DOCUMENTATION OF THE SAPRC-99 CHEMICAL MECHANISM FOR VOC REACTIVITY ASSESSMENT

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By

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ABSTRACT

An detailed mechanism for the gas-phase atmospheric reactions of volatile organic compounds (VOCs) and oxides of nitrogen (NO_x) in urban and regional atmospheres is comprehensively documented in this report. This can be used in airshed models to determine absolute and relative ozone impacts (reactivities) of the many types of VOCs that can be emitted into the atmosphere, and for other control strategy and research applications. This mechanism, designated SAPRC-99, represents a complete update of the SAPRC-90 mechanism of Carter (1990), and incorporates recent reactivity data from a wide variety of VOCs. The mechanism has assignments for ~400 types of VOCs, and can be used to estimate reactivities for ~550 VOC categories. A condensed version was developed for use in regional models. A unique feature of this mechanism is the use of a computerized system to estimate and generate complete reaction schemes for most non-aromatic hydrocarbons and oxygenates in the presence of NO_x, from which condensed mechanisms for the model can be derived. The mechanism was evaluated against the results of almost 1700 environmental chamber experiments carried out at the University of California at Riverside, including experiments to test ozone reactivity predictions for over 80 types of VOCs. The mechanism was used to update the various ozone reactivity scales developed by Carter (1994a), including the widely used Maximum Incremental Reactivity (MIR) scale. However, the reactivity estimates for many VOC classes are uncertain, which must be taken into account when using these data for regulatory applications. To aid this, uncertainty classifications have been assigned to all VOCs, and upper limit MIRs for VOCs with uncertain mechanisms are presented.

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I. INTRODUCTION

A. Background

Airshed models are essential for the development of effective control strategies for reducing photochemical air pollution because they provide the only available scientific basis for making quantitative estimates of changes in air quality resulting from changes in emissions. The chemical mechanism is the portion of the model that represents the processes by which emitted primary pollutants, such as volatile organic compounds (VOCs) and oxides of nitrogen (NO_x), interact in the gas phase to form secondary pollutants such as ozone (O_3) and other oxidants. This is an important component of airshed models because if the mechanism is incorrect or incomplete in significant respects, then the model's predictions of secondary pollutant formation may also be incorrect, and its use might result in implementation of inappropriate or even counter-productive air pollution control strategies.

One airshed model application where the accuracy of the chemical mechanism is particularly important is the assessment or implementation of control strategies to encourage use of VOCs that have lower impacts on ozone or other secondary pollutant formation than VOCs that are currently emitted. Such strategies require a means to quantify the impacts, or "reactivities" of the VOCs with respect to O_3 or other measures of air quality. There are several examples of control strategies where accurate O_3 reactivity estimates are important. In the California Air Resources Board (CARB)'s "Low Emissions Vehicle/Clean Fuels" regulations, "reactivity adjustment factors" are used to place exhaust emissions standards for alternatively-fueled vehicles on an equal ozone impact basis as those for vehicles using conventional gasoline (CARB, 1993). These are calculated using the Maximum Incremental Reactivity (MIR) scale (Carter, 1994a), which is a measure of effect of a VOC on O_3 formation in a set of standard airshed scenarios that represent NO_x conditions where ozone formation is most sensitive to VOCs (Carter, 1994a; CARB, 1993). The CARB is now considering using an updated MIR scale for reactivity adjustments in its proposed consumer products regulations (CARB, 1999). In addition, the EPA has used O_3 impacts of VOCs calculated for various environments among the factors they consider when evaluating proposals to exempt various compounds from controls as ozone precursors (Dimitriades, 1999).

The MIR scale adopted in the CARB vehicle regulation was calculated using the SAPRC-90 chemical mechanism (Carter, 1990), which had assigned or estimated mechanisms for over 100 types of VOCs. Although other state-of-the art mechanisms were available for airshed model applications (e.g., Gery et al, 1998, Stockwell et al, 1990), SAPRC-90 used for this purpose because it was the only mechanism that that represented a large number of VOCs that was evaluated against environmental chamber data. However, although this mechanism represented the state of the art at the time it was developed, since then there has been continued progress in basic atmospheric chemistry, and new information has become available concerning the reactions and O_3 impacts of many individual VOCs.

This mechanism has been updated several times to incorporate some of the new information that has become available, with the major documented updates being the "SAPRC-93" (Carter et al, 1993a; Carter, 1995) and the "SAPRC-97" (Carter et al, 1997a) versions. However, the reactions and rate constants for most of the inorganic species and common organic products have not been updated, and the latest documented update (SAPRC-97) does not incorporate important new information concerning mechanisms and reactivities of many classes of VOCs (e.g., Carter et al, 1999a, see also references cited below). This includes particularly improved estimation methods and new reactivity data on many types of oxygenated VOCs that have not previously been studied but that are or may be important in stationary source emissions, and updated mechanisms for components of mineral spirits and other high molecular weight alkanes.

Because of this, an updated mechanism that represents the current state of the art is needed to calculate an reactivity scale that is appropriate for the CARB's proposed reactivity-based consumer products regulations (CARB, 1999). In addition, the CARB vehicle regulations requires that the MIR scale it uses be updated approximately every three years, and therefore an update of that scale, using an updated and fully documented mechanism, is overdue. To address this need, the CARB contracted the author to an updated version of the SAPRC mechanism that represents the state of the art, that can appropriately represent the classes of compounds that need to be considered in stationary source VOC regulations, and that is comprehensively documented so that it can undergo peer review. This report documents the updated version of the mechanism, designated SAPRC-99, that represents the results of this effort.

B. Mechanism Overview

The major components of the SAPRC mechanisms are the base mechanism, the assignments and/or estimation procedures used to estimate the reactions of the represented VOCs that are not in the base mechanism, and the lumping procedures used to represent complex mixtures or VOCs for which assignments or estimates are not available. The base mechanism is the portion of the mechanism that represents the reactions of the inorganic species, the common organic products, the intermediate radicals leading to these products, including those formed from the initial reactions of the represented VOCs not in the base mechanism. Most of the VOCs that can be separately represented are not in the base mechanism, but can be added to the mechanism, either as explicit reactions for individual VOCs or as lumped model species whose parameters are derived from the mixture of detailed model species they represent, as needed in the model application. The updates to these various components are briefly summarized below, and are discussed in more detail in the remainder of this report. The remaining areas of uncertainty, and aspects of the mechanism additional work is needed, are also briefly summarized in this section.

1. Updates to the Base Mechanism

This version of the mechanism incorporates the first complete update of the base mechanism since SAPRC-90 was developed. The IUPAC (Atkinson et al, 1997a, 1999a) and NASA (1997) evaluations, the various reviews by Atkinson (1989, 1991, 1994, 1997a), and other available information were used to update all the applicable rate constants, absorption cross sections, quantum yields, and reaction mechanisms where appropriate. Although many small changes were made, most are not considered to have obviously important impacts on reactivity predictions. The one possible exception is the ~30% reduction in important OH + NO_2 rate constant based on the new evaluation by NASA (1997)[1]. However, a complete analysis of the effects of all the changes has not been carried out, so the possibility that other changes to the base mechanism may be important cannot be ruled out.

The base mechanism was also modified to improve somewhat the accuracy and level of detail in the mechanism in representing no-NO_x or low-NO_x conditions. The methyl peroxy and acetyl peroxy radical model species are not represented explicitly, without using "operator" approximations or the

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[1] The high rate constant in the current IUPAC (Atkinson et al, 1997) evaluation is probably inappropriate (Golden, personal communication, 1998).

steady-state approximation that was incorporated in previous mechanisms. This should give somewhat more accurate predictions of radical fates and C_1 product formation yields under low NO_x or nighttime conditions when peroxy + peroxy reactions become nonnegligible. The explicit treatment of methyl peroxy is based on the approach used in the RADM-2 mechanism (Stockwell et al, 1990), which was shown to give a good approximation to a version of the mechanism with explicit representation of all peroxy + peroxy reactions (Carter and Lurmann, 1990). However, “operator” and steady state approximation methods are still employed to represent the higher peroxy radicals, and the current mechanism, like the previous versions, is still not capable of predicting how the C_{2+} organic products may differ under conditions where peroxy + peroxy reactions compete with peroxy + NO reactions. But approximations have little or no effect on predictions of O_3 formation or O_3 reactivities, especially for the relatively high NO_x scenarios used for calculating the MIR scale (Carter, 1994a), and significantly reduce the number of active species that need to be included in the mechanism.

Although the base mechanism for SAPRC-99 employs a larger number of species than that for SAPRC-90 and as such is more detailed in most respects, a few condensations were employed. The separate model species used to predict formation of low-reactivity C_1-C_3 organic nitrates in the reactions of peroxy radicals with NO was lumped with the model species used to predict the formation of higher nitrates in these reactions because of the low total yield of the low reactivity nitrates. The PAN analogue formed from glyoxal, GPAN, is now lumped with the rest of the higher PAN analogues because of the relatively low amounts of GPAN predicted to be formed in atmospheric simulations. The effects of these approximations, which resulted in fewer species and significantly fewer reactions in the base mechanism, was shown to be small even in simulations of VOCs where these model species are predicted to be formed.

Because of the importance of isoprene emissions in many regional model applications, the base mechanism was expanded to include the isoprene photooxidation products used in the “four-product” condensed isoprene mechanism of Carter (1996). Thus, the base mechanism now includes explicit representation of methacrolein, methyl vinyl ketone, lumped C_5 unsaturated aldehyde products (ISOPROD), and the methacrolein PAN analogue (MPAN) formed when they react. Although the more condensed “one product” mechanism gives reasonably good approximations to predictions of effects of isoprene on ozone (Carter, 1996), the four product mechanism is considered to be more accurate, and allows prediction and appropriate representation of the major oxidation products of this important biogenic compound in ambient simulations.

2. Mechanism Generation and Estimation System

Probably the most important single advance in this version of the mechanism is the use of a new mechanism generation and estimation software system to derive fully detailed mechanisms for the atmospheric reactions of many classes of VOCs in the presence of NO_x, which can be used as the basis for deriving an appropriate representation of the VOC in the model. The automated procedure for generated alkane reaction mechanisms that was incorporated in SAPRC-90 (Carter, 1990) was updated based on the results of the evaluation of Atkinson (1997a) and an independent evaluation of alkoxy and peroxy radical reactions, as discussed in this report. More significantly, the software was completely revised and the capabilities of the system were extended to include not only alkanes, but also alkenes (with no more than one double bond), and many classes of oxygenates including alcohols, ethers, glycols, esters, aldehydes, ketones, glycol ethers, carbonates, etc. Although many of the estimated rate constants and rate constant ratios are highly uncertain, this procedure provides a consistent basis for deriving "best estimate" mechanisms for chemical systems which are too complex to be examined in detail in a reasonable amount of time. The system allows for assigning or adjusting rate constants or branching ratios in cases where data are available, or where adjustments are necessary for model simulations to fit chamber data. Therefore, it could be used for deriving fully detailed mechanisms for VOCs that fully incorporate whatever relevant data are available, relying on various estimation methods only when information is not otherwise available. The program also outputs documentation for the generated mechanism, indicating the source of the estimates or assumptions or explicit assignments that were used.

A major effort in developing this system involved incorporating results of various mechanistic, product, and environmental chamber studies that have been carried out in recent years to reduce uncertainties in mechanisms and reactivity predictions for various classes of oxygenated compounds. The branching ratios derived from experimental product studies or adjusted to fit environmental chamber reactivity experiments were used not only as a basis to derive explicit assignments for maximum accuracy of representation and reactivity predictions of the applicable compounds, but also to improve the reliability and scope of the estimation methods when applied to compounds for which data are not available. An important source of the environmental chamber data used for this purpose came from the CARB-funded study of the reactivity of selected consumer products VOCs (Carter et al, 1999a), as well as other recent studies of individual compounds of interest to various private sector groups (see references cited elsewhere in this report)[2].

This mechanism generation system is used as the primary means of deriving SAPRC-99 mechanistic parameters for all the classes of VOCs that it can handle, including alkanes, alkenes, and the variety of oxygenated species as indicated above. Although the program outputs mechanisms that can (for larger molecules) involve hundreds or even thousands of reactions or products, various "lumping rules" are used to convert the detailed generated mechanisms and product distributions into the lumped reactions incorporating the appropriate model species used in the base mechanism. The use of this program has permitted estimation of detailed mechanisms for a much larger number of compounds than otherwise would be possible without incorporating approximations that might significantly compromise the accuracy of reactivity predictions.

Although the mechanism generation system currently cannot be used to derive mechanisms for dialkenes and unsaturated aldehydes and ketones, the estimates in the detailed mechanism of Carter and Atkinson (1996) for isoprene and its major products were incorporated explicitly in the mechanism generation system, allowing full mechanisms for these species to be generated. The results are therefore are consistent with the detailed mechanism of Carter and Atkinson (1996) and the condensed mechanisms of Carter (1996) for these compounds. A similar approach was used so the system could be used to generate reactions of 1,3-butadiene acrolein, and various alkynes.

3. Assigned or Parameterized Mechanisms

Despite progress in recent years, there are still too many uncertainties concerning the details of the photooxidation mechanisms of aromatics and the reactive products they form to allow for explicit mechanisms to be derived or estimated. Therefore, simplified and parameterized mechanisms, with uncertain parameters adjusted to fit environmental chamber data, are still employed. However, the representation of the uncharacterized aromatic ring fragmentation products was revised somewhat based new data obtained for unsaturated dicarbonyls (e.g., Bierback et al, 1994), and to allow for explicit representation of the α-dicarbonyl products formed from the methylbenzenes. As with SAPRC-97, this version of the mechanisms appropriately represents reactivity differences among various xylene and

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[2] Reports on recent environmental chamber studies of various VOCs can be downloaded from http: //cert.ucr.edu/~carter/bycarter.htm

trimethylbenzene isomers, and is able to correctly simulate how aromatic reactivities vary with differing light sources. In addition, this version of the mechanism has reoptimized mechanisms for the naphthalenes and tetralin that can simulate environmental chamber experiments employing those compounds.

Because the mechanism generation system cannot derive mechanisms for bicyclic compounds, simplified mechanisms for these compounds were derived, based on environmental chamber data for several representative terpenes. Some parameters, such as overall organic nitrate yields and numbers of NO to NO_2 conversions in the OH reaction, were adjusted based on the chamber data, and the mechanism generation system for compounds for compounds with similar structures was employed to derive estimated mechanisms for their reactions with ozone. The mechanism correctly predicts observed reactivity differences among various terpene isomers, though some experiments, particularly with β-pinene, are not well simulated in some respects.

Assigned mechanisms were also derived for styrene, N-methyl-2-pyrroladone, toluene diisocyanate, and diphenylene diisocyanate, based on available kinetic and mechanistic data, estimated or parameterized mechanisms, and results of environmental chamber experiments employing those or related compounds.

Although ClO_x or BrO_x chemistries have been incorporated as extensions to the SAPRC-97 mechanism (Carter et al, 1996d, 1997d, 1997h), this is not yet incorporated in the current version of this updated mechanism. With the exception of chloropicrin, which appears to have relatively simple and unique chemistry (Carter et al, 1997h), the few halogenated compounds we have studied [trichloroethylene (Carter et al, 1996d) and alkyl bromides (Carter et al, 1997d)] indicate that we cannot account for the reactivities of those compounds with explicit mechanisms. Therefore, the current version of the mechanisms uses a highly simplified and parameterized “placeholder” mechanism to provide very rough estimates of the approximate range of reactivities of halogenated compounds under MIR conditions, given their OH radical rate constants. The predictions of these mechanisms must be considered to be highly uncertain, and the available chamber data indicate they are almost certainly not valid under low NO_x conditions.

A parameterized “placeholder” mechanism is also used to estimate the approximate reactivity ranges of amines, given their measured or estimated OH radical rate constants. The predictions of this mechanism for those compounds must also be considered to be highly uncertain, especially since they have not been evaluated using environmental chamber data. However, use of this mechanism allows at least approximate estimates to be made.

4. Mechanism Evaluation

The performance of the mechanism in simulating O_3 formation, rates of NO oxidation, and other measures of reactivity was evaluated by conducting model simulations of over 1600 environmental chamber experiments carried out the Statewide Air Pollution Research Center (SAPRC) and the College of Engineering Center for Environmental Research and Technology (CE-CERT) at the University of California at Riverside (UCR). These include 466 single VOC - NO_x experiments, 488 incremental reactivity experiments, and 664 experiments with mixtures, though approximately 500 of the mixture runs were replicate base case reactivity experiments of various types. These include not only experiments in the UCR database through 1993 (Carter et al, 1995d), but also experiments carried out at CE-CERT through mid 1999 for the purpose of developing and evaluating mechanisms for various types of VOCs[3].

The results of the evaluation indicated that this version of the mechanism performed approximately as well or better than the previous versions (Carter and Lurmann, 1991; Carter, 1995; Carter et al, 1997a) in simulating experiments with the major hydrocarbon classes found in ambient air and complex or surrogate mixtures. In addition, this version of the mechanism generally gave satisfactory fits to the reactivity data for most of the experiments using the various compounds that were studied more recently, which were either not represented or poorly represented in the previous versions. However, as with previous evaluations of this (Carter and Lurmann, 1991; Carter, 1995; Carter et al, 1997a) and other (Carter and Lurmann, 1990, Gery et al, 1988) mechanisms, there were cases where satisfactory simulations were not obtained. Many of these cases of poor performance in simulating the data can be attributed to problems with the mechanism, but this is probably not true in all cases.

For example, the mechanism did not perform particularly well in simulating the experiments with benzene, despite the fact that it generally performed satisfactorily in simulating experiments with most of the alkylbenzenes that were studied. The experiments with the 1-alkenes could only be simulated if it was assumed that the OH yields in the reaction of O_3 with those compounds were lower than indicated by laboratory data. The effects of varying reaction conditions on reactivities of some of the individual VOCs that were studied were not always successfully simulated, despite adjusting uncertain parameters in the mechanisms. These cases are noted in the summaries of the evaluation results for the various compounds. However, reactivities of most VOCs were reasonably well simulated, though in many cases adjustments to uncertain portions were made to achieve the fits. These cases are also noted in the summary of the evaluation results.

C. Updated Reactivity Estimates

The updated mechanism was used to calculate updated MIR and other ozone reactivity scales, using the scenarios and methodology developed previously for this purpose (Carter, 1994a,b). Reactivity estimates are given for a total of 557 VOC’s, including many that were not in previous tabulations, or whose estimates were based on much more uncertain or approximate mechanisms. The reactivity tabulations include footnotes indicating the type of mechanism or representation employed when calculating the reactivities, the extent to which the reactivity predictions were evaluated against experimental data, and an uncertainty ranking.

The updated reactivity scale given in this report supercedes those of Carter (1994a) and other interim updates that have been distributed previously. It is therefore recommended that these be used in any application that calls for use of the MIR scale or any of the other scales given by Carter (1994a). Although the estimates for many of the VOCs remain highly uncertain, the present scale provides the best estimates that are currently available. The uncertainty classification given with the scale and the other associated footnotes can be used to indicate the qualitative level of uncertainty for any given VOC. It is recommended that any regulatory application that employs any of the scales given in this report appropriately take uncertainty into account for those VOCs whose reactivities are indicated as having a high level of uncertainty.

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[3] The experiments used for mechanism evaluation include most of those described in the various reports on CE-CERT chamber studies that can be downloaded from http://cert.ucr.edu/~carter/bycarter.htm.

II. BASE MECHANISM

The base mechanism is the portion of the mechanism which must be incorporated when representing the reactions of any generic VOC, and includes the inorganic reactions, the reactions of the common organic products and the reactions of the common radicals formed from these products or any generic VOC. A complete listing of the base mechanism is given in Appendix A on Table A-1 through Table A-5. The species used in the base mechanism listed on Table A-1, their reactions and rate constants listed on Table A-2, the rate constant and mechanism documentation notes referred to there are given in Table A-4, and the absorption cross sections and quantum yields for the photolysis reactions listed on Table A-5. The major features of the mechanisms, and the changes made relative to the previous version (Carter et al, 1997a) are discussed in the following sections.

A. Inorganic Reactions

The inorganic reactions in the mechanism are essentially the same as in the previous versions, except all the rate constants have been updated based on the results of the most recent evaluations (Atkinson et al, 1997a,b, 1999a; Atkinson, 1997a; NASA, 1997). This resulted in changes to most of the rate constants, though in most cases the changes were small probably not of significance to model predictions. In addition, a few reactions that were previously judged to be negligible were added to extend the range of validity of the mechanism. The changes that may not be negligible, and the aspects of the inorganic mechanism that are still considered to be uncertain, are briefly summarized below, in the order that the reactions appear on Table A-2.

- Reactions of O^3P with O_3 and NO, which were omitted from the previous mechanism, are now included. These are believed to be negligible under most atmospheric conditions, but may not be in some high concentration experiments.
- The rate constant used for the “homogeneous” portion of the N_2O_5 hydrolysis reaction was decreased from 1×10^{-21} cm^3 $molec^{-1}$ s^{-1} to 2.6×10^{-22} cm^3 $molec^{-1}$ s^{-1}, based on the data of Mentel et al (1996). Note that this reaction may be primarily heterogeneous in nature, and the appropriate rate constant to use in atmospheric simulations is uncertain. However, the rate constant we use is not inconsistent with the IUPAC (Atkinson et al, 1997b) recommendation that the gas-phase rate constant is less than 2×10^{-21} cm^3 $molec^{-1}$ s^{-1}.
- The rate constant for OH + NO for 1 atmosphere and 300K increased by over a factor of 1.5, based on the NASA (1997) recommendation for the high pressure rate constant. The IUPAC (Atkinson et al, 1997a) recommendations is to use an even higher high pressure rate constant, but that recommendation is not used because the NASA value is more consistent with measurements made under near-atmospheric conditions.
- There is a significant discrepancy between the NASA (1997) and IUPAC (Atkinson et al, 1997a) recommendation concerning the important OH + NO_2 reaction. Again, the NASA recommendation is preferred because it is more consistent with measurements made under near-atmospheric conditions. [The rate parameters actually used are those that will be in the update to the NASA (1977) evaluation (Golden, private communication, 1999).] The high k_∞ recommended by IUPAC is based on very high pressure data in helium, and may be artifacts due to the contribution of a second reaction channel, involving HOONO formation, becoming important at higher pressures (Golden, personal communication, 1998). The value used in the current mechanism is about 20% lower than that used in the previous version. Given the importance of

this reaction as a radical termination and NO_x removal process, this change may have a non-negligible effect on model simulations.

- The reaction of OH with HONO, which was omitted in the previous mechanism because of its low importance in ambient simulations, is now included. This reaction can be important in simulations of experiments with HONO added as a radical source, which may be useful for assessing some aspects of VOC reactivity (unpublished results from this laboratory).
- A second photolysis channel for HONO, forming H. + NO_2, was added based on the IUPAC (Atkinson et al, 1997) recommendations. This channel is calculated to occur ~10% of the time under atmospheric conditions.
- The reaction of OH with NO_3, omitted from the previous mechanism, is now included. The possibility that it may be non-negligible under some nighttime conditions or in some dark experiments has not been ruled out.
- The rate constant for the reaction of HO_2 with NO_3 was increased based on recent laboratory data of Mellouki et al (1993).
- The reaction of NO_3 with itself, which may be non-negligible under some nighttime conditions (Stockwell et al, 1997) is now included.
- The reaction of OH with hydrogen was added because it may be a non-negligible sink for OH radicals in cleaner or remote atmospheres. The reaction is of negligible importance in urban or environmental chamber simulations, but may be needed in regional models.

The effects of these changes on model simulations have not been evaluated. It is expected the ~20% change in the OH + NO_2 may be the most important in terms of predictions of ozone formation, and in the model simulations of the environmental chamber experiments used to evaluate the mechanism, as discussed in Section V. However some of the changes concerning NO_3 reactions may have non-negligible effects on nighttime simulations. As indicated above, a number of changes were added that are not expected to influence ambient simulations, but which may be important in simulations of experiments that may be useful for evaluating other aspects of the mechanism. Since including these reactions did not add new species to the model, the impact of these reactions in terms of computational burden in airshed models should be minor.

B. Representation of Radical Species

The approaches used to represent the various types of radical species formed in the atmosphere are discussed in this section. As with the previous mechanism, most of the inorganic and a few of the organic radicals are represented explicitly, but most of the organic radicals are either lumped or not explicitly represented in the model. In particular, rapidly-reacting organic radicals which either react in only one way or whose reactions do not depend on other reacting species are replaced by the set of products they form, and most other radicals are either lumped or represented using a limited number of chemical “operators”. The various approaches employed are discussed in this section.

With regard to computational impacts of radical species incorporated in the model, a distinction is made between *active* species and species where the *steady state* approximation can be employed. Active species are model species whose concentrations need to be calculated by the solver software by integrating their rates of change, and which must be transported in multi-cell model simulations. Steady state species are model species (usually representing rapidly reacting radical or chemical operators representing radicals) for which the steady state approximation can be employed. In that approximation, the concentration of the species is calculated at each time step assuming that the instantaneous rate of formation is equal to the rate of destruction. This means that the species does not need to be transported or integrated by the model software, saving computer time and memory in multi-cell simulations. This approximation can appropriately be used by species such as alkyl and alkoxy radicals that always react rapidly with O_2 or have rapid unimolecular reactions, and is implicitly used when a radical is removed in the model by replacing it with the compound(s) it forms. However, experience has shown that it cannot be used for peroxy or NO_3 radicals, since their loss processes can become slow compared to their rates of change under low NO_x conditions or at nighttime. In addition because of limitations in the mechanism compiling software used in this work [and also implemented in the FCM version of the UAM (Kumar et al, 1995) and the CALGRID model], the steady state approximation cannot be used for species that react with themselves, other steady state species, or whose instantaneous concentrations cannot be calculated from the active species concentrations in a stepwise manner (Carter, 1988). Because of the latter restriction, the steady state approximation cannot be used for OH radicals when the mechanism is implemented with this software, though probably it is not a bad approximation for this species.

1. Inorganic Radicals

Most of the inorganic radicals in the mechanism are represented explicitly, as shown on Table A-1. The two exceptions are H atoms and $HOSO_2$ radicals, where the latter is formed in the reaction of OH with SO_2. H atoms are assumed to react exclusively and rapidly with O_2 to form HO_2, so any reaction that forms H atoms is represented as forming HO_2 instead. Likewise, $HOSO_2$ are assumed to react primarily with O_2 to form HO_2 and SO_3, so it is replaced by the HO_2 and sulfate (SULF) model species in the OH + SO_2 reaction. Table A-1 indicates those radicals for which the steady state approximation can be used. Note that this approximation should not be used for HO_2 or NO_3 radicals because they may build up significantly in concentration at nighttime or in the absence of NO_x. It probably could be used for OH radicals, but is not because of limitations of software used to implement the mechanism, as indicated above.

2. Rapidly Reacting Radicals.

As with the previous versions of the mechanism, many rapidly radicals are removed from the mechanism by replacing them by the species they are assumed to rapidly form. Note that this can only be done for radicals where (1) the steady state approximation is appropriate, (2) the product(s) they ultimately form do not depend on any other reactants, and (3) the products they form also do not depend on reaction conditions (e.g., temperature) or the variation can be assumed to be insignificant for the conditions of the model application. The specific types of rapidly reacting radical substitution reactions used in this mechanism are as follows. Except as indicated, the substitution is due to an expected rapid reaction of the radical with O_2.

- HCO is replaced by HO_2 + CO.
- Based on product data for reactions of OH radicals with alcohols and other species, α-Hydroxy alkyl radicals are assumed to react with O_2 primarily by abstraction from the α-hydroxy rather than by addition. Therefore, such radicals are replaced by HO_2 + the corresponding carbonyl compound formed when it reacts with O_2. For example, $CH_3CH(\cdot)OH$ is replaced by CCHO + HO_2, where CCHO is the model species for acetaldehyde.
- α-Nitrato alkyl radicals are assumed to decompose unimolecularly to NO_2 + the corresponding carbonyl compound sufficiently rapidly that the decomposition will dominate over reaction with O_2. Therefore, such radicals are replaced by NO_2 + the corresponding carbonyl compound formed in the decomposition. For example, $CH_3CH(\cdot)NO_2$ is replaced by CCHO + NO_2.

- All other carbon-centered radicals, including acyl (RCO•) and alkyl (R·) are assumed to react entirely by O_2 addition. Therefore, these are replaced by the corresponding peroxy radical whenever they are formed.
- With the exception of t-butoxy (model species TBU-O·) and phenoxy (model species BZ-O·) radicals, which are represented explicitly in the mechanism, all alkoxy radicals are replaced by the set of products they are assumed to form when they react under atmospheric conditions. This would include reactions with O_2 and/or unimolecular reactions, as applicable. If the alkoxy radical has more than one reaction pathway that is assumed to be non-negligible, then non-integer stoichiometric coefficients are used for the products, as appropriate. The reactions of alkoxy radicals are discussed in Section III.J.
- The Crigiee biradicals formed in the reactions of O_3 with alkenes are replaced by the set of products they are assumed to form when they react in the atmosphere, which includes stabilization as well as the various decomposition pathways. These reactions are probably temperature and pressure dependent, but since insufficient information is available to estimate these dependences, this is ignored. The reactions of Crigiee biradicals are discussed in the Section III.K.
- Stabilized Crigiee biradicals are replaced by the corresponding organic acid, on the assumption that their major fate under atmospheric conditions is reaction with H_2O to form the acid. The assumption that reaction with H_2O is the major fate of the biradicals is consistent with the rate constant ratios cited by Atkinson (1997a) for the reactions of $HCHO_2$ with H_2O, HCHO, CO, and NO_2. The mechanism for the reactions of stabilized $HCHO_2$ with water appear to be complex and may involve some formation of H_2O_2 or other peroxides, but based on the discussion of Atkinson (1999) we assume that acid formation is the major fate of all the stabilized Crigiee biradicals.

Note that branching ratios for some of the alkoxy radicals and the Crigiee biradicals may be temperature and pressure dependent, and this treatment ignores these dependencies. As discussed in Section III.J, the alkoxy radical branching ratios are estimated for $300^{o}C$ and 1 atmosphere total pressure, and thus they may not be optimum for simulations of high altitude or extreme temperature conditions. However, it should be pointed out that no other current mechanism represents these temperature and pressure dependences of product branching ratios, and doing so would require a significant increase in the complexity of the mechanism, or would require the model software to support temperature and pressure-varying parameters. Since no information is available concerning the temperature and pressure dependences of Crigiee biradical reactions, any representation of this in the model would be entirely speculative.

3. Explicitly Represented Organic Radicals

Most of the organic radical species are represented either by replacing them with the radicals or products they are expected to exclusively form, or by using the lumped peroxy radical species or “operators” as discussed in the following two sections. However, a few organic radical species are represented explicitly, either because their reactions are sufficiently different that they are not appropriately represented using the other approaches, or because it is believed representing them explicitly will improve the accuracy of the model sufficiently to make the added model species worthwhile. These are briefly discussed below.

Methyl Peroxy Radicals. In the previous mechanism, all peroxy radicals, including methyl peroxy, were represented using the general peroxy radical operators + the products they were expected to form, as discussed below. In this approach, the same organic products are assumed to be ultimately formed regardless of whether the radical reacts with NO, HO_2, or another peroxy radical. Although as discussed below this approach is still used for most of the higher peroxy radicals in this mechanism, in this mechanism methyl peroxy radicals ($CH_3OO\cdot$) are represented explicitly, using the model species C-O2·. Thus, the appropriate C_1 products are formed when it reacts with HO_2, itself, or other peroxy radicals, which are different than the formaldehyde formed when it reacts with NO. This allows for a more accurate representation of the reactions of at least this peroxy radical and gives this mechanism a level of detail approaching that of the RADM2 (Stockwell et al, 1990) or RACM (Stockwell et al, 1997) mechanisms in the way peroxy radical reactions are treated. As discussed by Carter and Lurmann (1990), the peroxy radical lumping approach used in the RADM2 mechanism appears to be somewhat less approximate than the lumping approach used in the previous SAPRC mechanisms.

Note that the reactions of peroxy radicals with NO_3 were not in the previous version of the mechanism. This reaction, which may be non-negligible at nighttime, was added based on the recommendations of the current evaluations (Atkinson et al, 1997a,b).

Acyl Peroxy Radicals. The previous mechanism used separate steady-state model species to represent acyl peroxy radicals (CCO-O2·), general lumped higher acyl peroxy radicals (C2CO-O2·), and the higher peroxy radicals formed from glyoxal (HCOCO-O2·) and benzaldehyde (BZCO-O2·). In addition, the model species (RCO3·) was used to compute the total concentration without using the steady state approximation, for the purpose of computing peroxy + peroxy reaction rates. The PAN analogues for these radicals (PAN, PPN, GPAN, and BZ-PAN) were also included in the mechanism as active species. In this mechanism, the acyl peroxy radical formed from glyoxal (and its PAN analogue) are removed by lumping them with the other higher general lumped peroxy radicals (or PAN analogues), the acyl peroxy radical (and PAN analogue) formed from methacrolein and other isoprene products are added, and the total acyl peroxy radical model species (RCO3·) is removed. The need for RCO3· is eliminated by treating all the acyl peroxy radical model species as active, and including all their cross reactions. Although this requires more reactions and active species in the mechanism than the approach used previously, it gives a somewhat more accurate representation of the peroxy + peroxy reactions of these species, which can be important at nighttime, and eliminates the need to include a separate total peroxy radical operator as a co-product in every reaction forming such radicals.

T-Butoxy Radicals. As indicated above, most alkoxy radicals are not represented explicitly in the mechanism, but are replaced by the set of species they are assumed to form when they react. In the previous mechanism this was the case for all organic alkoxy radicals except for phenoxy (see below), and in particular, t-butoxy radicals were assumed to react exclusively by decomposition to acetone and methyl radicals. However, the decomposition of t-butoxy is believed to be relatively slow (see Table A-2), and if NO_2 levels are sufficiently high then reaction with NO_2 may be non-negligible in high-NO_x scenarios or chamber experiments. In particular, the reaction of t-butoxy with NO_2 had to be included for the model to appropriately simulate results of incremental reactivity chamber experiments with isobutane (Carter et al, 1993a). Because the competition between decomposition and NO_2 depends on the NO_2 concentration, this requires that t-butoxy radicals be represented explicitly in the model. This is not necessary for most other alkoxy radicals, which can either react sufficiently rapidly with O_2, or have sufficiently rapid decomposition or isomerization pathways, that reaction with NO_2 can be neglected.

Phenoxy Radicals. Phenoxy radicals are represented explicitly in this and the previous mechanism because they are not expected to react with O_2 and have no known rapid decomposition pathway. In the presence of NO_x, the major fate of phenoxy radicals is believed to be reaction with NO_2, since it has no obvious unimolecular reaction route or mechanism for reaction with O_2. (Reaction with NO would be expected to form a nitrite that would rapidly photolyze to re-form NO and phenoxy.)

Nitrophenol formation has generally been assumed in this reaction (e.g., see Atkinson, 1990; Carter, 1990), presumably via some rearrangement of an initially formed unstable adduct. However, based on lower than expected yields of Nitrophenol in NO3 + cresol and OH + benzaldehyde systems (Atkinson, 1994), this may be an oversimplification. In the absence of NO_x, the major fate of phenoxy is assumed to be reaction with HO_2, though the model also includes a slow unimolecular loss to account for situations where NO_2 or HO_2 may be low. Note that the phenoxy radical model species is used as a surrogate for substituted phenoxy radicals as well, except for lumped nitro-substituted phenoxy radicals, discussed below.

Nitro-Phenoxy Radicals. Although their reaction mechanisms are assumed to be the same as phenoxy radicals, the NO_2-substituted phenoxy radicals assumed to be formed from the reactions of NO_3 with phenols are represented separately. This is done to account for nitrogen balance, and because the dinitroaromatics expected to be formed in the reaction with NO_2 are expected to be either non-volatile or non-reactive, and are thus represented in the model as “lost nitrogen”. This is the same representation as used in the previous mechanisms.

Formaldehyde + HO_2 Intermediate. The radical believed to be formed when HO_2 reacts with formaldehyde has to be represented explicitly because its subsequent fate is believed to be affected by NO levels, as shown on Table A-2. The mechanism used is based on the IUPAC (Atkinson et al, 1999a) recommendation, and is essentially the same as used in the previous mechanism.

4. Peroxy Radical Operators

Representation of peroxy radical reactions in mechanisms is complicated by the fact that a relatively large number of such radicals are formed even in condensed mechanisms, and they can react to a non-negligible extent with themselves and other peroxy radicals under some conditions. The approach employed in the Carter (1990) mechanism is to represent organic peroxy radicals with the set of products they would ultimately form if they reacted fully in the presence of NO_x and sunlight, together with a set of chemical “operators” that represent their other effects on the system. A total peroxy radical operator (RO2·) is used to compute the total peroxy radical concentrations for the purpose of computing peroxy + peroxy radical reaction rates; this allows the steady-state approximation to be used for the other peroxy radical operators.

The approach used in this mechanism is similar, except that as indicated above it is not used for methyl peroxy because it is now represented explicitly, and also the total peroxy radical species (RO2·) is eliminated. Instead of the latter, all the peroxy radical operators are treated as active species, and the cross-reactions between the operators are included. The elimination of RO2· simplifies the representation of peroxy radical chemistry and reduces the total number of species in the mechanism, though at the expense of having a somewhat larger number of active species and peroxy + peroxy radical cross reactions. The number of peroxy radical operators used to represent organic nitrate formation was reduced to reduce the number of species and cross-reactions. The peroxy radical operators employed in this mechanism are summarized below.

RO2-R·. This operator represents the effect of peroxy radical reactions that ultimately cause one NO to NO2 conversion and formation of HO_2 when they react with NO. It is representing as having zero carbons. When this operator reacts with HO_2, it is represented as forming ROOH, the lumped higher hydroperoxide species. Unlike the previous mechanism (Carter, 1990), which used a zero-carbon lumped hydroperoxide operator (-OOH) to represent the effect of hydroperoxide photolysis to form radicals, in this mechanism the higher hydroperoxides are represented by a model species whose reactions are based on those estimated for n-propyl hydroperoxide. In other words, a lumped molecule[4] approach is used rather than the lumped structure approach. Since the organic portion of the radicals already represented by the products formed if the radical reacted with NO (which is why the RO2-R· operators are zero carbon species), formation of the ROOH in the HO_2 reaction does not conserve carbon. To account for this, loss of three "lost carbon" (XC) species are included in this reaction to main carbon balance. Although this may appear to be a worse approximation than using a zero-carbon lumped structure species such as the -OOH in the previous mechanism, in fact for most radicals carbon is lost in the model when the peroxy reacts with NO (because of the use of relatively small products to represent most of the lumped products), so this tends to work towards compensating for that effect. Tracing the "lost carbon" (XC) levels in the model can be used to track the extent to which carbon is lost due to the way the product species are represented.

When this operator reacts with explicitly the represented radical species [i.e., NO_3, methyl peroxy, or any of the acyl peroxy species] the products formed are the same as would be formed if ethyl peroxy ($CH_3CH_2OO\cdot$) reacted with those species, except that any C_2 organic products (acetaldehyde or ethanol) are removed, and if ethoxy radicals are formed, they are replaced by HO_2 (based on the fact that ethoxy can be represented as rapidly forming acetaldehyde + HO_2, with acetaldehyde removed). In other words, since the since RO2-R· does not represent the organic portions of the peroxy radicals, the organic products formed in its reactions are ignored. Note that it is assumed that in $RO_2\cdot + RO_2\cdot$ reactions it is assumed that formation of 2 $RO\cdot + O_2$ and disproportionation to an alcohol + a carbonyl + O_2 occur with equal probability, based on available data for higher peroxy radicals (Atkinson et al, 1999a). In the case of reaction of methyl peroxy, it is assumed that the disproportionation forming methanol and that forming formaldehyde occur with equal probability.

R2O2·. This represents the effects of extra NO to NO_2 conversions caused by multi-step reaction mechanisms, as would occur, for example, in mechanisms involving alkoxy radical decompositions or isomerizations. Again, R2O2· is used so the model can account for the formation of RO_2, and [R2O2] is used for the actual reactions of the operator. Unlike the RO2-R· and the other peroxy operators, this is not strictly speaking a radical species, and it is not represented as having any effect on the system except when it reacts with NO. This is because it does not react to form radical or radical sink species, and is only appropriately used in conjunction with RO2-R.

RO2-N·. This represents the reactions of peroxy radicals with NO forming organic nitrates of various types, which are all represented in the model by the 6-carbon lumped alkyl nitrate model species RNO3 (see Section C.2). Note that in previous versions of the mechanisms two additional operators were used to represent these processes: RO2-XN· was used to represent peroxy radicals that reacted with NO to form relatively unreactive C_{3-} nitrates, and RO2-XN· was used to represent aromatic peroxy radicals that reacted with NO to form aromatic nitrates. In this mechanism RO2-XN· was removed because the amount of C_{3-} nitrate formation tends to be extremely small, and RO2-NP· was removed nitrate formation is assumed to be relatively minor for most aromatics. In addition, the reactions of the aromatic nitrates formed are so uncertain that representing them separately may not necessarily be any more accurate than lumping them with RNO3.

Since the RO2-N· operator is used to represent the organic nitrates formed when the peroxy radicals react with NO, it is represented as having the number of carbons of the nitrate it forms when it reacts with NO, and its reactions with species other than NO are based on this representation. The

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[4] The "lumped molecule" approach refers to representing a compound in the model by another compound, on a mole for mole basis. See Section VI.A.1.

products are derived based on what is considered to be appropriate for a C_{6+} alkyl peroxy radical, since those tend to be the radicals that are the largest precursors to alkyl nitrates in atmospheric simulations. In addition, since primary radicals tend to be formed in lower relative yields from such higher molecular weight compounds than secondary or tertiary radicals (because the C-H bonds tend to be more labile), the carbonyl products are represented by ketone model species (MEK or PROD2), rather than by aldehydes. The specific products used are indicated in the footnotes to Table A-2 for the various reactions.

RO_2 + RO_2 Reactions. Because the rate constants for peroxy + peroxy radical reactions can vary by orders of magnitude depending on the type of radical (e.g., Atkinson, 1997), the rate constant used for the peroxy + peroxy reactions of the peroxy radical operators must necessarily be very approximate. The value used for all these operators is based roughly on the range of rate constants for secondary peroxy radicals given by Atkinson (1997a) and Atkinson et al (1997b), and is 30 times higher than the 1×10^{-15} cm^3 $molec^{-1}$ s^{-1} value used in the previous mechanism (Carter 1990).

C. Reactions of Common Products

A total of 24 model species are used in this mechanism to represent the reactive organic product species, 11 of which are used for organic compounds that are represented explicitly, and 13 of which are used to represent groups of similar products using the “lumped molecule” approach. In most cases, the model species and mechanisms are not significantly different than in previous versions of the mechanisms, except that some of the rate constants were updated as indicated in footnotes to Table A-2. Most of the updates for the C_{3-} products are based on IUPAC (Atkinson et al, 1997a, 1999a) recommendations. The species used are summarized below.

1. Explicitly Represented and Lumped Molecule Products

Formaldehyde (HCHO) and Acetaldehyde (CCHO). The mechanisms for these two compounds are essentially the same as in the previous mechanism, except that some of the rate constants and absorption cross sections have been updated as recommended by IUPAC (Atkinson et al, 1997a, 1999a). Note that this mechanism differs from most condensed mechanisms in that acetaldehyde is represented explicitly, with most higher aldehydes lumped with propionaldehyde, as discussed below. The one exception is glycolaldehyde ($HOCH_2CHO$), which is expected to have a reactivity closer to acetaldehyde than propionaldehyde, and therefore is represented by acetaldehyde in this mechanism.

Propionaldehyde and Lumped Higher Aldehydes (RCHO). The reactions of the model species RCHO, which represents all C_{3+} aldehydes except glycolaldehyde, α-dicarbonyls, aromatic aldehydes, and acroleins, is based on the expected mechanism for propionaldehyde. Note that, based on structure-reactivity methods of Kwok and Atkinson (1995), as updated by Kwok et al (1996), approximately 4% of the reaction with OH radicals is estimated to occur by abstraction from the CH_2 group and ~1% at the methyl. The reactions of the radicals subsequently formed are derived using the general mechanism estimation methods, as discussed below. However, most of the OH reaction is analogous to the reaction of OH with acetaldehyde, forming RCO-O2·, the lumped higher acyl peroxy radical. The NO_3 and photolysis reactions are also assumed to be analogous to those for acetaldehyde, though a slightly higher NO_3 radical rate constant is assumed (based on the somewhat higher OH rate constant), and absorption cross sections and quantum yields specific to propionaldehyde are used.f

Acetone (ACET). Acetone is represented explicitly because it has significantly lower reactivity than other ketones, yet is sufficiently reactive that its reactivity is probably not negligible in long-range transport scenarios. Its mechanism is based on that discussed by Carter et al (1993b). Based on the data of

Jenkin et al (1993), the $CH_3COCH_2O\cdot$ radical is believed to primarily decompose to formaldehyde and $CH_3CO\cdot$. The absorption cross sections and quantum yields are based on the IUPAC (Atkinson et al, 1997a), except that the reported quantum yields at 230 and 330 nm are believed to be high, and were corrected as discussed by Carter et al (1993b) and the footnotes to Reaction K3HV on Table A-2.

Methyl Ethyl Ketone and Lumped Lower Reactivity Ketones (MEK). This model species is used to represent ketones and other reactive oxygenated product species whose OH radical rate constant is between 5×10^{-13} and 5×10^{-12} cm^3 $molec^{-1}$ s^{-1}. Note that this is different from previous versions of the SAPRC mechanism, where MEK was used for all higher non-aldehyde, non-aromatic oxygenated products that were more reactive than acetone. The MEK mechanism is based on that derived for methyl ethyl ketone using the general mechanism estimation methods discussed below, the IUPAC recommended OH rate constant (Atkinson et al, 1999a) and absorption cross sections provided by Moortgat (private communication, 1996). The overall photolysis quantum yield of 15% was derived by fits to MEK - NO_x and MEK incremental reactivity environmental chamber experiments carried out in our laboratories (see Section V and Carter et al, 1999a), and is somewhat higher than the ~10% overall quantum yield derived previously based on fits to a few UNC outdoor chamber experiments (Carter, 1990; Carter and Lurmann, 1991).

Methanol (MEOH). In previous SAPRC mechanisms methanol in emissions was represented as an assigned parameter detailed model species, which permitted it to be represented explicitly or lumped with other compounds, depending on the model application. However, this approach does not permit representing formation of methanol as a reaction product. In this mechanism methanol is assigned an explicit model species in order to permit its formation of a product in no-NO_x reactions of methyl peroxy reaction. These reactions, and the subsequent reactions of methanol so formed, may be non-negligible in some long-range transport scenarios. Since methanol is potentially important in emissions, most model applications would probably use a separate model species for it in any case. Indeed, methanol is now represented explicitly even in some condensed models such as expanded Carbon Bond IV (e.g., Carter, 1994b and references therein). The mechanism is based on IUPAC (Atkinson et al, 1997a, 1999a) recommendations.

Methyl Hydroperoxide (COOH) and Lumped Higher Peroxides (ROOH). In previous SAPRC mechanisms, the hydroperoxide species formed in peroxy + HO_2 reactions were represented by a single “lumped structure” model species “-OOH”, combined with the organic products formed in the peroxy + NO reactions. In this mechanism, for more accurate representation of low-NO_x chemistry, for regional or long-range transport simulations, methyl hydroperoxide is represented explicitly, and the other hydroperoxides are represented using a separate model species (ROOH) using the “lumped molecule” approach. In the case of methyl hydroperoxide, the OH reaction is assumed to occur at both the methyl and OOH positions as recommended by IUPAC (Atkinson et al, 1997a, 1999a), with the $\cdot CH_2OOH$ radical formed in the former reaction being assumed to rapidly decompose to formaldehyde + OH. The absorption cross sections are also based on IUPAC recommendations, with unit quantum yields assumed, and with the reaction assuming to proceed entirely by breaking the weak O-O bond.

The reactions of the lumped higher hydroperoxide (ROOH) are based on the estimated mechanism for n-propyl hydroperoxide. As discussed in footnotes to Table A-2 in Table A-4, the OH reaction is estimated to occur at the OOH group ~2/3 of the time, based on assuming the same rate constant as the same reaction of methyl hydroperoxide. Most of the remainder of the reaction is assumed to occur at the 1-position, yielding an α-hydroperoxy radical which is assumed to rapidly decompose to propionaldehyde (RCHO) and OH. The photolysis is assumed to have the same rate and an analogous mechanism as methyl hydroperoxide.

Glyoxal (GLY). Glyoxal, which is formed in the reactions of most aromatics, acetylene, and some other species [including some isoprene oxidation products (Carter and Atkinson, 1996)], continues to be represented explicitly in this mechanism. Since it is less reactive than some other aromatic products it is often not represented in condensed mechanisms, but it is known to make an important contribution to the reactivity of acetylene (Carter et al, 1997c) and benzene (see Section IV.A.1) and its reactivity is not well approximated by other model species. On the hand, this mechanism is somewhat more condensed than previous detailed SAPRC mechanisms in that the acyl peroxy radical and PAN analogue predicted to be formed from the OH + glyoxal reaction [HCO(CO)OO· and $HCO(CO)OONO_2$)] are not represented explicitly, but are lumped with RCO-O2· and PAN2 (see below). The mechanism for the OH reaction is based on the data of Niki et al (1985) as discussed by IUPAC (Atkinson et al, 1997a).

The glyoxal absorption cross sections were the same as used previously (Plum et al, 1983), as recommended by the IUPAC evaluation (Atkinson et al, 1997a). However, the quantum yields were significantly revised based modeling of acetylene - NO_x and acetylene reactivity environmental chamber data (Carter et al, 1997c), as discussed in the footnotes to Table A-2 in Table A-4. The model simulations of those chamber experiments were found to be highly sensitive to glyoxal absorption cross sections used in the mechanism, and no other reasonable adjustments to the mechanism would yield acceptable fits to the data (Carter et al, 1997c). Note that to fit the data quantum yields which are ~1.4 times higher than overall quantum yield reported by Plum et al (1983) for conditions of those experiments muse be used. Although use of acetylene reactivity data is a highly indirect way to obtain glyoxal quantum yields, we consider it to be a less uncertain way to estimate radical quantum yields then the data of Plum et al (1993), which uses a UV-poor light source, only measures rates of glyoxal decay. Clearly this is uncertain and direct measurements of glyoxal quantum yields as a function of wavelength are needed.

Methyl Glyoxal (MGLY) and Other Higher α-dicarbonyl aldehydes. Methyl glyoxal is formed in the reactions of methylbenzenes and from some carbonyl compounds is a highly reactive compound that can significantly affect the reactivity of compounds that form it. The MGLY model species is also used to represent other α-dicarbonyl aldehydes, such as ethylglyoxal, etc. However, unlike the SAPRC-97 mechanism of Carter et al (1997a), but like earlier versions of the mechanism (Carter, 1990, 1995; Carter et al, 1993b), it is not used in this version of the mechanism to represent any of the uncharacterized aromatic ring fragmentation products (see discussion of unknown aromatic fragmentation products, below). The mechanism for the OH and NO_3 reactions are similar to those in the previous mechanism, with the latter reaction assumed to have the same rate constant and analogous mechanism as for acetaldehyde.

The IUPAC recommended (Atkinson et al, 1997a, 1999a) absorption cross sections for methyl glyoxal are approximately a factor of 2 higher than the Plum et al (1983) values used in the previous mechanism. The current mechanism uses cross sections obtained from Moortgat (personal communication, 1996), which are consistent with the IUPAC recommendations but have higher resolution. Unit quantum yields were assumed in the low wavelength band ($\lambda \leq 340$ nm) and zero quantum yields were assumed for wavelengths above the cutoff of 421 nm, as determined by the thermochemistry. For the rest of the high wavelength regime, the quantum yield was assumed to decline linearly from unity at 344 nm to zero at a wavelength (407 nm) that was adjusted such that the calculated overall photolysis rates under the conditions of the experiments of Plum et al (1983) agreed with the experimentally measured values. (An analogous treatment was used in when deriving the quantum yields for glyoxal and biacetyl, though in the glyoxal case the adjustment was to fit the acetylene chamber data, as indicated above.) Note that this gives a different wavelength dependence than assumed in the previous mechanism, where a wavelength-dependent overall quantum yield was assumed for the entire high-wavelength band, including wavelengths above the high wavelength cutoff.

Biacetyl (BACL) and Other α-Dicarbonyl Ketones. Biacetyl or other α-dicarbonyl ketones are formed in significant yields from p-xylene, 1,2,4-trimethylbenzene and other o-dimethyl aromatics, and might be formed from the reactions of some carbonyl compounds. Biacetyl was not represented in previous versions of the mechanism, being in effect represented by methyl glyoxal. However, because its chemistry is in some ways quite different from methyl glyoxal (it reacts only slowly with OH, and its photolysis forms only PAN precursors), it was decided to represent it explicitly in this mechanism. The BACL model species is also used for other α-dicarbonyl ketones.

The reaction of biacetyl with OH radicals is ignored because the OH + biacetyl rate constant is probably not much different than that for acetone, making it a negligible loss process compared to photolysis. The photolysis is assumed to proceed via breaking the weak CO-CO bond, as shown on Table A-2. The absorption cross sections used were those from Plum et al (1983), and the wavelength-dependence of the quantum yields were derived from the data of Plum et al (1983) in a manner exactly analogous to that discussed above for methyl glyoxal (see footnotes to Table A-2 in Table A-4).

Phenol (PHEN) and Cresols (CRES). Phenol is formed from the reactions of benzene and is represented as being formed in the subsequent reactions of aromatic ring-retaining products such as cresols or benzaldehydes, and cresols are formed in the reactions of the substituted aromatics. Cresol is used to represent phenolic products formed from all alkyl-substituted benzenes, while phenol is used to represent such products formed from benzene and naphthalene, as well as phenolic products formed in secondary reactions of cresols. The relatively rapid reactions of these compounds with NO_3 represents a NO_x sink in the aromatic mechanisms that largely explains their predicted tendency to inhibit O_3 under low NO_x conditions. Therefore, it is important that these model species be in the mechanism. . They are kept as separate model species because the reactions of cresols are assumed to involve some PAN (or PAN analogue) formation, while this is assumed not to be the case for phenol.

There are still inadequate data concerning the atmospheric reactions of these compounds and the products they form, and the highly parameterized mechanisms used in the previous versions of the SAPRC mechanisms are essentially unchanged in this version. The main consumption reactions are with OH and NO_3, and the rate constants used are those recommended by Atkinson (1994). The OH + cresol mechanism is based on the highly parameterized mechanism derived by Carter (1990), but the version for this mechanism was reoptimized to fit the data from the single o-cresol - NO_x chamber experiment EC281 (Pitts et al, 1979; Carter et al, 1995d). The OH + phenol mechanism was derived by analogy with the resulting cresol mechanism. The NO_3 reactions are assumed to proceed via the formation of phenoxy radicals + HNO_3 (with the BZ-O·) model species used for substituted as well as unsubstituted radicals, when then reacts as discussed above in Section B.3. Note that although the mechanism for the NO_3 reaction (like that for the reaction with OH) is highly uncertain, it clearly must involve some sort of NO_x sink process in order for model simulations to fit chamber data for aromatics.

Nitrophenols (NPHE). The "nitrophenol" model species is used to represent whatever products are formed when phenoxy reacts with NO_2, which as indicated above is uncertain. It is assumed that the NO_2-substitution slows down the rate of reaction with OH radicals, and that its only significant consumption process is reaction with NO_3, for which it is assumed to have the same rate constant as phenol. This representation is unchanged from previous versions of the mechanism. Obviously this aspect of the mechanism is uncertain, but this representation appears to perform reasonably well in simulating effects of aromatics on peak O_3 yields, which are determined by NO_x-sink processes that are represented by the formation and reactions of NPHE.

Benzaldehyde (BALD) and Other Aromatic Aldehydes. Benzaldehyde, tolualdehydes and other aromatic aldehydes that are formed in a minor but non-negligible route in the reactions of OH with methylbenzenes are represented by the benzaldehyde (BALD) model species. Its OH and NO_3 reactions are assumed to be analogous to other aldehydes, except that separate model species (BZCO-O2· and BZ-PAN) are used to represent the acyl peroxy radical and PAN analogue formed. This is necessary because the reaction of the benzoyl peroxy radical with NO forms phenoxy radicals, which does not regenerate radicals like the radicals formed when the other acyl peroxy radicals react with NO.

The absorption cross sections for benzaldehyde (Majer et al, 1969) indicate that its photolysis can be significant if the quantum yield is sufficiently high. The quantum yields are unknown, but chamber data indicates that it is probably consumed to a non-negligible by photolysis, though the overall quantum yield is relatively low and the photolysis apparently does not involve significant radical formation, The overall quantum yield derived by Carter (1990) to fit SAPRC evacuable chamber data (Pitts et al, 1979) is retained in this mechanism. It was found to give reasonably good model simulations of benzaldehyde - NO_x experiments carried out in the CE-CERT Xenon Teflon Chamber (Carter et al, 1998a).

Methacrolein (METHACRO) and Methyl Vinyl Ketone (MVK). This version of the mechanism incorporates the “four product” isoprene mechanism (Carter, 1996) as part of the base mechanism, so it includes model species for methacrolein, MVK, and the lumped other isoprene products (ISOPROD). The mechanisms used for methacrolein and MVK are essentially the same as derived by Carter and Atkinson (1996), with some minor updates as indicated in footnotes to Table A-2 in Table A-4. The mechanisms were generated using the mechanism generation system discussed in Section III, which incorporated most of the estimates and assignments of Carter and Atkinson (1996) for the reactions specific to the isoprene and isoprene product system. This resulted in some minor changes to yields of minor product in some reactions. In addition, because of these changes and changes to the overall base mechanism, the overall quantum yield for the methacrolein MVK photolysis was reoptimized, using the same procedures and data as discussed by Carter and Atkinson (1996). This resulted the overall quantum yield for methacrolein being increased by ~14%, while that for MVK was reduced by over a factor of ~5. The reason for this large change in the optimized MVK quantum yield is not clear, but it may be due to a relatively low sensitivity of model simulation results to large changes in this parameter. (See Section V and Appendix B for results of model simulations of the methacrolein and MVK experiments.)

Methacrolein is also used to represent acrolein in reactions where acrolein is predicted to be formed as a product. This is to avoid adding a new model species to represent a relatively minor product in most ambient mixtures. However, this mechanism has a separate detailed model species for acrolein with mechanistic assignments appropriate for this compound, which can be used to more accurately represent acrolein when its reactivity is being assessed, or when emitted directly.

Lumped Isoprene Products (ISOPROD). The ISOPROD model species is used to represent reactive isoprene products other than methacrolein and MVK, and also to represent other unsaturated ketones or aldehydes (other than acrolein itself, which is represented by methacrolein) when formed in reactions of other VOCs. Its mechanism is based on the ISOPROD model species in the “four product” isoprene mechanism of Carter (1996), with some minor modifications as indicated in footnotes to Table A-2 in Table A-4. Its mechanism is derived from weighted averages of rate constants and parameters for a mixture of 30% hydroxymethacrolein and 23⅓% each cis-$HCOC(CH_3)$-$CHCH_2OH$, trans-$HCOC(CH_3)$-$CHCH_2OH$, and $HCOCH{=}C(CH_3)CH_2OH$. As with methacrolein and MVK, the mechanisms for these species were derived using the mechanism generation system discussed in Section III, incorporating estimates and assignments of Carter and Atkinson (1996) where applicable.

2. Lumped Parameter Products

"Lumped parameter" species refer to model species whose mechanisms are derived by averaging rate constants and product yield parameters from a representative mixture of compounds that they are designed to represent. Although the previous versions of the SAPRC mechanism used this approach only for model species representing emitted VOCs, this mechanism also uses this approach for two of the lumped organic product species, as discussed below.

Lumped Higher Reactivity Non-Aldehyde Oxygenates (PROD2). This model species, which is new to this version of the mechanism, is used to represent ketones, alcohols, and other reactive non-aromatic and non-double-bond-containing oxygenated products whose rate constants are higher than 5 x 10^{-12} cm^3 $molec^{-1}$ s^{-1}. This was added because it was judged that many of the bi- or polyfunctional product species that were previously represented by MEK when they were formed as products are in fact much more reactive than MEK, at least in terms of their reaction rate with OH radicals. The reaction mechanism of PROD2 is based on averaging mechanisms derived for a representative set of product species as discussed below.

Lumped Organic Nitrate Products (RNO3). This model species is used to represent various organic nitrates (other than PAN or PAN analogues), primarily those formed in the reactions of peroxy radicals from NO. This is consumed primarily by reaction with OH radicals, but a slow photolysis, which may be non-negligible in long-range transport simulations, is also included in the mechanism. Unlike previous SAPRC mechanisms, RNO3 is also used to represent those formed from aromatic peroxy radicals with NO; previously the nitrophenol (NPHE) model species was used for this purpose. As indicated above, this change was made to avoid having to add the separate peroxy radical "operator" needed to support separate representation of aromatic nitrates, which are formed in relatively low yields and for which the appropriateness of the NPHE vs the RNO3 representation is unknown. The reaction mechanism of RNO3 is based on averaging mechanisms derived for a representative set of product species as discussed below.

Derivation of PROD2 and RNO3 Mechanisms. Although in principle the mechanisms for the lumped parameter product species can be derived for each emissions inventory in the manner used for the lumped parameter model species used for emitted VOCs (see Section III.A), the necessary software to do this has not yet been developed. Instead, in this version of the mechanism the parameters are derived from sets of representative species representing products predicted to be formed from the reactions of the mixture of VOCs used as the "Base ROG" mixture in the atmospheric reactivity calculations (Carter, 1994a; see also Section VII.A.1), and are held fixed in the model simulations. The Base ROG mixture is used to represent reactive VOCs from all sources, and is derived from the "all city average" mixture derived by Jeffries et al (1989) from analysis of air quality data, with minor modifications as discussed by Carter (1994a,b)[5]. For the purpose of determining the contributions of the reactions of the compounds in the mixture to the formation of a lumped product, the contribution of each emitted VOC is weighed by the amount of each VOC that is estimated to react in a one-day scenario, multiplied by the yield of the lumped product used in the model for the reactions of the VOC. The amount reacted is obtained from the amount emitted multiplied by the "mechanistic reactivity" (Carter and Atkinson, 1989a; Carter, 1994a), which is the fraction of the VOC estimated to react. The latter is obtained from mechanistic reactivities in the "averaged conditions" scenario where the NO_x inputs are adjusted to yield maximum peak ozone

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[5] The complete mixture, indicating the specific detailed model species used to represent it in the model, is given in Table 50. See also Carter (1994b).

concentrations (the "MOIR" scenario)[6] (Carter, 1994a). Table 1 and Table 2 show the contributions of the reactions of various types of VOCs in the base ROG mixture to the formation of the RNO3 and PROD2 model species.

The set of compound that are represented by various model species can be calculated for those model species whose mechanisms can be derived using the mechanism generation/estimation system that is discussed in Section III. For each of these compounds, the system generates the set of products that are predicted to be formed using a fully explicit mechanism for the reactions in the presence of NO_x, which are then used, together with the "lumping rules" discussed in Section III.L, to determine the lumped product yields for the model. From this, the distribution of individual product VOCs represented by each lumped product model species can be determined, at least for the reactions of the VOCs whose mechanisms can be generated using this system. Although this system cannot generate mechanisms for aromatic compounds and terpenes, for which parameterized mechanisms must still be used, Table 1 and Table 2 show that their contributions to PROD2 or RNO3 formation from the base ROG mixture is minor. In particular, reactions of aromatics and terpenes account for less than 6% of the PROD2 formation, and for less than 5% of the formation of RNO3 in one-day scenarios.

Table 3 and Table 4 show the 35 most important products predicted to be formed from the reactions of the VOCs in the base ROG mixture that are represented by PROD2 (Table 3) or RNO3 (Table 4). The tables also show the contribution of each product to the total of all products represented by PROD2 or RNO3, their OH radical rate constant and carbon numbers, and the average OH rate constant and carbon number for all the products, weighed by their molar contribution to the total. Note that no single compounds dominate the lists, and in the case of the organic nitrates the top 35 compounds account for less than half of the products formed that are represented by RNO3. Therefore, in both cases there is no obvious choice of a single "representative" or "typical" compound to use for lumped molecule representations.

In the case of PROD2, the average OH radical rate constant is 1.5×10^{-11} cm^3 $molec^{-1}$ s^{-1}, and the average carbon number is slightly over 7. For the purpose of deriving a PROD2 mechanism in the model, five individual compounds, indicated by being underlined on Table 3, were chosen as being representative of the entire set. The choice was largely subjective, but was made such that the average OH rate constant and the average number of carbons was approximately the same as the average, and so they included examples of different types of compounds on the list. For each of these five compounds the reaction mechanism with OH and photolysis was generated using the mechanism estimation/generation procedure discussed in Section III, and the PROD2 parameters were derived by averaging the values obtained, weighing each of the five compounds equally[7]. Since most of these compounds are ketones, the ketone absorption cross sections and the quantum yields assumed to be appropriate for ketones with 7 carbons (see Section III.G.1) were used for the photolysis reactions. The mechanisms derived for these representative individual compounds are included with the mechanism listings for the detailed model species, given in Table A-6. Note that although the PROD2 mechanism is derived based on a set of model species with average carbon numbers of 7, this is represented as having 6 carbons in the mechanism for the purpose of computing carbon balance.

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[6] The MOIR mechanistic reactivities are used because they are typical mechanistic reactivities in a wide range of scenarios. MIR mechanistic reactivities tend to be lower than in other scenarios because the relatively high NO_x levels tend to suppress radical levels.

[7] The mechanisms derived for these representative individual compounds are included with the mechanism listings for the detailed model species, given in Section VI. The detailed model species names assigned to them are indicated on Table 3 or Table 4.

Table 1. Contributions of various types of model species in the base ROG mixture to the formation of the PROD2 lumped product species.

VOC	Cont’n	VOC	Cont’n	VOC	Cont’n	VOC	Cont’n
N-C5	14.5%	4-ME-C7	2.9%	1-C9E	1.0%	3-ME-C11	0.3%
N-C10	8.1%	1-HEPTEN	2.7%	24-DM-C5	0.9%	26DM-C9	0.2%
N-C6	6.2%	24-DM-C7	2.5%	3-ME-C6	0.9%	ME-CYCC6	0.2%
N-C7	5.8%	3-ME-C6	2.2%	1-HEXENE	0.8%	1-C10E	0.2%
Aromatics	5.2%	2-ME-C6	1.9%	N-C11	0.7%	4-ME-C10	0.2%
1-HEXENE	5.0%	4-ME-C8	1.9%	3-ME-C5	0.6%	3-ME-C10	0.2%
24-DM-C6	4.5%	2-ME-C8	1.8%	36DM-C10	0.6%	1-PENTEN	0.1%
2-ME-C7	4.2%	26DM-C8	1.7%	24-DM-C5	0.5%	23-DM-C5	0.1%
2-ME-C5	3.6%	4-ME-C9	1.6%	1-OCTENE	0.5%	1-PENTEN	0.1%
N-C8	3.5%	2-ME-C9	1.6%	ET-CYCC6	0.4%	N-C13	0.1%
N-C9	3.4%	N-C12	1.4%	1-C11E	0.3%	2-ME-C5	0.1%
CYCC6	3.0%	ME-CYCC6	1.1%	5-ME-C11	0.3%	3M-1-BUT	0.0%

Table 2. Contributions of various types of model species in the base ROG mixture to the formation of the RNO3 lumped product species.

VOC	Cont’n	VOC	Cont’n	VOC	Cont’n	VOC	Cont’n
2-ME-C4	7.7%	23-DM-C5	1.6%	N-C11	0.6%	C-2-BUTE	0.2%
N-C4	5.9%	Terpenes	1.4%	1-C11E	0.5%	1-PENTEN	0.2%
N-C10	5.8%	24-DM-C5	1.3%	ET-CYCC6	0.5%	1-C10E	0.2%
24-DM-C6	4.9%	2-ME-C3	1.3%	2M-1-BUT	0.5%	1-BUTENE	0.2%
N-C5	4.9%	2-ME-C9	1.3%	1-OCTENE	0.5%	1C6RCHO	0.2%
2-ME-C5	4.0%	2-ME-C8	1.3%	T-3-C7E	0.5%	T-2-C7E	0.2%
ME-CYCC5	3.1%	4-ME-C9	1.2%	1-PENTEN	0.4%	13-BUTDE	0.2%
Aromatics	2.7%	4-ME-C8	1.2%	PROPENE	0.4%	3M-1-BUT	0.2%
24-DM-C7	2.5%	1-C9E	1.2%	T-4-C9E	0.4%	T-4-C10E	0.2%
26DM-C8	2.5%	PROPANE	1.2%	T-2-C6E	0.4%	3-ME-C10	0.1%
3-ME-C5	2.4%	N-C12	1.1%	C-2-C6E	0.4%	1C5RCHO	0.1%
2-ME-C7	2.4%	CYCC5	1.0%	T-5-C11E	0.4%	4-ME-C10	0.1%
N-C7	2.4%	2-ME-C6	0.9%	22-DM-C4	0.3%	CYC-HEXE	0.1%
4-ME-C7	2.3%	CYCC6	0.9%	T-2-BUTE	0.3%	MEK	0.1%
3-ME-C6	2.1%	ISOBUTEN	0.9%	ME-CYCC6	0.3%	23-DM-C4	0.1%
N-C9	2.1%	3-ME-C6	0.9%	3-ME-C11	0.3%	2-ME-C5	0.1%
N-C8	1.9%	23-DM-C4	0.9%	5-ME-C11	0.3%	3-ME-C5	0.1%
N-C6	1.8%	C-2-PENT	0.8%	26DM-C9	0.3%	N-C13	0.1%
1-HEPTEN	1.8%	T-2-PENT	0.8%	T-4-C8E	0.3%	36DM-C11	0.0%
ME-CYCC6	1.7%	24-DM-C5	0.7%	2M-2-BUT	0.3%		
1-HEXENE	1.7%	36DM-C10	0.6%	1-HEXENE	0.2%		

Table 3. Product compounds predicted to be formed in the atmospheric reactions of compounds in the base ROG mixture that are represented by the PROD2 model species.

Cont'n [a]	kOH [b]	nC [c]	Model Species [d]	Product Structure [e]
	1.5e-11	7.19		Average of all Products
16.4%	9.6e-12	5	PROD2-1	CH3-CO-CH2-CH2-CH2-OH
6.1%	1.7e-11	6		CH3-CH(OH)-CH2-CH2-CO-CH2-OH
3.8%	1.5e-11	6	PROD2-2	CH3-CO-CH2-CH(CH3)-CH2-OH
3.4%	6.4e-12	6		*CH2-CH2-CH2-CH2-CH2-CO-*
3.1%	1.4e-11	6		CH3-CH(OH)-CH2-CH2-CO-CH3
2.9%	1.1e-11	6		CH3-CH2-CO-CH2-CH2-CH2-OH
2.9%	2.0e-11	7		CH3-CH2-CH(OH)-CH2-CH2-CO-CH2-OH
2.7%	5.5e-12	6		CH3-CO-CH2-C(CH3)(OH)-CH2-OH
2.7%	1.5e-11	7	PROD2-3	CH3-CH(OH)-CH2-CH2-CO-CH2-CH3
2.3%	2.7e-11	5		CH3-CH(OH)-CH2-CO-CH3
2.2%	1.7e-11	7		CH3-CH2-CH(OH)-CH2-CH2-CO-CH3
2.2%	2.3e-11	10		CH3-CH2-CH2-CH(OH)-CH2-CH2-CO-CH2-CH2-CH3
2.1%	2.1e-11	10		CH3-CH2-CH2-CH2-CH(OH)-CH2-CH2-CO-CH2-CH3
2.0%	7.1e-12	8		CH3-C(CH3)(OH)-CH2-CH2-CO-CH2-CH3
1.7%	2.1e-11	10		CH3-CH2-CH2-CH2-CH2-CH(OH)-CH2-CH2-CO-CH3
1.5%	1.9e-11	7		CH3-CH(OH)-CH(CH3)-CH2-CO-CH3
1.3%	2.2e-11	8		CH3-CH2-CH(OH)-CH(CH3)-CH2-CO-CH3
1.3%	1.8e-11	8	PROD2-4	CH3-CH2-CH(OH)-CH2-CH2-CO-CH2-CH3
1.3%	6.0e-12	7		CH3-C(CH3)(OH)-CH2-CH2-CO-CH3
1.3%	2.4e-11	10		CH3-CH2-CH(OH)-CH2-CH2-CO-CH2-CH2-CH2-CH3
1.3%	1.9e-11	8		CH3-CH(OH)-CH2-CH2-CO-CH2-CH2-CH3
1.2%	7.4e-12	8		CH3-C(CH3)(OH)-CH2-CH(CH3)-CO-CH3
1.2%	1.7e-11	8		CH3-CH(OH)-CH2-CH(CH3)-CO-CH2-CH3
1.2%	1.4e-11	7		CH3-CH2-CH2-CO-CH2-CH2-CH2-OH
1.1%	1.6e-11	7		CH3-CH(OH)-CH2-CH(CH3)-CO-CH3
1.1%	1.9e-11	8		CH3-CH2-CH2-CH(OH)-CH2-CH2-CO-CH3
1.1%	2.0e-11	9	PROD2-5	CH3-CH2-CH2-CH(OH)-CH2-CH2-CO-CH2-CH3
1.1%	2.2e-11	9		CH3-CH2-CH(OH)-CH2-CH2-CO-CH2-CH2-CH3
1.0%	1.4e-11	6		CH3-CH(CH3)-CH2-CO-CH3
1.0%	2.3e-11	9		CH3-CH2-CH2-CH2-CH(OH)-CH2-CH2-CO-CH2-OH
1.0%	2.2e-11	10		CH3-CH(OH)-CH2-CH2-CO-CH2-CH2-CH2-CH2-CH3
0.8%	2.0e-11	9		CH3-CH2-CH2-CH2-CH(OH)-CH2-CH2-CO-CH3
0.8%	1.9e-11	8		CH3-CH(CH3)-CH(OH)-CH2-CH2-CO-CH3
0.8%	1.7e-11	7		*CH(CH3)-CH2-CH2-CH2-CO-CH2-*
0.8%	1.7e-11	8		CH3-CH(OH)-CH2-CH2-CO-CH(CH3)-CH3
21.6%				All Others

[a] Amount of formation of this compound relative to all products represented as PROD2, on a molar basis.

[b] OH radical rate constant estimated using structure-reactivity methods of Kwok and Atkinson (1995), as updated by Kwok et al (1996), in units of cm^3 $molec^{-1}$ sec^{-1}.

[c] Number of carbons.

[d] Detailed model species name used when computing mechanism for compound that was used for deriving PROD2 mechanism for the model.

[e] Product structure as used in the mechanism generation system. The "*" symbol is used to indicate groups that are bonded in cyclic compounds. Underlined structures are those used to derive the PROD2 mechanism.

Table 4. Product compounds predicted to be formed in the atmospheric reactions of compounds in the base ROG mixture that are represented by the RNO3 model species.

Cont'n [a]	kOH [b]	nC [c]	Model Species [d]	Product Structure [e]
	7.8e-12	6.58		Average of all Products
6.5%	1.6e-12	4	RNO3-1	CH3-CH(ONO2)-CH2-CH3
3.6%	3.0e-12	5		CH3-CH(CH3)-CH(ONO2)-CH3
2.8%	4.2e-13	3		CH3-CH(ONO2)-CH3
2.6%	1.7e-12	5		CH3-C(CH3)(ONO2)-CH2-CH3
2.5%	3.0e-12	5		CH3-CH(ONO2)-CH2-CH2-CH3
1.4%	2.8e-12	5		CH3-CH2-CH(ONO2)-CH2-CH3
1.0%	4.7e-12	6	RNO3-3	CH3-CH(ONO2)-CH(CH3)-CH2-CH3
1.0%	1.2e-11	5	RNO3-2	CH3-CH(OH)-CH2-CH2-CH2-ONO2
1.0%	5.1e-13	4		CH3-C(CH3)(ONO2)-CH3
1.0%	3.1e-12	6		CH3-C(CH3)(ONO2)-CH2-CH2-CH3
0.9%	4.5e-12	4		CH3-C(CH3)(ONO2)-CH2-OH
0.9%	4.2e-12	6		CH3-CH(CH3)-CH(ONO2)-CH2-CH3
0.9%	9.9e-12	10	RNO3-6	CH3-CH2-CH(ONO2)-CH2-CH2-CH2-CH2-CH2-CH2-CH3
0.9%	9.9e-12	10		CH3-CH2-CH2-CH(ONO2)-CH2-CH2-CH2-CH2-CH2-CH3
0.9%	9.9e-12	10		CH3-CH2-CH2-CH2-CH(ONO2)-CH2-CH2-CH2-CH2-CH3
0.9%	5.6e-12	8	RNO3-5	CH3-CH(CH3)-CH2-C(CH3)(ONO2)-CH2-CH3
0.8%	9.9e-12	7	RNO3-4	CH3-CH2-CH2-CH2-CH2-CH(ONO2)-CH2-OH
0.8%	2.8e-12	6		CH3-CH2-C(CH3)(ONO2)-CH2-CH3
0.8%	1.0e-11	5		CH3-CH(OH)-CH(ONO2)-CH2-CH3
0.8%	1.2e-11	5		CH3-CH(ONO2)-CH(OH)-CH2-CH3
0.8%	4.4e-12	6		CH3-CH(CH3)-CH2-CH(ONO2)-CH3
0.8%	7.2e-12	6		*CH(ONO2)-CH2-CH2-CH2-CH2-CH2-*
0.7%	1.0e-11	10		CH3-CH(ONO2)-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH3
0.7%	6.2e-12	8		CH3-C(CH3)(ONO2)-CH2-CH(CH3)-CH2-CH3
0.7%	4.2e-12	7		CH3-CH2-C(CH3)(ONO2)-CH2-CH2-CH3
0.7%	4.2e-12	6		CH3-CH2-CH(ONO2)-CH2-CH2-CH3
0.7%	5.6e-12	7		CH3-CH2-CH(ONO2)-CH2-CH2-CH2-CH3
0.7%	8.5e-12	6		CH3-CH2-CH2-CH2-CH(ONO2)-CH2-OH
0.6%	8.9e-12	4		CH3-CH(OH)-CH(ONO2)-CH3
0.6%	1.9e-11	10		CH3-CH2-CH(OH)-CH2-CH2-CH(ONO2)-CH2-CH2-CH2-CH3
0.6%	1.9e-11	10		CH3-CH2-CH2-CH(OH)-CH2-CH2-CH(ONO2)-CH2-CH2-CH3
0.6%	3.1e-12	6		CH3-C(CH3)(ONO2)-CH(CH3)-CH3
0.6%	1.8e-11	6		CH3-CH(ONO2)-CH2-CH2-CH(OH)-CH2-OH
0.6%	3.4e-12	6		CH3-C(CH3)(OH)-CH2-CH2-CH2-ONO2
0.6%	4.4e-12	6		CH3-CH(ONO2)-CH2-CH2-CH2-CH3
58.0%				All Others

[a] Amount of formation of this compound relative to all products represented as RNO3, on a molar basis.

[b] OH radical rate constant estimated using structure-reactivity methods of Kwok and Atkinson (1995), as updated by Kwok et al (1996), in units of cm^3 molec^{-1} sec^{-1}.

[c] Number of carbons.

[d] Detailed model species name used when computing mechanism for compound that was used for deriving the RNO3 mechanism for the model.

[e] Product structure as used in the mechanism generation system. See Section ??. The "*" symbol is used to indicate groups that are bonded in cyclic compounds. Underlined structures are those used to derive the RNO3 mechanism.

In the case of RNO3, the average OH radical rate constant is 7.8 x 10^{-12} cm^3 $molec^{-1}$ s^{-1}, and the average carbon number is around 6.5. The RNO3 mechanism in the model is derived by choosing one representative compound each for carbon numbers of 4-8 and 10, such that the average OH rate constant is close to the average for the mixture. These six compounds are indicated by being underlined on Table 4. The mechanisms for these compounds were generated and the product yield parameters obtained[7] were averaged (weighing each equally) to obtain the product yields for the reactions of RNO3. The rate of photolysis is estimated by using the absorption cross sections given by IUPAC (Atkinson et al, 1997a, 1999a) for isopropyl nitrate, assuming unit quantum yield for production for NO_2.

3. Uncharacterized Aromatic Ring Fragmentation Products

Despite considerable progress in recent years towards understanding aromatic reaction mechanism (e.g., see Atkinson, 1999, and references therein), there is still insufficient information about the ring-opening products formed with OH radicals react with aromatic compounds to determine the appropriate mechanism for atmospheric modeling. In particular, the observed α-dicarbonyl and ring-retaining products from the aromatics are insufficient to account for the observed reactivity of aromatics in environmental chamber experiments, and it is necessary to assume formation of products that photolyze relatively rapidly to form radicals for model simulations to fit the environmental chamber data (e.g. Carter, 1990). To fit the data, the Carter (1990) mechanism included model species AFG1 and AFG2 to represent the contribution to reactivity of these uncharacterized ring-fragmentation products, with their yields and approximate photolysis rates adjusted to fit chamber data. Their mechanisms were based roughly on those for glyoxal and methyl glyoxal, respectively, although their action spectrum had a greater short wavelength contribution [eventually being based on that for acrolein (Carter et al, 1993b; Carter, 1995)] in order to fit reactivity data using differing types of light sources. More recently, to fit new aromatics environmental chamber data obtained using Teflon chambers with a xenon arc light source, it was found that it was also necessary to represent at least portion of the uncharacterized ring-opening products by model species with α-dicarbonyl action spectra (Carter et al, 1997a). These were represented in the model by methyl glyoxal – i.e., by increasing the methyl glyoxal yield by an adjustable amount in order to fit the chamber data (Carter et al, 1997a).

In this version of the mechanism, the general approach of using photoreactive model species with yields adjusted to fit the chamber data to represent the effects of unknown reactive aromatic ring fragmentation products is retained. However, the number of model species used for this purpose was increased to three, and their mechanisms were derived to be somewhat more consistent with the actual types of species expected to be involved. However, the mechanisms of the model species used were changed to be more consistent with the actual types of unsaturated dicarbonyl species expected to be involved, with their names being changed from AFGn to DCBn. A third model species (DCB3) was added to allow for separate representation of products with action spectra like α-dicarbonyls, and thus end the use the methyl glyoxal model species (MGLY) for this purpose. This was done so that the mechanism used may be more appropriate for an unsaturated carbonyl, and so model predictions of MGLY will actually represent methyl glyoxal and similar species. These are discussed in more detail below[8].

<u>DCB1</u> is used to represent the uncharacterized ring-opening products that do not undergo significant photodecomposition to form radicals. This includes not only the ring fragmentation formed from benzene and naphthalene, but also unsaturated diketones such as 3-hexene-2,5-dione, which the data of Bierbach et al (1994) and Tuazon et al (1985) do not undergo significant radical-forming

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[8] See also Section IV.A for a discussion of the derivations of the yields and photolysis rates of these species based on model simulations of the aromatic - NO_x chamber experiments.

photodecomposition. This non-photoreactive model species replaces the AFG1 used in the previous versions of the mechanism to represent the uncharacterized ring-fragmentation products from benzene because fits to the benzene - NO_x chamber data are not significantly improved if it is assumed that there are other photoreactive ring-opening products besides glyoxal. This is contrast with the previous version of the mechanism, where significant photolysis of AFG1 to radicals had to be assumed to fit these data. This change is because benzene also forms glyoxal, whose photolysis to radicals was increased significantly in this version of the mechanism in order to be consistent with new chamber data on the reactivity of acetylene (Carter et al, 1997c). Also, the reaction of this species with O_3 is an additional radical source that was not in the previous mechanism.

This species is also used in the mechanisms of the alkylbenzenes because at least some of the ring-opening products are expected to have low photoreactivity, yet are expected to react rapidly by other means, particularly with OH. In particular, o-substituted aromatics such as o-xylene and 1,2,4-trimethylbenzene are expected to form higher yields of unsaturated diketones, which as indicated above do not seem to be highly photoreactive (Bierbach et al, 1994; Tuazon et al, (1985). The fact that these o-substituted aromatics have relatively low reactivity in environmental chamber experiments, and that lower yields photoreactive products that give best fits to these data (Carter et al, 1997a), is consistent with the expected lower photoreactivity of these compounds. As discussed in Section IV.A, the yield of DCB1 is determined by assuming that the sum of all the DCBs (DCB1 + DCB2 + DCB3) is equal to the total ring fragmentation route, where the yields of the photoreactive DCB1 and DCB2 being determined by optimization. Note that this means the DCBs are used represent co-products formed with the measured α-dicarbonyls, as well as products formed in non-α-dicarbonyl-forming fragmentation routes.

The DCB1 reactions are based roughly on those estimated for HCOCH=CHCHO, with OH and O_3 rate constants based on the data of Bierbach et al (1994), and the mechanisms derived as discussed in Footnotes to Table A-2 in Table A-4. Although an OH reaction mechanism for an unsaturated diketone product such as might be formed from o-substituted aromatics may be somewhat different than that expected for 2-butene 1,4-dial, best fits to the p-xylene and 1,2,4-trimethylbenzene chamber data are obtained if the present DCB1 + OH mechanism is used.

DCB2 and DCB3 are used to represent the highly photoreactive ring-opening products formed from alkylbenzenes. As discussed by Carter et al (1997a), to fit chamber data using various light sources, it is necessary to assume two separate model species for this purpose, one with an action spectrum like acrolein, and the other with an action spectrum like an α-dicarbonyl. DCB2 is used to represent those compounds with action spectra like α-dicarbonyls, and thus uses absorption cross sections of methyl glyoxal, with a wavelength-independent overall quantum yield adjusted to give best fits to the chamber data as discussed in Section IV.A. Likewise, DCB3 uses the absorption cross sections of acrolein, with the overall quantum yield adjusted to fit the same chamber data. Note that the overall “quantum yield” used in the model for DCB3 is greater than unity, indicating that the absorption cross sections of the actual compounds being represented must be significantly greater than those for acrolein. However, in view of lack of information concerning the nature of these compounds and their photolysis reactions, it is assumed that the wavelength dependence of the action spectra are approximately the same as that for acrolein.

Other than the photolysis rates, the reactions of DCB2 and DCB3 are the same. They are based roughly on estimated mechanisms for $CH_3C(O)CH=CHCHO$. The rate constant for the OH reaction was assumed to be the same as that used for DCB1, with the mechanism estimated as indicated in footnotes to Table A-2 in Table A-4. Because of the rapid photolysis, it is assumed that consumption of these species by reaction with O_3 is negligible. The photolysis mechanisms are unknown, and are probably highly variable depending on the individual species involved. In this mechanism, these are very approximately represented by an estimated set of products is used which gives reasonably good performance in model simulations of available chamber data (see Section IV.A).

4. Unreactive Product Species

The mechanism has several model species whose subsequent reactions are ignored, either because they are unreactive or because the effects of their gas-phase reactions are expected to be small. These also include "counter species" for the purpose of tracking carbon and nitrogen balance. Since their computed concentrations do not effect transformations of any of the other gas-phase species, they could be eliminated from the model if their concentrations, or tracking carbon or nitrogen balance, are not of interest.

Formic Acid (HCOOH), Acetic Acid (CCO-OH), Lumped Higher Organic Acids (RCO-OH), Peroxy Acetic Acid (CCO-OOH), and Lumped Higher Organic Peroxy Acids (RCO-OOH). Formic acid is predicted to be formed in the reactions of formaldehyde with HO_2, acetic and higher organic acids are predicted to be formed from the reactions of acyl peroxy radicals with other peroxy radicals, and peroxy acetic and higher peroxy acids are predicted to be formed when acyl peroxy radicals react with HO_2. In addition, formation of formic and higher organic acids are assumed to be the major fate of stabilized Crigiee biradicals (Atkinson, 1997a, 1999). Their subsequent reactions with OH radicals is assumed to be negligible compared to other loss processes such as deposition, though the reaction with OH may in fact be non-negligible for the higher acids or peroxy acids. Formation of these acids is included in the model because of their potential involvement in acid deposition. Depending on the model application, it may be appropriate to remove them from the model or lump them into a single organic acid species.

Carbon Dioxide (CO2). Since CO_2 does not undergo gas-phase reactions and its formation is not expected to have any other effects on the environment (since background CO_2 concentrations are much higher), the only reason for having this species in the model is carbon balance.

Unreactive Carbon (NROG). This model species is used to represent emitted VOCs or VOC oxidation products whose subsequent reactions are assumed to be negligible, and which are not otherwise represented in the model. It can be removed from the model if carbon balance is not of interest. It is represented as having one carbon, with the other carbons in the unreactive VOC or product being represented by the "lost carbon" species.

Lost Carbon (XC). The lost carbon model species is used to account for carbons that are lost (or gained) if the model species has a different number of carbons than the VOC or VOC products being represented. Note that this is different from the "unreactive carbon" (NROG) model species in that the former is used to represent *molecules* that are treated as unreactive, while the latter represents *parts of molecules* that are not being represented (i.e., that are "lost") as a result of the mechanism condensation processes. This model species can be removed in model applications where carbon balance is not of interest.

Lost Nitrogen (XN). This model species is analogous to the lost carbon (XC) species except that in this case it is used for nitrogen balance. It is not recommended that this be removed from the mechanism, so that nitrogen balance can always be verified in any model simulation. Because of the importance of nitrogen species in affecting not only O_3 formation but also radical cycles and chain lengths, any modeling system that does not maintain proper nitrogen balance must be considered to be unreliable.

Hydrogen (H2). The mechanism includes the formation of H_2 from the photolysis of formaldehyde, but the subsequent reaction of H_2 with OH is ignored because of the low rate constant and the relatively small amount formed. Tracking H_2 in the model is useful only for mechanism evaluation studies if instrumentation to measure H_2 is available, and can be eliminated from the model for ambient simulations or other applications.

Sulfates (SULF). The SULF model species is used to represent the formation of SO_3 from the reactions of SO_2 with OH. It is assumed that the fate of SO_3 in the atmosphere would be formation of sulfate aerosol. This model species would be important in models for secondary aerosol formation in scenarios where SO_2 is emitted, but could be removed if aerosols are not represented in the model application.

III. GENERATED AND ESTIMATED MECHANISMS

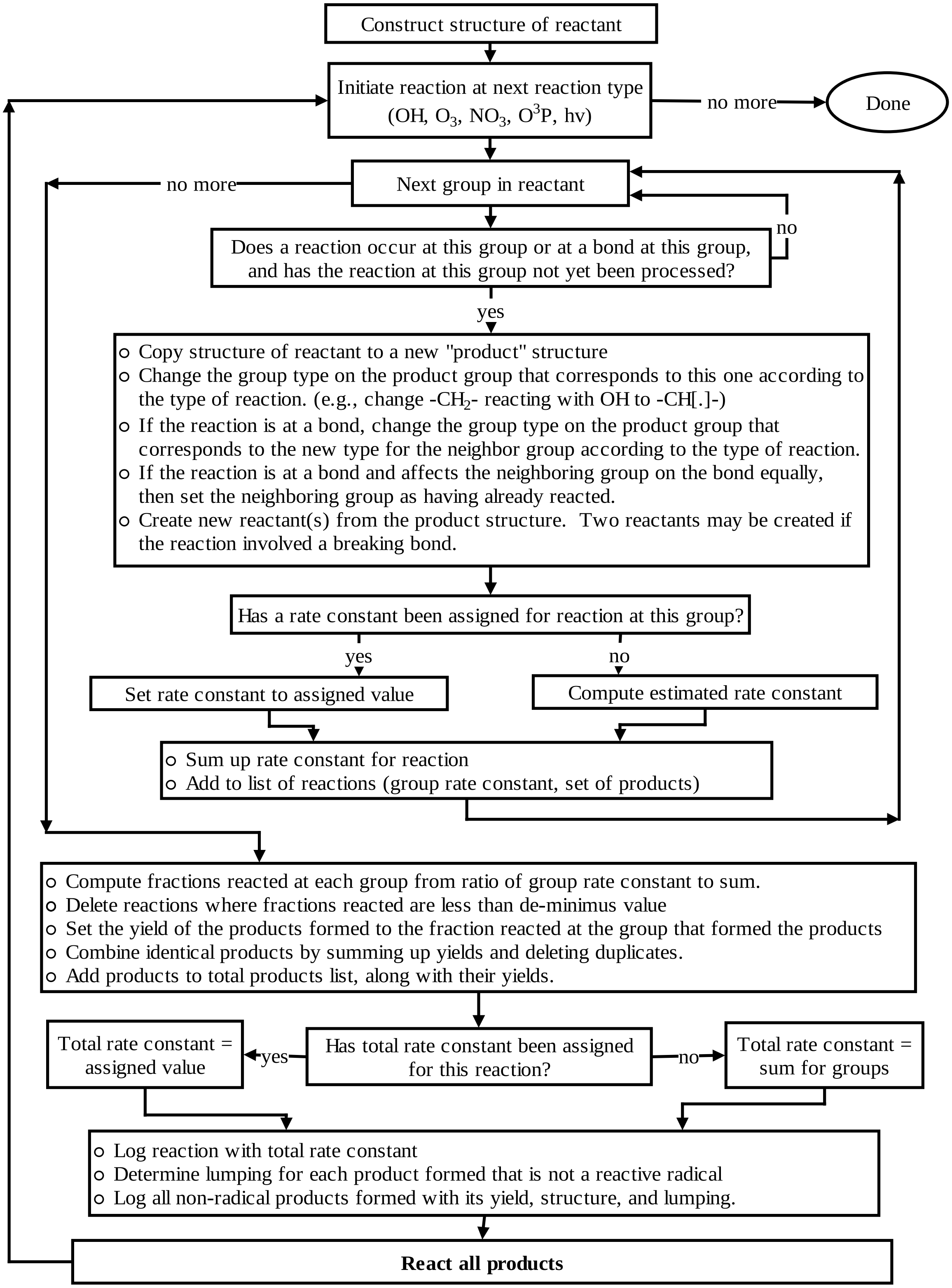
The atmospheric reaction mechanisms for most of the organic compounds that are represented by this mechanism are complex, can involve a large number of reactive intermediates (particularly for larger molecules), and in almost all cases involve reactions whose rate constants are unknown and have to be estimated. Because of the complexity, for practical reasons it is necessary either to greatly simplify the mechanisms for most VOCs, use extensive lumping or condensations in VOC representations, or use an automated procedure to generate the mechanisms. In the previous versions of the SAPRC mechanism, an automated procedure was used to derive mechanisms for the alkanes, but molecule-by-molecule assignments or various lumping or condensation approaches were used for all the other VOCs. In this version, an automated procedure is now used to derive the mechanisms for a much wider variety of compounds, which includes almost all compounds for which mechanistic assignments have been made except for the aromatics and terpenes. This procedures, estimation methods, and assignments that it employs are discussed in this section.

A. Mechanism Generation Procedure Overview

The mechanism generation is carried out using a set of object-oriented computer programs that derives explicit mechanisms for the major atmospherically-relevant reactions of a VOC in the presence of NO_x, given the structure of the VOC. The results are then used to determine the representation of these reactions in terms of the model species in the base mechanism. The current system can generate the atmospherically-relevant reactions of alkanes, monoalkenes, a variety of oxygenates, and selected dialkenes and alkynes with OH, reactions of monoalkenes and selected dialkenes with O_3, NO_3, and O^3P, and photolysis reactions of carbonyls and organic nitrates. The overall operation of the system involves the following steps:

- The user inputs the structure of the compound. The structure is specified in terms of "groups" such as $–CH_2$-, -CO-, -OH, etc., which are similar to those used in the group additivity thermochemical estimation methods of Benson (1976) or the structure-reactivity kinetic estimate methods of Atkinson (1987). The specific groups used are summarized in Section III.B.
- The initial reactions of the compound with OH, O_3, NO_3, O^3P or photolysis are processed as shown schematically on Figure 1. The rates of reactions at competing positions are estimated as discussed in Sections III.C through 0, and the products and radicals formed, together with their yields, are logged. Documentation text is generated and logged, as appropriate.
- For each reactive organic radical formed, either in the initial reaction with OH, etc., or through the reactions of a previously formed radical, the system generates the all the reactions that are believed to be potentially important for the radical in the presence of NO_x in air. The radicals and products formed, and their yields (obtained by multiplying the yield of the starting radical times the branching ratios for the reactions forming them) are logged for further processing. Documentation text is also generated and logged for those reactions where estimates are involved. The types of radicals involved, and the reactions the system considers, are as follows:

Figure 1. Flow diagram for the initial reactions of a VOC in the mechanism generation process.



  - <u>Carbon centered (e.g, alkyl) radicals</u>: Reaction with O_2. In most cases this involves formation of the corresponding peroxy radical, but in a few cases (e.g, α-hydroxy alkyl radicals) other reactions can occur. In all cases, only a single reaction pathway is assumed, so the yield of the product(s) are assigned the yield of the starting radical. These reactions are discussed in Section III.H.
  - <u>Peroxy radicals</u> (other than acetyl peroxy): Reaction with NO. This can involve formation of the corresponding alkyl nitrate ($RONO_2$) or formation of NO_2 and the corresponding alkoxy (RO·) radical. The conversion of NO to NO_2 in the latter reaction is logged as the formation of the "NO to NO_2 conversion product". Nitrate yield estimates, discussed in Section III.I, are used to determine the yields of the nitrate, alkoxy radical, and NO to NO_2 conversion products relative to the starting radical.
  - <u>Alkoxy radicals</u>: Reaction with O_2; β-scission decomposition; 1,4-H shift isomerization; or α-ester rearrangement (Tuazon et al, 1998b), when possible. The O_2 reaction involves the formation of HO_2 and a stable product, while the other reactions can involve formation of various carbon-centered radicals, in some cases with stable co-products. Various estimation methods or assignments, discussed in Section III.J are used to derive the relevant rate constants or branching ratios.

  Note that acetyl peroxy radicals (e.g. $RC(O)O_2\cdot$) are treated as product species and their reactions are not generated. This is because they are lumped with generic acyl peroxy radical species in the model (e.g., CCO-O2· or RCO-O2·), so the information obtained by generating their reactions is not used. Note that their ultimate products they form depend (PAN or RC(O)O· decomposition products) depend on environmental conditions and thus cannot be uniquely determined.

- For each "product" species formed, which includes acetyl peroxy radicals, HO_2 and the NO to NO_2 conversion product as well as stable organic products, the yield, structure, and generation (number of NO to NO_2 conversions involved before it is formed) is logged. The lumping assignment for the product (the way it is represented in the base mechanism) is also determined and logged. Lumping assignments are discussed in Section 0.
- Processing is completed once all the reactive radicals have been converted to stable products or radicals whose reactions are not generated (e.g., HO_2 or acyl peroxy radicals). The generated reaction list, product log (list of all products giving yields, structure and lumping), is saved for output or processing.
- Once all the relevant reactions for a VOC have been generated, the overall reactions or mechanistic parameters for the species can be derived, for use in model simulations. The sum of the yields of HO_2 and the NO to NO_2 conversion product in the product log are used to derive the corresponding HO2, RO2-R· and/or R2O2· yields. The yields of the lumped species representing the various organic products are summed to determine their total yields in the overall reaction. Loss or gain of carbon and nitrogens are tracked, and if necessary yields of "lost carbon" or "lost nitrogen" model species are determined to maintain balance.

Note that the system does not generate complete mechanisms for the VOCs, since peroxy + peroxy and peroxy + NO_2 reactions are ignored, and as indicated above acetyl peroxy radical reactions are not generated. However, even if the system generated all the peroxy + peroxy reactions, the current mechanism is not set up to use this information, because of the way the reactions of peroxy radicals are represented (see Section II.B.4). The present mechanism neglects the formation and decompositions of most peroxynitrates because their rapid decompositions at ambient temperatures result in no net reaction, so information on the formation and generation of these species would also be ignored. The current mechanism is also not set up to take advantage of any detailed product information concerning the reactions of individual acyl peroxy radicals and their corresponding PAN analogues. Therefore the present system is sufficient to provide all the information that the current version of the mechanism can use. Expanded capabilities can be added in the future as mechanisms and models that can use them are developed.

B. Specification of Reactants and Summary of Groups

In this section, the method used to specify structures of reactions, and the types of structures that can be represented, are discussed. A knowledge of this is necessary not only for those who wish to use the system, but also because some of the tables given in this report use this method to identify reactants and radicals.

The structure of a reactant VOC or radical is specified by giving the "groups" in the molecule, and indicating which groups they are bonded to. Groups are parts of the molecule that are treated as a unit by the system, and as indicated above are generally the same as the groups used in the structure-reactivity kinetic estimation method of Atkinson and co-workers (Atkinson, 1987; Kwok and Atkinson, 1995; Atkinson, 1997a). The list of groups that can be supported by the present system is given in Table 5 and Table 6. Table 5 shows the groups that can be used for constructing VOC structures to be reacted with OH, etc, and Table 6 shows the groups that can appear in reactive radical and product species that are formed.

If the molecule or radical contains atoms not shown on Table 5 or Table 6, then the reactions of that species cannot be generated by the current system. In addition, there are some groups for which there are insufficient thermochemical group additivity data in the system's thermochemical database to support the data requirements of the estimation methods, which means that reactions of molecules containing those groups usually cannot be generated. Those cases are indicated on. Table 5.

The structures of the molecules are specified as follows. Straight chain structures are given by groups separated by "-" or "=". For example:

Propane: CH3-CH2-CH3
Propionic acid: CH3-CH2-CO-OH
Ethyl acetate: CH3-CH2-O-CO-CH3
ethoxyethanol: HO-CH2-CH2-O-CH2-CH2-O-CH2-CH2-OH

Branched structures are indicated by using ()'s to show groups off to the side. For example:

Isobutane: CH3-CH(CH3)-CH3
3,3-diethyl pentan-2-ol: CH3-CH(OH)-C(CH2-CH3)(CH2-CH3)-CH2-CH3
4-isopropyl heptane: CH3-CH2-CH2-CH(CH(CH3)-CH3)-CH2-CH2-CH3

Cyclic structures are indicated by using a "*" character to mark the group which is used to close the ring. Note that the present system does not support specification of compounds with more than one ring, since no way of indicating such structures is presently defined.

3-methyl furan: *O-CH2-CH(CH3)-CH2-CH2-*

The system presently supports structures with single double bonds between carbon-centered groups only, and may not successfully generate reactions for non-hydrocarbon species with double bonds because of insufficient thermochemical group data in the present database. Double bonds are indicated using a "=" symbol in place of a "-", and *cis* and *trans* configurations are indicated using parentheses, as follows:

Table 5. Listing of groups for stable molecules that can be supported by the present mechanism generation system.

Group	Reactions at Group
Groups for which mechanisms can usually be generated	
-CH3	OH (H- Abstraction)
-CH2-	OH (H- Abstraction)
>CH-	OH (H- Abstraction)
>C<	none
-O-	none
-OH	OH (H- Abstraction)
-CHO	OH, NO_3 (H- Abstaction), hν (HCO..- Bond Scission)
-CO-	hν (CO..- Bond scission)
=CH2	OH, O_3, O^3P, NO_3 (Double Bond Addition)
=CH	OH, O_3, O^3P, NO_3 (Double Bond Addition)
=C<	OH, O_3, O^3P, NO_3 (Double Bond Addition)
Groups for which mechanisms can be generated in some cases	
-ONO2	hν (-O. + NO_2 formation)
Groups for which mechanisms usually cannot be generated	
-F	none
-Cl	none
-Br	none
-I	none
-NO2	none

cis-2-butene: CH3-CH=CH-CH3
trans-2-Hexene: CH3-CH=CH(CH2-CH2-CH3)

Although one can often enter structures in more than one way (for example, both CH3-CH(CH3)-CH2-CH3 and CH3-CH2-CH(CH3)-CH3 are acceptable ways to enter 2-methyl butane), the system uses an algorithm to generate a (usually) unique structure definition string for each structure. This is done so that the structure definition string can be used to determine if two products or intermediate species generated by the system are the same compound. Therefore, the structure specification generated by the system when a new molecule is specified may be slightly different than the one input by the user, though they would refer to the same compound. Note that the current version of the software is not completely finished in this regard, since unique structure definition strings are not always produced for some cyclic compounds. However, this only causes inefficiency in the mechanism generation algorithm, not errors in the generation of the reactions.

In order for the system to be useful for generating mechanisms for a wider variety of compounds, it is also possible to specify *special reactants* whose structures cannot be specified explicitly. Although the system cannot automatically generate reactions for these special reactants, it will accept assignments for their reactions. If the these assigned reactions form products that can be specified with known groups, the system then automatically generate the reactions of these products, thus generating the overall reaction mechanism of the special reactant. The special reactants that are supported in the present system are listed in Table 7

Table 6. Listing of radical center groups and non-reactive product groups that can be supported by the present mechanism generation system.

Group	Reactions at Group
Carbon-Centered Radical centers	
CH3.	O2 -> CH3OO.
-CH2.	O2 -> -CH2OO.
-CH[.]-	O2 -> -CH[OO.]-
>C[.]-	O2 -> >C[OO.]-
HCO.	O2 -> HO2. + CO
-CO.	O2 -> -CO[OO.]
Vinylic Radical centers	
=CH.	X=CH2 + O2 -> X=O + HCO., where X is =CH2, =CH-, or =C<
=C[.]	X=CH[.]- + O2 -> X=O + -C[OO.], where X is =CH2, =CH-, or =C<
Peroxy Radical Centers	
CH3OO.	NO -> CH3O.
-CH2OO.	NO -> -CH2O. + [NO conv NO2], NO -> -CH2-ONO2
-CH[OO.]-	NO -> -CH[O.]- + [NO conv NO2], NO -> -CH(ONO2)-
>C[OO.]-	NO -> >C[O.]- + [NO conv NO2], NO -> >C(ONO2)-
Acyl Peroxy Radical Centers	
-CO[OO.]	Not reacted
Alkoxy radical Centers	
CH3O.	O2 -> HO2 + HCHO
-CH2O.	O2 -> HO2 + -CHO, Decomposition, 1,5-H-shift isom, Ester rearrangement
-CH[O.]-	O2 -> HO2 + -CO-, Decomposition, 1,5-H shift isom, Ester rearrangement
>C[O.]-	Decomposition, 1,5-H shift isom.
HCO2.	O2 -> HO2 + CO2
-CO2.	Decomposition to R. + CO2
Carbene Radical Centers	
CH2:	O2 -> CH2OO[excited]
-CH:	O2 -> -CHOO[excited]
-C[:]-	O2 -> COO[excited]
Excited Crigiee Biradical Centers	
CH2OO[excited]	Various unimolecular reactions -- see text
-CHOO[excited]	Various unimolecular reactions -- see text
-COO[excited]-	Various unimolecular reactions -- see text
Stabilized Crigiee Biradical Centers	
CH2OO[stab]	Not reacted
-CHOO[stab]	Not reacted
-COO[stab]-	Not reacted
Elementary Product Groups	
CH4	Not reacted (elementary product)
HCHO	Not reacted (elementary product)
CO	Not reacted (elementary product)
CO2	Not reacted (elementary product)
NO2	Not reacted (elementary product)
[NO conv NO2]	Used for Mechanism Processing

Table 7. Special reactants that are presently supported as reactants or products in the mechanism generation system

Reactant	Designation	Reactions Supported
1,3-Butadiene	CH2=CH-CH=CH2	OH, O_3, O^3P, NO_3 (Double Bond Addition)
Isoprene	CH2=CH-C(CH3)=CH2	OH, O_3, O^3P, NO_3 (Double Bond Addition)
Acetylene	HC::CH	OH, O_3
Methyl Acetylene	HC::C-CH3	OH, O_3
1-Butyne	HC::C-CH2-CH3	OH, O_3
2-Butyne	CH3-C::C-CH3	OH, O_3
3-Methyl Furan	*O-CH=C(CH3)-CH=CH-*	Product only (formed from isoprene)

C. Reactions with OH Radicals

Reactions with OH radicals can occur by two mechanisms, depending on whether the group has a double bond or an abstractable hydrogen. If the group has an abstractable hydrogen, the reaction is

$$XH + OH \rightarrow X\cdot + H2O \qquad \text{(abstraction)}$$

where XH is any H-containing group and X· is the corresponding depending on whether the compound. If the group has a double bond, the reaction is

$$>C=C< + OH \rightarrow >C(OH)\text{-}C[\cdot]\text{-} \qquad \text{(addition)}$$

Note that two reactions are generated for each double bond, one where the OH adds to each side of the bond. (If the reactions are equivalent, as would be the case for symmetrical molecules, they are combined after they are generated – the system uses the products formed to determine equivalency.) For each molecule that reacts with OH, one reaction is generated for each group in the molecule that can react in this way. The fractions reacted at the various group are determined from the ratio of the estimated rate constant at each group, divided by the total of the estimated rate constants for all groups. The group rate constants are estimated as discussed below.

1. Assigned Total OH Radical Rate Constants

Total OH radical rate constants have been measured for many (indeed most) of the VOCs in the current mechanism, and in those cases assigned rate constants are used when generating the mechanisms rather than estimated values. Table 8 gives the OH radical rate constants assigned to all VOCs in the current mechanism, along with references and notes indicating the basis for the assignment. Most of the rate constants are based on recommendations by Atkinson (1989, 1994, 1997a). For completeness, this table has the rate constants for all VOCs in the current mechanism for which such assignments have been made, including those (e.g., aromatics and terpenes) whose mechanisms cannot be generated by the current system. For VOCs whose OH reactions can be automatically generated by the system, the table also shows the estimated T=300K rate constants, which were derived as discussed in the following section. The percentage differences between the assigned and estimated values are also shown.

Table 8. Rate constant and temperature dependence parameter assignments used for reactions of VOCs with OH radicals in the present mechanism.

Compound	DMS name	k(300)	A	B	Ea	Ref	Est'd k(300)	
		(cm^3 molec^{-1} s^{-1})			kcal/mole		k	(diff)
Alkanes								
Ethane	ETHANE	2.60e-13	1.37e-12	2.0	0.990	1	2.78e-13	7%
Propane	PROPANE	1.14e-12	1.40e-12	2.0	0.121	1	1.28e-12	12%
n-Butane	N-C4	2.47e-12	1.52e-12	2.0	-0.288	1	2.65e-12	7%
n-Pentane	N-C5	4.04e-12	2.20e-12	2.0	-0.364	1	4.07e-12	1%
n-Hexane	N-C6	5.47e-12	1.38e-12	2.0	-0.823	1	5.49e-12	0%
n-Heptane	N-C7	7.04e-12	1.43e-12	2.0	-0.950	1	6.91e-12	-2%
n-Octane	N-C8	8.76e-12	2.48e-12	2.0	-0.751	1	8.33e-12	-5%
n-Nonane	N-C9	1.00e-11	2.26e-12	2.0	-0.888	1	9.75e-12	-3%
n-Decane	N-C10	1.13e-11	2.82e-12	2.0	-0.827	1	1.12e-11	-1%
n-Undecane	N-C11	1.29e-11				1	1.26e-11	-2%
n-Dodecane	N-C12	1.39e-11				1	1.40e-11	1%
n-Tridecane	N-C13	1.60e-11				1	1.54e-11	-4%
n-Tetradecane	N-C14	1.80e-11				1	1.69e-11	-6%
n-Pentadecane	N-C15	2.10e-11				1	1.83e-11	-13%
n-C16	N-C16	2.30e-11				1	1.97e-11	-14%
Isobutane	2-ME-C3	2.21e-12	1.04e-12	2.0	-0.447	1	2.45e-12	11%
Iso-Pentane	2-ME-C4	3.70e-12				1	4.05e-12	9%
Neopentane	22-DM-C3	8.63e-13	1.62e-12	2.0	0.376	1	6.83e-13	-21%
2-Methyl Pentane	2-ME-C5	5.30e-12				1	5.47e-12	3%
3-Methylpentane	3-ME-C5	5.40e-12				1	5.75e-12	6%
2,3-Dimethyl Butane	23-DM-C4	5.79e-12	1.12e-12	2.0	-0.982	1	5.45e-12	-6%
2,2-Dimethyl Butane	22-DM-C4	2.38e-12	3.22e-11		1.552	1	1.84e-12	-23%
2,2-Dimethyl Pentane	22-DM-C5	3.40e-12				1	3.26e-12	-4%
2,4-Dimethyl Pentane	24-DM-C5	5.00e-12				1	6.87e-12	37%
2,2,3-Trimethyl Butane	223TM-C4	4.25e-12	7.61e-13	2.0	-1.025	1	3.24e-12	-24%
2,2,3,3-Tetrame. Butane	2233M-C4	1.06e-12	1.72e-12	2.0	0.286	1	1.02e-12	-4%
2,2,4-Trimethyl Pentane	224TM-C5	3.60e-12	1.87e-12	2.0	-0.389	1	4.66e-12	30%
2,3,4-Trimethyl Pentane	234TM-C5	7.10e-12				1	8.55e-12	20%
2,2-Dimethyl Hexane	22-DM-C6	4.80e-12				1	4.68e-12	-2%
2,3,5-Trimethyl Hexane	235TM-C6	7.90e-12				1	9.97e-12	26%
3,3-Diethyl Pentane	33-DE-C5	4.90e-12				1	5.31e-12	8%
2-Methyl Octane	2-ME-C8	1.01e-11				1	9.73e-12	-4%
4-Methyl Octane	4-ME-C8	9.70e-12				1	1.00e-11	3%
3,4-Diethyl Hexane	34-DE-C6	7.40e-12				2	1.25e-11	69%
2-Methyl Nonane	2-ME-C9	1.28e-11				3	1.12e-11	-12%
2,6-Dimethyl Octane	26DM-C8	1.29e-11				3	1.14e-11	-12%
Cyclopropane	CYCC3	8.40e-14				1	8.52e-14	1%
Cyclobutane	CYCC4	1.50e-12				1	1.59e-12	6%
Cyclopentane	CYCC5	5.06e-12	2.31e-12	2.0	-0.467	1	4.54e-12	-10%
Isopropyl Cyclopropane	IPR-CC3	2.70e-12				1	2.86e-12	6%
Cyclohexane	CYCC6	7.26e-12	2.59e-12	2.0	-0.614	1	8.52e-12	17%
Cycloheptane	CYCC7	1.30e-11				1	9.94e-12	-24%

Table 8 (continued)

Compound	DMS name	k(300)	A	B	Ea	Ref	Est'd k(300)	
		(cm^3 molec^{-1} s^{-1})			kcal/mole		k	(diff)
Methylcyclohexane	ME-CYCC6	1.00e-11				1	1.02e-11	2%
Cyclooctane	CYCC8	1.40e-11				1	1.14e-11	-19%
1,1,3-Trimethyl Cyclohex.	113MCYC6	8.70e-12				1	9.12e-12	5%
Hexyl Cyclohexane	C6-CYCC6	1.78e-11				4	1.77e-11	-1%
<u>Alkenes</u>								
Ethene	ETHENE	8.43e-12	1.96e-12		-0.870	1	8.44e-12	0%
Propene	PROPENE	2.60e-11	4.85e-12		-1.002	1	3.16e-11	21%
1-Butene	1-BUTENE	3.11e-11	6.55e-12		-0.928	1	3.16e-11	2%
3-Methyl-1-Butene	3M-1-BUT	3.14e-11	5.32e-12		-1.059	1	3.16e-11	1%
1-Pentene	1-PENTEN	3.11e-11	5.86e-12		-0.994	5	3.16e-11	2%
1-Hexene	1-HEXENE	3.66e-11	6.91e-12		-0.994	5	3.16e-11	-14%
3,3-Dimethyl-1-Butene	33M1-BUT	2.77e-11	5.23e-12		-0.994	5	3.16e-11	14%
1-Heptene	1-HEPTEN	3.96e-11	7.47e-12		-0.994	5	3.16e-11	-20%
Isobutene	ISOBUTEN	5.09e-11	9.47e-12		-1.002	1	5.79e-11	14%
2-Methyl-1-Butene	2M-1-BUT	6.04e-11	1.14e-11		-0.994	5	5.79e-11	-4%
2-Methyl-1-Pentene	2M1-C5E	6.23e-11	1.18e-11		-0.994	5	5.79e-11	-7%
trans-2-Butene	T-2-BUTE	6.32e-11	1.01e-11		-1.093	1	6.34e-11	0%
cis-2-Butene	C-2-BUTE	5.58e-11	1.10e-11		-0.968	1	6.34e-11	14%
2-Methyl-2-Butene	2M-2-BUT	8.60e-11	1.92e-11		-0.894	1	8.71e-11	1%
trans-2-Pentene	T-2-PENT	6.63e-11	1.25e-11		-0.994	5	6.34e-11	-4%
cis-2-Pentene	C-2-PENT	6.43e-11	1.21e-11		-0.994	5	6.34e-11	-1%
2,3-Dimethyl-2-Butene	23M2-BUT	1.09e-10	2.05e-11		-0.994	5	1.05e-10	-4%
Trans 4-Methyl-2-Hexene	T4M2-C5E	6.04e-11	1.14e-11		-0.994	5	6.34e-11	5%
2-Methyl-2-Pentene	2M-2-C5E	8.81e-11	1.66e-11		-0.994	5	8.71e-11	-1%
2,3-Dimethyl-2-Hexene	23M2-C5E	1.02e-10	1.92e-11		-0.994	5	1.05e-10	3%
Trans 4,4-dimethyl-2-Hexene	T44M2C5E	5.44e-11	1.03e-11		-0.994	5	6.34e-11	16%
Trans-2-Heptene	T-2-C7E	6.73e-11	1.27e-11		-0.994	5	6.34e-11	-6%
Trans-4-Octene	T-4-C8E	6.83e-11	1.29e-11		-0.994	5	6.34e-11	-7%
Cyclopentene	CYC-PNTE	6.63e-11	1.25e-11		-0.994	5	6.34e-11	-4%
Cyclohexene	CYC-HEXE	6.70e-11	1.26e-11		-0.994	5	6.34e-11	-5%
1,3-Butadiene	13-BUTDE	6.59e-11	1.48e-11		-0.890	1		
Isoprene	ISOPRENE	1.00e-10	2.55e-11		-0.815	1		
3-Carene	3-CARENE	8.71e-11	1.64e-11		-0.994	5		
Sabinene	SABINENE	1.16e-10	2.19e-11		-0.994	5		
b-Pinene	B-PINENE	7.82e-11	2.38e-11		-0.709	1		
d-Limonene	D-LIMONE	1.69e-10	3.19e-11		-0.994	5		
a-Pinene	A-PINENE	5.31e-11	1.21e-11		-0.882	1		
Styrene	STYRENE	5.80e-11				1		
2-(Cl-methyl)-3-Cl-Propene	CL2IBUTE	3.16e-11				1		
<u>Aromatics</u>								
Benzene	BENZENE	1.24e-12	2.47e-12		0.411	6		
Toluene	TOLUENE	5.91e-12	1.81e-12		-0.705	6		

Table 8 (continued)

Compound	DMS name	k(300)	A	B	Ea	Ref	Est'd k(300)	
		(cm^3 molec^{-1} s^{-1})			kcal/mole		k	(diff)
Ethyl Benzene	C2-BENZ	7.10e-12				6		
n-Propyl Benzene	N-C3-BEN	6.00e-12				6		
Isopropyl Benzene (cumene)	I-C3-BEN	6.50e-12				6		
s-Butyl Benzene	S-C4-BEN	6.00e-12				7		
m-Xylene	M-XYLENE	2.36e-11	2.36e-11		0.000	6		
o-Xylene	O-XYLENE	1.37e-11	1.37e-11		0.000	6		
p-Xylene	P-XYLENE	1.43e-11	1.43e-11		0.000	6		
1,2,4-Trimethyl Benzene	124-TMB	3.25e-11	3.25e-11		0.000	6		
1,3,5-Trimethyl Benzene	135-TMB	5.75e-11	5.75e-11		0.000	6		
1,2,3-Trimethyl Benzene	123-TMB	3.27e-11	3.27e-11		0.000	6		
Indan	INDAN	9.20e-12				8		
Naphthalene	NAPHTHAL	2.12e-11	1.07e-12		-1.779	6		
Tetralin	TETRALIN	3.43e-11				9		
1-Methyl Naphthalene	1ME-NAPH	5.30e-11				10		
2-Methyl Naphthalene	2ME-NAPH	5.23e-11				11		
Methyl Naphthalenes	ME-NAPH	5.20e-11				12		
2,3-Dimethyl Naphth.	23-DMN	7.68e-11				11		
Phenol	PHENOL	2.63e-11				6		
o-Cresol	O-CRESOL	4.20e-11				6		
m-Cresol	M-CRESOL	6.40e-11				6		
p-Cresol	P-CRESOL	4.70e-11				6		
Nitrobenzene	NO2-BENZ	1.50e-13				13		
Monochlorobenzene	CL-BEN	7.70e-13				6		
p-Dichlorobenzene	CL2-BEN	5.55e-13				14		
Benzotrifluoride	CF3-BEN	4.60e-13				15		
p-Trifluoromethyl-Cl-Benzene	PCBTF	2.40e-13				15		
Alkynes								
Acetylene	ACETYLEN	9.12e-13	9.40e-12		1.391	16		
Methyl Acetylene	ME-ACTYL	5.90e-12				16		
Ethyl Acetylene	ET-ACTYL	8.00e-12				16		
2-Butyne	2-BUTYNE	2.72e-11	1.00e-11		-0.596	16		
Alchohols and Glycols								
Methanol	MEOH	9.34e-13	3.10e-12		0.715	17	6.25e-13	-33%
Ethanol	ETOH	3.28e-12	5.56e-13		-1.057	17	3.61e-12	10%
Isopropyl Alcohol	I-C3-OH	5.32e-12	6.49e-13		-1.254	16	7.26e-12	37%
n-Propyl Alcohol	N-C3-OH	5.53e-12				16	5.51e-12	0%
t-Butyl Alcohol	T-C4-OH	1.13e-12	3.86e-13		-0.640	18	6.87e-13	-39%
n-Butyl Alcohol	N-C4-OH	8.57e-12				16	6.93e-12	-19%
Cyclopentanol	CC5-OH	1.07e-11				19	1.03e-11	-4%
Pentyl Alcohol	C5OH	1.11e-11				16	8.35e-12	-25%
2-Pentanol	2-C5OH	1.18e-11				19	1.14e-11	-3%
3-Pentanol	3-C5OH	1.22e-11				19	1.30e-11	7%

Table 8 (continued)

Compound	DMS name	k(300)	A	B	Ea	Ref	Est'd k(300)	
		(cm^3 molec^{-1} s^{-1})			kcal/mole		k	(diff)
2-Hexanol	2-C6OH	1.21e-11				19	1.28e-11	6%
1-Hexanol	1-C6OH	1.25e-11				16	9.78e-12	-22%
1-Heptanol	1-C7OH	1.37e-11				16	1.12e-11	-18%
1-Octanol	1-C8-OH	2.02e-11				20	1.26e-11	-38%
2-Octanol	2-C8-OH	2.52e-11				20	1.56e-11	-38%
3-Octanol	3-C8-OH	3.14e-11				20	1.73e-11	-45%
4-Octanol	4-C8-OH	2.87e-11				20	1.73e-11	-40%
Ethylene Glycol	ET-GLYCL	1.47e-11				21	8.38e-12	-43%
Propylene Glycol	PR-GLYCL	2.15e-11				21	1.28e-11	-40%
<u>Ethers and Glycol Ethers</u>								
Dimethyl Ether	ME-O-ME	3.01e-12	1.04e-11		0.739	16	2.30e-12	-24%
Trimethylene Oxide	TME-OX	1.03e-11				22	5.76e-12	-44%
Dimethoxy methane	METHYLAL	4.90e-12				52	6.69e-11	large
Tetrahydrofuran	THF	1.61e-11				16	1.41e-11	-12%
Diethyl Ether	ET-O-ET	1.31e-11	8.02e-13		-1.663	16	1.59e-11	22%
Alpha-Methyltetrahydrofuran	AM-THF	2.20e-11	2.52e-12		-1.292	23	2.08e-11	-5%
Tetrahydropyran	THP	1.38e-11				22	2.34e-11	70%
Methyl n-Butyl Ether	MNBE	1.48e-11				16	1.35e-11	-9%
Methyl t-Butyl Ether	MTBE	2.94e-12	5.89e-13		-0.960	16	1.66e-12	-44%
Ethyl t-Butyl Ether	ETBE	8.84e-12				16	8.48e-12	-4%
Di n-Propyl Ether	PR-O-PR	1.84e-11	1.18e-12		-1.639	16	2.18e-11	18%
Ethyl n-Butyl Ether	ENBE	2.13e-11				16	2.03e-11	-5%
Methyl t-Amyl Ether	MTAE	7.91e-12				19	2.82e-12	-64%
Di-n-butyl Ether	BU-O-BU	2.88e-11				16	2.46e-11	-15%
Di-Isobutyl Ether	IBU2-O	2.60e-11				24	2.46e-11	-5%
Di-n-Pentyl Ether	C5-O-C5	3.47e-11				25	2.75e-11	-21%
2-Methoxy-Ethanol	MEO-ETOH	1.33e-11	4.50e-12		-0.646	22	1.49e-11	12%
1-Methoxy-2-Propanol	MEOC3OH	2.00e-11				26	1.93e-11	-3%
2-Ethoxy-Ethanol	ETO-ETOH	1.87e-11				27	2.17e-11	16%
3-Ethoxy-1-Propanol	3ETOC3OH	2.20e-11				22	2.31e-11	5%
3-Methoxy-1-Butanol	3MEOC4OH	2.36e-11				22	2.67e-11	13%
2-Butoxy-Ethanol	BUO-ETOH	2.57e-11				28	2.61e-11	2%
2-(2-Ethoxyethoxy) EtOH	CARBITOL	5.08e-11				29	4.09e-11	-19%
<u>Esters</u>								
Methyl Formate	ME-FORM	2.27e-13				30	1.25e-13	-45%
Ethyl Formate	ET-FORM	1.02e-12				30	1.02e-12	0%
Methyl Acetate	ME-ACET	3.49e-13	8.30e-13		0.517	30	2.65e-13	-24%
Methyl Propionate	ME-PRAT	1.03e-12				30	6.87e-13	-33%
n-Propyl Formate	C3-FORM	2.38e-12				30	2.37e-12	0%
Ethyl Acetate	ET-ACET	1.60e-12				6	1.72e-12	7%

Table 8 (continued)

Compound	DMS name	k(300)	A	B	Ea	Ref	Est'd k(300)	
		(cm^3 molec^{-1} s^{-1})			kcal/mole		k	(diff)
Ethyl Propionate	ET-PRAT	2.14e-12				30	2.14e-12	0%
n-Butyl Formate	C4-FORM	3.12e-12				30	3.79e-12	21%
Methyl Butyrate	ME-BUAT	3.04e-12				30	1.91e-12	-37%
Propyl Acetate	PR-ACET	3.40e-12				6	3.21e-12	-6%
Isopropyl Acetate	IPR-ACET	3.40e-12				6	3.48e-12	2%
Methyl Isobutyrate	ME-IBUAT	1.73e-12				31	1.17e-12	-32%
t-Butyl Acetate	TBU-ACET	4.25e-13				32	5.56e-13	31%
s-Butyl Acetate	SBU-ACET	5.50e-12				6	5.34e-12	-3%
n-Propyl Propionate	PR-PRAT	4.02e-12				30	3.64e-12	-9%
Ethyl Butyrate	ET-BUAT	4.94e-12				30	3.36e-12	-32%
n-Butyl Acetate	BU-ACET	4.20e-12				6	4.63e-12	10%
n-Propyl Butyrate	PR-BUAT	7.41e-12				30	4.86e-12	-34%
n-Butyl Butyrate	BU-BUAT	1.06e-11				30	6.28e-12	-41%
Propylene Carbonate	PC	6.90e-13				33	3.79e-12	449%
Methyl Lactate	ME-LACT	2.76e-12				34	2.67e-12	-3%
Ethyl Lactate	ET-LACT	3.91e-12				34	4.12e-12	5%
Pr. Glycol Methyl Ether Acetate	PGME-ACT	1.44e-11				20	1.47e-11	2%
Dimethyl Succinate	DBE-4	1.50e-12				35	1.17e-12	-22%
Dimethyl Glutarate	DBE-5	3.50e-12				35	2.59e-12	-26%
Dimethyl Adipate	DBE-6	8.80e-12				35	4.01e-12	-54%
<u>Oxides</u>								
Ethylene Oxide	ETOX	7.60e-14				6	3.83e-13	404%
Propylene Oxide	PROX	5.20e-13				6	7.57e-13	46%
1,2-Epoxybutane	12BUOX	1.91e-12				36	2.00e-12	5%
<u>Acids</u>								
Formic Acid	FORMACID	4.50e-13	4.50e-13		0.000	6		
Acetic Acid	ACETACID	8.00e-13				16	2.10e-13	-74%
Propionic Acid	PROPACID	1.16e-12				16	1.34e-12	16%
<u>Aldehydes</u>								
Acetaldehyde	ACETALD	1.57e-11	5.60e-12		-0.616	37	1.58e-11	0%
Propionaldehyde	PROPALD	2.00e-11				37	2.01e-11	1%
2-Methylpropanal	2MEC3AL	2.60e-11	6.61e-12		-0.817	6	2.10e-11	-19%
Butanal	1C4RCHO	2.33e-11	5.26e-12		-0.886	6	2.14e-11	-8%
Pentanal	1C5RCHO	2.82e-11	6.34e-12		-0.890	6	2.28e-11	-19%
2,2-Dimethylpropanal (pivaldehyde)	22DMC3AL	2.63e-11	6.82e-12		-0.805	6	1.97e-11	-25%
3-Methylbutanal	3MC4RCHO	2.74e-11				6	2.28e-11	-17%
Acrolein	ACROLEIN	1.99e-11				6	3.16e-11	59%
Crotonaldehyde	CROTALD	3.64e-11				38	6.34e-11	74%
Methacrolein	METHACRO	3.33e-11	1.86e-11		-0.348	39	5.79e-11	74%
Hydroxy Methacrolein	HOMACR	4.30e-11				40	5.79e-11	35%

Table 8 (continued)

Compound	DMS name	k(300)	A	B	Ea	Ref	Est'd k(300)	
		(cm^3 molec^{-1} s^{-1})			kcal/mole		k	(diff)
Isoprene Product #1	IP-MHY1	7.00e-11				40	8.71e-11	24%
Isoprene Product #2	IP-MHY2	7.00e-11				40	8.71e-11	24%
Isoprene Product #3	IP-HMY	7.00e-11				40	8.71e-11	24%
<u>Ketones</u>								
Acetone	ACETONE	2.22e-13	2.80e-12		1.510	37	2.09e-13	-6%
Cyclobutanone	CC4-KET	8.70e-13				41	4.42e-12	408%
Methyl Ethyl Ketone	MEK	1.20e-12	1.30e-12		0.050	17	1.35e-12	13%
Cyclopentanone	CC5-KET	2.94e-12				41	6.83e-12	132%
3-Pentanone	DEK	2.00e-12				6	2.49e-12	25%
2-Pentanone	MPK	4.56e-12				42	4.78e-12	5%
Cyclohexanone	CC6-KET	6.39e-12				41	1.21e-11	89%
Methyl t-Butyl Ketone	MTBK	1.21e-12				43	1.72e-12	42%
4-Methyl-2-Pentanone	MIBK	1.41e-11				6	8.82e-12	-37%
Methyl n-Butyl Ketone	MNBK	9.10e-12				6	6.77e-12	-26%
Di-Isopropyl Ketone	DIPK	5.38e-12				44	5.07e-12	-6%
2-Heptanone	C7-KET-2	1.17e-11				42	8.19e-12	-30%
2-Octanone	C8-KET-2	1.10e-11				43	9.61e-12	-13%
2-Nonanone	C9-KET-2	1.22e-11				43	1.10e-11	-10%
Di-isobutyl ketone (2,6-dimethyl- 4-heptanone	DIBK	2.75e-11				6	1.74e-11	-37%
2-Decanone	C10-K-2	1.32e-11				43	1.24e-11	-6%
Methylvinyl ketone	MVK	1.87e-11	4.14e-12		-0.900	6	3.16e-11	69%
<u>Other Oxygenates</u>								
Hydroxy Acetone	HOACET	3.02e-12				22	3.11e-12	3%
Methoxy Acetone	MEOACET	6.77e-12				22	7.11e-12	5%
<u>Nitrogen-Containing Compounds</u>								
N-Methyl-2-Pyrrolidone	NMP	2.15e-11				33		
Ethyl Amine	ET-AMINE	2.76e-11	1.47e-11		-0.376	6		
Dimethyl Amine	DM-AMINE	6.58e-11	2.89e-11		-0.491	6		
Trimethyl Amine	TM-AMINE	6.07e-11	2.62e-11		-0.501	6		
Methyl Nitrite	ME-NITRT	2.20e-13				16		
Ethanolamine	ETOH-NH2	3.15e-11				45		
Diethanol Amine	ETOH2-NH	9.37e-11				46		
Triethanolamine	ETOH3-N	1.16e-10				47		
Toluene Diisocyanate	TDI	7.40e-12				48		
Para Toluene Isocyanate	P-TI	5.90e-12				49		
Methylene Diphenylene Diisocyanate	MDI	1.18e-11				50		
<u>Halogen-Containing Compounds</u>								
Methyl Chloride	CH3-CL	4.48e-14	3.15e-13	2.0	1.163	16		
Dichloromethane	CL2-ME	1.45e-13	7.69e-13	2.0	0.994	6		

Table 8 (continued)

Compound	DMS name	k(300)	A	B	Ea	Ref	Est'd k(300)	
		(cm^3 molec^{-1} s^{-1})			kcal/mole		k	(diff)
Methyl Bromide	ME-BR	4.12e-14	2.34e-13	2.0	1.035	6		
Chloroform	CHCL3	1.06e-13	5.67e-13	2.0	1.002	6		
Ethyl Chloride	C2-CL	4.18e-13	6.94e-13	2.0	0.302	16		
Ethylene Dichloride	12CL2-C2	2.53e-13	9.90e-13	2.0	0.813	16		
1,1-Dichloroethane	11CL2-C2	2.60e-13				6		
1,1,2-Trichloroethane	112CL3C2	2.00e-13	4.00e-13	2.0	0.413	16		
1,1,1-Trichloroethane	111-TCE	1.24e-14	5.33e-13	2.0	2.244	6		
Ethyl Bromide	C2-BR	3.08e-13	2.72e-11		2.671	6		
Ethylene Dibromide	11BR2-C2	2.27e-13	9.27e-13	2.0	0.839	16		
n-Propyl Bromide	C3-BR	1.18e-12				51		
n-Butyl Bromide	C4-BR	2.46e-12				51		
Vinyl Chloride	CL-ETHE	6.90e-12	1.69e-12		-0.839	16		
Trans-1,2-Dichloroethene	T-12-DCE	2.32e-12	1.01e-12		-0.497	16		
Trichloroethylene	CL3-ETHE	2.34e-12	5.63e-13		-0.849	16		
Perchloroethylene	CL4-ETHE	1.71e-13	9.64e-12		2.403	16		
Sulfur-Containing Compounds								
Dimethyl Sulfide	DMS	4.85e-12	1.13e-11		0.505	16		
Dimethyl Sulfoxide	DMSO	6.20e-11				6		
Silicon-Containing Compounds								
Hexamethyldisiloxane	SI2OME6	1.38e-12				6		
Hydroxymethyldisiloxane'	SI2OMEOH	1.89e-12				6		
D4 Cyclosiloxane	(SIOME)4	1.00e-12				6		
D5 Cyclosiloxane	(SIOME)5	1.55e-12				6		

References

1 Rate constant expression recommended by Atkinson (1997a)
2 Atkinson et al, paper in preparation (1999b)
3 Carter et al (1999d)
4 Room temperature rate constant from Carter et al (1999b).
5 T=298K rate constant recommended by Atkinson (1997a). Temperature dependence estimated based on data for similar alkenes.
6 Rate constant expression recommended by Atkinson (1989). Recommendation not changed in evaluation update by Atkinson (1994).
7 Assumed to have same rate constant as n-propyl benzene
8 Rate constant from Baulch et al (1989).
9 Rate constant from Atkinson and Aschmann (1988a)
10 Rate constant from Atkinson and Aschmann (1987).
11 Rate constant from Atkinson and Aschmann (1986).
12 Rate constant based on average of values for 1- and 2- isomers tabulated by Atkinson (1989).

Table 8 (continued)

References (continued)

13 Rate constant based on data tabulated by Atkinson (1989) and consistent with more recent measurement given by Atkinson (1994).

14 Rate constant from average of values for o-, m- and p- isomers tabulated by Atkinson (1989).

15 Rate constant from Atkinson et al (1985).

16 Rate constant expression recommended by Atkinson (1994)

17 Rate expression recommended by IUPAC panel (Atkinson et al, 1999a).

18 Rate constant used is Atkinson (1989) recommendation. k=8.1e-13 from Saunders et al (1994) not used because problems reported. k=1.43e-12 from Tuazon and co-workers (Carter et al, 1986c) does not fit chamber results (Carter et al, 1986c).

19 Rate constant from Wallington et al (1988a).

20 Rate constant from Carter et al (1999a).

21 Rate constant from Aschmann and Atkinson (1998).

22 Rate constant from Daguat et al (1988a).

23 Rate constant from Wallington et al (1990).

24 Rate constant from Bennett and Kerr (1989).

25 Rate constant from Wallington et al (1988b).

26 Average of values of Porter et al (1995) and Aschmann and Atkinson (1998)

27 Rate constant of Dagaut et al (1988a) used. Value of Hartmann et al (1986) not consistent with chamber data (Carter et al, 1993a)

28 Average of values of Dagaut et al (1988a), Stemmler et al (1996) and Aschmann and Atkinson (1998), as tabulated by Aschmann and Atkinson (1997).

29 Rate constant from Carter et al (1993a).

30 Rate constant from Wallington et al (1988d).

31 Rate constant from Wells et al. (1999).

32 Rate constant from Smith et al (1992). Average of values relative to propane and n-butane

33 Rate constant from Carter et al (1996c).

34 Rate constant from Atkinson and Carter (1995).

35 Rate constant from Carter et al (1997e).

36 Rate constant from Wallington et al (1988c).

37 Rate expression recommended by IUPAC panel (Atkinson et al, 1997a).

38 Rate constant from Atkinson et al (1983).

39 See Carter and Atkinson (1996) and references therein.

40 Rate constant estimated by Carter and Atkinson (1996).

41 Rate constant from Daguat et al (1988b).

42 Atkinson et al, paper in preparation (1999c)

43 Rate constant from Wallington and Kurylo (1987).

44 Rate constant from Atkinson et al (1982).

45 Rate constant estimated from the 298K rate constant for ethylamine and the difference between estimated rates of reaction at -CH3 or -CH2OH derived using the group-additivity methods of Kwok and Atkinson (1995).

46 Rate constant estimated by adding 2 times the difference between the rate constant for ethylene glycol and ethanol to the rate constant for dimethylamine.

Table 8 (continued)

References (continued)

47 Rate constant estimated by adding 3 times the difference between the rate constant for ethylene glycol and ethanol to the rate constant for trimethylamine.

48 Becker et al (1988)

49 Carter et al (1999g)

50 Estimated to have a rate constant that it twice that of pare-toluene isocyanate, based on the structure of the molecule (Carter et al, 1999g).

51 Donaghy et al. (1993)

52 Rate constant used is average of various measurements tabulated by Sidebottom et al (1997).

2. Estimation of OH Abstraction Rate Constants

Group rate constants for OH abstraction reactions are estimated using the group additivity method developed by Atkinson (1987), as updated by Kwok and Atkinson (1995), Kwok et al (1996) and in this work. The rate constant for the reaction of OH at any group is a function of the group and the groups bonded to it (the “neighbor groups”), and is derived from the equation

$$\mathrm{k(OH + group) = k(group)} \prod^{\text{neighbor groups}} \mathrm{F(neighbor\ group)} \tag{I}$$

where “k(group)” is the rate constant for OH reaction at the group if it were only bonded to methyl radicals, and “F(neighbor group)” is the substitutent correction factor for a neighbor group. The group rate constants and the currently implemented in the mechanism estimation system is given in Table 9. As indicated in the footnotes to the table, most of the group rate constants and correction factors were obtained from Kwok and Atkinson (1995), with one updated value from Kwok et al (1996) and with a few gaps filled in this work. Note that in some cases, the correction factor depends not only on the neighbor group but also the next nearest neighbor; these modified groups are referred to as “subgroups” on the table. Note also that formate -CHO groups are treated as separate groups as aldehyde -CHO for the purpose of OH rate constant estimates. This is because OH abstraction reaction appears to be essentially negligible for the former, but very rapid for the latter.

If the compound has a C=C double bond anywhere in the molecule, at present the system assumes the abstraction reactions from any H-containing group are all negligible compared to the addition to the C=C double bond, and the abstraction rate constant is set at zero. Although methods exist for estimating these abstraction rate constants (Kwok and Atkinson, 1997), it is currently necessary to make this approximation because general methods for generating and estimating the rates of all the possible reactions of the unsaturated radicals formed in these reactions have not yet been developed. Ignoring these abstraction reactions from unsaturated compounds is not a bad approximation for smaller molecules such as propene and the butenes, and all known mechanisms currently used in atmospheric models incorporate this approximation. However, abstraction at groups away from the double bonds can become non-negligible for the larger alkenes (see Atkinson, 1997a and references therein), so this approximation should be removed once methods to generate and estimate reactions of unsaturated radicals are developed.

Table 9. Group rate constants and substitutent factors used to estimate OH radical abstraction rate constants.

k(group) = A T^B $e^{-D/T}$ (cm^3 $molec^{-1}$ s^{-1})						F(group)		F(subgroup)		
Group	k(298)	A	B	D	Ref	F	Ref	Subgroup	F	Ref
-CH3	1.36e-13	4.49e-18	2	320	a	1.00	a			
-CH2-	9.34e-13	4.50e-18	2	-253	a	1.23	a	-CH2(CO-)	3.90	a
								-CH2(CO-O-)	1.23	a
								-CH2(F)	0.61	a
								-CH2(Cl)	0.36	a
								-CH2(Br)	0.46	a
>CH-	1.95e-12	2.12e-18	2	-696	a	1.23	a	-CH(CO-)-	3.90	a
								-CH(CO-O-)-	1.23	a
								-CH(F)-	0.21	a
								-CH(Cl)-	0.36	a
								-CH(Br)-	0.46	a
>C<						1.23		>C(CO-)-	3.90	a
								>C(CO-O-)-	1.23	a
								>C(F)-	0.21	a
								>C(Cl)-	0.36	a
								>C(Br)-	0.46	a
-O-						8.40	a	-O(CO-)	1.60	a
								-O(CHO)-	0.90	e
								-O(NO2)-	0.04	a
-OH	1.40e-13	2.10e-18	2	85	a	3.50	a			
-CHO	1.58e-11	5.55e-12	0	-311	b	0.75	a			
HCO(O)-	0.00e+00				c	-				
-CO-						0.75	a	-CO(O-)	0.31	d
-ONO2						0.04	a			
-F						0.09	a			
-Cl						0.38	a			
-Br						0.28	a			
-I						0.53	a			
-NO2						0.00	a			

References

a Kwok and Atkinson (1995)

b Based on kOH for acetaldehyde (Atkinson et al, 1997a, 1999)

c Reaction at formate group assumed to be negligible based on low OH + formate rate constants (Atkinson, 1989)

d Updated value from Kwok et al (1996)

e Adjusted to fit experimental kOH's for ethyl and methyl formate. (Does not work well for methyl formate, but assigned kOH is used for that compound.)

3. Estimation of OH Addition Rate Constants

Rate constant estimates for additions to double bonds are made by estimating total rate constants for reaction at a double bond with a given number and configuration of substituents, and then, for unsymmetrical molecules, estimating the fraction that reacts at the each end. These estimates are shown on Table 10, along with an indication of the derivation of the values used. The total rate constant estimates are based on measured rate constants for representative molecules, but only limited information is available upon which to base the branching ratio estimates, which are therefore more uncertain. These estimates are then used to derive a group rate constant for each of the two groups around the double bond. Note that since the present system does not support generating mechanisms with more than one C=C double bond (except for "special reactants", as discussed later), the estimates on this table are only applicable to monoalkenes.

The group rate constant estimates on Table 10 are somewhat different than those given by Kwok and Atkinson (1997) for several reasons. Propene is not used when deriving the group rate constants for monosubstituted alkenes because its OH rate constant is known and kinetic data for the higher 1-alkenes, which are expected to be more similar to the types of compounds for which estimates may be needed, are better fit by slightly higher values. The estimates of Kwok and Atkinson (1997) also take into account the possibility that some of the reaction may be occurring by abstraction from other groups, which is ignored in our estimates (see below). Kwok and Atkinson (1997) give correction factors for oxygenated substituents, but these are also not fully implemented in the present system because in this work estimates are mainly needed only for hydrocarbon species. The few unsaturated oxygenated species that are handled by the system (primarily acrolein and isoprene products) already have measured or assigned total OH rate constants (e.g., see Carter and Atkinson, 1996). However, correction factors from Kwok and Atkinson (1997) for -CHO and -CO- substituents, of 0.35 and 0.9, respectively, have been incorporated on a preliminary basis.

4. Comparison of Estimated and Assigned Rate Constants

Table 8, above, shows a comparison of the estimated and assigned OH radical rate constants, from which one can obtain an indication of the overall performance of the estimation methods for the various types of VOCs. Table 11 shows a summary of average percentage errors (biases) and average absolute percentage errors (errors) for OH radical rate constant estimates for various classes of VOCs. It can be seen that the estimation method performs reasonably well for alkanes and alkenes, having essentially no bias and an average error of less than 15%. The estimates do not perform as well for the oxygenated compounds, and appears to biased high in the case of aldehydes and ketones. Refinements to the estimation method may improve the performance for these oxygenates, but updating the work of Kwok and Atkinson (1995) was beyond the scope of this report.

5. Assigned Mechanisms for Initial OH Reactions

Because estimation methods for the branching ratios for the reactions of OH radicals at different positions of the molecule have some uncertainty, branching ratios are explicitly assigned for those compounds where experimental data are available, and indicate that the estimates may not be appropriate. In addition, as indicated in Table 7, several alkynes and dialkenes have also been incorporated into the mechanism generation system as "special reactants", whose reactions cannot be estimated and therefore need to be specified explicitly. The explicitly assigned branching ratios for initial OH radical reactions that are currently incorporated in the system are summarized on Table 12, along with the basis for the various assignments that are used.

Table 10. Group rate constants used for estimating rates of OH addition reactions.

Group	Estimated Total Rate Constant (300K) (cm3 molec-1 s-1)		Fraction reacting at least substituted end	
CH2=CH-	3.16e-11	Total rate constant based on average for 300K rate constants for 1-butene, 3-methyl-1-butene, 1-pentene, 1-hexene and 3-3-dimethyl-1-butene (Atkinson, 1997a).	0.65	Terminal bond addition fraction from Cvetanovic (1976).
CH2=C<	5.79e-11	Total rate constant based on average for 300K rate constants for isobutene, 2-methyl-1-butene and 2-methyl-1-pentene (Atkinson, 1997a).	1.00	100% addition at termal end assumed.
-CH=CH-	6.33e-11	Total rate constant based on average for 300K rate constants for the 2-butenes, the 2-pentenes, trans-4-methyl-2-pentene, trans-4,4-dimethyl-2-pentene, trans-2-heptene, trans-4-octene, cyclopentene, and cyclohexene (Atkinson, 1997a).	0.50	Equal addition at each position assumed.
-CH=C<	8.70e-11	Total rate constant based on average for 300K rate constants for 2-methyl-2-butene and 2-methyl-2-pentene (Atkinson, 1997a).	0.75	No information available concerning relative addition rates at the different positions. Roughly estimate 75% addition at the least substituted position.
>C=C<	1.05e-10	Total rate constant based on average for 300K rate constants for 2,3-dimethyl-2-butene and 2,3-dimethyl-2-pentene (Atkinson, 1997a).	0.50	Equal addition at each position assumed.

Table 11. Summary of average biases and errors in estimates of OH radical rate constants from data given on Table 8.

Class	Count	Average	
		Bias	Error
Alkanes	43	1%	10%
Alkenes	25	1%	7%
Alchohols and Glycols	41	-11%	22%
Esters	26	5%	36%
Aldehydes	14	16%	29%
Ketones	34	36%	56%
Others	2	4%	4%

Notes:

Bias is average of percentage differences between experimental and estimated values

Error is average of absolute value of percentage differences.

D. Reactions with NO_3 Radicals

Reactions with NO_3 radicals can be a non-negligible fate for alkenes and aldehydes under some conditions, and therefore are included in the mechanism. These reactions are considered in essentially the same way as reaction with OH radicals, except that HNO_3 or ONO_2-substituted products are formed. Thus, if the group has an abstractable hydrogen, the reaction is

$$XH + NO_3 \rightarrow X\cdot + HNO_3 \qquad \text{(abstraction)}$$

And if it has a double bond, the reaction is

$$>C=C< + NO_3 \rightarrow >C(ONO_2)\text{-}C[\cdot]\text{-} \qquad \text{(addition)}$$

However, the current system assumes that rate constants for all abstraction reactions are negligible except for reaction at aldehyde -CHO groups. Therefore, only H abstraction reactions of NO_3 with aldehydes or additions to alkenes are considered in the current mechanism.

1. Assigned NO_3 Radical Rate Constants

NO_3 radical rate constants have been measured for a number of VOCs in the current mechanism, though the coverage is nowhere near as complete as is the case for the OH radical reaction. Table 13 gives the NO_3 radical rate constants assigned to all VOCs in the current mechanism for which the reaction with NO_3 radicals is represented. Note that the table does not include measured NO_3 radical rate constants for alkanes and other species that the current mechanism neglects as being of negligible importance. Footnotes indicate the basis for the rate parameter assignments, most of which are based on Atkinson (1991, 1994, 1997a) recommendations.

Table 12. Assigned mechanisms for the initial reactions of OH radicals with compounds for which estimates could not be made, or where experimental data indicate that the estimates may not be appropriate.

Reactant and Products [a]	Factor	Documentation
1,3-Butadiene [CH2=CH-CH=CH2]		
CH2=CH-CH[.]-CH2-OH	100.0%	Terminal addition assumed to dominate because of formation of resonance-stabilized radical.
Isoprene [CH2=CH-C(CH3)=CH2]		
CH2=CH-C[.](CH3)-CH2-OH	52.4%	Mechanism assumed to be as discussed by Carter and Atkinson (1996).
CH2=C(CH3)-CH[.]-CH2-OH	42.6%	See above.
CH2=CH-C(OH)(CH2.)-CH3	2.5%	Based on observed 3-methyl furan yields as discussed by Carter and Atkinson (1996).
CH2=C(CH3)-CH(CH2.)-OH	2.5%	See above.
Acetylene [HC::CH]		
HO-CH=CH.	90.0%	Estimated mechanism is based on the data of Hatakeyama et al (1986) and modeling acetylene environmental chamber runs Carter et al (1997c).
HCO-CH2.	10.0%	See above. Adjusted to fit chamber data.
Methyl Acetylene [HC::C-CH3]		
CH3-C[.]=CH-OH	100.0%	Estimated to be the major reaction pathway.
Ethyl Acetylene [HC::C-CH2-CH3]		
CH3-CH2-C[.]=CH-OH	100.0%	Estimated to be the major reaction pathway.
2-Butyne [CH3-C::C-CH3]		
CH3-C(OH)=C[.]-CH3	100.0%	Estimated to be the major reaction pathway.
Methanol [CH3-OH]		
HO-CH2.	85.0%	Branching ratios recommended by IUPAC (Atkinson et al, 1997a, 1999).
CH3O.	15.0%	See above.
Ethanol [CH3-CH2-OH]		
CH3-CH[.]-OH	90.0%	Branching ratios recommended by IUPAC (Atkinson et al, 1997a, 1999).
CH3-CH2O.	5.0%	See above
HO-CH2-CH2.	5.0%	See Above
1-Octanol [CH3-CH2-CH2-CH2-CH2-CH2-CH2-CH2-OH]		
CH3-CH2-CH2-CH2-CH2-CH2-CH2-CH[.]-OH	19.2%	Based on yields of octanal from 1-octanol (Carter et al, 1999a).
HO-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2.	1.5%	Relative branching ratios of other routes estimated using method of Kwok and Atkinson (1995).
CH3-CH[.]-CH2-CH2-CH2-CH2-CH2-CH2-OH	10.8%	See above.
CH3-CH2-CH[.]-CH2-CH2-CH2-CH2-CH2-OH	13.3%	See above.
CH3-CH2-CH2-CH[.]-CH2-CH2-CH2-CH2-OH	13.3%	See above.
CH3-CH2-CH2-CH2-CH[.]-CH2-CH2-CH2-OH	13.3%	See above.
CH3-CH2-CH2-CH2-CH2-CH[.]-CH2-CH2-OH	13.3%	See above.
CH3-CH2-CH2-CH2-CH2-CH2-CH[.]-CH2-OH	13.3%	See above.
CH3-CH2-CH2-CH2-CH2-CH2-CH2-CH2O.	1.7%	See above.

Table 12 (continued)

Reactant and Products [a]	Factor	Documentation
<u>2-Octanol [CH3-CH(OH)-CH2-CH2-CH2-CH2-CH2-CH3]</u>		
CH3-C[.](OH)-CH2-CH2-CH2-CH2-CH2-CH3	36.5%	Based on yield of 2-octanone from 2-octanol (Carter et al, 1999a)
CH3-CH2-CH2-CH2-CH2-CH2-CH(CH2.)-OH	1.5%	Relative branching ratios of other routes estimated using method of Kwok and Atkinson (1995).
CH3-CH2-CH2-CH2-CH2-CH2-CH[O.]-CH3	1.5%	See above.
CH3-CH(OH)-CH[.]-CH2-CH2-CH2-CH2-CH3	12.3%	See above.
CH3-CH(OH)-CH2-CH[.]-CH2-CH2-CH2-CH3	12.3%	See above.
CH3-CH(OH)-CH2-CH2-CH[.]-CH2-CH2-CH3	12.3%	See above.
CH3-CH(OH)-CH2-CH2-CH2-CH[.]-CH2-CH3	12.3%	See above.
CH3-CH(OH)-CH2-CH2-CH2-CH2-CH[.]-CH3	9.9%	See above.
CH3-CH(OH)-CH2-CH2-CH2-CH2-CH2-CH2.	1.5%	See above.
<u>3-Octanol [CH3-CH2-CH(OH)-CH2-CH2-CH2-CH2-CH3]</u>		
CH3-CH2-C[.](OH)-CH2-CH2-CH2-CH2-CH3	42.4%	Based on yield of 3-octanone from 3-octanol (Carter et al, 1999a)
CH3-CH2-CH2-CH2-CH2-CH(OH)-CH2-CH2.	1.4%	Relative branching ratios of other routes estimated using method of Kwok and Atkinson (1995).
CH3-CH2-CH2-CH2-CH2-CH(OH)-CH[.]-CH3	9.4%	See above.
CH3-CH2-CH2-CH2-CH2-CH[O.]-CH2-CH3	1.4%	See above.
CH3-CH2-CH(OH)-CH[.]-CH2-CH2-CH2-CH3	11.5%	See above.
CH3-CH2-CH(OH)-CH2-CH[.]-CH2-CH2-CH3	11.5%	See above.
CH3-CH2-CH(OH)-CH2-CH2-CH[.]-CH2-CH3	11.5%	See above.
CH3-CH2-CH(OH)-CH2-CH2-CH2-CH[.]-CH3	9.4%	See above.
CH3-CH2-CH(OH)-CH2-CH2-CH2-CH2-CH2.	1.4%	See above.
<u>4-Octanol [CH3-CH2-CH2-CH(OH)-CH2-CH2-CH2-CH3]</u>		
CH3-CH2-CH2-C[.](OH)-CH2-CH2-CH2-CH3	36.6%	Based on yield of 4-octanone from 4-octanol (Carter et al, 1999a)
CH3-CH2-CH2-CH2-CH(OH)-CH2-CH2-CH2.	1.6%	Relative branching ratios of other routes estimated using method of Kwok and Atkinson (1995).
CH3-CH2-CH2-CH2-CH(OH)-CH2-CH[.]-CH3	10.3%	See above.
CH3-CH2-CH2-CH2-CH(OH)-CH[.]-CH2-CH3	12.7%	See above.
CH3-CH2-CH2-CH2-CH[O.]-CH2-CH2-CH3	1.6%	See above.
CH3-CH2-CH2-CH(OH)-CH[.]-CH2-CH2-CH3	12.7%	See above.
CH3-CH2-CH2-CH(OH)-CH2-CH[.]-CH2-CH3	12.7%	See above.
CH3-CH2-CH2-CH(OH)-CH2-CH2-CH[.]-CH3	10.3%	See above.
CH3-CH2-CH2-CH(OH)-CH2-CH2-CH2-CH2.	1.6%	See above.
<u>Methyl t-Butyl Ether [CH3-C(CH3)(CH3)-O-CH3]</u>		
CH3-C(CH3)(CH3)-O-CH2.	80.0%	Branching ratios based on product studies of Tuazon et al, (1991b); and Smith et al (1991), with overall yields increased to account for 100% reaction.
CH3-C(CH3)(CH2.)-O-CH3	20.0%	See Above

Table 12 (continued)

Reactant and Products [a]	Factor	Documentation
<u>1-Methoxy-2-Propanol [CH3-CH(OH)-CH2-O-CH3]</u>		
CH3-O-CH2-CH(CH2.)-OH	0.0%	Estimated to be minor
CH3-C[.](OH)-CH2-O-CH3	39.0%	Based on observed methoxyacetone yields (Tuazon et al, 1998a).
CH3-O-CH2-CH[O.]-CH3	0.0%	Estimated to be minor
CH3-CH(OH)-CH[.]-O-CH3	58.0%	Based on observed methyl formate and acetaldehyde yields, the expected products from this route (Tuazon et al, 1998a)
CH3-CH(OH)-CH2-O-CH2.	3.0%	Estimated to occur ~6% of the time. 3% yield assumed to account for 100% reaction.
<u>2-Butoxy-Ethanol [CH3-CH2-CH2-CH2-O-CH2-CH2-OH]</u>		
CH3-CH2-CH2-CH2-O-CH[.]-CH2-OH	57.0%	Branching ratio based on observed yield of n-butyl formate, which is the expected major product from this route (Tuazon et al, 1998a).
CH3-CH2-CH2-CH[.]-O-CH2-CH2-OH	22.0%	Branching ratio based on observed yields of 2-hydroxyetlyo formate and propanal, the expected major products from this route (Tuazon et al, 1998a).
HO-CH2-CH2-O-CH2-CH2-CH2-CH2.	0.5%	Relative branching ratios for this and the other routes estimated using method of Kwok and Atkinson (1996).
CH3-CH[.]-CH2-CH2-O-CH2-CH2-OH	3.5%	See above.
CH3-CH2-CH[.]-CH2-O-CH2-CH2-OH	4.3%	See above.
CH3-CH2-CH2-CH2-O-CH2-CH[.]-OH	12.2%	See above.
CH3-CH2-CH2-CH2-O-CH2-CH2O.	0.6%	See above.
<u>Methyl Acetate [CH3-O-CO-CH3]</u>		
CH3-CO-O-CH2.	100.0%	Environmental chamber reactivity data fit somewhat better if reaction at the CH3-CO end is assumed to be negligible.
CH3-O-CO-CH2.	0.0%	See above
<u>Propylene Carbonate [*CH(CH3)-CH2-O-CO-O-*]</u>		
CH(CH2.)-CH2-O-CO-O-	25.0%	Branching ratio estimated from ratio of estimate for reaction at this position using method of Kwok and Atkinson (1996) to measured total rate constant Carter et al, 1996c).
C[.](CH3)-CH2-O-CO-O-	37.5%	Model simulations are somewhat more consistent with environmental chamber reactivity data if the other two reaction routes are assumed to occur with approximately equal probability.
CH(CH3)-O-CO-O-CH[.]-	37.5%	See above
<u>Methyl Isobutyrate [CH3-CH(CH3)-CO-O-CH3]</u>		
CH3-C[.](CH3)-CO-O-CH3	67.0%	Branching ratio derived from total rate constant and estimated rate constants for the competing reaction routes. This results in higher predicted yields for acetone, which is more consistent with the product data of Wells et al (1999).
CH3-CH(CH2.)-CO-O-CH3	20.0%	Branching ratio derived from ratio of rate constant for this route estimated using the method of Kwok and Atkinson (1995), relative to the total rate constant.
CH3-CH(CH3)-CO-O-CH2.	13.0%	See above.

Table 12 (continued)

Reactant and Products [a]	Factor	Documentation
Propylene Glycol Methyl Ether Acetate [CH3-O-CH(CH3)-CH2-O-CO-CH3]		
CH3-CO-O-CH2-CH(CH3)-O-CH2.	7.9%	Group rate constant estimated using method of Kwok and Atkinson (1995)
CH3-O-C[.](CH3)-CH2-O-CO-CH3	45.3%	Group rate constant adjusted to fit environmental chamber reactivity data, and to be consistent with measured total rate constant.
CH3-O-CH(CH2.)-CH2-O-CO-CH3	1.2%	Group rate constant estimated using method of Kwok and Atkinson (1995)
CH3-O-CH(CH3)-CH[.]-O-CO-CH3	45.3%	Group rate constant adjusted to fit environmental chamber reactivity data, and to be consistent with measured total rate constant.
CH3-O-CH(CH3)-CH2-O-CO-CH2.	0.3%	Group rate constant estimated using method of Kwok and Atkinson (1995)
Dimethyl Adipate (DBE-5) [CH3-O-CO-CH2-CH2-CH2-CO-O-CH3]		
CH3-O-CO-CH2-CH2-CH2-CO-O-CH2.	39.0%	Based on yield of CH3-O-CO-CH2-CH2-CH2-CO-OH observed by Tuazon et al (1999)
CH3-O-CO-CH2-CH[.]-CH2-CO-O-CH3	41.0%	Yield of CH3-O-CO-CH2-CO-CH2-CO-O-CH3 observed by Tuazon et al (1999) corresponds to this route occurring 33% of the time.However, model simulations fit chamber data somewhat better if this route is assumed to be relatively more important; so the fraction reacted at in this position is estimated from the ratio of the rate constant derived using estimates of Kwok and Atkinson (1985) as updated by Kwok et al (1996) to the measured total rate constant. This is within the uncertainty of the yield measurement.
CH3-O-CO-CH2-CH2-CH[.]-CO-O-CH3	20.0%	See above
Dimethoxy Methane [CH3-O-CH2-O-CH3]		
CH3-O-CH2-O-CH2.	67.0%	Based on ratio of yields of CH3-O-CH2-O-CHO relative to CH3-O-CO-O-CH3 + CH3-O-CHO given by Sidebottom et al (1997), which is consistent with product data of Wallington et al (1997).
CH3-O-CH[.]-O-CH3	33.0%	See above.
Acrolein [CH2=CH-CHO]		
CH2=CH-CO.	75.0%	Estimated rate constant for reaction at this position is intermediate between the estimate based on the analogous reaction of methacrolein and estimation using method of Atkinson (1987).
HCO-CH[.]-CH2-OH	17.0%	Addition to double bond assumed to occur 25% of the time, based on total rate constant and estimate for reaction at the CHO position. Terminal/internal ratio based on the ratio determined for OH + propene.
HCO-CH(CH2.)-OH	8.0%	See above.

Table 12 (continued)

Reactant and Products [a]	Factor	Documentation
Crotonaldehyde [CH3-CH=CH(CHO)]		
CH3-CH=CH(CO.)	45.0%	Assumed to occur with the same rate constant as the analogous reaction for methacrolein.
CH3-CH[.]-CH(OH)-CHO	27.5%	Fraction reacted based on total rate constant, estimated rate for abstraction from -CHO, and assumption that addition at each side of the double bond is equal.
CH3-CH(OH)-CH[.]-CHO	27.5%	See above.
Methacrolein [CH2=C(CHO)-CH3]		
CH3-C[.](CHO)-CH2-OH	44.0%	Adjusted to give same product distribution as used by Carter and Atkinson (1996), and to be consistent with available product data.
CH3-C(OH)(CH2.)-CHO	6.0%	See above.
CH2=C(CO.)-CH3	50.0%	See above.
Hydroxy Methacrolein [CH2=C(CHO)-CH2-OH]		
CH2=C(CO.)-CH2-OH	38.0%	Mechanism of Carter and Atkinson (1996) is assumed.
HO-CH2-C[.](CHO)-CH2-OH	52.0%	See above.
HCO-C(OH)(CH2.)-CH2-OH	10.0%	See above.
Isoprene Product #1 [CH3-C(CHO)=CH(CH2-OH)]		
CH3-C(CO.)=CH(CH2-OH)	25.0%	Mechanism of Carter and Atkinson (1996) is assumed.
CH3-C[.](CHO)-CH(OH)-CH2-OH	50.0%	See above.
CH3-C(CHO)(OH)-CH[.]-CH2-OH	25.0%	See above.
Isoprene Product #2 [CH3-C(CHO)=CH-CH2-OH]		
CH3-C(CO.)=CH-CH2-OH	25.0%	Mechanism of Carter and Atkinson (1996) is assumed.
CH3-C[.](CHO)-CH(OH)-CH2-OH	50.0%	See above.
CH3-C(CHO)(OH)-CH[.]-CH2-OH	25.0%	See above.
Isoprene Product #3 [HCO-CH=C(CH3)-CH2-OH]		
HO-CH2-C(CH3)=CH-CO.	25.0%	Mechanism of Carter and Atkinson (1996) is assumed.
HCO-CH(OH)-C[.](CH3)-CH2-OH	50.0%	See above.
HCO-CH[.]-C(CH3)(OH)-CH2-OH	25.0%	See above.
Cyclohexanone [*CH2-CH2-CH2-CH2-CH2-CO-*]		
CH2-CH2-CH2-CH2-CO-CH[.]-	44.0%	Better fits of model simulations to results of environmental chamber reactivity experiments are obtained if equal probability of reaction at alpha and beta positions (Carter et al, 1999a).
CH2-CH2-CH2-CO-CH2-CH[.]-	44.0%	See above.
CH2-CH2-CO-CH2-CH2-CH[.]-	12.0%	Approximately the fraction reacted at this position estimated by method of Kwok and Atkinson (1995)
Methylvinyl ketone [CH2=CH-CO-CH3]		
CH3-CO-CH[.]-CH2-OH	70.0%	Based on product distribution of Tuazon and Atkinson (1989), as discussed by Carter and Atkinson (1996)
CH3-CO-CH(CH2.)-OH	30.0%	See above.
Formic Acid [HCO-OH]		
HCO2.	100.0%	Believed to be the major reaction route.

[a] Formation of H_2O, when applicable, is not shown.

Table 13. Rate constant and temperature dependence parameter assignments used for reactions of VOCs with NO_3 radicals in the present mechanism.

Compound	DMS name	k(300)	A	B	Ea	Ref	Est'd k(300)	
		(cm^3 $molec^{-1}$ s^{-1})			kcal/mole		k	(diff)
Propene	PROPENE	9.73e-15	4.59e-13		2.297	1	1.38e-14	42%
1-Butene	1-BUTENE	1.38e-14	3.14e-13		1.864	1	1.38e-14	0%
Isobutene	ISOBUTEN	3.32e-13	3.32e-13		0.000	2	3.32e-13	0%
cis-2-Butene	C-2-BUTE	3.47e-13	1.10e-13		-0.687	3	3.70e-13	7%
trans-2-Butene	T-2-BUTE	3.92e-13	1.10e-13	2.0	-0.759	1	3.70e-13	-6%
2-Methyl-2-Butene	2M-2-BUT	9.37e-12	9.37e-12		0.000	2	9.37e-12	0%
2,3-Dimethyl-2-Butene	23M2-BUT	5.72e-11	5.72e-11		0.000	2	5.72e-11	0%
Cyclopentene	CYC-PNTE	5.30e-13	5.30e-13		0.000	2	3.70e-13	-30%
Cyclohexene	CYC-HEXE	5.88e-13	1.05e-12		0.346	1	3.70e-13	-37%
1,3-Butadiene	13-BUTDE	1.00e-13	1.00e-13		0.000	2		
Isoprene	ISOPRENE	6.85e-13	3.03e-12		0.886	1		
a-Pinene	A-PINENE	6.09e-12	1.19e-12		-0.974	1		
3-Carene	3-CARENE	9.10e-12	9.10e-12		0.000	2		
b-Pinene	B-PINENE	2.51e-12	2.51e-12		0.000	2		
Sabinene	SABINENE	1.00e-11	1.00e-11		0.000	2		
d-Limonene	D-LIMONE	1.22e-11	1.22e-11		0.000	2		
2-(Cl-methyl)-3-Cl-Propene	CL2IBUTE	1.00e-15				4		
Styrene	STYRENE	1.51e-13				5		
Acetaldehyde	ACETALD	2.84e-15	1.40e-12		3.696	6		
Methylvinyl ketone	MVK	0.00e+00				7		
Methacrolein	METHACRO	4.76e-15	1.50e-12		3.430	8		
Isoprene Product #1	IP-MHY1	1.00e-13				9		
Isoprene Product #2	IP-MHY2	1.00e-13				9		
Isoprene Product #3	IP-HMY	1.00e-13				9		
Hydroxy Methacrolein	HOMACR	4.76e-15	1.50e-12		3.430	10		
Crotonaldehyde	CROTALD	5.12e-15				11		
N-Methyl-2-Pyrrolidone	NMP	1.26e-13				12		

References

1 Rate constant expression recommended by Atkinson (1997a)

2 Rate constant from Atkinson (1997a). Temperature dependence is assumed to be small.

3 T=298K rate constant recommended by Atkinson (1997a). Temperature dependence estimated by assuming the A factor is the same as for trans-2-butene.

4 This rate constant estimated by Atkinson (private communication, 1997) based on the rate constant for NO3 + Allyl chloride (Atkinson, 1991)

5 Rate constant from Atkinson and Aschmann (1988a).

6 Rate constant expression recommended by IUPAC, Supplement V (Atkinson et al, 1997a).

7 Data of Kwok et al (1997) indicate that the total rate constant is less than 6e-18 cm3 molec-1 s-1, which make it unimportant under atmospheric conditions.

8 Total rate constant from Kwok et al (1996). Temperature dependence estimated by Carter and Atkinson (1996)

9 Rate constant estimated by Carter and Atkinson (1996).

10 Rate constant assumed to be the same as for methacrolein (Carter and Atkinson, 1996)

11 Atkinson et al (1987)

12 Rate constant from Carter et al (1996c).

2. Estimated NO_3 Radical Rate Constants

Reaction of NO_3 with aldehyde groups are based on the measured rate constant for the reaction of NO_3 with acetaldehyde, which is (Atkinson et al, 1997a, 1999a),

$$k(NO_3 + X\text{-}CHO) = 1.40 \times 10^{-12}\ e^{-3.696/RT} \cdot F(X)\ cm^3\ molec^{-1}\ s^{-1}.$$

where F(X) is the substituent factor for groups other than $-CH_3$ bonded to the -CHO. The correlation between NO_3 and OH radical abstraction rate constants given by Atkinson (1991)[9] is used to estimate these group substituent correction factors, F(X), which are as follows:

- $F(-CH_2-) = F(-CH-) = F(>C<) = 1.34$ is derived from the correlation of Atkinson (1991) and the the rate constant for OH abstraction from -CHO groups derived by the group-additivity method of Kwok and Atkinson (1995).
- F(-CHO) = 0.18 is derived from the correlation and the OH rate constant for glyoxal.
- F(-CO-) = 0.89 is derived from the correlation and the OH rate constant for methyl glyoxal.

Note that rate constants for NO_3 abstraction from -CHO groups an oxygen (e.g., formates and acids) are estimated to be zero, so such reactions are not generated.

The group rate constants used for estimating NO_3 addition rate constants is given on Table 14, along with the documentation for the rate constant assignments. Note that in the case of NO_3 reactions we assume that addition always occurs to the least substituted position around the bond, based on the assumption that since NO_3 addition rate constants are lower than those for OH addition, they will tend to be more selective. Rate constant data are available for only a few compounds of each type, so the estimates are necessarily more uncertain than those for OH radical reactions. As with the OH addition estimates, the rate constant for propene is not used for making the estimates for general 1-alkenes because 1-butene is considered to be more representative of the types of the higher monoalkenes for which rate constant estimates would be needed.

The group rate constants shown on Table 14 are strictly speaking applicable only for estimating rate constants for unsaturated hydrocarbons. Group correction factors, which are multiplied by the group rate constants shown on Table 14, are used for estimating rate constants for NO_3 to double bonds in unsaturated carbonyls. These are as follows:

- A factor of 0.007 is used if the double bond has a -CHO substituent, based on the ratio of the estimated rate constant for NO_3 addition to methacrolein (Carter and Atkinson, 1996) to the group rate constant for CH2=C<.
- A factor of 2×10^{-4} is used if the double bond has a -CO- substituent, based on the upper limit rate constant for the reaction of NO_3 with methyl vinyl ketone (Carter and Atkinson, 1996). The actual upper limit rate constant of 6×10^{-18} cm^3 $molec^{-1}$ s^{-1} corresponds to a factor of $\sim 4 \times 10^{-4}$, but we arbitrarily use a factor which is half that. This is sufficiently small to make reactions of NO_3 with such compounds to be of negligible importance.

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[9] Atkinson (1993) noted a good correlation between OH and NO_3 abstraction rate constants per abstractable hydrogen, with the data being fit by $\ln k_{NO3} = 6.498 + 1.611 \ln k_{OH}$.

Table 14. Group rate constants and group substituent correction factors used for estimating rates of NO_3 addition reactions.

Groups	Estimated Total Rate Constant (300K) (cm3 molec-1 s-1)		Fraction reacting at least substituted end	
CH2=CH-	1.38e-14	Total rate constant based on 300K value for 1-butene (Atkinson, 1997a).	1.0	100% addition at termal end assumed.
CH2=C<	3.32e-13	Total rate constant based on 300K value for isobutene (Atkinson, 1997a)	1.0	100% addition at termal end assumed.
-CH=CH-	1.85e-13	Total rate constant based on averaging the 300K values for cis and trans 2-butene (Atkinson, 1997a).	0.5	Equal addition at each position assumed.
-CH=C<	9.37e-12	Total rate constant based on 300K value for 2-methyl-2-butene (Atkinson, 1997a).	1.0	100% Addition at the least substituted end is assumed.
>C=C<	2.86e-11	Total rate constant based on the 300K value for 2,3-dimethyl-2-butene (Atkinson, 1997a).	0.5	Equal addition at each position assumed.

The performance of the estimation method in predicting the measured NO_3 radical rate constants is indicated on Table 13. Except for propene (for which estimates are not needed) and the halogenated alkene on the list (whose subsequent reactions are not currently supported by the system), the estimates generally perform reasonably well. Of course, in most cases this is because the estimates are based on these data. There does seem to be a bias towards underpredicting the rate constants for the cycloalkenes, and it may be appropriate to add a ring correction term for such compounds.

3. Assigned Mechanisms for Initial NO_3 Reactions

As with OH reactions discussed above, explicit assignments are used for the initial reactions for those VOCs where estimates cannot be made, where available experimental data indicate the estimates are inappropriate, or where alternative estimates are used. The explicitly assigned branching ratios for the initial NO_3 radical reactions that are currently incorporated in the system are summarized on Table 15, along with the basis for the various assignments that are used.

E. Reactions with O_3

Reactions with O_3 are assumed to occur only at carbon-carbon double bonds[10], and the reactions are assumed to involve ultimately breaking the bond and forming a carbonyl and an excited Crigiee biradical, i.e.

$$>C{=}C< + O_3 \rightarrow >CO2[\text{excited}] + >C{=}O$$

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[10] Reactions of O_3 with alkynes are included as assigned reactions for special reactants (see Section III.E.4), but are not automatically generated by the system.

Table 15. Assigned mechanisms for the reactions of NO_3 radicals with compounds for which estimates could not be made, or where experimental data or other considerations indicate that the general estimates may not be appropriate.

Reactant and Products	Factor	Documentation
1,3-Butadiene [CH2=CH-CH=CH2]		
CH2=CH-CH[.]-CH2-ONO2	100.0%	Terminal addition assumed to dominate because of formation of resonance-stabilized radical.
Isoprene [CH2=CH-C(CH3)=CH2]		
CH2=CH-C[.](CH3)-CH2-ONO2	100.0%	Mechanism of Carter and Atkinson (1996) is assumed.
Crotonaldehyde [CH3-CH=CH(CHO)]		
CH3-CH=CH(CO.)	45.0%	Assumed to occur with the same rate constant as the analogous reaction for methacrolein.
CH3-CH[.]-CH(ONO2)-CHO	27.5%	Fraction reacted based on total rate constant, estimated rate for abstraction from -CHO, and assumption that addition at each side of the double bond is equal.
CH3-CH(ONO2)-CH[.]-CHO	27.5%	See above.
Methacrolein [CH2=C(CHO)-CH3]		
HNO3 + CH2=C(CO.)-CH3	50.0%	Mechanism of Carter and Atkinson (1996) is assumed.
CH3-C[.](CHO)-CH2-ONO2	50.0%	See above.
Hydroxy Methacrolein [CH2=C(CHO)-CH2-OH]		
HNO3 + CH2=C(CO.)-CH2-OH	50.0%	Mechanism of Carter and Atkinson (1996) is assumed.
HO-CH2-C[.](CHO)-CH2-ONO2	50.0%	See above.
Isoprene Product #1 [CH3-C(CHO)=CH(CH2-OH)]		
CH3-C[.](CHO)-CH(ONO2)-CH2-OH	100.0%	Mechanism of Carter and Atkinson (1996) is assumed. Abstraction from -CHO is estimated to occur only ~4% of the time.
Isoprene Product #2 [CH3-C(CHO)=CH-CH2-OH]		
CH3-C[.](CHO)-CH(ONO2)-CH2-OH	100.0%	Mechanism of Carter and Atkinson (1996) is assumed. Abstraction from -CHO is estimated to occur only ~4% of the time.
Isoprene Product #3 [HCO-CH=C(CH3)-CH2-OH]		
HCO-CH(ONO2)-C[.](CH3)-CH2-OH	100.0%	Mechanism of Carter and Atkinson (1996) is assumed. Abstraction from -CHO is estimated to occur only ~4% of the time.

Table 16. Rate constant and temperature dependence parameter assignments used for reactions of VOCs with O_3 in the present mechanism.

Compound	DMS name	k(300)	A	Ea	Ref	Est'd k(300)	
		(cm^3 molec^{-1} s^{-1})		kcal/mole		k	(diff)
<u>Alkanes</u>							
Ethene	ETHENE	1.68e-18	9.14e-15	5.127	1	1.68e-18	0%
Propene	PROPENE	1.05e-17	5.51e-15	3.732	1	1.01e-17	-4%
1-Butene	1-BUTENE	1.00e-17	3.36e-15	3.466	1	1.01e-17	1%
Isobutene	ISOBUTEN	1.17e-17	2.70e-15	3.243	1	1.18e-17	1%
cis-2-Butene	C-2-BUTE	1.28e-16	3.22e-15	1.924	1	1.15e-16	-10%
trans-2-Butene	T-2-BUTE	1.95e-16	6.64e-15	2.104	1	1.15e-16	-41%
1-Pentene	1-PENTEN	1.04e-17	3.36e-15	3.445	2	1.01e-17	-3%
2-Methyl-1-Butene	2M-1-BUT	1.66e-17	2.70e-15	3.037	3	1.18e-17	-29%
2-Methyl-2-Butene	2M-2-BUT	4.08e-16	2.87e-15	1.162	4	3.48e-16	-15%
3-Methyl-1-Butene	3M-1-BUT	1.14e-17	3.36e-15	3.388	2	1.01e-17	-12%
1-Hexene	1-HEXENE	1.14e-17	3.36e-15	3.388	2	1.01e-17	-12%
Cis-3-Hexene	C-3-C6E	1.53e-16	3.22e-15	1.816	5	1.15e-16	-25%
Trans-3-Hexene	T-3-C6E	1.74e-16	6.64e-15	2.170	6	1.15e-16	-34%
2-Methyl-1-Pentene	2M1-C5E	1.55e-17	2.70e-15	3.075	3	1.18e-17	-24%
3-Methyl-1-Pentene	3M1-C5E	5.12e-18	3.36e-15	3.867	2	1.01e-17	97%
4-Methyl-1-Pentene	4M1-C5E	9.57e-18	3.36e-15	3.494	2	1.01e-17	6%
Cis-3-Methyl-2-Hexene	C3M2-C5E	4.56e-16	2.87e-15	1.096	4	3.48e-16	-24%
Trans 3-Methyl-2-Hexene	T3M2-C5E	5.66e-16	2.87e-15	0.967	4	3.48e-16	-39%
23-Dimethyl-1-Butene	23M1-BUT	1.35e-17	2.70e-15	3.160	3	1.18e-17	-12%
3,3-Dimethyl-1-Butene	33M1-BUT	5.43e-18	3.36e-15	3.832	2	1.01e-17	86%
2,3-Dimethyl-2-Butene	23M2-BUT	1.14e-15	3.03e-15	0.584	1	6.74e-16	-41%
2-Ethyl-1-Butene	2E1-BUT	1.35e-17	2.70e-15	3.160	3	1.18e-17	-12%
1-Heptene	1-HEPTEN	1.25e-17	3.36e-15	3.337	2	1.01e-17	-19%
2,3,3-trimethyl-1-Butene	233M1BUT	8.63e-18	2.70e-15	3.426	3	1.18e-17	37%
1-Octene	1-OCTENE	1.45e-17	3.36e-15	3.246	2	1.01e-17	-30%
Cis-4-Octene	C-4-C8E	9.73e-17	3.22e-15	2.086	5	1.15e-16	18%
Trans-4-Octene	T-4-C8E	1.44e-16	6.64e-15	2.285	6	1.15e-16	-20%
Trans 2,5-Dimethyl 3-Hexene	T25M3C6E	4.24e-17	6.64e-15	3.013	6	1.15e-16	171%
Trans 2,2-Dimethyl 3-Hexene	T22M3C6E	4.34e-17	6.64e-15	2.998	6	1.15e-16	165%
2,4,4-trimethyl-2-Pentene	244M2C5E	1.43e-16	2.87e-15	1.788	4	3.48e-16	144%
3-Methyl-2-Isopropyl-1-Butene	3M2I1C4E	3.45e-18	2.70e-15	3.972	3	1.18e-17	242%
1-Decene	1-C10E	9.67e-18	3.36e-15	3.488	2	1.01e-17	4%
Cis-5-Decene	C-5-C10E	1.23e-16	3.22e-15	1.948	5	1.15e-16	-6%
3,4-Diethyl-2-Hexene	34E2-C6E	4.39e-18	2.87e-15	3.864	4	3.48e-16	<u>(large)</u>
Cyclopentene	CYC-PNTE	5.61e-16	1.80e-15	0.696	1	1.15e-16	-79%
1-Methyl cyclohexene	1M-CC5E	6.76e-16	2.70e-15	0.825	3	3.48e-16	-49%
Cyclohexene	CYC-HEXE	8.33e-17	2.88e-15	2.112	1	1.15e-16	38%
1-Methyl Cyclohexene	1M-CC6E	1.68e-16	2.87e-15	1.690	4	3.48e-16	107%
4-Methyl Cyclohexene	4M-CC6E	8.40e-17	2.88e-15	2.107	7	1.15e-16	37%

Table 16 (continued)

Compound	DMS name	k(300)	A	Ea	Ref	Est'd k(300)	
		(cm^3 molec^{-1} s^{-1})		kcal/mole		k	(diff)
1,2-Dimethyl Cyclohexene	12M-CC6E	2.11e-16	3.03e-15	1.589	8	6.74e-16	220%
1,3-Butadiene	13-BUTDE	6.64e-18	1.34e-14	4.537	1		
Isoprene	ISOPRENE	1.34e-17	7.86e-15	3.802	1		
a-Pinene	A-PINENE	8.80e-17	1.01e-15	1.455	1		
3-Carene	3-CARENE	3.78e-17	1.01e-15	1.958	9		
b-Pinene	B-PINENE	1.54e-17	1.01e-15	2.493	9		
Sabinene	SABINENE	8.74e-17	1.01e-15	1.459	9		
d-Limonene	D-LIMONE	2.04e-16	3.71e-15	1.729	10		
2-(Cl-methyl)-3-Cl-Propene	CL2IBUTE	3.90e-19			11		
Styrene	STYRENE	1.71e-17			12		
<u>Alkynes</u>							
Acetylene	ACETYLEN	8.61e-21	2.00e-14	8.739	13		
Methyl Acetylene	ME-ACTYL	1.56e-20	1.00e-14	7.970	14		
Ethyl Acetylene	ET-ACTYL	2.15e-20	1.00e-14	7.780	14		
2-Butyne	2-BUTYNE	2.15e-20	1.00e-14	7.780	15		
Methylvinyl ketone	MVK	4.74e-18	7.51e-16	3.020	12		
Methacrolein	METHACRO	1.19e-18	1.36e-15	4.200	12		
Isoprene Product #1	IP-MHY1	1.00e-17			16		
Isoprene Product #2	IP-MHY2	1.00e-17			16		
Isoprene Product #3	IP-HMY	1.00e-17			16		
Hydroxy Methacrolein	HOMACR	1.19e-18	1.36e-15	4.200	17		
Crotonaldehyde	CROTALD	9.00e-19			11		
Acrolein	ACROLEIN	3.07e-19	1.36e-15	5.006	18		

References

1 Rate constant expression recommended by Atkinson (1997a)

2 T=298K rate constant recommended by Atkinson (1997a). Temperature dependence estimated by assuming the A factor is the same as for 1-butene.

3 T=298K rate constant recommended by Atkinson (1997a). Temperature dependence estimated by assuming the A factor is the same as for isobutene.

4 T=298K rate constant recommended by Atkinson (1997a). Temperature dependence estimated by assuming the A factor is the same as the average of those for isobutene and 2,3-dimethyl-2-butene.

5 T=298K rate constant recommended by Atkinson (1997a). Temperature dependence estimated by assuming the A factor is the same as for cis-2-butene.

6 T=298K rate constant recommended by Atkinson (1997a). Temperature dependence estimated by assuming the A factor is the same as for trans-2-butene.

7 T=298K rate constant recommended by Atkinson (1997a). Temperature dependence estimated by assuming the A factor is the same as for cyclohexene.

8 T=298K rate constant recommended by Atkinson (1997a). Temperature dependence estimated by assuming the A factor is the same as for 2,3-dimethyl-2-butene.

9 T=298K rate constant recommended by Atkinson (1997a). Temperature dependence estimated by assuming the A factor is the same as for a-pinene.

Table 16 (continued)

References (continued)

10 T=298K rate constant recommended by Atkinson (1997a). Temperature dependence estimated by assuming the A factor is the sum of those for a-pinene and isobutene.

11 Rate constant recommended by Atkinson and Carter (1984)

12 Rate constant recommended by Atkinson (1994).

13 T=298K rate constant is from Atkinson and Aschmann (1984), as recommended by IUPAC (Atkinson et al, 1999). The temperature dependence is estimated based on assuming the A factor is roughly twice that for O3 + ethylene.

14 T=298K rate constant is from Atkinson and Aschmann (1984). The temperature dependence is estimated based on assuming the A factor is roughly twice that for O3 + propene.

15 Assumed to have approximately the same rate constant as 1-butyne, based on data given by Atkinson and Carter (1984).

16 Rate constant estimated by Carter and Atkinson (1996)

17 Estimated to have the same rate constant as methacrolein (Carter and Atkinson, 1996)

18 Rate constant at 298K of 2.9e-19 recommended by Atkinson (1994). Activation energy assumed to be the same as used for methacrolein.

Two reactions are generated for each C=C bond, involving formation of the biradical from each of the two groups around the bond. Therefore, it is necessary to know both the total rate constant and the fraction of biradical formation at each of the groups around the bond.

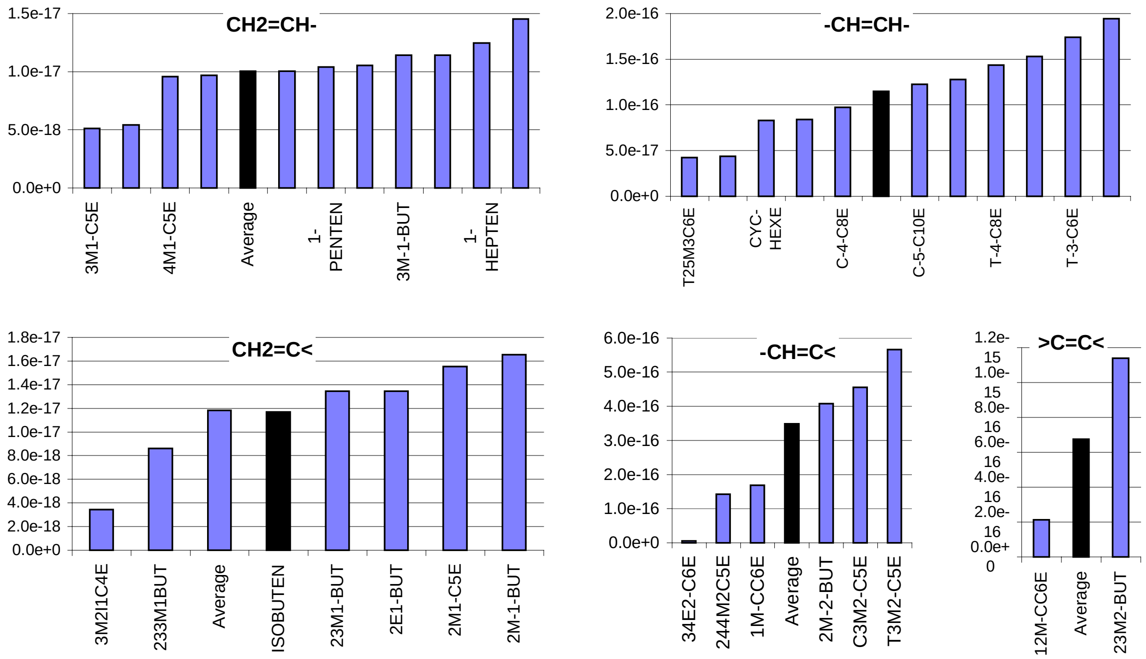
1. Assigned O_3 Rate constants

Rate constants for reaction with O_3 have been measured for most of the VOCs in the current mechanism for which O_3 reactions are assumed to be non-negligible. Table 16 lists the rate parameter assignments for all VOCs for which this is the case, and indicates the source of the assignments. Again, this includes all VOCs in the current mechanism, not just those whose reactions can be processed by the mechanism generation system. As with the other reactions, almost all of the assignments are based on recommendations from various Atkinson reviews (Atkinson and Carter, 1984; Atkinson, 1994, 1997a).

2. Estimated Total Rate Constants

As discussed by Atkinson and Carter (1984), ozone + alkene rate constants tend to be quite variable depending on the structure of the compound, even if grouped according to the number of substitutents on each side of the double bond. This is shown on Figure 2, which shows a comparison of the T=300K rate constants for the various monoalkenes tabulated by Atkinson (1997a), with a separate plot for each type of double bond structure. Note that cyclohexenes (which tend to have higher O_3 rate constants) and terpenes (whose structures the mechanism generation system cannot presently handle) are not shown. It can be seen that there is variability in the rate constants, particularly for the 1,1-disbustituted compounds. It is interesting to note that the more highly branched compounds tend to have the lowest rate constants, suggesting that steric effects may be important.

Figure 2. Comparison of O_3 + alkene rate constants for alkenes with the same configurations of constituents about the double bond.



Fortunately, measured O_3 rate constants are available for most of the alkenes that are important in current emissions, which tend to be the lower molecular weight compounds. However, it is still necessary to have a method to estimate rate constants for those compounds where no data are available, even if it is uncertain. For this purpose, we use the average of the rate constants for the reactions at the various types of double bonds, as shown on Figure 2, and as summarized on Table 17. Table 16, above, shows the discrepancies between the experimental and estimated values for all the alkenes in the current mechanism. The anomalously low value for 3,4-dietlyl-2-hexene (which may be low because of steric hindrance) was not used when computing the average for -CH=C<. Although there is variability, the averages are probably appropriate as best estimates for compounds whose rate constants are not known, at least for use by a the mechanism generation system at its current state of development. Obviously, compounds with large steric effects need to be estimated on a case-by-case basis.

3. Branching Ratios for Biradical Formation

Since the biradical and carbonyl formation in the initial O_3 reaction can occur on two different positions in unsymmetrical molecules, it is necessary to specify their relative importances. Information concerning this can be obtained from the measured yields of the primary carbonyl products, which are summarized by Atkinson (1997a). The averages of the primary yield data given by Atkinson (1997a) are summarized on Table 18 through Table 20 for the olefins with the various types of unsymmetrical groups where such data are available. In most cases the sum of these primary product yields are within experimental uncertainty of unity, indicating that these products account for the total O_3 + alkene reactions. (The main exceptions are propene [Table 18] and isobutene [Table 19], where higher than unit yields can be attributed to formaldehyde formation from the secondary reactions of the excited biradical.)

Table 17. Summary of rate constant estimates for reactions of O_3 at alkene groups.

Groups	Estimated Total Rate Constant (300K) (cm3 molec-1 s-1)	
CH2=CH-	1.01e-17	Average of 300K values for propene, 1-butene, 3-methyl-1-butene, 1-pentene, 1-hexene, 3-methyl-1-pentene, 3,3-dimethyl-1-butene, 4-methyl-1-pentene, 1-heptene, 1-octene, and 1-decene (Atkinson, 1997a).
CH2=C<	1.18e-17	Average of 300K values for isobutene, 2-methyl-1-butene, 23-dimethyl-1-butene, 2-ethyl-1-butene, 2-methyl-1-pentene, 2,3,3-trimethyl-1-butene, 3-methyl-2-isopropyl-1-butene, and 3,4-diethyl-2-hexene (Atkinson, 1997a).
-CH=CH-	1.15e-16	Average of 300K values for trans-2-butene, cis-2-butene, trans-3-hexene, cis-3-hexene, cis-4-octene, trans-4-octene, trans 2,5-dimethyl 3-hexene, trans 2,2-dimethyl 3-hexene, cis-5-decene, cyclohexene, and 4-methyl cyclohexene (Atkinson, 1997a).
-CH=C<	3.48e-16	Average of 300K values for 2-methyl-2-butene, cis-3-methyl-2-hexene, trans 3-methyl-2-hexene, 2,4,4-trimethyl-2-pentene, and 1-methyl cyclohexene (Atkinson, 1997a).
>C=C<	6.74e-16	Average of 300K values for 2,3-dimethyl-2-butene and 1,2-dimethyl cyclohexene (Atkinson, 1997a).

Atkinson (1997a) also summarizes carbonyl yield data for symmetrical alkenes (not shown here), and in most of those cases near-unit yields of the expected single carbonyl product are observed.

For alkenes with CH_2=CH- groups, Table 18 indicates that the data for most alkenes are consistent with assuming equal probability for each of the two possible reaction modes. This is therefore assumed when generating O_3 reaction mechanisms for all alkenes of this type. The major exception appears to be highly branched compounds such as 3,3-dimethyl-1-butene, where steric effects may tend to reduce biradical formation on the most substituted side. Since the current mechanism generation system is not capable of assessing steric effects, such compounds need to be handled on a case-by-case basis. However, present assignments are not made for such compounds because they are not important in current emissions inventories. The average error in assuming equal splits for the compounds where data are available is less than 10%, and the absolute value of the percentage error is less than 15%.

For alkenes with CH_2=C< groups, Table 19 indicates that the data are more consistent with assuming that fragmentation to formaldehyde + the disubstituted is essentially twice as probable as fragmentation to the ketone + $HCHO_2$ in essentially all cases. Steric effects appear to be less important in affecting this generalization, as suggested by the data for 2,3,3-trimethyl-1-butene. Therefore, the O_3 reactions of alkenes of this type are generated based on assuming that ketone + $HCHO_2$ formation occurs 33.3% of the time, as indicated on the table. This gives an average error of less than 5% and an average absolute percentage error of less than 15%.

For alkenes with -CH=C< groups, Table 20 indicates that aldehyde + disubstituted biradical formation occurs a larger fraction of the time than formation of the ketone + the monosubstituted biradical, but the limited data indicate somewhat variable ratios. For mechanism estimation and generation purposes, we assume that ketone + monosubstituted biradical formation occurs 30% of the

Table 18. Experimental and estimated yields of primary carbonyl products and OH radicals from the reactions of O_3 with alkenes with CH_2=CH- groups.

	Experimental			Estimated		OH Yield		
	HCHO	RCHO	Sum	RCHO	Error	Expt.	Est'd.	Error
CH2=CH- Average		0.54		0.5	-8%			-6%
Propene	0.71	0.48	1.20	0.5	3%	0.33	0.32	-3%
1-Butene	0.63	0.35	0.98	0.5	30%	0.41	0.32	-22%
1-Pentene	0.55	0.52	1.07	0.5	-4%	0.37	0.32	-14%
1-Hexene	0.54	0.53	1.07	0.5	-5%	0.32	0.32	0%
1-Heptene	0.52	0.55	1.07	0.5	-9%	0.27	0.32	19%
1-Octene	0.50	0.51	1.01	0.5	-2%	0.32	0.32	0%
1-Decene	0.53	0.49	1.02	0.5	2%			
3-Methyl-1-Butene	0.50	0.51	1.01	0.5	-2%			
3-Methyl-1-Pentene	0.39	0.63	1.03	0.5	-26%			
4-Methyl-1-Pentene	0.44	0.71	1.15	0.5	-41%			
3,3-Dimethyl-1-Butene	0.32	0.67	0.99	0.5	-34%			
Cyclohexene						0.68	0.52	-24%

Table 19. Experimental and estimated yields of primary carbonyl products and OH radicals from the reactions of O_3 with alkenes with CH_2=C< groups.

	Experimental			Estimated		OH Yield		
	HCHO	R-CO-R'	Sum	R-CO-R'	Error	Expt.	Calc	Error
CH2=C< Average		0.34		0.333	-2%			4%
Isobutene	0.98	0.32	1.29	0.333	4%	0.84	0.71	-16%
2-Methyl-1-Butene	0.64	0.28	0.92	0.333	16%	0.83	0.71	-15%
2-Methyl-1-Pentene	0.62	0.32	0.94	0.333	3%			
2-Ethyl-1-Butene	0.49	0.30	0.80	0.333	9%			
23-Dimethyl-1-Butene	0.72	0.38	1.10	0.333	-14%	0.5	0.71	41%
2,3,3-trimethyl-1-Butene	0.64	0.35	0.99	0.333	-6%			
3-Methyl-2-Isopropyl-1-Butene	0.61	0.43	1.03	0.333	-28%			

Table 20. Experimental and estimated yields of primary carbonyl products and OH radicals from the reactions of O_3 with alkenes with -CH=C< groups.

	Experimental			Estimated		OH Yield		
	RCHO	R-CO-R'	Sum	R-CO-R'	Error	Expt.	Calc	Error
-CH=C< Average		0.27		0.3	10%			-8%
2-Methyl-2-Butene	0.72	0.34	1.05	0.3	-13%	0.91	0.84	-8%
2,4,4-Trimethyl-2-Pentene	0.84	0.19	1.03	0.3	38%			
3,4-Diethyl-2-Hexene	0.71	0.29	0.99	0.3	4%			
1-Methyl Cyclohexene						0.90	0.84	-7%

time, as indicated on the table. This gives an average error of 10% and an average absolute percentage error of slightly less than 20% for the three compounds that were studied.

Atkinson (1997a) gives no information concerning primary carbonyl yields from unsymmetrical molecules with -CH=CH- or >C=C< groups – only data for symmetrical molecules are tabulated. For estimation and mechanism generation purposes, we assume equal probability for the two modes of reaction in such cases. The data for the other unsymmetrical molecules indicate that this is probably a good approximation, with the possible exception of molecules that are highly branched on one side where steric effects may come into play.

Table 18 through Table 20 also show measured yields of OH radicals, which are believed to be formed from secondary radicals of the biradical intermediates (see Section III.K). If it is assumed that the OH yields from the excited $HCHO_2$, $RCHO_2$, and $RR'CO_2$ biradicals are independent of the molecule from which they are formed and on the nature of the "R" or "R'" substitutents, then these OH yields should be consistent with the assumed branching ratios and the OH yields assumed for the various types of biradicals. As discussed in Section III.K, the current mechanism assumes that OH yields from excited $HCHO_2$, CH_3CHO_2, are respectively 12%, 52%, and 100%, based primarily on recommendations and data discussed by Atkinson (1997a). The "Calc'd" OH yields on Table 18 through Table 20 show the yields for the various molecules derived based on these assumptions, where they can be compared with the experimental data. In most cases these are consistent with the experimental data, with the percentage errors being no greater than those for the estimated carbonyl yields. Therefore, the estimates based on carbonyl yields and OH yields are self-consistent. However, as discussed in Section III.K, the experimental and estimated OH yields for the C_{4+} 1-alkenes are not consistent with the environmental chamber reactivity data for these compounds, and lower adjusted OH yields have to be used for the purpose of reactivity predictions. However, these adjustments do not affect the assumed branching ratios for the initial O_3 + alkene reactions.

4. Assigned Mechanisms for Initial O_3 Reactions

As with the other reactions discussed above, explicit assignments are used for the initial reactions for those VOCs where estimates cannot be made, where available experimental data indicate the estimates are inappropriate, or where alternative estimates are used. The explicitly assigned branching ratios for the initial O_3 reactions that are currently incorporated in the system are summarized on Table 21, along with the basis for the various assignments that are used.

F. Reactions with O^3P

O^3P atoms can react with compounds with C=C double bonds, forming an excited adduct that may decompose in various ways or undergo collisional stabilization. Although these reactions are generally of negligible importance under most ambient atmospheric conditions, they have been found to be non-negligible in some of the environmental chamber experiments used for mechanism evaluation, where NO_2 concentrations tend to be higher under ambient conditions[11]. They may also be non-negligible in plumes that have higher NO_x concentrations than ambient. For these reasons, O^3P + alkene reactions are included in the current mechanism and are supported by the mechanism generation system.

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[11] Reactions with O_3P increase in importance as NO_2 concentrations increase because NO_2 photolysis is the primary source of O^3P.

Table 21. Assigned mechanisms for the reactions of O_3 with compounds for which estimates could not be made, or where experimental data or other considerations indicate that the general estimates may not be appropriate.

Reactant and Products	Factor	Documentation
1,3-Butadiene [CH2=CH-CH=CH2]		
HCHO + CH2=CH-CHOO[excited]	50.0%	Estimated mechanism.
CH2=CH-CHO + CH2OO[excited]	50.0%	Estimated mechanism.
Isoprene [CH2=CH-C(CH3)=CH2]		
HCHO + CH2=CH-COO[excited]-CH3	20.0%	Mechanism of Carter and Atkinson (1996) is assumed.
HCHO + CH2=C(CHOO[excited])-CH3	20.0%	See above.
CH2=C(CHO)-CH3 + CH2OO[excited]	39.0%	See above.
CH2=CH-CO-CH3 + CH2OO[excited]	16.0%	See above.
O2 + *C(CH=CH2)(CH3)-CH2-O-*	2.5%	See above.
O2 + *CH(C(CH3)=CH2)-CH2-O-*	2.5%	See above.
Acetylene [HC::CH]		
HCO-CHOO[excited]	100.0%	The initially formed primary ozonide is assumed to rearrange to the Crigiee biradical via an O-O bond scission. [a]
Methyl Acetylene [HC::C-CH3]		
CH3-COO[excited]-CHO	50.0%	The initially formed primary ozonide is assumed to rearrange to the Crigiee biradical via an O-O bond scission. Equal probability of formation of each possible isomer is assumed. [a]
CH3-CO-CHOO[excited]	50.0%	See above.
Ethyl Acetylene [HC::C-CH2-CH3]		
CH3-CH2-COO[excited]-CHO	50.0%	The initially formed primary ozonide is assumed to rearrange to the Crigiee biradical via an O-O bond scission. Equal probability of formation of each possible isomer is assumed. [a]
CH3-CH2-CO-CHOO[excited]	50.0%	See above.
2-Butyne [CH3-C::C-CH3]		
CH3-CO-COO[excited]-CH3	100.0%	The initially formed primary ozonide is assumed to rearrange to the Crigiee biradical via an O-O bond scission. [a]
Methacrolein [CH2=C(CHO)-CH3]		
HCHO + CH3-COO[excited]-CHO	10.0%	Mechanism of Carter and Atkinson (1996) is assumed.
CH3-CO-CHO + CH2OO[excited]	90.0%	See above
Hydroxy Methacrolein [CH2=C(CHO)-CH2-OH]		
HCO-CO-CH2-OH + CH2OO[excited]	90.0%	Mechanism of Carter and Atkinson (1996) is assumed.
HCHO + HCO-COO[excited]-CH2-OH	10.0%	See above
Isoprene Product #1 [CH3-C(CHO)=CH(CH2-OH)]		
CH3-CO-CHO + HO-CH2-CHOO[excited]	90.0%	Mechanism of Carter and Atkinson (1996) is assumed.
HCO-CH2-OH + CH3-COO[excited]-CHO	10.0%	See above
Isoprene Product #2 [CH3-C(CHO)=CH-CH2-OH]		
CH3-CO-CHO + HO-CH2-CHOO[excited]	90.0%	Mechanism of Carter and Atkinson (1996) is assumed.
HCO-CH2-OH + CH3-COO[excited]-CHO	10.0%	See above

Table 21 (continued)

Reactant and Products	Factor	Documentation
Isoprene Product #3 [HCO-CH=C(CH3)-CH2-OH]		
CH3-CO-CH2-OH + HCO-CHOO[excited]	90.0%	Mechanism of Carter and Atkinson (1996) is assumed.
HCO-CHO + CH3-COO[excited]-CH2-OH	10.0%	See above
Methylvinyl ketone [CH2=CH-CO-CH3]		
HCHO + CH3-CO-CHOO[excited]	5.0%	Mechanism of Carter and Atkinson (1996) is assumed.
CH3-CO-CHO + CH2OO[excited]	95.0%	See above

[a] Although the biradical excitation energies are almost certainly different from those formed in the reactions of O3 with acroleins, because of lack of availabale information it is assumed to react to form the same products, and thus is represented by the same species.

1. Assigned O^3P Rate Constants

The rate constant assignments used for the O^3P reactions that are incorporated in the present mechanism are given on Table 22, where they are compared for the estimated values for those VOCs for which estimates can be made. The table also indicates the source of the rate constant assignments, which in most cases are from Atkinson (1997a).

2. Estimated O^3P Rate Constants

Since the reactions of alkenes with O^3P and OH radicals are both believed to involve primarily addition to the double bond, one might expect the rate constants for these reactions to be correlated. This is indeed the case for most of the alkenes where both rate constants have been measured, as is shown on Figure 3, which gives a log-log plot of O^3P and OH radical rate constants for the alkenes listed on Table 22. The line shows the least squares fit for the log-log plot for the monoalkenes, which was used for the purpose of estimating O^3P rate constants for those alkenes for which data are not available. This is given by:

$$\ln(kO^3P) = 19.160 + 1.864\ k(OH) \tag{II}$$

where kO^3P and kOH are the O^3P and OH radical rate constants in $cm^3\ molec^{-1}\ s^{-1}$. (Note that the third digits are significant since they are being used to compute logrithms.) Although the dialkens and the terpenes are not used when deriving this fit, Table 22 and Figure 3 show that the above equation performs reasonably well in predicting their rate constants in most cases. Including the terpenes and dialkenes, the average discrepancy is around 25%, and all the discrepancies in all cases except for d-limonene are less than 60%.

3. Estimated Mechanisms for O^3P Reactions

The mechanisms for the reactions of O^3P with the simpler alkenes have been recently reviewed by Atkinson (1997a), though the discussion there is based primarily on the earlier review of Atkinson and Lloyd (1984). The reaction presumably proceeds by O adding to the double bond forming an excited oxide, which can either be collisionally stabilized, undergo a 1,2-H shift to a carbonyl compound and then be stabilized, or decompose in various ways. Neglecting reactions requiring pentavalent transition states that are chemically unreasonable (e.g., formation of isobutyraldehyde from O^3P + 2-butenes), the alternative reaction routes given by Atkinson and Lloyd (1984) and Atkinson (1997a) can be classified as follows:

Table 22. Rate constant and temperature dependence parameter assignments used for reactions of VOCs with O^3P atoms in the present mechanism.

Compound	DMS name	k(300)	A	Ea	Ref	Est'd k(300)	
		(cm^3 $molec^{-1}$ s^{-1})		kcal/mole		k	(diff)
<u>Alkanes</u>							
Ethene	ETHENE	7.42e-13	1.04e-11	1.574	1		
Propene	PROPENE	4.01e-12	1.18e-11	0.644	1	3.91e-12	-2%
1-Butene	1-BUTENE	4.22e-12	1.25e-11	0.648	1	5.43e-12	29%
Isobutene	ISOBUTEN	1.69e-11			2	1.36e-11	-20%
cis-2-Butene	C-2-BUTE	1.76e-11			2	1.62e-11	-8%
trans-2-Butene	T-2-BUTE	2.18e-11			2	2.04e-11	-6%
1-Pentene	1-PENTEN	4.69e-12	1.48e-11	0.686	3	5.42e-12	16%
cis-2-Pentene	C-2-PENT	1.70e-11			2	2.09e-11	23%
3-Methyl-1-Butene	3M-1-BUT	4.18e-12	1.32e-11	0.686	3	5.55e-12	33%
2-Methyl-2-Butene	2M-2-BUT	5.10e-11			2	3.62e-11	-29%
1-Hexene	1-HEXENE	4.69e-12	1.48e-11	0.686	3	7.37e-12	57%
2,3-Dimethyl-2-Butene	23M2-BUT	7.64e-11			2	5.60e-11	-27%
Cyclopentene	CYC-PNTE	2.10e-11			2	2.23e-11	6%
Cyclohexene	CYC-HEXE	2.00e-11			2	2.26e-11	13%
1-Methyl Cyclohexene	1M-CC6E	9.00e-11			2	3.71e-11	-59%
1,3-Butadiene	13-BUTDE	1.98e-11			2		
Isoprene	ISOPRENE	3.60e-11			4		
a-Pinene	A-PINENE	3.20e-11			2		
3-Carene	3-CARENE	3.20e-11			2		
b-Pinene	B-PINENE	2.70e-11			2		
d-Limonene	D-LIMONE	7.20e-11			2		

<u>References</u>

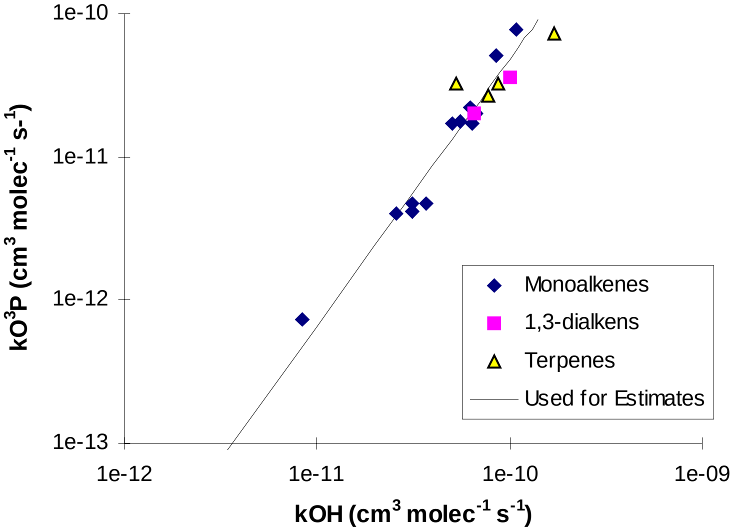
1 Rate constant expression from Atkinson and Lloyd (1984). T=298K value is consistent with recommendation of Atkinson (1997a).

2 Rate constant from Atkinson (1997a). Temperature dependence is expected to be small.

3 T=298K rate constant from Atkinson (1997a). Activation energy estimated from propene and 1-butene, as given by Atkinson and Lloyd (1984).

4 Rate constant from Paulson et al (1995).

Figure 3. Plot of OH radical vs. O^3P rate constants for VOCs in the mechanism where both rate constants are available. Rate constants are for T=300K.



$$O^3P + {>}C{=}C{<} + M \rightarrow \text{oxide} + M \qquad (S1)$$

$$O^3P + {>}C{=}C'H\text{-} + M \rightarrow {>}CH\text{-}C'O\text{-} + M \qquad (S2a)$$

$$O^3P + \text{-}CH{=}C\text{-}{<} + M \rightarrow \text{-}CO\text{-}CH{<} + M \qquad (S2b)$$

$$O^3P + \text{-}CX{=}C'{<} \rightarrow [\text{-}CX(O\cdot)\text{-}C(\cdot){<}] \rightarrow X\cdot + \text{-}CO\text{-}C(\cdot){<} \qquad (D1a)$$

$$O^3P + {>}C{=}C'X\text{-} \rightarrow [{>}C(\cdot)\text{-}C'(O\cdot)X\text{-}] \rightarrow {>}C(\cdot)\text{-}C'O\text{-} + X. \qquad (D1b)$$

$$O^3P + \text{-}CH{=}C'{<} \rightarrow [\text{-}CO\text{-}C'H{<}]^* \rightarrow \cdot CO\text{-} + {>}C'H\cdot \qquad (D2a)$$

$$O^3P + {>}C{=}C'H\text{-} \rightarrow [{>}CH\text{-}C'O\text{-}]^* \rightarrow {>}CH\cdot + \cdot CO\text{-} \qquad (D2b)$$

Where, for unsymmetrical molecules, C' refers to the carbon that has the greater number of substitutents.

Branching ratios estimated or interpolated based on these data are given in Table 23, where the branching ratio designations used are as indicated above, and footnotes indicate the source of the estimated mechanisms. Note that these ratios are applicable to one atmosphere total pressure only – the mechanism generation system currently does not support predicting the effects of total pressure on these yields[12]. Atkinson (1997a) and Atkinson and Lloyd (1994) gave no recommendations for compounds of with CH_2=C<, -CH=C<, or >C=C<, and highly approximate estimates are made based on considerations

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[12] Ignoring these pressure dependences is unlikely to introduce significant errors in tropospheric simulations because NO_2 concentrations are expected to be sufficiently low at higher altitudes that reactions of O^3P with alkenes is expected to be negligible.

Table 23. Estimated branching ratios for the reactions of O^3P with alkenes, based on the recommendations of Atkinson (1997a) and Atkinson and Lloyd (1984). Note that these ratios are not used in the final mechanism because of unsatisfactory results when simulating environmental chamber experiments.

Compound	Branching Ratio							Notes
	S1	S2a	S2b	D1a	D1b	D2a	D2b	
CH2=CH2								
Ethene	0%	0%		60%		40%		1
CH2=CH-								
Propene	30%	30%	0%	20%	0%	20%	0%	2
1-Butene	45%	40%	0%	15%	0%	0%	0%	2
C5 Alkenes	50%	45%	0%	5%	0%	0%	0%	3
C6+ Alkenes	55%	45%	0%	0%	0%	0%	0%	3
CH2=C>								
Isobutene	40%	-	30%	0%	15%	15%	-	4
C5 Alkenes	50%	-	38%	0%	6%	6%	-	3
C6 Alkenes	56%	-	40%	0%	2%	2%	-	3
C7+ Alkenes	60%	-	40%	0%	0%	0%	-	3
-CH=CH-								
2-Butenes	50%	20%		30%		0%		5
C5 Alkenes	64%	24%		12%		0%		3
C6 Alkenes	72%	24%		4%		0%		3
C7+ Alkenes	76%	24%		0%		0%		3
-CH=C<								
2-Methyl-2-Butene	50%	-	38%	6%	6%	0%	-	4
C6 Alkenes	56%	-	40%	2%	2%	0%	-	3
C7+ Alkenes	60%	-	40%	0%	0%	0%	-	3
>C=C<								
2,3-Dimethyl-2-Butene	96%	-		2%	2%	-		4
C7+ Alkenes	100%	-		0%	0%	-		3

1 Based on Atkinson (1997a) recommendation, ignoring ketene formation, which is lumped with the D2 decomposition route

2 Based on Atkinson (1997a) and Atkinson and Lloyd (1984) recommendation. Numbers rounded to nearest 5%

3 Based on extrapolating from data for lower molecular weight alkenes, assuming that stabilization will increase with the size of the molecule increases.

4 Estimated based on recommended mechanisms given by Atkinson and Lloyd (1994) for other alkenes.

5 Based on the Atkinson (1997a) and Atkinson and Lloyd (1984) recommendation, with the chemically unreasonable 20% CH3 shift represented by increasing oxide formation and

of data given by Atkinson and Lloyd (1994) for other compounds[13]. As indicated on the table, stabilization is assumed to become increasingly important for higher molecular weight compounds, and to dominate for C_{7+} alkenes.

Although the branching ratios shown on Table 23 represent our current best estimates based on available product data (Atkinson, 1997a), it was found that using these branching ratios gave unsatisfactory results when conducting model simulations of the available chamber database. This was found to be the case even after reasonable adjustment of the other uncertain parameters in the mechanism that affect radical initiation or termination processes. In order to fit the data, it was necessary to assume much lower radical yields from these O^3P reactions, i.e., that stabilization is much more important than indicated by the available product data. In particular, the model significantly overpredicts the reactivity of 1-butene and 1-hexene if any radical formation in the O^3P reaction is assumed, and consistent fits to the chamber data cannot be obtained unless it is assumed that radical formation from O^3P + propene is also negligible. In addition, assuming only 50% fragmentation in the O^3P + ethene rather than the recommended 100% removes biases in the simulation of the large database of ethene experiments.

The reason for this apparent inconsistency between the chamber data and the O^3P branching ratios indicated by the available product data is unknown, and needs to be investigated. Although O^3P reactions are not important under most atmospheric conditions, they are non-negligible in many of the chamber experiments used for mechanism evaluation, and using incorrect O^3P + alkene mechanisms may compensate for other errors in the mechanism. However, no reasonable adjustments of the other uncertainties in the alkene mechanisms that involve radical initiation/termination processes (such as nitrate yields from the peroxy radicals formed in the OH reaction, radical yields from the biradicals formed in the O_3 reaction, or radical generation in the alkene + NO_3 reactions) could be found to give satisfactory fits to the chamber data using the recommended O^3P branching ratios. Therefore, adjusted branching ratios, assuming no radical formation from C_{3+} alkenes and assuming only 50% fragmentation from ethene, are used in the current version of the mechanism that is developed in this work. These adjusted yields are given on Table 24.

4. Assigned Mechanisms for Dialkenes

Although it is expected that the reactions of O^3P with alkynes are unimportant and therefore are ignored in the mechanism, their reactions with isoprene and 1,3-butadiene may be non-negligible under some conditions, and need to be specified explicitly. The assigned O^3P mechanisms for these compounds are shown on Table 25. The O^3P + isoprene mechanism is based on that of Carter and Atkinson (1996), and the mechanism for 1,3-butadiene is assumed to be analogous. The current system does not have assigned mechanisms for any other VOCs.

G. Photolysis Reactions

Although the previous mechanism represented all aldehydes and ketones using the lumped molecule approach, this approach has proven to be unsatisfactory for the higher ketones (Carter et al, 1999a) and is therefore not used in this mechanism. Instead, specific mechanistic assignments are made for these compounds, based on generated mechanisms for their reactions with OH radicals, NO_3 (for

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[13] It is probable that improved estimates could be made for some of these compounds by reviewing the product data literature. This review was not carried out because of the relatively low importance of these O^3P reactions in most atmospheric simulations, and because in any case the branching ratios had to be revised to fit the chamber data.

Table 24. Adjusted branching ratios for the reactions of O^3P with alkenes that are found to give best fits to the available chamber database and are used in the final version of the mechanism developed in this work.

Groups	Branching Ratio				
	S1	S2a	S2b	D1a+D1b	D2a+D2b
CH_2=CH_2	25%	25%		20%	30%
CH_2=CH-	55%	45%	0%	0%	0%
CH_2=C>	60%	-	40%	0%	0%
-CH=CH-	76%	24%		0%	0%
-CH=C<	60%	-	40%	0%	0%
>C=C<	100%	-		0%	-

Table 25. Assigned mechanisms for the reactions of O^3P atoms with the dialkenes in the current mechanism.

Reactant and Products	Factor	Documentation
Isoprene [CH2=CH-C(CH3)=CH2]		
C(CH=CH2)(CH3)-CH2-O-	50.0%	As assumed by Carter and Atkinson (1996). Products represented by epoxides. Most of the reaction is assumed to occur at the more substituted position.
CH(C(CH3)=CH2)-CH2-O-	25.0%	See above.
CH2=CH-CO-CH2. + CH3.	25.0%	Fragmentation mechanism and yield as assumed by Carter and Atkinson (19896). Approximately 25% radical yield also necessary to obtain satisfactory fit to data with updated mechanism.
1,3-Butadiene [CH2=CH-CH=CH2]		
CH(CH=CH2)-CH2-O-	75.0%	Assumed to be analogous to the isoprene mecanism of Carter and Atkinson (1996). Products represented by epoxides.
CH2=CH-CH[.]-CHO + H.	25.0%	Analogous to the fragmentation mechanism in the isoprene system as assumed by Carter and Atkinson (1996).

aldehydes), and photolyses. Specific mechanistic assignments are also made for the OH radical and photolysis reactions of organic nitrates, which were used for determining the lumped organic nitrate mechanism as discussed in Section II.C.2. The estimation and generation of their initial reactions with OH radicals and NO_3 were discussed above. This section discusses the estimation and generation of their initial photolysis reactions.

Photolysis rates for the aldehydes and organic nitrates are estimated by assuming that they have the same absorption cross sections and quantum yields as the most chemically similar lower molecular weight analogue that is in the base mechanism. In the case of the ketones, it is assumed that the overall quantum yield decreases with the size of the molecule, based on overall quantum yields which give best fits of model simulations to environmental chamber data for methyl ethyl ketone, methyl propyl ketone, methyl isobutyl ketone, and methyl amyl ketone (see Section V and Appendix B). The specific assignments are as summarized on Table 26, along with footnotes indicating the derivations of the assignments and the groups used by the mechanism generation system to classify compounds according to photolysis type. Note that if the molecule has groups bonded to the carbonyl or nitrate groups that are different than those indicated on the table, then the system cannot currently generate photolysis reactions for compounds with that structure.

1. Default Carbonyl Photolysis Mechanisms

Although the actual mechanisms for the photolysis reactions of the higher molecular weight carbonyl compounds may well be more complex (Calvert and Pitts, 1966), unless information is available otherwise, it is assumed that all photolyses of carbonyls proceed by breaking the weakest CO-C bond. In the case of aldehydes (including glyoxals) this means the reaction is assumed to always proceed via

$$\text{R-CHO} + h\nu \rightarrow \text{R}\cdot + \text{HCO}\cdot$$

(where “R”. would be R’CO in the case of glyoxals) and in the case of α-dicarbonyl ketones it is assumed always to proceed via

$$\text{R-CO-CO-R'} + h\nu \rightarrow \text{RCO}\cdot + \text{R'CO}\cdot$$

In the case of unsymmetrical ketones, two possible reactions are considered:

$$\text{R-CO-R'} + h\nu \rightarrow \text{R}\cdot + \text{R'CO}\cdot$$

$$\text{R-CO-R'} + h\nu \rightarrow \text{RCO}\cdot + \text{R'}\cdot$$

In this case, the pathway with the lowest estimated heat of reaction is assumed to 100% of the time, regardless of the differences between them. This gives a prediction that is consistent with the assumed photolysis mechanism for methyl ethyl ketone in the base mechanism.

2. Unsaturated Carbonyl Photolysis

Somewhat different photolysis mechanisms are assigned for acrolein, methacrolein and methyl vinyl ketone, based on the mechanisms for the latter two given by Carter and Atkinson (1996). The base mechanism listing gives the assignments and documentation in the cases of methacrolein and MVK. In the case of acrolein, the following initial photolysis mechanism is used, which is derived by analogy to the Carter and Atkinson (1996) mechanism for methacrolein.

$$\text{CH}_2\text{=CH-CHO} + h\nu \rightarrow \text{HCO}\cdot + \text{CH}_2\text{=CH}\cdot \qquad (34\%)$$

$$\text{CH}_2\text{=CH-CHO} + h\nu \rightarrow \text{H}\cdot + \text{CH}_2\text{=CH-CO}\cdot \qquad (33\%)$$

$$\text{CH}_2\text{=CH-CHO} + h\nu \rightarrow \text{CO} + \text{CH}_3\text{CH:} \qquad (33\%)$$

The subsequent reactions of the radicals or carbenes formed are discussed in the following sections.

For the other unsaturated aldehydes, including specifically those used to derive the mechanism for the ISOPROD model species, the default mechanism, based on assuming 100% HCO· formation is assumed. The current mechanism has no mechanistic assignments for unsaturated ketones other than MVK, and in general specific assignments would need to be given for the individual compounds.

Table 26. Summary of assignments of absorption cross sections and quantum yields for carbonyl and organic nitrate photolysis reactions.

Compound Type	Phot. Set	Q.Yield	Note	Group Definition used to Determine Type
Aldehydes	C2CHO	-	1,2	-CHO groups bonded to $-CH_3$, $-CH_2-$, -CH< or -C<
Ketones (4 groups)	KETONE	0.15	3,4	-CO- groups bonded to $-CH_3$, $-CH_2-$, -CH< or -C<, with a total of 4 groups in the molecule.
Ketones (5)	KETONE	0.10	3,5	As above, but 5 groups in the molecule
Ketones (6)	KETONE	0.05	3,6	As above, but 6 groups in the molecule
Ketones (7)	KETONE	0.02	3,7	As above, but 7 groups in the molecule
Ketones (8)	KETONE	0.01	3,8	As above, but 8 groups in the molecule
Ketones (9+)	No photolysis		3,9	As above, but more than 8 groups in the molecule
Alkyl Glyoxal	MGLY_ADJ	-	1,4	-CHO- broups bonded to -CO-
Dialkyl Glyoxyl	BACL_ADJ	-	1,5	-CO- groups bonded to -CO-
Acrolein	ACROLEIN	2.0e-3	3,6	CH2=CH-CHO only.
Other Acroleins	ACROLEIN	4.1e-3	3,7	-CHO groups bonded to -CH= or >C=
Vinyl Ketone	ACROLEIN	2.1e-3	3,8	-CO- groups bonded to -CH= or >C=
Ester or Acid	No photolysis		9	-CO- or -CHO- groups bonded to -O- or -OH
Organic Nitrates	IC3ONO2	1.0	10	$-ONO_2$ groups bonded to $-CH_3$, $-CH_2-$ -CH< or -C<

Notes

1 The wavelength dependent quantum yields are given with the absorption cross sections in the photolysis set. See base mechanism documentation and mechanism listing.

2 Assumed to have same photolysis rate as propionaldehyde.

3 The photolysis set gives the absorption cross sections only, which are given with the base mechanism listing. The wavelength-independent quantum yield is shown on the table.

4 Overall quantum yield adjusted based on model simulations of environmetal chamber experiments with methyl ethyl ketone (Carter et al, 1999a).

5 Overall quantum yield adjusted based on model simulations of environmetal chamber experiments with methyl propyl ketone (Carter et al, 1999e).

6 Overall quantum yield adjusted based on model simulations of environmetal chamber experiments with methyl isobutyl ketone (Carter et al, 1999a).

7 Overall quantum yield adjusted based on model simulations of environmetal chamber experiments with 2-heptanone (Carter et al, 1999e).

8 Estimated to have an overall quantum yield which is half that estimated for ketones with seven groups.

9 Photodecomposition is estimated to be unimportant for ketones with nine or more groups.

4 Assumed to have the same photolysis rate as methyl glyoxal.

5 Assumed to have the same photolysis rate as biacetyl.

6 Overall quantum yield adjusted to fit model simulations of O3, NO, acrolein, and formaldehyde in acrolein - NOx chamber runs ITC941, 943, and 944.

7 Assumed to have same photolysis rate as methacrolein. See base mechanism documentaion.

8 Assumed to have same photolysis rate as methyl vinyl ketone. See base mechanism documentation.

9 Photolysis assumed to be negligible, based on absorption cross section data given by Calvert and Pitts

10 All alkyl nitrates are assumed to photolyze at the same rate and with a unit quantum yield. Absorption cross sections used are those recommended by IUPAC (Atkinson et al, 1997a, 1999) for isopropyl nitrate.

3. Organic Nitrate Photolysis

As discussed in Section II.C.2, although organic nitrate products are represented using the lumped molecule approach, the mechanism for the generic organic nitrate model species used for this purpose is derived based on generated mechanisms for individual organic nitrate compounds. The rates of their photolysis reactions are determined as shown on Table 26, which indicates that all organic nitrates are assumed to photolyze using the absorption cross sections recommended by IUPAC (Atkinson et al, 1997a, 1999a) for isopropyl nitrate. As discussed there, the quantum yield for NO_2 formation is assumed to be unity. In view of this, all organic nitrate photolysis reactions are represented by the general mechanism

$$RONO_2 + h\nu \rightarrow RO\cdot + NO_2$$

The subsequent reactions of the alkoxy radicals are then derived using the general methods discussed in Section III.J.

H. Reactions of Carbon Centered Radicals

Carbon-centered radicals are any radicals containing the groups CH3., -CH2., -CH[.]-, >C[.]-, HCO., -CO., =CH., or =C[.]. Except as indicated below or in Table 27, these are assumed to react exclusively by O_2 addition, forming the corresponding peroxy group. The general exceptions are as follows:

- Vinylic radicals are assumed to react via the mechanism

  $$HC{=}CH\cdot + O_2 \rightarrow HCHO + HCO.$$

  based on the data of Slagle et al (1984). Except as indicated below, substituted vinylic radicals are assumed to react analogously, e.g.,

  $$>C{=}CX\cdot + O_2 \rightarrow >C{=}O + XCO.$$

  Where -X is -H or any non-radical group. The exceptions are radicals of the type HO-C=C· formed in the reactions of OH with acetylenes, where specific mechanistic assignments are made as indicated below in Table 27.

- α-Hydroxy alkyl radicals are assumed to react by O_2 abstraction from the -OH, forming HO_2 and the corresponding carbonyl compound, e.g.,

  $$>C[\cdot]\text{-}OH + O_2 \rightarrow >C{=}O + HO_2$$

  The assumption that this reaction dominates for α-hydroxy radicals is based on results of product studies of reactions of alcohols and other OH-substituted compounds in the presence of O_2.

- α-Nitroxy alkyl radicals, which can be formed in the reactions of NO_3 radicals with alkenes, are assumed to undergo rapid unimolecular decomposition to NO_2 and the corresponding carbonyl compound, e.g.,

  $$>C[\cdot]\text{-}ONO_2 \rightarrow >C{=}O + NO_2$$

Table 27. Mechanistic assignments for carbon-centered radicals that are assumed not to react as as estimated for general carbon-centered radicals.

Reactant	Product(s)	Yield	Notes
<u>OH-Substituted Vinylic Radicals (from OH + Acetylenes)</u>			
HO-CH=CH.	HCO-OH + HCO.	33%	1
	HCO-CHO + OH	67%	
CH3-C[.]=CH(OH)	HCO-OH + CH3-CO.	33%	2
	CH3-CO-CHO + OH	67%	
CH3-C[.]=CH-OH	HCO-OH + CH3-CO.	33%	2
	CH3-CO-CHO + OH	67%	
CH3-C(OH)=C[.]-CH3	CH3-CO-OH + CH3-CO.	33%	2
	CH3-CO-CO-CH3 + OH	67%	
CH3-CH2-C[.]=CH-OH	HCO-OH + CH3-CH2-CO.	33%	2
	CH3-CH2-CO-CHO + OH	67%	
<u>Allylic Radicals</u>			
CH2=CH-C[.](CH3)-CH2-OH	CH2=CH-C[OO.](CH3)-CH2-OH	67%	3,4
	HO-CH2-C(CH3)=CH-CH2OO.	16.5%	
	HO-CH2-C(CH3)=CH(CH2OO.)	16.5%	
CH2=C(CH3)-CH[.]-CH2-OH	CH2=C(CH3)-CH[OO.]-CH2-OH	59.2%	3,5
	CH3-C(CH2OO.)=CH(CH2-OH)	20.4%	
	CH3-C(CH2OO.)=CH-CH2-OH	20.4%	
HO-CH2-C(CH2.)=CH(CH2-OH)	CH2=C(CH2-OH)-CH[OO.]-CH2-OH	100%	3,6
C(CH3)=CH-O-CH2-CH[.]-	*O-CH=C(CH3)-CH=CH-* + HO2.	100%	3,7
C[.](CH3)-CH=CH-O-CH2-	*O-CH=C(CH3)-CH=CH-* + HO2.	100%	3,7
CH2=CH-C[.](CH3)-CH2-ONO2	.OOCH2-CH=C(CH3)-CH2-ONO2	100%	3,8
CH2=CH-CH[.]-CH2-OH	CH2=CH-CH[OO.]-CH2-OH	50%	9
	HO-CH2-CH=CH-CH2OO.	25%	
	HO-CH2-CH=CH(CH2OO.)	25%	
CH2=CH-CH[.]-CH2-ONO2	.OOCH2-CH=CH-CH2-ONO2	50%	3,10
	.OOCH2-CH=CH(CH2-ONO2)	50%	

Table 27 (continued)

Reactant	Product(s)	Yield	Notes
Allylic Radical Precursors			
C(CH3)(OH)-CH2-O-CH2-CH[.]-	H2O + *C(CH3)=CH-O-CH2-CH[.]-*	100%	3,7
CH(OH)-C[.](CH3)-CH2-O-CH2-	H2O + *C[.](CH3)-CH=CH-O-CH2-*	100%	3,7

1 Estimated mechanism is based on the data of Hatakeyama et al (1986) and modeling acetylene environmental chamber runs Carter et al (1997c).

2 Estimated by analogy with assumed reactions of HO-CH=CH. from acetylene.

3 Ratios of reaction of O2 at different positions of the allylic radical is assumed to be as discussed by Carter and Atkinson (1996).

4 The relative importance of this reaction is based on observed yields of methyl vinyl ketone in the reactions of OH radicals with isoprene.

5 The relative importance of this reaction is based on observed yields of methyl vinyl ketone in the reactions of OH radicals with methacrolein.

6 This reaction is assumed to dominate to be consistent with results of API-MS isoprene + OH product studies of Kwok et al (1995), which indicate that C5-dihydroxycarbonyls, the predicted products of the competing reactions, are not formed.

7 It is necessary to assume this radical reacts as shown in order to explain the observed formation of 3-methyl furan from the reaction of OH radicals with isoprene (Carter and Atkinson, 1996).

8 Assumed to dominate over addition at the least substituted end of the allylic radical to be consistent with product data, as discussed by Carter and Atkinson (1996). Formation of only one of the two possible cis-trans isomers is shown because the reactions of the other isomer are expected to give the same products.

9 Equal probablity of addition at either radical center of the allylic radical is assumed.

10 100% terminal addition to allylic radical is assumed, to be consistent with mechanism assumed for isoprene (Carter and Atkinson, 1996). Equal probablity of cis and trans formation is assumed.

This is assumed to be an extremely rapid decomposition based on its high estimated exothermicity, combined with the expectation that the decomposition should not have a large activation energy. However, experimental (and theoretical) verification of this assumption would be useful.

- Carbenes are assumed to react with O_2, forming an excited Crigiee biradical, e.g.,

$$>C[:]- + O_2 \rightarrow >CO2[excited]-$$

Although the excitation energy is almost certainly different than those formed in O_3 + alkene reactions, for lack of available information otherwise the excited Crigiee biradicals are assumed to react with the same mechanism, and are therefore represented by the same species in the mechanism generation system. The reactions of Crigiee biradicals are discussed in Section III.K.

In addition to the above general exceptions, specific mechanistic assignments are made for some of the unsaturated carbon-centered radicals formed in the reactions of the special reactants that are currently supported by the system. These assignments are indicated on Table 27, along with footnotes documenting the reasons for the assignments. As shown there, there are three types of radicals that are considered, as follows:

1) OH-substituted vinylic radicals formed by OH addition to acetylenes whose mechanisms are assigned based on the assumed mechanism for acetylene (Carter et al, 1997c);
2) various allylic radicals where O_2 can add at more than one radical center, where the branching ratio assignments are based primarily on data from isoprene product studies (Carter and Atkinson, 1996); and
3) precursors to allylic radicals that are assumed to react with O_2 by abstraction forming HO_2 and allylic radicals, in order to account for the formation of 3-methyl furan from the reactions of OH with isoprene (Carter and Atkinson, 1996).

Note that the assignments for the allylic radicals that are based on product data are not always consistent with each other [e.g., addition of O_2 to the least substituted position is assumed for the nitrate-substituted radicals, while the opposite assumption is made for HO-CH2-C(CH2.)=CH(CH2-OH) to be consistent with product data]. Thus, these must be considered to be highly uncertain.

Although one might expect radicals of the type R-O-C(O)· to rapidly decompose to R· + CO_2, model simulations of reactivity experiments with methyl isobutyrate, which is predicted to form $CH_3OC(O)\cdot$ radicals in high yields, cannot fit the data if this is assumed (Carter et al, 1999a). Therefore, we assume that these radicals do not decompose, but instead add O_2 to form radicals of the type ROC(O)OO·, which can react with NO_2 to form PAN analogues of the type $ROC(O)OONO_2$. However, direct product data for systems where these radicals may be formed are needed to verify if this is indeed the case.

I. Reactions of Peroxy Radicals

Peroxy radicals are critical intermediates in almost all the generated mechanisms. Although under atmospheric conditions they can react with NO_2, NO_3, HO_2, and other peroxy radicals, the current version of the system only generates their reactions with NO. This is because reaction with NO is the major fate of peroxy radicals under conditions where reactions of VOCs contribute to tropospheric ozone, and the current base mechanism uses condensed approaches to represent the effects of the other reactions (see Section II.B.4). The reactions of non-acyl peroxy radicals with NO_2 are ignored because they are assumed to be rapidly reversed by the thermal decomposition of the peroxynitrate formed. The reactions of acyl peroxy radicals with NO_2 are not considered because acyl peroxy radicals are represented by lumped species so their reactions do not need to be generated. The products of peroxy + NO_3 and peroxy + peroxy reactions are represented by lumped species, so they are not considered in the mechanism generation system.

The main factor that needs to be determined when generating reactions of peroxy radicals with NO is the branching ratio between formation of NO_2 and the corresponding alkoxy radical, or addition and rearrangement forming the organic nitrate, e.g.

$$RO_2\cdot + NO \rightarrow RO\cdot + NO_2 \qquad (A)$$

$$RO_2\cdot + NO + M \rightarrow RONO_2 + M. \qquad (N)$$

The rate constant ratio $k_N/(k_A+k_N)$ is referred to as the “nitrate yield” in the subsequent discussion. This is a potentially important factor affecting a VOC’s atmospheric impact because if nitrate formation (process “N”) is a radical termination process and can significantly inhibit radical levels if it is sufficiently important compared to propagation (process “A). Unfortunately, except for secondary peroxy radicals formed from the C_3-C_{10} n-alkanes, direct information concerning nitrate yields is extremely limited, and nitrate yields have to be either estimated or (for those few cases where this is possible) adjusted to fit overall reactivity observed in environmental chamber experiments.

For the peroxy radicals formed from alkane photooxidations, the previous version of the mechanisms used yields estimated by Carter and Atkinson (1989b). These are based on data for nitrate yields from reactions of OH with C_3-C_8 n-alkanes and several C_5 and C_6 branched alkanes at ambient temperature and pressure, and on nitrate yields at different temperatures and pressures in OH reactions of several C_5 and C_7 alkanes. The data indicate that nitrate yields from alkyl peroxy radicals increase with the size of the molecule from less than 5% for C_3 to ~33% for C_8 (with an apparent upper limit of 40-50% for larger molecules), and also increase with decreasing temperature and decrease with decreasing pressure. This suggests that the rate of the nitrate formation reaction is governed by similar factors affecting other three-body reactions, whose temperature and pressure dependences can be parameterized using a modified version of the “Troe” falloff expression that is currently used in the evaluations. Based on this, Carter and Atkinson (1989b) used the following parameterization to fit the nitrate yield data for the secondary alkyl peroxy radicals:

$$Y_{sec}(n_C, T, M) = (k_N/k_R) / [1 + (k_N/k_R)] \qquad \text{(III)}$$

where Y_{sec} is the nitrate yield for secondary alkyl radicals with n_C carbons at temperature T (in ^oK) and total pressure M (in molecules cm^{-3}), and the rate constant ratio k_N/k_R is derived from

$$k_N/k_R = \{R_0(T,n_C)\cdot M/[1 + R_0(T,n_C)\cdot M/R_\infty(T)]\}\cdot F^Z \qquad \text{(IV)}$$

where

$$R_0(T,n_C) = \alpha \cdot e^{\beta\cdot n_C} \cdot (T/300)^{-m_0}$$

$$R_\infty(T) = R_\infty^{300} \cdot (T/300)^{-m_\infty}$$

$$Z = \{1 + [\log_{10}\{R_0(T,n_C)\cdot M)/R_\infty(T)\}]^2\}^{-1}$$

and α, β, R_∞^{300}, m_0, m_∞, and F are empirical parameters that are optimized to fit the data. Based on the data available at the time, Carter and Atkinson (1989b) derived α=1.94 x 10^{-22} cm^3 $molecule^{-1}$, β=0.97, R_∞^{300}=0.826, m_0=0, m_∞=8.1, and F=0.411. The limited (and somewhat inconsistent) data for primary and tertiary peroxy radicals indicate that lower nitrate yields are formed from these radicals, and Carter and Atkinson (1989b) recommended using scaling factors of 0.4±0.05 and 0.3±0.15 for secondary and tertiary peroxy radicals, respectively.

Most of the data concerning the effects of nitrate yields on carbon number come from the measurements of Atkinson et al (1982b, 1984), and the temperature and pressure effects data come from Atkinson et al (1983b). More recently, using what Atkinson (private communication, 1999) believes is improved chromatographic methods, Arey et al (1999) remeasured the nitrate yields from the C_3-C_8 n-alkanes. They obtained significantly lower nitrate yields for the C_{5+} radicals, and Atkinson and co-workers (unpublished results, 1999) obtained nitrate yield data from n-decane than estimated using the parameterization of Carter and Atkinson (1989b). For example, the new data indicate a nitrate yield of 24% for the C_8 secondary peroxy radicals, compared to the previous measurement of ~33%. As discussed below, these lower nitrate yields resulted in model being able to fit chamber data without having to make the chemically unreasonable assumption that hydroxy-substituted C_{6+} peroxy radicals formed after alkoxy radical isomerizations did not form nitrates when they reacted with NO, as had to be made in previous versions of the mechanism (Carter, 1990; Carter and Atkinson, 1985). Therefore, the earlier nitrate yields of Atkinson et al (1982b, 1983b, 1984), which are all based on similar analytical methods, appear to be low.

Because of this, the parameter values of Carter and Atkinson (1989b) are no longer appropriate for general estimation purposes and need to be re-derived to be consistent with the new data. To determine temperature and pressure effects, we assume that the data of Atkinson et al (1983b) are valid in a relative sense (i.e., the errors are in the nitrate calibrations), so relative changes with temperature and pressure are still correct), and correct all the data to be consistent with the remeasured yields at atmospheric temperature and pressure. Table 28 gives the nitrate yield data that were used to re-derive the parameterization, along with footnotes giving the source of the data or how they were derived. These include all the new data currently available from Atkinson's laboratory, together with the pentyl and heptyl nitrate yields at varying temperatures and pressures from Atkinson et al (1983b), corrected to be consistent with the new data. The temperature and pressure effects data for the branched secondary alkyl nitrate data from Atkinson et al (1983b) (see also Carter and Atkinson, 1989b) were not used because there are no more recent data available to correct the yields, and because the pentyl and heptyl nitrate data should be a sufficient basis for the optimization.

The new parameter values were derived using a non-linear optimization procedure to minimize the sum of squares of the quantity (estimated nitrate yield - measured nitrate yield) / max (0.1, observed nitrate yield). This was used because minimizing absolute errors resulted in giving undue weight to the (somewhat uncertain) data obtained at the lowest temperature causing the derivation of unreasonable optimized parameters. On the other hand, minimizing simply relative errors put undue weight on the lowest nitrate yields, which have the highest experimental uncertainty and are least important in affecting reactivity predictions. The parameter obtained in the optimization were as follows:

$\alpha = 3.94 \times 10^{-22}$ cm^3 molecule^{-1}
$\beta = 0.705$
$R_\infty^{300} = 0.380$
$m_0 = 2.15$
$m_\infty = 6.36$
$F = 0.745$

Note that the above value of R_∞^{300}, which is essentially the upper limit nitrate yield for high molecular weight compounds at ambient temperatures, is a factor of 1.6 lower than the upper limit derived from the previous parameterization. On the other hand, nitrate yield predictions for lower molecular weight compounds under ambient conditions are not as significantly affected.

Table 28 shows the nitrate yields estimated using these reoptimized parameters. These are used as the basis for the secondary nitrate yields estimates in the current mechanism, except as indicated below. A comparison for the experimental and calculated values for these data is also shown on Figure 4. It can be seen that reasonably good fits are obtained, though there may be a slight tendency for the parameterization to underpredict the yields at the lowest temperature and highest pressure.

Table 28. Alkyl nitrate yield data from the reactions of NO with secondary alkyl radicals that were used to derive the parameters to estimate secondary alkyl nitrate yields as a function of temperature, pressure, and carbon number.

Compound	nC	T	P	Yield				Fit	
or Radical		(K)	(molec cm^3)	Uncor	Corr	Ref	Calc	Wt	Err
Propane	3	300	2.37e+19		4.0%	1,2	5.0%	100%	11%
n-Butane	4	300	2.37e+19		8.3%	1,2	7.9%	100%	-4%
n-Pentane	5	300	2.37e+19	13.4%	11.5%	1,2	11.4%	100%	0%
n-Hexane	6	300	2.37e+19		15.0%	1,2	15.3%	100%	2%
n-Heptane	7	300	2.37e+19	29.1%	18.7%	1,2	18.9%	100%	1%
n-Octane	8	300	2.37e+19		23.6%	1,2	21.8%	100%	-7%
n-Decane	10	300	2.37e+19		24.1%	2,3	25.0%	100%	4%
Cyclohexyl	6	300	2.37e+19		16.5%	4	15.3%	100%	-7%
2-Pentyl	5	284	2.52e+19	15.8%	13.5%	5	14.3%	5%	6%
	5	284	1.21e+19	10.6%	9.1%		9.7%	5%	6%
	5	284	5.27e+18	6.8%	5.8%		5.5%	5%	-3%
	5	300	1.63e+19	9.9%	8.5%		9.5%	5%	10%
	5	300	1.13e+19	9.5%	8.1%		7.7%	5%	-4%
	5	300	4.96e+18	6.0%	5.1%		4.5%	5%	-7%
	5	300	1.82e+18	3.1%	2.7%		2.0%	5%	-7%
	5	328	2.18e+19	8.2%	7.0%		7.8%	5%	8%
	5	326	1.19e+19	6.4%	5.5%		5.9%	5%	5%
	5	327	4.46e+18	3.9%	3.3%		3.2%	5%	-2%
	5	337	2.12e+19	7.9%	6.8%		6.9%	5%	2%
3-Pentyl	5	284	2.52e+19	17.4%	14.9%	3,4	14.3%	5%	-4%
	5	284	1.21e+19	12.0%	10.3%		9.7%	5%	-6%
	5	284	5.27e+18	7.5%	6.4%		5.5%	5%	-9%
	5	300	1.63e+19	10.7%	9.2%		9.5%	5%	3%
	5	300	1.13e+19	10.3%	8.8%		7.7%	5%	-11%
	5	300	4.96e+18	5.9%	5.0%		4.5%	5%	-6%
	5	300	1.82e+18	3.1%	2.7%		2.0%	5%	-7%
	5	328	2.18e+19	8.4%	7.2%		7.8%	5%	6%
	5	326	1.19e+19	6.6%	5.6%		5.9%	5%	3%
	5	327	4.46e+18	4.4%	3.8%		3.2%	5%	-6%
	5	337	2.12e+19	8.1%	6.9%		6.9%	5%	0%
2-Heptyl	7	284	2.52e+19	29.8%	19.1%		23.9%	2.5%	25%
	7	285	1.18e+19	24.9%	16.0%		18.6%	2.5%	16%
	7	283	5.43e+18	16.3%	10.5%		13.6%	2.5%	30%
	7	284	1.97e+18	11.5%	7.4%		7.4%	2.5%	1%
	7	300	1.14e+19	23.1%	14.8%		15.1%	2.5%	2%
	7	300	5.15e+18	14.6%	9.4%		10.8%	2.5%	14%
	7	300	1.80e+18	10.1%	6.5%		5.9%	2.5%	-6%

Table 28 (continued)

Compound or Radical	nC	T (K)	P (molec cm^3)	Yield				Fit	
				Uncor	Corr	Ref	Calc	Wt	Err
2-Heptyl (cont'd)	7	323	2.21e+19	20.4%	13.1%		13.5%	2.5%	3%
	7	323	1.06e+19	16.3%	10.5%		10.9%	2.5%	4%
	7	324	4.65e+18	10.4%	6.7%		7.7%	2.5%	10%
	7	321	1.79e+18	7.1%	4.6%		4.7%	2.5%	2%
	7	339	2.11e+19	15.9%	10.2%		10.7%	2.5%	5%
	7	342	4.52e+18	8.9%	5.7%		6.1%	2.5%	4%
3-Heptyl	7	284	2.52e+19	35.2%	22.6%		23.9%	2.5%	6%
	7	285	1.18e+19	29.1%	18.7%		18.6%	2.5%	-1%
	7	283	5.43e+18	19.6%	12.6%		13.6%	2.5%	8%
	7	284	1.97e+18	14.1%	9.1%		7.4%	2.5%	-16%
	7	300	1.14e+19	29.3%	18.8%		15.1%	2.5%	-20%
	7	300	5.15e+18	17.7%	11.4%		10.8%	2.5%	-5%
	7	300	1.80e+18	12.2%	7.8%		5.9%	2.5%	-19%
	7	323	2.21e+19	22.6%	14.5%		13.5%	2.5%	-7%
	7	323	1.06e+19	17.9%	11.5%		10.9%	2.5%	-5%
	7	324	4.65e+18	12.2%	7.8%		7.7%	2.5%	-1%
	7	321	1.79e+18	8.8%	5.7%		4.7%	2.5%	-9%
	7	339	2.11e+19	17.2%	11.1%		10.7%	2.5%	-3%
	7	342	4.52e+18	9.6%	6.2%		6.1%	2.5%	0%
3-Heptyl	7	284	2.52e+19	31.4%	20.2%		23.9%	2.5%	18%
	7	285	1.18e+19	26.5%	17.0%		18.6%	2.5%	9%
	7	283	5.43e+18	17.6%	11.3%		13.6%	2.5%	20%
	7	284	1.97e+18	12.1%	7.8%		7.4%	2.5%	-3%
	7	300	1.14e+19	23.6%	15.2%		15.1%	2.5%	0%
	7	300	5.15e+18	15.3%	9.8%		10.8%	2.5%	10%
	7	300	1.80e+18	10.5%	6.7%		5.9%	2.5%	-8%
	7	323	2.21e+19	20.0%	12.9%		13.5%	2.5%	5%
	7	323	1.06e+19	16.0%	10.3%		10.9%	2.5%	6%
	7	324	4.65e+18	10.2%	6.6%		7.7%	2.5%	11%
	7	321	1.79e+18	7.3%	4.7%		4.7%	2.5%	0%
	7	339	2.11e+19	15.3%	9.8%		10.7%	2.5%	9%
	7	342	4.52e+18	8.4%	5.4%		6.1%	2.5%	7%

References

1 Nitrate yields for secondary radicals derived from total secondary nitrate yield from reactions of the n-alkane, divided by the fraction of formation of secondary radicals, as estimated using the method of Kwok and Atkinson (1995).

2 Total secondary nitrate yields from Arey et al (1999).

3 Total secondary nitrate yield from Atkinson (unpublished data, 1999).

4 Aschmann et al. (1997).

5 Nitrate yields relative to nitrate yields at ~300K and 1 atm total pressure from Atkinson et al (1983), as tabulated by Carter and Atkinson (1989). Data placed on an absolute basis using the ~300K, 1 atm total secondary nitrate yield data from Arey et al (1999), divided by the fraction of formation of secondary radicals as estimated by the method of Kwok and Atkinson (1995).

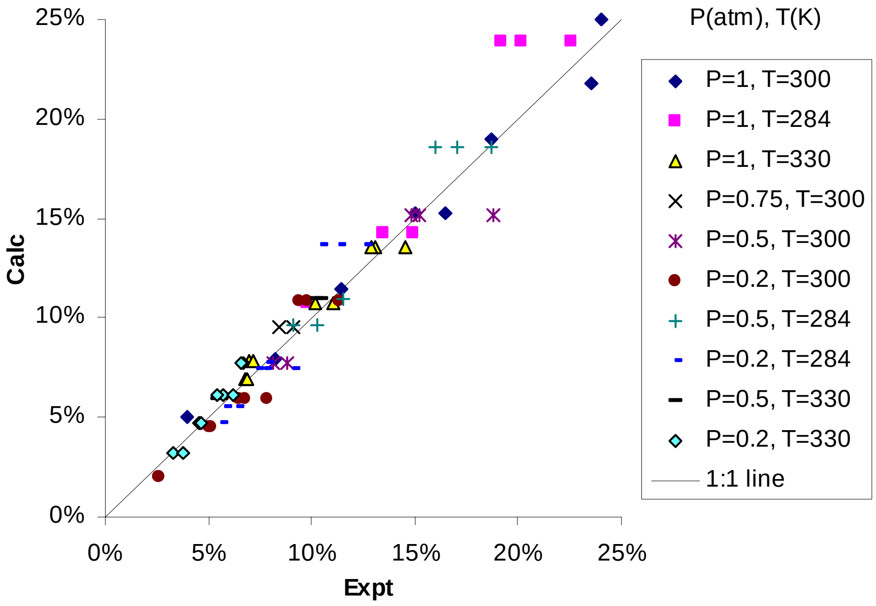

Figure 4. Plots of experimental vs calculated secondary alkyl nitrate yields that were used to optimize the parameters for estimation purposes.

The data summarized by Carter and Atkinson (1989b) indicate that the parameterization that fits the data for secondary alkyl nitrates does not perform well in predicting the limited nitrate yield data for primary and tertiary peroxy radicals. In addition, the presence of -OH, -O-, -CO-, ester, or other groups may also affect nitrate yields. Available information concerning nitrate yields that can serve as a basis for deriving estimates for substituted and non-secondary peroxy radicals is given in Table 29. As indicated on the table, most of these “nitrate yields” are not results of direct measurements, but results of optimizations of nitrate yield parameters in order to fit environmental chamber data. Although these chamber data are highly sensitive to this parameter, this is obviously a highly uncertain “measurement” because the results can be affected by other uncertainties in the VOCs’ mechanisms, as well in the ability of the model to simulate the conditions of the experiment (see Section V). Nevertheless, for most types of radicals this provides the only information available from which general estimates can be derived.

Table 29 shows that the estimates for secondary alkyl peroxy radicals (shown in the Y_{sec} column on the table) generally perform very poorly in fitting the data for these substituted or other radicals, in most cases overpredicting the observed or adjusted yields. This means that some correction is needed when estimating nitrate yields for substituted or non-secondary peroxy radicals. Carter and Atkinson (1989b) recommended using a correction factor for the purpose of estimating primary and tertiary nitrate yields, This is equivalent to assuming that

$$Y_i\,(n_C, T, M) = Y_{sec}\,(n_C, T, M) \cdot f_i \qquad \text{(V)}$$

where Yi is the yield computed for radicals of type i, Y_{sec} is the yield for secondary alkyl radicals computed as shown above, and f_i is a correction factor for this type of radical. This method, if generally applied, would mean that substitution or radical structure affects nitrate yields in a way that does not

Table 29. Alkyl nitrate yield assignments used in the current mechanism, including data used to derive general estimation methods for primary, tertiary, and substituted peroxy radicals.

Compound and Radical	Nitrate Yield			Ref.
	Value Used	Estimated		
		Y_{sec}	Y_{corr}	
<u>Propane</u>				
CH3-CH2-CH2OO.	2.0%	5.0%	0.0%	1
CH3-CH[OO.]-CH3	4.0%	5.0%	5.0%	2
<u>Neopentane</u>				
CH3-C(CH3)(CH2OO.)-CH3	5.1%	11.4%	6.4%	1
<u>2,2,4-Trimethyl Pentane [b]</u>				
CH3-C(CH3)(CH3)-CH2-C[OO.](CH3)-CH3	10.2%	21.8%	17.2%	3
CH3-C(CH3)(CH2OO.)-CH2-C(CH3)(OH)-CH3	10.2%	21.8%	17.2%	3
CH3-C(CH3)(CH3)-CH[OO.]-CH(CH3)-CH3	12.9%	21.8%	21.9%	3
CH3-C(CH3)(CH2OO.)-CH2-CH(CH3)-CH3	10.2%	21.8%	17.2%	3
CH3-C(CH3)(CH3)-CH2-CH(CH2OO.)-CH3	10.2%	21.8%	17.2%	3
CH3-C[OO.](CH3)-CH2-C(CH3)(CH3)-CH2-OH	10.2%	21.8%	17.2%	3
CH3-C(CH3)(OH)-CH2-C(CH3)(CH2OO.)-CH2-OH	10.2%	21.8%	17.2%	3
CH3-C(CH3)(OH)-CH2-C[OO.](CH3)-CH3	7.9%	19.0%	13.4%	3
CH3-C(OH)(CH2OO.)-CH2-C(CH3)(OH)-CH3	7.9%	19.0%	13.4%	3
CH3-CH(CH3)-CH2-C[OO.](CH3)-CH3	7.9%	19.0%	13.4%	3
CH3-C(CH3)(CH3)-CH2-CH[OO.]-CH3	11.2%	19.0%	19.0%	3
CH3-C(CH3)(CH2OO.)-CH2-CH(OH)-CH3	7.9%	19.0%	13.4%	3
CH3-C(CH3)(OH)-CH2-CH(CH2OO.)-CH3	7.9%	19.0%	13.4%	3
<u>2-Methyl Butane</u>				
CH3-C[OO.](CH3)-CH2-CH3	5.2%	11.4%	6.4%	1
CH3-CH(CH3)-CH[OO.]-CH3 [a]	14.1%	11.4%	11.4%	1
<u>Propene</u>				
CH3-CH[OO.]-CH2-OH	1.5%	5.0%	0.0%	4
CH3-CH(CH2OO.)-OH	1.8%	5.0%	0.0%	4
<u>1-Butene</u>				
CH3-CH2-CH(CH2OO.)-OH	3.1%	7.9%	3.9%	5
CH3-CH2-CH[OO.]-CH2-OH	2.2%	7.9%	3.9%	5
<u>1-Hexene</u>				
CH3-CH2-CH2-CH2-CH(CH2OO.)-OH	6.6%	15.3%	9.6%	6
CH3-CH2-CH2-CH2-CH[OO.]-CH2-OH	4.9%	15.3%	9.6%	6
<u>Cis-2-Butene</u>				
CH3-CH(OH)-CH[OO.]-CH3	3.5%	7.9%	3.9%	7

Table 29 (continued)

Compound and Radical	Nitrate Yield			Ref.
	Value Used	Estimated		
		Y_{sec}	Y_{corr}	
<u>Isoprene</u>				
HO-CH2-C(CH3)=CH-CH2OO.	8.8%	11.4%	6.4%	8
HO-CH2-C(CH3)=CH(CH2OO.)	8.8%	11.4%	6.4%	8
CH2=CH-C[OO.](CH3)-CH2-OH	8.8%	11.4%	6.4%	8
CH3-C(CH2OO.)=CH(CH2-OH)	8.8%	11.4%	6.4%	8
CH3-C(CH2OO.)=CH-CH2-OH	8.8%	11.4%	6.4%	8
CH2=C(CH3)-CH[OO.]-CH2-OH	8.8%	11.4%	6.4%	8
CH2=CH-C(OH)(CH2OO.)-CH3	8.8%	11.4%	6.4%	8
CH2=C(CH3)-CH(CH2OO.)-OH	8.8%	11.4%	6.4%	8
<u>T-Butyl Alcohol</u>				
CH3-C(OH)(CH2OO.)-CH3	7.0%	7.9%	3.9%	9
<u>MTBE</u>				
CH3-C(CH3)(CH3)-O-CH2OO.	7.0%	11.4%	6.4%	10
CH3-C(CH3)(CH2OO.)-O-CH3	7.0%	11.4%	6.4%	10
<u>Ethoxy Ethanol</u>				
CH3-CH[OO.]-O-CH2-CH2-OH	2.5%	7.9%	3.9%	11
CH3-CH2-O-CH[OO.]-CH2-OH	2.5%	7.9%	3.9%	11
HO-CH2-CH2-O-CH2-CH2OO.	2.5%	7.9%	3.9%	11
<u>Carbitol</u>				
HO-CH2-CH2-O-CH2-CH2-O-CH2-CH2OO.	12.2%	15.3%	9.6%	12
CH3-CH[OO.]-O-CH2-CH2-O-CH2-CH2-OH	12.2%	15.3%	9.6%	12
CH3-CH2-O-CH[OO.]-CH2-O-CH2-CH2-OH	12.2%	15.3%	9.6%	12
CH3-CH2-O-CH2-CH[OO.]-O-CH2-CH2-OH	12.2%	15.3%	9.6%	12
CH3-CH2-O-CH2-CH2-O-CH[OO.]-CH2-OH	12.2%	15.3%	9.6%	12
<u>Methyl Acetate</u>				
CH3-CO-O-CH2OO.	1.5%	5.0%	0.0%	13
<u>2-Butoxyethanol</u>				
HO-CH2-CH2-O-CH2-CH2-CH2-CH2OO.	11.8%	15.3%	9.6%	14
CH3-CH[OO.]-CH2-CH2-O-CH2-CH2-OH	11.8%	15.3%	9.6%	14
CH3-CH2-CH[OO.]-CH2-O-CH2-CH2-OH	11.8%	15.3%	9.6%	14
CH3-CH2-CH2-CH[OO.]-O-CH2-CH2-OH	11.8%	15.3%	9.6%	14
CH3-CH2-CH2-CH2-O-CH[OO.]-CH2-OH	11.8%	15.3%	9.6%	14

Table 29 (continued)

Compound and Radical	Nitrate Yield			Ref.
	Value Used	Estimated		
		Y_{sec}	Y_{corr}	
Ethyl Acetate				
CH3-CO-O-CH2-CH2OO.	4.0%	7.9%	3.9%	15
CH3-CO-O-CH[OO.]-CH3	4.0%	7.9%	3.9%	15
CH3-CH2-O-CO-CH2OO.	4.0%	7.9%	3.9%	15
Dimethyl Succinate (DBE-4)				
CH3-O-CO-CH2-CH2-CO-O-CH2OO.	8.0%	15.3%	9.6%	16
CH3-O-CO-CH2-CH[OO.]-CO-O-CH3	8.0%	15.3%	9.6%	16
CH3-O-CO-CH2-CH(OH)-CO-O-CH2OO.	8.0%	15.3%	9.6%	16
Dimethyl Glutyrate (DBE-5)				
CH3-O-CO-CH2-CH2-CH2-CO-O-CH2OO.	14.8%	19.0%	13.4%	17
CH3-O-CO-CH2-CH2-CH[OO.]-CO-O-CH3	14.8%	19.0%	13.4%	17
CH3-O-CO-CH2-CH[OO.]-CH2-CO-O-CH3	14.8%	19.0%	13.4%	17
CH3-O-CO-CH2-CH2-CH(OH)-CO-O-CH2OO.	14.8%	19.0%	13.4%	17
Methyl Isobutyrate				
CH3-CH(CH2OO.)-CO-O-CH3	6.4%	11.4%	6.4%	18
CH3-C[OO.](CH3)-CO-O-CH3	6.4%	11.4%	6.4%	18
CH3-CH(CH3)-CO-O-CH2OO.	6.4%	11.4%	6.4%	18
t-Butyl Acetate				
CH3-C(CH3)(CH2OO.)-O-CO-CH3	12.0%	15.3%	9.6%	19
CH3-C(CH3)(CH3)-O-CO-CH2OO.	12.0%	15.3%	9.6%	19
Propylene Carbonate [b]				
CH(CH3)-O-CO-O-CH[OO.]-	1.2%	7.9%	3.9%	20
C[OO.](CH3)-CH2-O-CO-O-	1.2%	7.9%	3.9%	20
CH(CH2OO.)-CH2-O-CO-O-	1.2%	7.9%	3.9%	20
CH3-CO-O-CO-O-CH2OO.	1.2%	7.9%	3.9%	20
CH3-CH[OO.]-O-CO-O-CHO	1.2%	7.9%	3.9%	20
Isobutene				
CH3-C[OO.](CH3)-CH2-OH	10.0%	7.9%	3.9%	21
n-Butyl Acetate				
CH3-CO-O-CH2-CH2-CH2-CH2OO.	10.0%	15.3%	9.6%	22
CH3-CO-O-CH2-CH2-CH[OO.]-CH3	10.0%	15.3%	9.6%	22
CH3-CH2-CH[OO.]-CH2-O-CO-CH3	10.0%	15.3%	9.6%	22
CH3-CH2-CH2-CH[OO.]-O-CO-CH3	10.0%	15.3%	9.6%	22
CH3-CH2-CH2-CH2-O-CO-CH2OO.	10.0%	15.3%	9.6%	22

Table 29 (continued)

Compound and Radical	Nitrate Yield			Ref.
	Value Used	Estimated		
		Y_{sec}	Y_{corr}	
Cyclohexanone				
CH2-CH2-CH2-CH2-CO-CH[OO.]-	15.0%	15.3%	9.6%	23
CH2-CH2-CH2-CO-CH2-CH[OO.]-	15.0%	15.3%	9.6%	23
CH2-CH2-CO-CH2-CH2-CH[OO.]-	15.0%	15.3%	9.6%	23
1-Methoxy-2-Propanol				
CH3-CH(OH)-CH[OO.]-O-CH3	1.6%	7.9%	3.9%	24
CH3-CH(OH)-CH2-O-CH2OO.	1.6%	7.9%	3.9%	24

[a] Experimental value is probably high. Not used for determining best fit parameters.

[b] Other uncertainties in the mechanism affect the nitrate yield that gives the best fits to the mechanism to such an extent that the adjusted yield for this compound was not used to determine the best fit parameters.

References

1 Based on nitrate yield data tabulated by Carter and Atkinson (1989).

2 Based on 2-propyl nitrate yields from propane from Arey et al (1999), corrected fraction of 2-propyl formation estimated using the method of Kwok and Atkinson (1995).

3 Nitrate yields from C7 and C8 peroxy radicals formed from 2,2,4-trimethyl pentane reduced by a factor of 1.7 to fit results of environmental chamber reactivity experiments.

4 Based on nitrate yield data from propene from Shepson et al (1985) and O’Brien et al (1998), corrected for estimated fraction of reaction from terminal position based on data of Cvetanocic (1976).

5 Based on nitrate yield data from 1-butene from O’Brien et al (1998), corrected for estimated fraction of reaction from terminal position based on data of Cvetanocic (1976) for propene.

6 Based on nitrate yield data from 1-hexene from O’Brien et al (1998), corrected for estimated fraction of reaction from terminal position based on data of Cvetanocic (1976) for propene.

7 Based on nitrate yield data from cis-2-butene from Muthuramu et al (1993) and O’Brien et al

8 Adjusted to fit environmental chamber reactivity data for isoprene (Carter and Atkinson, 1996).

9 Adjusted to fit environmental chamber reactivity data for t-butanol (Carter et al, 1997g).

10 Adjusted to fit environmental chamber reactivity data for MTBE (Carter et al, 1999a).

11 Adjusted to fit environmental chamber reactivity data for ethoxy ethanol (Carter et al, 1999a).

12 Adjusted to fit environmental chamber reactivity data for carbitol (Carter et al, 1999a).

13 Adjusted to fit environmental chamber reactivity data for methyl acetate (Carter et al, 1999a).

14 Adjusted to fit environmental chamber reactivity data for 2-butoxyethanol (Carter et al, 1999a).

15 Adjusted to fit environmental chamber reactivity data for ethyl acetate (Carter et al, 1999a).

Table 29 (continued)

References (continued)

16 Adjusted to fit environmental chamber reactivity data for DBE-4 (Carter et al, 1999a).
17 Adjusted to fit environmental chamber reactivity data for DBE-5 (Carter et al, 1999a).
18 Adjusted to fit environmental chamber reactivity data for methyl isobutyrate (Carter et al,
19 Adjusted to fit environmental chamber reactivity data for t-butyl acetate (Carter et al, 1999a).
20 Adjusted to fit environmental chamber reactivity data for propylene carbonate (Carter et al,
21 Adjusted to fit environmental chamber data for isobutene (Carter et al, 1999a).
22 Adjusted to fit environmental chamber reactivity data for n-butyl acetate (Carter et al, 1999a).
23 Adjusted to fit environmental chamber reactivity data for cyclohexanone (Carter et al, 1999a).
24 Adjusted to fit environmental chamber reactivity data for 1-Methoxy-2-Propanol (Carter et al, 1999f)

depend on the size of the radical. An alternative approach is to adjust the carbon number used to estimate the yields, i.e.,

$$Y_i\ (n_C, T, M) = Y_{sec}\ (n_C - n_i, T, M) \tag{VI}$$

where n_i is a correction term used to derive an “effective carbon number” for radicals of type i. This would predict that the effects of substitution or structure tend to become less important as the size of the radical increases, since the parameterization predicts that the nitrate yield becomes less dependent on n_C as n_C increases.

Figure 5 shows plots of the observed or adjusted overall nitrate yields derived for compounds forming non-secondary or substituted peroxy radicals against secondary nitrate yields (Y_{sec}) calculated for the same number of carbons using Equations (III and IV)[14]. It can be seen that in most cases the ratio of the observed or adjusted yields to Y_{sec} range from ~0.4 to 1, with no apparent dependence of the ratio on the nature of the radical or its substituents. The best fit line for all the data corresponds to a correction factor of ~0.65, if the constant correction factor method (Equation V) is employed, with an uncertainty of approximately a factor of 1.6. Because of the lack of a clear dependence of the correction on the type of radical, the most appropriate approach is probably to use this factor for all substituted or non-secondary radicals.

However, if the constant correction factor method (Equation V) is employed, then the model tends to overpredict the ozone reactivities of high molecular weight alkanes (e.g., n-octane and n-dodecane) in environmental chamber reactivity experiments. Better fits are obtained if higher nitrate yields from the C_{8+} OH-substituted peroxy radicals formed in the oxidations of these compounds (following 1,4-H shift isomerizations, as discussed in Section III.J.2) are assumed than predicted using Equation (V) and f=0.65. This suggests that the effects of substitution may decrease as the size of the radical increases, as is predicted by the “effective carbon number” adjustment approach (Equation VI). Therefore, “effective carbon number” adjustment this approach is adopted in this work.

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[14] The adjusted nitrate yield for methyl isobutyrate, whose mechanism is highly uncertain, is not shown.

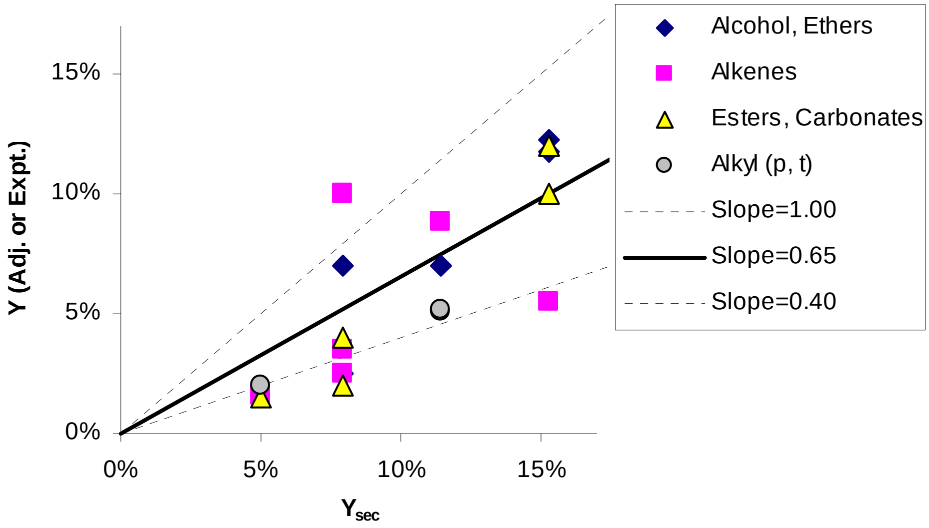

Figure 5. Plots of observed or adjusted overall nitrate yields against Y_{sec} values derived using Equations (III and IV) for compounds forming non-secondary and substituted peroxy radicals.

The best fits to the available experimental or adjusted nitrate yield data for are obtained by using Equation (VI) with the carbon numbers reduced by ~1.5 for non-secondary or substituted peroxy radicals, with no apparent dependence of the reduction on the type of radical or its substituents. Figure 6 shows the performance of this method in estimating overall nitrate yields for compounds forming substituted or non-secondary peroxy radicals that are used as the basis for deriving our estimates. The 1:1 line and lines showing a factor of 1.6 uncertainty range are also shown. A comparison of Figure 5 and Figure 6 shows that the carbon number adjustment method performs about as well (or poorly) as the factor adjustment method, with the data being an insufficient basis for choosing between them. However, the use of Equation (VI) with a carbon number reduction of 1.5 for all non-secondary or substituted radicals because of its superior performance in simulating the overall reactivities of the higher n-alkanes.

There are several cases where the observed or adjusted nitrate yields are not well fit by either method. These include $CH_3C(OH)(CH_3)CH_2OO\cdot$ from t-butanol, $CH_3C(OO\cdot)(CH_3)CH_2OH$ from isobutene, and $CH_3C(O)OC(CH_3)(CH_3)CH_2OO\cdot$ from t-butyl acetate, where the estimated yields are considerably lower than those that must be assumed for model simulations to fit the chamber data. On the other hand, the estimates tend to underpredict nitrate yields that were measured in the reactions of OH radicals with 1-butene and 1-hexene (O'Brein et al, 1998). It is interesting to note that the cases where the nitrate yields are higher than estimated all have the radical center is at or near a quaternary carbon. However, .the alkyl nitrate yield data for neopentyl, 2-methyl-2-butyl and 2-methyl-2-pentyl (Carter and Atkinson, 1989b) are reasonably consistent with the predictions using the estimated corrections discussed above, so no general conclusions can be made for radicals with this structure. The reason why the nitrate yields from radicals formed from 1-butene and 1-hexene are too low is unclear, and the possibility of experimental problems cannot necessarily be ruled out.

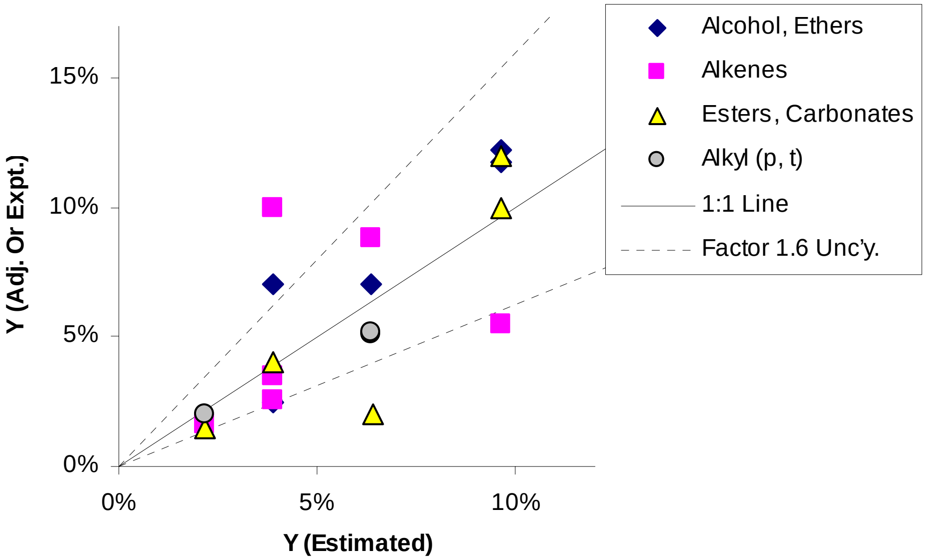

Figure 6. Plots of observed or adjusted overall nitrate yields for compounds forming non-secondary and substituted peroxy radicals against overall nitrate yields estimated using Equation (VI) and a carbon number reduction of 1.5.

The approach adopted in this work to use Equation (VII) with a carbon number reduction of 1.5 to derive the correction factors for estimating nitrate yields in cases of non-secondary or substituted radicals where no data are available, and to use explicit assignments for those radicals (including the outliers discussed above) for which available data indicate the estimates are not appropriate. These assignments are indicated on the "value used" column on Table 29.

J. Reactions of Alkoxy Radicals

Alkoxy radicals are also critical intermediates in the photooxidation mechanisms of most VOCs, and the variety of possible reactions that higher molecular weight alkoxy radicals can undergo is a major source of the complexity (and uncertainty) in the generated photooxidation mechanisms for most VOCs. Primary and secondary alkoxy radicals can react with O_2, C_{2+} alkoxy radicals can react via β-scission forming smaller molecules and radicals, long chain alkoxy radicals can undergo H-shift isomerizations ultimately forming disubstituted radicals, and certain substituted alkoxy radicals can undergo other reactions. Knowledge of the rate constants or branching ratios for all these processes need to be specified to generate the mechanisms. Unfortunately, relevant information concerning these processes is highly limited, and estimates are usually necessary. The methods used to estimate the various rate constants or branching ratios, and the specific assignments that are used in those cases where data are available, are discussed in this section.

1. Reaction with O_2

Primary and secondary alkoxy radicals can react with O_2, forming HO_2 and the corresponding carbonyl compound.

$$RCH_2O\cdot + O_2 \rightarrow RCHO + HO_2$$

$$RR'CO\cdot + O_2 \rightarrow R\text{-}CO\text{-}R' + HO_2$$

Absolute rate constants for these reactions are available only for methoxy, ethoxy, and isopropoxy radicals, and the IUPAC recommended rate parameters (Atkinson et al, 1998) are given on Table 30. Non-Arrhenius temperature dependences are observed and the A factors are much lower than expected for an abstraction reaction, indicating a possibly complex mechanism. However, the A factors are reasonably consistent for the reactions of the different radicals, increasing as expected with the number of abstractable hydrogens, though the A factor per hydrogen for isopropoxy is approximately half that of ethoxy.

For estimation purposes, we assume that all primary alkoxy radicals react with O_2 with the same A factor as does ethoxy, and that all secondary alkoxy + O_2 A factors are the same as for isopropoxy radicals:

$$A(O_2, \text{primary RO}\cdot) = 6.0 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

$$A(O_2, \text{secondary RO}\cdot) = 1.5 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

Because the low A factors and non-Arrhenius behavior these estimates must be considered to be uncertain, and quantitative data are clearly needed for other alkoxy radicals.

Table 30 shows that the apparent activation energies for the alkoxy + O_2 reaction appear to be correlated with the heat of reaction. In fact, a plot of the activation energy vs. ΔH_r (not shown) indicates that — perhaps by coincidence — the data for these three radicals fall almost exactly on a straight line, which is given by:

$$Ea(O_2) = 6.96 + 0.183\ \Delta H_r(O_2) \qquad \text{(VIII)}$$

where $Ea(O_2)$ is the activation energy and $\Delta H_r(O_2)$ is the heat of reaction[15] This therefore can be used to estimate activation energies, and therefore rate constants, for any alkoxy + O_2 reaction.

However, the above equation cannot be used for estimating activation energies for reactions of O_2 with alkoxy radicals such as $CH_3OCH_2O\cdot$, whose reaction with O_2 are sufficiently exothermic that Equation (VIII) predicts a negative activation energy. In those cases, we assume for estimation purposes that no alkoxy + O_2 reaction has an activation energy that is less than the a certain minimum value, which should be somewhere between 0 and 0.4 kcal/mole. We assume that the actual minimum is near the high end of this range, or 0.4 kcal/mole. Therefore, for estimation purposes we use:

$$Ea(O_2) = \max\ [\ 0.4,\ 6.96 + 0.183\ \Delta H_r(O_2)\ ] \qquad \text{(IX)}$$

Note that the 0 to 0.4 kcal/mole range for the minimum activation energy amounts to an uncertainty in the rate constant of a factor of ~2 for highly exothermic alkoxy + O_2 reactions. This is not a large uncertainty given the uncertainty in assuming that the A factors for the O_2 reactions are the same for all primary or all secondary alkoxy radicals.

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[15] Heats of reaction are estimated by group additivity as discussed in Section IV.A.5, based primarily on the thermochemical groups in the NIST (1994) database. Some reactants or products had groups that are not in the NIST (1994) database, and the thermochemical contributions of these groups had to be estimated. Tabulated heats of reaction may be uncertain by at least 2 kcal/mole.

Table 30. Recommended kinetic parameters for reactions of alkoxy radicals with O_2.

Radical	n	A	A/n	K(298)	ΔH_r	Ea
		(cm^3 molec^{-1} s^{-1})			(kcal/mol)	
CH3O.	3	7.20e-14	2.40e-14	1.92e-15	-26.28	2.15
CH3-CH2O.	2	6.00e-14	3.00e-14	9.48e-15	-32.03	1.09
CH3-CH[O.]-CH3	1	1.50e-14	1.50e-14	7.67e-15	-35.82	0.40

From Atkinson (1997a), Table 9

The estimates for the reactions of O_2 with the saturated hydrocarbon alkoxy radicals (i.e, alkoxy radicals containing only $-CH_3$, $-CH_2-$, >CH-, or >C< groups) are probably the least uncertain because they are the most similar to the simple alkoxy radicals used as the basis for the estimate. These estimates become increasingly uncertain for the oxygenated radicals with significantly higher reaction exothermicities (i.e., the reaction of O_2 with $CH_3OCH_2O\cdot$ has an estimated ΔH_r of -46.6 kcal/mole, compared to -35.8 for isopropoxy). The estimates used here predict that these highly exothermic alkoxy + O_2 reactions have 298K rate constants of ~3×10^{-14} cm^3 molec^{-1} s^{-1} for primary radicals and ~8×10^{-15} cm^3 molec^{-1} s^{-1} for secondary radicals. However, the possibility that these rate constants may be orders of magnitude higher cannot be ruled out. For example, if the approach of Atkinson (1997a), which uses a relationship between the rate constant (not the activation energy) and the heat of reaction, estimates the rate constant for the reaction of O_2 with, for example, $CH_3OCH_2O\cdot$, to be ~3.7×10^{-13} cm^3 molec^{-1} s^{-1}, which is a factor of ~12 higher than the estimation approach discussed above. This, of course, would imply that the effective A factors for these highly exothermic reactions are significantly higher than for those radicals whose rate constants have been measured – which we assume is not the case.

2. H-Shift Isomerizations

Long chain alkoxy radicals can react unimolecularly by abstraction by the alkoxy center from a C-H bond elsewhere in the radical, via a cyclic transition state, forming a hydroxy-substituted carbon-centered radical, e.g.,

$$CH_3CH_2CH_2CH_2O\cdot \rightarrow \cdot CH_2CH_2CH_2CH_2OH$$

Rate constants for these reactions can be estimated based on activation energies for bimolecular H-atom abstractions by alkoxy radicals plus ring strain energies for the cyclic transition states, and estimates of A factors (Carter et al, 1976; Baldwin et al, 1977; Carter and Atkinson, 1985; Atkinson, 1994). The results indicate that 1,5-H shift reactions (such as shown above), involving a relatively unstrained 6-member ring transition state, will be relatively rapid and should dominate over competing processes, at least for the hydrocarbon alkoxy radicals formed in alkane photooxidation systems. On the other hand, the estimates indicate that hydrogen shifts involving strained transition states, such as 1,3-H shifts involving a 5 member ring, as well as those involving more strained rings, are not likely to be sufficiently rapid to be important. Therefore except for the "ester rearrangement" reaction discussed below, only 1,4 H shift isomerizations are considered when the estimated mechanisms are generated.

The only data available concerning rates of 1,5-H shift isomerizations of alkoxy radicals are rate constants relative to competing alkoxy + O_2 or decomposition reactions. Although the rate constants for the competing reactions have also not been measured, they can be estimated in the case of the O_2 reactions as discussed above. Table 31 lists the isomerization reactions whose rate have been determined

Table 31. Rate constants for H abstraction reactions by alkoxy radicals.

Reaction	BDE [a] (kcal)	A [b]	Ea (kcal)	T (K)	k(T)	Refs [c]
Alkoxy Isomerizations (sec^{-1})						
1-Butoxy [d]	101.4	2.4e+11	8.42	298	1.60e+5	1,2
2-Pentoxy [d]	101.4	2.4e+11	8.16	298	2.50e+5	1,2
3-Hexoxy	101.4	2.4e+11	8.04	298	3.05e+5	2,3
2-Hexoxy	98.1	1.6e+11	6.44	298	3.05e+6	2,4
Methoxy + RH Reactions (cm^3 $molec^{-1}$ sec_{-1})						
CH_4	104.9	2.6e-13	8.84			5
C_2H_6 -> i-C_2H_5	101.2	4.0e-13	7.09			5
C_3H_8 -> i-C_3H_7	98.6	2.4e-13	4.57			6
$(CH_3)_2CHCH(CH_3)_2$	96.8	1.7e-13	4.11	373	6.64e-16	7,8
CH_3OH -> CH_2OH	98.1	5.0e-13	4.07			9
CH_3CHO	85.9	8.4e-14	0.63	298	2.88e-14	8,10
Alkoxy Isomerization Group Rate Constants for estimations (sec^{-1})						
$-CH_3$	101.4	2.4e+11	8.49	298	1.44e+5	2,11
$-CH_2-$	98.1	1.6e+11	6.33	298	3.63e+6	2,11
-CH<	96.8	8.0e+10	5.51	298	7.29e+6	2,11
-CHO	85.9	8.0e+10	5.75	299	5.02e+6	2,12

[a] Bond dissociation energies are derived from the NIST (1994) thermochemical database or from heats of formation given in the IUPAC evaluation (Atkinson et al, 1997).

[b] Underlined A, Ea, T, or k data are experimental measurements. Data not underlined are estimates.

[c] Notes and references:

1 Rate constant recommended by Atkinson (1997a)

2 A factors estimated for general alkoxy radical isomerizations by Atkinson (1997a), based on earlier estimates of Baldwin et al (1977)

3 Use middle value of range given by Eberhard et a. (1995). Varies from 1.8 - 4.3 x 10^5 sec^{-1}.

4 Use middle value of range given by Eberhard et a. (1995). Varies from 1.4 - 4.7 x 10^6 sec^{-1}.

5 Tsang and Hampson (1986)

6 Tsang (1988)

7 Alcock and Mile (1975)

8 A factor per abstracted hydrogen is assumed to be the average of that for the methoxy + ethane, propane and propane (to isopropyl) reactions.

9 Tsang (1987)

10 Weaver et al, (1975), Kelly and Keicklen (1978). These report rate constant ratios relative to methoxy + O2 of 14-15. Placed on an absolute basis using the methoxy + O2 rate constant.

11 Activation energy derived from correlation between methoxy + RH rate constants and BDE, with an added 1.6 kcal/mole "strain" correction for consistency with data for isomerization reactions, as discussed in the text.

12 Activation energy estimated from that estimated for the methoxy + acetaldehyde reaction, plus the 1.6 kcal/mole "strain" correction used for the other groups, plus an additional 3.5 kcal/mole "strain" correction for reactions with -CO- groups in the transition state, derived as discussed in the text.

[d] These parameters are explicitly assigned for this radical in the mechanism generation system.

relative to the competing O_2 reaction, together with the rate constant ratios as summarized by Atkinson (1997a). Table 31 also shows the A factors estimated by Atkinson (1997a) and the corresponding activation energies, which are based on assuming

$$A(\text{isom}) = 8.0 \times 10^{10} \times (\text{number of abstractable hydrogens})\ \text{sec}^{-1}.$$

This is based on the previous estimates of Baldwin et al (1977), and is incorporated in the 1,4-H shift estimates used in this work.

The limited number of species for which isomerization rate constants have been measured and the relative imprecision of the data for 2-hexoxy provide an inadequate data base from which to derive a general estimation method for the activation energies. It is reasonable to assume that the activation energy will be correlated with the C-H bond dissociation energy for the bond that is being attacked by the alkoxy center. To provide a somewhat larger database in this regard, it is useful to look at available kinetic information for a bimolecular analogue for this reaction, namely the H-atom abstraction reactions of methoxy radicals. Table 31 lists the rate constants or Arrhenius parameters found for such reactions in the NIST kinetics database (NIST, 1989). The Arrhenius parameters have been estimated for those species where temperature dependence information was not given by using the average of those determined for methoxy + methane and methoxy + ethane. The measured (IUPAC, 1997) or estimated (NIST, 1994) bond dissociation energies (BDE's) for the C-H bond being attacked are also shown on the Table.

Figure 7 shows plots of the activation energies for the internal or bimolecular alkoxy H-atom abstraction reactions against the relevant bond dissociation energy. [Data for the methoxy + isobutane reaction are inconsistent (NIST 1998), so they are not included.] It can be seen that if the methoxy + acetaldehyde data are not included, then a reasonably good straight line relationship is obtained. The limited data for the isomerization reactions are consistent with the relationship for the bimolecular methoxy reactions, with an offset of 1.6 kcal/mole. Although this offset is probably not outside the uncertainties of the BDE or activation energy determinations, it could also be rationalized as ring strain in the 6-member ring transition state for the isomerization reaction.

The solid line shown on Figure 7 is the least squares line through the data for the methoxy abstraction reactions, with the data for acetaldehyde not being used when determining the fit. The measurement for acetaldehyde is excluded because abstractions from (CO)-H bonds apparently do not have the same correlation with the bond energies as abstractions from hydrocarbon C-H bonds.

The dotted line on Figure 7 shows the line for the methoxy reaction offset by 1.6 kcal/mole to agree with the data for the isomerizations of the butoxy, pentoxy, and hexoxy radicals. Therefore, this can be used as a basis for estimating activation energies for alkoxy radical isomerizations in general, or at least those involving abstractions from alkyl C-H bonds.

The rate constants for any isomerization reaction can be estimated using a generalization of the structure-reactivity approach derived by Atkinson (Atkinson, 1987, Kwok and Atkinson, 1995, Atkinson, 1997a) for estimating OH radical reactions. In this approach, reaction by H-abstraction at each type of group, whether -CH3, -CH2-, -CH<, or -CHO is given by a group rate constant for that group, multiplied by an appropriate correction factor for each substituent other than methyl groups (whose correction factor is 1.0 by definition). Note that the substituting corrections are assumed to be due only to the substituting affecting the activation energy, not the A factor (Kwok and Atkinson, 1995; Atkinson, 1997a).

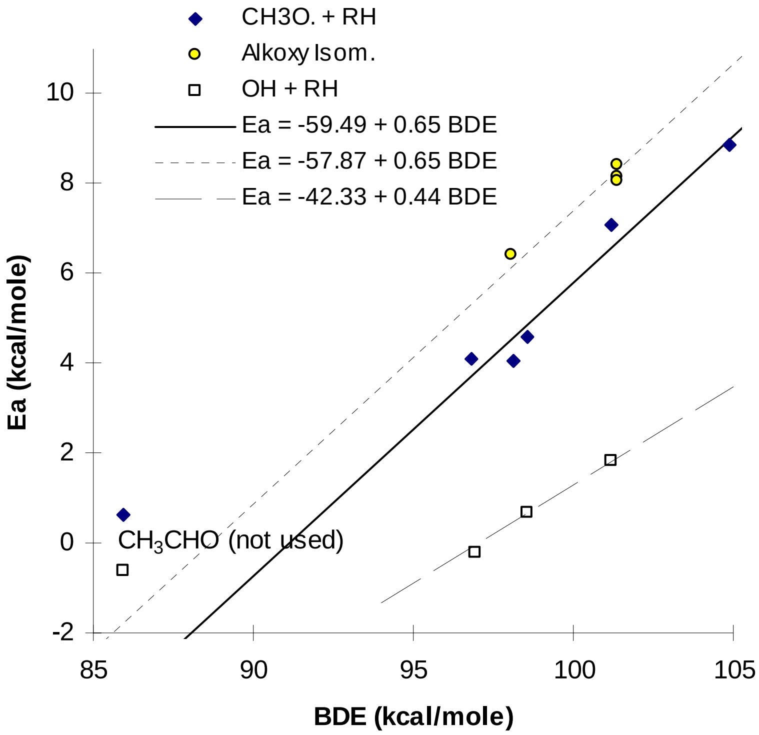

Figure 7. Plot of activation energies vs bond dissociation energies for methoxy abstraction reactions, alkoxy radical isomerizations, and OH abstraction reactions.

Obviously a large kinetic database is necessary to derive the substituent correction factors, and this is not available for these alkoxy radical abstraction reactions. However, if we assume that (1) the substituent corrections are due only to the substituent affecting the activation energy and not the A factor, and (2) the activation energy is linearly related to the bond dissociation energy for both the OH and the alkoxy radical abstraction reactions, then one can derive the substituent correction factors for the alkoxy reactions from those for the corresponding OH radical reaction. The latter have been derived by Kwok and Atkinson (1996) using the large kinetic database for OH radical reactions. The first assumption is reasonable, and is already incorporated in the way the Atkinson estimation methods derive temperature dependences. The second assumption is already incorporated in our alkoxy radical estimation methods discussed above, but needs to be examined in the case of OH radical rate constants.

The 298K group rate constants used in estimating OH radical reactions and parameters used by Kwok and Atkinson (1996) to determine their temperature dependences, are given in Table 9, above. Kwok and Atkinson (1996) gave the temperature dependences in the form k=C T^2 exp(-B/T), but these can be recast to the Arrhenius activation energy (adjusted to be valid for T around 298K), to place it on the same basis as used for the alkoxy radical reactions. The corresponding activation energies are 1.82, 0.68, -0.20, and -0.62 kcal/mole for -CH3, -CH2-, -CH<, and -CHO, respectively. These activation energies are plotted against the bond dissociation energies associated with the group on Figure 7. It can be seen that the activation energies are reasonably well fit by a linear relationship with the bond dissociation energy for reactions at alkyl C-H bonds, but not for reaction at -CHO groups. In the case of OH radicals, the correlation breaks down for bond dissociation energies less than ~95 kcal/mole because there is essentially no energy barrier for bonds weaker than that. However, for stronger bonds, the correlation between group activation energy and BDE seems to hold reasonably well.

It is of interest to note that the slope for the line relating Ea to BDE for the alkoxy reactions is somewhat greater than that for the OH reactions, by a factor of ~1.5. This means that the activation energies for the alkoxy reactions would be more sensitive to substituents than is the case for OH reactions, as might be expected given the slower rates of these reactions. If these linear relationships between Ea and BDE are assumed to hold for the substituted species, this suggests that the group correction factors for the alkoxy radical isomerizations (F_{isom}) should be related to those for the OH radical reactions (F_{OH}) by

$$F_{isom} \approx f_{OH}^{1.5} \tag{X}$$

Thus, the group correction factors given by Kwok and Atkinson (1996) for estimating rate constants for OH radical reactions can be used as a basis for estimating alkoxy radical isomerization reactions.

The dotted line on Figure 7 was derived to fit data primarily for radicals that have a -CH2- attached to the -CH3 group where the reaction is occurring. The OH group correction factor at ~300K for a -CH2- substituent is 1.23, which from Equation (X) corresponds to a correction factor of 1.5 for alkoxy radical reactions. This corresponds to an activation energy reduction of 0.18 kcal/mole. This means that the intercept for the line adjusted to fit the activation energy for these radicals (the dotted line on Figure 7) should be increased by 0.18 for the purpose of estimating group rate constants, which are defined based on $-CH_3$ substituents. Based on this, the activation energies for group rate constants for alkoxy radical isomerizations involving abstractions from -CH3, -CH2- and -CH< can be estimated from

$$\text{Ea (group isom)} = -57.87 + 0.65\ \text{BDE} + 0.18 = 57.69 + 0.65\ \text{BDE} \tag{XI}$$

where BDE is the bond dissociation energy for the breaking bond. To place the BDE’s on the same basis as those used to derive the equation, the BDE’s for Equation (XII) should be calculated for groups with one -CH2- substituent, with the other substituents, if any, being CH3 groups.

Table 31 shows the activation energies for the various alkyl groups derived using Equation (XI), along with their corresponding A factors and 298K rate constants. In the case of -CHO groups, the activation energy is estimated from the estimated methoxy + acetaldehyde activation energy, plus the estimated 1.6 kcal/mole strain energy, derived as discussed above, plus an additional 3.5 kcal/mole of strain for reactions with -CO- groups in the cyclic transition state, derived as discussed in Section III.J.4, below. These group rate constants, together with the substituent factors derived for Equation (XI) using the substituent factors for estimating OH radical rate constants from Table 9, above, can then be used for estimating isomerization rate constants for any alkoxy radicals where the abstraction is at the given group.

As indicated above, a comparison of the activation energies for the bimolecular methoxy reactions with the estimation activation energies for isomerization of butoxy, pentoxy and hexoxy suggests that the ring strain for these isomerizations is ~1.6 kcal/mole. Note that this is reasonably consistent with the ring strain given by Benson (1976) for a six member ring with one oxygen. However, the strain may be different if the ring in the transition state involves groups other than just -CH2-. We assume that there is no strain difference if the transition state ring also has -CH< or >C< groups, but this does not appear to be the case if the ring also contains -O-, -CO- or -O-CO- groups. In particular, predictions are more consistent with available data if activation energies for isomerization involving -O-, -CO- or -O-CO- in the transition states are increased by an additional ~3.5 kcal/mole. Before giving the basis for this, which is discussed in Section III.J.4, it is necessary to first discuss the rate constant estimates for the competing decomposition reactions. This is given in the following section.

3. Beta Scission Decomposition

The most common unimolecular reactions of alkoxy radicals are β-scission decompositions. These involve breaking the C-C bond next to the alkoxy group, forming a carbonyl compound and a carbon center radical (where the latter will react further, as discussed above). For primary, secondary, and tertiary alkoxy radicals, the respective reactions are:

$$RCH_2O\cdot \rightarrow R\cdot + HCHO$$

$$RCH(O\cdot)R' \rightarrow RCHO + R'\cdot \ \underline{\text{or}}\ R'CHO + R\cdot$$

$$RC(O\cdot)(R')R'' \rightarrow R\text{-}CO\text{-}R' + R''\cdot \ \underline{\text{or}}\ R\text{-}CO\text{-}R'' + R'\cdot \ \underline{\text{or}}\ R'\text{-}CO\text{-}R'' + R\cdot$$

Note that for secondary and tertiary radicals there may be more than one possible reaction route, if the R, R' and/or R" substituents are different.

No direct measurements of absolute rate constants for alkoxy radical decompositions are available, but information is available concerning ratios of these rate constants relative to those for other alkoxy radical reactions. The only information concerning temperature dependent rate constants come from the measurements relative to alkoxy + NO reactions, whose absolute rate constants are known or can be estimated (Atkinson, 1994, and references therein). Based on these data, Atkinson (1994, 1997b) recommends estimating the Arrhenius A factors using

$$A = 2.0 \times 10^{14} \cdot n \text{ sec-1}, \qquad \text{(XIII)}$$

where n is the reaction path degeneracy. The recommended decomposition rate constants and kinetic parameters are summarized on Table 32. The A factors derived using Equation (XIII) are assumed to be applicable to all alkoxy radical decompositions. Table 32 also gives alkoxy radical decomposition rate constants obtained from rate constant ratios obtained from results of various mechanistic and product studies, and placed on an absolute basis using estimates for the competing decomposition reactions. This is discussed below.

Table 33 lists the various alkoxy radicals for which relevant data are available concerning the branching ratios for their various competing reactions, or at least concerning upper or lower limits for those branching ratios. These are determined from product yields observed in various studies of OH radical + organic + NO_x systems where these alkoxy radicals are expected to be formed, as indicated in the comments on the table. In some cases product yield ratios can be used to derive ratios of rate constants involving an alkoxy radical decomposition; these are indicated in Table 33 and the relevant data are also included in Table 32. (In those cases Table 32 also gives the radical number used on Table 33 to aid the reader in finding the data on that radical.) In many other cases, only upper or lower branching ratios can be derived. For example, lower limits for a reaction route can be based on observing high yields of a product expected from a reaction, and upper limits for another route can be inferred from the failure to observe an expected product from the reaction. Many of the upper or lower limit estimates are subjective and approximate, and probably in many cases they could be refined based on a detailed analysis of the experimental methods. However, these approximate upper and lower limit data are useful for assessing the overall performance of the estimation methods because of the relatively large number and variety of reactions involved.

Table 32. Summary of measured or estimated rate constants for alkoxy radical decompositions.

Reaction	Rate Parameters [a]				Relative to			Note	Ea (est.)	
	ΔH_r	A	Ea	k(298)	Type	Ratio	k(ref) [b]		Value	Err
Reactions forming CH3.										
CH3-CH2O. -> CH3. + HCHO	13.04	2.0e+14	20.20	3.1e-1	k(NO)		-	[c]	19.8	-0.4
CH3-CH[O.]-CH3 -> CH3-CHO + CH3.	7.86	4.0e+14	17.60	5.0e+1	k(NO)		-	[c]	17.5	-0.1
CH3-CH2-CH[O.]-CH3 -> CH3-CH2-CHO + CH3.	7.63	2.0e+14	16.60	1.3e+2	k(NO)		-	[c]	17.4	0.8
CH3-C[O.](CH3)-CH3 -> CH3-CO-CH3 + CH3.	4.98	7.5e+14	16.20	9.9e+2	k(NO)		-	[c,d]	16.2	0.0
CH3-C[O.](CH3)CH2-CH3 -> CH3-CH2-CO-CH3 + CH3.	4.82	4.0e+14	18.30	1.5e+1	k(NO)		-	[c,e,f]	16.2	-2.1
CH3-C(CH3)(CH3)-O-CH[O.]-CH3 -> CH3. + CH3-C(CH3)(CH3)-O-CHO	-4.81	2.0e+14	12.30	1.9e+5	k(O2)	4.85	3.9e+4	12 [f]	11.9	-0.4
CH3-CH2-O-CH[O.]-CH3 -> CH3-CH2-O-CHO + CH3.	-4.81	2.0e+14	11.49	7.5e+5	k(O2)	19	3.9e+4	10 [f]	11.9	0.4
CH3-CO-O-CH2-CH2-O-CH[O.]-CH3 -> CH3. + CH3-CO-O-CH2-CH2-O-CHO	-4.81	2.0e+14	11.92	3.6e+5	k(O2)	9.3	3.9e+4	35 [f]	11.9	0.0
CH3-CH[O.]-O-CH2-CH2-OH -> CH3. + HCO-O-CH2-CH2-OH	-4.81	2.0e+14	12.33	1.8e+5	k(O2)	4.62	3.9e+4	21 [f]	11.9	-0.4
Reactions forming CH3-CH2. and CH3-CH2-CH2.										
CH3-CH2-CH[O.]-CH3 -> CH3-CHO + CH3-CH2.	6.94	2.0e+14	13.58	2.2e+4	k(O2)	0.56	3.9e+4	2 [f]	14.3	0.7
CH3-CH2-CH[O.]-CH2-CH3 -> CH3-CH2-CHO + CH3-CH2.	6.71	4.0e+14	13.92	2.5e+4	k(O2)	0.63	3.9e+4	3 [f]	14.2	0.3
CH3-CH2-CH2-CH[O.]-CH3 -> CH3-CH2-CH2. + CH3-CHO	6.13	2.0e+14	14.10	9.1e+3	k(NO)		-	[c]	13.9	-0.2
CH3-C[O.](CH3)-CH2-CH3 -> CH3-CO-CH3 + CH3-CH2.	4.06	2.0e+14	13.90	1.3e+4	k(NO)		-	[c]	13.0	-0.9
Reactions forming CH3-C[.](CH3)-CH3										
CH3-C(CH3)(CH2O.)-CH3 -> HCHO + CH3-C[.](CH3)-CH3	10.40	2.0e+14	11.16	1.3e+6	k(O2)	39	3.4e+4	1 [f]	11.2	0.0
Reactions forming alpha-Hydroxy Alkyl Radicals										
HO-CH2-CH2O. -> HO-CH2. + HCHO	11.79	2.0e+14	12.62	1.1e+5	k(O2)	3.59	3.1e+4	4 [f]	12.6	0.0
CH3-CH(CH3)-CH[O.]-CH2-OH -> CH3-CH(CHO)-CH3 + HO-CH2.	7.15	2.0e+14	11.48	7.6e+5	kd(R$_2$CH.)	2.45	3.1e+5	7 [f]	10.6	-0.9
Reactions forming CH$_3$C(O)CH$_2$. Radicals										
CH3-CO-CH2-CH[O.]-CH3 -> CH3-CHO + CH3-CO-CH2.	3.86	2.0e+14	12.38	1.7e+5	k(O2)	4.26	3.9e+4	41 [f]	12.9	0.6
Reactions forming Alkoxy Radicals										
CH3-C[O.](CH3)-O-CH3 -> CH3-CO-CH3 + CH3O.	9.50	2.0e+14	11.90	3.7e+5	kd(CH3.)	0.15	2.5e+6	14 [f]	12.6	0.7
CH3-CH(CH3)-CH2-O-C[O.](CH3)-CH3 -> CH3-CH(CH2O.)-CH3 + CH3-CO-CH3	9.29	2.0e+14	11.69	5.4e+5	kd(CH3.)	0.21	2.5e+6	18 [f]	12.5	0.8
CH3-C[O.](CH3)-O-CH2-CH3 -> CH3-CH2O. + CH3-CO-CH3	9.28	2.0e+14	11.26	1.1e+6	kd(CH3.)	0.44	2.5e+6	15 [f]	12.5	1.3
Reactions forming R-CO-O. Radicals										
CH3-C[O.](CH3)-O-CO-CH3 -> CH3-CO-CH3 + CH3-CO2.	10.73	2.0e+14	16.72	1.1e+2?	kd(CH3.)	0.32	3.5e+2?	40 [f]	16.7	0.0

Table 32 (continued)

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[a] Data from Table 33 unless noted otherwise. Rate constants and A factors in units of sec-1, and Ea;s and heats of reaction are in units of kcal/mole. Underlined Ea from references, otherwise Ea's computed from tabiuated k(298) and A. These parameters are explicitly assigned for this radical in the mechanism generation system, unless indicated otherwise.

[b] k(ref) for O_2 reaction is $k(O_2)[O_2]$ for $[O_2] = 5.16 \times 10^{18}$ molec cm^{-3} at 1 atm and 298K.

[c] Atkinson (1997b). Relative to $k(RO+NO) = 2.3 \times 10^{-11} \exp(150/T)$.

[d] High pressure limit. Batt and Robinson (1987) calculate that rate constant under atmospheric conditions is ~80% of this. However, to fit chamber data, the A factor for atmospheric modeling is increased to from 6.0 to 7.5×10^{14} sec-1.

[e] Not used when computing best fit parameters for reactions forming methyl radicals. No explicit assignments made for this radical.

[f] Number is the radical number on Table 33 from which the data are taken. See footnotes to that table for documentation.

[g] Not used for deriving general estimates for reactions forming this radical because of uncertainties in the rate constant ratio and the value of the reference rate constant.

[h] The reference rate constant is almost certainly incorrect, since it would mean that the competing isomerization reaction, which isn't observed, would dominate. No explicit assignments made for this radical.

Table 33 also includes the heats of reaction for the various reactions where relevant and the estimated rate constants and corresponding branching ratios for the competing reactions. (The predictions for the O_2 reactions and the isomerizations are as discussed in the previous section, the predictions for the decompositions are discussed below.) An indication of how well the predicted branching ratios agree with the observed ratios is also shown. Table 34 gives a subset of the information on Table 33, organized by alkoxy reaction type rather than by radical. This is useful for obtaining an indication of how well the estimates are performing for a particular type of reaction. For that reason, Table 34 includes results using several alternative assumptions, as discussed where applicable below.

Based on the approach used by Atkinson (1996), the activation energies for the decomposition reactions are estimated assuming

$$\text{Ea (decomposition)} = \text{EaA} + \text{EaB} \cdot \Delta H_r \qquad \text{(XIV)}$$

where EaA and EaB are parameters which are assumed to depend only on the type of radical which is formed in the decomposition. The derivation of these parameters for the various types of decomposition reactions is discussed below.

We will first consider decompositions forming methyl radicals, for which, as shown on Table 32, there are the most extensive and best characterized data. These come in two groups: decompositions of hydrocarbon alkoxy radicals (i.e., alkoxy radicals containing only $-CH_3$, $-CH_2-$, $>CH-$, or $>C<$ groups) which tend to be endothermic by ~5 to ~13 kcal/mole and relatively slow, and decompositions of alkoxy radicals with α-O groups such as formed in photooxidations of ethers, which are exothermic by ~5 kcal/mole and tend to be much more rapid. Note that the rate constants for the latter are uncertain because of uncertainty in the estimates for the O_2 reaction used to place the experimental rate constant ratio on an absolute basis. It is possible that the O_2 reaction is significantly faster than estimated in this work, in which case these decompositions will also be faster.

Figure 8 shows plots of the estimated activation energy for selected decompositions reactions vs. the estimated heats of reaction. It can be seen that the data for reactions forming methyl radicals fall reasonably well on a straight line, if the point for the 2-methyl-2-butoxy radical, which seems to be somewhat inconsistent with the other data, is excluded. The least squares line (excluding the point for 2-methyl-2-butoxy) is

Table 33. Experimental and estimated branching ratios for radicals where relevant data are available.

Radical Reaction	Type	ΔH_r (kcal)	Estimated [a] k (s^{-1})	Estimated [a] %	Expt. Branching [b] Min	Expt. Branching [b] Exp'd	Expt. Branching [b] Max	Fit [c]	k Ratios [d] Expt	k Ratios [d] Calc
1 <u>CH3-C(CH3)(CH2O.)-CH3</u>										
CH3-C(CH3)(CH2O.)-CH3 + O2 -> CH3-C(CH3)(CHO)-CH3 + HO2.	O2	-30.8	3.35e+4	3%	0%	3%	5%	ok	<u>kd/kO2</u>	
CH3-C(CH3)(CH2O.)-CH3 -> HCHO + CH3-C[.](CH3)-CH3	D	10.4	1.31e+6	98%	75%	98%	100%	ok	39	39
Based on data summarized by Atkinson (1997b)										
2 <u>CH3-CH2-CH[O.]-CH3</u>										
CH3-CH2-CH[O.]-CH3 + O2 -> CH3-CH2-CO-CH3	O2	-36.0	3.94e+4	86%	46%	64%	76%	High	<u>kd/kO2</u>	
CH3-CH2-CH[O.]-CH3 -> CH3-CHO + CH3-CH2.	D	6.9	6.46e+3	14%	24%	36%	54%	Low	<u>0.56</u>	0.16
CH3-CH2-CH[O.]-CH3 -> CH3-CH2-CHO + CH3.	D	7.6	3.43e+1	0%						
Average of rate constant ratios reported by Carter et al (1979) and Cox et al (1981) as given by Atkinson (1997b).										
3 <u>CH3-CH2-CH[O.]-CH2-CH3</u>										
CH3-CH2-CH[O.]-CH2-CH3 + O2 -> CH3-CH2-CO-CH2-CH3 + HO2.	O2	-36.3	3.94e+4	72%	42%	61%	74%	ok	<u>kd/kO2</u>	
CH3-CH2-CH[O.]-CH2-CH3 -> CH3-CH2-CHO + CH3-CH2.	D	6.7	1.53e+4	28%	26%	39%	58%	ok	0.63	0.39
Based on data of Atkinson et al (1995).										
4 <u>HO-CH2-CH2O.</u>										
HO-CH2-CH2O. + O2 -> HO2. + HCO-CH2-OH	O2	-30.6	3.10e+4	22%	15%	22%	30%	ok	<u>kd/kO2</u>	
HO-CH2-CH2O. -> HO-CH2. + HCHO	D	11.8	1.11e+5	78%	70%	78%	85%	ok	3.59	3.59
Based on product data for ethene, as recommended by Atkinson (1997a).										
5 <u>CH3-CH[O.]-CH2-OH</u>										
CH3-CH[O.]-CH2-OH + O2 -> HO2. + CH3-CO-CH2-O	O2	-34.6	2.68e+4	1%						
CH3-CH[O.]-CH2-OH -> HO-CH2. + CH3-CHO	D	6.6	5.19e+6	99%	85%	100%	100%	ok		
Based on product data for propene, as discussed by Atkinson (1997a).										
6 <u>CH3-CH(OH)-CH[O.]-CH3</u>										
CH3-CH(OH)-CH[O.]-CH3 + O2 -> CH3-CH(OH)-CO-CH3 + HO2	O2	-34.8	2.91e+4	0%	0%	0%	0%	ok		
CH3-CH(OH)-CH[O.]-CH3 -> CH3-CHO + CH3-CH[.]-OH	D	2.9	2.56e+9	100%	100%	100%	100%	ok		
CH3-CH(OH)-CH[O.]-CH3 -> CH3-CH(OH)-CHO + CH3.	D	9.1	1.18e+1	0%						
Based on upper limit yields of hydroxy carbonyls from OH + trans-2-butene (Atkinson, personal communication, 1999). Similar results were obtained from OH + trans-3-hexene.										

Table 33 (continued)

Radical	Type	ΔH_r	Estimated [a]		Expt. Branching [b]			Fit	k Ratios [d]	
Reaction	Type	(kcal)	k (s^{-1})	%	Min	Exp'd	Max	[c]	Expt	Calc
7 CH3-CH(CH3)-CH[O.]-CH2-OH										
CH3-CH(CH3)-CH[O.]-CH2-OH + O2 -> CH3-CH(CH3)-CO-CH2-OH + HO2	O2	-34.4	2.52e+4	1%	0%	0%	10%	ok	kd/kd(R2CH.)	
CH3-CH(CH3)-CH[O.]-CH2-OH -> HCO-CH2-OH + CH3-CH[.]-CH3	D	8.1	3.11e+5	8%	15%	29%	50%	Low	2.45	11.26
CH3-CH(CH3)-CH[O.]-CH2-OH -> CH3-CH(CHO)-CH3 + HO-CH2.	D	7.2	3.50e+6	91%	50%	71%	90%	High		
Based on yields of 2-methyl propanal, acetone, and glycolaldehyde from OH + 3-methyl-1-butene (Atkinson et al, 1998), assuming that OH addition occurs an estimated ~65% of the time at the 1-position relative to total OH addition.										
8 CH3-O-CH2-O-CH2O.										
CH3-O-CH2-O-CH2O. + O2 -> HO2. + CH3-O-CH2-O-CHO	O2	-46.6	1.58e+5	96%	70%	84%	100%	ok	kd/kO2	
CH3-O-CH2-O-CH2O. -> CH3-O-CH2O. + HCHO	D	13.3	6.50e+3	4%	0%	16%	30%	ok	0.19	0.04
Based on observation of CH3-O-CH2-O-CHO in 64% yield from dimethoxy methane (Wallington et al, 1997). The 24% yield of CH3-O-CO-CH3 (Wallington et al, 1997) suggests that reaction at the methyl group occurs ~75% of the time. This would mean that decomposition from this radical may be non-negligible.										
9 CH3-C(CH3)(CH3)-O-CH2O.										
CH3-C(CH3)(CH3)O-CH2O. + O2 -> CH3-C(CH3)(CH3)O-CHO + HO2.	O2	-46.6	1.58e+5	97%	65%	95%	100%	ok		
CH3-C(CH3)(CH3)O-CH2O. -> CH3-C[O.](CH3)CH3 + HCHO	D	14.3	3.09e+3	2%	0%	0%	25%	ok		
CH3-C(CH3)(CH3)O-CH2O. -> CH3-C(CH3)(CH2.)O-CH2-OH	I(O)		1.59e+3	1%	0%	0%	25%	ok		
Based on observation of t-butyl formate as the major product from MTBE (Tuazon et al, 1991b; Smith et al, 1991).										
10 CH3-CH2-O-CH[O.]-CH3										
CH3-CH2-O-CH[O.]-CH3 + O2 -> CH3-CH2-O-CO-CH3 + HO2.	O2	-49.4	3.94e+4	8%	0%	5%	10%	ok		
CH3-CH2-O-CH[O.]-CH3 -> CH3-CH2O. + CH3-CHO	D	10.1	7.44e+4	16%	0%	0%	15%	High	kd/kO2	
CH3-CH2-O-CH[O.]-CH3 -> CH3-CH2-O-CHO + CH3.	D	-4.8	3.54e+5	76%	60%	95%	100%	ok	19.00	8.99
CH3-CH2-O-CH[O.]-CH3 -> CH3-CH(OH)O-CH2-CH2.	I(O)		5.31e+2	0%	0%	0%	25%	ok		
Based on ethyl formate from diethyl ether in 92% (Wallington and Japar, 1991) or 66% (Eberhard et al, 1993) yields and ethyl acetate in 4% yield (Eberhard et al, 1993) Average of yields for ethyl formate used in computing yield ratio. (Acetaldehyde also observed, but could be formed in other ways)										

Table 33 (continued)

Radical Reaction	Type	ΔH_r (kcal)	Estimated [a] k (s^{-1})	 %	Expt. Branching [b] Min	 Exp'd	 Max	Fit [c]	k Ratios [d] Expt	 Calc
11 CH3-CH2-CH2-CH[O.]-O-CH3										
CH3-CH2-CH2-CH[O.]-O-CH3 + O2 -> HO2. + CH3-CH2-CH2-CO-O-CH3	O2	-49.7	3.94e+4	0%	0%	0%	30%	ok		
CH3-CH2-CH2-CH[O.]-O-CH3 -> CH3-CH2-CH2. + CH3-O-CHO	D	-6.5	1.45e+8	100%	50%	66%	100%	ok		
CH3-CH2-CH2-CH[O.]-O-CH3 -> CH3O. + CH3-CH2-CH2-CHO	D	10.3	6.04e+4	0%	0%	0%	30%	ok		
CH3-CH2-CH2-CH[O.]-O-CH3 -> CH3-O-CH(OH)-CH2-CH2-CH2.	I		1.96e+5	0%	0%	0%	30%	ok		
Based on observations of 43% propionaldehyde and 51% methyl formate from methyl n-butyl ether (Aschmann and Atkinson, 1999). This radical is predicted to be formed ~71% of the time. The observed products account for ~70% of the reaction.										
12 CH3-C(CH3)(CH3)-O-CH[O.]-CH3										
CH3-C(CH3)(CH3)O-CH[O.]-CH3 + O2 -> CH3-C(CH3)(CH3)O-CO-CH3 + HO2.	O2	-49.4	3.94e+4	9%	0%	17%	25%	ok		
CH3-C(CH3)(CH3)-O-CH[O.]-CH3 -> CH3-C[O.](CH3)-CH3 + CH3-CHO	D	11.1	3.51e+4	8%	0%	0%	20%	ok		
CH3-C(CH3)(CH3)-O-CH[O.]-CH3 -> CH3. + CH3-C(CH3)(CH3)-O-CHO	D	-4.8	3.54e+5	82%	70%	83%	100%	ok	kd/kO2 3.3	 9.0
CH3-C(CH3)(CH3)O-CH[O.]-CH3 -> CH3-C(CH3)(CH2.)O-CH(OH)CH3	I(O)		1.59e+3	0%	0%	0%	20%	ok		
Based on observed t-butyl formate and t-butyl acetate yields from ETBE (Smith et al, 1992).										
13 CH3-CH(CH3)-O-CH[O.]-CH(CH3)-CH3										
CH3-CH(CH3)-O-CH[O.]-CH(CH3)-CH3 + O2 -> HO2. + CH3-CH(CH3)-O-CO-CH(CH3)-CH3	O2	-49.2	3.94e+4	0%	0%	0%	25%	ok		
CH3-CH(CH3)-O-CH[O.]-CH(CH3)-CH3 -> CH3-CH[O.]-CH3 + CH3-CH(CHO)-CH3	D	11.4	2.75e+4	0%	0%	0%	25%	ok		
CH3-CH(CH3)-O-CH[O.]-CH(CH3)-CH3 -> CH3-CH[.]-CH3 + CH3-CH(CH3)-O-CHO	D	-6.1	1.14e+10	100%	50%	100%	100%	ok		
CH3-CH(CH3)-O-CH[O.]-CH(CH3)-CH3 -> CH3-CH(CH3)-CH(OH)-O-CH(CH2.)-CH3	I(O)		5.31e+2	0%	0%	0%	25%	ok		
Based on observation of 48% yield of t-butyl formate from isobutyl isopropyl ether (Stemmler et al, 1997a). This radical is predicted to be formed ~33% of the time.										
14 CH3-C[O.](CH3)-O-CH3										
CH3-C[O.](CH3)-O-CH3 -> CH3-O-CO-CH3 + CH3.	D	-6.5	2.51e+6	96%	50%	87%	95%	High		
CH3-C[O.](CH3)-O-CH3 -> CH3-CO-CH3 + CH3O.	D	9.5	1.13e+5	4%	5%	13%	25%	Low	kd/kd(CH$_3$) 0.15	 0.05
Based on ratios of methyl acetate to acetone yields from MTBE (Tuazon et al, 1991, Smith et al, 1991)										

Table 33 (continued)

Radical Reaction	Type	ΔH_r (kcal)	Estimated [a] k (s^{-1})	 %	Expt. Branching [b] Min	 Exp'd	 Max	Fit [c]	k Ratios [d] Expt	 Calc
15 CH3-C[O.](CH3)-O-CH2-CH3										
CH3-C[O.](CH3)-O-CH2-CH3 -> CH3. + CH3-CH2-O-CO-CH3	D	-6.5	2.51e+6	95%	0%	69%	100%	ok		
CH3-C[O.](CH3)-O-CH2-CH3 -> CH3-CH2O. + CH3-CO-CH3	D	9.3	1.33e+5	5%	0%	31%	100%	ok	0.44	0.05
CH3-C[O.](CH3)-O-CH2-CH3 -> CH3-C(CH3)(OH)-O-CH2-CH2.	I(O)		5.31e+2	0%						
Based on ratios of acetone and ethyl acetate yields from ETBE (Smith et al, 1992), assuming they are all formed from this radical, which is estimated to be formed 5% of the time. (Total yields of both are ~6%). This is uncertain.										
16 CH3-CH(CH3)-O-C[O.](CH3)-CH3										
CH3-CH(CH3)-O-C[O.](CH3)-CH3 -> CH3-CH[O.]-CH3 + CH3-CO-CH3	D	10.1	7.28e+4	3%	0%		20%	ok		
CH3-CH(CH3)-O-C[O.](CH3)-CH3 -> CH3. + CH3-CH(CH3)-O-CO-CH3	D	-6.5	2.51e+6	97%	80%	100%	100%	ok		
CH3-CH(CH3)-O-C[O.](CH3)-CH3 -> CH3-C(CH3)(OH)-O-CH(CH2.)-CH3	I(O)		1.06e+3	0%	0%		20%	ok		
Based on observations of isopropyl acetate as major product (nearly 100% yield) from di-isopropyl acetate (Wallington et al, 1993).										
17 CH3-C(CH3)(CH3)-O-C[O.](CH3)-CH3										
CH3-C(CH3)(CH3)-O-C[O.](CH3)-CH3 -> CH3-C[O.](CH3)-CH3 + CH3-CO-CH3	D	10.3	6.27e+4	2%	0%	0%	20%	ok		
CH3-C(CH3)(CH3)-O-C[O.](CH3)-CH3 -> CH3. + CH3-C(CH3)(CH3)-O-CO-CH3	D	-6.5	2.51e+6	97%	75%	100%	100%	ok		
CH3-C(CH3)(CH3)-O-C[O.](CH3)-CH3 -> CH3-C(CH3)(CH2.)-O-C(CH3)(OH)-CH3	I(O)		1.59e+3	0%	0%	0%	20%	ok		
Based on observed 85% yield of isopropyl acetate from di-t-butyl ether (Langer et al, 1996).										
18 CH3-CH(CH3)-CH2-O-C[O.](CH3)-CH3										
CH3-CH(CH3)-CH2-O-C[O.](CH3)-CH3 -> CH3-CH(CH2O.)-CH3 + CH3-CO-CH3	D	9.3	1.32e+5	5%	0%	18%	40%	ok	kd/kd(CH_3)	
CH3-CH(CH3)-CH2-O-C[O.](CH3)-CH3 -> CH3. + CH3-CH(CH3)-CH2-O-CO-CH3	D	-6.5	2.51e+6	94%	40%	82%	100%	ok	0.21	0.05
CH3-CH(CH3)-CH2-O-C[O.](CH3)-CH3 -> CH3-C(CH3)(OH)-O-CH2-C[.](CH3)-CH3	I(O)	H3	2.70e+4	1%	0%	0%	30%	ok		
Based on 6% yields of CH3-CH(CHO)-CH3 and 28% of CH3-CH(CH3)-CH2-O-CO-CH3 from isopropyl isobutyl ether (Stemmler et al, 1997a), assuming that the former is formed from subsequent reactions from this radical. This radical is predicted to be formed ~50% of the time.										

Table 33 (continued)

Radical Reaction	Type	ΔH_r (kcal)	Estimated [a] k (s^{-1})	%	Expt. Branching [b] Min	Exp'd	Max	Fit [c]	k Ratios [d] Expt	Calc
15 <u>CH3-C[O.](CH3)-O-CH2-CH3</u>										
CH3-C[O.](CH3)-O-CH2-CH3 -> CH3. + CH3-CH2-O-CO-CH3	D	-6.5	2.51e+6	95%	0%	69%	100%	ok		
CH3-C[O.](CH3)-O-CH2-CH3 -> CH3-CH2O. + CH3-CO-CH3	D	9.3	1.33e+5	5%	0%	31%	100%	ok	0.44	0.05
CH3-C[O.](CH3)-O-CH2-CH3 -> CH3-C(CH3)(OH)-O-CH2-CH2.	I(O)		5.31e+2	0%						
Based on ratios of acetone and ethyl acetate yields from ETBE (Smith et al, 1992), assuming they are all formed from this radical, which is estimated to be formed 5% of the time. (Total yields of both are ~6%). This is uncertain.										
16 <u>CH3-CH(CH3)-O-C[O.](CH3)-CH3</u>										
CH3-CH(CH3)-O-C[O.](CH3)-CH3 -> CH3-CH[O.]-CH3 + CH3-CO-CH3	D	10.1	7.28e+4	3%	0%		20%	ok		
CH3-CH(CH3)-O-C[O.](CH3)-CH3 -> CH3. + CH3-CH(CH3)-O-CO-CH3	D	-6.5	2.51e+6	97%	80%	100%	100%	ok		
CH3-CH(CH3)-O-C[O.](CH3)-CH3 -> CH3-C(CH3)(OH)-O-CH(CH2.)-CH3	I(O)		1.06e+3	0%	0%		20%	ok		
Based on observations of isopropyl acetate as major product (nearly 100% yield) from di-isopropyl acetate (Wallington et al, 1993).										
17 <u>CH3-C(CH3)(CH3)-O-C[O.](CH3)-CH3</u>										
CH3-C(CH3)(CH3)-O-C[O.](CH3)-CH3 -> CH3-C[O.](CH3)-CH3 + CH3-CO-CH3	D	10.3	6.27e+4	2%	0%	0%	20%	ok		
CH3-C(CH3)(CH3)-O-C[O.](CH3)-CH3 -> CH3. + CH3-C(CH3)(CH3)-O-CO-CH3	D	-6.5	2.51e+6	97%	75%	100%	100%	ok		
CH3-C(CH3)(CH3)-O-C[O.](CH3)-CH3 -> CH3-C(CH3)(CH2.)-O-C(CH3)(OH)-CH3	I(O)		1.59e+3	0%	0%	0%	20%	ok		
Based on observed 85% yield of isopropyl acetate from di-t-butyl ether (Langer et al, 1996).										
18 <u>CH3-CH(CH3)-CH2-O-C[O.](CH3)-CH3</u>										
CH3-CH(CH3)-CH2-O-C[O.](CH3)-CH3 -> CH3-CH(CH2O.)-CH3 + CH3-CO-CH3	D	9.3	1.32e+5	5%	0%	18%	40%	ok	<u>kd/kd(CH_3)</u>	
CH3-CH(CH3)-CH2-O-C[O.](CH3)-CH3 -> CH3. + CH3-CH(CH3)-CH2-O-CO-CH3	D	-6.5	2.51e+6	94%	40%	82%	100%	ok	0.21	0.05
CH3-CH(CH3)-CH2-O-C[O.](CH3)-CH3 -> CH3-C(CH3)(OH)-O-CH2-C[.](CH3)-CH3	I(O)	H3	2.70e+4	1%	0%	0%	30%	ok		
Based on 6% yields of CH3-CH(CHO)-CH3 and 28% of CH3-CH(CH3)-CH2-O-CO-CH3 from isopropyl isobutyl ether (Stemmler et al, 1997a), assuming that the former is formed from subsequent reactions from this radical. This radical is predicted to be formed ~50% of the time.										

Table 33 (continued)

Radical Reaction	Type	ΔH_r (kcal)	Estimated [a] k (s^{-1})	 %	Expt. Branching [b] Min	 Exp'd	 Max	Fit [c]	k Ratios [d] Expt	 Calc
19 CH3-CH(CH3)-O-CH2-C[O.](CH3)-CH3										
CH3-CH(CH3)-O-CH2-C[O.](CH3)-CH3 -> CH3-CH(CH3)-O-CH2. + CH3-CO-CH3	D	3.7	6.96e+4	13%	0%	0%	25%	ok		
CH3-CH(CH3)-O-CH2-C[O.](CH3)-CH3 -> CH3. + CH3-CH(CH3)-O-CH2-CO-CH3	D	6.2	1.93e+2	0%	0%	0%	25%			
CH3-CH(CH3)-O-CH2-C[O.](CH3)-CH3 -> CH3-C(CH3)(OH)-CH2-O-C[.](CH3)-CH3	I(O)	H3	4.81e+5	87%	75%	100%	100%	ok		
Based on observed formation of ~25% of CH3-C(CH3)(OH)-CH2-O-CO-CH3 from isobutyl isopropyl ether (Stemmler et al, 1997a), which can only be formed by the isomerization reaction. However, this radical is predicted to be formed only ~8% of the time.										
20 CH3-CH(OH)-CH[O.]-O-CH3										
CH3-CH(OH)-CH[O.]-O-CH3 + O2 -> HO2. + CH3-CH(OH)-CO-O-CH3	O2	-48.5	3.94e+4	0%	0%	0%	15%	ok		
CH3-CH(OH)-CH[O.]-O-CH3 -> CH3-CH[.]-OH + CH3-O-CHO	D	-9.8	3.14e+13	100%	80%	100%	100%	ok		
CH3-CH(OH)-CH[O.]-O-CH3 -> CH3O. + CH3-CH(OH)-CHO	D	11.5	2.57e+4	0%	0%	0%	15%	ok		
Based on observation of 59% yield of methyl formate and 56% yield of acetaldehyde from 1-methoxy-2-propanol (Tuazon et al, 1998a). This radical is predicted to be formed ~55% of the time, and the observed products account for ~98% of the overall reaction.										
21 CH3-CH[O.]-O-CH2-CH2-OH										
CH3-CH[O.]-O-CH2-CH2-OH + O2 -> HO2. + CH3-CO-O-CH2-CH2-OH	O2	-49.4	3.94e+4	7%	5%	18%	30%	ok		
									kd/kO2	
CH3-CH[O.]-O-CH2-CH2-OH -> CH3. + HCO-O-CH2-CH2-OH	D	-4.8	3.54e+5	64%	70%	82%	100%	Low	4.62	8.99
CH3-CH[O.]-O-CH2-CH2-OH -> HO-CH2-CH2O. + CH3-CHO	D	10.1	7.39e+4	13%	0%	0%	25%	ok		
CH3-CH[O.]-O-CH2-CH2-OH -> CH3-CH(OH)-O-CH2-CH[.]-OH	I(O)		8.80e+4	16%	0%	0%	25%	ok		
Based on the observed formation of 36% HO-CH2-CH2-O-CHO and 8% CH3-CO-O-CH2-CH2-OH from 2-ethoxy ethanol (Stemmler et al, 1996). This radical is predicted to be formed ~36% of the time. The observed products account for essentially all the reaction.										
22 CH3-CH2-O-CH[O.]-CH2-OH										
CH3-CH2-O-CH[O.]-CH2-OH + O2 -> HO2. + CH3-CH2-O-CO-CH2-OH	O2	-48.3	3.94e+4	0%	0%	0%	25%	ok		
CH3-CH2-O-CH[O.]-CH2-OH -> CH3-CH2O. + HCO-CH2-OH	D	11.5	2.48e+4	0%	0%	0%	25%	ok		
CH3-CH2-O-CH[O.]-CH2-OH -> HO-CH2. + CH3-CH2-O-CHO	D	-6.1	6.36e+10	100%	75%	100%	100%	ok		
Based on the observed formation of ~43% ethyl formate from 2-ethoxy ethanol (Stemmler et al, 1996). This radical is predicted to be formed ~36% of the time. The observed products account for essentially all the reaction.										

Table 33 (continued)

Radical		ΔH_r	Estimated [a]		Expt. Branching [b]			Fit	k Ratios [d]	
Reaction	Type	(kcal)	k (s^{-1})	%	Min	Exp'd	Max	[c]	Expt	Calc
23 CH3-CH(CH3)-O-CH[O.]-CH2-OH										
CH3-CH(CH3)-O-CH[O.]-CH2-OH + O2 -> HO2. + CH3-CH(CH3)-O-CO-CH2-OH	O2	-48.3	3.94e+4	0%	0%	0%	15%	ok		
CH3-CH(CH3)-O-CH[O.]-CH2-OH -> CH3-CH[O.]-CH3 + HCO-CH2-OH	D	12.4	1.36e+4	0%	0%	0%	15%	ok		
CH3-CH(CH3)-O-CH[O.]-CH2-OH -> HO-CH2. + CH3-CH(CH3)-O-CHO	D	-6.1	6.36e+10	100%	80%	100%	100%	ok		
CH3-CH(CH3)-O-CH[O.]-CH2-OH -> CH3-CH(CH2.)-O-CH(OH)-CH2-OH	I(O)		1.06e+3	0%	0%	0%	15%	ok		
Based on formation of 57% isopropyl formate from 2-isopropoxy ethanol (Aschmann and Atkinson, 1999). This radical is predicted to be formed ~30% of the time, and the observed products account for essentially all the reaction routes.										
24 CH3-CH2-CH2-CH[O.]-O-CH2-CH2-OH										
CH3-CH2-CH2-CH[O.]-O-CH2-CH2-OH + O2 -> HO2. + CH3-CH2-CH2-CO-O-CH2-CH2-OH	O2	-49.7	3.94e+4	0%	0%	0%	25%	ok		
CH3-CH2-CH2-CH[O.]-O-CH2-CH2-OH -> CH3-CH2-CH2. + HCO-O-CH2-CH2-OH	D	-6.5	1.45e+8	100%	50%	100%	100%	ok		
CH3-CH2-CH2-CH[O.]-O-CH2-CH2-OH -> HO-CH2-CH2O. + CH3-CH2-CH2-CHO	D	10.1	7.06e+4	0%	0%	0%	25%	ok		
CH3-CH2-CH2-CH[O.]-O-CH2-CH2-OH -> HO-CH2-CH2-O-CH(OH)-CH2-CH2-CH2.	I		1.96e+5	0%	0%	0%	25%	ok		
CH3-CH2-CH2-CH[O.]-O-CH2-CH2-OH -> CH3-CH2-CH2-CH(OH)-O-CH2-CH[.]-OH	I(O)		8.80e+4	0%	0%	0%	25%	ok		
Based on observations of propionaldehyde and HO-CH2-CH2-O-CHO in ~20% yields from 2-butoxy ethanol by Tuazon et al. (1998), with somewhat higher yields observed by Stemmler et al. (1997b). This radical is belived to be formed ~20% of the time.										
25 CH3-CH2-CH2-CH2-O-CH[O.]-CH2-OH										
CH3-CH2-CH2-CH2-O-CH[O.]-CH2-OH + O2 -> HO2. + CH3-CH2-CH2-CH2-O-CO-CH2-OH	O2	-48.3	3.94e+4	0%	0%	0%	25%	ok		
CH3-CH2-CH2-CH2-O-CH[O.]-CH2-OH -> CH3-CH2-CH2-CH2O. + HCO-CH2-OH	D	11.6	2.46e+4	0%	0%	0%	25%	ok		
CH3-CH2-CH2-CH2-O-CH[O.]-CH2-OH -> HO-CH2. + CH3-CH2-CH2-CH2-O-CHO	D	-6.1	6.36e+10	100%	80%	100%	100%	ok		
CH3-CH2-CH2-CH2-O-CH[O.]-CH2-OH -> CH3-CH2-CH[.]-CH2-O-CH(OH)-CH2-OH	I(O)		1.83e+4	0%	0%	0%	25%	ok		
Based on observations of n-butyl formate from 2-butoxy ethanol with yields of 57% (Tuazon et al, 1998) or ~35% (Stemmler et al., 1997b). This radical is believed to be formed ~50% of the time.										

Table 33 (continued)

Radical		ΔH_r	Estimated [a]		Expt. Branching [b]			Fit	k Ratios [d]	
Reaction	Type	(kcal)	k (s^{-1})	%	Min	Exp'd	Max	[c]	Expt	Calc
26 CH3-C[O.](CH3)-O-CH2-CH2-OH										
CH3-C[O.](CH3)-O-CH2-CH2-OH -> CH3. + CH3-CO-O-CH2-CH2-OH	D	-6.5	2.51e+6	92%	60%	90%	100%	ok		
CH3-C[O.](CH3)-O-CH2-CH2-OH -> HO-CH2-CH2O. + CH3-CO-CH3	D	9.3	1.32e+5	5%	0%	0%	20%	ok		
CH3-C[O.](CH3)-O-CH2-CH2-OH -> CH3-C(CH3)(OH)-O-CH2-CH[.]-OH	I(O)		8.80e+4	3%	0%	0%	20%	ok		
Based on formation of 44% CH3-CO-O-CH2-CH2-OH from 2-isopropoxy ethanol (Aschmann and Atkinson, 1999). This radical is predicted to be formed ~50% of the time, and the observed products account for essentially all the reaction routes.										
27 CH3-C(CH3)(OH)-CH2-O-C[O.](CH3)-CH3										
CH3-C(CH3)(OH)-CH2-O-C[O.](CH3)-CH3 -> CH3-C(OH)(CH2O.)-CH3 + CH3-CO-CH3	D	9.3	1.32e+5	5%	0%	0%	25%	ok		
CH3-C(CH3)(OH)-CH2-O-C[O.](CH3)-CH3 -> CH3. + CH3-C(CH3)(OH)-CH2-O-CO-CH3	D	-6.5	2.51e+6	95%	75%	100%	100%	ok		
Based on observed formation of ~25% of CH3-C(CH3)(OH)-CH2-O-CO-CH3 from isobutyl isopropyl ether (Stemmler et al, 1997a), which can only be formed by this reaction. However, this radical is predicted to be formed only ~5% of the time.										
28 CH3-CO-CH2O.										
CH3-CO-CH2O. + O2 -> CH3-CO-CHO + HO2.	O2	-26.9	1.01e+4	0%	0%		25%	ok		
CH3-CO-CH2O. -> HCHO + CH3-CO.	D	2.6	1.74e+9	63%	75%	100%	100%	Low		
Based on data of Jenkin et al (1993) indicating that decomposition dominates.										
29 CH3-CH2-O-CO-CH2O.										
CH3-CH2-O-CO-CH2O. + O2 -> CH3-CH2-O-CO-CHO + HO2.	O2	-23.3	3.23e+3	14%	30%	75%	100%	Low		
CH3-CH2-O-CO-CH2O. -> HCHO + CH3-CH2-O-CO.	D	13.5	1.39e+1	0%	0%	0%	70%	ok		
CH3-CH2-O-CO-CH2O. -> CH3-CH[.]-O-CO-CH2-OH	I(O)		1.99e+4	86%	0%	25%	70%	High		
The most reasonable explanation for the observation of ~25% of CH3-CH2-O-CO-CHO from ethyl 3-ethoxypropionate (Baxley et al, 1997) is to assume that this radical reacts with O_2 to a significant extent. This radical is predicted to be formed ~33% of the time.										
30 CH3-CH(CH2O.)-O-CO-CH3										
CH3-CH(CH2O.)-O-CO-CH3 + O2 -> HO2. + CH3-CH(CHO)-O-CO-CH3	O2	-30.8	3.37e+4	41%	0%	0%	75%	ok		
CH3-CH(CH2O.)-O-CO-CH3 -> CH3-CO-O-CH[.]-CH3 + HCHO	D	12.8	4.93e+4	59%	25%	100%	100%	ok		
Necessary to assume decomposition is non-negligible to explain observation of acetic acid as a 9% product from isopropyl acetate (Tuazon et al, 1998b).										

Table 33 (continued)

Radical Reaction	Type	ΔH_r (kcal)	Estimated [a] k (s^{-1})	 %	Expt. Branching [b] Min	 Exp'd	 Max	Fit [c]	k Ratios [d] Expt	 Calc
31 CH3-CH2-CH[O.]-CH2-O-CO-CH3										
CH3-CH2-CH[O.]-CH2-O-CO-CH3 + O2 -> HO2. + CH3-CH2-CO-CH2-O-CO-CH3	O2	-34.8	2.91e+4	89%	25%	50%	100%	ok		
CH3-CH2-CH[O.]-CH2-O-CO-CH3 -> CH3-CH2. + CH3-CO-O-CH2-CHO	D	8.4	2.15e+3	7%	0%		75%	ok		
CH3-CH2-CH[O.]-CH2-O-CO-CH3 -> CH3-CO-O-CH2. + CH3-CH2-CHO	D	8.8	1.57e+3	5%	0%		75%	ok		
Based on observed formation of ~15% CH3-CH2-CO-CH2-O-CO-CH3 from n-butyl acetate (Veillerot et al. 1995). This radical predicted to be formed ~30% of the time. Only ~30% of the reaction route are accounted for, and the yields are only approxmiate.										
32 CH3-CO-O-CH2-CH2-CH[O.]-CH3										
CH3-CO-O-CH2-CH2-CH[O.]-CH3 + O2 -> HO2. + CH3-CO-CH2-CH2-O-CO-CH3	O2	-36.0	3.94e+4	62%	25%	65%	100%	ok		
CH3-CO-O-CH2-CH2-CH[O.]-CH3 -> CH3-CO-O-CH2-CH2. + CH3-CHO	D	5.2	2.41e+4	38%	0%	35%	75%	ok		
CH3-CO-O-CH2-CH2-CH[O.]-CH3 -> CH3. + CH3-CO-O-CH2-CH2-CHO	D	7.9	2.76e+1	0%	0%		75%			
Based on observed formation of ~15% CH3-CO-CH2-CH2-O-CO-CH3 from n-butyl acetate (Veillerot et al. 1995). This radical predicted to be formed ~23% of the time. Only ~30% of the reaction route are accounted for, and the yields are only approxmiate.										
33 CH3-O-CO-CH2-CH[O.]-CO-O-CH3										
CH3-O-CO-CH2-CH[O.]-CO-O-CH3 + O2 -> CH3-O-CO-CH2-CO-CO-O-CH3 + HO2.	O2	-30.2	6.90e+3	76%	0%	10%	10%	High		
CH3-O-CO-CH2-CH[O.]-CO-O-CH3 -> CH3-O-CO-CHO + CH3-O-CO-CH2.	D	16.7	4.48e+0	0%	0%	0%	10%	ok		
CH3-O-CO-CH2-CH[O.]-CO-O-CH3 -> CH3-O-CO-CH2-CHO + CH3-O-CO.	D	7.3	1.37e+3	15%	0%	0%	20%	ok		
CH3-O-CO-CH2-CH[O.]-CO-O-CH3 -> CH3-O-CO-CH2-CH(OH)-CO-O-CH2.	I(OCO)		7.88e+2	9%	80%	90%	100%	Low		
It is necessary to assume that the isomerization of this radical dominates in order for model calculations to approximately fit results of DBE-4 reactivity experiments. The reaction with O2, which is predicted to be the most important competing route, is arbitrarily assumed to occur ~10% of the time.										
34 CH3-CH2-O-CH[O.]-CH2-O-CO-CH3										
CH3-CH2-O-CH[O.]-CH2-O-CO-CH3 + O2 -> HO2. + CH3-CH2-O-CO-CH2-O-CO-CH3	O2	-48.3	3.94e+4	0%	0%	0%	30%	ok		
CH3-CH2-O-CH[O.]-CH2-O-CO-CH3 -> CH3-CH2O. + CH3-CO-O-CH2-CHO	D	11.5	2.48e+4	0%	0%	0%	30%	ok		
CH3-CH2-O-CH[O.]-CH2-O-CO-CH3 -> CH3-CO-O-CH2. + CH3-CH2-O-CHO	D	-3.6	1.63e+7	100%	50%	90%	100%	ok		
CH3-CH2-O-CH[O.]-CH2-O-CO-CH3 -> CH3-CO-O-CH2-CH(OH)-O-CH2-CH2.	I(OCO)		5.31e+2	0%	0%	0%	30%	ok		
Based on observed yield of ethyl formate (33%) from 2-ethoxyethyl acetate (Wells et al., 1996). This is somewhat lower than the predicted 44% formation for this radical, but within the uncertainty of the estimate.										

Table 33 (continued)

Radical Reaction	Type	ΔH_r (kcal)	Estimated [a] k (s^{-1})	%	Expt. Branching [b] Min	Exp'd	Max	Fit [c]	k Ratios [d] Expt	Calc
35 <u>CH3-CO-O-CH2-CH2-O-CH[O.]-CH3</u>										
CH3-CO-O-CH2-CH2-O-CH[O.]-CH3 + O2 -> HO2. + CH3-CO-O-CH2-CH2-O-CO-CH3	O2	-49.4	3.94e+4	8%	5%	10%	25%	ok		
CH3-CO-O-CH2-CH2-O-CH[O.]-CH3 -> CH3-CO-O-CH2-CH2O. + CH3-CHO	D	10.1	7.39e+4	15%	0%	0%	25%	ok	<u>kd/kO2</u>	
CH3-CO-O-CH2-CH2-O-CH[O.]-CH3 -> CH3. + CH3-CO-O-CH2-CH2-O-CHO	D	-4.8	3.54e+5	72%	50%	90%	100%	ok	9.3	9.0
CH3-CO-O-CH2-CH2-O-CH[O.]-CH3 -> CH3-CH(OH)-O-CH2-CH[.]-O-CO-CH3	I(O)		2.72e+4	6%	0%	0%	25%	ok		
Based on yields of CH3-CO-O-CH2-CH2-O-CHO (37%) and CH3-CO-O-CH2-CH2-O-CO-CH3 (4%) from 2-ethoxyethyl acetate (Wells et al, 1996). This radical is predicted to be formed ~36% of the time, which is consistent with these product yields.										
36 <u>CH3-CH2-O-CO-CH2-CH[O.]-O-CH2-CH3</u>										
CH3-CH2-O-CO-CH2-CH[O.]-O-CH2-CH3 + O2 -> HO2. + CH3-CH2-O-CO-CH2-CO-O-CH2-CH3	O2	-51.8	3.94e+4	0%	0%	0%	20%	ok		
CH3-CH2-O-CO-CH2-CH[O.]-O-CH2-CH3 -> CH3-CH2-O-CO-CH2. + CH3-CH2-O-CHO	D	-5.8	8.34e+7	100%	50%	84%	100%	ok		
CH3-CH2-O-CO-CH2-CH[O.]-O-CH2-CH3 -> CH3-CH2O. + CH3-CH2-O-CO-CH2-CHO	D	8.0	3.46e+5	0%	0%	16%	20%	ok		
CH3-CH2-O-CO-CH2-CH[O.]-O-CH2-CH3 -> CH3-CH2-O-CO-CH2-CH(OH)-O-CH2-CH2.	I(O)		5.31e+2	0%	0%	0%	20%	ok		
Based on yield ratios for ethyl formate and CH3-CH2-O-CO-CH2-CHO from ethyl 3-ethoxypropionate (Baxley et al, 1997). Total yield is ~42%, while predicted amount of this radical formed is ~50%.										
37 <u>CH3-CH2-O-CO-CH2-CH2-O-CH[O.]-CH3</u>										
CH3-CH2-O-CO-CH2-CH2-O-CH[O.]-CH3 + O2 -> HO2. + CH3-CH2-O-CO-CH2-CH2-O-CO-CH3	O2	-49.4	3.94e+4	8%	0%	0%	50%	ok		
CH3-CH2-O-CO-CH2-CH2-O-CH[O.]-CH3 -> CH3-CH2-O-CO-CH2-CH2O. + CH3-CHO	D	10.1	7.39e+4	16%	0%	0%	50%	ok		
CH3-CH2-O-CO-CH2-CH2-O-CH[O.]-CH3 -> CH3. + CH3-CH2-O-CO-CH2-CH2-O-CHO	D	-4.8	3.54e+5	75%	50%	75%	100%	ok		
CH3-CH2-O-CO-CH2-CH2-O-CH[O.]-CH3 -> CH3-CH(OH)-O-CH2-CH[.]-CO-O-CH2-CH3	I(O)		2.32e+3	0%	0%	0%	50%	ok		
Based on formation of 30% CH3-CH2-O-CO-CH2-CH2-O-CHO from ethyl 3-ethoxypropionate (Baxley et al, 1977). Note that this radical is predicted to be formed 40% of the time, so the observed yield is higher than maximum predicted.										

Table 33 (continued)

Radical Reaction	Type	ΔH_r (kcal)	Estimated [a] k (s^{-1})	 %	Expt. Branching [b] Min	 Exp'd	 Max	Fit [c]	k Ratios [d] Expt	 Calc
38 CH3-C[O.](CHO)-CH2-OH										
CH3-C[O.](CHO)-CH2-OH -> HCO-CO-CH2-OH + CH3.	D	19.0	7.13e-3	0%	0%	0%	25%	ok		
CH3-C[O.](CHO)-CH2-OH -> CH3-CO-CH2-OH + HCO.	D	-0.7	1.53e+7	94%	75%	100%	100%			
CH3-C[O.](CHO)-CH2-OH -> CH3-CO-CHO + HO-CH2.	D	8.9	9.82e+5	6%	0%	0%	25%	ok		
Based on observations of hydroxyacetone as a major product in the reaction of OH with methacrolein (Tuazon and Atkinson, 1990). This and products from other radicals formed believed to account for all the reaction routes.										
39 CH3-C[O.](CH3)-CO-O-CH3										
CH3-C[O.](CH3)-CO-O-CH3 -> CH3-O-CO-CO-CH3 + CH3.	D	12.2	1.16e+0	0%	0%	0%	50%	ok		
CH3-C[O.](CH3)-CO-O-CH3 -> CH3-CO-CH3 + CH3-O-CO.	D	5.7	4.62e+3	85%	50%	100%	100%	ok		
CH3-C[O.](CH3)-CO-O-CH3 -> CH3-C(CH3)(OH)-CO-O-CH2.	I(O)		7.88e+2	15%	0%	0%	50%	ok		
It is necessary to assume that the decomposition to CH3-O-CO. is a major route in order for model to simulate results of methyl isobutyrate reactivity experiments (Carter et al, 1999a).										
40 CH3-C[O.](CH3)-O-CO-CH3										
CH3-C[O.](CH3)-O-CO-CH3 -> CH3-CO-O-CO-CH3 + CH3.	D [e]	10.0	3.48e+2	66%	50%	76%	90%	ok	kd/kd(CH_3)	
CH3-C[O.](CH3)-O-CO-CH3 -> CH3-CO-CH3 + CH3-CO2.	D	10.7	1.09e+2	21%	10%	24%	50%	ok	0.32	0.31
CH3-C[O.](CH3)-O-CO-CH3 -> CH3-C(CH3)(OH)-O-CO-CH2.	I(OCO)		6.72e+1	13%	0%	0%	25%	ok		
Based on yields of acetone and acetic anhydride from isopropyl acetate and t-butyl acetate (Tuazon et al. 1998b).										
41 CH3-CO-CH2-CH[O.]-CH3										
CH3-CO-CH2-CH[O.]-CH3 + O2 -> CH3-CO-CH2-CO-CH3 + HO2.	O2	-38.1	3.94e+4	38%	10%	19%	30%	High	kd/kO2	
CH3-CO-CH2-CH[O.]-CH3 -> CH3-CHO + CH3-CO-CH2.	D	3.9	6.37e+4	62%	70%	81%	90%	Low	4.3	1.6
CH3-CO-CH2-CH[O.]-CH3 -> CH3-CO-CH2-CHO + CH3.	D	5.8	1.35e+2	0%	0%	0%	10%	ok		
CH3-CO-CH2-CH[O.]-CH3 -> CH3-CH(OH)-CH2-CO-CH2.	I(CO)		2.53e+2	0%	0%	0%	10%	ok		
Based on ratios of acetaldehyde to 2,4-pentadione yields from OH + 2-pentanone (Atkinson et al, 1999b).										

Table 33 (continued)

Radical		ΔH_r	Estimated [a]		Expt. Branching [b]			Fit	k Ratios [d]	
Reaction	Type	(kcal)	k (s^{-1})	%	Min	Exp'd	Max	[c]	Expt	Calc
44 CH3-O-CO-CH2-CH[O.]-CH2-CO-O-CH3										
CH3-O-CO-CH2-CH[O.]-CH2-CO-O-CH3 + O2 -> CH3-O-CO-CH2-CO-CH2-CO-O-CH3 + HO2.	O2	-40.5	3.94e+4	38%	90%	100%	100%	Low		
CH3-O-CO-CH2-CH[O.]-CH2-CO-O-CH3 -> CH3-O-CO-CH2-CHO + CH3-O-CO-CH2.	D	4.8	6.34e+4	62%	0%	0%	10%	High		
Necessary to assume that reaction with O2 dominates for model simulations of dimethyl glutarate (DBE-5) chamber experiments. The observation of CH3-O-CO-CH2-CO-CH2-CO-O-CH3 as a product of the OH + DBE-5 reaction (Tuazon et al, 1999) also indicates that the O2 reaction is important.										
45 CH3-O-CO-CH2-CH2-CH[O.]-CO-O-CH3										
CH3-O-CO-CH2-CH2-CH[O.]-CO-O-CH3 + O2 -> CH3-O-CO-CH2-CH2-CO-CO-O-CH3 + HO2.	O2	-28.1	3.57e+3	77%	0%	10%	10%	High		
CH3-O-CO-CH2-CH2-CH[O.]-CO-O-CH3 -> CH3-O-CO-CHO + CH3-O-CO-CH2-CH2.	D	15.0	1.67e+1	0%	0%	0%	10%	ok		
CH3-O-CO-CH2-CH2-CH[O.]-CO-O-CH3 -> CH3-O-CO-CH2-CH2-CHO + CH3-O-CO.	D	9.5	2.80e+2	6%	0%	0%	10%	ok		
CH3-O-CO-CH2-CH2-CH[O.]-CO-O-CH3 -> CH3-O-CO-CH2-CH2-CH(OH)-CO-O-CH2.	I(OCO)		7.88e+2	17%	80%	90%	100%	Low		
Isomerization is assumed to dominate by analogy with the assumptions made for CH3-O-CO-CH2-CH[O.]-CO-O-CH3 radicals. This also results in somewhat better fits of model simulations to dimethyl glutarate (DBE-5) reactivity experiments. Reaction with O2, predicted to be the major competing process, is arbitrarily assumed to occur ~10% of the time.										
46 *C[O.](CH3)-CH2-O-CO-O-*										
C[O.](CH3)-CH2-O-CO-O- -> *CH2-O-CO-O-CO-* + CH3.	D [e]	11.1	7.40e+1	0%	0%	0%	20%	ok		
C[O.](CH3)-CH2-O-CO-O- -> CH3-CO-O-CO-O-CH2.	D [e]	4.9	8.61e+5	99%	75%	100%	100%	ok		
C[O.](CH3)-CH2-O-CO-O- -> CH3-CO-CH2-O-CO2.	D	5.6	5.12e+3	1%	0%	0%	20%	ok		
Necessary to assume that the decomposition to CH3-CO-O-CO-O-CH2. dominates in order for model to fit results of propylene carbonate reactivity chamber experiments.										
47 CH3-O-CH[O.]-O-CH3										
CH3-O-CH[O.]-O-CH3 + O2 -> CH3-O-CO-O-CH3 + HO2.	O2	-53.3	3.94e+4	0%	50%	84%	95%	Low	kd/kO2	
CH3-O-CH[O.]-O-CH3 -> CH3-O-CHO + CH3O.	D	-1.7	9.07e+8	100%	0%	16%	50%	High	0.2	2e+4
Based on CH3-O-CHO / CH3-O-CO-O-CH3 yield ratios from dimethoxy methane (Sidebottom et al, 1997), assuming they are both formed from the CH3-O-CH[O.]-CH3 radical.										

Table 33 (continued)

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[a] Rate constants estimated for T=298K using recommended parameters as discussed in the text. Units are sec-1. Unimolecular rate constants for O2 reaction calculated assuming [O2] = 5.18 x 10-18 molec cm-3. "%" is the estimated percentage of the radical which reacts with this reaction.

[b] Minimum, expected, and maximum fractions for this reaction route relative to all reactions of this radical, based on analysis of the experimental data. Minimum and maximum values are subjective estimates. Underlined branching ratios are used for explicit estimates for this radical -- overriding the temperature-dependent rate constant estimates.

[c] "High" means that the estimated branching ratio is greater than the maximum value estimated from analysis of the experimental data; "Low" means that the estimated ratio is lower than the minimum; "ok" means that the estimated branching ratio lies between the minimum and maximum considered consistent with the experimental data.

[d] Rate constant ratios which can be used for quantitative rate constant estimates.

[e] The activation energy is reduced by 2 kcal/mole for reactions that form products with -CO-O-CO- groups. If this correction were not applied, the estimated rate constant would be a factor of ~30 lower.

$$\text{Ea (decomp. to CH3.)} = 14.05 + 0.44\ \Delta H_r \qquad \text{(XV)}$$

where Ea is the activation energy and ΔH_r is the estimated heat of reaction, both in kcal/mole. This corresponds to EaA = 14.05 kcal/mole and EaB = 0.44. These are used for estimating activation energies for all the alkoxy radical decompositions forming methyl radicals.

Figure 8 shows that Equation (XV) overpredicts the activation energies for reactions forming ethyl and propyl radicals. However, the data for these decompositions are reasonably well fit if EaB is assumed to be the same as form reactions forming methyl radicals, and EaA is reduced to 11.25 kcal/mole, i.e.,

$$\text{Ea (decomp. to RCH2.)} = 11.25 + 0.44\ \Delta\text{Hr} \qquad \text{(XVI)}$$

Although the data are not sufficient to determine whether the EaB for decompositions forming these radicals is necessarily the same as for those forming methyl, this is assumed for lack of sufficient data to determine otherwise. Likewise, the single measurement for a decomposition forming tertiary radicals is fit using EaA = 6.58 kcal/mole, and the least uncertain measurement for a decomposition forming $HOCH_2\cdot$ is fit using EaA = 7.42 kcal/mole, if it is assumed that the same EaB is applicable for reactions assuming these radicals as well. Thus,

$$\text{Ea (decomp. to } R_3C.) = 6.58 + 0.44\ \Delta H_r \qquad \text{(XVII)}$$

$$\text{Ea (decomp. to } HOCH_2\cdot) = 7.43 + 0.44\ \Delta\text{Hr} \qquad \text{(XVIII)}$$

can be used to estimate activation energies for these types of decompositions.

Quantitative information concerning decompositions forming alkoxy radicals is sparse, though as shown on Table 33 and Table 34 there are a number of cases where upper or lower limit estimates can be obtained. As shown on Table 32, the only quantitative information concerns two radicals where decomposition to an alkoxy radical competes with a decomposition forming a methyl radical. If equation (XIII) and (XV) are used to estimate the Arrhenius parameters and thus the rate constants for these competing decompositions to methyl radicals, then the rate constants forming alkoxy radicals can be placed on an absolute basis. If this is assumed, and if the same EaB is used as assumed for the reactions forming alkyl or $HOCH_2\cdot$ radicals, then a value of EaA = 7.42 kcal/mole can be derived, i.e.,

$$\text{Ea (decomp to RO. - initial estimate)} = 7.50 + 0.44\ \Delta H_r \qquad \text{(XIX)}$$

Table 34. Experimental and estimated branching ratios for radicals where relevant data are available, sorted by type of reaction. Estimated branching ratios derived using alternative mechanistic assumptions are also shown.

Reaction Type and Reaction	Rad. [a]	Hr (kcal)	Estimated k (min^{-1})	Estimated %	Expt. Fract React. Min	Expt. Fract React. Exp'd	Expt. Fract React. Max	Estimation vs Experimental
Estimates using Recommended Parameters								
Decomposition Forming CH3.								
CH3-C[O.](CH3)-O-CO-CH3 -> CH3-CO-O-CO-CH3 + CH3.	40	9.99	3.48e+2	66%	50%	76%	90%	ok
CH3-CH2-O-CH[O.]-CH3 -> CH3-CH2-O-CHO + CH3.	10	-4.81	3.54e+5	76%	60%	95%	100%	ok
CH3-C(CH3)(CH3)-O-CH[O.]-CH3 -> CH3. + CH3-C(CH3)(CH3)-O-CHO	12	-4.81	3.54e+5	82%	70%	83%	100%	ok
CH3-CH2-O-CO-CH2-CH2-O-CH[O.]-CH3 -> CH3. + CH3-CH2-O-CO-CH2-CH2-O-CHO	37	-4.81	3.54e+5	75%	50%	75%	100%	ok
CH3-CO-O-CH2-CH2-O-CH[O.]-CH3 -> CH3. + CH3-CO-O-CH2-CH2-O-CHO	35	-4.81	3.54e+5	72%	50%	90%	100%	ok
CH3-CH[O.]-O-CH2-CH2-OH -> CH3. + HCO-O-CH2-CH2-OH	21	-4.81	3.54e+5	64%	70%	82%	100%	Low: 64% vs 70%
CH3-C[O.](CH3)-O-CH3 -> CH3-O-CO-CH3 + CH3.	14	-6.51	2.51e+6	96%	50%	87%	95%	High: 96% vs 95%
CH3-CH(CH3)-O-C[O.](CH3)-CH3 -> CH3. + CH3-CH(CH3)-O-CO-CH3	16	-6.51	2.51e+6	97%	80%	100%	100%	ok
CH3-C[O.](CH3)-O-CH2-CH3 -> CH3. + CH3-CH2-O-CO-CH3	15	-6.51	2.51e+6	95%	0%	69%	100%	ok
CH3-C(CH3)(CH3)-O-C[O.](CH3)-CH3 -> CH3. + CH3-C(CH3)(CH3)-O-CO-CH3	17	-6.51	2.51e+6	97%	75%	100%	100%	ok
CH3-CH(CH3)-CH2-O-C[O.](CH3)-CH3 -> CH3. + CH3-CH(CH3)-CH2-O-CO-CH3	18	-6.51	2.51e+6	94%	40%	82%	100%	ok
CH3-C(CH3)(OH)-CH2-O-C[O.](CH3)-CH3 -> CH3. + CH3-C(CH3)(OH)-CH2-O-CO-CH3	27	-6.51	2.51e+6	95%	75%	100%	100%	ok
CH3-C[O.](CH3)-O-CH2-CH2-OH -> CH3. + CH3-CO-O-CH2-CH2-OH	26	-6.51	2.51e+6	92%	60%	90%	100%	ok
Decomposition Forming RCH2.								
CH3-CH2-CH[O.]-CH3 -> CH3-CHO + CH3-CH2.	2	6.94	6.46e+3	14%	24%	36%	54%	Low: 14% vs 24%
CH3-CH2-CH[O.]-CH2-CH3 -> CH3-CH2-CHO + CH3-CH2.	3	6.71	1.53e+4	28%	26%	39%	58%	ok
CH3-CH2-CH2-CH[O.]-O-CH3 -> CH3-CH2-CH2. + CH3-O-CHO	11	-6.54	1.45e+8	100%	50%	66%	100%	ok
CH3-CH2-CH2-CH[O.]-O-CH2-CH2-OH -> CH3-CH2-CH2. + HCO-O-CH2-CH2-OH	24	-6.54	1.45e+8	100%	50%	100%	100%	ok
CH3-CO-O-CH2-CH2-CH[O.]-CH3 -> CH3-CO-O-CH2-CH2. + CH3-CHO	32	5.17	2.41e+4	38%	0%	35%	75%	ok
Decomposition Forming R2CH.								
CH3-CH(CH3)-O-CH[O.]-CH(CH3)-CH3 -> CH3-CH[.]-CH3 + CH3-CH(CH3)-O-CHO	13	-6.09	1.14e+10	100%	50%	100%	100%	ok

Table 34 (continued)

Reaction Type and Reaction	Rad. [a]	Hr (kcal)	Estimated k (min^{-1})	Estimated %	Expt. Fract React. Min	Expt. Fract React. Exp’d	Expt. Fract React. Max	Estimation vs Experimental
<u>Decomposition Forming R3C.</u>								
CH3-C(CH3)(CH2O.)-CH3 -> HCHO + CH3-C[.](CH3)-CH3	1	10.40	1.31e+6	98%	75%	98%	100%	ok
<u>Decomposition Forming RO. (Rate constants estimated to minimize bias [Equation (XX)].</u>								
CH3-C(CH3)(CH3)O-CH2O. -> CH3-C[O.](CH3)CH3 + HCHO	9	14.34	3.09e+3	2%	0%	0%	25%	ok
CH3-O-CH2-O-CH2O. -> CH3-O-CH2O. + HCHO	8	13.34	6.50e+3	4%	0%	0%	25%	ok
CH3-CH(CH3)-O-CH[O.]-CH2-OH -> CH3-CH[O.]-CH3 + HCO-CH2-OH	23	12.35	1.36e+4	0%	0%	0%	15%	ok
CH3-CH2-CH2-CH2-O-CH[O.]-CH2-OH -> CH3-CH2-CH2-CH2O. + HCO-CH2-OH	25	11.55	2.46e+4	0%	0%	0%	25%	ok
CH3-CH2-O-CH[O.]-CH2-O-CO-CH3 -> CH3-CH2O. + CH3-CO-O-CH2-CHO	34	11.54	2.48e+4	0%	0%	0%	30%	ok
CH3-CH2-O-CH[O.]-CH2-OH -> CH3-CH2O. + HCO-CH2-OH	22	11.54	2.48e+4	0%	0%	0%	25%	ok
CH3-CH(OH)-CH[O.]-O-CH3 -> CH3O. + CH3-CH(OH)-CHO	20	11.49	2.57e+4	0%	0%	0%	15%	ok
CH3-C(CH3)(CH3)-O-CH[O.]-CH3 -> CH3-C[O.](CH3)-CH3 + CH3-CHO	12	11.07	3.51e+4	8%	0%	0%	20%	ok
CH3-C[O.](CH3)-O-CO-CH3 -> CH3-CO-CH3 + CH3-CO2.	40	10.73	1.09e+2	21%	10%	24%	50%	ok
CH3-CH2-CH2-CH[O.]-O-CH3 -> CH3O. + CH3-CH2-CH2-CHO	11	10.34	6.04e+4	0%	0%	0%	30%	ok
CH3-C(CH3)(CH3)-O-C[O.](CH3)-CH3 -> CH3-C[O.](CH3)-CH3 + CH3-CO-CH3	17	10.29	6.27e+4	2%	0%	0%	20%	ok
CH3-CH2-CH2-CH[O.]-O-CH2-CH2-OH -> HO-CH2-CH2O. + CH3-CH2-CH2-CHO	24	10.13	7.06e+4	0%	0%	0%	25%	ok
CH3-CH(CH3)-O-C[O.](CH3)-CH3 -> CH3-CH[O.]-CH3 + CH3-CO-CH3	16	10.09	7.28e+4	3%	0%	0%	20%	ok
CH3-CH2-O-CO-CH2-CH2-O-CH[O.]-CH3 -> CH3-CH2-O-CO-CH2-CH2O. + CH3-CHO	37	10.07	7.39e+4	16%	0%	0%	50%	ok
CH3-CO-O-CH2-CH2-O-CH[O.]-CH3 -> CH3-CO-O-CH2-CH2O. + CH3-CHO	35	10.07	7.39e+4	15%	0%	0%	25%	ok
CH3-CH[O.]-O-CH2-CH2-OH -> HO-CH2-CH2O. + CH3-CHO	21	10.07	7.39e+4	13%	0%	0%	25%	ok
CH3-CH2-O-CH[O.]-CH3 -> CH3-CH2O. + CH3-CHO	10	10.06	7.44e+4	16%	0%	0%	15%	High: 16% vs 15%
CH3-C[O.](CH3)-O-CH3 -> CH3-CO-CH3 + CH3O.	14	9.50	1.13e+5	4%	5%	13%	25%	Low: 4% vs 5%
CH3-CH(CH3)-CH2-O-C[O.](CH3)-CH3 -> CH3-CH(CH2O.)-CH3 + CH3-CO-CH3	18	9.29	1.32e+5	5%	0%	18%	40%	ok
CH3-C[O.](CH3)-O-CH2-CH2-OH -> HO-CH2-CH2O. + CH3-CO-CH3	26	9.29	1.32e+5	5%	0%	0%	20%	ok
CH3-C(CH3)(OH)-CH2-O-C[O.](CH3)-CH3 -> CH3-C(OH)(CH2O.)-CH3 + CH3-CO-CH3	27	9.29	1.32e+5	5%	0%	0%	25%	ok

Table 34 (continued)

Reaction Type and Reaction	Rad.	Hr	Estimated		Expt. Fract React.			Estimation vs
	[a]	(kcal)	k (min^{-1})	%	Min	Exp'd	Max	Experimental
CH3-C[O.](CH3)-O-CH2-CH3 -> CH3-CH2O. + CH3-CO-CH3	15	9.28	1.33e+5	5%	0%	31%	100%	ok
CH3-CH2-O-CO-CH2-CH[O.]-O-CH2-CH3 -> CH3-CH2O. + CH3-CH2-O-CO-CH2-CHO	36	7.99	3.46e+5	0%	0%	16%	20%	ok
CH3-O-CH[O.]-O-CH3 -> CH3-O-CHO + CH3O.	47	-1.67	9.07e+8	100%	0%	16%	50%	High: 100% vs 50%
Decomposition Forming RCO.								
CH3-CO-CH2O. -> HCHO + CH3-CO.	28	2.59	1.74e+9	63%	75%	100%	100%	Low: 63% vs 75%
CH3-CH2-O-CO-CH2O. -> HCHO + CH3-CH2-O-CO.	29	13.50	1.39e+1	0%	0%	0%	70%	ok
Decomposition forming HCO.								
CH3-C[O.](CHO)-CH2-OH -> CH3-CO-CH2-OH + HCO.	38	-0.66	1.53e+7	94%	75%	100%	100%	ok
Decomposition Forming a-Hydroxy Radicals								
HO-CH2-CH2O. -> HO-CH2. + HCHO	4	11.79	1.11e+5	78%	70%	78%	85%	ok
CH3-CH[O.]-CH2-OH -> HO-CH2. + CH3-CHO	5	6.62	5.19e+6	99%	85%	100%	100%	ok
CH3-CH(CH3)-CH[O.]-CH2-OH -> CH3-CH(CHO)-	7	7.15	3.50e+6	91%	50%	71%	90%	High: 91% vs 90%
CH3-CH(OH)-CH[O.]-CH3 -> CH3-CHO + CH3-CH[.]-OH	6	2.87	2.56e+9	100%	100%	100%	100%	ok
CH3-CH2-CH2-CH2-O-CH[O.]-CH2-OH -> HO-CH2. + CH3-CH2-CH2-CH2-O-CHO	25	-6.05	6.36e+10	100%	80%	100%	100%	ok
CH3-CH(CH3)-O-CH[O.]-CH2-OH -> HO-CH2. + CH3-CH(CH3)-O-CHO	23	-6.05	6.36e+10	100%	80%	100%	100%	ok
CH3-CH2-O-CH[O.]-CH2-OH -> HO-CH2. + CH3-CH2-O-CHO	22	-6.05	6.36e+10	100%	75%	100%	100%	ok
CH3-CH(OH)-CH[O.]-O-CH3 -> CH3-CH[.]-OH + CH3-O-CHO	20	-9.80	3.14e+13	100%	80%	100%	100%	ok
Decompositions Forming ROCH2.								
CH3-CH(CH3)-O-CH2-C[O.](CH3)-CH3 -> CH3-CH(CH3)-O-CH2. + CH3-CO-CH3	19	3.74	6.96e+4	13%	0%	0%	25%	ok
CH3-CH2-CH[O.]-CH2-O-CO-CH3 -> CH3-CO-O-CH2. + CH3-CH2-CHO	31	8.84	1.57e+3	5%	0%		75%	ok
Decompositions Forming ROCH[.]R								
CH3-CH(CH2O.)-O-CO-CH3 -> CH3-CO-O-CH[.]-CH3 + HCHO	30	12.81	4.93e+4	59%	25%	100%	100%	ok
Decomposition Forming RO-CO-CH2. or R-CO-O-CH2.								ok
CH3-CH2-O-CO-CH2-CH[O.]-O-CH2-CH3 -> CH3-CH2-O-CO-CH2. + CH3-CH2-O-CHO	36	-5.80	8.34e+7	100%	50%	84%	100%	ok
CH3-CH2-O-CH[O.]-CH2-O-CO-CH3 -> CH3-CO-O-CH2. + CH3-CH2-O-CHO	34	-3.60	1.63e+7	100%	50%	90%	100%	ok
Decompositions forming RO-CO.								
CH3-C[O.](CH3)-CO-O-CH3 -> CH3-CO-CH3 + CH3-O-CO.	39	5.69	4.62e+3	85%	50%	100%	100%	ok

Table 34 (continued)

Reaction Type and Reaction	Rad.	Hr	Estimated		Expt. Fract React.			Estimation vs
	[a]	(kcal)	k (min^{-1})	%	Min	Exp'd	Max	Experimental
CH3-CH2-O-CO-CH2O. -> HCHO + CH3-CH2-O-CO.	29	13.50	1.39e+1	0%	0%	0%	70%	ok
CH3-O-CO-CH2-CH[O.]-CO-O-CH3 -> CH3-O-CO-CH2-CHO + CH3-O-CO.	33	7.33	1.37e+3	15%	0%	0%	20%	ok
<u>Isomerizations (no -O- or -CO- in transition state ring)</u>								
CH3-CH2-CH2-CH[O.]-O-CH2-CH2-OH -> HO-CH2-CH2-O-CH(OH)-CH2-CH2-CH2.	24		1.96e+5	0%	0%	0%	25%	ok
<u>Isomerizations with -O- or -CO- in transition state ring (3.5 kcal/mole strain energy assumed)</u>								
CH3-CH2-O-CH[O.]-CH3 -> CH3-CH(OH)O-CH2-CH2.	10		5.31e+2	0%	0%	0%	25%	ok
CH3-C(CH3)(CH3)O-CH2O. -> CH3-C(CH3)(CH2.)O-CH2-OH	9		1.59e+3	1%	0%	0%	25%	ok
CH3-C(CH3)(CH3)O-CH[O.]-CH3 -> CH3-C(CH3)(CH2.)O-CH(OH)CH3	12		1.59e+3	0%	0%	0%	20%	ok
CH3-CH(CH3)-O-C[O.](CH3)-CH3 -> CH3-C(CH3)(OH)-O-CH(CH2.)-CH3	16		1.06e+3	0%	0%	0%	20%	ok
CH3-C(CH3)(CH3)-O-C[O.](CH3)-CH3 -> CH3-C(CH3)(CH2.)-O-C(CH3)(OH)-CH3	17		1.59e+3	0%	0%	0%	20%	ok
CH3-CH2-O-CO-CH2-CH[O.]-O-CH2-CH3 -> CH3-CH2-O-CO-CH2-CH(OH)-O-CH2-CH2.	36		5.31e+2	0%	0%	0%	20%	ok
CH3-CH2-O-CO-CH2-CH2-O-CH[O.]-CH3 -> CH3-CH(OH)-O-CH2-CH[.]-CO-O-CH2-CH3	37		2.32e+3	0%	0%	0%	50%	ok
CH3-CO-O-CH2-CH2-O-CH[O.]-CH3 -> CH3-CH(OH)-O-CH2-CH[.]-O-CO-CH3	35		2.72e+4	6%	0%	0%	25%	ok
CH3-CH2-CH2-CH[O.]-O-CH2-CH2-OH -> CH3-CH2-CH2-CH(OH)-O-CH2-CH[.]-OH	24		8.80e+4	0%	0%	0%	25%	ok
CH3-CH2-CH2-CH2-O-CH[O.]-CH2-OH -> CH3-CH2-CH[.]-CH2-O-CH(OH)-CH2-OH	25		1.83e+4	0%	0%	0%	25%	ok
CH3-CH2-CH2-CH[O.]-O-CH3 -> CH3-O-CH(OH)-CH2-CH2-CH2.	11		1.96e+5	0%	0%	0%	30%	ok
CH3-CH(CH3)-CH2-O-C[O.](CH3)-CH3 -> CH3-C(CH3)(OH)-O-CH2-C[.](CH3)-CH3	18		2.70e+4	1%	0%	0%	30%	ok
CH3-CH(CH3)-O-CH2-C[O.](CH3)-CH3 -> CH3-C(CH3)(OH)-CH2-O-C[.](CH3)-CH3	19		4.81e+5	87%	75%	100%	100%	ok
CH3-C[O.](CH3)-O-CH2-CH2-OH -> CH3-C(CH3)(OH)-O-CH2-CH[.]-OH	26		8.80e+4	3%	0%	0%	20%	ok
CH3-CH[O.]-O-CH2-CH2-OH -> CH3-CH(OH)-O-CH2-CH[.]-OH	21		8.80e+4	16%	0%	0%	25%	ok
CH3-CO-CH2-CH[O.]-CH3 -> CH3-CH(OH)-CH2-CO-CH2.	41		2.53e+2	0%	0%	0%	10%	ok
CH3-C[O.](CH3)-O-CO-CH3 -> CH3-C(CH3)(OH)-O-CO-CH2.	40		6.72e+1	13%	0%	0%	25%	ok

Table 34 (continued)

Reaction Type and Reaction	Rad. [a]	Hr (kcal)	Estimated		Expt. Fract React.			Estimation vs Experimental
			k (min^{-1})	%	Min	Exp’d	Max	
Estimates using alternative assumptions (see text)								
Decomposition Forming RO. (Rate constants estimated to best fit data on Table 32 [Equation (XIX)].)								
CH3-C(CH3)(CH3)O-CH2O. -> CH3-C[O.](CH3)CH3 + HCHO	9	14.34	1.49e+4	9%	0%	0%	25%	ok
CH3-O-CH2-O-CH2O. -> CH3-O-CH2O. + HCHO	8	13.34	3.14e+4	17%	0%	0%	25%	ok
CH3-CH(CH3)-O-CH[O.]-CH2-OH -> CH3-CH[O.]-CH3 + HCO-CH2-OH	23	12.35	6.55e+4	0%	0%	0%	15%	ok
CH3-CH2-CH2-CH2-O-CH[O.]-CH2-OH -> CH3-CH2-CH2-CH2O. + HCO-CH2-OH	25	11.55	1.19e+5	0%	0%	0%	25%	ok
CH3-CH2-O-CH[O.]-CH2-O-CO-CH3 -> CH3-CH2O. + CH3-CO-O-CH2-CHO	34	11.54	1.20e+5	1%	0%	0%	30%	ok
CH3-CH2-O-CH[O.]-CH2-OH -> CH3-CH2O. + HCO-CH2-OH	22	11.54	1.20e+5	0%	0%	0%	25%	ok
CH3-CH(OH)-CH[O.]-O-CH3 -> CH3O. + CH3-CH(OH)-CHO	20	11.49	1.24e+5	0%	0%	0%	15%	ok
CH3-C(CH3)(CH3)-O-CH[O.]-CH3 -> CH3-C[O.](CH3)-CH3 + CH3-CHO	12	11.07	1.70e+5	30%	0%	0%	20%	High: 30% vs 20%
CH3-C[O.](CH3)-O-CO-CH3 -> CH3-CO-CH3 + CH3-CO2.	40	10.73	2.18e+5	100%	10%	24%	50%	High: 100% vs 50%
CH3-CH2-CH2-CH[O.]-O-CH3 -> CH3O. + CH3-CH2-CH2-CHO	11	10.34	2.92e+5	0%	0%	0%	30%	ok
CH3-C(CH3)(CH3)-O-C[O.](CH3)-CH3 -> CH3-C[O.](CH3)-CH3 + CH3-CO-CH3	17	10.29	3.03e+5	11%	0%	0%	20%	ok
CH3-CH2-CH2-CH[O.]-O-CH2-CH2-OH -> HO-CH2-CH2O. + CH3-CH2-CH2-CHO	24	10.13	3.41e+5	0%	0%	0%	25%	ok
CH3-CH(CH3)-O-C[O.](CH3)-CH3 -> CH3-CH[O.]-CH3 + CH3-CO-CH3	16	10.09	3.51e+5	12%	0%	0%	20%	ok
CH3-CH2-O-CO-CH2-CH2-O-CH[O.]-CH3 -> CH3-CH2-O-CO-CH2-CH2O. + CH3-CHO	37	10.07	3.57e+5	47%	0%	0%	50%	ok
CH3-CO-O-CH2-CH2-O-CH[O.]-CH3 -> CH3-CO-O-CH2-CH2O. + CH3-CHO	35	10.07	3.57e+5	46%	0%	0%	25%	High: 46% vs 25%
CH3-CH[O.]-O-CH2-CH2-OH -> HO-CH2-CH2O. + CH3-CHO	21	10.07	3.57e+5	43%	0%	0%	25%	High: 43% vs 25%
CH3-CH2-O-CH[O.]-CH3 -> CH3-CH2O. + CH3-CHO	10	10.06	3.59e+5	48%	0%	0%	15%	High: 48% vs 15%
CH3-C[O.](CH3)-O-CH3 -> CH3-CO-CH3 + CH3O.	14	9.50	5.45e+5	0%	5%	13%	25%	Low: 0% vs 5%
CH3-CH(CH3)-CH2-O-C[O.](CH3)-CH3 -> CH3-CH(CH2O.)-CH3 + CH3-CO-CH3	18	9.29	6.37e+5	20%	0%	18%	40%	ok
CH3-C[O.](CH3)-O-CH2-CH2-OH -> HO-CH2-CH2O. + CH3-CO-CH3	26	9.29	6.37e+5	20%	0%	0%	20%	ok
CH3-C(CH3)(OH)-CH2-O-C[O.](CH3)-CH3 -> CH3-C(OH)(CH2O.)-CH3 + CH3-CO-CH3	27	9.29	6.37e+5	20%	0%	0%	25%	ok
CH3-C[O.](CH3)-O-CH2-CH3 -> CH3-CH2O. + CH3-CO-CH3	15	9.28	6.41e+5	20%	0%	31%	100%	ok

Table 34 (continued)

Reaction Type and Reaction	Rad.	Hr	Estimated		Expt. Fract React.			Estimation vs
	[a]	(kcal)	k (min^{-1})	%	Min	Exp'd	Max	Experimental
CH3-CH2-O-CO-CH2-CH[O.]-O-CH2-CH3 -> CH3-CH2O. + CH3-CH2-O-CO-CH2-CHO	36	7.99	1.67e+6	2%	0%	16%	20%	ok
CH3-O-CH[O.]-O-CH3 -> CH3-O-CHO + CH3O.	47	-1.67	4.38e+9	100%	0%	16%	50%	High: 100% vs 50%
<u>Isomerizations with -O- in transition state ring (Estimates assuming no excess ring strain energy)</u>								
CH3-CH2-O-CH[O.]-CH3 -> CH3-CH(OH)O-CH2-CH2.	10		2.15e+5	29%	0%	0%	25%	High: 29% vs 25%
CH3-C(CH3)(CH3)O-CH2O. -> CH3-C(CH3)(CH2.)O-CH2-OH	9		6.46e+5	80%	0%	0%	25%	High: 80% vs 25%
CH3-C(CH3)(CH3)O-CH[O.]-CH3 -> CH3-C(CH3)(CH2.)O-CH(OH)CH3	12		6.46e+5	57%	0%	0%	20%	High: 57% vs 20%
CH3-CH(CH3)-O-C[O.](CH3)-CH3 -> CH3-C(CH3)(OH)-O-CH(CH2.)-CH3	16		4.31e+5	13%	0%	0%	20%	ok
CH3-C(CH3)(CH3)-O-C[O.](CH3)-CH3 -> CH3-C(CH3)(CH2.)-O-C(CH3)(OH)-CH3	17		6.46e+5	18%	0%	0%	20%	ok
CH3-CH2-O-CO-CH2-CH[O.]-O-CH2-CH3 -> CH3-CH2-O-CO-CH2-CH(OH)-O-CH2-CH2.	36		2.15e+5	0%	0%	0%	20%	ok
CH3-CH2-O-CO-CH2-CH2-O-CH[O.]-CH3 -> CH3-CH(OH)-O-CH2-CH[.]-CO-O-CH2-CH3	37		9.19e+5	63%	0%	0%	50%	High: 63% vs 50%
CH3-CO-O-CH2-CH2-O-CH[O.]-CH3 -> CH3-CH(OH)-O-CH2-CH[.]-O-CO-CH3	35		1.08e+7	95%	0%	0%	25%	High: 95% vs 25%
CH3-CH2-CH2-CH[O.]-O-CH2-CH2-OH -> CH3-CH2-CH2-CH(OH)-O-CH2-CH[.]-OH	24		3.49e+7	18%	0%	0%	25%	ok
CH3-CH2-CH2-CH2-O-CH[O.]-CH2-OH -> CH3-CH2-CH[.]-CH2-O-CH(OH)-CH2-OH	25		7.26e+6	0%	0%	0%	25%	ok
CH3-CH2-CH2-CH[O.]-O-CH3 -> CH3-O-CH(OH)-CH2-CH2-CH2.	11		2.15e+5	0%	0%	0%	30%	ok
CH3-CH(CH3)-CH2-O-C[O.](CH3)-CH3 -> CH3-C(CH3)(OH)-O-CH2-C[.](CH3)-CH3	18		1.06e+7	78%	0%	0%	30%	High: 78% vs 30%
CH3-CH(CH3)-O-CH2-C[O.](CH3)-CH3 -> CH3-C(CH3)(OH)-CH2-O-C[.](CH3)-CH3	19		1.89e+8	100%	75%	100%	100%	ok
CH3-C[O.](CH3)-O-CH2-CH2-OH -> CH3-C(CH3)(OH)-O-CH2-CH[.]-OH	26		3.49e+7	92%	0%	0%	20%	High: 92% vs 20%
CH3-CH[O.]-O-CH2-CH2-OH -> CH3-CH(OH)-O-CH2-CH[.]-OH	21		3.49e+7	99%	0%	0%	25%	High: 99% vs 25%
CH3-CO-CH2-CH[O.]-CH3 -> CH3-CH(OH)-CH2-CO-CH2.	41		9.32e+4	47%	0%	0%	10%	High: 47% vs 10%

[a] Radical number on Table 33

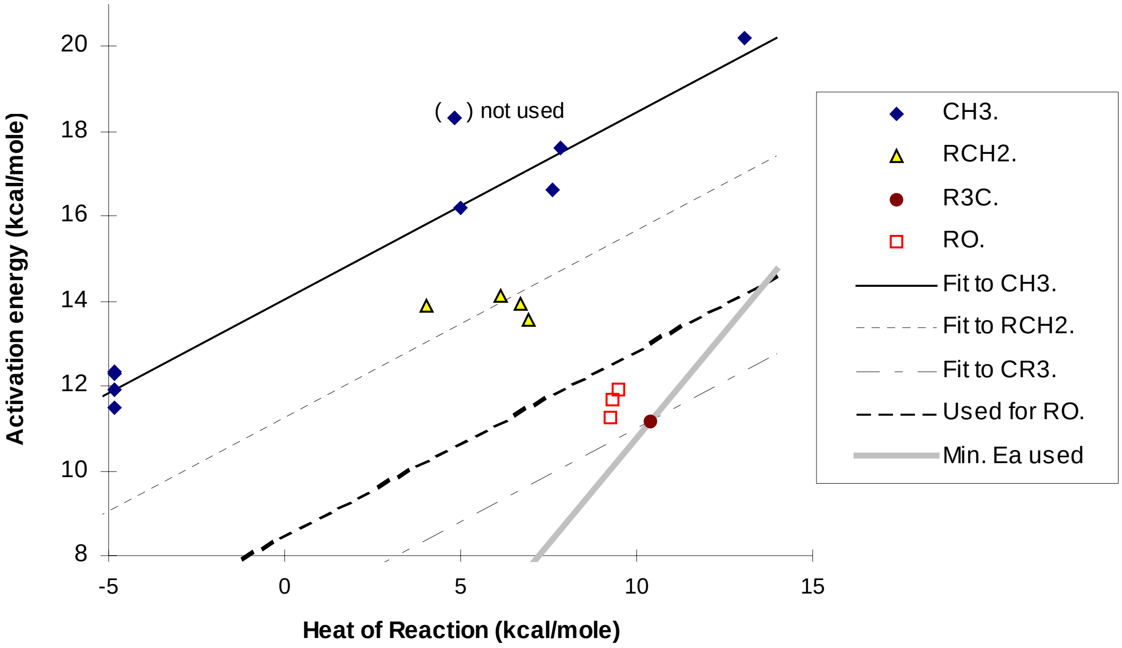

Figure 8. Plots of estimated or measured activation energies vs. heats of reaction for various alkoxy radical decompositions.

Note that using Equation (XIX) gives a reasonably good fit to the data for the decomposition determined relative to the O_2 reaction, even though this was not used in its derivation.

However, although use of Equation (XIX) to predict alkoxy-forming decomposition activation energies gives good fits to the limited quantitative product yield data, Table 34 shows that there are many cases where it results in predictions which are inconsistent with upper limit data concerning the relative importance of this reaction (see “rate constants estimated to best fit data on Table 32” in the “alternative assumptions” section of the table). In particular, use of Equation (XIX) appears to be biased towards overpredicting the relative importance of this reaction. Such a bias is not acceptable as a basis for deriving a general methodology for deriving estimated VOC reaction mechanisms, and if uniformly good predictions cannot be obtained, at a minimum the prediction method should be as likely to underpredict as overpredict.

To obtain unbiased estimates for the relative importances of these decompositions, an optimization was performed to minimize the cases where the estimates were outside of the estimated upper and lower limit ranges, as well as to minimize the discrepancies between estimated and experimental quantitative yield ratios[16]. This optimization was done in two ways: one where EaA was adjusted and EaB was held fixed at the 0.44 value as assumed for the reactions forming alkyl radicals, and the other where both EaA and EaB were optimized. However, the qualities of the fits were not significantly different in either case, so for consistency with the estimates for the other reactions we will

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[16] The data for the $CH_3OCH(O\cdot)OCH_3$ radical, where the estimates appear to fail by orders of magnitude more than was the case for any other radicals, were not used in the optimization.

only use the data where we assumed EaB = 0.44. The results of this optimization yielded EaA = 8.44 kcal/mole, i.e.,

$$\text{Ea (decomp to RO. - recommended)} = 8.43 + 0.44\ \Delta H_r \qquad \text{(XX)}$$

This resulted in overpredicting the apparent activation energies for the three alkoxy-forming decompositions on Table 32 by ~1 kcal/mole each, which corresponds to an underprediction of the 298K rate constant by a factor of ~6. However, use of Equation (XX) for predicting activation energies for alkoxy-forming decompositions is preferred over Equation (XIX) because the latter removes the apparent bias towards overpredicting upper limit rate constants. In particular, this gives only three cases (as opposed to six for Equation XIX) where the prediction is outside the estimation is outside the estimated uncertainty range of the experimental data.

The estimates discussed above do not cover all the types of radicals that may be formed in alkoxy radical decompositions, and methods are needed to estimate EaA values for cases where there are no data. Atkinson (1997b) observed that there is an apparent correlation between the EaA and the ionization potential of the radical formed, and used this to derive a general estimation method for all alkoxy radical decompositions. Plots of the EaA values obtained as discussed above against ionization potential of the radical formed is shown on Figure 9. The IP's used are given in Table 35 and are from the NIST (1994) database. It can be seen that the three points for the alkyl (methyl, ethyl, propyl and t-butyl) radicals are reasonably well fit by a straight line, which is given by

$$\text{EaA (decomp. to hydrocarbon radicals)} = -8.73 + 2.35\ \text{IP} \qquad \text{(XXI)}$$

where EaA is in kcal/mole and IP is the ionization potential of the radical formed in eV. When combined with Equation (XIV), and using EaB = 0.44 as discussed above, this yields

$$\text{Ea (decomp. to hydrocarbon radicals)} = -8.73 + 2.35\ \text{IP} + 0.44\ \Delta H_r \qquad \text{(XXII)}$$

where IP is in eV and Ea and ΔH_r is in kcal/mole. This is close to the general relationship derived by Atkinson (1997a), which is

$$\text{Ea (general decompositions)} = -8.1 + 2.4\ \text{IP} + 0.36\ \Delta H_r. \qquad \text{(XXIII)}$$

The small differences between these equations are due to the fact that in this work the EaB parameter is determined using only the reactions forming methyl radicals, and that Atkinson (1996) did not include the exothermic decompositions of the radicals from the ether systems in his analysis, but did include the reaction forming $HOCH_2\cdot$.

Figure 9 shows that Equation (XXI) overpredicts the EaA for the reaction forming $HOCH_2\cdot$ by 1.65 kcal/mole, resulting in an underprediction of the 298K rate constant by a factor of ~16. However, it can be argued that the discrepancy is not large considering the data and the assumptions behind the empirical correlations. Equation (XXI) clearly fails in the case of reactions forming alkoxy radicals, overpredicting activation energies by over 4.5 kcal/mole and the decomposition rate constants by three orders of magnitude. For that reason, we conclude that Equations (XXI) should only be used for reactions forming carbon-centered radicals. For substituted radicals the actual data should be used to derive EaA estimates whenever possible.

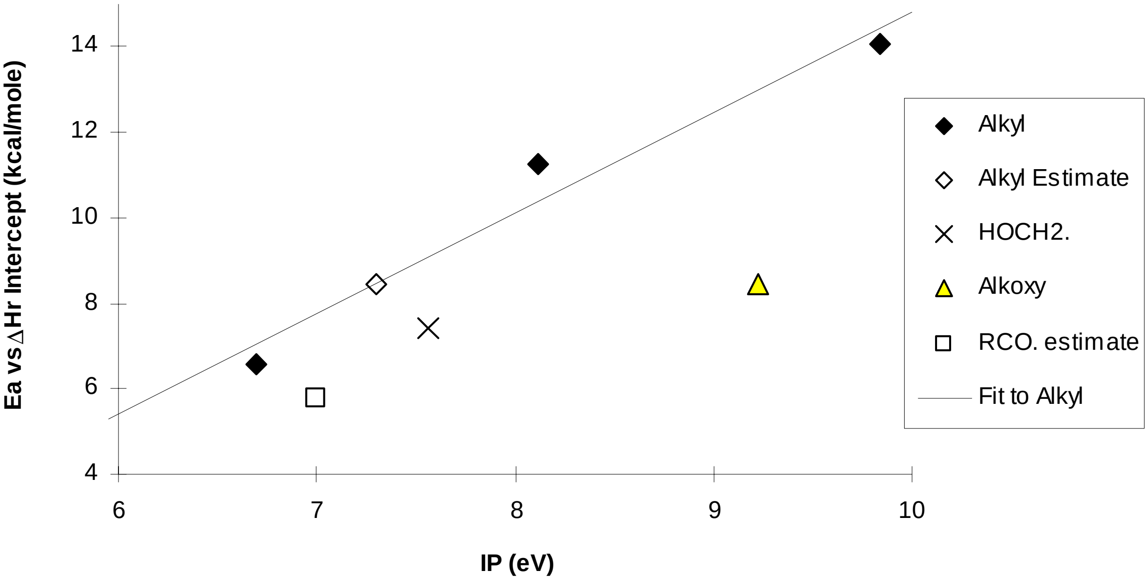

Figure 9. Plots of intercepts of lines used to predict activation energies from heats of reactions for various types of alkoxy radical decompositions vs. the ionization potential of the radical formed. These are based on assuming all lines have the same slope as fits the data for reactions forming methyl radicals.

Based on these considerations, together with the availability of IP data, Equation (XXI) can therefore be used to derive the EaA parameters for decompositions forming secondary alkyl radicals ($R_2CH\cdot$), and a modified version of Equation (XXI), where the EaA is reduced by 1.65 kcal/mole so its predictions are consistent with the data for the reaction forming $HOCH_2O\cdot$, can be used to estimate EaA for reactions forming $CH_3C(.)OH$. In the case of reactions forming HCO and RC(O)· radicals, predictions that are reasonably consistent with the limited upper and lower limit data (see Table 34) if the EaA predicted using Equation (XXI) is reduced by ~2 kcal/mole. These estimates are given on Table 35, together with the EaA values derived for the decompositions discussed above, and the associated ionization potentials. Obviously, these EaA estimates are the least uncertain for secondary alkyl radicals, are highly uncertain for formyl and acetyl radicals.

Available IP data and Equation (XXI) (or the modified version of it) can also be used to derive an EaA for reactions forming $CH_3OCH_2\cdot$ radicals, which presumably could also be applied to reactions forming other radicals of the type $ROCH_2\cdot$. However, applying this approach to reactions forming these radicals predict that this type of reaction is extremely rapid (having rate constants > 10^9 sec^{-1}) in at least two cases where available data are inconsistent with this reaction dominating (see Table 34 and radicals 19 and 31 on Table 33). Predictions are more consistent with the data if the activation energies are derived assuming the same EaA as employed for reactions forming alkyl $RCH_2\cdot$ radicals. For other radicals, Equation (XII) is either not applicable or cannot be used because of lack of available IP data.

Table 35. Summary of ionization potentials and EaA parameters used to estimate activation energies for alkoxy radical decompositions from the heats of reactions.

Type of radical Formed [a]	IP [b] (eV)	EaA (kcal/mole)	Derivation of EaA
CH_3.	9.84	14.05	Derived from least squares fits of Ea vs Hr as discussed in the text (Equation (XV). The EaB derived from these data are assumed to be applicable for all alkoxy radical decompositions.
RCH_2.	8.12	11.25	Derived to by adjusting EaA to fit the data as discussed in the text (Equation (XVI).
RCH[.]R	7.30	8.46	EaA is estimated from the IP using Equation (XXI). See text.
R_2C[.]R	6.70	6.58	Derived to by adjusting EaA to fit the data as discussed in the text (Equation (XVII).
RO.	9.22	8.43	Derived to minimize errors and biases in predictions of relative product yield data as discussed in the text (Equation XX).
OH	13.00	8.43	EaA assumed to be the same as derived for decompositions forming alkoxy radicals. This is highly uncertain.
HCO.	~8.8? [c]	9.99	Estimated from the IP using Equation (XXI), with the intercept reduced by 2.0 kcal/mole to give predictions which are more consistent with the limited available upper and lower limit data. Highly uncertain and may be upper limit.
R’C(O).	7.00	5.76	(see above)
R’C(O)O.		12.00	Necessary to assume that decompositions forming RCO2. radicals is slow to be consistent with product data from reaction of OH with isopropyl and t-butyl acetates, and for model simulations to fit chamber data for propropylene carbonate. The EaA value used is the lowest value that is consistent with the data for propylene carbonate.
$HOCH_2$.	7.56	7.43	Derived to by adjusting EaA to fit the data as discussed in the text (Equation (XVIII).
RCH[.]OH	6.70	5.41	Estimated from the IP using Equation (XXI), with the intercept reduced by 1.65 kcal/mole to correctly predict the data for the decomposition of HOCH2CH2O. to HOCH2.
R_2C[.]OH		4.21	Ratio of EaA for R_2C[.]OH to R2C[.]R assumed to be the same as ratio of EaA’s for RCH[.]OH to RCH[.]R.
R’OCH_2.	6.94	11.25	Better fits to available data are obtained if reactions forming $ROCH_2$. Radicals have the same activation energies as those forming RCH_2 radicals.
RCH[.]OR’		7.46	R’O- substitution assumed to reduce EaA by 1 kcal/mole relative to alkyl substitution to fit data for a minor product from isopropyl acetate. This is highly uncertain, and the data are also consistent with reducing EaA even further.
R_2C[.]OR’		5.58	R’O- substitution assumed to reduce EaA by 1 kcal/mole to be consistent with assumption made when estimating EaA for RCH[.]OR’. This is highly uncertain.
ROC(O).		12.00	Derived to be such that this decomposition is predicted to be minor for CH3-O-CO-CH2-CH[O.]-CO-O-CH3 radicals, but is the dominant process for CH3-C[O.](CH3)-CO-O-CH3, for model predictions to be consistent with environmental chamber reactivity data for dimethyl succinate (DBE-4) and methyl isobutyrate, respectively.
XC(O)CH_2.		11.25	For lack of available data, R’C(O)- and HC(O)- substitution is assumed to have no effect on EaA.
RCH[.]C(O)X		8.46	(see above)
R_2C[.]C(O)X		6.58	(see above)

[a] "R" is any substituent where the radical center is bonded to a non-carbonyl carbon. "R’" is any substituent other than H. "X" is any substituent, including H.

[b] IP data from NIST (1994) and is given for the methyl substituted species except where indicated.

[c] Not in NIST database. Entry of "8.8?" given in Lange’s handbook of chemistry (1985).

For reactions forming substituted alkyl radicals (i.e., reactions forming radicals with non-alkyl substituents) we assume that β- or further substituents on the radical formed have no effect, and make various estimates concerning the effects of various types of α-substituents, based on highly uncertain assumptions or fits to a very limited data base. In several cases, adjustments were made so the predictions would be consistent with product data or with environmental chamber reactivity data for several compounds. For example, it was initially assumed that decompositions forming RC(O)O· radicals have the same parameters as those forming simple alkoxy (RO·) radicals, but,, as indicated on Table 35, this better fits to product and environmental chamber data for several compounds were obtained if a much higher EaA value was used. These estimates, which are obviously very uncertain, are summarized on Table 35.

Although this is not the case with any of the radicals listed on Table 33, there may be cases where Equation (XIV) and the recommended EaA and EaB values may predict unreasonably low or negative activation energies. For general estimation purposes, we assume a minimum decomposition energy of ~0.75 kcal/mole. Thus if Equation (XIV) predicts a lower activation energy lower than that, then 0.75 kcal/mole is used. Although the possibility of a lower minimum cannot be ruled out, the data for the decomposition of neopentoxy and $HOCH_2CH_2O\cdot$ radicals tend to rule out the minimum being higher than this.

The above discussion, based on the use of Equation (XIV), all incorporate the assumption that the activation energy for the decomposition only depends on the nature of the radical formed and the overall heat of reaction. With appropriate choices of EaA, as shown on Table 35, this gives predictions which, though not always consistent with the data to within the experimental uncertainty, are at least good to within an order of magnitude in most cases. Note that this assumption implies that the activation energy does not depend on the nature of the carbonyl compound that is formed. This appears to work in the case of reactions forming aldehydes, ketones, or esters, which is the case for most of the reactions listed on Table 33.

However, this assumption appears to fail in the case of reactions where the carbonyl group formed is in an anhydride or carbonate anhydride, i.e., is contained in a -C(O)OC(O)- structure. The data of Tuazon et al (1989b) indicate that the $CH_3C[O.](CH_3)OC(O)CH_3$ radical formed in the reactions of OH radicals with t-butyl and isopropyl acetates (radical 40 on Table 33) decomposes to a significant extent to form acetic anhydride and methyl radicals, while Equation (XIV) and the parameters that fit the data for most of the other methyl radical-forming reactions predict that this reaction is sufficiently slow that the competing isomerization pathway, which is not observed, would dominate[17]. In addition, reactivity and product data recently obtained from a carbonate compound can only be explained if an analogous reaction of a carbonate-containing radical is much more rapid than predicted by these estimates (unpublished results from this laboratory). The data of Tuazon et al (1998b), together with the estimated rate constant for the competing decomposition of $CH_3C[O.](CH_3)OC(O)CH_3$ to acetone and $CH_3CO_2\cdot$, can be predicted if the reactions forming anhydride products have a 2 kcal/mole lower reaction energy than predicted using Equation (XIV), and other data from our laboratory are also better fit if this is assumed.

Therefore, for estimating activation energies for β-scission decompositions that form carbonyl compounds with -C(O)OC(O)- structures, the following modified version of Equation (XIV) is employed:

$$\text{Ea (decomposition forming R}\cdot + \text{-CO-O-CO-)} = \text{EaA} + \text{EaB} \cdot \Delta H_r - 2 \text{ kcal/mole} \qquad \text{(XXIV)}$$

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[17] The decomposition is predicted to dominate even after the ring strain correction of 3.5 kcal/mole for transition states containing -O- or -CO- groups is added, as discussed in Section III.J.4.

where EaA is derived based on the radical, R·, that is formed as shown on Table 35, and the same EaB value is used as assumed for all other reactions. This is obviously uncertain because it is derived based on highly uncertain estimates for competing rate constants (see radical 40 on Table 33), and is based on only a limited number of reactions. However, employing this correction means that the mechanism estimation system gives branching ratio predictions that are consistent with the limited data that are currently available.

One area where the estimation methods discussed above clearly fails is the predictions of the branching ratios of the $CH_3OCH(O\cdot)OCH_3$ radical (radical 47 on Table 33). The data of Sidebottom et al (1997) indicate that decomposition and O_2 reaction occur at competitive rates (with O_2 reaction being somewhat more important), while the estimation methods derived in this work predict that decomposition will dominate by orders of magnitude. It is unclear whether the problem is with the estimation of the O_2 reaction, the estimates of the decomposition rates, the thermochemical estimates, or (least likely) the experimental data or its interpretation. Until data are available for other similar radicals with similar discrepancies between the estimates and the data, it is unclear what, if any, adjustments may be appropriate. Therefore, estimates for reactions of alkoxy radicals with two alkoxy substituents near the radical center must be considered suspect. However, dimethoxy methane is the only compound of this structure in the current detailed mechanism, and because of the experimental data of Sidebottom et al (1997) it is not necessary to use estimates to determine its mechanism.

The decomposition activation energy and rate constant estimates discussed in this section are obviously highly uncertain in many (if not most) cases, being based in many cases on very uncertain alkoxy + O_2 rate constants, employing many highly uncertain and untested assumptions, and not giving satisfactory predictions in all cases. Clearly, additional data are needed, particularly for reactions of oxygen-containing alkoxy radicals, to test, refine, and improve these estimates and the many assumptions they incorporate. Indeed, it may not be possible to develop a totally satisfactory estimation method that can accurately predict rate constants for the full variety of these reactions, without carrying out detailed theoretical calculations for each system. Thus, rate constants or branching ratios derived from experimental data should always be used whenever possible when developing reaction mechanisms for atmospheric reactivity predictions. However, when no data are available, we have no choice but to use estimates such as those discussed in this section.

4. Isomerization Corrections

As discussed above, when estimating alkoxy radical isomerization rate constants, an additional 3.5 kcal/mole is added to the activation energy if the cyclic transition state contains -O-, -C(O)- or -OC(O)- groups. The need for this correction is shown on Table 34, which compares the experimental and predicted upper and lower limit branching ratios for these isomerizations with and without this correction. It can be seen that if the additional 3.5 kcal/mole is not added to the activation energy, there are 8 cases where isomerization is predicted to be important where the experimental data indicate it is not. This overprediction of the importance of isomerization is removed when the additional 3.5 kcal/mole activation energy is assumed. On the other hand, if a strain energy of greater than that is assumed, then the estimation becomes inconsistent with the observation that the $CH_3CH(CH_3)\text{-}OCH_2C(O\cdot)(CH_3)CH_3$ reacts primarily by isomerization (Stemmler et al, 1997a).

Note that if it is assumed that the reactions of O_2 with the O-substituted alkoxy radicals are much more rapid than estimated in this work, as predicted, for example, by the estimation method of Atkinson (1997a), then many of the competing decompositions would also be predicted to be faster, and this isomerization strain correction may not be necessary. Obviously this isomerization correction, as well as all our estimates concerning the decomposition reactions, would need to be revisited if new data indicate that our estimates concerning these alkoxy + O_2 reactions are incorrect.

5. Ester Rearrangement

Tuazon et al (1998b) recently reported data indicating that α-ester-substituted alkoxy radicals undergo a second type of hydrogen shift isomerization, where the hydrogen α to the alkoxy center shifts, via a 5-member ring transition state, to the ester carbonyl oxygen atom, forming an acid and an acyl radical, e.g.,

$$RCH(O\cdot)\text{-}O\text{-}CO\text{-}R' \rightarrow RC(O)\cdot + O{=}C(OH)\text{-}R'.$$

In the case of the alkoxy radical formed from ethyl acetate [$CH_3CH(O\cdot)O\text{-}CO\text{-}CH_3$], this reaction dominates over the competing reactions of this alkoxy radical (primarily reaction with O_2 and decomposition to CH_3CHO and $CH_3CO_2\cdot$), which are estimated to have a total rate constant of ~5 x 10^4 sec^{-1} under atmospheric conditions. This means that these “ester rearrangements” must react with a rate constant of at least ~3 x 10^5 sec^{-1} under these conditions. Obviously provisions for these reactions need to be included in the mechanism estimation and generation system.

There is no information available upon which to base quantitative estimates for the rate constant for this reaction, other than the fact that the rate constant for $CH_3CH(O\cdot)O\text{-}CO\text{-}CH_3$ radicals is at least ~3 x 10^5 sec^{-1}, assuming the estimates for the competing reactions of this radical are correct. However, if the reaction is assumed to be much faster than this, then significant yields of PAN precursors are predicted to be formed in the photooxidation of n-butyl acetate, and models assuming this give predictions that are not consistent with results of environmental chamber experiments with this compound (Carter et al, 1999a). The PAN precursor $CH_3C(O)\cdot$ would result from the ester rearrangement of the $CH_3CH_2CH_2CH(O\cdot)O\text{-}CO\text{-}CH_3$ radical, which competes with the 1,4-H shift isomerization to $\cdot CH_2CH_2CH_2CH(OH)O\text{-}CO\text{-}CH_3$, which has an estimated rate constant of 2 x 10^5 sec^{-1}. To minimize this apparent inconsistency, we assume that all ester rearrangements occur with the estimated lower limit rate constant of 3 x 10^5 sec^{-1}.

To obtain a rough estimate of temperature dependence, we assume that these ester rearrangements have an A factor which is approximately the same as that used for 1,4-H shift isomerizations, based on expected similarities in the structure of the transition states. If a T=298K rate constant of 3 x 10^5 sec^{-1} is assumed, this corresponds to

$$k(\text{ester rearrangement}) \approx 8 \times 10^{10}\ e^{-3723/T}\ \text{sec-1} \qquad \text{(XXV)}$$

Obviously, this is highly uncertain, and quantitative information concerning relative rates of competing reactions involving this rearrangement, or at least more upper or lower limit data, would significantly reduce the uncertainty of these estimates.

Tuazon et al (1998b) saw no evidence that the analogous ester rearrangement reaction involving a 6-member ring transition state that might be expected to occur in the t-butyl acetate system, e.g.,

$$\cdot OCH_2C(CH_3)_2O\text{-}CO\text{-}CH_3 \rightarrow HC(O)C(\cdot)(CH_3)CH_3 + O{=}C(OH)\text{-}CH_3$$

in fact occurs to any significant extent. Of course, this could be because the competing decomposition to $HCHO + CH_3C(\cdot)(CH3)\text{-}O\text{-}CO\text{-}CH_3$ is predicted to be very fast, with an estimated rate constant of ~3 x 10^7 sec^{-1}. Nevertheless, we tentatively assume that these reactions are not important, and the possibility that they may occur is not presently incorporated in the mechanism generation system. However, the possibility that this occurs needs to be investigated.

6. Acyloxy Radicals

Acyloxy radicals are radicals of the form RC(O)O· or HC(O)O·. It is expected that the decomposition of RC(O)O· to R· and CO_2,

$$RC(O)O\cdot \rightarrow R\cdot + CO_2$$

should be rapid, based on thermochemical considerations, so this is assumed to be its major fate when it is generated in the mechanisms. In the case of HC(O)O·, the it is assumed to be consumed by rapid reaction with O_2.

$$HC(O)O\cdot + O_2 \rightarrow HO_2 + CO_2$$

Although it is also possible that it may primarily decompose to H· + CO_2, under atmospheric conditions the net effect would be the same because the major fate of H· atoms is reaction with O_2, forming HO_2.

7. Explicit Alkoxy Reaction Assignments

Because of the uncertainties in estimating alkoxy radical rate constants, explicit assignments of alkoxy radical rate constants or branching ratios are used rather than estimates whenever there are sufficient data available to make such assignments. These are shown on Table 30 through Table 33, above, where Table 30 contains the explicit assignments for the three measured alkoxy + O_2 reactions, Table 31 shows the assignments used for the butoxy and pentoxy isomerizations, Table 32 shows the assignments for those decompositions where quantitative rate constant assignments could be made, and Table 33 shows the assignments where the available data are appropriate for assigning branching ratios only. Note that many of these are quite uncertain, in most cases being based on highly indirect determinations or adjustments in complex mechanisms to fit reactivity data in chamber experiments, and having highly uncertain, usually estimated, reference rate constants. Note also that the system does not incorporate temperature dependence estimates for those reactions on Table 33 where only branching ratio assignments could be made, so the estimates may not be applicable for temperatures much different from ~300K. Nevertheless, these are less uncertain than the rate constants or branching ratios that have to be based entirely on estimates.

The reactions of isoprene, isoprene products and alkynes involve the formation of radicals whose mechanisms cannot be estimated because of lack of available thermochemical data, so explicit assignments have to be made in those cases so reactions of those compounds could be generated. These assignments are listed on Table 36, along with footnotes indicating the basis for the assignments. Note that those for radicals formed from isoprene and its products are based on estimates incorporated in the isoprene and isoprene products mechanism of Carter and Atkinson (1996), and those for other radicals are based on analogy for reactions of similar radicals for which estimates could be made.

8. Thermochemical Assignments Used in Estimates

Many of the estimates of alkoxy radical rate constants discussed above require a knowledge or estimate of the heats of reaction for the reactions being considered. These are estimated using the group additivity methods of Benson (1976), using updated group additivity data that were obtained primarily from the NIST (1994) thermochemical database. Although that database is extensive, it is not sufficient for many of the reactions that need to be considered, and assignments or estimates for additional groups had to be added. Table 37 and Table 38 give a complete listing of the thermochemical group assignments currently incorporated in the database. Table 37 gives the data obtained from the NIST (1994) database,

Table 36. Explicit assignments for reactions of alkoxy radicals whose mechanisms could not be estimated.

Radical	Products	Ratio	Notes
Isoprene Intermediates			
HO-CH2-C(CH3)=CH-CH2O.	HO-CH2-CH=C(CH3)-CH[.]-OH		1
HO-CH2-C(CH3)=CH(CH2O.)	HO-CH2-C(CH2.)=CH(CH2-OH)		1
CH2=C(CH2-OH)-CH[O.]-CH2-OH	CH2=C(CHO)-CH2-OH + HO-CH2.		1
CH2=CH-C[O.](CH3)-CH2-OH	CH2=CH-CO-CH3 + HO-CH2.		1
CH3-C(CH2O.)=CH(CH2-OH)	HO-CH2-C(CH3)=CH-CH[.]-OH		1
CH3-C(CH2O.)=CH-CH2-OH	CH3-C(CHO)=CH-CH2-OH + HO2.		1
CH2=C(CH3)-CH[O.]-CH2-OH	CH2=C(CHO)-CH3 + HO-CH2.		1
CH2=CH-C(OH)(CH2O.)-CH3	*C(CH3)(OH)-CH2-O-CH2-CH[.]-*		1
CH2=C(CH3)-CH(CH2O.)-OH	*CH(OH)-C[.](CH3)-CH2-O-CH2-*		1
CH2=CH-CO-CH2O.	HCHO + CH2=CH-CO.		1
Isoprene Product Intermediates			
HCO-CO-CH2O.	HCHO + HCO-CO.		1
.OCH2-CH=C(CH3)-CH2-ONO2	HCO-CH=C(CH3)-CH2-ONO2 + HO2.	80%	1
	HO-CH2-CH=C(CH3)-CH[.]-ONO2	20%	
Alkyne and Diene Intermediates			
CH3-CH[O.]-CO-CHO	CH3-CHO + HCO-CO.		2
CH3-CO-CO-CH2O.	HCHO + CH3-CO-CO.		3
CH2=CH-CH[O.]-CH2-OH	CH2=CH-CHO + HO-CH2.		4
HO-CH2-CH=CH(CH2O.)	HCO-CH=CH(CH2-OH) + HO2.		5
HO-CH2-CH=CH-CH2O.	HO-CH2-CH=CH-CH[.]-OH		6
CH2=CH-CH[O.]-CHO	CH2=CH-CHO + HCO.		7
.OCH2-CH=CH(CH2-ONO2)	HCO-CH=CH(CH2-ONO2) + HO2.		5
.OCH2-CH=CH-CH2-ONO2	HO-CH2-CH=CH-CH[.]-ONO2		6
CH2=CH-CH[O.]-CH2-ONO2	CH2=CH-CO-CH2-ONO2 + HO2.		8

Notes

1 As assumed by Carter and Atkinson (1996).

2 Assumed to be fast by analogy with estimated reactions for CH3-CH[O.]-CO-R radicals.

3 Assumed to be fast by analogy with estimated reactions for CH3-CO-CH2O. radicals.

4 Assumed to be fast by analogy with estimated reactions for R-CH[O.]-CH2-OH radicals.

5 Assumed to be fast based on lack of facile decomposition routes, and the fact that isomerization would involve a trans cyclic transition state.

6 Isomerization, which is permitted by the cis configuration, is expected to dominate.

7 Assumed to be fast by analogy with estimated reactions for R-CH[O.]-CHO radicals.

8 Reaction with O2 estimated to be the major route based on the estimated mechanism for CH3-CH2-CH[O.]-CH2-ONO2.

Table 37. Thermochemical group assignments used for estimating heats of reaction for rate constant estimation purposes that were obtained from the NIST (1994) database, or assigned as zero. Estimation methods and notation based on Benson (1976).

Group	kcal/mole	Group	kcal/mole	Group	kcal/mole
From NIST (1994)					
C*_(C)	39.10	C_(C)(C*)(C)(C)	1.50	Cd_(Cd)(Cd)	6.78
C*_(C)(C)	40.95	C_(C)(Cd)	-4.76	Cd_(Cd)(Cd)(Cd)	4.60
C*_(C)(C)(C)	42.60	C_(C)(Cd)(O)	-6.50	Cd_(Cd)(Cd)(O)	8.90
C*_(C)(O)	35.10	C_(C)(Cl)	-15.60	Cd_(Cd)(CO)	5.00
C*_(CO)	37.90	C_(C)(Cl)(Cl)	-18.90	Cd_(Cd)(CO)(O)	11.60
C@_(C)(Cl)	28.40	C_(C)(Cl)(Cl)(Cl)	-24.90	Cd_(Cd)(O)	8.60
C_(*CO)	-5.40	C_(C)(Cl)(F)(F)	-106.30	CO_(C)	-29.10
C_(*CO)(C)	-0.30	C_(C)(Cl)(O)	-21.60	CO_(C)(C)	-31.40
C_(*CO)(C)(C)	2.60	C_(C)(CO)	-5.20	CO_(C)(C*)	-31.40
C_(Br)(Br)(Br)(C)	3.90	C_(C)(CO)(Cl)	-22.00	CO_(C)(Cl)	-47.92
C_(Br)(C)	-5.40	C_(C)(F)	-51.50	CO_(C)(CO)	-29.20
C_(Br)(C)(C)	-3.40	C_(C)(F)(F)	-102.30	CO_(C)(F)	-95.50
C_(Br)(C)(C)(C)	-0.40	C_(C)(F)(F)(F)	-158.00	CO_(C)(I)	-20.00
C_(Br)(C)(Cl)	-10.10	C_(C)(I)	8.00	CO_(C)(O)	-35.10
C_(C)	-10.20	C_(C)(I)(I)	26.00	CO_(Cd)	-29.10
C_(C)(C)	-4.93	C_(C)(NO2)	-14.40	CO_(Cd)(O)	-32.00
C_(C)(C)(C)	-1.90	C_(C)(O)	-8.10	CO_(Cl)(O)	-49.20
C_(C)(C)(C)(C)	0.50	C_(C)(O)(O)	-16.30	CO_(CO)	-25.30
C_(C)(C)(C)(Cd)	1.68	C_(C)(O)(O)(O)	-29.60	CO_(CO)(Cl)	-40.15
C_(C)(C)(C)(Cl)	-12.80	C_(C)(O*)	6.10	CO_(CO)(O)	-29.30
C_(C)(C)(C)(CO)	1.40	C_(C)(O*)	6.10	CO_(O)	-32.10
C_(C)(C)(C)(F)	-48.50	C_(C*)	-10.08	CO_(O)(O)	-29.70
C_(C)(C)(C)(I)	13.00	C_(Cd)	-10.20	N_(C)(F)(F)	-7.80
C_(C)(C)(C)(NO2)	-11.70	C_(Cd)(Cd)	-4.29	O_(C)	-37.90
C_(C)(C)(C)(O)	-6.60	C_(Cd)(CO)	-3.80	O_(C)(C)	-23.20
C_(C)(C)(C)(O*)	8.60	C_(CO)	-10.20	O_(C)(C*)	-23.20
C_(C)(C)(Cd)	-1.48	C_(CO)(Cl)	-10.20	O_(C)(Cd)	-30.50
C_(C)(C)(Cl)	-14.80	C_(CO)(Cl)(Cl)	-12.00	O_(C)(CO)	-43.10
C_(C)(C)(Cl)(Cl)	-22.00	C_(CO)(Cl)(Cl)(Cl)	-11.80	O_(C)(NO2)	-19.40
C_(C)(C)(CO)	-1.70	C_(CO)(CO)	-7.60	O_(C)(O)	-4.50
C_(C)(C)(F)	-49.00	C_(I)(O)	3.80	O_(C*)	-37.90
C_(C)(C)(F)(F)	-97.00	C_(O)	-10.20	O_(Cd)(Cd)	-33.00
C_(C)(C)(I)	10.50	C_(O)(O)	-16.10	O_(Cd)(CO)	-45.20
C_(C)(C)(NO2)	-13.60	Cd_(C)(C)(Cd)	10.34	O_(CO)	-58.10
C_(C)(C)(O)	-7.20	Cd_(C)(Cd)	8.59	O_(CO)(CO)	-46.50
C_(C)(C)(O)(O)	-18.60	Cd_(C)(Cd)(Cd)	8.88	O_(CO)(O)	-19.00
C_(C)(C)(O*)	7.80	Cd_(C)(Cd)(CO)	7.50	O_(NO2)(O)	4.00
C_(C)(C*)	-4.95	Cd_(C)(Cd)(O)	10.30	O_(O)	-16.30
C_(C)(C*)(C)	-1.90	Cd_(Cd)	6.26	O_(O)(O)	14.70
Assigned to Zero					
*CO_(C)	0.00	Cl_(CO)	0.00	NO2_(C)	0.00
Br_(C)	0.00	F_(C)	0.00	NO2_(O)	0.00
Br_(C*)	0.00	F_(CO)	0.00	ONO2_(C)	0.00
Br_(CO)	0.00	I_(C)	0.00		
Cl_(C)	0.00	I_(CO)	0.00		

Table 38. Thermochemical group assignments used for estimating heats of reaction for rate constant estimation purposes that were derived for this work. Estimation methods and notation based on Benson (1976).

Group	kcal/mole	Documentation [a]
*CO_(O)	-4.20	C-H bond energy in formates is estimated to be 95 kcal/mole or higher based on correlation between BDE and CO-H + OH rate constants.
*CO_(ONO2)	-19.40	Calculated from O_(C)(NO2) + *CO_(O), *CO_(O) assignment: Assigned
C*_(Br)(C)	41.78	Estimated using correlation between kOH and BDE for alkanes and methanol, and kOH estimated using group additivity.
C*_(C)(C)(CO)	42.25	Estimated using: force-hr ch3-c[.](ch3)-cho + ch3-ch2-cho = ch3-ch(ch3)-cho + ch3-ch[.]-cho
C*_(C)(C)(O)	31.50	Estimated using: force-hr ch3-c[.](ch3)oh + ch3-ch(ch3)ch3 + ch3-ch2-oh + ch3-ch[.]-ch3 = ch3-ch(ch3)oh + ch3-c[.](ch3)ch3 + ch3-ch[.]-oh + ch3-ch2-ch3
C*_(C)(C)(ONO2)	12.10	Estimated using: force-hr CH3-C[.](ONO2)-CH3 = CH3-C[.](O-NO2)-CH3
C*_(C)(CO)	38.58	Estimated using: force-hr ch3-co-ch2. + ch3-ch2-co-ch3 + ch3-ch2-ch3 + ch3-ch2-ch[.]-ch3 = ch3-co-ch3 + ch3-ch[.]-co-ch3 + ch3-ch2-ch2. + ch3-ch2-ch2-ch3
C*_(C)(CO)(O)	32.46	Assumed to be the same as normal secondary alcohols, i.e., that carbonyl group does not affect BDE.
C*_(C)(O)(O)	24.50	Estimated using: force-hr HO-CH(CH3)-OH + HO-CH[.]-CH3 = HO-C[.](CH3)-OH + HO-CH2-CH3
C*_(C)(ONO2)	15.70	Calculated from O_(C)(NO2) + C*_(C)(O)
C*_(CO)(O)	34.95	Assumed to be the same as normal primary alcohols, i.e., that carbonyl group does not affect BDE.
C*_(CO)(ONO2)	15.55	Estimated using: FORCE-HR HCO-CH[.]-ONO2 = HCO-CH[.]-O-NO2
C*_(O)	35.75	WPC: Was 33.7. Adjusted to agree with Hf (.CH2OH) given by IUPAC (1996)
C*_(O)(O)	29.93	Estimated using: force-hr HO-CH2-OH + HO-CH2. = HO-CH[.]-OH + HO-CH3
C*_(ONO2)	16.35	Calculated from O_(C)(NO2) + C*_(O), C*_(O) assignment: WPC: Was 33.7. Adjusted to agree with Hf (.CH2OH) given by IUPAC (1996)
C_(*CO)(C)(C)(C)	5.70	CH3-C(CH3)(CH3)-CHO assumed to have the same CO..H BDE as CH3-CH(CH3)-CHO.
C_(*CO)(C)(ONO2)	-20.53	CH3-CH(ONO2)-CHO is assumed to have the same (CO)..H BDE as CH3-CH2-CHO.
C_(*CO)(CO)	-2.41	HCO-CH2-CHO is assumed to have the same (CO)..H BDE as CH3-CH2-CHO.
C_(*CO)(O)	-1.76	CH3-O-CH2-CHO is assumed to have the same (CO)..H BDE as CH3-CH2-CHO.
C_(*CO)(ONO2)	-21.17	ref HCO-CH2-ONO2 assumed to have same (CO)..H BDE as CH3-CH2-CHO.
C_(Br)(C)(CO)	4.00	Reaction [ch3-ch(cho)-br + ch3. = ch3-ch(cho)-ch3 + br.] is assumed to have same HR as analogous reactions for CH3-CH(Cl)-Br.
C_(Br)(C)(O)	-2.50	Reaction [ch3-ch(oh)-br + ch3. = ch3-ch(oh)-ch3 + br.] is assumed to have same HR as analogous reactions for CH3-CH(Cl)-Br.
C_(Br)(C)(O*)	12.50	Reaction [ch3-ch[o.]-br + ch3. = ch3-ch[o.]-ch3 + br.] is assumed to have same HR as analogous reactions for CH3-CH(Cl)-Br.
C_(Br)(C*)	-6.67	Reaction [.ch2-ch2-br + ch3. = .ch2-ch2-ch3 + br.] is assumed to have same HR as analogous reactions for alkyl groups.
C_(Br)(CO)	-6.27	Reaction [ch3-co-ch2-br + ch3. = ch3-co-ch2-ch3 + br.] is assumed to have same HR as analogous reactions for alkyl groups.
C_(Br)(O)	-3.70	Estimated using: force-hr br-ch2o. + ch3-oh = br-ch2-oh + ch3o.
C_(Br)(O*)	10.79	Reaction [.och2-br + ch3. = .och2-ch3 + br.] is assumed to have same HR as analogous reactions for CH3-CH(Cl)-Br.

Table 38 (continued)

Group	kcal/mole	Documentation [a]
C_(Br)(OO*)	9.30	Estimated using: force-hr br-ch2oo. + ch3-o-oh = br-ch2-o-oh + ch3oo.
C_(C)(C)(C)(C*)	-1.20	Estimated using: force-hr ch3-c(ch3)(ch3)-ch3 = ch3-c(ch3)(ch3)ch2. + h. is 99.7
C_(C)(C)(C)(ONO2)	-26.00	Calculated from O_(C)(NO2) + C_(C)(C)(C)(O)
C_(C)(C)(C)(OO*)	5.50	BDE for ROO..H assumed to be 85.0 based on IUPAC Hf's for CH3OO. and C2H5OO.
C_(C)(C)(C*)	-3.60	Estimated using: force-hr ch3-ch(ch3)ch3 = ch3-ch(ch3)ch2. + h. is 99.7
C_(C)(C)(C*)(O)	-8.90	Estimated using: force-hr ch3-c(ch3)(oh)-ch2. + ch3-ch(oh)-ch3 = ch3-c(ch3)(oh)-ch3 + ch3-ch(oh)-ch2.
C_(C)(C)(C*)(ONO2)	-28.30	Estimated using: force-hr .CH2-C(CH3)(CH3)-ONO2 = .CH2-C(CH3)(CH3)-O-NO2
C_(C)(C)(CO)(CO)	-1.47	Estimated using: force-hr hco-ch(ch3)-cho + ch3-c(ch3)(ch3)-cho = hco-c(ch3)(ch3)-cho + ch3-ch(ch3)-cho
C_(C)(C)(CO)(O)	-5.70	Estimated using: force-hr ch3-c(oh)(ch3)-cho + ch3-c(ch3)(ch3)ch3 = ch3-c(ch3)(ch3)cho + ch3-c(oh)(ch3)-ch3
C_(C)(C)(CO)(O*)	9.50	Estimated using: force-hr ch3-c(oh)(ch3)cho + ch3-c[o.](ch3)ch3 = ch3-c[o.](ch3)cho + ch3-c(oh)(ch3)ch3
C_(C)(C)(CO)(ONO2)	-25.10	Estimated using: force-hr CH3-C(CH3)(ONO2)-CO-CH3 = CH3-C(CH3)(O-NO2)-CO-CH3
C_(C)(C)(O)(O*)	-3.40	Assumed to have same O..H BDE as t-butanol
C_(C)(C)(O)(ONO2)	-38.00	Calculated from O_(C)(NO2) + C_(C)(C)(O)(O)
C_(C)(C)(O)(OO*)	-6.50	BDE for ROO..H assumed to be 85.0 based on IUPAC Hf's for CH3OO. and C2H5OO.
C_(C)(C)(O*)(ONO2)	-23.80	Calculated from O_(C)(NO2) + C_(C)(C)(O)(O*), C_(C)(C)(O)(O*) assignment: WPC: Assumed to have same BDE as used for C_CCHO*
C_(C)(C)(ONO2)	-26.60	Calculated from O_(C)(NO2) + C_(C)(C)(O)
C_(C)(C)(OO*)	4.90	BDE for ROO..H assumed to be 85.0 based on IUPAC Hf's for CH3OO. and C2H5OO.
C_(C)(C*)(CO)	-3.40	Estimated using: force-hr ch3-co-ch(ch3)-ch2. + ch3-ch(ch3)-ch3 = ch3-co-ch(ch3)-ch3 + ch3-ch(ch3)-ch2.
C_(C)(C*)(CO)(O)	-8.00	Estimated using: force-hr ch3-o-c(ch3)(cho)-ch2. + ch3-o-c(ch3)(ch3)-ch3 = ch3-o-c(ch3)(cho)-ch3 + ch3-o-c(ch3)(ch3)-ch2.
C_(C)(C*)(CO)(ONO2	-27.40	HCO-C(CH3)(ONO2)-CH3 is assumed to have same CH2..H BDE as HCO-C(CH3)(OH)-CH3.
C_(C)(C*)(O)	-9.50	WPC: Assumed to have BDE of 100 (between ethane and propane)
C_(C)(C*)(ONO2)	-28.90	Calculated from O_(C)(NO2) + C_(C)(C*)(O), C_(C)(C*)(O) assignment: WPC: Assumed to have BDE of 100 (between ethane and propane)
C_(C)(Cd)(ONO2)	-25.90	Calculated from O_(C)(NO2) + C_(C)(Cd)(O)
C_(C)(Cl)(O*)	-6.60	Reaction [ch3-ch[o.]-cl + ch3. = ch3-ch[o.]-ch3 + cl.] Is assumed to have same HR as analogous reactions of compounds with the C_ClHO group.
C_(C)(Cl)(ONO2)	-41.00	Calculated from O_(C)(NO2) + C_(C)(Cl)(O)
C_(C)(CO)(CO)	-4.57	Estimated using: force-hr ch3-co-ch2-co-ch3 + ch3-ch2-ch(ch3)-ch2-ch3 = ch3-co-ch(ch3)-co-ch3 + ch3-ch2-ch2-ch2-ch3
C_(C)(CO)(CO)(O)	-8.57	Estimated using: force-hr hco-c(ch3)(oh)-cho + hco-c(ch3)(ch3)-ch3 = hco-c(ch3)(ch3)-cho + hco-c(ch3)(oh)-ch3
C_(C)(CO)(O)	-6.32	WPC: Estimated assuming Hr (ch3-ch2-oh + ch3-cho -> ch3-ch3 + hoch2-cho) = Hr (ch3-ch(oh)-ch3 + ch3-ch2-cho -> ch3-ch(oh)-cho + ch3-ch2-ch3). Depends on C_(CO)OHH
C_(C)(CO)(O)(O)	-17.70	Estimated using: force-hr ch3-o-c(cho)(ch3)-o-ch3 + ch3-o-c(ch3)(ch3)-ch3 = ch3-o-c(ch3)(ch3)-o-ch3 + ch3-o-c(cho)(ch3)-ch3

Table 38 (continued)

Group	kcal/mole	Documentation [a]
C_(C)(CO)(O)(O*)	-2.50	Assumed to have the same O..H BDE as other tertiary alcohols.
C_(C)(CO)(O*)	7.87	WPC: H-O BDE of 104.2 assumed
C_(C)(CO)(ONO2)	-25.72	Estimated using: force-hr CH3-CH(ONO2)-CO-CH3 = CH3-CH(O-NO2)-CO-CH3
C_(C)(NO2)(NO2)	-9.90	DIPPR value -16.5, No Benson H-value, this from literature [6]
C_(C)(O)(O)(ONO2)	-49.00	Calculated from O_(C)(NO2) + C_(C)(O)(O)(O)
C_(C)(O)(O*)	-2.10	WPC: Assumed to have same BDE as CH3-CH2-CH2-O
C_(C)(O)(ONO2)	-35.70	Calculated from O_(C)(NO2) + C_(C)(O)(O)
C_(C)(O)(OO*)	-4.20	BDE for ROO..H assumed to be 85.0 based on IUPAC Hf's for CH3OO. and C2H5OO.
C_(C)(O*)(ONO2)	-21.50	Calculated from O_(C)(NO2) + C_(C)(O)(O*), C_(C)(O)(O*) assignment: WPC: Assumed to have same BDE as CH3-CH2-CH2-O
C_(C)(ONO2)	-27.50	Calculated from O_(C)(NO2) + C_(C)(O)
C_(C)(OO*)	3.34	Based on IUPAC Hf for CH3-CH2OO.
C_(C*)(Cl)	-18.01	Reaction [.ch2-ch2-cl + ch3. = .ch2-ch2-ch3 + cl.] is assumed to have same HR as analogous reactions of chloroalkanes.
C_(C*)(CO)	-6.90	WPC: H-CH2-CH2-CHO assumed to have same BDE as propane.
C_(C*)(CO)(O)	-8.02	Estimated using: force-hr HCO-CH(CH2.)OH + ch3-ch(ch3)ch3 = hco-ch(ch3)oh + ch3-ch(ch2.)ch3
C_(C*)(CO)(ONO2)	-27.42	HCO-CH(ONO2)-CH3 is assumed to have same CH2..H BDE as HCO-CH(OH)-CH3.
C_(C*)(O)	-9.73	WPC: Estimated assuming same BDE as n-propyl.
C_(C*)(O)(O)	-18.60	BDE for CH3-O-CH(OH)-CH2..H is assumed to be the same as for CH3-CH(OH)-CH2...H.
C_(C*)(ONO2)	-29.13	Calculated from O_(C)(NO2) + C_(C*)(O), C_(C*)(O) assignment: WPC: Estimated assuming same BDE as n-propyl.
C_(Cd)(O)	-8.05	Missing from NIST table. Set to give same estimated HF for CH2=CH-CH2-OH as NIST
C_(Cd)(O*)	5.25	CH2=CH-CH2-OH is assumed to have the same O..H BDE as other primary alcohols.
C_(Cd)(OO*)	3.39	Allylic hydroperoxides assumed to have same O..H BDE as alkyl hydroperoxides.
C_(Cl)(Cl)(O*)	-10.10	Reaction [cl-ch[o.]-cl + ch3. = cl-ch[o.]-ch3 + cl.] is assumed to have same HR as analogous reactions for dichlroralkanes.
C_(CO)(CO)(O)	-9.19	Estimated using: force-hr hco-ch(oh)-cho + hco-ch(ch3)-ch3 = hco-ch(ch3)-cho + hco-ch(oh)-ch3
C_(CO)(CO)(O*)	5.81	Assumed to have same O..H BDE as other secondary alcohols.
C_(CO)(CO)(ONO2)	-28.59	Estimated using: force-hr HCO-CH(ONO2)-CHO = HCO-CH(O-NO2)-CHO
C_(CO)(O)	-6.95	WPC: Estimated assuming Heat of reaction of -CO-CH2-CO- + CH2Cl2 = 2 -CO-CH2-Cl is the same as that for -CO-CH2-CO- + -O-CH2-O- = 2 -CO-CH2-O-.
C_(CO)(O)(O)	-15.42	Estimated using: force-hr hco-ch(oh)-o-ch3 + ch3-ch(oh)-ch3 = hco-ch(oh)-ch3 + ch3-ch(oh)-o-ch3
C_(CO)(O)(O*)	-1.22	CH3-O-CH(OH)-CO-CH3 is assumed to have the same O..H BDE as CH3-CH2-CH2-OH.
C_(CO)(O*)	7.24	WPC: Assumed to have same BDE as CH3-CH2-CH2-O. Note that this depends on highly uncertain assignment for C(CO)HHO.
C_(CO)(ONO2)	-26.36	Calculated from O_(C)(NO2) + C_(CO)(O), C_(CO)(O) assignment: WPC: Estimated assuming Heat of reaction of -CO-CH2-CO- + CH2Cl2 = 2 -CO-CH2-Cl is the same as that for -CO-CH2-CO- + -O-CH2-O- = 2 -CO-CH2-O-.
C_(CO)(OO*)	6.05	Estimated using: force-hr ch3-co-ch2-o-oh + ch3oo. = ch3-co-ch2oo. + ch3-o-oh
C_(I)(ONO2)	-15.60	Calculated from O_(C)(NO2) + C_(I)(O)

Table 38 (continued)

Group	kcal/mole	Documentation [a]
C_(O)(O)(O)	-26.92	Based on average of the heats of formation of trimethoxy methane tabulated by NIST at //http://webbook.nist.gov/
C_(O)(O)(O)(O)	-40.25	Based on average of the heats of formation of tetramethoxy methane tabulated by NIST at //http://webbook.nist.gov/
C_(O)(O)(O*)	-12.72	CH3-O-CH(OH)-O-CH3 is assumed to have the same O..H BDE as CH3-O-CH(OH)-CH3
C_(O)(O)(O)(O*)	-25.05	Assumed to have same O..H BDE as other tertiary alcohols.
C_(O)(O*)	-1.90	WPC: Assumed to have same BDE as CH3-CH2-CH2-O
C_(O)(ONO2)	-35.50	Calculated from O_(C)(NO2) + C_(O)(O)
C_(O)(OO*)	-4.00	BDE for ROO..H assumed to be 85.0 based on IUPAC Hf's for CH3OO. and C2H5OO.
C_(O*)(ONO2)	-21.30	Calculated from O_(C)(NO2) + C_(O)(O*), C_(O)(O*) assignment: WPC: Assumed to have same BDE as CH3-CH2-CH2-O
C_(ONO2)	-29.60	Calculated from O_(C)(NO2) + C_(O)
C_(OO*)	2.49	Estimated using IUPAC (1996) Hf's for CH3OOH and CH3OO.
CO_(Br)	-25.73	Reaction [hco-br + ch3. = hco-ch3 + br.] is assumed to have same HR as analogous reactions for CH3-CH(Cl)-Br.
CO_(Br)(C)	-27.81	Reaction [ch3-co-br + ch3. = ch3-co-ch3 + br.] is assumed to have same HR as analogous reactions for CH3-CH(Cl)-Br.
CO_(C)(Cd)	-34.06	Derived to fit HF in NIST database for CH2=CH-CO-CH3.
CO_(C)(O*)	-39.36	WPC: Derived from IUPAC Hf for ch3cooh, and CRC O..H BDE.
CO_(C)(OO*)	-30.91	Derived using IUPAC Hf for ch3-c(o)oo.
CO_(C*)	-29.10	WPC: Assumed to have same BDE as used for ch3-co-ch2.
CO_(C*)(CO)	-31.10	Estimated assuming the C..H BDE is the same in biacetyl as in acetone.
CO_(C*)(O)	-34.10	Estimated using correlation between kOH and BDE for alkanes and methanol, and kOH estimated using group additivity.
CO_(Cl)	-45.84	Reaction [hco-cl + ch3. = hco-ch3 + cl.] Is assumed to have same HR as analogous reaction of R-CO-Cl
CO_(Cl)(ONO2)	-68.60	Calculated from O_(C)(NO2) + CO_(Cl)(O)
CO_(CO)(CO)	-26.89	Hr for elimination of CO from CH3-CO-CO-CO-CH3 is assumed to be the same as for elimination of CO from biacetyl.
CO_(O)(O*)	-34.10	Estimated using: force-hr ch3-co-oh + ch3-o-co2. = ch3-co2. + ch3-o-co-oh
CO_(O)(OO*)	-25.51	BDE for ch3-o-co-oo..h Assumed to be same as for ch3-co-oo..h.
CO_(O*)	-36.84	Estimated using: force-hr ch3-co-oh + hco2. = ch3-co2. + hco-oh
O_(*CO)	-42.64	HCO-OH is assumed to have same (CO)..H BDE as CH3-O-CHO.
O_(*CO)(C)	-27.30	WPC: BDE for H-CO-O-R estimated to be relatively high (~100) based on low OH radical rate constant. Highly uncertain.
O_(C*)(CO)	-40.65	WPC: H-CH2-O-CO- assumed to have same BDE as ethane.
O_(C*)(NO2)	-12.45	Estimated using correlation between kOH and BDE for alkanes and methanol, and kOH estimated using group additivity.
O_(C*)(O)	-4.50	Estimated using: force-hr *ch(ch3)-o-c[.](ch3)-o-o-o-* + ho-ch2-ch3 = *ch(ch3)-o-ch(ch3)-o-o-o-* + ho-ch[.]-ch3
O_(Cd)	-44.86	Derived to fit HF in NIST database for CH2=CH-OH (-30).
O_(O)(O*)	17.50	Estimated using: force-hr ch3-o-o-oh + ch3oo. = ch3-o-o-o. + ch3-o-oh

Table 38 (continued)

Group	kcal/mole	Documentation [a]
O_(O*)(ONO2)	14.00	Calculated from O_(C)(NO2) + O_(O)(O*)
ONO2_(C*)	6.95	Estimated using: force-hr .ch2-ono2 = .ch2-o-no2

[a] The documentation text in this version is preliminary. These will be cleaned up for the final draft, and footnotes will be added to explain the notation used.

and Table 38 gives the thermochemical assignments that were added for this work, indicating the source of the assignments.

Note that there were insufficient resources in this project to comprehensively review the available and most up-to-date thermochemical group data, so some of the assignments shown on Table 38 may not necessarily represent the state of the art, and they probably can be improved significantly in some cases. However, given the other uncertainties of the estimation methods discussed above, it is suspected that this probably does not represent the largest source of uncertainty involved, at least in most cases.

The more significant problem with the thermochemical assignment database in the current mechanism generation system is a lack of assignments for certain groups, which limits the overall scope of the mechanism generation system. In particular, the limited number of assignments for halogenated groups (particularly those containing radicals) means that mechanisms cannot be generated for most halogenated compounds. Also, the lack of assignments for unsaturated radicals means the system cannot automatically generate mechanisms for abstraction reactions from alkenes [which are believed to be non-negligible for longer chain alkenes (Atkinson, 1997a)] or reactions of OH or NO_3 radicals with dialkenes. Lack of thermochemical group estimates also prevents mechanisms from being generated for certain highly substituted groups as well. Because of this, improving the thermochemical database needs to be a priority when this system is updated.

K. Reactions of Crigiee Biradicals

Crigiee biradicals, i.e., species of the type >C[·]OO·, are assumed to be formed in the reactions of O_3 with alkenes or alkynes, and by the reactions of carbenes (that are assumed to be formed in the photolyses of some unsaturated compounds) with O_2. These radicals are believed to be formed with initial vibrational excitation, and can undergo various unimolecular decompositions or be collisionally stabilized. The ranges of excitation energies of the biradicals formed from the reactions of carbenes with O_2 or O_3 with alkynes are almost certainly different from those formed in the reactions of O_3 with alkenes, so in general one might expect the branching ratios for the decomposition and stabilization routes to differ depending on the source of the biradicals. However, because of lack of information concerning the former reactions we assume that they react with the same mechanism as determined from O_3 + alkene systems.

1. $HCHO_2$ Biradicals

Atkinson (1997a) reviewed available information concerning reactions of O_3 with alkenes, and recommended the following mechanisms for the reactions of excited $HCHO_2$ biradicals:

$$HCHO_2(\text{excited}) + M \rightarrow HCHO_2(\text{stabilized}) \qquad (37\%)$$

$$HCHO_2(\text{excited}) \rightarrow HCO + OH \qquad (12\%)$$

$$HCHO_2(\text{excited}) \rightarrow CO_2 + H_2 \qquad (13\%)$$

$$HCHO_2(\text{excited}) \rightarrow CO + H_2O \qquad (38\%)$$

These branching ratios are used in the current mechanism. As indicated in Section II.B.2, the stabilized biradicals are assumed to react primarily with H_2O, forming the corresponding acid, i.e.,

$$HCHO_2(\text{stabilized}) + H_2O \rightarrow HC(O)OH + H_2O$$

2. $RCHO_2$ Biradicals

The reactions of substituted Crigiee biradicals are more uncertain. In the case of excited CH_3CHO_2, the following routes, discussed by Atkinson (1997a), appear to be the most reasonable to consider[18]:

$$CH_3CHOO(\text{excited}) + M \rightarrow CH_3CHOO(\text{stabilized}) + M \qquad (A)$$

$$CH_3CHO_2(\text{excited}) \rightarrow CH_3\cdot + CO + OH \qquad (B)$$

$$CH_3CHO_2(\text{excited}) \rightarrow CH_3\cdot + CO_2 + H\cdot \qquad (C)$$

$$CH_3CHO_2(\text{excited}) \rightarrow CH_4 + CO_2 \qquad (D)$$

Based on examination of the available literature, Atkinson (1997a) recommends assuming branching ratios of 15%, 54%, 17%, and 14% for pathways A-D, respectively. In the case of other substituted biradicals, this scheme can be generalized to

$$RCHOO(\text{excited}) + M \rightarrow RCHOO(\text{stabilized}) + M \qquad (A')$$

$$RCHO_2(\text{excited}) \rightarrow R\cdot + CO + OH \qquad (B')$$

$$RCHO_2(\text{excited}) \rightarrow R\cdot + CO_2 + H\cdot \qquad (C')$$

$$RCHO_2(\text{excited}) \rightarrow RH + CO_2 \qquad (D')$$

Note that Pathway B can account for much of the OH radical formation observed in the reactions of O_3 with 1-alkenes. The measured yields of OH radicals from the reactions of O_3 with 1-butene through 1-octene, as summarized by Atkinson (1997a) (see also Table 18, above), do not appear to be greatly different from that for the reaction of O_3 with propene, suggesting that the branching ratios may not change as the size of the biradical increases.

However, assuming the relatively high branching ratios recommended by Atkinson (1997a) for Pathways B and C results in positive biases in model simulations of the large data base of propene - NO_x environmental chamber experiments, and in significant overpredictions of O_3 formation rates in 1-butene - NO_x and (especially) 1-hexene - NO_x environmental chamber experiments. Although there are other uncertainties in the mechanisms that could be causing these discrepancies, reasonably consistent fits to the data cannot be obtained unless it is assumed that (1) somewhat lower radical yields (i.e., lower yields of Pathways B and C) are assumed for the excited CH_3CHOO reactions than recommended by Atkinson (1997a), and (2) the radical yields (i.e., the yields of Pathways B' and C') decrease as the size of the

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[18] Two other routes, involving formation of $CH_3O\cdot$ + HCO and CH_3OH + CO, are also given by Atkinson (1997a), but are not considered here because they do not involve chemically reasonable transition states for vibrationally excited molecules.

molecule increases. Note that both assumptions are inconsistent with the observed OH yields in the reactions of O_3 with 1-alkenes (Atkinson, 1997a – see also Table 18, above), so there is an apparent inconsistency between the laboratory measurements of the OH yields in the O_3 + alkene reactions and the results of modeling the 1-alkene - NO_x chamber experiments used to evaluate the mechanism.

The reason for this apparent inconsistency is unknown, and it might be due in part to the fact that NO_x is present in the environmental chamber experiments but not in the laboratory systems used to measure the OH yields. However, the possibility that the problems with modeling the 1-alkene chamber experiments using the Atkinson (1997a)-recommended branching ratios are due to other problems with the mechanism certainly cannot be ruled out. Nevertheless, satisfactory fits to the available data cannot be obtained even after adjusting or making reasonable modifications in the other uncertain aspects of the alkene photooxidation mechanisms. Because the objective of this project is to develop a mechanism that correctly predicts O_3 reactivities and other impacts of VOCs in simulated smog systems, it is necessary to use branching ratios that give predictions that are consistent with the large environmental chamber data.

The adjusted branching ratios for the reactions of excited $RCHO_2$ biradicals that are used in the current version of the mechanism are summarized on Table 39. As shown there, to fit the chamber data the biradicals are assumed to be increasingly likely to be stabilized as the size of the “R” substituent on the radical is increased. For this purpose, the “size” of the substituent is defined as the number of groups used by the mechanism generation system to define the substituent, as indicated in

Table 5, above. Note that for biradicals formed from unsubstituted alkenes the number of groups is the same as the number of carbons. Footnotes to the table indicate the rationalizations for the particular sets of branching ratios used.

3. R_2COO Biradicals

Available information on OH yields from reactions of O_3 with alkenes such as isobutene, 2-methyl-2-butene, 2,3-dimethyl-2-butene and other compounds (Atkinson, 1997a – see also Table 18, above) are most easily rationalized if it is assumed that most excited R_2COO react forming OH radicals in near-unit yields. In contrast with the case with 1-alkenes, model simulations assuming high radical yields in the reactions of O_3 with such alkenes are also reasonably consistent with the available chamber data, at least in the case of isobutene and several of the terpenes that are expected to form this type of biradical (see Section V and Appendix B). If one of the R groups has an α hydrogen, the reaction is assumed to proceed via rearrangement to an unsaturated hydroperoxide, which subsequently decomposes (Atkinson, 1997a):

$$>CH\text{-}C(\cdot)(OO\cdot)R \rightarrow >C=C(OOH)R \rightarrow >C=C(O\cdot)R + OH$$

$$>C=C(O\cdot)R \leftrightarrow >C(\cdot)C(O)R$$

Although other reactions probably occur to some extent, this is assumed to be the dominant reaction pathway for R_2COO biradicals which have the necessary α hydrogen. It may be that this reaction also occurs with the stabilized biradical, which may explain why there is no indication of decreased OH yield as the size of the molecule increases.

If the two substituents on the biradical are different and both have abstractable α hydrogens, then two possible OH-forming reactions can occur. In these cases, we estimate that the branching ratio is roughly proportional to the ratio of OH radical abstraction from the abstracted α hydrogens involved. This is uncertain because there is no experimental basis for this estimate.

Table 39. Adjusted branching ratios used for the reactions of excited $RCHO_2$ biradicals.

Pathway		Branching Ratio				
Number of Groups in R.		1	2	3	4	5+
Stabilization -> RC(O)OH	(A)	34%	89%	92%	95%	100%
R. + CO + OH	(B)	52%	11%	8%	5%	0%
R. + CO2 + H	(C)	0%	0%	0%	0%	0%
RH + CO2	(D)	14%	0%	0%	0%	0%
Notes		1	2	3	4	5

1 OH yield and methane formation (Pathways B and D) approximately as recommended by Atkinson (1997a). Radical formation from Pathway C is assumed to be negligible to improve fits of model simulation to propene - NOx chamber experiments, and fraction of stabilization (Pathway A) is increased accordingly.

2 Radical formation from Pathway (C) is assumed to be negligible and OH formation from Pathway (B) is reduced to improve fits of model simulations to 1-butene - NOx chamber experiments. Rest of reaction is assumed to be stabilization.

3 Branching ratios intermediate between those derived for the 1-butene and 1-hexene systems.

4 Model simulations are most consistent with results of 1-hexene - NOx chamber experiments if radical formation from the reactions of this biradical is assumed to invlove no more than ~5% radical formation routes. The rest of the reaction is assumed to involve stabilization.

5 100% stabilization is assumed by extrapolation from the mechanisms assumed for the smaller biradicals.

The above mechanism cannot occur for those disubstituted Crigiee biradicals that do not have substituents with α hydrogens. It is also considered to be unlikely if the only substituent(s) with α hydrogens are -CHO groups, since it is expected that formation of a ketene hydroperoxide intermediate would involve a strained transition state. In those cases (which probably do not occur in many cases for the VOCs currently considered in the mechanism), we arbitrarily assume that 90% is stabilized and 10% decomposes to CO_2 + 2 R·.

4. Assigned Reactions of α-Carbonyl or Unsaturated Crigiee Biradicals

Carter and Atkinson (1996) gave estimated mechanisms for several α-carbonyl or unsaturated Crigiee biradicals that are different from the general mechanisms discussed above. In most cases, these are adopted in this work. These are summarized on Table 40. Note that the reactions shown for HC(O)CHOO, CH_2=CHCHOO, and CH_2=C(CH_3)CHOO are assigned mechanisms applicable for those biradicals only, while that shown for RC(O)CHOO is a general mechanism that is derived based on the mechanism assumed by Carter and Atkinson (1996) for CH_3C(O)CHOO, but is assumed to be applicable for all radicals of this type, regardless of the nature of the "R" group.

Table 40. Assigned mechanisms for the reactions of excited α-carbonyl or unsaturated Crigiee biradicals.

Reactant and Products	Factor	Documentation
R-CO-CHOO[excited]		
R-COO[excited]-CHO	100.0%	O-shifts of alpha-carbonyl biradicals, via a primary ozonide transition state, are assumed to be rapid if they form a more substituted biradical (Carter and Atkinson, 1996)
CH2=C(CH3)-CHOO[excited]		
CO2 + CH2=CH-CH3	25.0%	As assumed by Carter and Atkinson (1996).
CH2=C(CHOO[stab])-CH3	75.0%	See above.
CH2=CH-CHOO[excited]		
CO2 + CH2=CH2	25.0%	Assumed to be analogous to mechanism assumed for methyl-substituted radical formed from O3 + isoprene (Carter and Atkinson, 1996).
CH2=CH-CHOO[stab]	75.0%	See above.
HCO-CHOO[excited]		
CO + HCO. + OH	50.0%	Assumed that decomposition is much more facile than in the CH3-CHOO[excited] case because of the weaker H..CO and C..CO bonds. The two most likely decomposition routes are arbitrarily assumed to have equal probability.
HCO2. + HCO.	50.0%	See above.

L. Lumping Assignments

Once the reactions of a given VOC with OH, NO_3, O_3, etc. have been fully generated, the system summarizes the overall yields of all products (including the $NO \rightarrow NO_2$ conversion operator), so that each initial reaction of the VOC in the presence of NO_x can be represented by one overall process

$$X + VOC \rightarrow p_1\ HO_2 + p_2\ (NO \rightarrow NO_2 \text{ conversions}) + \sum_i p_i\ Product_i$$

Here X refers to the species reacting with the VOC (OH, hν, etc.), $product_i$ represents each of the products that are formed, and p_i represents its overall yield. Since many hundreds and even thousands of products might be formed in the reactions of larger molecules, it is clearly not possible that they all be represented explicitly in the model simulations. As discussed in Section II.C, above, the current mechanism represents most oxidation products using a limited number of model species based on various "lumped molecule" assignments.

These assignments, which provide the interface between the mechanism generation system discussed above and the base mechanism discussed in Section II, are summarized on Table 41. For each product that is formed in the overall reaction, the system checks the "lumping rules" associated with each model species in the order they are given on this table, and assigns the product to the first model species on the list whose associated rules describe the products being considered. Note that the last model species on the list is "INERT", which means that if the product satisfies none of the other criteria, it is treated as unreactive in the model. The total yield of each of the model species formed in the overall reaction are then summed up, and the overall reaction is then recast into the form

$$X. + VOC \rightarrow m_1\ HO2. + m_2\ RO2\text{-}R. + m_3\ R2O2. + \sum_i m_i\ ModSpe_i$$

Table 41. Summary of lumping assignments used to determine how individual explicit product species are represented in the base mechanism.

Model Species	Structure or Lumping Critieria
Radical Operators (see text)	
RO2-N.	Any organic nitrate that is formed in a RO2 + NO reaction
Total HO2	HO2.
Total NO->NO2	NO->NO2 conversion operator
Explicit Radicals	
CCO-O2.	CH3-CO[OO.]
C-O2.	CH3OO.
HO.	OH
Cl.	Cl.
TBU-O.	CH3-C[O.](CH3)-CH3
Lumped Radicals	
MA-RCO3.	Any compound containing a C=C double-bonded group next to a CO[OO.] group.
RCO-O2.	Any other compound containing a CO[OO.] group.
Explicit Products	
HNO3	HNO3
NO2	NO2
CO	CO
CO2	CO2
HCHO	HCHO
ACET	CH3-CO-CH3
GLY	HCO-CHO
Lumped Products	
CCHO	CH3-CHO or HO-CH2-CHO
HCOOH	CH2OO[stab] or HCO-OH
CCO-OH	CH3-CHOO[stab] or CH3-CO-OH
MGLY	Any compound containing a -CO- next to a -CHO group.
BACL	Any compound containing a -CO- next to another -CO- group.
METHACRO	CH2=C(CHO)-CH3 or CH2=CH-CHO
MVK	Any compound containing CH2=CH-CO- groups except as indicated above.
ISOPROD	Any compound containing a C=C double-bonded group next to a -CHO or -CO- group except as indicated above, or 3-methyl furan.
RCHO	Any compound containing a -CH2-, >CH- or >C< group next to a -CHO group.
RCO-OH	Any compound containing a -CHOO[stab] group or a -CO- group next to a -OH group.
RNO3	Any compound containing a -ONO2 group that reacts with OH faster than 5 x 10^{-13} cm^3 $molec^{-1}$ s^{-1}, that is not formed in a peroxy + NO reaction.
XN	Any other compound containing a -ONO2 group except as indicated above.
PROD2	Anythingthat reacts with OH faster than 5 x 10^{-12} cm^3 $molec^{-1}$ s^{-1}, except as indicated above.
MEK	Anythingthat reacts with OH faster than 5 x 10^{-13} cm^3 $molec^{-1}$ s^{-1}, except as indicated above.
INERT	Anything not satisfying any of the above criteria

where HO2., RO2-R., R2O2., or ModSpe$_i$ are model species in the base mechanism (see Table A-1 in Appendix A), and m$_i$, …, m$_i$ are their corresponding yields. Reactions expressed in this way can be inserted directly into the mechanism, or the values of the overall rate constant and product yield parameters (the set of m$_i$'s) can serve as a basis for deriving parameters for lumped parameter species used to represent the compound in complex mixtures (see Section VI).

Although most of Table 41 is reasonably self-explanatory, some explanation is needed concerning how overall yields of HO2., RO2-R., R2O2., and RO2-N. are determined. In the case of RO2-N., just determining if the product contains a nitrate (-ONO2) group is not always appropriate, since the starting reactant itself may contain nitrate groups, and nitrate-containing species are formed when NO_3 reacts with double bonds. Because of this, the system stores a flag with the product log whenever a RO_2+NO reaction forming a nitrate is generated, which can be used to determine if it is appropriate to represent the product by RO2-N. In the case of HO2., RO2-R., and RO2-N., the total yields are computed from the total HO_2 and total $NO \rightarrow NO_2$ counts as follows:

Condition:	[Total HO_2] ≥ [Total $NO \rightarrow NO_2$]	[Total $NO \rightarrow NO_2$] > [Total HO_2]
HO2. Yield =	[Total HO_2] - [Total $NO \rightarrow NO_2$]	0
RO2-R. yield =	[Total $NO \rightarrow NO_2$]	[Total HO_2]
R2O2. Yield =	0	[Total $NO \rightarrow NO_2$] - [Total HO_2]

Note that this is an approximate treatment, since the system lumps HO_2 that is formed with no NO toNO_2 conversions (e.g., in reactions of alcohols forming α-hydroxy alkyl groups) with extra NO to NO_2 conversions from another reaction pathway. However, the effect of this approximation should be small, and would only be non-negligible under low NO_x conditions where peroxy + peroxy reactions convert with NO to NO_2 conversion processes.

IV. PARAMETERIZED MECHANISMS

The mechanism generation system discussed in the previous system cannot be used for VOCs where the nature of the radical intermediates are unknown, or that involve formation of intermediates that cannot be processed by the present system. These include the aromatics (whose intermediates are highly uncertain and almost certainly involve highly unsaturated radicals for which thermochemical estimates cannot be made), terpenes (whose polycyclic structure cannot be represented by the current system), halogenated compounds (for which insufficient thermochemical information is available on the current database implemented with the system), and compounds containing groups, such as amins, for which general estimation methods have not been developed.

These VOCs must continue to be represented by parameterized or highly simplified mechanisms, as is the case in other mechanisms and previous versions of this mechanism. The representation and mechanisms used in these cases are discussed in this section.

A. Representation of Aromatics

Aromatic hydrocarbons are believed to react in the atmosphere primarily with OH radicals, forming a variety of ring-containing and fragmentation products (Atkinson, 1990, 1999, and references therein). Despite progress in recent years towards improving our understanding of the atmospheric chemistry of aromatic hydrocarbons (e.g., see Atkinson, 1999, and references therein), there is still insufficient understanding of the details of these mechanisms to derive, or even estimate, predictive mechanisms. Therefore, it is still necessary to use parameterized mechanisms, with yields of model species representing reactive uncharacterized products adjusted to fit chamber data, in order to represent the atmospheric reactions of this important class of compounds.

All current photochemical mechanisms are based on assuming that the reactions of OH radicals with aromatics involve two initial processes. The first, which is applicable only for aromatics with substituents about the ring, involves H-atom abstraction from the side group, ultimately forming primarily aromatic aldehydes and ketones, and possibly small yields of aromatic nitrates as well:

$$\text{OH} + \text{aromatic} \rightarrow \text{H}_2\text{O} + (\text{benzyl type radical, e.g., } \Phi\text{CH}_2\cdot)$$

$$(\text{benzyl type radical}) + \text{O}_2 \rightarrow (\text{benzyl peroxy type radical, e.g., } \Phi\text{CH}_2\text{OO}\cdot)$$

$$(\text{benzyl peroxy type radical}) + \text{NO} \rightarrow \text{aromatic nitrate, e.g., } \Phi\text{CH}_2\text{ONO}_2$$

$$(\text{benzyl peroxy type radical}) + \text{NO} \rightarrow \text{NO}_2 + (\text{benzyl oxy type radical, e.g., } \Phi\text{CH}_2\text{O}\cdot)$$

$$(\text{benzyl oxy type radical}) + \text{O}_2 \rightarrow \text{HO}_2 + \text{aromatic aldehyde or ketone, e.g., } \Phi\text{CHO}$$

The other reaction route, which is generally the more important (and also the most uncertain), involves addition of OH to the aromatic ring, ultimately forming phenols or cresols to some extent, but primarily forming various ring fragmentation products:

OH + aromatic → (OH-aromatic adduct)

(OH-aromatic adduct) + O_2 → HO_2 + phenol or cresol

(OH-aromatic adduct) + O_2 → (OH-aromatic-O_2 adduct)

(OH-aromatic-O_2 adduct) + NO → uncharacterized nitrate products

(OH-aromatic-O_2 adduct) + NO → NO_2 + (uncharacterized radical intermediates)

(uncharacterized radical intermediates) → → HO_2 + α-dicarbonyls and other fragmentation products

Alternative mechanism formulations, e.g., assuming the OH-aromatic reacts with NO_2 at a rate competing with or exceeding its reaction with O_2, assuming radical intermediates react with NO_2 to form stable products, or assuming that additional NO to NO_2 conversions are involved in the formation of α-dicarbonyls or other fragmentation products, can also be considered. However, except for the naphthalenes and tetralin (discussed below), experience has shown that parameterizations based on these alternative mechanisms do not fit the available environmental chamber data as well as those based on the general reaction schemes shown above.

The exception to this general scheme is that as discussed below improved fits of model simulations to chamber data for naphthalene, 2,3-dimethyl naphthalene, and tetralin are obtained if it is assumed that at least some of the uncharacterized radical intermediates react in a manner analogous to a PAN precursor (e.g., acyl peroxy) radicals. This involves radicals where the reaction with NO_2 forming a relatively stable termination product, e.g.,

(uncharacterized radical intermediates) + NO_2 → (uncharacterized PAN analogue)

competes with the reaction with NO forming radical propagation products (shown above). The data for these compounds are not fit if it is assumed that there is no significant radical termination process, nor are they well fit if it is assumed that the extent of termination is not strongly affected by reaction conditions. The latter would be the case if the termination were due to organic nitrate formation from the reactions of peroxy radicals with NO, or to the formation of some intermediate, such as phenoxy radicals, that only reacts by a termination process.

Therefore, the parameterization used to represent the reactions of the aromatics in this version is similar to that employed previously (Carter et al, 1997a), except that, as discussed above in Sections II.C.1 and II.C.3, a larger number of model species are used to represent the reactions of the various known and uncharacterized aromatic ring fragmentation projects. In this version, all three of the α-dicarbonyl products from the methylbenzenes are represented explicitly, and three different model species are used to represent the non-photoreactive (DCB1) and the two types of photoreactive (DCB2 and DCB3) uncharacterized ring fragmentation products. In addition, the mechanisms for the DCB's are are estimated based roughly on those estimated for unsaturated dicarbonyls (see Section II.C.3), unlike the previous mechanism where they were based on reactions of α-dicarbonyls (Carter, 1990). In addition, to at least approximately fit chamber data for the naphthalenes and tetralin, the possibility for the formation of PAN precursor radicals, represented by the RCO-O2· model species, is also included in the parameterization.

In terms of model species used in the current mechanism, the overall reactions of the aromatics are represented as follows:

$$\begin{aligned}\text{OH + aromatic} \rightarrow\ & y_{RH}\ \text{HO2.} + y_{RR}\ \text{RO2-R.} + y_{NR}\ \text{RO2-N.} + y_{Q2}\ \text{RCO-O2.} + \\ & y_{PH}\ \text{PHEN} + y_{CR}\ \text{CRES} + y_{BL}\ \text{BALD} + y_{K6}\ \text{PROD2} + \\ & y_{GL}\ \text{GLY} + y_{MG}\ \text{MGLY} + y_{BA}\ \text{BACL} + y_{D1}\ \text{DCB1} + y_{D2}\ \text{DCB2} + y_{D3}\ \text{DCB3.}\end{aligned}$$

Here the y_{PH}, …, y_{D3} are the stoichiometric parameters that must be specified to define the mechanism. Note that the products shown in the first line represents the formation of various radical products and their effects of NO to NO_2 or organic nitrate formation from reactions of peroxy radicals, those shown in the second line represent the aromatic ring-retaining products (with PROD2 being used to represent aromatic ketones such as methyl phenyl ketone that may be formed from ethylbenzene), and those in the third line represent the various known or uncharacterized ring fragmentation products.

Note that based on the reaction mechanism formulation discussed above, and considerations of factors such as radical conservation, relationships between some of the parameters can be derived, to reduce the number of parameters that have to be estimated or optimized. Radical conservation requires that

$$y_{RH} + y_{RR} + y_{RN} + y_{Q2} = 1.$$

If it is assumed that cresol or phenol formation occurs as shown above and that all the other processes involve a NO to NO_2 conversion, then

$$y_{RH} = y_{PH} + y_{CR}$$

This means that y_{RR} can be derived given the y_{Q2} value that best fits the data and the assigned phenol and cresol yields and the assigned nitrate yield (y_{RN}) parameter.

$$y_{RR} = 1 - (y_{PH} + y_{CR} + y_{Q2} + y_{RN}) \qquad \text{(XXVI)}$$

In addition, we assume that all the ring fragmentation processes, including those that form α-dicarbonyls, but probably excluding those involving involve formation of radicals represented by RCO-O2·, involve formation of some type of reactive dicarbonyl product. This implies that

$$\text{Total DCB Yield} = y_{D1} + y_{D2} + y_{D3} = 1 - (y_{Q2} + y_{NR} + y_{PH} + y_{CR} + y_{BL} + y_{K6}) \qquad \text{(XXVII)}$$

This is used to derive y_{D1} given the optimized yields of y_{D1}, y_{D3}, and y_{Q2} and the assigned yields of the other parameters.

The stoichiometric yield parameters that were assigned or derived for the various aromatic compounds currently incorporated in the mechanism are summarized on Table 42. Footnotes to that table indicating the sources of the derivations are given on Table 43. As indicated in the footnotes, some of the product yield parameters are based on experimental data, some are estimated, and some are adjusted to fit chamber data. The adjustments were done by using a non-linear optimization method to minimize the sum of squares error between experimental and calculated values of the data indicated on the footnotes, with the errors normalized relative to the maximum values of the measurements for each experiment.

The following points are noted concerning these assignments and the resulting mechanisms for the various types of compounds.

Table 42. Summary of assigned and optimized stoichiometric yield parameters used to represent the reactions of the aromatics.

Parameters and Products		Benzene	Toluene	Ethyl Benzene	o-Xylene	m-Xylene	p-Xylene
OH abstraction pathway							
yBL	BALD		0.085		0.054	0.037	0.083
yK6	PROD2			0.239			
yNR	RO2-N.		0.008	0.024	0.008	0.008	0.008
Notes		1	6,7	10	6,14	6,14	6,14
Phenol/Cresol patheay							
yPH	PHEN	0.236					
yCR	CRES		0.234	0.190	0.161	0.210	0.188
Notes		2,3	6	11	15	15	15
α-Dicarbonyl products							
yGL	GLY	0.207	0.116	0.094	0.084	0.107	0.195
yMG	MGLY		0.135	0.109	0.238	0.335	0.112
yBA	BACL				0.139		
Notes		4,3	8	11,12	8	8	8
Optimized Fragmentation Products							
yD2	DCB2		0.156		0.060	0.290	0.000
yD3	DCB3		0.057	0.049	0.145	0.108	0.012
Notes		5	9	13	16	17	18,19
Derived Yields [a]							
yRH	HO2.	0.236	0.234	0.190	0.161	0.210	0.188
yRR	RO2-R.	0.764	0.758	0.786	0.831	0.782	0.804
yD1	DCB1	0.764	0.460	0.498	0.572	0.347	0.709

Parameters and Products		1,2,3-Trimethyl Benzene	1,2,4-Trimethyl Benzene	1,3,5 Trimethyl Benzene	Naphthalene	Methyl Naphthalene	2,3-Dimethyl Naphthalene	Tetralin
OH abstraction pathway								
yBL	BALD	0.044	0.044	0.025				
yNR	RO2-N.	0.010	0.010	0.010	0.070	0.070	0.070	0.129
Notes [b]		20	20	20	24	29	24	31
Phenol/Cresol patheay								
yPH	PHEN				0.236			0.600
yCR	CRES	0.186	0.186	0.186		0.236	0.236	
Notes [b]		20	20	20	24	29	24	
α-Dicarbonyl products								
yGL	GLY	0.065	0.063	0.000	0.084	0.084	0.084	0.084
yMG	MGLY	0.166	0.364	0.621		0.038	0.076	
yBA	BACL		0.079		25	29	25,30	25
Notes [b]		8	8	8				
Optimized Fragmentation Products								
yD2	DCB2	0.077	0.000	0.097	0.049	0.076	0.103	0.046
yD3	DCB3	0.149	0.027	0.114	0.049	0.076	0.103	0.046
yQ2	RCO-O2.				0.479	0.539	0.600	0.163
Notes [b]		21	22	23	26,27,28	29	26,27,30	26,31
Derived Yields [a]								
yRH	HO2.	0.186	0.186	0.186	0.236	0.236	0.236	0.600
yRR	RO2-R.	0.804	0.804	0.804	0.215	0.155	0.094	0.108
yD1	DCB1	0.533	0.733	0.569	0.117	0.003	0 [c]	0.016

[a] Parameters calculated using Equations (XXVI) and (XXVII).

[b] Documentation notes are given on Table 42.

[c] Equation (XXVII) predicts a slightly negative DCB1 yield for this compound. Zero yield assumed.

Table 43. Documentation notes for the assigned and optimized stoichiometric yield parameters used to represent the reactions of the aromatics.

No.	Note
1	Organic nitrate yields from reaction of NO to OH - aromatic - O_2 adducts is assumed not to be significant
2	Glyoxal yields from Tuazon et al (1986).
3	See also yield data summarized by Atkinson (1994).
4	Phenol yield from Atkinson et al (1989).
5	Best fits to the D([O_3]-[NO]) data in benzene - NOx runs ITC560, ITC561, ITC562, ITC710, CTC159A, CTC159B, CTC160A, and CTC160B are obtained if yields of photoreactive DCB products are assumed to be negligible..
6	Aromatic aldehyde and and total phenolic product yields are averages of data tabulated by Atkinson (1994), except that the benzaldehyde and tolualdehyde yields of Gery et al (1987) are not used because they are substantially higher than the other measurements.
7	The approximate yield of organic nitrates in the RO_2+NO reaction are estimated from the benzyl nitrate yields tabulated by Atkinson (1994). Note that this corresponds to an approximately 9.5% yield from benzyl peroxy radicals, which is in the expected range for a molecule of this size.
8	Alpha-dicarbonyl yields are averages of data tabulated by Atkinson (1994), with low values from Shepson et al (1984) and the high values of Tagkagi et al (1980) excluded from the averages.
9	The DCB2 and DCB3 yields were adjusted to fit the concentration-time data for D([O_3]-[NO]) and toluene in toluene - NOx - air runs CTC079, CTC048, CTC026, CTC034, CTC065, DTC042B, DTC155A, DTC151A, DTC170A, and DTC042A.
10	The fraction reacted by abstraction from -CH_2- group is estimated from the rate constants for ethylbenzene and toluene, and from the benzaldehyde yield form toluene, assuming OH addition to the aromatic ring occurs with the same rate constant as with toluene. The expected abstraction product is benzophenone, which is very approximately represented in the mechanism by the lumped higher oxygenate product PROD2. The organic nitrate yield is estimated to be 10% of reaction of peroxy radical formed after abstraction from the -CH_2- group. Since abstraction is estimated to occur ~24% of the time and nitrate formation from the OH-aromatic-O_2 adducts is assumed to be negligible, this gives a 2.4% overall nitrate yield.
11	The phenolic product and alpha-dicarbonyl yields, relative to OH addition to aromatic ring, are assumed to be the same as for toluene
12	Methyl glyoxal is used to represent ethyl glyoxal.
13	The DCB2 and DCB3 yields were adjusted to fit the concentration-time data for D([O_3]-[NO]) and ethylbenzene in ethylbenzene - NOx - air runs CTC057, CTC092A, CTC092B, CTC098B, DTC223A, DTC223B, DTC224A, and DTC224B.
14	Nitrate yields for the xylenes are based approximately on the methylbenzyl nitrate yields tabulated by Atkinson (1994). The yields are consistent with 10-20% nitrate formation from reaction of NO with methylbenzyl peroxy radicals.
15	Phenolic product yields from Atkinson et al (1991).
16	The DCB2 and DCB3 yields were adjusted to fit the concentration-time data for D([O_3]-[NO]) and o-xylene in o-xylene - NOx - air runs CTC038, CTC039, CTC046, CTC068, CTC081, CTC091A, DTC207A, DTC207B, DTC208A, DTC208B, DTC209A, and DTC209B.
17	The DCB2 and DCB3 yields were adjusted to fit the concentration-time data for D([O_3]-[NO]) and and m-xylene in m-xylene - NOx - air runs CTC029, CTC035, CTC036, CTC094A, DTC193B, DTC192B, DTC206B, DTC295A, DTC188B, and DTC191B.
18	The DCB2 and DCB3 yields were adjusted to fit the concentration-time data for D([O_3]-[NO]) and p-xylene in p-xylene - NOx - air runs CTC041, CTC043, CTC044, CTC047, CTC070, DTC198A, DTC198B, and DTC199A.

No.	Note
19	Note that the apparent low photoreactive DCB yields from p-xylene and 1,2,4-trimethylbenzene can be attributed to the expected formation of diketone as well as dialdehyde products, where the diketones apparently do not photolyze as rapidly as dialdehydes.
20	The extent of reaction via abstraction from CH_3 groups is estimated from average rate constant per CH_3 group derived for toluene and the xylenes, which is 4.7 x 10^{-13} cm3 $molec^{-1}$ s^{-1}. The overall yields of organic nitrates and phenolic products are estimated to be comparable to those for the xylenes, and to be similar for all isomers.
21	The DCB2 and DCB3 yields were adjusted to fit the concentration-time data for D([O_3]-[NO]) and the reactant aromatic in the 1,2,3-trimethylbenzene - NOx - air runs CTC054, CTC075, CTC076, DTC211A, DTC211B, DTC212A, DTC212B, DTC213A, and DTC213B.
22	The DCB2 and DCB3 yields were adjusted to fit the concentration-time data for D([O_3]-[NO]) and the reactant aromatic in the 1,2,4-trimethylbenzene - NOx - air runs CTC056, CTC091B, CTC093A, CTC093B, DTC201A, DTC201B, DTC203A, DTC203B, DTC204A, and DTC204B.
23	The DCB2 and DCB3 yields were adjusted to fit the concentration-time data for D([O_3]-[NO]) and the reactant aromatic in the 1,3,5-trimethylbenzene - NOx - air runs CTC030, CTC050, CTC071, CTC073, DTC194A, DTC194B, DTC195A, DTC195B, DTC196A, DTC196B, and DTC206A.
24	The naphthalenes are assumed to have the same yield of phenol-like products as benzene. Abstraction from the methyl group in the methyl naphthalenes is assumed to be relatively unimportant. However, model simulations of naphthalene - NOx and 2,3-dimethyl naphthalene runs are best fit by assuming relatively high nitrate yields of 12% and 7%, respectively, though assuming 7% overall yields for both compounds gives satisfactory fits to the data. Note that the actual reactions that this "nitrate formation" parameterization represents may be something other than nitrate formation from peroxy + NO.
25	The glyoxal yield from the naphthalenes and tetralin is assumed to be approximately the same as the glyoxal yield from o-xylene.
26	Since the only difference between DCB2 and DCB3 is the action spectrum of the photolysis reaction and since the available naphthalene, 2,3-dimethyl naphthalene and tetralin chamber experiments were all carried out using the same light source, the data are not sufficient to determine the yield ratio for these products. Based on the optimization results for the alkylbenzenes, where the optimized DCB2/DCB3 yield ratios varied from 0 to 3 with an average of about 1, we assume that the best fit yields for these two should be roughly equal for the naphthalenes and tetralins.
27	Satisfactory fits to the chamber data could not be obtained unless it was assumed that the ring fragmentation process included substantial formation of a peroxynitrate precursor, which was represented by the model species RCO-O2., the precursor of PAN2. See text.
28	The yields of RCO-O2. and DCB2 + DCB3 were optimized to fit D([O3]-[NO]) data for the naphthalene - NOx runs ITC751, ITC755, ITC756, ITC798, and ITC802.
29	No chamber data are available to derive a best fit mechanism for this compound. All its mechanistic parameters were derived by averaging those estimated or optimized for naphthalene and 2,3-dimethylnaphthalene.
30	The yields of RCO-O2. DCB2 + DCB3 and MGLY were optimized to fit D([O3]-[NO]) and PAN data for the 2,3-DMN - NOx runs ITC771, ITC774, ITC775, and ITC806. Best fits were obtained when the yield of the PAN precursor species was ~0.8, but using a value of 0.6, which is more consistent with the expected upper limit for ring opening, gave similar results. The DCB1 yield calculated using Equation XXVIII was slightly negative, so a zero DCB1 yield is used.

No.	Note
31	Best fits to the chamber data are obtained if relatively high organic nitrate yields and high yields of phenol-like products are assumed. Higher nitrate yields could result if significant abstraction from -CH2- groups occurred, forming alkane-like peroxy radicals. It is also necessary to assume some formation of peroxynitrate precursors, represented by RCO-O2., to obtain satisfactory fits to the data, though the optimum yield for tetralin is less than derived for that for the naphthalenes. The total yield of phenol-like products was set at 0.6, which is reasonably consistent with the maximum value assuming that DCB, nitrate and peroxynitrate precursor formation account for the other pathways. The total alkyl nitrate yields, and yields of RCO-O2. and DCB2 + DCB3 from ring fragmentation were optimized to fit D([O3]-[NO]) data for the tetralin - NOx runs ITC739, ITC747, ITC748, ITC750, and ITC832.

1. Benzene

The glyoxal and phenol yields used were based on experimental data summarized by Atkinson (1997). Contrary to the previous version of the mechanisms (Carter, 1990; Carter et al, 1997a), the data are best fit if it is assumed that the uncharacterized ring fragmentation product does not photolyze to a significant extent. This change can be attributed to the fact that the photoreactivity of glyoxal is increased significantly in the present mechanism. This is based on results of modeling chamber studies of acetylene, where the reactivity of this compound could not be simulated unless significantly higher photoreactivity for glyoxal, its major photoreactive product, is assumed (Carter et al, 1997c; see also footnotes to Table A-2 in Table A-4). Therefore, only DCB1 is used to represent the uncharacterized fragmentation products from this compound.

Figure 10 shows plots of the $\Delta([O_3]-[NO])$ data for the benzene - NO_x experiments that were used for evaluating and deriving the mechanism for this compound. (See Section V for a summary of the model simulation methods and a more complete discussion of the evaluation results for all experiments used.) The results of model simulations using the assigned mechanism are also shown. It can be seen that the mechanism does not perform particularly well in simulating some of the data, tending to overpredict the rate of O_3 formation and NO oxidation in some of the xenon arc chamber runs and significantly underpredicting it in some of the blacklight chamber runs. However, no reasonable alternative parameterization that was examined resulted in a mechanism that better fit the data. Assuming any additional radical source from photolysis of uncharacterized products (or their reaction with O_3 for that matter) exacerbated the overprediction of the reactivity of the xenon arc chamber runs. Assuming higher radicals sources and countering them by increasing termination processes, such as using higher nitrate yield or assuming formation of products represented by PAN precursors (as found to improve simulations of data for the naphthalenes) did not solve the problem. Assuming alternative mechanisms such as formation of radicals that react with NO_2 also did not improve the fits.

More data are needed concerning the products formed in the photooxidation of benzene and their reactivities, including *direct* studies on the photoreactivity of glyoxal, before the uncertainties in the benzene photooxidation mechanism can be reduced. In addition, the possibility that there are experimental problems with some of the older ITC experiments, where the results appear to be inconsistent, cannot be ruled out. More comprehensive chamber data are needed to more unambiguously evaluate the mechanism for benzene. Although the model performs much better in simulating the data for the alkylbenzenes, and benzene is relatively unimportant in affecting atmospheric O_3 formation (because of its low reactivity and relatively low emissions amounts), the problems with the mechanism for what is presumably the simplest aromatic suggests fundamental problems with all aromatics mechanisms.

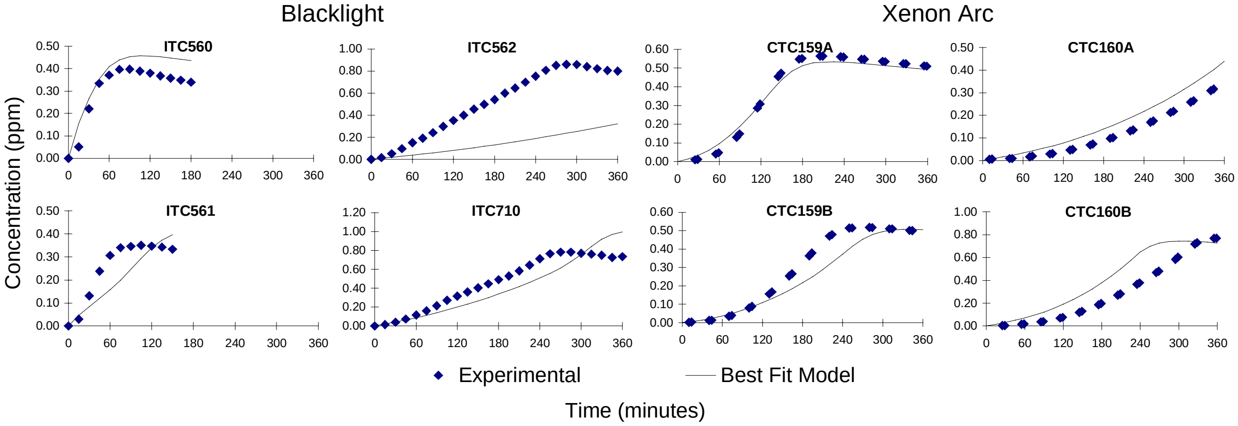

Figure 10. Plots of experimental and calculated $\Delta([O_3]-[NO])$ data for the experiments used to evaluate the benzene mechanism.

2. Methylbenzenes

The methylbenzenes (toluene, the xylenes and the trimethylbenzenes) are representative of the most important class of aromatic hydrocarbons in terms of both emissions and reactivity, and for that reason have the most extensive database of environmental chamber experiments for mechanism evaluation, as well information concerning yields of known products. The yields of phenolic products, benzaldehyde or tolualdehydes, and the α-dicarbonyls are based on experimental data summarized by Atkinson (1994). Averages of the reported data were used in those cases where more than one measurement is listed, though in some cases, measurements that appeared to fall outside the distribution of data from other studies were not used when computing the averages. The nitrate yields are somewhat uncertain, but they appear to be relatively low and not highly important in affecting alkylbenzene reactivity.

As discussed above, the yields of model species DCB2 and DCB3, used to represent the uncharacterized photoreactive products, were optimized to fit the chamber data (see the footnotes to Table 42 in Table 43 for the specific data used). As discussed previously (Carter et al, 1997a) it is necessary to assume varying action spectra to fit the data in chambers with different light sources, requiring, and data from chambers with both blacklight and xenon arc light source are needed to determine their yields. Such data are available for all the methylbenzenes through the trimethylbenzenes, permitting their mechanisms to be optimized.

In contrast with benzene, the adjusted mechanism generally performs reasonably well in simulating the available chamber data, with no large or consistent differences in model performance in chambers with differing light sources. The performance of the model in simulating the individual alkylbenzene - NO_x chamber experiments is similar to that observed with previous versions of the mechanism (Carter et al, 1997a) and is presented in Section V.

3. Ethylbenzene

The mechanism for ethylbenzene is important because it is used as a surrogate (or surrogate species) for all the higher monoalkylbenzenes, such as propylbenzene or cumene. No product data for this compound is given by Atkinson (1994), and thus yields of all products had to be estimated. It is estimated that OH abstraction from the side group is more important than in the case of methylbenzenes because of the more reactive -CH_2- group, as indicated in the footnotes to Table 42 in Table 43. Other than that, the phenolic and α-dicarbonyl products are estimated based on those for toluene, reduced by the appropriate factor to correspond to the relatively lower fraction of reaction by OH addition to the aromatic ring.

As with the methylbenzenes, the DCB2 and DCB3 yields were adjusted to optimize the fit of model calculation to the chamber data, which also included experiments with both blacklight and xenon arc light sources. The model fit the data reasonably well (see Section V), performing comparably as the model for the methyl benzenes. However, it is interesting to note that the best fit DCB2 yield for ethylbenzene is zero, while the yield for toluene is relatively high, being larger than that for DCB3 (see Table 42). On the other hand, the DCB3 yields for ethylbenzene and toluene are not greatly different. There is no obvious explanation for the large difference in DCB2 yields, which will have a significant effect on predicted reactivity, and suggests that estimates of comparable reactivity for aromatics with "comparable" structure may not always be reliable.

4. Naphthalenes and Tetralin

Relatively little is known about the details of the atmospheric reactions of naphthalenes and tetralins, except that appears that there are probably significant differences between the mechanisms for the alkylbenzenes and the naphthalenes (e.g., Atkinson, 1999, and references therein). The limited environmental chamber data for these compounds indicate that the naphthalenes and tetralin are considerably less reactive than the alkylbenzenes, despite their relatively high OH rate constants (Carter et al, 1981, 1987). Therefore, it is not appropriate to represent the naphthalenes and tetralins using general aromatic model species, and separate mechanisms are necessary to appropriately predict the reactivities of these compounds.

There was insufficient time and resources in this project to evaluate all available data for the naphthalenes (or tetralins) to determine the most appropriate parameterization for their mechanisms, so the parameterization used for the alkylbenzenes was used as the starting point. The yields of the phenolic products, organic nitrates, and α-dicarbonyls were very approximately estimated as discussed in the footnotes to Table 42 in Table 43, and optimizations were carried out to determine the best fit DCB2 + DCB3 yields. Because naphthalene and tetralin environmental chamber data are only available with a blacklight light source, it was not possible to separately optimize both products, so their yields were assumed to be the same (see footnotes to the table).

Although adjusting DCB2 and DCB3 yields was found to be sufficient to fit the chamber data for the alkylbenzene runs, this was found not to be the case when attempting to fit the mechanism to the data for the naphthalenes and tetralins. This is shown, for example, on Figure 11, which shows experimental and calculated $\Delta([O_3]-[NO])$ data for the naphthalene experiments. The calculated lines labeled "Optimize $y_{D2}=y_{D3}$" show the results of optimizing the photoreactive DCB yields only, using the initial estimates for the other parameters. It can be seen that the O_3 formation and NO oxidation rates in some runs are overpredicted and some are underpredicted, depending on the initial reactant concentrations. The results for 2,3-dimethyl naphthalene and tetralin are similar. In an attempt to improve the fits, a second set of optimizations were carried out where the nitrate yields, y_{NR}, were optimized along with the photoreactive DCB yields. This also did not result in acceptable fits to the data, as shown on the curves labeled "Optimize $y_{D2}=y_{D3}$, y_{NR}" on Figure 11. Reparameterizing mechanism to represent the possible formation of radicals that react with NO_2 to form termination products (such as phenoxy) and adjusting the yields of those radicals along with the photoreactive DCB yields gives similar results as adjusting the nitrate yields. Using alternative parameterizations where the product yields depend on the absolute NO_2 concentration

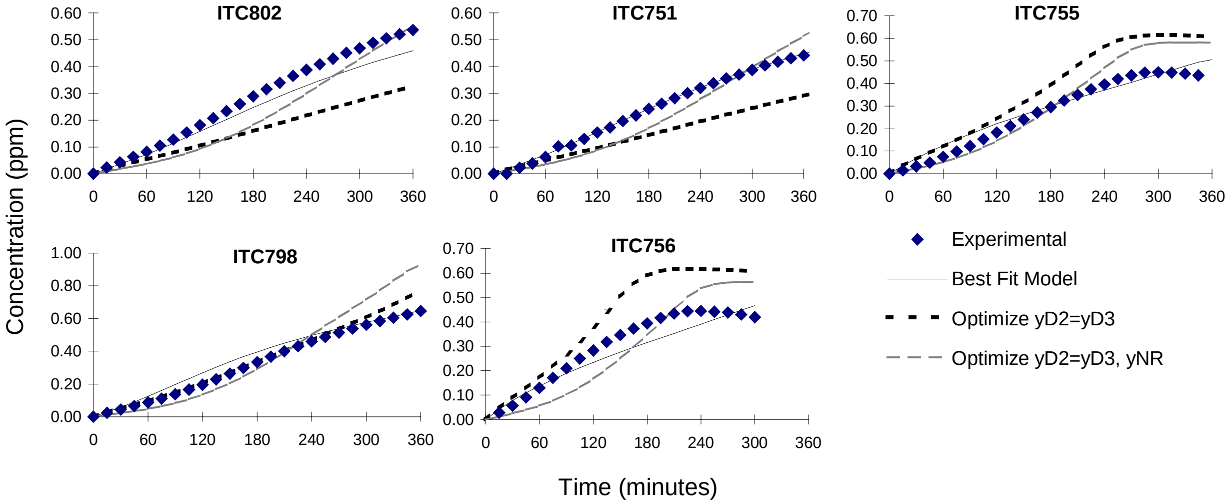

Figure 11. Plots of experimental and calculated $\Delta([O_3]-[NO])$ data for the naphthalene - NO_x used to derive the naphthalene mechanism.

(as would occur if radicals which react with both NO_2 and O_2 were involved) also did not yield acceptable fits to the data.

Improved fits of the parameterized model to the naphthalene, dimethylnaphthalene, and tetralin data were only obtained when it was assumed that the reactions involved the formation of radicals that in a manner to PAN precursors, which were represented in the model by RCO-O2·. The simulations of the naphthalene experiments using the best fit mechanism with the optimized PAN precursor and photoreactive DCB yields given on Table 42 are shown on Figure 11, where it can be seen that reasonably good performance in simulating the data is obtained. The results are similar for 2,3-dimethylnaphthalene and tetralin. However, in the case of 2,3-dimethylnaphthalene the yields of MGLY were also adjusted to optimize fits to the PAN data for these experiments, while for tetralin it was found that it was necessary also to adjust the overall nitrate yield for the model to satisfactorily simulate the data. The higher apparent nitrate yields in the case of tetralin could be due to reactions of radicals formed from OH abstractions from the non-aromatic ring.

These parameterized mechanisms for the naphthalenes and tetralin are clearly highly uncertain. Since the only currently available chamber data came from using a blacklight light source, the mechanism may not be correctly predicting the reactivity contributions of the photoreactive products in sunlight, where the spectrum is more similar to the xenon arc light sources. Perhaps more significantly, if the parameterization employed correspond reasonably well to the underlying chemistry of these compounds, the model may not be correctly extrapolating from the conditions of these experiments to the conditions of the atmosphere. However, these mechanisms represent our current best estimates at the present time.

5. Estimated Mechanisms for Other Aromatics

Table 8, above, shows that there are several other aromatic compounds whose OH rate constants are known, but for which no environmental chamber data are available for deriving mechanistic product yield parameters. These compounds are represented in the mechanism with model species using the appropriate measured rate constant, with but product yield parameters that are estimated based on those for most structurally similar compound(s) whose parameters are given in Table 42. These are as follows:

- Chlorobenzene (CL-BEN), dichlorobenzene (CL2-BEN) and nitrobenzene (NO2-BENZ) are assumed to have the same product yield parameters as derived for benzene.
- Parachlorobenzyltrifluoride (PCBTF) and trifluromethyl benzene (CF3-BEN) are assumed to have the same product yield parameters as derived for toluene.
- Isopropyl benzene (I-C3-BEN), n-propyl benzene (N-C3-BEN) and s-butyl benzene (S-C4-BEN) are assumed to have the same product yield parameters as derived for ethylbenzene.
- Monomethylnaphthalene (ME-NAPH) is assumed to have parameters that are averages of the corresponding parameters for naphthalene and 2,3-dimethylnaphthalene. The parameters so derived are shown on Table 42.

Obviously these estimates are uncertain, especially in view of the differences for the parameters for toluene and ethylbenzene, as discussed above. However, these provide the best available estimates concerning the mechanisms for these compounds, and at least incorporate their known OH rate constants. In this respect, their representation is presumed to be somewhat less uncertain than those aromatics that are not incorporated in the mechanism, but are represented by other aromatics using the “lumped molecule” approach (see Table C-1 in Appendix C).

B. Representation of Other Compounds

Table 44 shows the representation used for the reactions of the other compounds or classes of compounds that are incorporated in the present mechanism and that do not fall into the categories discussed above. The assignments for the various types of compounds are discussed in more detail below.

1. Terpenes

Terpenes are bicyclic alkenes or dialkenes or cyclic alkenes, and as such their reactions cannot be processed by the current mechanism generation system. The rate constants for their initial reactions are given above in Table 8 (for OH radicals), Table 13 (for NO_3 radicals) Table 16 (for O_3) and Table 22 (for O^3P atoms). Although some product data are available for their reactions with OH radicals and O_3 (see Atkinson, 1997a), the available information is not sufficient to completely determine their mechanisms. Their representation is therefore estimated based on simplified or parameterized mechanisms, or using mechanisms generated for similar monocyclic, monoalkene structures.

The terpenes whose reactions are represented in this mechanism are α- and β-pinenes, Δ^3-carene, d-limonene, and sabinene, the only terpenes for which environmental chamber data are available. The mechanisms used for these compounds, given in terms of model species in the base mechanism, are given in Table 44. The considerations used when deriving mechanisms for the terpenes are discussed below. The performance of these mechanisms in simulating the chamber data for these compounds is summarized in Section V.

Reaction with OH radicals. In the case of the reaction with OH radicals, the simplest mechanism would involve OH adding to the double bond, forming a β-hydroxy radical which will react with O_2 to form the corresponding peroxy radical, which reacts with NO to form either the corresponding nitrate or alkoxy radical, and where the alkoxy radical can react in various ways, including decomposing to ultimately forming HO_2 and carbonyl compounds.

Table 44 Assigned mechanisms for terpenes and other non-aromatic compounds or groups of compounds that are not processed using the mechanism generation system.

Compound	Kinetic Parameters [a,b]			Reaction [c]
	A	Ea	B	Reaction
				Assigned Mechanisms
α-Pinene	1.21e-11	-0.882		A-PINENE + HO. = #.75 RO2-R. + #.25 RO2-N. + #.5 R2O2. + #.75 RCHO + #6.5 XC
	1.01e-15	1.455		A-PINENE + O3 = #.7 HO. + #.081 RO2-R. + #.321 RO2-N. + #1.375 R2O2. + #.298 RCO-O2. + #.051 CO + #.339 HCHO + #.218 RCHO + #.345 ACET + #.002 GLY + #.081 BACL + #.3 RCO-OH + #3.875 XC
	1.19e-12	-0.974		A-PINENE + NO3 = #.75 NO2 + #.25 RO2-N. + #.75 R2O2. + #.75 RCHO + #6.25 XC + #.25 XN
	3.20e-11			A-PINENE + O3P = PROD2 + #4 XC
β-Pinene	2.38e-11	-0.709		B-PINENE + HO. = #.75 RO2-R. + #.25 RO2-N. + #.5 R2O2. + #.75 HCHO + #.75 PROD2 + #3.25 XC
	1.01e-15	2.493		B-PINENE + O3 = #.34 HO. + #.09 HO2. + #.05 RO2-N. + #.2 R2O2. + #.2 RCO-O2. + #.375 CO + #.1 CO2 + #.25 HCHO + #.75 PROD2 + #.28 HCOOH + #3.595 XC
	2.51e-12			B-PINENE + NO3 = #.75 RO2-R. + #.25 RO2-N. + #.75 R2O2. + #.75 RNO3 + #4 XC + #.25 XN
	2.70e-11			B-PINENE + O3P = #.4 RCHO + #.6 PROD2 + #5.2 XC
Δ^3 Carene	1.64e-11	-0.994		3-CARENE + HO. = #.75 RO2-R. + #.25 RO2-N. + #.5 R2O2. + #.75 RCHO + #6.25 XC
	1.01e-15	1.958		3-CARENE + O3 = #.7 HO. + #.161 RO2-N. + #.539 R2O2. + #.482 CCO-O2. + #.058 RCO-O2. + #.058 HCHO + #.482 RCHO + #.3 RCO-OH + #5.492 XC
	9.10e-12			3-CARENE + NO3 = #.75 NO2 + #.25 RO2-N. + #.75 R2O2. + #.75 RCHO + #6.25 XC + #.25 XN
	3.20e-11			3-CARENE + O3P = PROD2 + #4 XC
Sabinene	2.19e-11	-0.994		SABINENE + HO. = #.75 RO2-R. + #.25 RO2-N. + #.5 R2O2. + #.75 HCHO + #.75 PROD2 + #3.25 XC
	1.01e-15	1.459		SABINENE + O3 = #.34 HO. + #.09 HO2. + #.05 RO2-N. + #.2 R2O2. + #.2 RCO-O2. + #.375 CO + #.1 CO2 + #.25 HCHO + #.75 PROD2 + #.28 HCOOH + #3.595 XC
	1.00e-11			SABINENE + NO3 = #.75 RO2-R. + #.25 RO2-N. + #.75 R2O2. + #.75 RNO3 + #4 XC + #.25 XN
	1.69e-11			SABINENE + O3P = #.4 RCHO + #.6 PROD2 + #5.2 XC
D-Limonene	3.19e-11	-0.994		D-LIMONE + HO. = #.75 RO2-R. + #.25 RO2-N. + #.5 R2O2. + #.75 RCHO + #6.25 XC
	3.71e-15	1.729		D-LIMONE + O3 = #.7 HO. + #.161 RO2-N. + #.539 R2O2. + #.482 CCO-O2. + #.058 RCO-O2. + #.058 HCHO + #.482 RCHO + #.3 RCO-OH + #5.492 XC
	1.22e-11			D-LIMONE + NO3 = #.75 NO2 + #.25 RO2-N. + #.75 R2O2. + #.75 RCHO + #6.25 XC + #.25 XN
	7.20e-11			D-LIMONE + O3P = PROD2 + #4 XC

Table 44 (continued)

Compound	Kinetic Parameters [a,b]			Reaction [c]
	A	Ea	B	Reaction
Styrene	5.80e-11			STYRENE + HO. = #.87 RO2-R. + #.13 RO2-N. + #.87 HCHO + #.87 BALD + #.26 XC
	1.71e-17			STYRENE + O3 = #.4 HCHO + #.6 BALD + #.6 HCOOH + #.4 RCO-OH + #1.6 XC
	1.51e-13			STYRENE + NO3 = #.22 NO2 + #.65 RO2-R. + #.13 RO2-N. + #.22 R2O2. + #.22 HCHO + #.22 BALD + #.65 RNO3 + #1.56 XC + #.13 XN
	1.76e-11			STYRENE + O3P = PROD2 + #2 XC
N-Methyl-2-Pyrrolidone	2.15e-11			NMP + HO. = #.92 HO2. + #.08 RO2-N. + #.46 RCHO + #.46 PROD2 + #.38 XC + XN
	1.26e-13			NMP + NO3 = #.92 HO2. + #.08 RO2-N. + HNO3 + #.92 PROD2 + #-1 XC + XN
				Adjusted Parameterized Mechanisms
Toluene Diisocyanate	7.40e-12			TDI + HO. = #.5 HO. + CRES
Para Toluene Isocyanate	5.90e-12			P-TI + HO. = #.2 HO. + #.7 HO2. + #.15 MGLY + CRES
Diphenylene Diisocyanate	1.18e-11			MDI + HO. = #.2 HO. + #.7 HO2. + #.15 MGLY + CRES
				"Placeholder" Mechanisms for Approximate Estimates [c]
Trichloro-ethylene	5.63e-13	-0.849		CL3-ETHE + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
n-Propyl Bromide	1.18e-12			C3-BR + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
n-Butyl Bromide	2.46e-12			C4-BR + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
Methyl Chloride	3.15e-13	1.163	2	CH3-CL + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
Dichloro-methane	7.69e-13	0.994	2	CL2-ME + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
Methyl Bromide	2.34e-13	1.035	2	ME-BR + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
Chloroform	5.67e-13	1.002	2	CHCL3 + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
Ethyl Chloride	6.94e-13	0.302	2	C2-CL + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
1,2-Dichloro-ethane	9.90e-13	0.813	2	12CL2-C2 + HO. = RO2-R. + #.5 HCHO + #.5 RCHO

Table 44 (continued)

Compound	Kinetic Parameters [a,b]			Reaction [c]
	A	Ea	B	Reaction
1,1-Dichloroethane	2.60e-13			11CL2-C2 + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
1,1,2-Trichloroethane	4.00e-13	0.413	2	112CL3C2 + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
1,1,1-Trichloroethane	5.33e-13	2.244	2	111-TCE + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
Ethyl Bromide	2.72e-11	2.671		C2-BR + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
1,2-Dibromoethane	9.27e-13	0.839	2	11BR2-C2 + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
Vinyl Chloride	1.69e-12	-0.839		CL-ETHE + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
t-1,2-Dichloroethene	1.01e-12	-0.497		T-12-DCE + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
Perchloroethylene	9.64e-12	2.403		CL4-ETHE + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
Ethyl Amine	1.47e-11	-0.376		ET-AMINE + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
Dimethyl Amine	2.89e-11	-0.491		DM-AMINE + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
Trimethyl Amine	2.62e-11	-0.501		TM-AMINE + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
Ethanolamine	3.15e-11			ETOH-NH2 + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
Diethanol Amine	9.37e-11			ETOH2-NH + HO. = #.96 RO2-R. + #.04 RO2-N. + #.5 HCHO + #.5 RCHO
Triethanolamine	1.16e-10			ETOH3-N + HO. = #.905 RO2-R. + #.095 RO2-N. + #.5 HCHO + #.5 RCHO

[a] Rate constant given by A exp(-Ea/RT) $(T/300)^B$, where the rate constant and A factor are in cm^3 $molec^{-1}$ s^{-1} and the

[b] See Table 8 for the derivation of the OH radical rate constants used.

[c] See text for a discussion of how the mechanisms were derived.

[d] These mechanisms are for approximate estimates only, and are based on assuming formation of relatively reactive

$$\text{Terpene} + \text{OH} \rightarrow \text{>C}(\cdot)\text{-C(OH)<}$$

$$\text{>C}(\cdot)\text{-C(OH)<} + O_2 \rightarrow \text{>C(OO}\cdot\text{)-C(OH)<}$$

$$\text{>C(OO}\cdot\text{)-C(OH)<} + \text{NO} \rightarrow \text{>C(ONO}_2\text{)-C(OH)<}$$

$$\text{>C(OO}\cdot\text{)-C(OH)<} + \text{NO} \rightarrow NO_2 + \text{>C(O}\cdot\text{)-C(OH)<}$$

$$\text{>C(O}\cdot\text{)-C(OH)<} \rightarrow \text{>C=O} + \text{-C}(\cdot)\text{(OH)-}$$

$$\text{-C}(\cdot)\text{(OH)-} + O_2 \rightarrow HO_2 + \text{>C=O}$$

$$\text{>C(O}\cdot\text{)-C(OH)<} \rightarrow \text{other radicals (additional NO to NO}_2\text{ conversions)}$$

If the decomposition involves breaking what was the double bond to form an α-hydroxy radical, which is the dominant process for most of the simpler alkenes, then no additional NO to NO_2 conversions would be involved. However, additional NO to NO_2 conversions may occur if other decompositions can compete, which are estimated to be non-negligible for compounds with similar structures as the terpenes. If the reacting double bond is in the ring, the carbonyl products would be expected to be bifunctional compounds with at least one aldehyde group, which is represented in the model by the RCHO model species. If the reacting double bond is a $=CH_2$ group outside the ring, then the products would be formaldehyde + a ketone, the latter represented by PROD2 in the model.

Therefore, for compounds with the double bond in the ring, such as α-pinene, Δ^3-carene, and d-limonene, the following parameterized mechanism is employed:

$$\text{OH} + \text{Terpene(ring d.bond)} \rightarrow y_N\ \text{RO2-N}\cdot + (1\text{-}y_N)\ \{\text{RO2-R}\cdot + \text{RCHO}\} + y_{R2O2}\ \text{R2O2}\cdot$$

where the nitrate yield, y_N, and the amount of extra NO to NO_2 conversions, y_{R2O2}, are determined based on model simulations of the available terpene - NO_x chamber data. For compounds with $=CH_2$ groups, such as β-pinene and sabinene, the parameterized mechanism is

$$\text{OH} + \text{Terpene}(=CH_2) \rightarrow y_N\ \text{RO2-N}\cdot + (1\text{-}y_N)\ \{\text{RO2-R}\cdot + \text{HCHO} + \text{PROD2}\} + y_{R2O2}\ \text{R2O2}\cdot$$

Best fits to most of the chamber data are obtained using $y_N = 0.25$ and $y_{R2O2} = 0.5$, and as indicated on Table 44 this is assumed for all the terpenes.

Reaction with O_3 The Crigiee biradicals expected to be formed in the reactions of O_3 with α-pinene, Δ^3-carene and d-limonene could all be represented in the mechanism generation system, so the overall O_3 reactions could be generated in the same way as used for the other alkenes, if the mechanism for the initial reaction is assigned. This is the approach used for these compounds. All three of these compounds have trisubstituted double bond in the ring, and as discussed above in Section III.E.3, it is assumed that the formation of -CO- + -CHOO[excited] and -CHO + -COO[excited]- occur respectively 30% and 70% of the time, based on ketone yields from acyclic trisubstituted alkenes. Although d-limonene has a second double bond outside the ring, it is assumed that most of the reaction occurs at the more substituted bond in the ring, and reactions at the second double bond is ignored when estimating the overall mechanism. Note that this procedure results in predicted OH yields of 70% for these compounds, which is reasonably close to the experimentally-determined values of 0.76-0.85 for α-pinene and 86% for d-limonene (Atkinson, 1997b). The overall processes generated in this way are shown in Table 44.

The mechanism generation system cannot be used as readily to estimate the reactions of O_3 with β-pinene and sabinene, since reaction to form formaldehyde + a Crigiee biradical with a bicyclic structure is expected to be formed to a non-negligible extent. However, the expected overall reactions of these biradicals are not expected to differ greatly with the structure, at least in terms of model species in the base mechanism. This is expected to be as follows,

ring-COO[excited]-ring $\rightarrow$ ring-C=C(OOH)-ring $\rightarrow$ OH + ring-C(·)-CO-ring
ring-C(·)-CO-ring + O_2 $\rightarrow$ ring-C(OO·)-CO-ring
ring-C(OO·)-CO-ring + NO $\rightarrow$ 0.2 ring-C(ONO_2)-ring + 0.8 ring-C(O·)-CO-ring
ring-C(O·)-CO-ring $\rightarrow$ -CO-chain-CO·

where the 20% nitrate yield is the value derived by the mechanism generation system for a substituted C_9 peroxy radical, such as expected to be formed in this case. Therefore, in terms of model species in the base mechanism, reaction of the terpene with O_3 to form this biradical yields the following overall process:

O_3 + Terpene(=CH_2) $\rightarrow$ HCHO + OH + 0.2 RO2-N· + 0.8 {R2O2· + RCO-O2·} (A)

Of course, part of the time the reaction would also involve formation of the cyclic ketone + HCHO2[excited], whose subsequent reactions are as discussed above. In this case, the overall process is

O_3 + Terpene(=CH_2) $\rightarrow$ PROD2 + 0.12 HO2 + 0.12 OH + 0.5 CO + 0.13 CO2 + 0.37 HCOOH (B)

The branching ratio for these two routes is derived based on assuming an overall OH yield of ~35%, which is the measured value for β-pinene and close to the measured values of 26% and 33% for sabinene (Atkinson, 1997a and references therein). This is predicted if Pathways (A) and (B) are assumed to occur respectively 25% and 75% of the time, which gives the following overall process:

O_3 + Terpene(=CH_2) $\rightarrow$ 0.25 HCHO + 0.75 PROD2 + 0.34 OH + 0.05 RO2-N· + 0.2 R2O2·
+ 0.2 RCO-O2· + 0.09 HO2. + 0.375 CO + 0.1 CO2 + 0.28 HCOOH

Note, however, that assuming ~75% ketone + HCHO2[excited] formation is not consistent with the observed yields of only 22-23% nopinone from β-pinene and 50% ketone from sabinene (Atkinson, 1997a, and references therein), so this is clearly an oversimplification of the actual mechanisms for these terpenes.

Reaction with NO_3 Radicals. The mechanisms for the terpene + NO_3 reactions are represented in a manner similar to that used for the OH reactions as discussed above, being based on assuming the following set of reactions:

Terpene + NO_3 $\rightarrow$ >C(·)-C(ONO_2)<
>C(·)-C(ONO_2)< + O_2 $\rightarrow$ >C(OO·)-C(ONO_2)<
>C(OO·)-C(ONO_2)< + NO $\rightarrow$ >C(ONO_2)-C(ONO_2)<
>C(OO·)-C(ONO_2)< + NO $\rightarrow$ NO_2 + >C(O·)-C(ONO_2)<
>C(O·)-C(ONO_2)< $\rightarrow$ >C=O + -C(·)(ONO_2)-
-C(·)(ONO_2)- $\rightarrow$ >C=O + NO_2

The alkoxy radical estimation methods discussed above predict that the >C(O·)-C(ONO_2)< radicals of the types formed in these reactions should primarily decompose, so the possible competing reactions are not considered. As with the OH reaction, the carbonyls formed would either be a bifunctional aldehyde (represented by the RCHO model species) in the case of terpenes with double bonds in the ring, or formaldehyde + a ketone (represented by PROD2) in the case of terpenes with =CH_2 groups. If a the same overall nitrate yield is assumed as is used in the OH reaction (~25%), then the overall process is:

$$NO_3 + \text{Terpene(ring d.bond)} \rightarrow 0.25\ \{RO2\text{-}N\cdot + XN\} + 0.75\ \{RCHO + R2O2\cdot + NO2\}$$

for terpenes with the double bond in the ring, and

$$NO_3 + \text{Terpene}(=CH_2) \rightarrow 0.25\ \{RO2\text{-}N\cdot + XN\} + 0.75\ \{HCHO + PROD2 + R2O2\cdot + NO2\}$$

for terpenes with $=CH_2$ groups.

Reaction with O^3P. As discussed above in Section III.F.3, it is assumed that the reactions of O^3P with the higher alkenes involve formation of ~60% of the corresponding oxide, and ~40% formation of a carbonyl compound. The oxide formed in the reactions of O^3P with the terpenes are represented by the PROD2 model species For terpenes with the double bond in the ring, the carbonyl product is expected to be primarily a ketone, which is also represented in the model by PROD2, while if the terpene has a $=CH_2$ group, the predicted product is an aldehyde, whose formation is represented by RCHO. Thus, the overall reactions are

$$O^3P + \text{Terpene(ring d.bond)} \rightarrow PROD2$$

for terpenes with the double bond in the ring, and

$$O^3P + \text{Terpene}(=CH_2) \rightarrow 0.6\ PROD2 + 0.4\ RCHO$$

for terpenes with $=CH_2$ groups.

2. Styrene

The mechanism used for the reactions of styrene is based on that derived by Carter et al (1999c) based on environmental chamber experiments employing that compound. Note that to fit the environmental chamber reactivity data it is necessary to assume that essentially no radical formation occurs in the O_3 reaction. The only modification to the mechanism of Carter et al (1999c) is that the nitrate yield for the OH reaction was increased from 10% to 13% to reduce biases in the model simulations of the mini-surrogate incremental reactivity experiments. The nitrate yield in the NO_3 reaction was also increased from 10% to 13%, since it is assumed to be the same in the OH reaction.

3. N-Methyl-2-Pyrrolidone

The mechanism for the reactions of N-methyl-2-pyrrolidone (NMP) is based on that derived by Carter et al (1996c), based on environmental chamber experiments employing that compound. The main differences are that the products 1-formyl-2-pyrrolidinone and N-methyl succimide were represented by PROD2 and RCHO, respectively, rather than by separate model species with parameterized mechanisms. In addition, the nitrate yields used in the mechanism had to be reduced from 15% to 8% for the model to give reasonably good simulations of the data. The fits of the model simulations to the chamber data are given in Appendix B (see also Section V).

4. Aromatic Isocyanates

Environmental chamber reactivity experiments have been carried out for toluene diisocyanate (TDI) (Carter et al, 1997i) and para-toluene isocyanate (P-TI) (Carter et al, 1999g), allowing simplified parameterized mechanisms for these compounds to be developed. Based on the P-TI mechanism, a simplified estimated mechanism for the structurally similar (and commercially more important) compound methylene diphenylene diisocyanate (MDI) was also derived (Carter et al, 1999g). Although the details of the atmospheric reactions of these compounds are unknown, highly simplified mechanisms, such as those shown on Table 44, were shown to simulate the data reasonably well (Carter et al, 1997i, 1999g).

These parameterized aromatic isocyanate mechanisms were incorporated in the updated mechanism and reoptimized to fit the chamber data. In the case of TDI, the OH yield in had to be increased from 0.3 to 0.6 in order to simulate the data approximately as well as the mechanism reported by Carter et al (1997i). In other words, with the updated base mechanism the chamber data are fit with a parameterized model with considerably less radical termination than the model used with the SAPRC-97 mechanism. In the case of P-TI, the extent of radical termination (which in any case is considerably less than for TDI) did not have to be readjusted, but the yield of product compounds represented by methyl glyoxal was reduced from 0.3 to 0.15. The reoptimized mechanisms are shown on Table 44, along with the estimated MDI mechanism, which was derived from the P-TI mechanism as discussed by Carter et al (1999g).

5. Halogenated Compounds

Although we have previously carried out experimental studies of the ozone reactivities of chloropicrin (CCl_3ONO_2) (Carter et al, 1997h), n-propyl and n-butyl bromides (Carter et al, 1997d) and trichloroethylene (Carter et al, 1996d), and developed mechanisms for those compounds that were evaluated using the data obtained, satisfactory fits of the model to chamber data were obtained only for chloropicrin. In particular, no reasonable adjustments of uncertain portions of the mechanisms would result in satisfactory fits to the data for the alkyl bromides (Carter et al, 1997d) or trichloroethylene (Carter et al, 1996d), especially after the times in the experiment when O_3 formation began. Additional data are needed, with chemically simpler systems, before mechanisms can be developed that can reliably predict ozone impacts of halogenated compounds.

Because the explicit mechanisms with the ClO_x or BrO_x chemistry did not adequately fit the data for two of the three compounds studied, it was decided that our knowledge of these systems is not sufficient to include this chemistry in the base mechanism. Instead, a highly simplified and parameterized “placeholder” mechanism is used in the current mechanism to provide very rough estimates of the approximate range of reactivities of halogenated compounds under MIR conditions, given their OH radical rate constants. This parameterized mechanism, which is shown on Table 44, is based on the assumption that the overall reactions involve at least one NO to NO_2 conversion, form relatively reactive products (which are represented by formaldehyde and the lumped higher aldehyde), and do not involve any significant radical termination processes such as nitrate formation. The appropriate OH rate constant for the compound, given on Table 8, is used in conjunction with the placeholder mechanism given on Table 44.

Note that this mechanism is not appropriate for chloropicrin because it does not represent VOCs that are photoreactive. The reactions of chloropicrin are not represented in the current version of the mechanism, since the necessary ClO_x chemistry has not yet been incorporated in the base mechanism.

The performance of the placeholder mechanisms in simulating the reactivities of the two other halogenated compounds that were studied was evaluated by simulating the results of the incremental reactivity experiments. The results, which are given in Appendix B (see also Section V), indicate that the simplified mechanism performs remarkably well in simulating the experiments with trichloroethylene, especially in the higher NO_x experiments that are more representative of MIR conditions. The simulations of the higher NO_x reactivity experiments with the alkyl bromides were variable, with some experiments being reasonably well simulated, and others with the O_3 reactivity being overestimated by about a factor of 1.5-2. The parameterized mechanism performed very poorly in simulating the reactivities of these compounds under low NO_x conditions, with the model predicting they enhance O_3 in all cases, while O_3 was not enhanced in the low NO_x trichloroethylene runs, and inhibited in the low NO_x runs with the bromides.

Based on the results of this evaluation with a very limited number of compounds, it is possible that the parameterized mechanism may give at least rough estimates of reactivities under MIR (i.e., relatively high NO_x) conditions, but would likely significantly overestimate ozone impacts of such compounds under low NO_x conditions, where many may actually be O_3 inhibitors. Appropriately representing reactivities of these compounds under low NO_x conditions would require incorporating ClO_x or BrO_x reactions into the mechanism, and a better understanding of how they interact with the VOCs and NO_x species under ambient conditions, as well as how they interact with the chamber walls.

6. Amines

There are a number of amines and alcohol amines in the emissions inventories, and an ability to estimate at least their approximate ranges of reactivities, at least under MIR conditions, would be desirable. However, there is insufficient information available to derive or estimate atmospheric reaction mechanisms for amines, and no environmental chamber data available that are suitable for deriving parameterized mechanisms. For that reason, no attempt was made to derive or estimate mechanisms for these compounds. Instead, as with halogenated compounds, simplified and parameterized “placeholder” mechanisms were used for this purpose. These are given on Table 44. As with the amines, the placeholder mechanisms are based on the assumption that there is at least one NO to NO_2 conversion, that relatively reactive products, represented by formaldehyde and the lumped higher aldehyde, are formed, and that no significant radical termination occurs for C_1-C_3 compounds. For the higher molecular weight alcohol amines, the nitrate yield is estimated based on that for a substituted, non-secondary peroxy radical with the same number of carbons (see Section III.I).

Since it assumes relatively reactive products and no inhibition other than the expected nitrate formation for the higher molecular weight compounds, the mechanism may be biased towards overpredicting the reactivities of these compounds. However, until more data are available this cannot be adequately assessed. In any case, reactivities estimated using these mechanisms must be considered to be highly uncertain.

C. Unrepresented Compounds

Although Table 8 includes OH radical rate constants for the atmospheric reactions of representatives of other classes of organic compounds, including several sulfur- and silicon-containing compounds, these are not represented in the current version of the mechanism. With the exception of several volatile siloxanes (Carter et al, 1992), which were shown to be ozone inhibitors under all conditions, there is insufficient information available to develop or evaluate mechanisms for these compounds. Although highly approximate estimated mechanisms could be developed in some cases, there was insufficient time and resources available to carry this out for this version of the mechanism.

V. MECHANISM EVALUATION

The base mechanism and the mechanisms for the individual VOCs were evaluated by comparing results of model simulations of with results of primarily indoor environmental chamber experiments carried out at the University of California at Riverside. These include not only experiments from the large data base of UCR chamber experiments through 1993 (Carter et al, 1995d), but also the large number of experiments carried out subsequently at CE-CERT. These include the experiments used in the development and evaluation of the SAPRC-97 mechanism (Carter et al, 1997a), and reactivity studies of a wide variety of individual VOCs (Carter et al, 1996a-d, 1997b-g,i, 1999b-g), and studies of representative consumer product VOCs (Carter et al, 1999a). The experiments used in the evaluation, and references to the reports documenting the experiments, are summarized on Table B-1 in Appendix B. These consisted of the following:

- 76 characterization runs, including 3 pure air runs, 8 acetaldehyde - air runs to determine NO_x offgasing effects, and 65 CO - NO_x or n-butane - NO_x experiments to measure the chamber radical source.
- 484 single VOC runs involving 37 types of VOCs.
- 447 incremental reactivity experiments involving 84 types of VOCs or mineral spirits samples. These experiments consisted of determining the effect of adding the VOC or sample to a “base case” reactive organic gas (ROG) - NO_x “surrogate” mixture simulating ambient mixtures. The types of incremental reactivity experiments used in this evaluation, and the codes used to identify them in the tables and figures in Appendix B, are indicated on Table 45.
- 477 mixture runs involving various types of simple or complex mixtures or ambient ROG surrogates. Most of these (561 runs) were "base case" surrogate - NO_x runs carried out in conjunction with the incremental reactivity experiments. The types of mixtures or surrogates employed, and the codes used to identify them in Appendix B, are indicated on Table 45.

The environmental chambers used to generate the data used in this evaluation are summarized on Table 46. Note that a two- or three-letter code is used to designate each chamber. The individual experiments in any given chamber are numbered sequentially, and as shown on Table B-1, the runs are designated by the chamber code followed by the run number. Note that the DTC, OTC, and (in most cases) CTC had dual reactors where two mixtures could be irradiated simultaneously. In those cases, the suffix "A" or "B" is used to indicate the reactor used to obtain the data. For incremental reactivity experiments, the designation refers to the reactor where the test VOC was added, with the understanding that the other reactor contained the same mixture without the added VOC.

There is also a large database of outdoor environmental chamber experiments that were carried out at the University of North Carolina that can be used for mechanism evaluation. These have been used for evaluations of the SAPRC-99 (Carter and Lurmann, 1991) and other (e.g., Carter and Lurmann, 1990; Gery et al, 1988) mechanisms, as well as for evaluation of the detailed isoprene mechanism of Carter and Atkinson (1996). Unfortunately, there was insufficient time to conduct a comprehensive evaluation of this mechanism using the UNC chamber data base, because of the need to update and re-evaluate the chamber model for that chamber. However, results of previous evaluation studies have shown that mechanisms that perform reasonably well in simulating the UCR indoor chamber data base also perform reasonably well in simulating the UNC chamber data (Carter and Lurmann, 1990, 1991; Carter and Atkinson, 1996).

Table 45. Designations used for types of incremental reactivity experiments and complex mixtures in the summaries of the evaluation experiments and results.

Designation	Description
	<u>Types of Incremental Reactivity Experiments</u>
MR3	Experiments using the 3-component "mini-surrogate" at relatively high NO_x levels. This type of experiment was used in our first major experimental incremental reactivity study (Carter et al, 1993a), and is still used as part of our experimental protocol to evaluate VOC reactivity. This employs relatively high NOx levels and uses an ethene, n-hexane, and m-xylene mixture as a simple representation of ambient VOCs. As discussed by Carter et al (1995b), experiments using this surrogate are very sensitive to effects of VOCs on radical levels (e.g., aspects of the mechanism that affect radical initiation or inhibition).
MR8	Experiments using the 8-component "full surrogate" at relatively high NO_x levels. This type of experiment was first employed by Carter et al (1995b) as a more realistic representation of maximum incremental reactivity (MIR) conditions than the mini-surrogate system, and that is also used as part of our standard experimental protocol to evaluate reactivity. Like the mini-surrogate, this also employs relatively high NOx conditions, but uses a mixture as of of n-butane, n-octane, ethene, propene, trans-2-butene, toluene, m-xylene, and formaldehyde as a more realistic representation of ambient conditions. Incremental reactivities measured using these experiments have been shown to give the best correlation to atmospheric MIR's than the other types of surrogate - NOx systems we employ for reactivity studies (Carter et al, 1995b).
R8	Experiments using the 8-component "full surrogate" at lower NO_x levels. This uses the same surrogate mixture as the "MR8" experiments, but with NO_x levels reduced by a factor of ~2. This type of experiment was also developed by Carter et al (1995b) and is also used as part of our standard experimental protocol to evaluate reactivity. These experiments evaluate the effects of VOCs on O3 formation under conditions where NOx is limited.
MRE	Experiments using ethene alone as the ROG surrogate, at relatively high NO_x levels. This was used in the study of Carter et al (1995b) when evaluating the effects of using simplified surrogate systems, and in some experiments to evaluate reactivities of terpenes. It has not been used subsequently because evaluation results are highly sensitive to the ability of the model to simulate the base case experiment, which tend to be variable.
MR4	Similar to "MR3" except that toluene and 1,3,5-trimethylbenzene is used in place of m-xylene. This was used in some recent experiments as an alternative to the standard mini-surrogate because the more rapidly reacting 1,3,5-trimethylbenzene gives a somewhat better measure of the effects of the VOC on radical levels. It is not widely used because the results are similar to those using the standard mini-surrogate, and use of the standard surrogate gives better comparability to the large existing data base.
R3	Experiments using the standard "MR3" mini-surrogate, but at lower NOx levels than the standard mini-surrogate. This was used in a few cases as part of specialized studies, or because of errors in reactant injections.
RE	Experiments using ethene as the surrogate and carried out under NOx limited conditions. This was used in a few experiments with terpenes (i.e., ethene + terpene experiments were carried out to evaluate terpene mechanisms).
RX	Experiments using other miscellaneous or non-standard surrogate - NO_x mixtures for the base case. These were used either for special studies, because gas chromatographic interferences prevented use of the standard surrogate, or because of injection errors.

Table 45 (continued)

Designation	Description
	Types of Simple Mixtures
MIX-A	Mixture of alkanes
MIX-E	Mixture of alkenes
MIX-AE	Mixture of alkanes and alkenes
MIX-AO	Mixtures of alkanes and oxygenates (generally aldehydes)
MIX-RO	Mixtures of aromatics and oxygenates (generally aldehydes)
MIX-AR	Mixtures of alkanes and aromatics
MIX-ER	Mixtures of alkenes and aromatics
	Ambient Surrogate Mixtures used in Base Case Incremental Reactivity Experiments.
SURG-3M	Base case for the "MR3" incremental reactivity experiments. Employed the standard 3-component "mini-surrogate" at relatively high NO_x concentrations.
SURG-8M	Base case for the "MR8" incremental reactivity experiments. Employed the standard 8-component "full surrogate" at relatively high NO_x concentrations.
SURG-8	Base case for the "R8" incremental reactivity experiments. Employed the standard 8-component "full surrogate" at lower NO_x concentrations.
SURG-3	Base case for the "R3" incremental reactivity experiments. Employed the standard 3-component "mini-surrogate" at lower NO_x concentrations.
SURG-4M	Base case for the "MR4" incremental reactivity experiments. Employed the modified version of the 3-component "mini-surrogate" at relatively high NO_x concentrations.
SURG-X	Base case for the "MRX" incremental reactivity experiments. Employed various miscellaneous surrogates, usually (but not always) at relatively high NO_x concentrations.
	Ambient Surrogate Mixtures used in Various Complex Mixture Experiments.
SURG-4	Experiments in the ITC using a 4-component surrogate, low NO_x mixture used in the early incremental reactivity study of Carter and Atkinson (1987).
SURG-4R	Modified versions of the "SURG-4" mixture used in the study of Carter and Atkinson (1987).
SURG-7	A surrogate mixture of seven hydrocarbons used in several runs in the SAPRC EC (Pitts et al, 1979).
SURG-8S	A surrogate mixture of 8 hydrocarbons used in the "multi-day effects" study of Carter et al (1984b).

Table 46. Summary of environmental chambers used to obtain the data used for mechanism evaluation.

Chamber	Light Source	Type	Volume (liters)	Surface	RH	Period for Runs	Additional Information
ITC	Blaclkight	Single	~6400	Semi-collapsible 2 mil FTP Teflon bag held by frame	~50%	1982-86	See Carter et al (1995d)
ETC	Blacklight	Single	~3000	Semi-collapsible 2 mil FTP Teflon bag held by frame	Dry	1989-93	See Carter et al (1995d)
DTC	Blacklight	Dual	2 x ~5000	Two semi-collapsible 2 mil FTP Teflon bags held by frames	Dry	1993-99	See Carter et al (1995d)
EC	25 KW Xenon Arc	Single	5774	Teflon coated aluminum, evacuable cylinder	~50%	1975-84	See Carter et al (1995d)
XTC	4 x 6 KW Xenon Arc	Single	~5000	Semi-collapsible 2 mil FTP Teflon bag held by frame	Dry	1993	See Carter et al (1995d)
CTC (11-82)	4 x 6 KW Xenon Arc	Single	~5000	Semi-collapsible 2 mil FTP Teflon bag held by frame	Dry	1994-95	Very similar to XTC.
CTC (83+)	4 x 6 KW Xenon Arc	Dual	2 x ~2500	Two semi-collapsible 2 mil FTP Teflon bags held by frames	Dry	1995-99	Similar to XTC except dual bags.
OTC	Sunlight	Dual	2 x ~20,000	Dividable and completely collapsible 2 mil FEP Teflon bag.	Dry	1992-93	See Carter et al (1995c,d)

Data from seven different chambers were used in these evaluations, and their major characteristics are summarized in Table 46. As indicated on the table, most of these chambers are described in detail by Carter et al (1995d), or references therein. The only exception is the CTC, which is the most recently constructed of these chambers. This is essentially the XTC after it was moved from SAPRC to CT-CERT, and employed the same light source and general design.

A. Chamber Simulation Methods

Evaluations of mechanisms using chamber data require an appropriate representation of the conditions of the chamber experiments that affect the simulation results. These include initial reactant concentrations, physical conditions such as temperature and dilution, light intensity and spectrum, and the major wall effects such as the chamber radical source, O_3 decays, NO_x offgasing, etc. These considerations are discussed in detail elsewhere (e.g., Carter and Atkinson, 1990, 1991; Carter et al, 1995c,d, 1997a), and generally the approach employed in this work was similar. This is summarized briefly in the following sections.

1. Light Characterization

Light characterization requires specification of both the intensity and the spectrum of the light source used in the experiments. As discussed by Carter et al (1995c,d) for indoor chamber runs, this is determined by the NO_2 photolysis rate (usually derived from results of NO_2 actinometry experiments), and the relative spectral distribution of the light source. For blacklight chambers the spectrum is assumed to be constant and the spectrum recommended by Carter et al (1995d) is used. For Xenon arc chambers, the spectrum tends to vary with time, and the spectrum used for modeling is based on measurements made during or around the time of the experiment as discussed by Carter et al (1995d). For the outdoor chamber, the spectrum was calculated as a function of solar zenith angle as described by Carter et al. (1995c).

For the blacklight chambers and the EC, the NO_2 photolysis rates were determined by carrying out periodic NO_2 actinometry experiments, with the values assigned to individual runs being based on the trends or averages of the measurements carried out around the time of the experiment (Carter et al, 1995d, 1997a). For the XTC and CTC, the relative trends in light intensity with time were determined primarily using absolute spectral intensity measurements, whose data were placed on an absolute basis using occasional in-chamber steady-state or Cl_2 actinometry measurements (Carter et al, 1995d, 1997a). For the outdoor chamber, the absolute light intensities were obtained using continuous UV radiometer and total solar radiometer (TSR) data. These were used to derive absolute spectra for calculating photolysis rates by fitting outputs of a solar radiation model to these measurements (Carter et al, 1995c).

For the DTC and CTC experiments carried out since 1994, a check on the accuracy of the light intensity assignments can be obtained from the trends of the results of the many replicate "base case" experiments carried out in conjunction with the incremental reactivity experiments. As the light intensity gradually decreases over time, the rate of O_3 formation and NO oxidation also decrease accordingly, and these rates take step increases when the changes are made that increase the light intensity. There are two periods when the trends of the results of these experiments were not consistent with the photolysis rates as indicated by the NO_2 actinometry or spectral intensity results. One case involved DTC runs 624-647 that were carried out using 75% lights (Carter et al, 1999h), but no runs in this group were used in this evaluation. The other case consisted of the CTC runs after CTC170, which includes a number of runs used in this evaluation. For these experiments, the rates of decrease in the rates of NO oxidation and O_3 formation in the base case runs decreased more rapidly with time than did the light intensity as measured by NO_2 actinometry or spectral measurements made outside the chamber (Carter et al, 1999c). On the other hand, the Cl_2 actinometry measurements made inside the chamber, though less precise than the other measurement methods, were consistent with the trend in base case surrogate reactivity results. This suggests that the chamber walls may be contributing to the decreasing intensity trend. For these CTC runs, the method for assigning NO_2 photolysis rates was adjusted to be consistent with the trend in replicate base case surrogate results (Carter et al, 1999c).

2. Representation of Chamber Wall Effects

The chamber wall effects that were represented in the simulations of these experiments were the chamber radical source (Carter et al, 1982), NO_x offgasing, heterogeneous formation of HONO from NO_2, N_2O_5 hydrolysis, O_3 dark decay, and background effects causing excess NO to NO_2 conversions. These by the following psuedo-reactions:

$$\text{Walls} + h\nu \rightarrow \text{HONO} \qquad \text{(RN)}$$

$$\text{Walls} + NO_2 + h\nu \rightarrow 0.5\ \{\text{HONO} + \text{Wall-}NO_x\} \qquad \text{(RS)}$$

$$\text{Walls} + NO_2 \rightarrow y_{HONO}\ \text{HONO} + (1-y_{HONO})\ \text{Wall-}NO_x \qquad (NO_2W)$$

$$N_2O_5 + \text{walls} \rightarrow 2\ \text{Wall-}NO_x \qquad (N_{25}I)$$

$$N_2O_5 + H_2O + \text{walls} \rightarrow 2\ \text{Wall-}NO_x \qquad (N_{25}S)$$

$$\text{Walls} + O_3 \rightarrow (\text{loss of } O_3) \qquad (O_3W)$$

Note that “Wall-NO_x” in the above reactions is an inert counter species that us used to account for nitrogen balance only, since it undergoes no subsequent reaction in the model. The rate constants for these processes, and the stoichiometric parameter y_{HONO} were assigned based on the results of appropriate characterization runs or estimates as indicated on Table 47. See Carter and Lurmann (1990, 1991) and Carter et al (1995d) for a more detailed discussion of how these processes are represented in chamber models and how their rate parameters are derived.

The formation of HONO from the walls (Reaction RN) us used to represent both the chamber radical source and NO_x offgasing, because the HONO so formed would photolyze rapidly to form both OH radicals and NO

$$\mathrm{HONO} + h\nu \rightarrow \mathrm{OH} + \mathrm{NO}$$

Previously, the radical source and NO_x offgasing were represented as separate processes, as

$$\mathrm{Walls} + h\nu \rightarrow \mathrm{OH} \qquad \text{(RS)}$$

$$\mathrm{Walls} + h\nu \rightarrow \mathrm{NO_2} \qquad (\mathrm{ENO_2})$$

with the rates of each being assigned independently based on appropriate characterization runs (n-butane - NO_x or CO - NO_x runs for the radical source, and pure air or acetaldehyde-air runs for NO_x offgasing) (Carter and Lurmann, 1990, 1991; Carter et al, 1995d, 1997a). However, in most cases the rates of these two reactions tended to be the same to within the uncertainty of the determination, suggesting that they may be due to the same process. For that reason, the revised representation, using Reactions (RN) and (RS), is used in this work. Note that the NO_2 dependence of the radical source, represented by Reaction (RS), appears to be significant only in the case of the EC, so that reaction is assigned a nonzero rate constant only for runs in that chamber. If there is an NO_2 dependence for the radical source in the other chambers, it is much less than the run-to-run variability of the radical source.

Table 47 gives the rate constants and other wall-dependent parameters that were assigned to the experiments used in this evaluation. Note that the “Set(s)” column on the table indicates the “characterization set” (Carter et al, 1995d), which refers to a group of runs that are all assumed to have the same characterization parameters. The characterization set assigned to each experiment is given with the run listing in Table B-1 in Appendix B. In most cases, this refers to runs in a given reaction bag, though sometimes the characterization set changes if the results of characterization runs indicate that the wall effects parameters have changed. For the CTC, characterization sets are also used to refer to runs that are assumed to have the same spectral distribution. Since the spectral distribution changes more rapidly then the reactor characteristics, for that chamber there are many characterization sets where the same wall effects parameters are assigned.

3. Other Reaction Conditions

The other reaction conditions that need to be represented in the simulations are the initial reactant concentrations, temperature, humidity and dilution. In most cases the initial reactant concentrations are determined from measurements made prior to the start of the irradiation, but in some reactivity experiments with missing data for a “base case” reactant the average concentration measured in similar experiments is used. The one exception to this is the initial HONO that may be introduced as a contaminant with the NO_x injections; this is represented by the parameter “HONO-F”, whose value is derived based on results of radical source characterization runs as indicated on Table 47. The humidity used in the simulations is also indicated on Table 47.

Table 47. Chamber wall effect and background characterization parameters used in the environmental chamber model simulations for mechanism evaluation.

Cham.	Set(s)	Value	Discussion
RN-I (ppb)			Ratio of the rate of **wall + hv -> HONO** to the NO2 photolysis rate.
ITC	All	0.045	Average of value of RS-I which gave best fits to n-butane - NOx chamber experiments carried out in this chamber. The initial HONO was optimized at the same time. Temperature does not vary significantly in the ITC runs used for evaluation.
ETC	2-3	9.00e+9 exp(-9712/T) 0.078 @ 300K	The few n-butane - NOx experiments in this chamber appear to be anomalous. The preexpodential factor is derived to minimize biases in model simulations of the large number of mini-surrogate - NOx chamber experiments carried out in this chamber. The activation energy is based on the value that gives best fits to temperature dependences of RN-I values which fit n-butane - NOx and CO - NOx experiments in the OTC and other Teflon bag chambers.
DTC	1	0.058	Average of value of RS-I which gave best fits to n-butane - NOx chamber experiments carried out in this chamber. The initial HONO was optimized at the same time. If a temperature dependence is shown, it was derived from the temperature dependence of the RN-I values that best fit characterization data in outdoor chamber experiments, with the same activation energy used in all cases. If a temperature dependence is not shown, then the temperature variation for experiments in this set is small compared to the run-to-run variability in the best fit RN-I values. Note that the radical source in Sets 3, 12, 13, and 16 runs was anomalously high.
	3	2.16e+10 exp(-9712/T) 0.188 @ 300K	
	10	8.14e+9 exp(-9712/T) 0.071 @ 300K	
	11	0.080	
	12	0.277	
	13	0.146	
	14	0.082	
	15	0.057	
	16	0.212	
	17	0.073	
	18	0.066	
XTC	1	5.25e+9 exp(-9712/T) 0.0457 @ 300K	
CTC	1-8,10	0.064	
	9	0.097	
		0.064	
OTC		6.04e+9 exp(-9712/T) 0.053 @ 300K	
EC	1	0.308	Based on the NO2 dependence radical source derived by Carter et al (1981), adjusted downward by 20% to reduce biases in simulations of n-butane - NOx experiments carried out in this chamber. The NO2-dependent radical source term, RS-S, was reduced by an equal factor.

Table 47 (continued)

Cham.	Set(s)	Value	Discussion
RS-S (unitless)			Ratio of the rate of **NO2 + hv -> 0.5 HONO + 0.5 wall NOx** to the NO2 photolysis rate.
EC	1	0.17%	Based on the NO2 dependence radical source derived by Carter et al (1981), adjusted downward by 20% to reduce biases in simulations of n-butane - NOx experiments carried out in this chamber. The NO2-independent radical source term, RN-I, was reduced by an equal factor.
All others		0	Any dependence of apparent radical source on initial NOx levels in Teflon bag chambers was found to be much less than the run-to-run variability.
HONO-I (ppb)			Initial HONO in experiment, assumed to be independent of other reactants.
ITC	All	1.7	Average of initial HONO value which gave best fits to n-butane - NOx chamber experiments carried out in this chamber. The RN-I parameter was optimized at the same time. The best fit initial HONO values appear to be approximately independent of the initial NO2.
HONO-F (unitless)			Ratio of the initial HONO concentration to the measured initial NO2. [The initial NO2 in the experiment is reduced by a factor of 1 - (HONO-F)]. Unless the characterization data indicate otherwise, it is assumed that the initial HONO is introduced with the NO2 injection, so is it is assumed to be proportional to the initial NO2 concentration.
ETC	2-3	0	Initial HONO assumed to be small for these experiments, where special procedures were employed to minimize HONO contamination. See Carter et al (1993a).
DTC	1	0.1%	Average of value of initial HONO to initial NO2 which gave best fits to n-butane - NOx chamber experiments carried out in this chamber. The RN-I parameter was optimized at the same time
	3	0.4%	
	10	0.8%	
	11	0.6%	
	12	0.5%	
	13	0.9%	
	14	0.6%	
	15	0.7%	
	16	0.5%	
	17	0.3%	
	18	0.8%	
XTC	1	1.2%	
CTC	1-8,10	0.8%	
	9	0.8%	
OTC	10-12	0	Apparently not significant compared to RN-I.

Table 47 (continued)

Cham.	Set(s)	Value	Discussion
E-NO2/K1 (ppb)			Ratio of rate of NO2 offgasing from the walls to the NO2 photolysis rate.
EC	1	0.10	Adjusted to fit O3 formation in acetaldehyde/air run EC-253.
All Teflon Bag Chambers		0	The NOx offgasing caused by representing the radical source by HONO offgasing appears to be sufficient for accounting for NOx offgasing effects in most cases. RN-I parameters adjusted to fit experiments sensitive to the radical source are consistent with NOx offgasing rates adjusted to fit pure air or aldehyde - air runs, to within the uncertainty and variability.
k(NO2W) (min^{-1})			Rate of unimolecular loss (or hydrolysis) of NO2 to the walls.
All Teflon Bag Chambers		1.6e-4	Based on dark NO2 decay and HONO formation measured in the ETC by Pitts et al. (1984). Assumed to be the same in all Teflon bag chambers, regardless of volume.
EC	1	2.8e-4	Based on dark NO2 decay and HONO formation measured in the EC by Pitts et al. (1984).
YHONO			Yield of HONO in the unimolecular reaction (hydrolysis) of NO2 on the walls.
All Teflon Bag Chambers		0.2	Based on dark NO2 decay and HONO formation measured in the ETC by Pitts et al. (1984). Assumed to be the same in all Teflon bag chambers, regardless of volume.
EC	1	0.5	Based on dark NO2 decay and HONO formation measured in the EC by Pitts et al. (1984).
k(O3W) (min^{-1})			Unimolecular loss rate of O3 to the walls.
ITC	All	1.5e-4	Based on results of O3 decay in Teflon bag chambers experiments as discussed by Carter et al (1995d).
ETC	All	1.5e-4	
DTC	All	1.5e-4	
XTC	All	1.5e-4	
CTC	All	8.5e-5	Based on results of O3 decay experiments in this chamber
OTC	All	1.7e-4	
EC	All	1.1e-3	Based on results of O3 decay in Teflon bag chambers experiments as discussed by Carter et al (1995d).
k(N26I) (min^{-1})			Rate constant for **N2O5 -> 2 Wall-NOx**. This represents the humidity-independent portion of the wall loss of N_2O_5, or the intercept of plots of rates of N_2O_5 loss against humidity.
All Teflon Bag Chambers		2.8e-3	Based on N_2O_5 decay rate measurements made by Tuazon et al (1983) for the ETC. Assumed to be independent of chamber size (Carter et al, 1995d).
EC	1	4.7e-3	Based on N_2O_5 decay rate measurements made by Tuazon et al (1983) for the EC. See also Carter et al (1995d).

Table 47 (continued)

Cham.	Set(s)	Value	Discussion
k(N26S) (ppm^{-1} min^{-1})			Rate constant for **N2O5 + H2O -> 2 Wall-NOx**. This represents the humidity dependent portion of the wall loss of N_2O_5, or the slope of plots of rates of N_2O_5 loss against humidity.
All Teflon Bag Chambers		1.1e-6	Based on N_2O_5 decay rate measurements made by Tuazon et al (1983) for the ETC. Assumed to be independent of chamber size (Carter et al, 1995d).
EC	1	1.8e-6	Based on N_2O_5 decay rate measurements made by Tuazon et al (1983) for the EC. See also Carter et al (1995d).
k(XSHC) (min^{-1})			Rate constant for **OH -> HO2**. This represents the effects of reaction of OH with reactive VOCs in the background air or offgased from the chamber walls. This parameter does not significantly affect model simulations of experiments other than pure air runs.
All Teflon Bag Chambers		250	Estimated from modeling several pure air in the ITC (Carter et al, 1996d), and also consistent with simulations of pure air runs in the ETC (Carter et al, 1997a).
EC	1	0	Assumed to be negligible because the EC is generally evacuated overnight between experiments (Carter et al, 1995d).
H2O (ppm)			Default water vapor concentration for runs where no humidity data are available.
ITC	all	2.0e+4	This corresponds to ~50% RH at 303K, which is the condition for most experiments in this chamber.
All Other Teflon Bag Chambers		1.0e+3	Experiments in these chambers were carried out using dried purified air. The limited humidity data for such runs indicate that the humidity was less than 5%, probably no more than ~2.5%, and possibly much less than that. The default value corresponds to ~2.5 - 3% RH for the conditions of most experiments.
EC	1	2.0e+4	This corresponds to ~50% RH at 303K, which is the condition for most experiments in this chamber. Humidity data are available for most EC runs, so the default is usually not used.

The temperature used in the simulations is derived from the measurements made during the experiments, as discussed by Carter et al (1995d). The dilution varies depending on the chamber, and is derived as also discussed by Carter et al (1995d). The dilution is relatively small for all experiments used for mechanism evaluation in this work, being about 2% per hour in the EC, and generally less than 1% per hour in the Teflon bag chambers, which can collapse as samples are withdrawn.

Most experiments used in this evaluation were 6-hour runs. A few multi-day runs were included in the evaluation set, but only the simulation results for the first day are shown. Except for the few outdoor runs, most of the experiments were carried out with constant light intensity and approximately constant temperature.

4. Incremental Reactivity Simulations

Most incremental reactivity experiments consisted of simultaneous irradiations of two mixtures in the two reactors (or "sides") of the chamber, one with and one without the added test compound. Those were simulated by separately simulating the experiment on each side, using the reactant concentrations and conditions measured for that side. The incremental reactivity data (i.e., change in measured quantities caused by adding the VOC, divided by the amount added) were then calculated from the results of these two simulations in exactly the same way the experimental reactivity data were calculated from the experimental measurements.

This procedure could not be used when simulating incremental reactivity experiments carried out in the ECT, where base case and added test VOC irradiations were carried out as separate experiments, and temperature and some other conditions tended to vary from run to run (Carter et al, 1993a). In those cases, the base case conditions used to derive the experimental incremental reactivity measurement was derived using correlations between experimental conditions and results of the separate base case experiments (Carter et al, 1993a). In the model simulations, the base case was simulated by simulating the test VOC experiment without the test compound added, and the incremental reactivities were calculated from the differences in the results of that simulation and the simulation of the actual experiment.

5. Chemical Mechanism Employed

The chemical mechanism employed in the chamber simulations consisted of the base mechanism with reactions added as needed to represent the VOCs present, together with the reactions used to represent the chamber effects. The base mechanism used is listed in Table A-2 in Appendix A. The reactions used to represent the individual VOCs not in the base mechanism, which were derived as discussed in previous sections, are listed in Table A-6 in Appendix A[19]. No lumping of initially present VOCs was employed except when simulating the components of the mineral spirits samples (MS-A through MS-D), where lumped species with averaged parameters were used to represent the alkanes and (for MS-A) aromatics and alkenes present. The reactions and parameters added to represent chamber effects are as discussed above in Section V.A.2.

B. Chamber Simulation Results

The results of the simulation of the chamber experiments are summarized in Table B-1 and in the various figures in Appendix B. Table B-1 gives the experimental and calculated values of the quantity $\Delta(O_3\text{-NO})$[20] for 2, 4, and 6-hours into the experiments for all experiments used in the evaluation except for the pure air and acetaldehyde-air runs. The quantity $\Delta\ (O_3\text{-NO})$ is defined as

$$\Delta\ (O_3\text{-NO})_t = [O_3]_t - [NO]_t - ([O_3]_0 - [NO]_0) \qquad \text{(XXIX)}$$

where $[O_3]_0$, $[NO]_0$, $[O_3]_t$, and $[NO]_t$ are the initial and time=t concentrations of ozone, and NO, respectively. As discussed previously (e.g., Carter and Lurmann, 1990, 1991); Carter and Atkinson, 1984), this gives a measure of the ability of the model to simulate the chemical processes that cause ozone

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[19] The VOCs were actually represented in the software using generalized reactions with variable parameters, whose values were assigned depending on the particular VOC being represented. However, the effect is the same as explicitly incorporating the reactions as shown in Table A-6.

[20] Note that $\Delta(O_3\text{-NO})$ is sometimes referred to as d(O3-NO) or D(O3-NO) on some of the tabulations of the results.

formation that gives a useful measure even where ozone is suppressed by the presence of excess NO. Table B-1 also shows the percentage error in the calculation for each experiment where $\Delta(O_3\text{-}NO)$ is greater than 1 pphm (0.01 ppm). This is defined as

$$\Delta\% = 100 \text{ x } (\text{Calculated value - Experimental value}) / \text{Calculated value} \qquad (XXX)$$

This gives a measure of the performance of the model in simulating the rates of O_3 formation and NO oxidation at various times in the individual experiments.

Because of the large number of experiments, Table B-1 is not very useful for giving a sense of the overall model performance in simulating the various types of experiments. For that reason, most of Appendix B consists of various figures displaying the model performance in graphical form. Depending on the types and numbers of runs involved, these can consist of concentration - time plots of $\Delta(O_3\text{-}NO)$ or (in a few cases) of other species; distribution plots of percentage errors in model simulations of $\Delta(O_3\text{-}NO)$ (calculated using Equation XXX), or plots of incremental reactivity data.

The incremental reactivity data plots include plots of experimental and calculated $\Delta(O_3\text{-}NO)$ for the base case and added VOC ("test") experiment, and plots of experimental and calculated incremental reactivities (IR)'s for $\Delta(O_3\text{-}NO)$ and IntOH. These quantities are defined as follows:

$$\text{IR } \Delta(O_3\text{-}NO)_t = \{\Delta(O_3\text{-}NO)_t^{\text{Added VOC Experiment}} - \Delta(O_3\text{-}NO)_t^{\text{Base Case Experiment}}\} / [\text{VOC added}]$$

$$\text{IR IntOH}_t = \{\text{IntOH}_t^{\text{Added VOC Experiment}} - \text{IntOH}_t^{\text{Base Case Experiment}}\} / [\text{VOC added}]$$

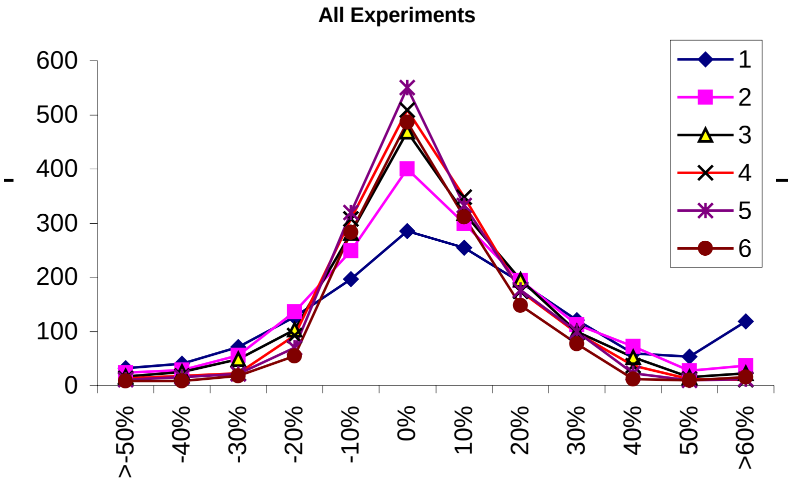
and IntOH is the integrated OH radical levels, calculated from the rates of consumption of the most reactive VOC in the base case mixture that reacts only with OH radicals (usually m-xylene) (Carter et al, 1993a). Note that there are no "base case" data shown for incremental reactivity experiments carried out in the ETC, since there is no single base case experiment associated with those runs (see above).

As observed in previous mechanism evaluation studies, although there were runs that were not particularly well simulated by the model, overall the model fit most of $\Delta(O_3\text{-}NO)$ data to within ±30% or better. The overall performance of the model in simulating all the runs listed in Table B-1 is shown on Figure 12. The model simulated the 6-hour $\Delta(O_3\text{-}NO)$ to within ±5% for ~1/3 of the experiments, to within ±15% for ~3/4 of the runs, and to within ±25% for almost 90% of the experiments. The model has a slight bias (average Δ% of 9%) towards overpredicting the t=1 hour $\Delta(O_3\text{-}NO)$ data, but this bias decreases to ~4% for the later periods of the runs. This is a somewhat better model performance than the simulations of the previous versions of the SAPRC mechanism (e.g., Carter and Lurmann, 1991). However, this better overall performance may be more a result of eliminating poorly characterized experiments or more difficult to characterize outdoor runs from the evaluation set than to changes or improvements in the mechanism.

Table 48 gives a summary of the results of the evaluations of the mechanisms for the various types of experiments, and indicates the figures in Appendix B where the various evaluation results are shown. For the VOC runs, the table also gives codes indicating the overall mechanism performance. These include

1. Fits the data to within the experimental uncertainty or with biases that are not considered to be significant.
2. Poor fits for some runs or non-negligible overall biases indicate possible problems with the mechanism for this compound, or there are insufficient data for satisfactory mechanism evaluation.

Figure 12. Distribution plots of model simulations of the hourly $\Delta(O_3\text{-}NO)$ data for all the experiments used for mechanism evaluation.



3. The mechanism either does not satisfactorily fit the data, or is considered to be too unrepresentative of the chemistry involved to give reliable atmospheric reactivity predictions.

The compounds where the evaluation results indicated possible adjustments to the mechanism may be appropriate or where there was insufficient data for satisfactory evaluation included the following: Cresols, naphthalene, dimethyl naphthalene, and tetralin are included because the data are considered insufficient for satisfactory mechanism development; ,4-diethyl hexane, cyclohexanone, t-butyl alcohol, and dimethyl glutarate, because there are non-negligible biases in simulations of full surrogate experiments after adjusting the nitrate yields to fit the mini-surrogate runs; β-pinene is included because of poor fits to the data for some runs; and benzene is included because of poor fits to the data in some runs and for some measures of reactivity. Reactivity predictions for these compounds are therefore considered to be somewhat uncertain, though not as uncertain as those for compounds for which no data are available for mechanism evaluation.

The compounds where the mechanism does not satisfactorily fit the data or is considered to be too uncertain for reliable reactivity predictions are the alkyl bromides and trichloroethylene. As discussed in Section IV.B.5, halogen chemistry is not included in this version of the mechanism, and highly simplified "placeholder" mechanisms are used to make approximate estimates of likely reactivity ranges. The reactivity predictions for these compounds should be considered to be almost as uncertain as those for compounds where no data are available.

However, as indicated on the table, the evaluation results for most VOCs are given code "1", indicating acceptable fits to the data. Of course, as also indicated on the table, this is often a result of adjusting uncertain aspects of the mechanism to fit the data. For the aromatics this consisted of the various adjustments to the parameterized mechanisms as discussed in Section IV.A, while in most other cases this consisted of adjusting the nitrate yield in the OH reaction (see Section III.I).

Table 48. Summary of results of mechanism evaluation for the various types of experiments, and figures in Appendix B where the evaluation results are shown.

Run Type	Figure no. [a]				Fit	Comments [d,e]
	C	D	R	P	[c]	
NOx Offgasing Characterization	1					NOx offgasing parameter adjusted to fit data for various characterization sets. Ozone fit in most runs, but overpredicted in some cases.
Radical Source Characterization Runs		2				Radical source parameter adjusted to fit data for each characterization set. Scatter indicates run-to-run variability, with most of the data being fit to within +/- 40%. No consistent biases.
Carbon Monoxide			3		1	Slight tendency to underpredict d(O3-NO) reactivity in some experiments, but generally good fits. No adjustments. (MRE, MR3, MR8, R8) (B)
Formaldehyde	4		8		1	Tendency to somewhat overpredict initial NO oxidation rates in most (but not all) blacklight chamber runs.. Good fits to the xenon arc chamber runs. No adjustments. (S, MRE, MR3, MR8, R8) (B, X)
Acetaldehyde	5		9		1	Reasonably good fits with no consistent biases. No adjustments. (S, MR3, MR8, R8) (B, X)
Acetone	6		10		1	Reasonably good fits to most data. May be slightly biased towards overpredicting d(O3-NO). No adjustments for this evaluation. (S, MRE, MR3, MR8, R8) (B, X, O)
Methyl Ethyl Ketone	7		11	7	1	Necessary to increase the overall quantum yield to 0.15 to remove biases in simulations.. Good fits to d(O3-NO), and formaldehyde data. Underpredicts acetaldehyde in two runs, fits it in two others. (S, MR3, MRX, MR8) (B, X)
Benzaldehyde			12		1	Reasonably good fit for one experiment and fair fit to the other, where the model does not simulate the base case well. No adjustments. (MR4, R8) (B)
o-Cresol	13				2	Mechanism adjusted to fit d(O3-NO) data in o-cresol run. Reasonably good fit to d(O3-NO) in p-cresol run, but d(O3-NO) underpredicted in run with m-cresol. (S) (X)
Methacrolein	14				1	Overall quantum yield optimized to fit d(O3-NO) data. Quality of fits similar to that reported by Carter and Atkinson (1996). (S) (B, X, O)
Methylvinyl keton	14				1	Overall quantum yield optimized to fit d(O3-NO) data. Quality of fits similar to that reported by Carter and Atkinson (1996). (S) (B, X)
Ethane			15		1	Fits most data to within experimental uncertainty. No adjustments. (MRE, MR3) (B)
Propane			16		1	Good fits to data in two MR3 runs; underpredicts d(O3-NO) reactivity in the third. No adjustments. (MR3) (B)
n-Butane			17		1	Significantly underpredicts d(O3-NO) reactivity in MRE experiments, but base case is not particularly well simulated. Good fits to MR3, R3, MR8, and R8 reactivity data. No adjustments. (MRE, MR3, R3, MR8, R8) (B) [e]
n-Hexane			18		1	Significantly overpredicts d(O3-NO) inhibition in the MRE run, but good fits to MR3 reactivity data. No adjustments. (MR3) (B)
n-Octane			18		1	Good fits to data in most runs, but somewhat underpredicts d(O3-NO) reactivity in some runs. No adjustments. (MR3, MR8, R8) (B, X)
n-Dodecane			19		1	Slight bias towards overpredicting inhibition in MR3 runs, but reasonably good fits for full surrogate runs. No adjustments. MR3, MR8, R8) (B)

Table 48 (continued)

Run Type	Figure no. [a] C	D	R	P	Fit [c]	Comments [d,e]
n-Tetradecane			20		1	Similar bias towards overrpredicting d(O3-NO) reactivity as in n-dodecane runs, but slight bias towards underpredicting d(O3-NO) inhibition in some (but not all) MR8 runs. No adjustments. (MR3, MR8) (B)
n-Pentadecane			21		1	No consistent biases. Somewhat overpredicts inhibition in MR3 run, underpredicts in MR8 run. (MR3, MR8) (B).
n-Hexadecane			21		1	No consistent biases for MR3 runs. Fair fits for MR8 runs. (MR3, MR8) (B, X)
Isobutane			22		1	Rate of decomposition of t-butoxy radicals adjusted in part based on simulations of these experiments. No consistent biases after adjustment. Generally fits within experimental uncertainty and variability. (MR3) (B)
2,2,4-Trimethyl Pentane			22		1	Nitrate yields from C7 and C8 peroxy radicals adjusted to fit data. Good fits after adjustment. (MR3) (B)
2,6-Dimethyl Octane			22		1	Slight tendency to overpredict d(O3-NO) reactivities in MR4 and MR8 runs may indicate need to adjust nitrate yield slightly, but no adjustments made. Good fit to d(O3-NO) reactivity in R8 run. (MR4, MR8, R8) (B)
2-Methyl Nonane			23		1	Very slight tendency to overpredict d(O3-NO) reactivities in MR3 and MR8 runs may indicate a need to slightly adjust nitrate yield slightly, but no adjustments made. (MR3, MR8, R8) (B)
3,4-Diethyl Hexane			23		2	Non-negligible tendency to overpredict d(O3-NO) inhibition in MR4 experiments and to overpredict d(O3-NO) reactivity in low NOx (R8) runs indicate that adjustments need to be made to the mechanism, but no adjustments made. (MR3, MR8, R8) (B).
Cyclohexane			24		1	Slight bias towards underpredicting inhibition in MR3 runs but good fits for full surrogate runs. No adjustments (MR3, MR8, R8) (B)
Hexyl Cyclohexane			24		1	Fits most data to within experimental uncertainty. No adjustments. (MR3, MR8, R8) (B)
Octyl Cyclohexane			25		1	Fits data to within uncertainty for all but one MR3 run, where d(O3-NO) inhibition is slightly overpredicted. No adjustments. (MR3, MR8, R8) (B)
Ethene	27	26	28		1	Variable fits to the large number of ethene - NOx experiments, but overall bias in d(O3-NO) predictions is small (may be slightly high). Tends to underpredict O3 in the outdoor chamber ethene - NOx runs. Good fits to reactivity experiments. No adjustments (S, MR3, MR8, R8) (B, O)
Propene	29	30	31		1	Radical yields in O3P reaction had to be assumed to be low and radical yields in O3 reaction had to be reduced in order to remove bias in simulations of the large number of propene - NOx runs. No bias in d(O3-NO) simulations of propene - NOx runs in blacklight chambers, negative bias for XTC, CTC, and OTC runs and positive bias for EC runs. Fits reactivity data to within experimental uncertainty and variability. (S, MRE, MR3, MR8, R8) (B, X, O)

Table 48 (continued)

Run Type	Figure no. [a]				Fit	Comments [d,e]
	C	D	R	P	[c]	
1-Butene	32				1	Radical yields in both O3P and O3 reaction had to be assumed to be low to approximately fit data, even though assuming low OH yield in O3 reaction is inconsistent with laboratory data. Some variability in fits to data, but no consistent biases after adjustment. (S) (B,X)
1-Hexene	32					Radical yields in both O3P and O3 reaction had to be assumed to be low to approximately fit data, even though assuming low OH yield in O3 reaction is inconsistent with laboratory data. Reasonably good fits to the data after adjustment. (S) (B)
Isobutene	32		33		1	Nitrate yield in OH reaction adjusted upwards to fit data. Somewhat overpredicts maximum O3 in isobutene - NOx runs. Good fits to reactivity data. (S, MR3) (B)
trans-2-Butene	32		33		1	Good fits to data for most runs without adjustments. (S, MRE, MR3, MR8, R8, RE) (B, X)
Isoprene	34		35		1	Reasonably good fits to most (but not all) isoprene - NOx runs; similar to the fits reported by Carter and Atkinson (1996). Bias towards underpredicting O3 reactivity at end of MRE and RE runs, but good fits to MR3 reactivity data. (S, MRE, MR3, RE) (B, X, O)
2-Pentanone	36		37		1	Overall quantum yield for photodecomposition had to be reduced to 0.1 to fit data. Good fits to MPK - NOx and reactivity data after this adjustment. (S, MR3, MR8, R8) (X)
Cyclohexanone			37		2	Branching ratio for reactions of OH radicals at different positions and overall nitrate yield in OH reaction had to be adjusted to improve model simulations to reactivity data. Photolysis is assumed not to form radicals, so overall quantum yield not adjusted. Fair fits to reactivity data after adjustment, but d(O3-NO) reactivity is still overpredicted in some full surrogate experiments. (MR3, MR8, R8) (B, X)
4-Methyl-2-Pentanone			38		1	Need to adjust quantum yield to 0.04 to fit reactivity data. Reasonably good fits for mini-surrogate and high NOx full surrogate. Somewhat overpredicts reactivity at end of low NOx full surrogate runs.
2-Heptanone	36		38		1	Overall quantum yield for photodecomposition had to be reduced to 0.02 to fit data. Good fits to MPK - NOx and reactivity data after this adjustment. (S, MR3, MR8, R8) (X)
Methanol			39		1	Fits data to within experimental uncertainty without adjustments. (MR3) (B)
Ethanol			39		1	Fits data to within experimental uncertainty without adjustments. (MR3) (B)
Isopropyl Alcohol			41		1	Variable fits. Good fits to some mini-surrogate runs, some where d(O3-NO) reactivity underpredicted. No consistent biases for full surrogate runs. No adjustments. (MR3, MR8, R8) (B)
t-Butyl Alcohol			40		2	Nitrate yields adjusted to fit data in the MR3 experiments. The resulting mechanism overpredicts d(O3-NO) reactivities by about 30-50%, but is more consistent with the data for the R8 experiments. Data are somewhat better fit if the rate constant is reduced by about a factor of 1.6 to the estimated value, but the rate constant was not adjusted in the mechanism used. (MR3, MR8, R8) (B)

Table 48 (continued)

Run Type	Figure no. [a] C	D	R	P	Fit [c]	Comments [d,e]
1-Octanol			42		1	Good fits to two experiments and tendency to overpredict d(O3-NO) reactivity in two others. No adjustments (MR3, MR8, R8) (B)
2-Octanol			42		1	Fits data to within experimental uncertainty and variability. No adjustments (MR3, MR8, R8) (B)
3-Octanol			42		1	Slight bias towards overpredicting d(O3-NO) reactivity. No adjustments. (MR3, MR8, R8) (B)
Propylene Glycol			43		1	Mechanism fits data to within experimental uncertainty. No adjustments (MR3, MR8, R8) (B)
Dimethyl Ether			45		1	Mechanism fits data to within experimental uncertainty. No adjustments (MR3) (B)
Diethyl Ether			45		1	Mechanism may be slightly biased towards overpredicting d(O3-NO) reactivity. No adjustments. (MR3, MR8, R8) (B)
Methyl t-Butyl Ether			44		1	Fits data to within experimental uncertainty after adjusting overall nitrate yield (MR3) (B)
1-Methoxy-2-Propanol			46		1	Fits data to within experimental uncertainty after adjusting overall nitrate yield (MR3, MR8, R8) (B)
2-Ethoxyethanol			47		1	Fits data to within experimental uncertainty after adjusting overall nitrate yield (MR3) (B)
2-(2-Ethoxy-ethoxy) Ethanol			47		1	Fits data to within experimental uncertainty after adjusting overall nitrate yield (MR3) (B)
2-Butoxyethanol			48		1	Fits most data to within experimental uncertainty after adjusting overall nitrate yield (MR3, MR8, R8) (B)
Methyl Acetate			49		1	Chamber data are somewhat better fit is it is assumed that reaction at the acetate group is assumed to be negligible. Also necessary to adjust overall nitrate yield somewhat. Adjusted mechanism fits data without consistent biases. (MR3, MR8, R8) (B)
Ethyl Acetate			50		1	Nitrate yield adjusted to improve fits to data. Model fits data for all but one MR8 experiment within experimental uncertainty. (MR3, MR8, R3, R8) (B, X)
Isopropyl Acetate			51	52	1	Reactivity data fit to within experimental uncertainty. Formaldehyde and acetone yields may be slightly underpredicted. No adjustments. (MR3, MR8) (B).
Methyl Isobutyrate			53	54	1	In order to even approximately fit the reactivity data for this compound, it is necessary to assume that radicals such as CH3-O-CO. react with NO2 to form a PAN analogue rather than decompose. Overall nitrate yields and initial OH reaction branching ratios adjusted to improve fits to chamber data. (MR3, MR8, R8) (B)
t-Butyl Acetate			51	52	1	Overall nitrate yield adjusted to fit data, but these is still a slight bias towards overpredicting d(O3-NO) reactivity. Model gives good fits to formaldehyde data but may slightly underpredict acetone yields. (MR3, MR8, R8) (X)

Table 48 (continued)

Run Type	Figure no. [a]				Fit	Comments [d,e]
	C	D	R	P	[c]	
n-Butyl Acetate			55		1	Nitrate yield adjusted to fit data. Fits most data to within experimental uncertainty, though may be slight bias towards overpredicting d(O3-NO) reactivity in the MR8 runs. (MR3, MR8, R8) (B)
Propylene Carbonate			56		1	Nitrate yields reduced to by relatively large factor to fit mini-surrogate (MR3) runs, and branching ratio for initial OH reaction had to be adjusted also to reduce biases in simulations of full surrogate reactivity runs. Adjusted model still slightly overpredicted reactivity in full surrogate runs. Run DTC243 appears to be anomalous and wasn't used in judging fits. (MR3, MR8, R8) (B)
1-Methoxy-2-Propyl Acetate			57		1	Model gives reasonably good fits to the data without adjustments. May be slight bias towards overpredicting d(O3-NO) reactivity in the MR8 experiments. (MR3, MR8) (B)
Dimethyl Succinate			58		1	Mechanism needed a number of adjustments to yield acceptable fits to the data. Isomerization of the CH3-O-CO-C[O.]-R radical had to be assumed to dominate, which is within the uncertainty of the estimates. Adjusted model fits data to within experimental uncertainty. (MR3, MR8, R8) (X)
Dimethyl Glutarate			58		2	Had to adjust branching ratio for initial OH reaction, overall nitrate yield, and an alkoxy intermediate branching ratio in order for model to be consistent with the chamber data and available product data. Adjusted model somewhat overpredicts d(O3-NO) reactivity in MR8 experiments, but gives good fits to the data for the MR3 and R8 runs. (MR3, MR8, R8) (X)
Acetylene	59		60		1	Quantum yields for radical formation from the photolysis of glyoxal had to be assumed to be much higher than estimated previously in order to even approximately fit reactivity data for acetylene (see documentation of base mechanism). Model gives reasonably good fits to data from acetylene - NOx runs and reactivity runs, but there may be a slight bias towards underpredicting d(O3-NO) reactivity in the MR3 runs. (S, MR3, MR8, R8) (B, X)
Acrolein	61				2	Overall quantum yield adjusted to fit data for acrolein - NOx runs. Good fits for runs at lower acrolein / NOx ratios, but initial NO oxidation rate underpredicted in higher acrolein / NOx run ITC946. (S) (B)
a-Pinene	62		63		1	Overall nitrate yield and number of NO to NO2 conversions in OH reaction adjusted to fit chamber data. Very good fits to a-pinene - NOx runs, reactivity runs fit to within experimental variability and uncertainty. (S, MRE, R8, RE) (B, X, O)
b-Pinene	62		63		2	Overall nitrate yield and numbers of NO to NO2 conversions assumed to be the same as best fits a-pinene data since using significantly different values did not improve fits for this compound. Although initial NO oxidation rates reasonably well fit in the b-pinene - NOx runs, the maximum ozone yield is consistently overpredicted. Fair fits to the incremental reactivity data. (S, MRE, RE) (B, X, O)

Table 48 (continued)

Run Type	Figure no. [a]				Fit [c]	Comments [d,e]
	C	D	R	P		
3-Carene	62				1	Overall nitrate yield and numbers of NO to NO2 conversions assumed to be the same as best fits a-pinene data since using significantly different values did not improve fits for this compound. Although initial NO oxidation rates reasonably well fit, the maximum ozone yield was underpredicted in three of the four runs. (S) (B)
Sabinene	62				1	Overall nitrate yield and numbers of NO to NO2 conversions assumed to be the same as best fits a-pinene data since using significantly different values did not improve fits for this compound. Slight tendency to overpredict O3 formation rate in middle of run, but maximum O3 concentration reasonably well simulated in most cases. (S) (B)
d-Limonene	62				1	Overall nitrate yield and numbers of NO to NO2 conversions assumed to be the same as best fits a-pinene data since using significantly different values did not improve fits for this compound. Slight tendency to overpredict O3 formation rate in middle of run (though not as much as for sabinene) but maximum O3 concentration reasonably well simulated in most cases. (S) (B)
Benzene	64		72		2	Representation of reactive products adjusted to fit benzene - NOx experiments as discussed in the aromatic mechanism documentation section. Tendency of model to overpredict peak O3 yields in some benzene - NOx runs, and very poor fits to data for one run (ITC562). Reasonably good fits to d(O3-NO) reactivity in reactivity runs, but tendency to underpredict IntOH reactivity. (S, MR3, R8) (B)
Toluene	65		72		1	Representation of reactive products adjusted to fit aromatic - NOx experiments as discussed with aromatic mechanism documentation. Reasonably good fits to most toluene - NOx runs. Fits d(O3-NO) reactivity in reactivity experiments within experimental uncertainty and variability, but tends to somewhat underpredict IntOH reactivity. (S, MR3, MR8, R8) (B, X)
Ethyl Benzene	66		72		1	Representation of reactive products adjusted to fit aromatic - NOx experiments as discussed with aromatic mechanism documentation. Reasonably good fits to most ethylbenzene - NOx runs. Fits reactivity runs to within the uncertainty of the data, but effect of added ethylbenzene too small for good mechanism evaluation. (S, MR3) (B, X)
m-Xylene	67		73		1	Representation of reactive products adjusted to fit aromatic - NOx experiments as discussed with aromatic mechanism documentation. Reasonably good fits to most m-xylene - NOx runs. Fits most reactivity runs to within the uncertainty of the data. (S, MR3, MR8, R8) (B, X)
o-Xylene	68				1	Representation of reactive products adjusted to fit aromatic - NOx experiments as discussed with aromatic mechanism documentation. Fair fits to most o-xylene - NOx runs. (S) (B, X)

Table 48 (continued)

Run Type	Figure no. [a] C	D	R	P	Fit [c]	Comments [d,e]
p-Xylene	69		73		1	Representation of reactive products adjusted to fit aromatic - NOx experiments as discussed with aromatic mechanism documentation. Fair fits to most p-xylene - NOx runs, though some variability in simulations of some CTC runs. Fits the one reactivity run to within the uncertainty of the data, but effect of added p-xylene too small for good mechanism evaluation. No adjustments were made. (S, MR3) (B, X)
1,2,3-Trimethyl Benzene	70		74		1	Representation of reactive products adjusted to fit aromatic - NOx experiments as discussed with aromatic mechanism documentation. Good fits to most 123-TMB - NOx runs, but incremental reactivities somewhat underpredicted in MR3 experiments.. (S, MR3) (B, X)
1,2,4-Trimethyl Benzene	70		74		1	Representation of reactive products adjusted to fit aromatic - NOx experiments as discussed with aromatic mechanism documentation. Fair fits to most 124-TMB - NOx runs. (S) (B, X)
1,3,5-Trimethyl Benzene	71		74		1	Representation of reactive products adjusted to fit aromatic - NOx experiments as discussed with aromatic mechanism documentation. Good fits to most 135-TMB - NOx runs, but incremental reactivities somewhat overpredicted in the MR3 experiment. (S, MR3) (B, X)
Naphthalene	75				2	Representation of reactive products adjusted to fit aromatic - NOx experiments as discussed with aromatic mechanism documentation. Unlike the alkylbenzenes, it is necessary to assume significant formation of products that react like PAN analogues in order to approximately fit the naphthalene - NOx runs. Fair fits to most runs, but peak O3 may be somewhat overpredicted in some low NOx experiments. (S) (B)
2,3-Dimethyl Naphthalene	75				2	Representation of reactive products adjusted to fit aromatic - NOx experiments as discussed with aromatic mechanism documentation. Unlike the alkylbenzenes, it is necessary to assume significant formation of products that react like PAN analogues in order to approximately fit the 2,3-dimethylnaphthalene - NOx runs. Good fits to most runs. (S) (B)
Tetralin	75				2	Representation of reactive products adjusted to fit aromatic - NOx experiments as discussed with aromatic mechanism documentation. Unlike the alkylbenzenes, it is necessary to assume significant formation of products that react like PAN analogues in order to approximately fit the tetralin - NOx runs. Fair fits to most runs, with some discrepancies but no consistent biases. (S) (B)
Styrene			76		1	Necessary to adjust the nitrate yield in the OH reaction and the radical yield in the O3 reaction to fit the chamber data. Reasonably good fits to most of the reactivity data. (MR3, MR8, R8) (X)
Toluene Diisocyanate			77		1	A highly simplified parameterized mechanism was adjusted to fit the chamber data. Reasonably good fits were obtained, with no consistent biases. (MR3, MR8, R8) (B).

Table 48 (continued)

Run Type	Figure no. [a]				Fit [c]	Comments [d,e]
	C	D	R	P		
Para Toluene Isocyanate			78		1	A highly simplified parameterized mechanism was adjusted to fit the chamber data. Reasonably good fits were obtained, with no consistent biases. (MR3, MR8, R8) (B).
N-Methyl-2-Pyrrolidone			79		1	The nitrate yield in the OH reaction was adjusted to fit the chamber data. Reasonably good fits to the reactivity data were obtained.
n-Propyl Bromide			80		3	Bromine chemistry is not represented in this version of the mechanism. The highly simplified "placeholder" mechanism used for all halocarbons (with the appropriate OH rate constant) somewhat overpredicted reactivity in the high NOx runs and incorrectly predicted positive reactivity in the low NOx runs, where the compound actually inhibited O3. (MR3, MR8, R8) (B)
n-Butyl Bromide			80		3	Bromine chemistry is not represented in this version of the mechanism. The highly simplified "placeholder" mechanism used for all halocarbons (with the appropriate OH rate constant) approximately fit initial reactivity data in the MR3 experiments, overpredicted reactivity in the high MR8 runs by about a factor of 2, and incorrectly predicted positive reactivity in the low NOx runs, where the compound actually inhibited O3. No adjustments were made. (MR3, MR8, R8) (B)
Trichloroethylene			81		3	Chlorine chemistry is not represented in this version of the mechanism. The highly simplified "placeholder" mechanism used for all halocarbons (with the appropriate OH rate constant) gave surpassingly good fits to the reactivity data, considering the crudity of the mechanism and the fact that no adjustments were made. (MR3, MR8, R8) (B)
Mineral Spirits Samples			82		1	Model fits the reactivity data to within the experimental uncertainties for samples "B", "C", and "D", but slightly underpredicted the reactivity of sample "A" under higher NOx conditions. Much better mechanism performance than observed previously (Carter et al, 1997f). No adjustments were made. (MR3, MR8, R8) (B)
"MIX-A" Mix		83				Fits are variable, but the model does not have a significant bias for the group as a whole. D(O3-NO) is predicted to within +/- 40% for most runs.
"SURG-4" Mix		84				Model has definite bias towards overpredicting O3 in these experiments, and even more towards overpredicting initial NO oxidation rate. Possible experimental problems with these low NOx runs; NOx zeros do not appear to be correct in some cases.
"SURG-7" Mix		85				Model has a tendency to overpredict d(O3-NO) by about 20% on the
"SURG-8S" Mix		86				Fits are highly variable for this group, with the model having a bias towards underpredicitng by about 20%.
"SURG-3M" Mix		87				Fits are variable, with overall biases being small but somewhat different in different chambers. D(O3-NO) is usually simulated to within +/- 30%.
"SURG-8M" Mix		88				Generally good fits with no or small overall bias. D(O3-NO) is usually simulated by +/- 20%.

Table 48 (continued)

Run Type	Figure no. [a] C	 D	 R	 P	Fit [c]	Comments [d,e]
"SURG-8" Mix		89				Generally good fits with no or small overall bias. D(O3-NO) is usually simulated by +/- 20%.
"SURG-X" Mix		90				Most runs are reasonably well simulated, but there are more cases where d(O3-NO) is overpredicted than underpredicted.

[a] Figure types codes: C = concentration/time plots; D = distribution plots; R = reactivity data; P = product data plots.

[b] Types of experiments used to evaluate mechanisms for VOC or mixture is indicated in parentheses after comments. S = single VOC - NOx, MR3 = "MR3" reactivity, etc. (See Table 45 for reactivity experiment type codes.). Types of light source indicated in parentheses after experiment type codes. B = blacklight chambers, X = xenon arc chambers, O = outdoor chambers.

[c] Fit codes for evaluations of mechanisms of individual VOCs are as follows:

1 Model fits data to within experimental uncertainty, no consistent biases, or biases are considered not large enough to be significant. This code also used if data are not adequate to sufficiently evaluate mechanism.

2 Some poor fits or biases indicate possible mechanism problems or needs for improvement.

3 The mechanism either does not satisfactorily fit the data, or is considered to be too unrepresentative of the chemistry involved to give reliable atmospheric reactivity predictions.

[d] Model tends to consistently underpredict IntOH reactivities in all low NOx (e.g., R8) incremental reactivity experiment, possibly due to problems in representation of radical reactions under low NOx conditions. This is not noted in the comments for the individual VOCs.

[e] Although there are a large number of single VOC - NOx runs for n-butane and some for a few other alkanes, these are not useful for mechanism evaluation because of their large sensitivity to the chamber radical source (Carter and Lurmann, 1990).

VI. LUMPED MECHANISM FOR AIRSHED MODELS

Airshed model applications require simulations of highly complex mixtures of large numbers of VOCs, and in most cases it is not necessary or practical to represent each of them separately. For such applications, models with lumped model species that represent reactions of a large number of species with similar reaction rates and mechanisms, are generally employed. Even for VOC reactivity assessment it is only really necessary to separately represent the VOC whose reactivity is being assessed, the reactions of most of the other VOCs present in the ambient simulation can be represented using appropriate lumped model species. This was the approach that was employed in our previous reactivity studies (e.g., Carter and Atkinson, 1989a, Carter, 1994a), and continues to be the approach used in this work.

In this section, we describe the lumping approach we recommend for use when employing this mechanism in regional model simulations, which is also the approach used in the EKMA models when calculating the reactivity scales discussed in Section VII.A. Before discussing the specific approach, we briefly summarize the various types of lumping methods that can be employed, and the factors that need to be considered when determining the recommended method.

A. Summary of Lumping Approaches

As with the previous mechanism (Carter, 1988), two different approaches, referred to as lumped molecule and variable lumped parameter condensation, can be employed to represent VOCs in complex mixtures. A third approach, referred to here as fixed parameter condensation is used in condensed models such as the LCC (Lurmann et al, 1987), RADM-2 (Stockwell et al, 1990), and RACM (Stockwell et al, 1997) can also be employed, and may be appropriate or necessary in some applications. A fourth approach, referred to as lumped structure is employed in the widely-used Carbon Bond mechanism (Gery et al, 1988) and was used to represent hydroperoxides in the previous SAPRC mechanism (Carter, 1990), though it is not used in the current mechanism. These are discussed below.

1. Lumped Molecule Approach

The lumped molecule approach involves representing the VOC by a model species in the base mechanism, on a molecule-for-molecule basis. This is the same as the approach used to represent most of the product species in the various VOC reactions, as discussed above in Section II.C.1. For example, the lumped higher aldehyde species, RCHO, can be used to represent all aldehydes present in emissions or other complex mixtures, if it is not necessary to represent them explicitly for the purpose of estimating their reactivities. Although this is less accurate than the lumped or fixed parameter approaches discussed below, it is appropriate for classes of compounds that are believed to react very similarly, or are not sufficiently important in the emissions to justify more complex approaches.

2. Variable Lumped Parameter Approach

The variable lumped parameter approach representing a group of VOCs that react with similar rate constants with model species whose kinetic and product yield parameters are weighted averages of the mixture of VOCs they are being used to represent. This is potentially the most accurate lumping method, permitting lumping of species with quite different mechanisms, provided that they react with the same species with similar rate constants, or at least have similar kinetic reactivities (fractions reacted) in the model scenarios (Carter, 1988). Two weighting methods can be used when deriving the parameter values given the mixture of emitted or ambient VOCs being represented.

In reactivity weighting, the contribution of a given VOC to the parameters derived for the lumped model species is proportional to the amount of the VOC that is estimated to react in the scenario, which, if the VOC reacts only with OH radicals, is given by

$$\text{Amount Reacted} = \text{Amount Emitted} \cdot \text{Fraction Reacted} \qquad \text{(XXXI)}$$

where

$$\text{Fraction Reacted} = \text{Kinetic Reactivity} \approx (1 - e^{-kOH \cdot IntOH}) \qquad \text{(XXXII)}$$

and kOH is the OH radical rate constant and IntOH is an effective integrated OH radical rate constant that is characteristic of the type of model scenario (Carter, 1988; Middleton et al, 1990), which is estimated to be ~110 ppt-min for regional model applications (Middleton et al, 1990). This is most appropriate when lumping VOCs with widely varying kinetic reactivities, as is necessary when lumping slowly reacting VOCs into a single group. However, this has the disadvantage that the number of moles of model species is different from the number of moles of compounds being represented, which detracts from the chemical realism of the mechanism. In addition, the value of IntOH appropriate for a single day urban or EKMA simulation will not be appropriate for a multi-day regional simulation, and vise-versa.

In molar weighting, the contribution of a given VOC to the parameters of the lumped model species is simply proportional to the amount of VOC emitted or input into the scenario. This is appropriate if the VOCs being lumped have similar kinetic reactivities, as is generally the case for rapidly reacting VOCs[21]. This lumping is also more chemically realistic because it preserves moles, and does not depend on any aspect of the scenario other than the emissions.

Note that a variant of the lumped parameter approach is used when representing the individual VOCs for the purpose of evaluating the mechanism against chamber data or calculating its atmospheric reactivity. However, in this case there is no lumping involved, one model species, with parameters set equal to those of the compound being represented, is used for each VOC whose mechanism is being evaluated or whose reactivity is being calculated. The one exception is model simulations of experiments or reactivities of complex mixtures (such as mineral spirits or vehicle exhausts), where species in the mixtures are lumped in the same way as recommended for regional model simulations.

Although potentially the most accurate, the lumped parameter approach has the disadvantages that nature of the model species depends on the emissions, and requires special emissions processing procedures that involves software that is not available on most modeling systems. In addition, emissions speciation is often highly uncertain, and model simulations using scenario-specific parameters for the lumped species may not necessarily be significantly more accurate than those using parameters derived using a “typical” or “representative” ambient mixture or emissions profile.

3. Fixed Parameter Approach

The fixed parameter approach is a variant of the lumped parameter approach where the parameters for the lumped species are derived using a typical or representative ambient mixture or emissions profile, and then used in all subsequent model applications regardless of the actual emissions

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[21] VOCs with OH rate constants $\geq 10^{-11}$ cm^3 $molec^{-1}$ s^{-1} have kinetic reactivities greater than 80% for IntOH = 110 ppt-min. Since kinetic reactivities can be no greater than 100%, this means that kinetic reactivities of VOCs with this or higher rate constants are all within ± 20%.

involved. This is the approach that was used in the RADM-2 mechanism (Stockwell et al, 1990), where the parameters for the lumped alkane, alkene, and aromatic species were derived based on the RADM-2 emissions inventory, and then held fixed for all model applications using that mechanism (Carter and Lurmann, 1990). This greatly simplifies mechanism implementation and emissions processing, and is potentially as accurate as the variable lumped parameter approach if the emissions composition is uncertain or reasonably well represented by the composition used when deriving the mechanism.

In this work we present a fixed parameter version of this mechanism that can be used to permit implementation of this mechanism in modeling systems that do not support the emissions processing needed for implementing the variable parameter approach. This is discussed in Section VI.B, below. It is based on the ambient mixture of VOCs obtained from analysis of air quality data (Jeffries et al, 1989; Carter, 1994a,b) which was used to represent the base case reactive organic gas (ROG) mixture in the previous (e.g., Carter, 1994a,b) and current (see Section VII) reactivity scale calculation.

However, it is recommended that the variable parameter approach be used in model applications where it is believed that the composition of the initial and/or emitted VOC species are known with reasonable accuracy. In particular, it should be used in applications where the composition of the emitted or ambient species is believed to be significantly different from that of the base ROG mixture used to derive the lumped parameters in the fixed parameter mechanism.

4. Lumped Structure Approach

The widely-used Carbon Bond IV mechanism uses the “lumped structure” approach, where different parts of the molecule are treated as if they react independently (Gery et al, 1988). This permits representation of a large number of compounds with a relatively small number of model species, and performs reasonably well in simulating experiments with complex mixtures that are representative of those used when the mechanism was developed (Gery et al, 1988). However, as seen from the detailed mechanistic discussion given above in Section III, different parts of molecules actually do not react independently. Examples of where the lumped structure approximation break down include the dependence of nitrate yields on the size of the peroxy radicals (Section III.I) the importance of internal isomerization and rearrangement reactions undergone by larger alkoxy radicals (Section III.J). For that reason, this approximation is not used in the current version of the mechanism.

B. Recommended Lumping for Regional Model Applications

1. Lumping Approach

The optimum lumping approach in terms of minimizing the number of model species without introducing nonnegligible approximations depends on the model application and type of scenario employed. The use of the variable parameter approach permits a high degree of lumping with very little approximation in single box or EKMA model scenarios, which involve only a single day simulation with all the VOCs being introduced together (Carter, 1988). However, the requirements of multi-cell and multi-day regional models are more demanding. This is because different compositions of VOCs can be emitted at different times and locations, so no single parameterization may represent the emissions profile in all locations at all times. In addition, representing slowly reacting VOCs with more rapidly reacting model species using reactivity weighting may not appropriately represent these VOCs in multi-day simulations, since they would persist longer than the model species used to represent them. More lumped classes are therefore needed to minimize the time and space variation of the reactivity characteristics of the VOCs represented by any given lumped species, and to permit the slowly reacting species to be more appropriately represented in multi-day scenarios.

The approach adopted in this work is to recommend a lumping approach that addresses the requirements of regional, multi-cell, multi-day model applications. Since that is the most demanding requirement, this will then give a mechanism that should be appropriate for most applications, albeit with more species than may be necessary for some applications such as EKMA. This permits use of a consistent mechanism and degree of condensation, regardless of the application.

Table 49 gives a summary of the lumped classes recommended for use with regional models. The lumping for the more reactive classes of compounds are similar to that used in other mechanisms such as the RADM-2 (Stockwell et al. 1990) and RACM (Stockwell et al, 1997) mechanisms, and condensed versions of the SAPRC-90 mechanism (Lurmann et al, 1991; Kumar et al, 1995). However, there is a larger number of slowly reacting “alkane and others” classes, to allow for appropriate representations of compounds such as ethane and propane in regional model simulations. Separate classes are used for ethane and propane and compounds with similar reactivities, with non-methane organics that react slower than half that of ethane being treated as inert. The dividing lines in terms of OH rate constants are somewhat arbitrary in the case of the alkane classes, but are chosen in the recommended lumping to be consistent with those used in the RADM-2 emissions processing system, as discussed by Middleton et al (1990). This permits the mechanism to be used in models with emissions data processed for the RADM-2 mechanism, as discussed in the following section.

Biogenic compounds are represented in separate classes because their emissions can have significantly different spatial and temporal profiles than anthropogenic emissions, and their reactivity characteristics are quite different from those of the anthropogenic alkenes they otherwise would be lumped with. Isoprene, which is the dominant biogenic in many U.S. scenarios, is represented explicitly, and a separate lumped class is used is used for terpenes.

Note that the lumped molecule assignments takes advantage of the fact that this version of the mechanism uses a relatively large number of model species represent reactive products, compared to previous mechanisms. This permits, for example, unsaturated aldehydes and ketones to be represented using isoprene product species whose mechanisms are probably closer to the compounds being represented than the generic higher saturated aldehyde or ketone species used in most mechanisms. Although the saturated higher aldehydes and ketones could be represented using the lumped parameter approach since explicit mechanisms for such compounds can be generated, the lumped molecule approach is employed because they are not sufficiently important in emissions or ambient air masses to justify using separate model species for them.

Table 49 shows that that the lumping approach for representing most oxygenated species when present in mixtures is the same as used when representing them when formed as products in the oxidations of other VOCs, as discussed above in Sections II.C.1 and II.C.2. The major exceptions are oxygenated compounds that react only with OH radicals, such as esters, acids, etc. These are represented using the appropriate lumped alkane class (ALK1, … ALK5) depending on their OH rate constant when they are primary VOCs, but are represented by MEK, PROD2, or (for acids) RCO-OH if they are formed as reactive products of other VOCs. This is because in principle the use of lumped parameter species can permit a more accurate representation of the impacts of these compounds when present in complex mixtures, if the parameters are derived to take the contributions of these species into account. The MEK and PROD2 model species are only used to represent ketones, whose photolysis reactions cannot be represented using lumped alkane classes.

Table 49. Summary of lumped classes and lumped molecule representations recommended for representing complex mixtures in ambient model applications.

Model Species	Description
Emitted Compounds Represented Explicitly	
CH4	Methane
ETHENE	Ethene
ISOPRENE	Isoprene
HCHO	Formaldehyde
ACET	Acetone
MEOH	Methanol
PHEN	Phenol
Lumped Molecule Groups	
CCHO	Acetaldehyde and Glycolaldehyde
RCHO	Lumped C3+ Aldehydes
MEK	Ketones that react with OH radicals slower than 5 x 10^{-12} cm^3 $molec^{-2}$ sec^{-1}.
PROD2	Ketones that react with OH radicals faster than 5 x 10^{-12} cm^3 $molec^{-2}$ sec^{-1}.
CRES	Cresols
BALD	Aromatic aldehydes (e.g., benzaldehyde)
METHACRO	Methacrolein and acrolein
ISOPROD	Unsaturated aldehydes other than acrolein and methacrolein.
MVK	Unsaturated ketones
Unreactive Compounds	
INERT	Compounds other than CO or methane that do not react, or react only with OH with a rate constant less than approximately half that of ethane, or ~2 x 10^2 ppm-1 min-1.
Lumped Parameter Groups (Lumped using molar weighting except as indicated)	
ALK1	Alkanes and other non-aromatic compounds that are react only with OH, and have an OH rate constant (kOH) between ~2 x 10^2 and 5 x 10^2 ppm-1 min-1. (Primarily ethane)
ALK2	Alkanes and other non-aromatic compounds that react only with OH, and have kOH between 5 x 10^2 and 2.5 x 10^3 ppm-1 min-1. (Primarily propane and acetylene)
ALK3	Alkanes and other non-aromatic compounds that react only with OH, and have kOH between 2.5 x 10^3 and 5 x 10^3 ppm-1 min-1.
ALK4	Alkanes and other non-aromatic compounds that react only with OH, and have kOH between 5 x 10^3 and 1 x 10^4 ppm-1 min-1.
ALK5	Alkanes and other non-aromatic compounds that react only with OH, and have kOH greater than 1 x 10^4 ppm-1 min-1.
ARO1	Aromatics with kOH < 2x10^4 ppm-1 min-1. (Primarily toluene and other monoalkyl benzenes.) Benzene and slower reacting aromatics such as halobenzens are lumped with reactivity weighting based on their OH rate constant relative to that of toluene, all others are lumped using molar weighting. Group given kOH of toluene.
ARO2	Aromatics with kOH > 2x10^4 ppm-1 min-1. (Primarily xylenes and polyalkyl benzenes)
OLE1	Alkenes (other than ethene) with kOH < 7x10^4 ppm-1 min-1. (Primarily terminal alkenes)
OLE2	Alkenes with kOH > 7x10^4 ppm-1 min-1. (Primarily internal or disubstituted alkenes)
TRP1	Biogenic alkenes other than isoprene (primarily terpenes)

The mechanisms for the model species ALK_n, ARO_n, OLE_n, and TRP1 are derived depending on the mixture of VOCs they are being used to represent, which depends on the emissions or initial VOCs in the model simulation. To conserve moles and for greater chemical realism, it is recommended that molar weighting rather reactivity weighting be used in most cases. Note that for the lowest reactivity "alkane and others" class, ALK1, this means that compounds reacting much slower than the rate constant for the class should not be lumped with the class. For this reason, compounds with OH rate constants lower than about half that of ethane are treated as "inert", i.e., not lumped with ALK1. (The one exception is methane, which, because of the relatively large amount present, is represented explicitly.) Although these slowly reacting compounds, such as HCFC's, etc., may eventually react to some extent in multi-day regional episodes, the amounts emitted and therefore the amounts reacted are very small, and would have negligible effect. Of course, if the reactivities or persistence of these compounds are of interest, then separate model species should be used to represent them.

The one area where it is recommended that reactivity weighting be used concerns the representation of benzene and other slowly reacting aromatics. Because they are emitted in relatively small amounts and contribute relatively little to the overall reactivity of the mixture, it is not considered worthwhile to represent them separately, so they are represented using the ARO1 group, which is dominated by toluene and the alkylbenzenes. However, benzene has a kinetic reactivity which is less than 1/3 that of toluene, so representing it using a group that represents primarily monoalkylbenzenes would not be appropriate. For that reason, the recommended approach is to use reactivity weighting for benzene and other slowly reacting when being represented by the ARO1 group, but use molar weighting for toluene and the alkylbenzenes, and give the group the OH rate constant of toluene. If an IntOH of 110 ppt-min, as used for the RADM-2 mechanism (Middleton et al, 1990), this means that one mole of benzene would be represented by 0.295 moles of ARO1. Of course, if calculations of the persistence or role of benzene are of particular interest, then a separate model species should be used for this purpose.

The mechanisms for the model species ALK_n, ARO_n, OLE_n, and TRP1 can be derived from the emissions inventory as discussed by Carter (1988). This requires assigning all the emissions classes in the emissions inventory to detailed model species in the present mechanism, which is beyond the scope of this report. However, they can also be derived using the mixture of reactive organic measured in ambient air, as discussed in the following section.

2. Fixed Parameter Mechanism

Although state-of-the-art modeling systems should include the ability to derive the most appropriate parameters for the model species from the VOC emissions data, in practice very few modeling systems presently support this capability. In addition, use of variable parameter mechanism to represent ambient or emitted VOCs may not be necessary or appropriate in all cases. These include model applications where the compositions of the emissions input are uncertain or highly variable, or model applications that employ idealized scenarios representing a wide distribution of conditions are employed. The latter includes developing general reactivity scales such as the Carter (1994a) scales that are updated in this work. Therefore, a fixed parameter version of this mechanism is derived to address these needs, as discussed in this section.

The base case model scenarios used to derive the Carter (1994a) reactivity scales use a standard mixture of hydrocarbons and oxygenates to represent the reactive VOCs that are emitted or initially present in the scenarios. The composition of this mixture, which is given in Table 50, was derived from an analysis of hydrocarbons in urban atmospheres in the United States (Jeffries et al, 1998) and from oxygenate measurements in the California South Coast Air Basin (Carter, 1994a,b and references therein). Table 50 also shows the detailed model species used to represent each of measured components in the

Table 50. Composition of the base ROG mixture used in the reactivity simulations and to derive the lumped parameters in the fixed parameter mechanism.

VOC Name	Moles VOC / Mole C Mix	Represented By	Lumped with
Ethane	0.01685	ETHANE	ALK1
Propane	0.01413	PROPANE	ALK2
n-Butane	0.01807	N-C4	ALK3
n-Pentane	0.00613	N-C5	ALK4
n-Hexane	0.00132	N-C6	ALK4
n-Heptane	0.00120	N-C7	ALK5
n-Octane	0.00074	N-C8	ALK5
n-Nonane	0.00074	N-C9	ALK5
n-Decane	0.00184	N-C10	ALK5
n-Undecane	0.00016	N-C11	ALK5
n-Dodecane	0.00033	N-C12	ALK5
n-Tridecane	0.00001	N-C13	ALK5
Isobutane	0.00788	2-ME-C3	ALK3
Iso-Pentane	0.01516	2-ME-C4	ALK4
2-Methyl Pentane	0.00355	2-ME-C5	ALK4
3-Methylpentane	0.00253	3-ME-C5	ALK4
2,2-Dimethyl Butane	0.00046	22-DM-C4	ALK3
2,3-Dimethyl Butane	0.00095	23-DM-C4	ALK4
2,4-Dimethyl Pentane	0.00060	24-DM-C5	ALK4
3-Methyl Hexane	0.00127	3-ME-C6	ALK5
2,3-Dimethyl Pentane	0.00112	23-DM-C5	ALK5
Cyclopentane	0.00071	CYCC5	ALK4
Methylcyclopentane	0.00161	ME-CYCC5	ALK4
Cyclohexane	0.00068	CYCC6	ALK5
Methylcyclohexane	0.00068	ME-CYCC6	ALK5
Ethylcyclohexane	0.00018	ET-CYCC6	ALK5
Branched C6 Alkanes	0.00024	0.5 23-DM-C4 + 0.25 3-ME-C5 + 0.25 2-ME-C5	ALK4
Branched C7 Alkanes	0.00209	0.5 24-DM-C5 + 0.25 3-ME-C6 + 0.25 2-ME-C6	0.5 ALK4 + 0.5 ALK5
Branched C8 Alkanes	0.00403	0.5 24-DM-C6 + 0.25 4-ME-C7 + 0.25 2-ME-C7	ALK5
Branched C9 Alkanes	0.00171	0.5 24-DM-C7 + 0.25 4-ME-C8 + 0.25 2-ME-C8	ALK5
Branched C10 Alkanes	0.00156	0.5 26DM-C8 + 0.25 4-ME-C9 + 0.25 2-ME-C9	ALK5
Branched C11 alkanes	0.00016	0.5 26DM-C9 + 0.25 4-ME-C10 + 0.25 3-ME-C10	ALK5
Branched C12 Alkanes	0.00033	0.5 36DM-C10 + 0.25 5-ME-C11 + 0.25 3-ME-C11	ALK5
Branched C13 Alkanes	0.00001	0.5 36DM-C11 + 0.25 5-ME-C12 + 0.25 3-ME-C12	ALK5
C7 Cycloalkanes	0.00012	ME-CYCC6	ALK5
Ethene	0.01346	ETHENE	ETHE
Propene	0.00318	PROPENE	OLE1
1-Butene	0.00115	1-BUTENE	OLE1
C4 Terminal Alkenes	0.00014	1-BUTENE	OLE1
3-Methyl-1-Butene	0.00032	3M-1-BUT	OLE1
1-Pentene	0.00080	1-PENTEN	OLE1
1-Hexene	0.00033	1-HEXENE	OLE1
Isobutene	0.00115	ISOBUTEN	OLE2
2-Methyl-1-Butene	0.00092	2M-1-BUT	OLE2
trans-2-Butene	0.00115	T-2-BUTE	OLE2
cis-2-Butene	0.00091	C-2-BUTE	OLE2
2-Methyl-2-Butene	0.00052	2M-2-BUT	OLE2
1,3-Butadiene	0.00062	13-BUTDE	OLE2
Isoprene	0.00130	ISOPRENE	ISOP
Cyclohexene	0.00018	CYC-HEXE	OLE2
C5 Terminal Alkenes	0.00044	1-PENTEN	OLE1
C6 Terminal Alkenes	0.00223	1-HEXENE	OLE1

Table 50 (continued)

VOC Name	Moles VOC / Mole C Mix	Represented By	Lumped As
C7 Terminal Alkenes	0.00119	1-HEPTEN	OLE1
C8 Terminal Alkenes	0.00024	1-OCTENE	OLE1
C9 Terminal Alkenes	0.00052	1-C9E	OLE1
C10 Terminal Alkenes	0.00010	1-C10E	OLE1
C11 Terminal Alkenes	0.00019	1-C11E	OLE1
C4 Internal Alkenes	0.00014	0.5 T-2-BUTE + 0.5 C-2-BUTE	OLE2
C5 Internal Alkenes	0.00317	0.5 C-2-PENT + 0.5 T-2-PENT	OLE2
C6 Internal Alkenes	0.00100	0.5 C-2-C6E + 0.5 T-2-C6E	OLE2
C7 Internal Alkenes	0.00044	T-3-C7E	OLE2
C8 Internal Alkenes	0.00021	T-4-C8E	OLE2
C9 Internal Alkenes	0.00024	T-4-C9E	OLE2
C10 Internal Alkenes	0.00010	T-4-C10E	OLE2
C11 Internal Alkenes	0.00019	T-5-C11E	OLE2
C7 Cyclic or di-olefins	0.00019	T-2-C7E	OLE2
a-Pinene	0.00051	A-PINENE	TRP1
3-Carene	0.00019	3-CARENE	TRP1
C9 Styrenes	0.00048	STYRENE	ARO2
C10 Styrenes	0.00036	STYRENE	ARO2
Benzene	0.00329	BENZENE	0.295 ARO1
Toluene	0.00923	TOLUENE	ARO1
Ethyl Benzene	0.00128	C2-BENZ	ARO1
n-Propyl Benzene	0.00036	N-C3-BEN	ARO1
Isopropyl Benzene (cumene)	0.00019	I-C3-BEN	ARO1
C9 Monosub. Benzenes	0.00016	N-C3-BEN	ARO1
s-Butyl Benzene	0.00023	S-C4-BEN	ARO1
C10 Monosub. Benzenes	0.00018	N-C3-BEN	ARO1
C11 Monosub. Benzenes	0.00065	N-C3-BEN	ARO1
C12 Monosub. Benzenes	0.00002	N-C3-BEN	ARO1
o-Xylene	0.00183	O-XYLENE	ARO2
p-Xylene	0.00218	P-XYLENE	ARO2
m-Xylene	0.00218	M-XYLENE	ARO2
C9 Disub. Benzenes	0.00247	0.34 M-XYLENE + 0.33 O-XYLENE + 0.33 P-XYLENE	ARO2
C10 Disub. Benzenes	0.00154	0.34 M-XYLENE + 0.33 O-XYLENE + 0.33 P-XYLENE	ARO2
C11 Disub. Benzenes	0.00010	0.34 M-XYLENE + 0.33 O-XYLENE + 0.33 P-XYLENE	ARO2
C12 Disub. Benzenes	0.00009	0.34 M-XYLENE + 0.33 O-XYLENE + 0.33 P-XYLENE	ARO2
1,3,5-Trimethyl Benzene	0.00072	135-TMB	ARO2
1,2,3-Trimethyl Benzene	0.00075	123-TMB	ARO2
C9 Trisub. Benzenes	0.00236	0.34 135-TMB + 0.33 123-TMB + 0.33 124-TMB	ARO2
C10 Trisub. Benzenes	0.00160	0.34 135-TMB + 0.33 123-TMB + 0.33 124-TMB	ARO2
C11 Trisub. Benzenes	0.00010	0.34 135-TMB + 0.33 123-TMB + 0.33 124-TMB	ARO2
C12 Trisub. Benzenes	0.00009	0.34 135-TMB + 0.33 123-TMB + 0.33 124-TMB	ARO2
C10 Tetrasub. Benzenes	0.00042	0.34 135-TMB + 0.33 123-TMB + 0.33 124-TMB	ARO2
Acetylene	0.00974	ACETYLEN	ALK2
Formaldehyde	0.00792	FORMALD	HCHO
Acetaldehyde	0.00477	ACETALD	CCHO
Propionaldehyde	0.00070	PROPALD	RCHO
C4 aldehydes	0.00031	1C4RCHO	RCHO
C5 Aldehydes	0.00107	1C5RCHO	RCHO
C6 Aldehydes	0.00073	1C6RCHO	RCHO
Benzaldehyde	0.00016	BENZALD	BALD
Acetone	0.00309	ACETONE	ACET
Methyl Ethyl Ketone	0.00110	MEK	MEK

.mixture, and groups used to represent them in the lumped mechanism. Since this mixture is based on VOC measurements in a variety of urban areas, it serves as an appropriate basis for deriving parameters for those lumped species that represent anthropogenic emissions.

This base ROG mixture cannot serve as a basis for deriving the parameters for the biogenic terpene (TRP1) group, since that mixture represents purely ambient VOCs. For this we use the estimated annual North American biogenic terpene emissions rates summarized by Guenther et al (1999), where the five most abundant terpenes are as follows:

Terpene	Tg C/year
α-Pinene	4.3
β-Pinene	3.1
Δ^3 Carene	1.9
Sabinene	1.1
d-Limonene	1.0

Although other terpenes listed by Guenther et al (1999) total more than 3 Tg C/year and other classes of compounds, such as alcohols and aldehydes, are also important in the biogenic inventory, this profile is used as the basis for deriving the recommended parameters for the TRP1 lumped group for the present mechanism. Note that since the appropriate lumped group used for anthropogenic species can be used to represent the biogenic alcohols and aldehydes, the contributions of these compounds to the biogenic emissions do not affect the parameters derived for TRP1.

Table 51 gives a summary of the compounds used to derive the mechanism for each of the lumped model species in the fixed parameter mechanism. The relative contributions of the species to the parameters of each group are also shown. Except for benzene (see discussion above) the relative contributions were determined by the mole fractions of the compounds in the mixtures.

The rate constants and mechanisms for the reactions for these lumped species that are derived using this set of anthropogenic base ROG and biogenic terpene mixtures are given in Table A-3 in Appendix A. The reactions of ethene and isoprene that are used for these explicitly represented species are also shown on that table. These explicit and lumped primary VOC reactions are added to the base mechanism to constitute the full fixed parameter SAPRC-99 mechanism for use in ambient simulations. This mechanism is used in the base case simulations in the incremental reactivity calculations discussed in Section VII.

It should be emphasized, however, that for model applications where the emissions inventory is known, or where the effects of changing the composition of the inventory is being assessed, the parameters should be derived using the specific inventories used in the simulations. This is particularly true if the inventories indicate significant contributions of classes of compounds that are not in the base ROG mixture used to derive the current fixed parameter mechanism. In particular, the base ROG mixture consists primarily of the hydrocarbons of the type found in gasoline vehicle exhausts, and the parameters derived using this mixture may not be appropriate if sources involving emissions of other types of VOCs, such as glycols or alcohols, are important.

Table 51. Summary of compounds used to derive mechanisms for lumped parameter groups in the fixed parameter mechanism.

Compound	Cont'n	Compound	Cont'n
ALK1		ARO2	
Ethane	100%	m-Xylene	22%
ALK2		p-Xylene	22%
Propane	59%	o-Xylene	20%
Acetylene	41%	1,3,5-Trimethyl Benzene	14%
ALK3		1,2,3-Trimethyl Benzene	14%
n-Butane	68%	1,2,4-Trimethyl Benzene	9%
Isobutane	30%	OLE1	
2,2-Dimethyl Butane	2%	Propene	29%
ALK4		1-Hexene	24%
Iso-Pentane	45%	1-Butene	12%
n-Pentane	18%	1-Pentene	11%
2-Methyl Pentane	11%	1-Heptene	11%
3-Methylpentane	8%	1-Nonene	5%
2,4-Dimethyl Pentane	5%	3-Methyl-1-Butene	3%
Methylcyclopentane	5%	1-Octene	2%
n-Hexane	4%	1-Undecene	2%
2,3-Dimethyl Butane	3%	1-Decene	1%
Cyclopentane	2%	OLE2	
ALK5		trans-2-Pentene	13%
2,4-Dimethyl Hexane	11%	cis-2-Pentene	13%
n-Decane	10%	trans-2-Butene	10%
3-Methyl Hexane	10%	Isobutene	10%
n-Heptane	7%	cis-2-Butene	8%
2,3-Dimethyl Pentane	6%	2-Methyl-1-Butene	8%
2-Methyl Heptane	6%	Styrene	7%
4-Methyl Heptane	6%	1,3-Butadiene	5%
2,4-Dimethyl Heptane	5%	2-Methyl-2-Butene	4%
Methylcyclohexane	4%	Trans-2-Hexene	4%
2,6-Dimethyl Octane	4%	Cis-2-Hexene	4%
n-Nonane	4%	Trans-3-Heptene	4%
n-Octane	4%	Trans-4-Nonene	2%
Cyclohexane	4%	Trans-4-Octene	2%
2-Methyl Hexane	3%	Trans-2-Heptene	2%
4-Methyl Octane	2%	Trans-5-Undecene	2%
2-Methyl Octane	2%	Cyclohexene	1%
4-Methyl Nonane	2%	Trans-4-Decene	1%
2-Methyl Nonane	2%	TRP1	
n-Dodecane	2%	a-Pinene	38%
Ethylcyclohexane	1%	b-Pinene	27%
n-Undecane	1%	3-Carene	17%
3,6-Dimethyl Decane	1%	Sabinene	10%
ARO1		d-Limonene	9%
Toluene	70%		
n-Propyl Benzene	10%		
Ethyl Benzene	10%		
Benzene [a]	7%		
s-Butyl Benzene	2%		
Isopropyl Benzene (cumene)	1%		

[a] Reactivity weighting factor of 0.295 used for benzene. See text.

VII. ATMOSPHERIC REACTIVITY ESTIMATES

To estimate the effects of VOC emissions on ozone formation under conditions more representative of polluted urban atmospheres, incremental reactivities were calculated for all VOCs that are represented in the current mechanism. This includes not only the VOCs whose mechanisms were derived or estimated as discussed in the previous sections, but also VOCs, or mixtures of isomeric VOCs, that are represented by other VOCs using the "lumped molecule" approach. In addition to "best estimate" reactivity estimates that were derived using the mechanisms discussed above, upper limit reactivity estimates were made for the purpose of estimating maximum likely ozone impacts. The latter may be useful in some regulatory approaches as a means to take uncertainties into account. Qualitative uncertainty classifications are given for all VOCs to aid the use of uncertainty information in regulatory applications, and for determining where further studies are most needed.

Atmospheric reactivities are derived for the Maximum Incremental Reactivity (MIR) and other scales, with ozone impacts quantified in terms of both effects on peak O_3 concentration and 8-hour averages. However, the emphasis in this work is on the MIR scale because this is the scale used in the California vehicle emissions regulations (CARB, 1993), and being considered for use in consumer product regulations (CARB, 1999). Because of this, upper limit reactivity estimates are made only for the MIR scale, though an analogous approach could be applied for other scales.

A. Atmospheric Reactivity Modeling Methods

The modeling approach and scenarios used for estimating atmospheric reactivities of VOCs is generally the same as used by Carter (1994a) when developing the MIR and other scales with the SAPRC-90 mechanism. The only modification made in this work is that the MIR and other "adjusted NO_x" scales were derived by averaging the incremental reactivities of the individual adjusted NO_x scenarios (rather than by separately averaging the kinetic and mechanistic reactivities), and that reactivities are calculated for 8-hour averages rather than integrated ozone. Since the general methods and scenarios are the same as described in detail previously (Carter et al, 1994a,b), they are only briefly summarized here.

1. Scenarios Used for Reactivity Assessment

Base Case Scenarios. The scenarios employed were those used by Carter (1994a,b) to develop various reactivity scales to quantify impacts of VOCs on ozone formation in various environments. These were based on a series of single-day EKMA box model scenarios (EPA, 1984) derived by the EPA for assessing how various ROG and NO_x control strategies would affect ozone nonattainment in various areas of the country (Baugues, 1990). The characteristics of these scenarios and the methods used to derive their input data are described in more detail elsewhere (Baugues, 1990; Carter, 1994b). Briefly, 39 urban areas in the United States were selected based on geographical representativeness of ozone nonattainment areas and data availability, and a representative high ozone episode was selected for each. The initial non-methane organic carbon (NMOC) and NO_x concentra-tions, the aloft O_3 concentrations, and the mixing height inputs were based on measurement data for the various areas, the hourly emissions in the scenarios were obtained from the National Acid Precipitation Assessment Program emissions inventory (Baugues, 1990), and biogenic emissions were also included. Table 52 gives a summary of the urban areas represented and other selected characteristics of the scenarios.

Table 52. Summary of the conditions of the scenarios used for atmospheric reactivity assessment.

	Scenario	Max O$_3$ (ppb)	Max 8-Hr Avg O$_3$ (ppb)	ROG / NOx	NO$_x$ / MOIR NO$_x$	Height (kM)	Init., Emit ROG (m.mol m^{-2})	O$_3$ aloft (ppb)	Integrated OH (ppt-min)
Avg.	Max React (MIR)	189	117	3.1	1.5	1.8	15	70	139
Cond.	Max O$_3$ (MOIR)	242	166	4.5	1.0	1.8	15	70	239
	Equal Benefit (EBIR)	230	176	6.4	0.7	1.8	15	70	245
Base	Atlanta, GA	176	134	7.3	0.6	2.1	12	63	222
Case	Austin, TX	171	144	9.3	0.4	2.1	11	85	200
	Baltimore, MD	333	227	5.2	0.9	1.2	17	84	223
	Baton Rouge, LA	239	178	6.8	0.8	1.0	11	62	209
	Birmingham, AL	237	203	6.9	0.5	1.8	13	81	234
	Boston, MA	190	167	6.5	0.5	2.6	14	105	302
	Charlotte, NC	138	124	7.8	0.3	3.0	7	92	240
	Chicago, IL	266	224	11.6	0.5	1.4	25	40	181
	Cincinnati, OH	201	156	6.4	0.6	2.8	17	70	253
	Cleveland, OH	251	186	6.6	0.8	1.7	16	89	215
	Dallas, TX	221	153	4.7	1.0	2.3	18	75	219
	Denver, CO	208	146	6.3	1.0	3.4	29	57	164
	Detroit, MI	239	181	6.8	0.6	1.8	17	68	274
	El Paso, TX	186	140	6.6	0.9	2.0	12	65	154
	Hartford, CT	166	144	8.4	0.4	2.3	11	78	249
	Houston, TX	308	223	6.1	0.8	1.7	25	65	264
	Indianapolis, IN	210	153	6.6	0.7	1.7	12	52	242
	Jacksonville, FL	151	116	7.6	0.5	1.5	8	40	228
	Kansas City, MO	155	127	7.1	0.5	2.2	9	65	266
	Lake Charles, LA	272	207	7.4	0.5	0.5	7	40	262
	Los Angeles, CA	567	420	7.6	0.9	0.5	23	100	151
	Louisville, KY	210	159	5.5	0.7	2.5	14	75	300
	Memphis, TN	219	180	6.8	0.5	1.8	15	58	284
	Miami, FL	128	110	9.6	0.3	2.7	9	57	201
	Nashville, TN	162	137	8.0	0.4	1.6	7	50	251
	New York, NY	344	293	8.1	0.6	1.5	39	103	179
	Philadelphia, PA	242	175	6.2	0.8	1.8	19	53	267
	Phoenix, AZ	280	200	7.6	0.9	3.3	40	60	169
	Portland, OR	163	128	6.5	0.6	1.6	6	66	265
	Richmond, VA	234	176	6.2	0.7	1.9	16	64	252
	Sacramento, CA	204	147	6.6	0.7	1.1	7	60	235
	St Louis, MO	325	221	6.1	0.9	1.6	26	82	207
	Salt Lake City, UT	184	152	8.5	0.5	2.2	11	85	201
	San Antonio, TX	138	103	3.9	0.9	2.3	6	60	226
	San Diego, CA	193	155	7.1	0.8	0.9	8	90	169
	San Francisco, CA	255	136	4.8	1.7	0.7	25	70	66
	Tampa, FL	232	162	4.4	0.9	1.0	8	68	254
	Tulsa, OK	224	164	5.3	0.7	1.8	15	70	313
	Washington, DC	276	213	5.3	0.7	1.4	13	99	280

Several changes to the scenario inputs were made based on discussions with the California ARB staff and others (Carter, 1994b). Two percent of the initial NOx and 0.1% of the emitted NO_x in all the scenarios was assumed to be in the form of HONO. The photolysis rates were calculated using solar light intensities and spectra calculated by Jeffries (1991) for 640 meters, the approximate mid-point of the mixed layer during daylight hours. The composition of the VOCs entrained from aloft was based on the analysis of Jeffries et al. (1989).

The composition of the initial and emitted reactive organics (referred to as the "base ROG" mixture) is given on Table 50, above. It is derived from the “all city average” mixture derived by Jeffries et al (1989) from analysis of air quality data, with minor modifications as discussed by Carter (1994a,b). Note that this same mixture is used to derive the parameters for the lumped parameter products (RNO3 and PROD2) in the base mechanism, and for the lumped species in the recommended fixed parameter condensed mechanism (see Sections II.C.2 and VI.B.2, respectively).

Complete listings of the input data for the scenarios are given elsewhere (Carter, 1994b).These are referred to as "base case" scenarios, to distinguish them from those where NOx inputs are adjusted as discussed below.

Adjusted NO_x Scenarios. In addition to these 39 base case scenarios, adjusted NO_x scenarios were developed to represent different conditions of NOx availability. NO_x levels were found to be the most important factor affecting differences in relative ozone impacts among most VOCs (Carter and Atkinson, 1989a; Carter, 1994a). Because of this, separate scales were derived to represent different conditions of NO_x availability, as follows:

- In the "Maximum Incremental Reactivity" (MIR) scenarios, the NO_x inputs for each of the 39 base case scenarios are adjusted such that the final O_3 level is most sensitive to changes in VOC emissions. This represents relatively high NO_x conditions where VOC control is the most effective means to reduce ozone formation. Note that the MIR NO_x levels vary from scenario to scenario, so it is not correct to say that there is a characteristic ROG/NO_x ratio that corresponds to MIR conditions.
- In the "Maximum Ozone Incremental Reactivity" (MOIR) scenarios the NOx inputs are adjusted to yield the highest maximum O_3 concentration. This represents conditions that are optimum for ozone formation. This represents moderate NO_x conditions where O_3 formation is just starting to become NO_x limited. Generally, NO_x levels of MOIR scenarios are about 70% of those of MIR conditions (Carter, 1994a). Although O_3 formation is also sensitive to VOC control under these conditions, it is less sensitive than in the higher NO_x MIR scenarios.
- In the "Equal Benefit Incremental Reactivity" (EBIR) scenarios, the NOx inputs are adjusted such that relative changes in VOC and NOx emissions had equal effect on ozone formation. This represents conditions where O_3 formation is NO_x limited to such an extent, but not to such a large extent that VOC controls are ineffective. Generally, NO_x levels in EBIR scenarios are about 70% those of MOIR scenarios, and about half those of MIR scenarios.

As discussed by Carter (1994a), there represent respectively the high, medium and low ranges of NO_x conditions that are of relevance when assessing VOC control strategies for reducing ozone. Although lower NO_x conditions than EBIR occur in many areas (especially non-urban areas), O_3 formation under such conditions is primarily sensitive to NO_x emissions, and VOC control is not as important as NO_x control under those conditions.

Averaged Conditions Scenarios. In addition to the above, “averaged conditions” MIR, MOIR, and EBIR scenarios were developed for use for screening or sensitivity calculations. This consists of developing a scenario whose inputs are based on averaging those representing the 39 urban areas, with NO_x inputs adjusted to yield MIR, MOIR, or EBIR conditions as discussed above (Carter, 1994a,b). These scenarios are also summarized on Table 52.

2. Quantification of Atmospheric Reactivity

The reactivity of a VOC in an airshed scenario is measured by its incremental reactivity. For ambient scenarios, this is defined as the change in ozone caused by adding the VOC to the emissions, divided by the amount of VOC added, calculated for sufficiently small amounts of added VOC that the incremental reactivity is independent of the amount added[22].

$$\mathrm{IR(VOC, Scenario)} = \lim_{VOC \to 0} \left[\frac{\mathrm{O_3(Scenario\ with\ VOC)\ \text{-}\ O_3(Base\ Scenario)}}{\mathrm{Amount\ of\ VOC\ Added}} \right] \qquad \text{(XXXIII)}$$

The specific calculation procedure is discussed in detail elsewhere (Carter, 1994a,b).

Incremental reactivities derived as given above tend to vary from scenario to scenario because they differ in their overall sensitivity of O_3 formation to VOCs. These differences can be factored out to some extent by using “relative reactivities”, which are defined as ratios of incremental reactivities to the incremental reactivity of the base ROG mixture.

$$\mathrm{RR(VOC, Scenario)} = \frac{\mathrm{IR(VOC, Scenario)}}{\mathrm{IR\ (Base\ ROG, Scenario)}} \qquad \text{(XXXIV)}$$

These relative reactivities can also be thought of as the relative effect on O3 of controlling emissions of the particular VOC by itself, compared to controlling emissions from all VOC sources equally. Thus, they are more meaningful in terms of control strategy assessment than absolute reactivities, which can vary greatly depending on the episode and local meteorology.

In addition to depending on the VOC and the scenario, the incremental and relative reactivities depend on how the amounts of VOC added and amounts of ozone formed are quantified. In this work, the amount of added VOC is quantified on a mass basis, since this is how VOCs are regulated, and generally approximates how VOC substitutions are made in practice. Note that relative reactivities will be different if they are quantified on a molar basis, with VOCs with higher molecular weight having higher reactivities on a mole basis than a gram basis.

Relative reactivities can also depend significantly on how ozone impacts are quantified (Carter, 1994a). Two different ozone quantification methods are used in this work, as follows:

- "Ozone Yield" incremental reactivities measure the effect of the VOC on the total amount of ozone formed in the scenario at the time of its maximum concentration. Incremental reactivities are quantified as grams O_3 formed per gram VOC added. Most previous recent studies of incremental reactivity (Dodge, 1984; Carter and Atkinson, 1987, 1989a, Chang and Rudy, 1990;

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[22] Note that this differs from how the term “incremental reactivity” is used in the context of chamber experiments. In that case, the incremental reactivity refers to the relative change observed in the individual experiments, which in general depends on the amount added.

Jeffries and Crouse, 1991) have been based on this quantification method. The MIR, MOIR, and EBIR scales of Carter (1994a) also use this quantification.

- "Max 8 Hour Average" incremental measure the effect of the VOC on the average ozone concentration during the 8-hour period when the average ozone concentration was the greatest, which in these one-day scenarios was the last 8 hours of the simulation. This provides a measure of ozone impact that is more closely related to the new Federal ozone standard that is given in terms of an 8 hour average. This quantification is used for relative reactivities in this work.

In previous reports, we have reported reactivities in terms of integrated O_3 over a standard concentration of 0.09 or 0.12 ppm. This provides a measure of the effect of the VOC on exposure to unacceptable levels of ozone. This is replaced by the Max 8 Hour Average reactivities because it is more representative of the new Federal ozone standard and because reactivities relative to integrated O_3 over a standard tend to be between those relative to ozone yield and those relative to 8-hour averages. Therefore, presenting both ozone yield and maximum 8-hour average relative reactivities should be sufficient to provide information on how relative reactivities vary with ozone quantification method. Incremental reactivities are quantified as ppm O_3 per milligram VOC emitted per square meter.

If a reactivity scale is developed based on incremental reactivities in more than one scenario, then the method used to derive the scale from the reactivities in the individual scenarios will also affect the scale. Although as discussed by Carter (1994a) a number of aggregation methods can be used, in this work we use only simple averaging of incremental or relative reactivities, as discussed below. Note that this differs somewhat from the method used by Carter (1994a) to derive the MIR and other adjusted NO_x scales, where averages of kinetic and mechanistic reactivities were used.

Based on these considerations, reactivities in the following scales were derived in this work, as follows:

- The MIR scale consists of averages of the incremental reactivities in the 39 MIR scenarios (i.e., the 39 base case scenarios with NO_x adjusted to represent MIR conditions), with O_3 quantified by ozone yields, and VOCs quantified by mass. The units are grams O_3 formed per gram VOC added.
- The MOIR and EBIR scales are derived from averages of the ozone yield incremental reactivities in the 39 MOIR or EBIR scenarios, in a manner analogous to the derivation of the MIR scale.
- The Averaged Conditions MIR, MOIR, and EBIR scales are the ozone yield incremental reactivities in the corresponding averaged conditions scenario. For most VOCs, the averaged conditions reactivities are very close to those derived from the 39 adjusted NO_x scales as discussed above.
- The Base Case O_3 Yield Scales are O_3 yield incremental and relative reactivities in the 39 base case scenarios. Thus there are 39 such scales, one for each of the 39 urban areas. Averages and standard deviations of the relative reactivities are also presented.
- The Base Case Maximum 8-Hour Average Scales are relative reactivities based on effects of the VOCs on the maximum 8-hour average ozone in the 39 base case scenarios. Averages and standard deviations of the relative reactivities in these 39 scales are also presented.

Note that the MIR scale is the one recommended by Carter (1994a) for regulatory applications requiring use of a single scale, and is preferred by the California ARB for regulatory use (e.g., CARB, 1993, 1998). This is because MIR reactivities reflect conditions that are most sensitive to VOC controls, and serve as an appropriate complement to NO_x controls in a comprehensive control strategy. Relative reactivities in the MIR scale also correspond reasonably well to integrated O_3 reactivities in lower NO_x scenarios, because both are strongly influenced by factors of a VOCs mechanism that affect O_3 formation rates (Carter, 1994a). However, relative reactivities can differ depending on the scenarios or quantification method used, and regulatory applications that do not require use of a single scale should be based on considerations of reactivities in multiple scales.

3. Chemical Mechanism Used

The chemical mechanism employed in the atmospheric reactivity simulations consisted of the lumped mechanism discussed in Section VI with reactions added as needed to represent the VOC or mixture whose reactivity is being assessed. The lumped mechanism, which consists of the base mechanism listed in Table A-1 and the mechanism for the lumped species listed in Table A-3 is used in the "base case" simulations without the added VOCs. No lumping was employed when representing an individual VOC for calculating its reactivity, and Table A-6 in Appendix A gives the reactions used for those VOCs that are not in the base mechanism[19]. When calculating reactivities of complex mixtures (e.g., MS-A or the base ROG mixture), the components were lumped using the approach recommended in Table 49, with the parameters for the lumped model species being derived based on the specific mixtures being represented. Note that separate model species were used to represent components whose reactivities were being assessed than used to represent VOCs in the base mixture, except for components that are already represented explicitly in the mechanism.

B. VOC Classes and Uncertainty Classifications

Atmospheric reactivity estimates were made for all VOC classes that can be used to represent emitted VOCs in the current mechanism. These classes, which are also referred to as "detailed model species", can represent either a single compound or a mixture of isomers that are assumed to have similar mechanisms, or whose detailed compositions are unknown. The individual compounds include compounds whose reactions are represented explicitly, and compounds represented by other compounds using the lumped molecule approach. The mixtures of isomers are represented by one or more compounds that are assumed to be representative of the types of compounds in the mixtures.

Table C-1 in Appendix C lists all the detailed model species used in the current version of the mechanism (including some for which mechanistic and therefore reactivity estimates have not been made), and gives other summary information concerning these species. This includes the following:

- Name. Each detailed model species has a 2-8 character detailed model species name that is used to identify it in the modeling system. Note that this name is primary means to identify these species in some of the tabulations in this report, so can be used to identify what the name represents if this is not obvious.
- Description. The name of the VOC or the group of the VOCs that are represented by this class.
- Molecular Weight (Mwt). Because each detailed model species refers to either a single compound or set of isomeric compounds, each has a unique molecular weight associated with it. The molecular weight is used when processing mass-based emissions data, or when computing impacts of compounds on a weight basis.
- The uncertainty code (Unc) assigned to the mechanism for this model species. These codes, which are defined in Table C-2, indicate the author's subjective opinion of the likelihood that the mechanism, and the ozone impact predictions resulting from using the mechanism, will change significantly in the

future as new data become available. Note a higher number means a higher uncertainty (with 6 being the highest), and it is recommended that any reactivity-based regulation use uncertainty adjustments for those VOCs whose uncertainty classifications are greater than 4.

- The experimental data availability code (Exp.). These codes, which are defined in Table C-3, indicate the extent to which the mechanism for the compound has been or can be experimentally evaluated. Reference is also made in some cases to the availability of data to test the mechanism under MIR conditions; this refers to experiments testing the effects of the compounds on O_3 formation in surrogates representing relatively high NO_x conditions. Note that a code of "-" means there are no data available to evaluate the mechanism. The evaluation of mechanism is discussed in Section V (see also Appendix B).

- Additional information and comments (Notes). These footnotes, which are defined in Table C-4, give additional information about the representation of the detailed model species and the status of its evaluation. For example, note “1” indicates the mechanism is considered to be reasonably well established, “2” means the evaluation of mechanism for this species is discussed in this report, “4” means that the mechanism was adjusted to improve fits to chamber data, “7” means that the appropriateness of the lumped molecule representation used is uncertain, etc.

- The method used to represent the chemical reactions of the DMS in the model. This could be one of the following:

  - Explicit in the base mechanism (Expl). This means that reactions of this model species are part of the base mechanism because it is used, in part, to represent organic oxidation products. The mechanisms for the organic product species in the base mechanism are discussed in Section II.C

  - Mechanism Generated (Gen’d). This means that the mechanism was generated using the mechanism estimation and generation system that is discussed in Section III. The structure that was used when generating the mechanism (see Section III.B) is also shown.

  - Assigned Parameters (Asn’d). This means that the mechanism for this compound was derived or estimated as discussed in Section IV. This includes aromatics, terpenes, and other compounds for which the mechanism generation system cannot be used.

  - Lumped Molecule (L.Mol). This means that this detailed model species is represented in the model by another model species (or mixture thereof), on a mole for mole basis. The model species or mixture used to represent it is also shown. Note that mixtures are used for detailed model species that refer to an unspecified mixture of isomers that have different reactivity. Because of analytical limitations, such unspecified mixture classes tend to occur in many speciation profiles in emissions inventories.

  - Not in model (-). The current version of the mechanism does not have mechanistic assignments for this class of compounds. It is included in the list because it occurs in speciated emissions inventories. The molecular weight and carbon number information can be used when determining an approximate representation of the compound in model applications when mixtures containing these species are emitted.

  - Mixture (Mix). This is a complex mixture. This is not strictly a detailed model species, but is included in the tabulation of reactivity results for comparison purposes.

- Lumped Group. This is the lumped or explicit model species that is used in the condensed mechanism when representing the representing the detailed model species when present in mixtures, or in lumped model simulations when its reactivity is not being assessed. The footnote indicates abbreviations that are used.

C. Reactivity Results

The results of the reactivity calculations in the different scales are given in various tables in Appendix C. The incremental reactivity in the MIR scale is given in Table C-1, along with the estimated upper limit MIR, derived as discussed in the following section. Table C-5 gives reactivity data in various scales, including MIR, MOIR, EBIR, and averages, standard deviations, minima, and maxima in the O_3 yield and maximum 8-hour average relative reactivities calculated for the various scales. The incremental reactivities calculated for all the individual scenarios are given in Tables Table C-6 and Table C-7, where Table C-6 gives the data for the ozone yield reactivities, and Table C-7 gives the data for the maximum 8-hour average reactivities. Because of their size, the latter tables are not included with the printed version of this report, but are included with the electronic version, which can be downloaded from http://cert.ucr.edu/~carter/reactdat.htm.

It can be seen that there have been changes in the incremental and relative reactivities for a number of VOCs, relative to previous versions. The largest changes are for the VOCs whose mechanisms have been changed because of new data or revised estimates, but other changes have resulted from changes in the base mechanism and treatment of reactive products. For example, MIR's for some high molecular weight species whose mechanisms have not otherwise changed increased because of the use or PROD2 rather than the less reactive MEK to represent reactive ketone or other non-aldehyde oxygenated products. A complete analysis of the changes to the reactivity scale due to the mechanism updates has not been carried out, but may give useful insights concerning the effects of chemical mechanism uncertainties on incremental reactivity scales.

As indicated on Table C-5, the mechanisms for some VOCs are considered to be highly uncertain, and it is recommended that any regulations that use incremental reactivity data take these uncertainties into account. In particular, it is recommended that appropriate uncertainty adjustments be used for those VOCs that are given an uncertainty code of "4" or greater. A discussion of exactly what constitutes an appropriate uncertainty adjustment is beyond the scope of this work. However, at the request of the CARB, the author developed a means to estimate “upper limit” MIR’s for VOCs, given available information concerning the reaction rates and chemical type of the VOC, and the calculated MIRs for VOCs with known or estimated mechanisms (Carter, 1997). These upper limit estimates were updated for the current version of the mechanism, and the results are included on Table C-1. The methods and data used to derive these upper limit estimates are given in Appendix D to this report.

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APPENDIX A.

MECHANISM LISTING AND TABULATIONS

This Appendix contains the tables giving a complete listing of the both the detailed and the condensed versions of the SAPRC-99 mechanism. Table A-1 contains a list of all the model species used in both versions. Table A-2 lists all the reactions and rate parameters in the base mechanism, and Table A-3 gives the additional reactions and rate parameters used in the fixed parameter version of the lumped mechanism. Both tables have footnotes documenting the rate parameters and reactions used, and the text of these footnotes are given in Table A-4. Table A-5 lists the absorption cross sections and photolysis reactions used in the mechanism. Finally, Table A-6 lists the reactions and rate parameters derived or assigned to all the VOCs that are not incorporated in the base or condensed mechanisms. These are added to the base mechanism as needed to evaluate the mechanism for the individual VOC, or to assess its atmospheric reactivity. Note that the reactions of the VOCs that are explicitly represented in the condensed mechanism, such as ethylene and isoprene, are given in Table A-2 rather than Table A-6.

Table A-1. Listing of model species used in the base and lumped mechanisms.

Type and Name	Description
	Species used in Base Mechanism
Constant Species.	
O2	Oxygen
M	Air
H2O	Water
HV	Light
Active Inorganic Species.	
O3	Ozone
NO	Nitric Oxide
NO2	Nitrogen Dioxide
NO3	Nitrate Radical
N2O5	Nitrogen Pentoxide
HONO	Nitrous Acid
HNO3	Nitric Acid
HNO4	Peroxynitric Acid
HO2H	Hydrogen Peroxide
CO	Carbon Monoxide
SO2	Sulfur Dioxide
Active Radical Species and Operators.	
HO.	Hydroxyl Radicals
HO2.	Hydroperoxide Radicals
C-O2.	Methyl Peroxy Radicals
RO2-R.	Peroxy Radical Operator representing NO to NO2 conversion with HO2 formation.
R2O2.	Peroxy Radical Operator representing NO to NO2 conversion without HO2 formation.
RO2-N.	Peroxy Radical Operator representing NO consumption with organic nitrate formation.
CCO-O2.	Acetyl Peroxy Radicals
RCO-O2.	Peroxy Propionyl and higher peroxy acyl Radicals
BZCO-O2.	Peroxyacyl radical formed from Aromatic Aldehydes
MA-RCO3.	Peroxyacyl radicals formed from methacrolein and other acroleins.
Steady State Radical Species	
O3P	Ground State Oxygen Atoms
O*1D2	Excited Oxygen Atoms
TBU-O.	t-Butoxy Radicals
BZ-O.	Phenoxy Radicals
BZ(NO2)-O.	Nitro-substituted Phenoxy Radical
HOCOO.	Radical formed when Formaldehyde reacts with HO2
PAN and PAN Analogues	
PAN	Peroxy Acetyl Nitrate
PAN2	PPN and other higher alkyl PAN analogues
PBZN	PAN analogues formed from Aromatic Aldehydes
MA-PAN	PAN analogue formed from Methacrolein

Table A-1 (continued)

Type and Name	Description
Explicit and Lumped Molecule Reactive Organic Product Species	
HCHO	Formaldehyde
CCHO	Acetaldehyde
RCHO	Lumped C3+ Aldehydes
ACET	Acetone
MEK	Ketones and other non-aldehyde oxygenated products which react with OH radicals slower than 5 x 10^{-12} cm^3 $molec^{-2}$ sec^{-1}.
MEOH	Methanol
COOH	Methyl Hydroperoxide
ROOH	Lumped higher organic hydroperoxides
GLY	Glyoxal
MGLY	Methyl Glyoxal
BACL	Biacetyl
PHEN	Phenol
CRES	Cresols
NPHE	Nitrophenols
BALD	Aromatic aldehydes (e.g., benzaldehyde)
METHACRO	Methacrolein
MVK	Methyl Vinyl Ketone
ISOPROD	Lumped isoprene product species
Lumped Parameter Products	
PROD2	Ketones and other non-aldehyde oxygenated products which react with OH radicals faster than 5 x 10^{-12} cm^3 $molec^{-2}$ sec^{-1}.
RNO3	Lumped Organic Nitrates
Uncharacterized Reactive Aromatic Ring Fragmentation Products	
DCB1	Reactive Aromatic Fragmentation Products that do not undergo signficant photodecomposition to radicals.
DCB2	Reactive Aromatic Fragmentation Products which photolyze with alpha-dicarbonyl-like action spectrum.
DCB3	Reactive Aromatic Fragmentation Products which photolyze with acrolein action spectrum.
Non-Reacting Species	
CO2	Carbon Dioxide
XC	Lost Carbon
XN	Lost Nitrogen
SULF	Sulfates (SO_3 or H_2SO_4)

Table A-1 (continued)

Type and Name	Description
Low Reactivity Compounds or Unknown Products Represented as Unreactive	
H2	Hydrogen
HCOOH	Formic Acid
CCO-OH	Acetic Acid
RCO-OH	Higher organic acids
CCO-OOH	Peroxy Acetic Acid
RCO-OOH	Higher organic peroxy acids
CONO2	Methyl Nitrate
NROG	Unspecified Unreactive Carbon
Species used in Lumped Mechanisms for Base Case and Ambient Simulations	
Primary Organics Represented explicitly	
CH4	Methane
ETHENE	Ethene
Lumped Parameter Species	
ALK1	Alkanes and other non-aromatic compounds that react only with OH, and have kOH < 5 x 10^2 ppm-1 min-1. (Primarily ethane)
ALK2	Alkanes and other non-aromatic compounds that react only with OH, and have kOH between 5 x 10^2 and 2.5 x 10^3 ppm-1 min-1. (Primarily propane and acetylene)
ALK3	Alkanes and other non-aromatic compounds that react only with OH, and have kOH between 2.5 x 10^3 and 5 x 10^3 ppm-1 min-1.
ALK4	Alkanes and other non-aromatic compounds that react only with OH, and have kOH between 5 x 10^3 and 1 x 10^4 ppm-1 min-1.
ALK5	Alkanes and other non-aromatic compounds that react only with OH, and have kOH greater than 1 x 10^4 ppm-1 min-1.
ARO1	Aromatics with kOH < 2x10^4 ppm-1 min-1.
ARO2	Aromatics with kOH > 2x10^4 ppm-1 min-1.
OLE1	Alkenes (other than ethene) with kOH < 7x10^4 ppm-1 min-1.
OLE2	Alkenes with kOH > 7x10^4 ppm-1 min-1.
TRP1	Terpenes

Table A-2. Listing and documentation of the reactions in the base mechanism.

Label	Rate Parameters [a]				Refs & Notes [b]	Reaction and Products [c]
	k(298)	A	Ea	B		
Inorganic Reactions						
1	Phot Set= NO2				1,2	NO2 + HV = NO + O3P
2	5.79e-34	5.68e-34	0.00	-2.8	3	O3P + O2 + M = O3 + M
3	7.96e-15	8.00e-12	4.09		4,5	O3P + O3 = #2 O2
4	1.01e-31	1.00e-31	0.00	-1.6	6,7,5	O3P + NO + M = NO2 + M
5	9.72e-12	6.50e-12	-0.24		4,5	O3P + NO2 = NO + O2
6	1.82e-12	Falloff, F=0.80			4,7,5,7a	O3P + NO2 = NO3 + M
	0:	9.00e-32	0.00	-2.0		
	inf:	2.20e-11	0.00	0.0		
8	1.81e-14	1.80e-12	2.72		6	O3 + NO = NO2 + O2
9	3.52e-17	1.40e-13	4.91		6	O3 + NO2 = O2 + NO3
10	2.60e-11	1.80e-11	-0.22		6	NO + NO3 = #2 NO2
11	1.95e-38	3.30e-39	-1.05		6	NO + NO + O2 = #2 NO2
12	1.54e-12	Falloff, F=0.45			6,7	NO2 + NO3 = N2O5
	0:	2.80e-30	0.00	-3.5		
	inf:	2.00e-12	0.00	0.2		
13	5.28e-2	Falloff, F=0.45			6,7	N2O5 = NO2 + NO3
	0:	1.00e-3	21.86	-3.5		
	inf:	9.70e+14	22.02	0.1		
14	2.60e-22	2.60e-22			8	N2O5 + H2O = #2 HNO3
15	(Slow)				9	N2O5 + HV = NO3 + NO + O3P
16	(Slow)				9	N2O5 + HV = NO3 + NO2
17	6.56e-16	4.50e-14	2.50		10	NO2 + NO3 = NO + NO2 + O2
18	Phot Set= NO3NO				1,11,12	NO3 + HV = NO + O2
19	Phot Set= NO3NO2				1,11,12	NO3 + HV = NO2 + O3P
20	Phot Set= O3O3P				1,13,14	O3 + HV = O3P + O2
21	Phot Set= O3O1D				1,13,14	O3 + HV = O*1D2 + O2
22	2.20e-10	2.20e-10			4	O*1D2 + H2O = #2 HO.
23	2.87e-11	2.09e-11	-0.19		15	O*1D2 + M = O3P + M
24	7.41e-12	Falloff, F=0.60			16	HO. + NO = HONO
	0:	7.00e-31	0.00	-2.6		
	inf:	3.60e-11	0.00	-0.1		
25	Phot Set= HONO-NO				1,17,18	HONO + HV = HO. + NO
26	Phot Set= HONO-NO2				1,17,18	HONO + HV = HO2. + NO2
27	6.46e-12	2.70e-12	-0.52		6	HO. + HONO = H2O + NO2
28	8.98e-12	Falloff, F=0.60			19	HO. + NO2 = HNO3
	0:	2.43e-30	0.00	-3.1		
	inf:	1.67e-11	0.00	-2.1		
29	2.00e-11	2.00e-11			6,20	HO. + NO3 = HO2. + NO2
30	1.47e-13	k = k0+k3M(1+k3M/k2)			21,22	HO. + HNO3 = H2O + NO3
	k0:	7.20e-15	-1.56	0.0		
	k2:	4.10e-16	-2.86	0.0		
	k3:	1.90e-33	-1.44	0.0		
31	Phot Set= HNO3				1,23	HNO3 + HV = HO. + NO2

Table A-2 (continued)

Label	Rate Parameters [a]				Refs & Notes [b]	Reaction and Products [c]
	k(298)	A	Ea	B		
32	2.09e-13	k = k1 + k2 [M]			24	HO. + CO = HO2. + CO2
	k1:	1.30e-13	0.00	0.0		
	k2:	3.19e-33	0.00	0.0		
33	6.63e-14	1.90e-12	1.99		6	HO. + O3 = HO2. + O2
34	8.41e-12	3.40e-12	-0.54		6	HO2. + NO = HO. + NO2
35	1.38e-12	Falloff, F=0.60			6	HO2. + NO2 = HNO4
	0:	1.80e-31	0.00	-3.2		
	inf:	4.70e-12	0.00	0.0		
36	7.55e-2	Falloff, F=0.50			6	HNO4 = HO2. + NO2
	0:	4.10e-5	21.16	0.0		
	inf:	5.70e+15	22.20	0.0		
37	Phot Set= HO2NO2				1,25	HNO4 + HV = #.61 {HO2. + NO2} + #.39 {HO. + NO3}
38	5.02e-12	1.50e-12	-0.72		6	HNO4 + HO. = H2O + NO2 + O2
39	1.87e-15	1.40e-14	1.19		6	HO2. + O3 = HO. + #2 O2
40A	2.87e-12	k = k1 + k2 [M]			26	HO2. + HO2. = HO2H + O2
	k1:	2.20e-13	-1.19	0.0		
	k2:	1.85e-33	-1.95	0.0		
40B	6.46e-30	k = k1 + k2 [M]			26	HO2. + HO2. + H2O = HO2H + O2 + H2O
	k1:	3.08e-34	-5.56	0.0		
	k2:	2.59e-54	-6.32	0.0		
41	4.00e-12	4.00e-12			27	NO3 + HO2. = #.8 {HO. + NO2 + O2} + #.2 {HNO3 + O2}
42	2.28e-16	8.50e-13	4.87		28	NO3 + NO3 = #2 NO2 + O2
43	Phot Set= H2O2				1,29	HO2H + HV = #2 HO.
44	1.70e-12	2.90e-12	0.32		6	HO2H + HO. = HO2. + H2O
45	1.11e-10	4.80e-11	-0.50		6	HO. + HO2. = H2O + O2
S2OH	9.77e-13	Falloff, F=0.45			6,30	HO. + SO2 = HO2. + SULF
	0:	4.00e-31	0.00	-3.3		
	inf:	2.00e-12	0.00	0.0		
H2OH	6.70e-15	7.70e-12	4.17		4	HO. + H2 = HO2. + H2O
Methyl peroxy and methoxy reactions						
MER1	7.29e-12	2.80e-12	-0.57		31,32	C-O2. + NO = NO2 + HCHO + HO2.
MER4	5.21e-12	3.80e-13	-1.55		31	C-O2. + HO2. = COOH + O2
MEN3	1.30e-12	1.30e-12			31	C-O2. + NO3 = HCHO + HO2. + NO2
MER5	2.65e-13	2.45e-14	-1.41		33	C-O2. + C-O2. = MEOH + HCHO + O2
MER6	1.07e-13	5.90e-13	1.01		33	C-O2. + C-O2. = #2 {HCHO + HO2.}
Peroxy Racical Operators						
RRNO	9.04e-12	2.70e-12	-0.72		34,35,32	RO2-R. + NO = NO2 + HO2.
RRH2	1.49e-11	1.90e-13	-2.58		35,36	RO2-R. + HO2. = ROOH + O2 + #-3 XC
RRN3	2.30e-12	2.30e-12			37,38	RO2-R. + NO3 = NO2 + O2 + HO2.
RRME	2.00e-13	2.00e-13			39,40	RO2-R. + C-O2. = HO2. + #.75 HCHO + #.25 MEOH
RRR2	3.50e-14	3.50e-14			41,40	RO2-R. + RO2-R. = HO2.
R2NO	Same k as rxn RRNO				42,43	R2O2. + NO = NO2
R2H2	Same k as rxn RRH2				42,43	R2O2. + HO2. = HO2.
R2N3	Same k as rxn RRN3				42,43	R2O2. + NO3 = NO2

Table A-2 (continued)

Label	Rate Parameters [a]				Refs & Notes [b]	Reaction and Products [c]
	k(298)	A	Ea	B		
R2ME	Same k as rxn RRME				42,43	R2O2. + C-O2. = C-O2.
R2RR	Same k as rxn RRR2				42,43,40	R2O2. + RO2-R. = RO2-R.
R2R3	Same k as rxn RRR2				42,43	R2O2. + R2O2. =
RNNO	Same k as rxn RRNO				42,44	RO2-N. + NO = RNO3
RNH2	Same k as rxn RRH2				42,44,45	RO2-N. + HO2. = ROOH + #3 XC
RNME	Same k as rxn RRME				42,44,46	RO2-N. + C-O2. = HO2. + #.25 MEOH + #.5 {MEK + PROD2} + #.75 HCHO + XC
RNN3	Same k as rxn RRN3				42,44,47	RO2-N. + NO3 = NO2 + O2 + HO2. + MEK + #2 XC
RNRR	Same k as rxn RRR2				42,44,46	RO2-N. + RO2-R. = HO2. + #.5 {MEK + PROD2} + O2 + XC
RNR2	Same k as rxn RRR2				42,43	RO2-N. + R2O2. = RO2-N.
RNRN	Same k as rxn RRR2				42,44,46	RO2-N. + RO2-N. = MEK + HO2. + PROD2 + O2 + #2 XC
Reactions of Acyl Peroxy Radicals, PAN, and PAN analogues						
APN2	1.05e-11	Falloff, F=0.30			48	CCO-O2. + NO2 = PAN
	0:	2.70e-28	0.00	-7.1		
	inf:	1.20e-11	0.00	-0.9		
DPAN	5.21e-4	Falloff, F=0.30			49	PAN = CCO-O2. + NO2
	0:	4.90e-3	24.05	0.0		
	inf:	4.00e+16	27.03	0.0		
APNO	2.13e-11	7.80e-12	-0.60		50	CCO-O2. + NO = C-O2. + CO2 + NO2
APH2	1.41e-11	4.30e-13	-2.07		51	CCO-O2. + HO2. = #.75 {CCO-OOH +O2} + #.25 {CCO-OH + O3}
APN3	4.00e-12	4.00e-12			52	CCO-O2. + NO3 = C-O2. + CO2 + NO2 + O2
APME	9.64e-12	1.80e-12	-0.99		53	CCO-O2. + C-O2. = CCO-OH + HCHO + O2
APRR	7.50e-12	7.50e-12			54,55	CCO-O2. + RO2-R. = CCO-OH
APR2	Same k as rxn APRR				42,43	CCO-O2. + R2O2. = CCO-O2.
APRN	Same k as rxn APRR				42,55,46	CCO-O2. + RO2-N. = CCO-OH + PROD2
APAP	1.55e-11	2.90e-12	-0.99		31	CCO-O2. + CCO-O2. = #2 {C-O2. + CO2} + O2
PPN2	1.21e-11	1.20e-11	0.00	-0.9	56,57	RCO-O2. + NO2 = PAN2
PAN2	4.43e-4	2.00e+15	25.44		58,57	PAN2 = RCO-O2. + NO2
PPNO	2.80e-11	1.25e-11	-0.48		58a,57	RCO-O2. + NO = NO2 + CCHO + RO2-R. + CO2
PPH2	Same k as rxn APH2				59,57	RCO-O2. + HO2. = #.75 {RCO-OOH + O2} + #.25 {RCO-OH + O3}
PPN3	Same k as rxn APN3				59,57	RCO-O2. + NO3 = NO2 + CCHO + RO2-R. + CO2 + O2
PPME	Same k as rxn APME				59,57	RCO-O2. + C-O2. = RCO-OH + HCHO + O2
PPRR	Same k as rxn APRR				59,57	RCO-O2. + RO2-R. = RCO-OH + O2
PPR2	Same k as rxn APRR				59,43	RCO-O2. + R2O2. = RCO-O2.
PPRN	Same k as rxn APRR				59,46,57	RCO-O2. + RO2-N. = RCO-OH + PROD2 + O2
PPAP	Same k as rxn APAP				59,57	RCO-O2. + CCO-O2. = #2 CO2 + C-O2. + CCHO + RO2-R. + O2
PPPP	Same k as rxn APAP				59,57	RCO-O2. + RCO-O2. = #2 {CCHO + RO2-R. + CO2}
BPN2	1.37e-11	1.37e-11			60	BZCO-O2. + NO2 = PBZN
BPAN	3.12e-4	7.90e+16	27.82		61	PBZN = BZCO-O2. + NO2

Table A-2 (continued)

Label	Rate Parameters [a] k(298)	A	Ea	B	Refs & Notes [b]	Reaction and Products [c]
BPNO	Same k as rxn PPNO				62,63	BZCO-O2. + NO = NO2 + CO2 + BZ-O. + R2O2.
BPH2	Same k as rxn APH2				62,63	BZCO-O2. + HO2. = #.75 {RCO-OOH + O2} + #.25 {RCO-OH + O3} + #4 XC
BPN3	Same k as rxn APN3				62,63	BZCO-O2. + NO3 = NO2 + CO2 + BZ-O. + R2O2. + O2
BPME	Same k as rxn APME				62,63	BZCO-O2. + C-O2. = RCO-OH + HCHO + O2 + #4 XC
BPRR	Same k as rxn APRR				62,63	BZCO-O2. + RO2-R. = RCO-OH + O2 + #4 XC
BPR2	Same k as rxn APRR				43,62	BZCO-O2. + R2O2. = BZCO-O2.
BPRN	Same k as rxn APRR				46,62,63	BZCO-O2. + RO2-N. = RCO-OH + PROD2 + O2 + #4 XC
BPAP	Same k as rxn APAP				62,63	BZCO-O2. + CCO-O2. = #2 CO2 + C-O2. + BZ-O. + R2O2.
BPPP	Same k as rxn APAP				62,57,63	BZCO-O2. + RCO-O2. = #2 CO2 + CCHO + RO2-R. + BZ-O. + R2O2.
BPBP	Same k as rxn APAP				62,63	BZCO-O2. + BZCO-O2. = #2 {BZ-O. + R2O2. + CO2}
MPN2	Same k as rxn PPN2				62,64	MA-RCO3. + NO2 = MA-PAN
MPPN	3.55e-4	1.60e+16	26.80		65	MA-PAN = MA-RCO3. + NO2
MPNO	Same k as rxn PPNO				62,64	MA-RCO3. + NO = NO2 + CO2 + HCHO + CCO-O2.
MPH2	Same k as rxn APH2				62,64	MA-RCO3. + HO2. = #.75 {RCO-OOH + O2} + #.25 {RCO-OH + O3} + XC
MPN3	Same k as rxn APN3				62,64	MA-RCO3. + NO3 = NO2 + CO2 + HCHO + CCO-O2. + O2
MPME	Same k as rxn APME				62,64	MA-RCO3. + C-O2. = RCO-OH + HCHO + XC + O2
MPRR	Same k as rxn APRR				62,64	MA-RCO3. + RO2-R. = RCO-OH + XC
MPR2	Same k as rxn APRR				43,62	MA-RCO3. + R2O2. = MA-RCO3.
MPRN	Same k as rxn APRR				62,64	MA-RCO3. + RO2-N. = #2 RCO-OH + O2 + #4 XC
MPAP	Same k as rxn APAP				62,64	MA-RCO3. + CCO-O2. = #2 CO2 + C-O2. + HCHO + CCO-O2. + O2
MPPP	Same k as rxn APAP				62,64	MA-RCO3. + RCO-O2. = HCHO + CCO-O2. + CCHO + RO2-R. + #2 CO2
MPBP	Same k as rxn APAP				62,64	MA-RCO3. + BZCO-O2. = HCHO + CCO-O2. + BZ-O. + R2O2. + #2 CO2
MPMP	Same k as rxn APAP				62,64	MA-RCO3. + MA-RCO3. = #2 {HCHO + CCO-O2. + CO2}
Other Organic Radical Species						
TBON	2.40e-11	2.40e-11			66,67	TBU-O. + NO2 = RNO3 + #-2 XC
TBOD	9.87e+2	7.50e+14	16.20		68,67	TBU-O. = ACET + C-O2.
BRN2	3.80e-11	2.30e-11	-0.30		69	BZ-O. + NO2 = NPHE
BRH2	Same k as rxn RRH2				70	BZ-O. + HO2. = PHEN
BRXX	1.00e-3	1.00e-3			71	BZ-O. = PHEN
BNN2	Same k as rxn BRN2				72	BZ(NO2)-O. + NO2 = #2 XN + #6 XC
BNH2	Same k as rxn RRH2				70	BZ(NO2)-O. + HO2. = NPHE
BNXX	Same k as rxn BRXX				71	BZ(NO2)-O. = NPHE
Explicit and Lumped Molecule Organic Products						
FAHV	Phot Set= HCHO_R				73	HCHO + HV = #2 HO2. + CO

Table A-2 (continued)

Label	Rate Parameters [a] k(298)	 A	 Ea	 B	Refs & Notes [b]	Reaction and Products [c]
FAVS	Phot Set= HCHO_M				73	HCHO + HV = H2 + CO
FAOH	9.20e-12	8.60e-12	-0.04		31	HCHO + HO. = HO2. + CO + H2O
FAH2	7.90e-14	9.70e-15	-1.24		31	HCHO + HO2. = HOCOO.
FAHR	1.51e+2	2.40e+12	13.91		31	HOCOO. = HO2. + HCHO
FAHN	Same k as rxn MER1				74	HOCOO. + NO = HCOOH + NO2 + HO2.
FAN3	5.74e-16	2.00e-12	4.83		75	HCHO + NO3 = HNO3 + HO2. + CO
AAOH	1.58e-11	5.60e-12	-0.62		31	CCHO + HO. = CCO-O2. + H2O
AAHV	Phot Set= CCHO_R				76	CCHO + HV = CO + HO2. + C-O2.
AAN3	2.73e-15	1.40e-12	3.70		77	CCHO + NO3 = HNO3 + CCO-O2.
PAOH	2.00e-11	2.00e-11			78,31,79,80	RCHO + HO. = #.034 RO2-R. + #.001 RO2-N. + #.965 RCO-O2. + #.034 CO + #.034 CCHO + #-0.003 XC
PAHV	Phot Set= C2CHO				78,76	RCHO + HV = CCHO + RO2-R. + CO + HO2.
PAN3	3.67e-15	1.40e-12	3.52		78,81	RCHO + NO3 = HNO3 + RCO-O2.
K3OH	1.92e-13	1.10e-12	1.03		31,82	ACET + HO. = HCHO + CCO-O2. + R2O2.
K3HV	Phot Set= ACETONE				83	ACET + HV = CCO-O2. + C-O2.
K4OH	1.18e-12	1.30e-12	0.05	2.0	31,79,80	MEK + HO. = #.37 RO2-R. + #.042 RO2-N. + #.616 R2O2. + #.492 CCO-O2. + #.096 RCO-O2. + #.115 HCHO + #.482 CCHO + #.37 RCHO + #.287 XC
K4HV	Phot Set= KETONE, qy= 1.5e-1				84	MEK + HV = CCO-O2. + CCHO + RO2-R.
MeOH	9.14e-13	3.10e-12	0.72	2.0	85	MEOH + HO. = HCHO + HO2.
MER9	5.49e-12	2.90e-12	-0.38		86	COOH + HO. = H2O + #.35 {HCHO + HO.} + #.65 C-O2.
MERA	Phot Set= COOH				87	COOH + HV = HCHO + HO2. + HO.
LPR9	1.10e-11	1.10e-11			88,89	ROOH + HO. = H2O + RCHO + #.34 RO2-R. + #.66 HO.
LPRA	Phot Set= COOH				90	ROOH + HV = RCHO + HO2. + HO.
GLHV	Phot Set= GLY_R				91,92	GLY + HV = #2 {CO + HO2.}
GLVM	Phot Set= GLY_ABS, qy= 6.0e-3				91,93	GLY + HV = HCHO + CO
GLOH	1.10e-11	1.10e-11			31,94,95	GLY + HO. = #.63 HO2. + #1.26 CO + #.37 RCO-O2. + #-.37 XC
GLN3	9.63e-16	2.80e-12	4.72		95,96	GLY + NO3 = HNO3 + #.63 HO2. + #1.26 CO + #.37 RCO-O2. + #-.37 XC
MGHV	Phot Set= MGLY_ADJ				97	MGLY + HV = HO2. + CO + CCO-O2.
MGOH	1.50e-11	1.50e-11			31	MGLY + HO. = CO + CCO-O2.
MGN3	2.43e-15	1.40e-12	3.77		96	MGLY + NO3 = HNO3 + CO + CCO-O2.
BAHV	Phot Set= BACL_ADJ				91a,98	BACL + HV = #2 CCO-O2.
PHOH	2.63e-11	2.63e-11			99,100	PHEN + HO. = #.24 BZ-O. + #.76 RO2-R. + #.23 GLY + #4.1 XC
PHN3	3.78e-12	3.78e-12			99,101	PHEN + NO3 = HNO3 + BZ-O.

Table A-2 (continued)

Label	Rate Parameters [a]				Refs & Notes [b]	Reaction and Products [c]
	k(298)	A	Ea	B		
CROH	4.20e-11	4.20e-11			99,102	CRES + HO. = #.24 BZ-O. + #.76 RO2-R. + #.23 MGLY + #4.87 XC
CRN3	1.37e-11	1.37e-11			99,101	CRES + NO3 = HNO3 + BZ-O. + XC
NPN3	Same k as rxn PHN3				103	NPHE + NO3 = HNO3 + BZ(NO2)-O.
BZOH	1.29e-11	1.29e-11			99	BALD + HO. = BZCO-O2.
BZHV	Phot Set= BZCHO, qy= 5.0e-2				104	BALD + HV = #7 XC
BZNT	2.62e-15	1.40e-12	3.72		105	BALD + NO3 = HNO3 + BZCO-O2.
MAOH	3.36e-11	1.86e-11	-0.35		106,80,107	METHACRO + HO. = #.5 RO2-R. + #.416 CO + #.084 HCHO + #.416 MEK + #.084 MGLY + #.5 MA-RCO3. + #-0.416 XC
MAO3	1.13e-18	1.36e-15	4.20		106,108, 109,110	METHACRO + O3 = #.008 HO2. + #.1 RO2-R. + #.208 HO. + #.1 RCO-O2. + #.45 CO + #.117 CO2 + #.2 HCHO + #.9 MGLY + #.333 HCOOH + #-0.1 XC
MAN3	4.58e-15	1.50e-12	3.43		106,111, 80,112	METHACRO + NO3 = #.5 {HNO3 + RO2-R. + CO +MA-RCO3.} + #1.5 XC + #.5 XN
MAOP	6.34e-12	6.34e-12			113,5	METHACRO + O3P = RCHO + XC
MAHV	Phot Set= ACROLEIN, qy= 4.1e-3				106,114	METHACRO + HV = #.34 HO2. + #.33 RO2-R. + #.33 HO. + #.67 CCO-O2. + #.67 CO + #.67 HCHO + #.33 MA-RCO3. + #-0 XC
MVOH	1.89e-11	4.14e-12	-0.90		106,80	MVK + HO. = #.3 RO2-R. + #.025 RO2-N. + #.675 R2O2. + #.675 CCO-O2. + #.3 HCHO + #.675 RCHO + #.3 MGLY + #-0.725 XC
MVO3	4.58e-18	7.51e-16	3.02		106,108, 109,80, 110	MVK + O3 = #.064 HO2. + #.05 RO2-R. + #.164 HO. + #.05 RCO-O2. + #.475 CO + #.124 CO2 + #.1 HCHO + #.95 MGLY + #.351 HCOOH + #-0.05 XC
MVN3	(Slow)				106	MVK + NO3 = #4 XC + XN
MVOP	4.32e-12	4.32e-12			113,5	MVK + O3P = #.45 RCHO + #.55 MEK + #.45 XC
MVHV	Phot Set= ACROLEIN, qy= 2.1e-3				106,114, 115	MVK + HV = #.3 C-O2. + #.7 CO + #.7 PROD2 + #.3 MA-RCO3. + #-2.4 XC
IPOH	6.19e-11	6.19e-11			116,106, 80	ISOPROD + HO. = #.705 RO2-R. + #.006 RO2-N. + #.0 R2O2. + #.289 MA-RCO3. + #.357 CO + #.056 HCHO + #.134 CCHO + #.015 RCHO + #.158 MEK + #.352 PROD2 + #.158 GLY + #.179 MGLY + #-0.514 XC
IPO3	4.18e-18	4.18e-18			116,106, 80,117, 109,118, 110	ISOPROD + O3 = #.4 HO2. + #.048 RO2-R. + #.048 RCO-O2. + #.285 HO. + #.498 CO + #.14 CO2 + #.125 HCHO + #.047 CCHO + #.21 MEK + #.023 GLY + #.742 MGLY + #.1 HCOOH + #.372 RCO-OH + #-.33 XC
IPN3	1.00e-13	1.00e-13			116,106, 80	ISOPROD + NO3 = #.85 RO2-R. + #.15 MA-RCO3. + #.609 CO + #.15 HNO3 + #.241 HCHO + #.233 RCHO + #.008 MGLY + #.609 RNO3 + #.241 XN + #-.827 XC
IPHV	Phot Set= ACROLEIN, qy= 4.1e-3				116,106, 80,119	ISOPROD + HV = #1.233 HO2. + #.467 CCO-O2. + #.3 RCO-O2. + #1.233 CO + #.3 HCHO + #.467 CCHO + #.233 MEK + #-.233 XC

Table A-2 (continued)

Label	Rate Parameters [a]				Refs &	Reaction and Products [c]
	k(298)	A	Ea	B	Notes [b]	
Lumped Parameter Organic Products						
K6OH	1.50e-11	1.50e-11			120	PROD2 + HO. = #.379 HO2. + #.473 RO2-R. + #.07 RO2-N. + #.029 CCO-O2. + #.049 RCO-O2. + #.213 HCHO + #.085 CCHO + #.559 RCHO + #.116 MEK + #.329 PROD2 + #.88 XC
K6HV	Phot Set= KETONE, qy= 2.0e-2				120,121	PROD2 + HV = #.915 RO2-R. + #.085 RO2-N. + #.677 R2O2. + #.4 CCO-O2. + #.6 RCO-O2. + #.304 HCHO + #.163 CCHO + #.782 RCHO + #-.09 XC
RNOH	7.80e-12	7.80e-12			122	RNO3 + HO. = #.339 NO2 + #.113 HO2. + #.376 RO2-R. + #.172 RO2-N. + #.597 R2O2. + #.01 HCHO + #.44 CCHO + #.214 RCHO + #.006 ACET + #.177 MEK + #.048 PROD2 + #.31 RNO3 + #.351 XN + #.56 XC
RNHV	Phot Set= IC3ONO2				122,123	RNO3 + HV = NO2 + #.341 HO2. + #.565 RO2-R. + #.094 RO2-N. + #.152 R2O2. + #.134 HCHO + #.431 CCHO + #.147 RCHO + #.02 ACET + #.243 MEK + #.436 PROD2 + #.35 XC
Uncharacterized Reactive Aromatic Ring Fragmentation Products						
D1OH	5.00e-11	5.00e-11			124,125	DCB1 + HO. = RCHO + RO2-R. + CO
D1HV		(Slow)			124,126	DCB1 + HV = HO2. + #2 CO + RO2-R. + GLY + R2O2.
D1O3	2.00e-18	2.00e-18			124,127, 117	DCB1 + O3 = #1.5 HO2. + #.5 HO. + #1.5 CO + #.5 CO2 + GLY
D2OH	5.00e-11	5.00e-11			128,129	DCB2 + HO. = R2O2. + RCHO + CCO-O2.
D2HV	Phot Set= MGLY_ABS, qy= 3.7e-1				128,130	DCB2 + HV = RO2-R. + #.5 {CCO-O2. + HO2.} + CO + R2O2. + #.5 {GLY + MGLY + XC}
D3OH	5.00e-11	5.00e-11			128,129	DCB3 + HO. = R2O2. + RCHO + CCO-O2.
D3HV	Phot Set= ACROLEIN, qy= 7.3e+0				128,130	DCB3 + HV = RO2-R. + #.5 {CCO-O2. + HO2.} + CO + R2O2. + #.5 {GLY + MGLY + XC}

[a] Except as indicated, the rate constants are given by $k(T) = A \cdot (T/300)^{B} \cdot e^{-Ea/RT}$, where the units of k and A are $cm^{3}\ molec^{-1}\ s^{-1}$, Ea are $kcal\ mol^{-1}$, T is ^{o}K, and R=0.0019872 $kcal\ mol^{-1}\ deg^{-1}$. The following special rate constant expressions are used:

<u>Phot Set = *name*</u>: The absorption cross sections and quantum yields for the photolysis reaction are given in Table 5, where "*name*" indicates the photolysis set used. If a "qy=*number*" notation is given, the number given is the overall quantum yield, which is assumed to be wavelength independent.

<u>Falloff</u>: The rate constant as a function of temperature and pressure is calculated using $k(T,M) = \{k0(T)\cdot[M]/[1 + k0(T)\cdot[M]/kinf(T)]\}\cdot F^{Z}$, where $Z = \{1 + [\log_{10}\{k0(T)\cdot[M])/kinf(T)\}]^{2}\}^{-1}$, [M] is the total pressure in molecules cm^{-3}, F is as indicated on the table, and the temperature dependences of k0 and kinf are as indicated on the table.

<u>(Slow)</u>: The reaction is assumed to be negligible and is not included in the mechanism. It is shown on the listing for documentation purposes only.

<u>k = k0+k3M(1+k3M/k2)</u>: The rate constant as a function of temperature and pressure is calculated using $k(T,M) = k0(T) + k3(T)\cdot[M]\cdot(1 + k3(T)\cdot[M]/k2(T))$, where [M] is the total bath gas (air) concentration in molecules cm^{-3}, and the temperature dependences for k0, k2 and k3 are as indicated on the table.

Table A-2 (continued)

k = k1 + k2 [M]: The rate constant as a function of temperature and pressure is calculated using k(T,M) = k1(T) + k2(T) [M], where [M] is the total bath gas (air) concentration in molecules cm^{-3}, and the temperature dependences for k1, and k2 are as indicated on the table.

Same k as Rxn *label*: The rate constant is the same as the reaction with the indicated label.

[b] Documentation text is in Table A-4..

[c] Format of reaction listing: “=” separates reactants from products; “#*number*” indicates stoichiometric coefficient, “#*coefficient* { *product list* }” means that the stoichiometric coefficient is applied to all the products listed.

Table A-3. Listing and documentation of reactions added to the base mechanism to constitute the fixed parameter lumped mechanism.

Label	Rate Parameters [a]				Refs & Notes [b]	Reaction and Products [a]
	k(298)	A	Ea	B		
Explicitly Represented Primary Organics						
c1OH	6.37e-15	2.15e-12	3.45		31	CH4 + HO. = H2O + C-O2.
etOH	8.52e-12	1.96e-12	-0.87		136	ETHENE + HO. = RO2-R. + #1.611 HCHO + #.195 CCHO
etO3	1.59e-18	9.14e-15	5.13		136	ETHENE + O3 = #.12 HO. + #.12 HO2. + #.5 CO + #.13 CO2 + HCHO + #.37 HCOOH
etN3	2.05e-16	4.39e-13	4.53	2.0	136	ETHENE + NO3 = RO2-R. + RCHO + #-1 XC + XN
etOA	7.29e-13	1.04e-11	1.57		136	ETHENE + O3P = #.5 HO2. + #.2 RO2-R. + #.3 C-O2. + #.491 CO + #.191 HCHO + #.25 CCHO + #.009 GLY + #.5 XC
isOH	9.82e-11	2.50e-11	-0.81		136,137	ISOPRENE + HO. = #.907 RO2-R. + #.093 RO2-N. + #.079 R2O2. + #.624 HCHO + #.23 METHACRO + #.32 MVK + #.357 ISOPROD + #-0.167 XC
isO3	1.28e-17	7.86e-15	3.80		136,137	ISOPRENE + O3 = #.266 HO. + #.066 RO2-R. + #.008 RO2-N. + #.126 R2O2. + #.192 MA-RCO3. + #.275 CO + #.122 CO2 + #.592 HCHO + #.1 PROD2 + #.39 METHACRO + #.16 MVK + #.204 HCOOH + #.15 RCO-OH + #-0.258 XC
isN3	6.74e-13	3.03e-12	0.89		136,137	ISOPRENE + NO3 = #.187 NO2 + #.749 RO2-R. + #.064 RO2-N. + #.187 R2O2. + #.936 ISOPROD + #-0.064 XC + #.813 XN
isOP	3.60e-11	3.60e-11			136,137	ISOPRENE + O3P = #.01 RO2-N. + #.24 R2O2. + #.25 C-O2. + #.24 MA-RCO3. + #.24 HCHO + #.75 PROD2 + #-1.01 XC
Lumped Primary Organics (Based on base ROG mixture used in reactivity scenarios)						
A1OH	2.54e-13	1.37e-12	0.99	2.0	136,138	ALK1 + HO. = RO2-R. + CCHO
A2OH	1.04e-12	9.87e-12	1.33		136,139	ALK2 + HO. = #.246 HO. + #.121 HO2. + #.612 RO2-R. + #.021 RO2-N. + #.16 CO + #.039 HCHO + #.155 RCHO + #.417 ACET + #.248 GLY + #.121 HCOOH + #0.338 XC
A3OH	2.38e-12	1.02e-11	0.86		136,140	ALK3 + HO. = #.695 RO2-R. + #.069 RO2-N. + #.559 R2O2. + #.236 TBU-O. + #.026 HCHO + #.446 CCHO + #.122 RCHO + #.024 ACET + #.333 MEK + #-0.05 XC
A4OH	4.39e-12	5.95e-12	0.18		136,140	ALK4 + HO. = #.836 RO2-R. + #.142 RO2-N. + #.937 R2O2. + #.011 C-O2. + #.011 CCO-O2. + #.002 CO + #.024 HCHO + #.455 CCHO + #.244 RCHO + #.452 ACET + #.11 MEK + #.125 PROD2 + #-.099 XC
A5OH	9.34e-12	1.11e-11	0.10		136,140	ALK5 + HO. = #.655 RO2-R. + #.345 RO2-N. + #.95 R2O2. + #.026 HCHO + #.099 CCHO + #.204 RCHO + #.072 ACET + #.089 MEK + #.418 PROD2 + #2.014 XC

Table A-3 (continued)

Label	Rate Parameters [a] k(298)	 A	 Ea	 B	Refs & Notes [b]	Reaction and Products [a]
B1OH	5.95e-12	1.81e-12	-0.71		136,141	ARO1 + HO. = #.224 HO2. + #.765 RO2-R. + #.011 RO2-N. + #.055 PROD2 + #.118 GLY + #.119 MGLY + #.017 PHEN + #.207 CRES + #.059 BALD + #.491 DCB1 + #.108 DCB2 + #.051 DCB3 + #1.288 XC
B2OH	2.64e-11	2.64e-11	0.00		136,140	ARO2 + HO. = #.187 HO2. + #.804 RO2-R. + #.009 RO2-N. + #.097 GLY + #.287 MGLY + #.087 BACL + #.187 CRES + #.05 BALD + #.561 DCB1 + #.099 DCB2 + #.093 DCB3 + #1.68 XC
O1OH	3.23e-11	7.10e-12	-0.90		136,140	OLE1 + HO. = #.91 RO2-R. + #.09 RO2-N. + #.206 R2O2. + #.732 HCHO + #.294 CCHO + #.497 RCHO + #.005 ACET + #.119 PROD2 + #.92 XC
O1O3	1.06e-17	2.62e-15	3.26		136,140	OLE1 + O3 = #.155 HO. + #.056 HO2. + #.022 RO2-R. + #.001 RO2-N. + #.076 C-O2. + #.345 CO + #.086 CO2 + #.5 HCHO + #.154 CCHO + #.363 RCHO + #.001 ACET + #.185 HCOOH + #.05 CCO-OH + #.335 RCO-OH + #1.297 XC
O1N3	1.26e-14	4.45e-14	0.75		136,140	OLE1 + NO3 = #.826 RO2-R. + #.174 RO2-N. + #.489 R2O2. + #.009 CCHO + #.038 RCHO + #.024 ACET + #.512 RNO3 + #.68 XC + #.488 XN
O1OA	4.90e-12	1.07e-11	0.47		136,140	OLE1 + O3P = #.45 RCHO + #.437 MEK + #.113 PROD2 + #1.224 XC
O2OH	6.33e-11	1.74e-11	-0.76		136,140	OLE2 + HO. = #.919 RO2-R. + #.081 RO2-N. + #.001 R2O2. + #.244 HCHO + #.733 CCHO + #.512 RCHO + #.127 ACET + #.072 MEK + #.061 BALD + #.025 METHACRO + #.025 ISOPROD + #-.053 XC
O2O3	1.07e-16	5.02e-16	0.92		136,140	OLE2 + O3 = #.378 HO. + #.003 HO2. + #.033 RO2-R. + #.002 RO2-N. + #.137 R2O2. + #.197 C-O2. + #.137 CCO-O2. + #.006 RCO-O2. + #.265 CO + #.07 CO2 + #.269 HCHO + #.456 CCHO + #.305 RCHO + #.045 ACET + #.026 MEK + #.006 PROD2 + #.042 BALD + #.026 METHACRO + #.073 HCOOH + #.129 CCO-OH + #.303 RCO-OH + #.155 XC
O2N3	7.27e-13	7.27e-13	0.00		136,140	OLE2 + NO3 = #.392 NO2 + #.443 RO2-R. + #.135 RO2-N. + #.712 R2O2. + #.03 C-O2. + #.079 HCHO + #.508 CCHO + #.151 RCHO + #.102 ACET + #.001 MEK + #.015 BALD + #.048 MVK + #.321 RNO3 + #.079 XC + #.287 XN
O2OA	2.09e-11	2.09e-11			136,140	OLE2 + O3P = #.013 HO2. + #.012 RO2-R. + #.001 RO2-N. + #.012 CO + #.069 RCHO + #.659 MEK + #.259 PROD2 + #.012 METHACRO + #.537 XC

Table A-3 (continued)

Label	Rate Parameters [a] k(298)	 A	 Ea	 B	Refs & Notes [b]	Reaction and Products [a]
Lumped Terpenes (Based on estimated North America annual emissions rate of top 5 terpenes.)						
T1OH	8.27e-11	1.83e-11	-0.89		136,142	TRP1 + HO. = #.75 RO2-R. + #.25 RO2-N. + #.5 R2O2. + #.276 HCHO + #.474 RCHO + #.276 PROD2 + #5.146 XC
T1O3	6.88e-17	1.08e-15	1.63		136,142	TRP1 + O3 = #.567 HO. + #.033 HO2. + #.031 RO2-R. + #.18 RO2-N. + #.729 R2O2. + #.123 CCO-O2. + #.201 RCO-O2. + #.157 CO + #.037 CO2 + #.235 HCHO + #.205 RCHO + #.13 ACET + #.276 PROD2 + #.001 GLY + #.031 BACL + #.103 HCOOH + #.189 RCO-OH + #4.183 XC
T1N3	6.57e-12	3.66e-12	-0.35		136,142	TRP1 + NO3 = #.474 NO2 + #.276 RO2-R. + #.25 RO2-N. + #.75 R2O2. + #.474 RCHO + #.276 RNO3 + #5.421 XC + #.25 XN
T1OA	3.27e-11	3.27e-11			136,142	TRP1 + O3P = #.147 RCHO + #.853 PROD2 + #4.442 XC

[a] See footnotes to Table 50.

[b] Documentation text is in Table 52.

Table A-4. Documentation notes for the base and lumped mechanisms.

No.	Note
1	See Table A-5 for listing of absorption cross sections and quantum yields. Set used is given in the "Type" column.
2	Absorption cross sections and quantum yields from IUPAC recommendation (Atkinson et al, 1997a), except that quantum yields for wl > 410 nm are from NASA (1997), which are consistent with IUPAC (Atkinson et al, 1997a) values except they are more precise. Note that more recent IUPAC recommendations (Atkinson et al, 1997b) gives slightly different absorption cross sections based on data from a more recent study, but the differences are not significant.
3	Rate constant expression derived from IUPAC (Atkinson et al, 1997b) recommendations for M = 20.9% O2 and 79.1% N2.
4	Rate constant is IUPAC, Supplement VI (Atkinson et al, 1997b) and NASA (1997) recommendation.
5	This reaction is probably not important in the troposphere, but is included to increase range of applicability.
6	Rate constant expression is IUPAC (Atkinson et al, 1997b) recommendation.
7	Recommended rate constant given for N2 is assumed to be applicable to air.
7a	The falloff parameters recommended by NASA (1997) give a 300K, 1 atm rate constant which is approximately 13% lower than the IUPAC-recommended values that were used.
8	The data of Mentel et al (1996) indicate that the reaction occurs through pathways which are first order and second order in H2O, where the latter is presumed to be surface-dependent. We assume that the process which is first order in H2O represents a gas-phase reaction, and use the rate expression of Mentel et al (1996) for this process. Note that the IUPAC (Atkinson et al, 1997b) recommendation that the gas-phase rate constant is less than 2×10^{-21} cm-3 molec-1 s-1.
9	Photolysis of N2O5 is assumed to be negligible compared to decomposition under atmospheric conditions.
10	The NASA (1997) evaluation states that the existence of this channel has not been firmly established, but results of a number of studies indicate it may occur. Rate constant expression used is that NASA (1997) states gives best fits to the data. Uncertainty is at least a factor of 2. This reaction was not discussed in the recent IUPAC evaluations (Atkinson et al, 1997a,b).
11	Absorption cross sections from IUPAC (Atkinson et al, 1997a). Values recommended by more recent IUPAC evaluation (Atkinson et al, 1997b) appear to be the same for 298K, though different at lower temperature. Temperature dependence ignored.
12	IUPAC (1997b) and NASA (1997) give no useable recommendations for quantum yields except to recommend that qy(NO2+O)=1 for wl <= 583. Quantum yields of Magnotta and Johnsom (1980), scaled down by a factor of 1.5 to give unit maximum quantum yields, as incorporated in mechanism of Carter (1990) were retained in this mechanism. The calculated rate constant for solar overhead sun is consistent with the recommendations of Magnotta and Johnson (1980), and reasonably consistent with the IUPAC (1997a) recommendation.

Table A-4 (continued)

No.	Note
13	Absorption cross sections from IUPAC, given for T=273K (Atkinson et al, 1997b). Temperature dependences for cross section (NASA, 1997) are ignored.
14	Quantum yields for O1D are those tabulated by IUPAC (Atkinson et al, 1997b), which are significantly higher than previous recommendations at wl > 310 nm. Quantum yields for O3P based on assuming total quantum yield of unity, though this was not adequately discussed in the evaluations.
15	Calculated using IUPAC (Atkinson et al, 1997b) recommended rate constants for reaction with O2 and N2, assuming 20.9% O2 and 79.1% N2. Temperature dependence optimized to fit rate constants calculated for T= 270, 300, and 330K.
16	Falloff expression recommended by NASA (1997) used because it gives rate constant for 1 atm N2 which is consistent with measurement near those conditions. IUPAC (Atkinson et al, 1997a,b) recommendations are not used because k (1 atm N2) are not consistent with these data, being based on high pressure data in He. This is consistent with current recommendation of Atkinson (private communication, 1997).
17	The cross sections from Stockwell and Calvert (1978), used in the previous version of the mechanism, are retained because they are higher resolution than the averaged data recommended by IUPAC (1997b), and the areas under the spectra appear to be consistent.
18	Absorption cross sections from the NASA (1997) evaluation..
19	NASA (1997) and IUPAC (Atkinson et al, 1997a,b) give significantly different recommendations for rate parameters for this important reaction. The falloff expression used here is based on a NASA (1997) and IUPAC (Atkinson et al, 1997a,b) give significantly different recommendations for rate parameters for this important reaction. The falloff expression used here is based on a re-evaluation of the data by Golden (Personal communication, 1998), and is expected to be the recommendation in the next NASA evaluation. This is essentially the same as the NASA (1997) recommendation except for the temperature dependence, which Golden says was due to improper uncertainty weighting. The data with "weak colliders (i.e., bath gases other than SF6 or CF4) appear to be well fit by this parameterization, including the data of Donahue et al (1997). The data of Forster et al (1995), which are the basis for the high 1997 IUPAC recommendation, are not used because they may be due to a HOONO-forming channel becoming importa
20	No recommendation is given concerning the temperature dependence of this rate constant, which is assumed to be small.
21	The rate parameters were derived to fit the rate constants calculated using the NASA (1997) recommended expression for T 270 - 330 K range and 1 atm. total pressure.
22	This rate constant is strictly valid for 1 atm air only, but the error introduced by neglecting the pressure dependence of this reaction is expected to be small.
23	Absorption cross-sections from IUPAC (Atkinson et al, 1997b). Recommend quantum yield for the OH + NO2 pathway is "close to unity" for wl > 260 nm, though other pathways become important at lower wavelengths.
24	The rate constants for the OH + CO reactions are based on expression given by IUPAC (Atkinson et al, 1997a). NASA (1997) gives a similar expression, but without temperature dependence.

Table A-4 (continued)

No.	Note
25	Absorption cross sections and quantum yields from IUPAC (Atkinson et al, 1997b). Quantum yields are uncertain and based on data for a single wavelength only.
26	Reactions and rate constants used for the HO2 + HO2 and HO2 + HO2 + H2O system based on the data of Kircher and Sander (1984) as discussed in the IUPAC (Atkinson et al, 1997b) evaluation.
27	Rate constant recommended by IUPAC (Atkinson et al, 1997b). Measurement of the branching ratios vary, so the mechanism is uncertain. The branching ratio assumed is approximately in the middle of the range given by IUPAC (Atkinson et al, 1997b) and NASA (1997) evaluations, which is 0.6 - 1.0 for the OH-forming channel.
28	Rate expression from NASA (1994) evaluation. More recent evaluations neglect this reaction, though it may be non-negligible under some nighttime conditions (Stockwell et al, 1997).
29	Absorption cross sections recommended by IUPAC (Atkinson et al, 1997a,b) used. Quantum yield assumed to be unity.
30	The initially formed $HOSO_2$ is believed to react primarily with O_2, forming HO2 and SO_3 (Stockwell and Calvert, 1983). The SO_3 is assumed to be converted into sulfates, which are represented by the SULF model species.
31	Rate constant expression recommended by IUPAC, Supplement VII (Atkinson et al, 1999a).
32	The reaction of NO2 is ignored because it is rapidly reversed by the decomposition of the peroxynitrate, resulting in no net reaction. Calculations not neglecting peroxynitrate formation give essentially the same results. However, this may not be valid in low temperature simulations.
33	Total rate constant and rate constant for methoxy radical formation from IUPAC (Atkinson et al, 1997a, 1999a) recommendation. Temperature dependence for rate constant for methanol + HCHO formation derived to be consistent with these.
34	The RO2-R. operator represents the effects of peroxy radicals which react with NO to form NO2 and HO2, and also the effects of peroxy radical reactions on other species. Except as indicated, the organic products from this peroxy radical are not represented.
35	Rate constant recommended by Atkinson (1997a) for general peroxy radicals.
36	The organic products from the HO2 reaction are represented by the lumped higher hydroperoxide species. Negative "lost carbons" are added because this is a zero-carbon operator.
37	Rate constant based on that recommenced by IUPAC (Atkinson et al, 1999a) for ethyl peroxy + NO3. Formation of alkoxy + NO2 + O2 stated to occur >85% of the time.
38	The reaction is assumed to form the corresponding alkoxy radical. The HO2 represents the radicals regenerated by the alkoxy radical.
39	Based on rate constant for methyl peroxy + ethyl peroxy rate given by Atkinson (1997a). This is near the middle of the range of rate constants given for other methyl peroxy + higher alkyl peroxy radical reactions given by Atkinson (1997a) or Atkinson et al (1997a).
40	Approximately half of the peroxy + peroxy reaction is assumed to form two O2 + alkoxy radicals, where the latter react to form HO_2 and organic products, where the formaldehyde from the

No.	Note
	methoxy is represented in this reaction. The HO2 represents the radicals regenerated in the fraction of this peroxy radical which reacts in this way. The other half of the time the reaction is assumed to proceed via H-atom transfer, with half of that involving transfer from the methyl peroxy, forming formaldehyde, and the other half involving transfer to the methyl peroxy, forming methanol. Note that the organic products from RO2-R· are not represented in this reaction because this is a “massless” operator.
41	The rate constants for peroxy + peroxy radical reactions can vary by orders of magnitude depending on the type of radical (e.g., Atkinson, 1997), so the value used here must be approximate. The value used is the geometric mean of the values recommended by Atkinson (1997a) for primary + primary and secondary + secondary peroxy radicals.
42	Assumed to have same rate constant as used for general higher peroxy radical (see notes for RO2-R.).
43	The R2O2. operator represents the effects of peroxy radical reactions causing extra NO to NO2 conversions. Its reactions with species other than NO are represented as having no effect other than to consume this operator.
44	The RO2-N. operator represents the effects of peroxy radicals which react with NO to form higher organic nitrates (represented by RNO3), and also the effects of peroxy radical reactions on other species. It has five carbons.
45	The organic products from the HO2 reaction are represented by the lumped higher hydroperoxide species. "Lost carbons" are added because this is a five-carbon operator.
46	Approximately half of the peroxy + peroxy reaction for radicals represented by RO2-N. is assumed to form two O2 + alkoxy radicals. The MEK + HO2. represents the products and radicals formed from the alkoxy radical from this species. The other half is assumed to involve disproportionation, forming O2 + and an alcohol and carbonyl compound. These are represented by PROD2.
47	This reaction is assumed to form the corresponding alkoxy radical, which is assumed to react products represented by MEK + HO2.
48	Falloff expression recommended by IUPAC (Atkinson et al, 1997a, 1999a), based on data of Bridier et al (1991).
49	Falloff expression recommended by IUPAC (Atkinson et al, 1992), based on data of Bridier et al (1991). Note: NASA (1997) also recommends using Bridier et al (1991) data, but gives a revised expression which gives a different k at 298K. Based on new data on PAN decomposition which give a factor of ~2 lower rate 298K rate constants, The more recent IUPAC evaluations (Atkinson et al., 1997a, 1999a) recommend the a high pressure rate constant expression of $5.4\text{x}10^{16}$ exp(-13830/T), derived by averaging the data. We are staying with the earlier IUPAC Recommendations based on the data of Bridier et al (1991) because it gives good agreement with the data of Tuazon et al (1991a) and is consistent with the NASA (1997) recommended equilibrium constant.

Table A-4 (continued)

No.	Note
50	Rate constant expression recommended by IUPAC (Atkinson et al, 1999a). This is almost the same as the earlier IUPAC(Atkinson et al, 1997a) recommended value of $2.0x10^{-11}$ and close to the NASA (1997) value of $1.8x10^{-11}$.
51	Branching ratio and rate constant expression recommended by IUPAC (Atkinson et al, 1997a, 1999).
52	Rate constant from Canosa-Mass et al (1996)
53	Rate constant expression recommended by IUPAC (Atkinson et al, 1999a) evaluation. As discussed there, the data are inconclusive as to the importance of the competing reaction forming CH3O + CH3CO2 + O2, but the study which indicate that it occurs, which was used in the previous IUPAC (Atkinson et al, 1997a) evaluation, indicates that it occurs less than ~15% under atmospheric conditions. Therefore, the reaction is assumed to involve disproportionation 100% of the time.
54	Rate constant is the average of the the IUPAC (Atkinson et al, 1999a) recommendations of 1×10^{-11} for the acetyl peroxy + ethyl peroxy reaction and 5×10^{-12} for the acetyl peroxy + $CH_3C(O)CH_2O_2$ reaction.
55	This reaction is assumed to proceed primarily by disproportionation to form the organic acid and a carbonyl compound, based on data for the acetyl peroxy + methyl peroxy reaction.
56	The rate parameters are assumed to be approximately the same as those for the reaction of $CH_3C(O)OO\cdot$ at the high pressure limit. This assumption is employed in the IUPAC (Atkinson et al, 1999a) evaluation when deriving the recommended value of the $CH_3CH_2C(O)OO\cdot + NO_2$ rate constant.
57	The products of the reactions of RCO-O2. are based on R=ethyl. Mechanism assumed to be similar to corresponding reaction of acetyl peroxy radicals.
58	Rate parameters based on the IUPAC (Atkinson et al, 1999a) recommendation for PPN.
58a	Rate constant expression based on the data of Seefeld and Kerr (1997), which gives k(PPN2)/k(PPNO) = 2.33±0.38, and the value of k(PPN2) used in the mechanism. This is as recommended by IUPAC (Atkinson et al, 1999a).
59	Assumed to have same rate constant as corresponding reaction of $CH_3C(O)OO$.
60	Rate constant based on $k(NO_2)/k(NO)$ ratio measured by Kirchner et al (1992) and the k(NO) used for general higher acyl peroxy radical species.
61	Rate constant expression based on the data of Kirchner et al (1992).
62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue
63	The mechanism is assumed to be analogous to the mechanism of the corresponding reaction of acetyl peroxy radicals. Note that the formation of benzyl peroxy radicals results in the formation of phenoxy after 1 NO to NO2 conversion, so it can be represented by BZ-O. + R2O2. The general lumped higher orgainc acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the aromatic acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.

Table A-4 (continued)

No.	Note
64	MA-RCO3. And MA-PAN are used to represent the acyl peroxy radical and PAN analogue formed from any acrolein compound. Their reactions are are based on those formed from methacrolein. Generally, the reaction mechanisms are assumed to be analogous to those for the corresponding reactions of acetyl peroxy radicals. The alkoxy radical is assumed to decompose to CO2 + CH2=CH(.)CH3, while the latter reacts with O2 to form HCHO + CH3CO., as discussed by Carter and Atkinson (1996). The general lumped higher orgainc acid (RCO-OH) and peroxyacid (RCO-OOH) are used to represent the unsaturated acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.
65	Rate parameters from Roberts and Bertman (1992), as used by Carter and Atkinson (1996).
66	The rate expression recommended by Atkinson (1997) for general alkoxy + NO_2 reactions is 2.3x10^{-11} exp(+150/T). This is reduced by a factor of 1.58 to be consistent with environmental chamber data, as discussed in a separate note.
67	The effects of isobutane on ozone formation and radical levels in environmental chamber experiments are not consistent with predictions of models which assume the recommended rate constant ratios for the decomposition of t-butoxy radicals relative to reaction with NO_2. The data are better fit if the ratio is increased by a factor of 2.5. The error is assumed to be equally distributed in each rate constant, so they are both adjusted by the a factor of 1.58, which is the square root of 2.5. This rate constant must be considered to be uncertain by at least this amount.
68	Atkinson (1997b) recommends the high-pressure rate expression of 6.0x10+14 exp(-16.2/RT). Batt and Robinson (1987) calculate that at one atmosphere the rate constant is 79% the high pressure limit, giving an estimated rate expression of 4.74x10-14 exp(-16.2/RT). This is increased by a factor of 1.58 to be consistent with environmental chamber data, as discussed in a separate note. This rate constant must be considered to be uncertain by at least this amount.
69	The rate constant is based on the general recommendation of Atkinson (1994) for alkoxy + NO2 reactions at the high pressure limit. Nitrophenol formation has generally been assumed in this reaction (e.g., see Atkinson, 1990; Carter, 1990), presumably via some rearrangement of an initially-formed unstable adduct. However, based on lower than expected yields of nitrophenols in NO3 + cresol and OH + benzaldehyde systems (Atkinson, 1994), this may be an oversimplification.
70	Assumed to have the same rate constant as the reaction of HO2 with peroxy radicals. This may underestimate the actual rate constant because alkoxy radicals tend to be more reactive than peroxy radicals.
71	This is included to avoid problems if these radicals are ever formed under conditions where both HO_2 and NO_2 are very low (which is considered to be unlikely under most ambient conditions), and can be considered to represent its reaction with organics present. The rate constant is arbitrary, and is such that this process becomes significant only if $[NO_2] < \sim 3 \times 10^{-6}$ ppm and $[HO_2] < 1 \times 10^{-5}$ ppm.
72	The rate constant is based on the general recommendation of Atkinson (1994) for alkoxy + NO2 reactions at the high pressure limit. The products of this reaction (presumed to be aromatic dinitro compounds) are expected to have very low vapor pressures and are represented as unreactive nitrogen and carbon.

Table A-4 (continued)

No.	Note
73	Absorption cross sections and quantum yields recommended by IUPAC (Atkinson et al, 1997a) used. Absorption cross sections used are those given for T = 285K.
74	Rate constant assumed to be the same as used for methylperoxy + NO.
75	T=298K Rate constant recommended by IUPAC (Atkinson et al, 1979a). Temperature dependence is as estimated by IUPAC (Atkinson et al, 1979a).
76	Absorption cross sections and quantum yields recommended by IUPAC (Atkinson et al, 1997a, 1999a) used. Reaction assumed to occur primarily by breaking the C-CHO bond. Pathway forming molecular products is assumed to be negligible under atmospheric conditions, based on calculated rate for analogous reaction of acetaldehyde.
77	Rate constant expression recommended by IUPAC, Supplement V (Atkinson et al, 1997a).
78	The mechanism for RCHO is based on reactions estimated for propionaldehyde.
79	OH reactions at various positions in the molecule estimated using the group-additivity methods of Kwok and Atkinson (1995), as updated by Kwok et al (1996).
80	Except as indicated by other footnotes, the overall reaction mechanism was derived using the general estimation methods for atmospheric reactions of alkyl, alkyl peroxy, and alkoxy radicals and the automated mechanism generation system as discussed by Carter (1999).
81	The rate constant is based on the estimated rate constant for the reaction of NO_3 with propionaldehyde. This is based on the correlation noted by Atkinson (1991) between HO and NO_3 radical H-atom abstraction rate constants, the assumption that the reaction only occurs at the -CHO group, and the estimated rate constant for OH reaction at that group. Atkinson (1991) noted that 298K H abstraction rate constants per abstractable hydrogen are approximately fit by $\ln k_{NO3} \approx 6.498 + 1.611 \ln k_{OH}$, and the rate constant for OH abstraction from the -CHO group estimated by group additivity methods is $k_{OH} = 1.94 \times 10^{-11}$ cm^3 molec^{-1} s^{-1}. These correspond to $k_{NO3} \approx 3.67 \times 10^{-15}$ cm^3 molec^{-1} s^{-1} at 298K. The temperature dependence is derived by assuming the same A factor as that for the reaction of NO_3 with acetaldehyde.
82	Reaction in the presence of NOx is assumed to involve formation of $CH_3C(O)CH2O.$, after one NO to NO2 conversion. Based on the data of Jenkin et al (1993), this radical is believed to rapidly decompose to HCHO + CH3CO.
83	Absorption cross sections and quantum yields used are those recommended by IUPAC (Atkinson et al, 1997a) except as noted. The reported quantum yields at 230 and 330 are expected to be high and an estimated correction was made as discussed by Carter et al (1993b). The corrected quantum yield data for wavelengths less than 290 nm were then fit to a smooth curve to estimate the quantum yields for higher wavelengths, with no weight being given to the highly uncertain 330 nm point. As discussed by Carter et al (1993b), using these corrections results in better fits of model calculations to environmental chamber experiments involving acetone.
84	The absorption coefficients used for MEK are from Moortgat (Private communication, 1996). The overall MEK quantum yield of 0.15 was found to give best fits to the MEK-NOx and MEK reactivity data our laboratories (Carter et al, 1999a). This is slightly higher than the overall quantum yield of 0.1 used in the previous version of the mechanism, based on fits to UNC outdoor chamber data (Carter, 1990). Using an overall quantum yield was found to give better fits

Table A-4 (continued)

No.	Note
	to the data using both xenon arc and blacklight light sources than assuming wavelength-dependence quantum yields such as for acetone. The reaction is assumed to proceed primarily by breaking the weakest CO-C bond.
85	The mechanism and rate constants are as recommended by IUPAC (Atkinson et al, 1997a, 1999a). 85% of the reaction is believed to involve formation of $\cdot CH_2OH$, with the remainder involving formation of $CH_3O\cdot$. However, both these radicals react primarily with O_2 forming formaldehyde + HO_2, so the overall process is as shown.
86	Rate constant and branching ratio for initial OH reaction based on IUPAC (Atkinson et al, 1997a, 1999a) recommendation. The .CH2OOH radical is assumed to rapidly decompose to HCHO + OH, based on its high estimated exothermicity.
87	Absorption cross sections from IUPAC (Atkinson et al, 1997a, 1999a), which also recommends assuming unit total quantum yield, but gives no recommendation as to the exact mechanism. Breaking the O-O bond assumed to be the major pathway.
88	The mechanism for ROOH is based on reactions estimated for n-propyl hydroperoxide.
89	Reaction at the OOH position is assumed to be as fast as in CH3OOH. Reaction at the 1-position is estimated to be ~7x10-12 (i.e., ~2/3 of the time) based on comparing rates of analogous reactions for methanol, ethanol, and CH3OOH (Atkinson et al., 1997a, 1999a). The alpha-hydroperoxy radicals are assumed to decompose rapidly to OH and the carbonyl on the basis of estimated high exothermicity. Reaction at the 2- or 3-positions are estimated to occur no more than ~10% of the time and are neglected.
90	Reaction assumed to occur with the same rate and analogous mechanism as methyl hydroperoxide.
91	Absorption cross sections from Plum et al (1983), as recommended by IUPAC (Atkinson et al, 1997a, 1999a).
91a.	Absorption cross sections from Plum et al (1983). The evaluations give no recommendations for biacetyl.
92	For the low wavelength band, a constant quantum yield of 0.4 is assumed, based on data of Langford and Moore (1984). For the high wavelength band, quantum yield is assumed to decrease linearly to zero at the threshold wavelength of 418 nm, starting at a "falloff" wavelength, which is adjusted to yield fits to chamber data for acetylene - NOx and acetylene reactivity experiments, as discussed by Carter et al (1997c). "Best fit" falloff wavelength of 380 nm used. Note that this gives overall quantum yields which are ~1.4 times higher than overall quantum yield reported by Plum et al (1983) for conditions of those experiments. Although use of acetylene reactivity data is a highly indirect way to obtain glyoxal quantum yields, it is considered to be a less uncertain way to estimate radical quantum yields then the data of Plum et al (1993), which uses a UV-poor light source and only measures rates of glyoxal decay.
93	Plum et al (1983) observed 13% formaldehyde yield in photodecomposition, so overall quantum yield adjusted to give this yield relative to the radical forming process for the spectral distribution of those experiments. A wavelength-independent quantum yield is used because of lack of information on wavelength dependence.

No.	Note
94	Product distribution based on the data of Niki et al (1985), as discussed by IUPAC (Atkinson et al, 1997a). Product distribution is calculated for 1 atm air at 298K.
95	HCO(CO)OO. is represented by the lumped higher acyl peroxy species RCO-OO.
96	The rate constant is estimated based on the correlation noted by Atkinson (1991) between HO and NO_3 radical H-atom abstraction rate constants, where the 298K H abstraction rate constants per abstractable hydrogen are approximately fit by $\ln k_{NO3} = 6.498 + 1.611 \ln k_{OH}$. The 298K rate constant is then derived from the 298K OH radical rate constant, assuming that all the reaction is at the OH group, and the temperature dependence is derived by assuming the same A factor per abstractable hydrogen as that for the reaction of NO_3 with acetaldehyde.
97	Absorption cross sections obtained from Moortgat (personal communication, 1996). These are essentially the same as those recommended by IUPAC (Atkinson et al, 1997a, 1999a), except slightly better resolution. Photolysis at the low wavelength band is assumed to have unit quantum yields, based on data for biacetyl. Photolysis above the cutoff wavelength of 421 nm (Atkinson et al, 1977a) is assumed to have zero quantum yields. For the rest of the high wavelength region, the wavelength dependence was derived by assuming the quantum yields decline linearly from 1 at 344 nm to 0 at a wavelength (407 nm) which was adjusted to be such that the calculated overall quantum yields for the conditions of the experiments of Plum et al (1983) agreed with the overall quantum yield they observed experimentally. The quantum yields recommended by IUPAC (Atkinson et al, 1999a) lack sufficient wavelength resolution to be useful for modeling.
98	Assumed to have unit quantum yield at low wavelength band based on data cited by Atkinson (1994). For the high wavelength band, the quantum yields were assumed to decline linearly from 1 at 350 nm to 0 at a wavelength (420 nm) which was adjusted to be such that the calculated overall quantum yields for the conditions of the experiments of Plum et al (1983) agreed with the overall quantum yield they observed experimentally.
99	Rate constant recommended by Atkinson (1994) for o-cresol.
100	The parameterized mechanism is estimated by analogy to the parameterized mechanism derived for cresols (see footnotes for OH + cresol reaction).
101	In absence of definitive data concerning this reaction, the same mechanism is used as assumed by Carter (1990). However, see footnotes concerning phenoxy reactions.
102	The parameterized mechanism is based on that used by Carter (1990), but was reoptimized to fit the NO, ozone, PAN, and cresol data in the o-cresol - NOx experiment EC281.
103	Assumed to have the same rate constant as the reaction of NO_3 with phenol. Reaction with NO_3 is assumed to dominate over reaction with OH radicals and other loss processes.
104	Absorption coefficients are from Majer et al (1969). The overall quantum yield derived by Carter (1990), which are based on model simulations of benzaldehyde decay rates in SAPRC evacuable chamber experiments, is used. Because of lack of data, the quantum yield is assumed to be independent of wavelength. The products formed from benzaldehyde photolysis are unknown, except that both radical formation and benzene formation appear to be minor (Carter, 1990). This benzaldehyde photolysis mechanism gives reasonably good model simulations of benzaldehyde -

Table A-4 (continued)

No.	Note
	NOx experiments recently carried out in the CE-CERT xenon Teflon chamber (Carter et al, 1998a).
105	T=298K rate constant recommended by Atkinson (1994). Temperature dependence estimated by assuming the reaction has the same A factor as the reaction of NO_3 with acetaldehyde.
106	The rate constant and mechanism of Carter and Atkinson (1996) was used with no significant changes (except as indicated in other footnotes, if applicable). Some minor changes in product yields may result in some cases from use of the general mechanism estimation system (Carter, 1999a) to generate the overall reaction scheme.
107	MEK is used to represent hydroxyacetone.
108	The excited $HCHO_2$ biradical is assumed to react as recommended by Atkinson (1997) based on data for the O3 + ethene system, i.e., 37% stabilization, 12% decomposition to HCO + OH, 13% decomposition to CO_2 + H_2, and 38% decomposition to CO + H_2O. Note that this is different than used for this species when formed in the isoprene products mechanisms of Carter and Atkinson (1996) and Carter (1996).
109	The vibrationally excited $HCOC(CH_3)CO_2$ biradicals are assumed to rearrange and decompose to $HCOC(O)CH_2$. + OH, where the former forms HCOC(O). + HCHO after O2 addition and NO to NO_2 conversion. RCO-O2. is used to represent HCOC(O)OO. in this reaction. Vibrationally excited $CH_3C(O)CHO_2$ is assumed to rapidly convert to $HCOC(CH_3)CO_2$ as discussed by Carter and Atkinson (1996).
110	The organic acid(s) formed in this reaction represent the formation of stabilizied Crigiee biradicals, which are assumed to be consumed primairly by reaction with H_2O forming the corresponding acid.
111	NO_3 radical addition assumed to occur primarily at the least substituted position.
112	The product CH3C(O)CH2ONO2 is expected to be relatively unreactive and is represented as "lost nitrogen" + 3 "lost carbons".
113	Rate constant estimated from linear correlation between log k for OH and O3P reaction. Chamber data for C_{3+} alkenes are better fit by models assuming O3P reactions with C_{3+} species do not form radicals. Stable products represented by the lumped higher aldehyde or ketone, depending on type of product(s) expected to be formed.
114	The overall quantum yield was reoptimized to fit the same data as discussed by Carter and Atkinson (1996). In the case of methacrolein, he changes to the other portion of the mechanism resulted in an ~14% increase in the best fit overall quantum yield compared to that derived by Carter and Atkinson (1996). In the case of MVK, the best fit overall quantum yield decreased by a factor of 5.
115	CH_2=CHC(O)OO. Is represented by MA-RCO3.
116	As discussed by Carter (1996), ISOPROD is the "four product" lumped isoprene product species whose mechanism is derived by lumping rate constant and product parameters for a mixture of 30% hydroxymethacrolein, and 70% equal amounts of cis and trans $HCOC(CH_3)=CHCH_2OH$ and $HCOCH=C(CH_3)CH_2OH$. These proportions are based on the estimated yields of these products

Table A-4 (continued)

No.	Note
	in the reactions of OH with isoprene (Carter and Atkinson, 1996), which are represented by ISOPROD in the four product condensed mechanism (Carter, 1996). The other footnotes refer to the estimated mechanisms for these four individual compounds which were used to derive the lumped ISOPROD mechanism. RCHO, PROD2, MA-RCO3, etc. are used to represent various compounds as indicated in the descriptions of these lumped model species. See Carter and Atkinson (1996) for the specific compounds which can be formed in the various reactions of these species.
117	The $HC(O)CHO_2$ biradical can decopose either to OH + HCO + CO via an internal H abstraction from HCO, or to HCO + HCO_2 via rearrangement to HCOCH(O.)O. and decomposition. (The HCO would form HO_2 + CO and the HCO_2 would form HO_2 + CO_2 after reaction with O_2.) These two pathways are assumed to have equal probability. Note that decomposition for these biradicals is assumed to be faster than for biradicals such as CH_3CHO_2 because of the weaker H-CO and C-CO bonds.
118	The excited $CH_3C(O_2)CH_2OH$ biradical is assumed to react primarily via rearrangement to the unsaturated hydroperoxide followed by decomposition to OH radicals and the corresponding carbonyl compound, as is assumed in the general alkene mechanism (Carter, 1999b). Two possible such rearrangements can occur in the case of this biradical, one to $CH_2=C(OOH)CH_2OH$, which decomposes to OH + $HOCH_2C(O)CH_2$., and the other to $HOCH=C(OOH)CH_3$, which decomposes to OH + $CH_3C(O)CH(.)OH$. The relative importances of the competing rearrangements in such cases is estimated by assuming they are approximately proportional to the estimated OH abstracting rate constant from the H-donating group (Carter, 1999b). Based on this, the overall reaction is estimated to be OH + 0.04 $HOCH_2C(O)CH_2$. + 0.96 $CH_3C(O)CH(.)OH$, with the subsequent reactions of these radicals being derived by the general estimation methods (Carter, 1999a).
119	All the species represented by ISOPROD are assumed to have the same overall photolysis rate as used for methacrolein.
120	The PROD2 mechanism was derived by averaging mechanisms for $CH_3C(O)CH_2CH_2CH_2OH$, $CH_3C(O)CH_2CH(CH_3)CH_2OH$, $CH_3CH(OH)CH_2CH_2C(O)CH_2CH_3$, $CH_3CH_2CH(OH)CH_2CH_2C(O)CH_2CH_3$, and $CH_3CH_2CH_2CH(OH)CH_2CH_2C(O)CH_2CH_3$, which were taken as representative of the products formed from VOCs measured in ambient air that are represented by PROD2 in the model (Carter, 1999). The mechanisms for these five representative PROD2 compounds were derived using the mechanism generation and estimation methods discussed by Carter (1999).
121	Assumed to photolyze with the same rate absorption cross section as used for MEK and other higher ketones. The overall quantum yield is assumed to be the same as that which gives best fits to chamber data for 2-heptanone (Carter et al, 1999e), which has the approximately the same number of carbons as the average for the set of compounds used to derive the PROD2 mechanism.
122	The RNO3 mechanism was derived by averaging mechanisms for $CH_3CH(ONO_2)CH_2CH_3$, $CH_3CH(OH)CH_2CH_2CH_2ONO_2$, $CH_3CH(ONO_2)CH(CH_3)CH_2CH_3$, $CH_3CH_2CH_2CH_2CH_2CH(ONO_2)CH_2OH$, $CH_3CH(CH_3)CH_2C(CH_3)(ONO_2)CH_2CH_3$, and CH_3CH_2CH(ONO2)CH2CH_2CH2-CH_2CH_2CH2CH_3, which were taken as representative of the products formed from VOCs

Table A-4 (continued)

No.	Note
	measured in ambient air that are represented by RNO3 in the model (Carter, 1999). The mechanisms for these three representative RNO3 compounds were derived using the mechanism generation and estimation methods discussed by Carter (1999).
123	Absorption cross sections given by IUPAC (Atkinson et al, 1997a, 1999a) for isopropyl nitrate are used. As discussed by IUPAC (Atkinson et al, 1999a), the quantum yield is expected to be near unity for formation of NO2.
124	DCB1 is used to represent aromatic ring fragmentation products that do not undergo signficant photodecomposition to radicals. Its mechanism is largely parameterized, but it is based roughly on that expected for unsaturated dicarbonys such as 2-butene-1,3-dial.
125	The rate constant is based on data of Bierbach et al (1994). The reaction is assumed to proceed via addition of OH to double bond, followed by decomposition of the alkoxy radical to HCO and HC(O)CH(OH)CHO, where the latter is represented by RCHO. Although this mechanism may not be what one would estimate for the non-photoreactive unsaturated diketones (Bierback et al, 1994; Tuazon et al, 1985) expected to be formed from o-substitued aromatics, best fits to the o-xylene and 1,2,4-trimethylbenzene chamber data are obtained if this mechanism is used.
126	The photolysis action spectra of these products are assumed to be similar to that for acrolein, so the absorption cross sections of acrolein are used, with a wavelength-independent overall quantum yield. The overall quantum yield is adjusted to optimize fits of model simulations to the benzene - NOx experiments used in the optimization of the previous version of the mechanism by Carter et al (1997a), The photolyisis mechanism is represented as being similar to that used for DCB2 and DCB3. However, best fits to benzene - NOx experiments are obtained if this photolysis is assumed to be slow, so the reaction is not included in the mechanism.
127	The rate constant is based on the data of Bierbach et al (1994). The reaction is assumed to involve initial formation of glyoxal and $HC(O)CHO_2$.
128	DCB2 and DCB3 represent the highly photoreactive unsaturated dicarbonyl product formed from the ring-opening reactions of the alkylbenzenes. To fit chamber data using differing light sources, they are represented by two species, which differ only in their action spectra and overall quantum yields, with the action spectrum of DCB2 being like methyl glyoxal, and that of DCB3 being like acrolein, and with the overall quantum yields adjusted separately to fit chamber data. Its reactions are based roughly on estimated reactions of a 5-carbon compound with general structure XC(O)CX=CXC(O)X, where X can be H or alkyl.
129	Assumed to have the same rate constant as used for DCB1. Mechanism represented as OH adding to double bond in XC(O)CX=CXC(O)X, with alkoxy radical decomposing to CH3CO. and XCO-CH(OH)-CXO, the latter being represented by RCHO. Note that the general alkoxy radical estimation method (Carter, 1999) predicts that alkoxy radicals like RCH(OH)CH(O.)C(O)R' will decompose primarily to RCH(OH)CHO + RC(O).
130	The overall quantum yields for DCB2 and DCB3 were optimized to give best fits of model simulations of NO oxidation, O3 formation and xylene consumption in m-xylene - NOx chamber runs with various light sources, and also to mini-surrogate - NOx runs. The DCB2 and DCB3 quantum yields had to be adjusted as well as the yields of these products from m-xylene to best fit the data for the various light sources, and also to fit the results of the mini-surrogate as well as the

Table A-4 (continued)

No.	Note
	m-xylene only runs. (For the other aromatics, only the DCB2 and DCB3 yields are optimized.) The photolysis mechanisms are unknown, and probably highly variable depending on the species involved. For an RC(O)CH=CHC(O)H structure, the most energetically favored initial reaction is formation of R. + HCOCH=CHCO., but assuming that mechanism results in a model that consistently underpredicts PAN yields in alkylbenzene - NOx chamber experiments. Therefore, a set of products is assumed to be formed that may result from various different reaction
131	Isoprene mechanism used is based on the "four product" condensed isoprene mechanism of Carter (1996) which in turn is based on the detailed isoprene mechanism of Carter and Atkinson (1996). The rate constants and the major initial reaction pathways are the same as used in those mechanisms. Some minor changes in product yields resulted in some cases from use of the general mechanism estimation system (Carter, 1999a) to generate the overall reaction schemes, or as indicated in other footnotes.
132	The overall nitrate yield is slightly higher than the adjusted nitrate yields in the Carter and Atkinson (1996) mechanism because the mechanism generation system included some nitrate formation from peroxy radicals formed in secondary reactions. Although the yields were not readjusted, the mechanism still gives satisfactory fits to the isoprene chamber data used in the nitrate yield adjustments by Carter and Atkinson (1996).
133	The excited $CH_2=CHC(O_2)CH_3$ and $CH_2=C(CH_3)CHO_2$. biradical reactions are the same as given by Carter and Atkinson (1996), except that the $CH_2=CHC(O)O_2$. formed from the former is represented by MA-RCO3, and the propene formed from the latter is represented by PROD2.
134	All the organic products formed in this reaction are represented by ISOPROD. A small amount of nitrate formation is estimated to occur from the reactions of the substituted peroxy radicals with NO (Carter, 1999a).
135	PROD2 is used to represent the various isoprene oxide products. And MA-RCO3 us used to represent $CH_2=CHC(O)OO$. Note that this mechanism, which is based on that of Carter and Atkinson (1996) is inconsistent with the mechanisms for the reactions of O^3P with the other higher alkenes, which are assumed not to form radical products. However, assuming no radical formation in the reaction of O^3P with isoprene results in somewhat degraded model performance in simulations of the results of the isoprene experiments discussed by Carter and Atkinson (1996).
136	See discussion of mechanism generation system for documentation details for individual VOCs.
137	Based largely on "four product" isoprene mechanism of Carter (1996).
138	Mechanism for ethane, the only compound in this lumped class present in the base ROG mixture that is used to derive the mechanisms of these lumped species.
139	Mechanism based on 41% acetylene and 59% propane, the two compounds in this class present in the base ROG mixture that is used to derive the mechanisms for the lumped species. The ratio is based on the relative number of moles of each present in the mixture. The reaction of acetylene with O3 is ignored.
140	Mechanism and rate parameters are averages for the compounds in this class that are present in the base ROG mixture that is used to derive the mechanisms of these lumped species.

Table A-4 (continued)

No.	Note
141	Mechanism is the average for the compounds in this class that are present in the base ROG mixture that is used to derive the mechanisms of these lumped species. The rate parameters are those for toluene, the major compound in this class. The contribution of benzene to the mixture is given a reactivity weighting factor of 0.295, based on its kinetic reactivity [calculated using an IntOH of 110 ppt-min (Middleton et al, 1990)] relative to that of toluene.
142	Mechanisms and rate parameters are emissions-weighed averages of those for the five terpenes with the highest estimated total annual North American emissions as given by Guenther et al (1999).

Table A-5. Listing of the absorption cross sections and quantum yields for the photolysis reactions.

WL (nm)	Abs (cm^2)	QY (nm)	WL	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY
							NO2							
205.0	4.31e-19	1.000	210.0	4.72e-19	1.000	215.0	4.95e-19	1.000	220.0	4.56e-19	1.000	225.0	3.79e-19	1.000
230.0	2.74e-19	1.000	235.0	1.67e-19	1.000	240.0	9.31e-20	1.000	245.0	4.74e-20	1.000	250.0	2.48e-20	1.000
255.0	1.95e-20	1.000	260.0	2.24e-20	1.000	265.0	2.73e-20	1.000	270.0	4.11e-20	1.000	275.0	4.90e-20	1.000
280.0	5.92e-20	1.000	285.0	7.39e-20	1.000	290.0	9.00e-20	1.000	295.0	1.09e-19	1.000	300.0	1.31e-19	1.000
305.0	1.57e-19	1.000	310.0	1.86e-19	1.000	315.0	2.15e-19	0.990	320.0	2.48e-19	0.990	325.0	2.81e-19	0.990
330.0	3.13e-19	0.990	335.0	3.43e-19	0.990	340.0	3.80e-19	0.990	345.0	4.07e-19	0.990	350.0	4.31e-19	0.990
355.0	4.72e-19	0.990	360.0	4.83e-19	0.980	365.0	5.17e-19	0.980	370.0	5.32e-19	0.980	375.0	5.51e-19	0.980
380.0	5.64e-19	0.970	385.0	5.76e-19	0.970	390.0	5.93e-19	0.960	395.0	5.85e-19	0.935	400.0	6.02e-19	0.820
405.0	5.78e-19	0.355	410.0	6.00e-19	0.130	411.0	5.93e-19	0.110	412.0	5.86e-19	0.094	413.0	5.79e-19	0.083
414.0	5.72e-19	0.070	415.0	5.65e-19	0.059	416.0	5.68e-19	0.048	417.0	5.71e-19	0.039	418.0	5.75e-19	0.030
419.0	5.78e-19	0.023	420.0	5.81e-19	0.018	421.0	5.72e-19	0.012	422.0	5.64e-19	0.008	423.0	5.55e-19	0.004
424.0	5.47e-19	0.000												
							NO3NO							
585.0	2.89e-18	0.000	586.0	3.32e-18	0.050	587.0	4.16e-18	0.100	588.0	5.04e-18	0.150	589.0	6.13e-18	0.200
590.0	5.96e-18	0.250	591.0	5.44e-18	0.280	592.0	5.11e-18	0.310	593.0	4.58e-18	0.340	594.0	4.19e-18	0.370
595.0	4.29e-18	0.400	596.0	4.62e-18	0.370	597.0	4.36e-18	0.340	598.0	3.67e-18	0.310	599.0	3.10e-18	0.280
600.0	2.76e-18	0.250	601.0	2.86e-18	0.240	602.0	3.32e-18	0.230	603.0	3.80e-18	0.220	604.0	4.37e-18	0.210
605.0	4.36e-18	0.200	606.0	3.32e-18	0.200	607.0	2.40e-18	0.200	608.0	1.85e-18	0.200	609.0	1.71e-18	0.200
610.0	1.77e-18	0.200	611.0	1.91e-18	0.180	612.0	2.23e-18	0.160	613.0	2.63e-18	0.140	614.0	2.55e-18	0.120
615.0	2.26e-18	0.100	616.0	2.09e-18	0.100	617.0	2.11e-18	0.100	618.0	2.39e-18	0.100	619.0	2.56e-18	0.100
620.0	3.27e-18	0.100	621.0	5.24e-18	0.090	622.0	1.02e-17	0.080	623.0	1.47e-17	0.070	624.0	1.21e-17	0.060
625.0	8.38e-18	0.050	626.0	7.30e-18	0.050	627.0	7.53e-18	0.050	628.0	7.37e-18	0.050	629.0	6.98e-18	0.050
630.0	6.76e-18	0.050	631.0	4.84e-18	0.046	632.0	3.27e-18	0.042	633.0	2.17e-18	0.038	634.0	1.64e-18	0.034
635.0	1.44e-18	0.030	636.0	1.69e-18	0.024	637.0	2.07e-18	0.018	638.0	2.03e-18	0.012	639.0	1.58e-18	0.006
640.0	1.23e-18	0.000												
							NO3NO2							
400.0	0.00e+00	1.000	401.0	0.00e+00	1.000	402.0	0.00e+00	1.000	403.0	2.00e-20	1.000	404.0	0.00e+00	1.000
405.0	3.00e-20	1.000	406.0	2.00e-20	1.000	407.0	1.00e-20	1.000	408.0	3.00e-20	1.000	409.0	0.00e+00	1.000
410.0	1.00e-20	1.000	411.0	2.00e-20	1.000	412.0	5.00e-20	1.000	413.0	5.00e-20	1.000	414.0	2.00e-20	1.000
415.0	6.00e-20	1.000	416.0	6.00e-20	1.000	417.0	7.00e-20	1.000	418.0	5.00e-20	1.000	419.0	8.00e-20	1.000
420.0	8.00e-20	1.000	421.0	8.00e-20	1.000	422.0	9.00e-20	1.000	423.0	1.10e-19	1.000	424.0	9.00e-20	1.000
425.0	7.00e-20	1.000	426.0	1.40e-19	1.000	427.0	1.40e-19	1.000	428.0	1.20e-19	1.000	429.0	1.10e-19	1.000
430.0	1.70e-19	1.000	431.0	1.30e-19	1.000	432.0	1.50e-19	1.000	433.0	1.80e-19	1.000	434.0	1.80e-19	1.000
435.0	1.60e-19	1.000	436.0	1.50e-19	1.000	437.0	1.80e-19	1.000	438.0	2.10e-19	1.000	439.0	2.00e-19	1.000
440.0	1.90e-19	1.000	441.0	1.80e-19	1.000	442.0	2.10e-19	1.000	443.0	1.80e-19	1.000	444.0	1.90e-19	1.000
445.0	2.00e-19	1.000	446.0	2.40e-19	1.000	447.0	2.90e-19	1.000	448.0	2.40e-19	1.000	449.0	2.80e-19	1.000
450.0	2.90e-19	1.000	451.0	3.00e-19	1.000	452.0	3.30e-19	1.000	453.0	3.10e-19	1.000	454.0	3.60e-19	1.000
455.0	3.60e-19	1.000	456.0	3.60e-19	1.000	457.0	4.00e-19	1.000	458.0	3.70e-19	1.000	459.0	4.20e-19	1.000
460.0	4.00e-19	1.000	461.0	3.90e-19	1.000	462.0	4.00e-19	1.000	463.0	4.10e-19	1.000	464.0	4.80e-19	1.000
465.0	5.10e-19	1.000	466.0	5.40e-19	1.000	467.0	5.70e-19	1.000	468.0	5.60e-19	1.000	469.0	5.80e-19	1.000
470.0	5.90e-19	1.000	471.0	6.20e-19	1.000	472.0	6.40e-19	1.000	473.0	6.20e-19	1.000	474.0	6.20e-19	1.000
475.0	6.80e-19	1.000	476.0	7.80e-19	1.000	477.0	7.70e-19	1.000	478.0	7.30e-19	1.000	479.0	7.30e-19	1.000
480.0	7.00e-19	1.000	481.0	7.10e-19	1.000	482.0	7.10e-19	1.000	483.0	7.20e-19	1.000	484.0	7.70e-19	1.000
485.0	8.20e-19	1.000	486.0	9.10e-19	1.000	487.0	9.20e-19	1.000	488.0	9.50e-19	1.000	489.0	9.60e-19	1.000
490.0	1.03e-18	1.000	491.0	9.90e-19	1.000	492.0	9.90e-19	1.000	493.0	1.01e-18	1.000	494.0	1.01e-18	1.000
495.0	1.06e-18	1.000	496.0	1.21e-18	1.000	497.0	1.22e-18	1.000	498.0	1.20e-18	1.000	499.0	1.17e-18	1.000
500.0	1.13e-18	1.000	501.0	1.11e-18	1.000	502.0	1.11e-18	1.000	503.0	1.11e-18	1.000	504.0	1.26e-18	1.000
505.0	1.28e-18	1.000	506.0	1.34e-18	1.000	507.0	1.28e-18	1.000	508.0	1.27e-18	1.000	509.0	1.35e-18	1.000
510.0	1.51e-18	1.000	511.0	1.73e-18	1.000	512.0	1.77e-18	1.000	513.0	1.60e-18	1.000	514.0	1.58e-18	1.000
515.0	1.58e-18	1.000	516.0	1.56e-18	1.000	517.0	1.49e-18	1.000	518.0	1.44e-18	1.000	519.0	1.54e-18	1.000
WL (nm)	Abs (cm^2)	QY (nm)	WL	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY
520.0	1.68e-18	1.000	521.0	1.83e-18	1.000	522.0	1.93e-18	1.000	523.0	1.77e-18	1.000	524.0	1.64e-18	1.000
525.0	1.58e-18	1.000	526.0	1.63e-18	1.000	527.0	1.81e-18	1.000	528.0	2.10e-18	1.000	529.0	2.39e-18	1.000
530.0	2.23e-18	1.000	531.0	2.09e-18	1.000	532.0	2.02e-18	1.000	533.0	1.95e-18	1.000	534.0	2.04e-18	1.000
535.0	2.30e-18	1.000	536.0	2.57e-18	1.000	537.0	2.58e-18	1.000	538.0	2.34e-18	1.000	539.0	2.04e-18	1.000
540.0	2.10e-18	1.000	541.0	2.04e-18	1.000	542.0	1.88e-18	1.000	543.0	1.68e-18	1.000	544.0	1.70e-18	1.000

Table A-5 (continued)

WL (nm)	Abs (cm^2)	QY (nm)	WL	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY
520.0	1.68e-18	1.000	521.0	1.83e-18	1.000	522.0	1.93e-18	1.000	523.0	1.77e-18	1.000	524.0	1.64e-18	1.000
525.0	1.58e-18	1.000	526.0	1.63e-18	1.000	527.0	1.81e-18	1.000	528.0	2.10e-18	1.000	529.0	2.39e-18	1.000
530.0	2.23e-18	1.000	531.0	2.09e-18	1.000	532.0	2.02e-18	1.000	533.0	1.95e-18	1.000	534.0	2.04e-18	1.000
535.0	2.30e-18	1.000	536.0	2.57e-18	1.000	537.0	2.58e-18	1.000	538.0	2.34e-18	1.000	539.0	2.04e-18	1.000
540.0	2.10e-18	1.000	541.0	2.04e-18	1.000	542.0	1.88e-18	1.000	543.0	1.68e-18	1.000	544.0	1.70e-18	1.000
545.0	1.96e-18	1.000	546.0	2.42e-18	1.000	547.0	2.91e-18	1.000	548.0	2.98e-18	1.000	549.0	2.71e-18	1.000
550.0	2.48e-18	1.000	551.0	2.43e-18	1.000	552.0	2.47e-18	1.000	553.0	2.53e-18	1.000	554.0	2.78e-18	1.000
555.0	3.11e-18	1.000	556.0	3.26e-18	1.000	557.0	3.29e-18	1.000	558.0	3.51e-18	1.000	559.0	3.72e-18	1.000
560.0	3.32e-18	1.000	561.0	2.98e-18	1.000	562.0	2.90e-18	1.000	563.0	2.80e-18	1.000	564.0	2.72e-18	1.000
565.0	2.73e-18	1.000	566.0	2.85e-18	1.000	567.0	2.81e-18	1.000	568.0	2.85e-18	1.000	569.0	2.89e-18	1.000
570.0	2.79e-18	1.000	571.0	2.76e-18	1.000	572.0	2.74e-18	1.000	573.0	2.78e-18	1.000	574.0	2.86e-18	1.000
575.0	3.08e-18	1.000	576.0	3.27e-18	1.000	577.0	3.38e-18	1.000	578.0	3.31e-18	1.000	579.0	3.24e-18	1.000
580.0	3.34e-18	1.000	581.0	3.55e-18	1.000	582.0	3.28e-18	1.000	583.0	2.93e-18	1.000	584.0	2.82e-18	1.000
585.0	2.89e-18	1.000	586.0	3.32e-18	0.950	587.0	4.16e-18	0.900	588.0	5.04e-18	0.850	589.0	6.13e-18	0.800
590.0	5.96e-18	0.750	591.0	5.44e-18	0.720	592.0	5.11e-18	0.690	593.0	4.58e-18	0.660	594.0	4.19e-18	0.630
595.0	4.29e-18	0.600	596.0	4.62e-18	0.590	597.0	4.36e-18	0.580	598.0	3.67e-18	0.570	599.0	3.10e-18	0.560
600.0	2.76e-18	0.550	601.0	2.86e-18	0.540	602.0	3.32e-18	0.530	603.0	3.80e-18	0.520	604.0	4.37e-18	0.510
605.0	4.36e-18	0.400	606.0	3.32e-18	0.380	607.0	2.40e-18	0.360	608.0	1.85e-18	0.340	609.0	1.71e-18	0.320
610.0	1.77e-18	0.300	611.0	1.91e-18	0.290	612.0	2.23e-18	0.280	613.0	2.63e-18	0.270	614.0	2.55e-18	0.260
615.0	2.26e-18	0.250	616.0	2.09e-18	0.240	617.0	2.11e-18	0.230	618.0	2.39e-18	0.220	619.0	2.56e-18	0.210
620.0	3.27e-18	0.200	621.0	5.24e-18	0.190	622.0	1.02e-17	0.180	623.0	1.47e-17	0.170	624.0	1.21e-17	0.160
625.0	8.38e-18	0.150	626.0	7.30e-18	0.130	627.0	7.53e-18	0.110	628.0	7.37e-18	0.090	629.0	6.98e-18	0.070
630.0	6.76e-18	0.050	631.0	4.84e-18	0.040	632.0	3.27e-18	0.030	633.0	2.17e-18	0.020	634.0	1.64e-18	0.010
635.0	1.44e-18	0.000												
							O3O3P							
175.4	8.11e-19	0.050	177.0	8.11e-19	0.050	178.6	7.99e-19	0.050	180.2	7.86e-19	0.050	181.8	7.63e-19	0.050
183.5	7.29e-19	0.050	185.2	6.88e-19	0.050	186.9	6.22e-19	0.050	188.7	5.76e-19	0.050	190.5	5.26e-19	0.050
192.3	4.76e-19	0.050	194.2	4.28e-19	0.050	196.1	3.83e-19	0.050	198.0	3.47e-19	0.050	200.0	3.23e-19	0.050
202.0	3.14e-19	0.050	204.1	3.26e-19	0.050	206.2	3.64e-19	0.050	208.3	4.34e-19	0.050	210.5	5.42e-19	0.050
212.8	6.99e-19	0.050	215.0	9.20e-19	0.050	217.4	1.19e-18	0.050	219.8	1.55e-18	0.050	222.2	1.99e-18	0.050
224.7	2.56e-18	0.050	227.3	3.23e-18	0.050	229.9	4.00e-18	0.050	232.6	4.83e-18	0.050	235.3	5.79e-18	0.050
238.1	6.86e-18	0.050	241.0	7.97e-18	0.050	243.9	9.00e-18	0.050	246.9	1.00e-17	0.050	250.1	1.08e-17	0.050
253.2	1.13e-17	0.050	256.4	1.15e-17	0.050	259.7	1.12e-17	0.050	263.2	1.06e-17	0.050	266.7	9.65e-18	0.050
270.3	8.34e-18	0.050	274.0	6.92e-18	0.050	277.8	5.42e-18	0.050	281.7	4.02e-18	0.050	285.7	2.77e-18	0.050
289.9	1.79e-18	0.050	290.0	1.77e-18	0.050	294.1	1.09e-18	0.050	295.0	9.95e-19	0.050	298.5	6.24e-19	0.050
300.0	5.30e-19	0.050	303.0	3.43e-19	0.015	305.0	2.76e-19	0.020	306.0	2.42e-19	0.050	307.0	2.09e-19	0.123
307.7	1.85e-19	0.196	308.0	1.80e-19	0.227	309.0	1.61e-19	0.333	310.0	1.43e-19	0.400	311.0	1.25e-19	0.612
312.0	1.07e-19	0.697	312.5	9.80e-20	0.718	313.0	9.32e-20	0.738	314.0	8.36e-20	0.762	315.0	7.40e-20	0.765
316.0	6.44e-20	0.779	317.0	5.48e-20	0.791	317.5	5.00e-20	0.799	318.0	4.75e-20	0.806	319.0	4.25e-20	0.822
322.5	2.49e-20	0.906	327.5	1.20e-20	0.940	332.5	6.17e-21	0.950	337.5	2.74e-21	0.975	342.5	1.17e-21	1.000
347.5	5.90e-22	1.000	352.5	2.70e-22	1.000	357.5	1.10e-22	1.000	362.5	5.00e-23	1.000	367.5	0.00e+00	1.000
400.0	0.00e+00	1.000	410.0	1.20e-23	1.000	420.0	2.20e-23	1.000	440.0	1.12e-22	1.000	460.0	3.28e-22	1.000
480.0	6.84e-22	1.000	500.0	1.22e-21	1.000	520.0	1.82e-21	1.000	540.0	2.91e-21	1.000	560.0	3.94e-21	1.000
580.0	4.59e-21	1.000	600.0	5.11e-21	1.000	620.0	4.00e-21	1.000	640.0	2.96e-21	1.000	660.0	2.09e-21	1.000
680.0	1.36e-21	1.000	700.0	9.10e-22	1.000	750.0	3.20e-22	1.000	800.0	1.60e-22	1.000	900.0	0.00e+00	1.000

Table A-5 (continued)

WL (nm)	Abs (cm^2)	QY (nm)	WL	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY
O3O1D														
175.4	8.11e-19	0.870	177.0	8.11e-19	0.870	178.6	7.99e-19	0.870	180.2	7.86e-19	0.870	181.8	7.63e-19	0.870
183.5	7.29e-19	0.870	185.2	6.88e-19	0.870	186.9	6.22e-19	0.870	188.7	5.76e-19	0.870	190.5	5.26e-19	0.870
192.3	4.76e-19	0.870	194.2	4.28e-19	0.870	196.1	3.83e-19	0.870	198.0	3.47e-19	0.870	200.0	3.23e-19	0.870
202.0	3.14e-19	0.870	204.1	3.26e-19	0.870	206.2	3.64e-19	0.870	208.3	4.34e-19	0.870	210.5	5.42e-19	0.870
212.8	6.99e-19	0.870	215.0	9.20e-19	0.870	217.4	1.19e-18	0.870	219.8	1.55e-18	0.870	222.2	1.99e-18	0.870
224.7	2.56e-18	0.870	227.3	3.23e-18	0.870	229.9	4.00e-18	0.870	232.6	4.83e-18	0.870	235.3	5.79e-18	0.870
238.1	6.86e-18	0.870	241.0	7.97e-18	0.870	243.9	9.00e-18	0.870	246.9	1.00e-17	0.870	250.1	1.08e-17	0.870
253.2	1.13e-17	0.870	256.4	1.15e-17	0.870	259.7	1.12e-17	0.870	263.2	1.06e-17	0.870	266.7	9.65e-18	0.870
270.3	8.34e-18	0.870	274.0	6.92e-18	0.881	277.8	5.42e-18	0.896	281.7	4.02e-18	0.911	285.7	2.77e-18	0.926
289.9	1.79e-18	0.942	290.0	1.77e-18	0.942	294.1	1.09e-18	0.950	295.0	9.95e-19	0.950	298.5	6.24e-19	0.950
300.0	5.30e-19	0.950	303.0	3.43e-19	0.985	305.0	2.76e-19	0.980	306.0	2.42e-19	0.950	307.0	2.09e-19	0.877
307.7	1.85e-19	0.804	308.0	1.80e-19	0.773	309.0	1.61e-19	0.667	310.0	1.43e-19	0.600	311.0	1.25e-19	0.388
312.0	1.07e-19	0.303	312.5	9.80e-20	0.283	313.0	9.32e-20	0.262	314.0	8.36e-20	0.238	315.0	7.40e-20	0.235
316.0	6.44e-20	0.221	317.0	5.48e-20	0.209	317.5	5.00e-20	0.202	318.0	4.75e-20	0.194	319.0	4.25e-20	0.178
322.5	2.49e-20	0.095	327.5	1.20e-20	0.060	332.5	6.17e-21	0.050	337.5	2.74e-21	0.025	342.5	1.17e-21	0.000
347.5	5.90e-22	0.000												
HONO-NO														
309.0	0.00e+00	0.410	310.0	1.30e-20	0.410	311.0	1.90e-20	0.411	312.0	2.80e-20	0.421	313.0	2.20e-20	0.432
314.0	3.60e-20	0.443	315.0	3.00e-20	0.454	316.0	1.40e-20	0.464	317.0	3.10e-20	0.475	318.0	5.60e-20	0.486
319.0	3.60e-20	0.496	320.0	4.90e-20	0.507	321.0	7.80e-20	0.518	322.0	4.90e-20	0.529	323.0	5.10e-20	0.539
324.0	7.10e-20	0.550	325.0	5.00e-20	0.561	326.0	2.90e-20	0.571	327.0	6.60e-20	0.582	328.0	1.17e-19	0.593
329.0	6.10e-20	0.604	330.0	1.11e-19	0.614	331.0	1.79e-19	0.625	332.0	8.70e-20	0.636	333.0	7.60e-20	0.646
334.0	9.60e-20	0.657	335.0	9.60e-20	0.668	336.0	7.20e-20	0.679	337.0	5.30e-20	0.689	338.0	1.00e-19	0.700
339.0	1.88e-19	0.711	340.0	1.00e-19	0.721	341.0	1.70e-19	0.732	342.0	3.86e-19	0.743	343.0	1.49e-19	0.754
344.0	9.70e-20	0.764	345.0	1.09e-19	0.775	346.0	1.23e-19	0.786	347.0	1.04e-19	0.796	348.0	9.10e-20	0.807
349.0	7.90e-20	0.818	350.0	1.12e-19	0.829	351.0	2.12e-19	0.839	352.0	1.55e-19	0.850	353.0	1.91e-19	0.861
354.0	5.81e-19	0.871	355.0	3.64e-19	0.882	356.0	1.41e-19	0.893	357.0	1.17e-19	0.904	358.0	1.20e-19	0.914
359.0	1.04e-19	0.925	360.0	9.00e-20	0.936	361.0	8.30e-20	0.946	362.0	8.00e-20	0.957	363.0	9.60e-20	0.968
364.0	1.46e-19	0.979	365.0	1.68e-19	0.989	366.0	1.83e-19	1.000	367.0	3.02e-19	1.000	368.0	5.20e-19	1.000
369.0	3.88e-19	1.000	370.0	1.78e-19	1.000	371.0	1.13e-19	1.000	372.0	1.00e-19	1.000	373.0	7.70e-20	1.000
374.0	6.20e-20	1.000	375.0	5.30e-20	1.000	376.0	5.30e-20	1.000	377.0	5.00e-20	1.000	378.0	5.80e-20	1.000
379.0	8.00e-20	1.000	380.0	9.60e-20	1.000	381.0	1.13e-19	1.000	382.0	1.59e-19	1.000	383.0	2.10e-19	1.000
384.0	2.41e-19	1.000	385.0	2.03e-19	1.000	386.0	1.34e-19	1.000	387.0	9.00e-20	1.000	388.0	5.60e-20	1.000
389.0	3.40e-20	1.000	390.0	2.70e-20	1.000	391.0	2.00e-20	1.000	392.0	1.50e-20	1.000	393.0	1.10e-20	1.000
394.0	6.00e-21	1.000	395.0	1.00e-20	1.000	396.0	4.00e-21	1.000	400.0	0.00e+00	1.000			
HONO-NO2														
309.0	0.00e+00	0.590	310.0	1.30e-20	0.590	311.0	1.90e-20	0.589	312.0	2.80e-20	0.579	313.0	2.20e-20	0.568
314.0	3.60e-20	0.557	315.0	3.00e-20	0.546	316.0	1.40e-20	0.536	317.0	3.10e-20	0.525	318.0	5.60e-20	0.514
319.0	3.60e-20	0.504	320.0	4.90e-20	0.493	321.0	7.80e-20	0.482	322.0	4.90e-20	0.471	323.0	5.10e-20	0.461
324.0	7.10e-20	0.450	325.0	5.00e-20	0.439	326.0	2.90e-20	0.429	327.0	6.60e-20	0.418	328.0	1.17e-19	0.407
329.0	6.10e-20	0.396	330.0	1.11e-19	0.386	331.0	1.79e-19	0.375	332.0	8.70e-20	0.364	333.0	7.60e-20	0.354
334.0	9.60e-20	0.343	335.0	9.60e-20	0.332	336.0	7.20e-20	0.321	337.0	5.30e-20	0.311	338.0	1.00e-19	0.300
339.0	1.88e-19	0.289	340.0	1.00e-19	0.279	341.0	1.70e-19	0.268	342.0	3.86e-19	0.257	343.0	1.49e-19	0.246
344.0	9.70e-20	0.236	345.0	1.09e-19	0.225	346.0	1.23e-19	0.214	347.0	1.04e-19	0.204	348.0	9.10e-20	0.193
349.0	7.90e-20	0.182	350.0	1.12e-19	0.171	351.0	2.12e-19	0.161	352.0	1.55e-19	0.150	353.0	1.91e-19	0.139
354.0	5.81e-19	0.129	355.0	3.64e-19	0.118	356.0	1.41e-19	0.107	357.0	1.17e-19	0.096	358.0	1.20e-19	0.086
359.0	1.04e-19	0.075	360.0	9.00e-20	0.064	361.0	8.30e-20	0.054	362.0	8.00e-20	0.043	363.0	9.60e-20	0.032
364.0	1.46e-19	0.021	365.0	1.68e-19	0.011	366.0	1.83e-19	0.000						

Table A-5 (continued)

WL (nm)	Abs (cm^2)	QY (nm)	WL	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY
HNO3														
190.0	1.36e-17	1.000	195.0	1.02e-17	1.000	200.0	5.88e-18	1.000	205.0	2.80e-18	1.000	210.0	1.04e-18	1.000
215.0	3.65e-19	1.000	220.0	1.49e-19	1.000	225.0	8.81e-20	1.000	230.0	5.75e-20	1.000	235.0	3.75e-20	1.000
240.0	2.58e-20	1.000	245.0	2.11e-20	1.000	250.0	1.97e-20	1.000	255.0	1.95e-20	1.000	260.0	1.91e-20	1.000
265.0	1.80e-20	1.000	270.0	1.62e-20	1.000	275.0	1.38e-20	1.000	280.0	1.12e-20	1.000	285.0	8.58e-21	1.000
290.0	6.15e-21	1.000	295.0	4.12e-21	1.000	300.0	2.63e-21	1.000	305.0	1.50e-21	1.000	310.0	8.10e-22	1.000
315.0	4.10e-22	1.000	320.0	2.00e-22	1.000	325.0	9.50e-23	1.000	330.0	4.30e-23	1.000	335.0	2.20e-23	1.000
340.0	1.00e-23	1.000	345.0	6.00e-24	1.000	350.0	4.00e-24	1.000	355.0	0.00e+00	1.000			
HO2NO2														
190.0	1.01e-17	1.000	195.0	8.16e-18	1.000	200.0	5.63e-18	1.000	205.0	3.67e-18	1.000	210.0	2.39e-18	1.000
215.0	1.61e-18	1.000	220.0	1.18e-18	1.000	225.0	9.32e-19	1.000	230.0	7.88e-19	1.000	235.0	6.80e-19	1.000
240.0	5.79e-19	1.000	245.0	4.97e-19	1.000	250.0	4.11e-19	1.000	255.0	3.49e-19	1.000	260.0	2.84e-19	1.000
265.0	2.29e-19	1.000	270.0	1.80e-19	1.000	275.0	1.33e-19	1.000	280.0	9.30e-20	1.000	285.0	6.20e-20	1.000
290.0	3.90e-20	1.000	295.0	2.40e-20	1.000	300.0	1.40e-20	1.000	305.0	8.50e-21	1.000	310.0	5.30e-21	1.000
315.0	3.90e-21	1.000	320.0	2.40e-21	1.000	325.0	1.50e-21	1.000	330.0	9.00e-22	1.000	335.0	0.00e+00	1.000
H2O2														
190.0	6.72e-19	1.000	195.0	5.63e-19	1.000	200.0	4.75e-19	1.000	205.0	4.08e-19	1.000	210.0	3.57e-19	1.000
215.0	3.07e-19	1.000	220.0	2.58e-19	1.000	225.0	2.17e-19	1.000	230.0	1.82e-19	1.000	235.0	1.50e-19	1.000
240.0	1.24e-19	1.000	245.0	1.02e-19	1.000	250.0	8.30e-20	1.000	255.0	6.70e-20	1.000	260.0	5.30e-20	1.000
265.0	4.20e-20	1.000	270.0	3.30e-20	1.000	275.0	2.60e-20	1.000	280.0	2.00e-20	1.000	285.0	1.50e-20	1.000
290.0	1.20e-20	1.000	295.0	9.00e-21	1.000	300.0	6.80e-21	1.000	305.0	5.10e-21	1.000	310.0	3.90e-21	1.000
315.0	2.90e-21	1.000	320.0	2.20e-21	1.000	325.0	1.60e-21	1.000	330.0	1.30e-21	1.000	335.0	1.00e-21	1.000
340.0	7.00e-22	1.000	345.0	5.00e-22	1.000	350.0	4.00e-22	1.000	355.0	0.00e+00	1.000			
HCHO_R														
240.0	6.40e-22	0.270	241.0	5.60e-22	0.272	242.0	1.05e-21	0.274	243.0	1.15e-21	0.276	244.0	8.20e-22	0.278
245.0	1.03e-21	0.280	246.0	9.80e-22	0.282	247.0	1.35e-21	0.284	248.0	1.91e-21	0.286	249.0	2.82e-21	0.288
250.0	2.05e-21	0.290	251.0	1.70e-21	0.291	252.0	2.88e-21	0.292	253.0	2.55e-21	0.293	254.0	2.55e-21	0.294
255.0	3.60e-21	0.295	256.0	5.09e-21	0.296	257.0	3.39e-21	0.297	258.0	2.26e-21	0.298	259.0	5.04e-21	0.299
260.0	5.05e-21	0.300	261.0	5.49e-21	0.308	262.0	5.20e-21	0.316	263.0	9.33e-21	0.324	264.0	8.23e-21	0.332
265.0	4.30e-21	0.340	266.0	4.95e-21	0.348	267.0	1.24e-20	0.356	268.0	1.11e-20	0.364	269.0	8.78e-21	0.372
270.0	9.36e-21	0.380	271.0	1.79e-20	0.399	272.0	1.23e-20	0.418	273.0	6.45e-21	0.437	274.0	6.56e-21	0.456
275.0	2.23e-20	0.475	276.0	2.42e-20	0.494	277.0	1.40e-20	0.513	278.0	1.05e-20	0.532	279.0	2.55e-20	0.551
280.0	2.08e-20	0.570	281.0	1.48e-20	0.586	282.0	8.81e-21	0.602	283.0	1.07e-20	0.618	284.0	4.49e-20	0.634
285.0	3.59e-20	0.650	286.0	1.96e-20	0.666	287.0	1.30e-20	0.682	288.0	3.36e-20	0.698	289.0	2.84e-20	0.714
290.0	1.30e-20	0.730	291.0	1.75e-20	0.735	292.0	8.32e-21	0.740	293.0	3.73e-20	0.745	294.0	6.54e-20	0.750
295.0	3.95e-20	0.755	296.0	2.33e-20	0.760	297.0	1.51e-20	0.765	298.0	4.04e-20	0.770	299.0	2.87e-20	0.775
300.0	8.71e-21	0.780	301.0	1.72e-20	0.780	302.0	1.06e-20	0.780	303.0	3.20e-20	0.780	304.0	6.90e-20	0.780
305.0	4.91e-20	0.780	306.0	4.63e-20	0.780	307.0	2.10e-20	0.780	308.0	1.49e-20	0.780	309.0	3.41e-20	0.780
310.0	1.95e-20	0.780	311.0	5.21e-21	0.764	312.0	1.12e-20	0.748	313.0	1.12e-20	0.732	314.0	4.75e-20	0.716
315.0	5.25e-20	0.700	316.0	2.90e-20	0.684	317.0	5.37e-20	0.668	318.0	2.98e-20	0.652	319.0	9.18e-21	0.636
320.0	1.26e-20	0.620	321.0	1.53e-20	0.585	322.0	6.69e-21	0.550	323.0	3.45e-21	0.515	324.0	8.16e-21	0.480
325.0	1.85e-20	0.445	326.0	5.95e-20	0.410	327.0	3.49e-20	0.375	328.0	1.09e-20	0.340	329.0	3.35e-20	0.305
330.0	3.32e-20	0.270	331.0	1.07e-20	0.243	332.0	2.89e-21	0.216	333.0	2.15e-21	0.189	334.0	1.71e-21	0.162
335.0	1.43e-21	0.135	336.0	1.94e-21	0.108	337.0	4.17e-21	0.081	338.0	2.36e-20	0.054	339.0	4.71e-20	0.027
340.0	2.48e-20	0.000												

Table A-5 (continued)

WL (nm)	Abs (cm^2)	QY (nm)	WL	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY
							HCHO_M							
240.0	6.40e-22	0.490	241.0	5.60e-22	0.490	242.0	1.05e-21	0.490	243.0	1.15e-21	0.490	244.0	8.20e-22	0.490
245.0	1.03e-21	0.490	246.0	9.80e-22	0.490	247.0	1.35e-21	0.490	248.0	1.91e-21	0.490	249.0	2.82e-21	0.490
250.0	2.05e-21	0.490	251.0	1.70e-21	0.490	252.0	2.88e-21	0.490	253.0	2.55e-21	0.490	254.0	2.55e-21	0.490
255.0	3.60e-21	0.490	256.0	5.09e-21	0.490	257.0	3.39e-21	0.490	258.0	2.26e-21	0.490	259.0	5.04e-21	0.490
260.0	5.05e-21	0.490	261.0	5.49e-21	0.484	262.0	5.20e-21	0.478	263.0	9.33e-21	0.472	264.0	8.23e-21	0.466
265.0	4.30e-21	0.460	266.0	4.95e-21	0.454	267.0	1.24e-20	0.448	268.0	1.11e-20	0.442	269.0	8.78e-21	0.436
270.0	9.36e-21	0.430	271.0	1.79e-20	0.419	272.0	1.23e-20	0.408	273.0	6.45e-21	0.397	274.0	6.56e-21	0.386
275.0	2.23e-20	0.375	276.0	2.42e-20	0.364	277.0	1.40e-20	0.353	278.0	1.05e-20	0.342	279.0	2.55e-20	0.331
280.0	2.08e-20	0.320	281.0	1.48e-20	0.312	282.0	8.81e-21	0.304	283.0	1.07e-20	0.296	284.0	4.49e-20	0.288
285.0	3.59e-20	0.280	286.0	1.96e-20	0.272	287.0	1.30e-20	0.264	288.0	3.36e-20	0.256	289.0	2.84e-20	0.248
290.0	1.30e-20	0.240	291.0	1.75e-20	0.237	292.0	8.32e-21	0.234	293.0	3.73e-20	0.231	294.0	6.54e-20	0.228
295.0	3.95e-20	0.225	296.0	2.33e-20	0.222	297.0	1.51e-20	0.219	298.0	4.04e-20	0.216	299.0	2.87e-20	0.213
300.0	8.71e-21	0.210	301.0	1.72e-20	0.211	302.0	1.06e-20	0.212	303.0	3.20e-20	0.213	304.0	6.90e-20	0.214
305.0	4.91e-20	0.215	306.0	4.63e-20	0.216	307.0	2.10e-20	0.217	308.0	1.49e-20	0.218	309.0	3.41e-20	0.219
310.0	1.95e-20	0.220	311.0	5.21e-21	0.236	312.0	1.12e-20	0.252	313.0	1.12e-20	0.268	314.0	4.75e-20	0.284
315.0	5.25e-20	0.300	316.0	2.90e-20	0.316	317.0	5.37e-20	0.332	318.0	2.98e-20	0.348	319.0	9.18e-21	0.364
320.0	1.26e-20	0.380	321.0	1.53e-20	0.408	322.0	6.69e-21	0.436	323.0	3.45e-21	0.464	324.0	8.16e-21	0.492
325.0	1.85e-20	0.520	326.0	5.95e-20	0.548	327.0	3.49e-20	0.576	328.0	1.09e-20	0.604	329.0	3.35e-20	0.632
330.0	3.32e-20	0.660	331.0	1.07e-20	0.650	332.0	2.89e-21	0.640	333.0	2.15e-21	0.630	334.0	1.71e-21	0.620
335.0	1.43e-21	0.610	336.0	1.94e-21	0.600	337.0	4.17e-21	0.590	338.0	2.36e-20	0.580	339.0	4.71e-20	0.570
340.0	2.48e-20	0.560	341.0	7.59e-21	0.525	342.0	6.81e-21	0.490	343.0	1.95e-20	0.455	344.0	1.14e-20	0.420
345.0	3.23e-21	0.385	346.0	1.13e-21	0.350	347.0	6.60e-22	0.315	348.0	1.22e-21	0.280	349.0	3.20e-22	0.245
350.0	3.80e-22	0.210	351.0	1.04e-21	0.192	352.0	7.13e-21	0.174	353.0	2.21e-20	0.156	354.0	1.54e-20	0.138
355.0	6.76e-21	0.120	356.0	1.35e-21	0.102	357.0	3.60e-22	0.084	358.0	5.70e-23	0.066	359.0	5.80e-22	0.048
360.0	8.20e-22	0.000												
							CCHO_R							
262.0	2.44e-20	0.326	266.0	3.05e-20	0.358	270.0	3.42e-20	0.390	274.0	4.03e-20	0.466	278.0	4.19e-20	0.542
280.0	4.50e-20	0.580	281.0	4.69e-20	0.575	282.0	4.72e-20	0.570	283.0	4.75e-20	0.565	284.0	4.61e-20	0.560
285.0	4.49e-20	0.555	286.0	4.44e-20	0.550	287.0	4.59e-20	0.545	288.0	4.72e-20	0.540	289.0	4.77e-20	0.535
290.0	4.89e-20	0.530	291.0	4.78e-20	0.520	292.0	4.68e-20	0.510	293.0	4.53e-20	0.500	294.0	4.33e-20	0.490
295.0	4.27e-20	0.480	296.0	4.24e-20	0.470	297.0	4.38e-20	0.460	298.0	4.41e-20	0.450	299.0	4.26e-20	0.440
300.0	4.16e-20	0.430	301.0	3.99e-20	0.418	302.0	3.86e-20	0.406	303.0	3.72e-20	0.394	304.0	3.48e-20	0.382
305.0	3.42e-20	0.370	306.0	3.42e-20	0.354	307.0	3.36e-20	0.338	308.0	3.33e-20	0.322	309.0	3.14e-20	0.306
310.0	2.93e-20	0.290	311.0	2.76e-20	0.266	312.0	2.53e-20	0.242	313.0	2.47e-20	0.218	314.0	2.44e-20	0.194
315.0	2.20e-20	0.170	316.0	2.04e-20	0.156	317.0	2.07e-20	0.142	318.0	1.98e-20	0.128	319.0	1.87e-20	0.114
320.0	1.72e-20	0.100	321.0	1.48e-20	0.088	322.0	1.40e-20	0.076	323.0	1.24e-20	0.064	324.0	1.09e-20	0.052
325.0	1.14e-20	0.040	326.0	1.07e-20	0.032	327.0	8.58e-21	0.024	328.0	7.47e-21	0.016	329.0	7.07e-21	0.008
							C2CHO							
294.0	5.80e-20	0.890	295.0	5.57e-20	0.885	296.0	5.37e-20	0.880	297.0	5.16e-20	0.875	298.0	5.02e-20	0.870
299.0	5.02e-20	0.865	300.0	5.04e-20	0.860	301.0	5.09e-20	0.855	302.0	5.07e-20	0.850	303.0	4.94e-20	0.818
304.0	4.69e-20	0.786	305.0	4.32e-20	0.755	306.0	4.04e-20	0.723	307.0	3.81e-20	0.691	308.0	3.65e-20	0.659
309.0	3.62e-20	0.627	310.0	3.60e-20	0.596	311.0	3.53e-20	0.564	312.0	3.50e-20	0.532	313.0	3.32e-20	0.500
314.0	3.06e-20	0.480	315.0	2.77e-20	0.460	316.0	2.43e-20	0.440	317.0	2.18e-20	0.420	318.0	2.00e-20	0.400
319.0	1.86e-20	0.380	320.0	1.83e-20	0.360	321.0	1.78e-20	0.340	322.0	1.66e-20	0.320	323.0	1.58e-20	0.300
324.0	1.49e-20	0.280	325.0	1.30e-20	0.260	326.0	1.13e-20	0.248	327.0	9.96e-21	0.236	328.0	8.28e-21	0.223
329.0	6.85e-21	0.211	330.0	5.75e-21	0.199	331.0	4.94e-21	0.187	332.0	4.66e-21	0.174	333.0	4.30e-21	0.162
334.0	3.73e-21	0.150	335.0	3.25e-21	0.133	336.0	2.80e-21	0.117	337.0	2.30e-21	0.100	338.0	1.85e-21	0.083
339.0	1.66e-21	0.067	340.0	1.55e-21	0.050	341.0	1.19e-21	0.033	342.0	7.60e-22	0.017	343.0	4.50e-22	0.000

Table A-5 (continued)

WL (nm)	Abs (cm^2)	QY (nm)	WL	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY
							KETONE							
198.5	3.95e-19	1.000	199.0	1.61e-19	1.000	199.5	7.75e-20	1.000	200.0	3.76e-20	1.000	200.5	2.51e-20	1.000
201.0	1.83e-20	1.000	201.5	1.36e-20	1.000	202.0	1.16e-20	1.000	202.5	8.97e-21	1.000	203.0	4.62e-21	1.000
203.5	3.18e-21	1.000	204.0	2.42e-21	1.000	204.5	2.01e-21	1.000	205.0	1.77e-21	1.000	205.5	1.64e-21	1.000
206.0	1.54e-21	1.000	206.5	1.52e-21	1.000	207.0	1.54e-21	1.000	207.5	1.62e-21	1.000	208.0	1.64e-21	1.000
208.5	1.60e-21	1.000	209.0	1.57e-21	1.000	209.5	1.49e-21	1.000	210.0	1.47e-21	1.000	210.5	1.52e-21	1.000
211.0	1.50e-21	1.000	211.5	1.62e-21	1.000	212.0	1.81e-21	1.000	212.5	2.10e-21	1.000	213.0	2.23e-21	1.000
213.5	2.06e-21	1.000	214.0	1.69e-21	1.000	214.5	1.49e-21	1.000	215.0	1.42e-21	1.000	215.5	1.42e-21	1.000
216.0	1.42e-21	1.000	216.5	1.48e-21	1.000	217.0	1.48e-21	1.000	217.5	1.53e-21	1.000	218.0	1.56e-21	1.000
218.5	1.67e-21	1.000	219.0	1.68e-21	1.000	219.5	1.78e-21	1.000	220.0	1.85e-21	1.000	220.5	1.92e-21	1.000
221.0	2.01e-21	1.000	221.5	2.11e-21	1.000	222.0	2.23e-21	1.000	222.5	2.33e-21	1.000	223.0	2.48e-21	1.000
223.5	2.60e-21	1.000	224.0	2.74e-21	1.000	224.5	2.85e-21	1.000	225.0	3.04e-21	1.000	225.5	3.15e-21	1.000
226.0	3.33e-21	1.000	226.5	3.55e-21	1.000	227.0	3.73e-21	1.000	227.5	3.93e-21	1.000	228.0	4.11e-21	1.000
228.5	4.34e-21	1.000	229.0	4.56e-21	1.000	229.5	4.75e-21	1.000	230.0	5.01e-21	1.000	230.5	5.27e-21	1.000
231.0	5.53e-21	1.000	231.5	5.83e-21	1.000	232.0	6.15e-21	1.000	232.5	6.45e-21	1.000	233.0	6.73e-21	1.000
233.5	7.02e-21	1.000	234.0	7.42e-21	1.000	234.5	7.83e-21	1.000	235.0	8.11e-21	1.000	235.5	8.45e-21	1.000
236.0	8.82e-21	1.000	236.5	9.21e-21	1.000	237.0	9.65e-21	1.000	237.5	1.00e-20	1.000	238.0	1.05e-20	1.000
238.5	1.10e-20	1.000	239.0	1.15e-20	1.000	239.5	1.20e-20	1.000	240.0	1.23e-20	1.000	240.5	1.28e-20	1.000
241.0	1.32e-20	1.000	241.5	1.38e-20	1.000	242.0	1.44e-20	1.000	242.5	1.50e-20	1.000	243.0	1.57e-20	1.000
243.5	1.63e-20	1.000	244.0	1.68e-20	1.000	244.5	1.75e-20	1.000	245.0	1.81e-20	1.000	245.5	1.88e-20	1.000
246.0	1.96e-20	1.000	246.5	2.03e-20	1.000	247.0	2.11e-20	1.000	247.5	2.19e-20	1.000	248.0	2.25e-20	1.000
248.5	2.33e-20	1.000	249.0	2.40e-20	1.000	249.5	2.48e-20	1.000	250.0	2.56e-20	1.000	250.5	2.64e-20	1.000
251.0	2.73e-20	1.000	251.5	2.81e-20	1.000	252.0	2.88e-20	1.000	252.5	2.98e-20	1.000	253.0	3.07e-20	1.000
253.5	3.16e-20	1.000	254.0	3.25e-20	1.000	254.5	3.34e-20	1.000	255.0	3.43e-20	1.000	255.5	3.51e-20	1.000
256.0	3.59e-20	1.000	256.5	3.67e-20	1.000	257.0	3.75e-20	1.000	257.5	3.84e-20	1.000	258.0	3.94e-20	1.000
258.5	4.03e-20	1.000	259.0	4.13e-20	1.000	259.5	4.22e-20	1.000	260.0	4.28e-20	1.000	260.5	4.33e-20	1.000
261.0	4.41e-20	1.000	261.5	4.49e-20	1.000	262.0	4.57e-20	1.000	262.5	4.65e-20	1.000	263.0	4.72e-20	1.000
263.5	4.78e-20	1.000	264.0	4.85e-20	1.000	264.5	4.92e-20	1.000	265.0	4.99e-20	1.000	265.5	5.04e-20	1.000
266.0	5.12e-20	1.000	266.5	5.22e-20	1.000	267.0	5.28e-20	1.000	267.5	5.34e-20	1.000	268.0	5.41e-20	1.000
268.5	5.46e-20	1.000	269.0	5.51e-20	1.000	269.5	5.55e-20	1.000	270.0	5.59e-20	1.000	270.5	5.63e-20	1.000
271.0	5.66e-20	1.000	271.5	5.70e-20	1.000	272.0	5.74e-20	1.000	272.5	5.78e-20	1.000	273.0	5.81e-20	1.000
273.5	5.86e-20	1.000	274.0	5.90e-20	1.000	274.5	5.93e-20	1.000	275.0	5.96e-20	1.000	275.5	5.97e-20	1.000
276.0	5.98e-20	1.000	276.5	5.98e-20	1.000	277.0	5.99e-20	1.000	277.5	5.99e-20	1.000	278.0	5.98e-20	1.000
278.5	5.96e-20	1.000	279.0	5.96e-20	1.000	279.5	5.95e-20	1.000	280.0	5.94e-20	1.000	280.5	5.92e-20	1.000
281.0	5.90e-20	1.000	281.5	5.88e-20	1.000	282.0	5.86e-20	1.000	282.5	5.83e-20	1.000	283.0	5.79e-20	1.000
283.5	5.75e-20	1.000	284.0	5.71e-20	1.000	284.5	5.67e-20	1.000	285.0	5.61e-20	1.000	285.5	5.56e-20	1.000
286.0	5.51e-20	1.000	286.5	5.45e-20	1.000	287.0	5.41e-20	1.000	287.5	5.37e-20	1.000	288.0	5.33e-20	1.000
288.5	5.27e-20	1.000	289.0	5.21e-20	1.000	289.5	5.15e-20	1.000	290.0	5.08e-20	1.000	290.5	4.99e-20	1.000
291.0	4.89e-20	1.000	291.5	4.82e-20	1.000	292.0	4.73e-20	1.000	292.5	4.62e-20	1.000	293.0	4.53e-20	1.000
293.5	4.41e-20	1.000	294.0	4.32e-20	1.000	294.5	4.23e-20	1.000	295.0	4.15e-20	1.000	295.5	4.11e-20	1.000
296.0	4.01e-20	1.000	296.5	3.94e-20	1.000	297.0	3.88e-20	1.000	297.5	3.77e-20	1.000	298.0	3.69e-20	1.000
298.5	3.63e-20	1.000	299.0	3.54e-20	1.000	299.5	3.46e-20	1.000	300.0	3.36e-20	1.000	300.5	3.24e-20	1.000
301.0	3.16e-20	1.000	301.5	3.06e-20	1.000	302.0	2.95e-20	1.000	302.5	2.82e-20	1.000	303.0	2.70e-20	1.000
303.5	2.59e-20	1.000	304.0	2.49e-20	1.000	304.5	2.42e-20	1.000	305.0	2.34e-20	1.000	305.5	2.28e-20	1.000
306.0	2.19e-20	1.000	306.5	2.11e-20	1.000	307.0	2.04e-20	1.000	307.5	1.93e-20	1.000	308.0	1.88e-20	1.000
308.5	1.80e-20	1.000	309.0	1.73e-20	1.000	309.5	1.66e-20	1.000	310.0	1.58e-20	1.000	310.5	1.48e-20	1.000
311.0	1.42e-20	1.000	311.5	1.34e-20	1.000	312.0	1.26e-20	1.000	312.5	1.17e-20	1.000	313.0	1.13e-20	1.000
313.5	1.08e-20	1.000	314.0	1.04e-20	1.000	314.5	9.69e-21	1.000	315.0	8.91e-21	1.000	315.5	8.61e-21	1.000
316.0	7.88e-21	1.000	316.5	7.25e-21	1.000	317.0	6.92e-21	1.000	317.5	6.43e-21	1.000	318.0	6.07e-21	1.000
318.5	5.64e-21	1.000	319.0	5.19e-21	1.000	319.5	4.66e-21	1.000	320.0	4.36e-21	1.000	320.5	3.95e-21	1.000
321.0	3.64e-21	1.000	321.5	3.38e-21	1.000	322.0	3.17e-21	1.000	322.5	2.80e-21	1.000	323.0	2.62e-21	1.000

Table A-5 (continued)

WL (nm)	Abs (cm^2)	QY (nm)	WL	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY
323.5	2.29e-21	1.000	324.0	2.13e-21	1.000	324.5	1.93e-21	1.000	325.0	1.70e-21	1.000	325.5	1.58e-21	1.000
326.0	1.48e-21	1.000	326.5	1.24e-21	1.000	327.0	1.20e-21	1.000	327.5	1.04e-21	1.000	328.0	9.51e-22	1.000
328.5	8.44e-22	1.000	329.0	7.26e-22	1.000	329.5	6.70e-22	1.000	330.0	6.08e-22	1.000	330.5	5.15e-22	1.000
331.0	4.56e-22	1.000	331.5	4.13e-22	1.000	332.0	3.56e-22	1.000	332.5	3.30e-22	1.000	333.0	2.97e-22	1.000
333.5	2.67e-22	1.000	334.0	2.46e-22	1.000	334.5	2.21e-22	1.000	335.0	1.93e-22	1.000	335.5	1.56e-22	1.000
336.0	1.47e-22	1.000	336.5	1.37e-22	1.000	337.0	1.27e-22	1.000	337.5	1.19e-22	1.000	338.0	1.09e-22	1.000
338.5	1.01e-22	1.000	339.0	9.09e-23	1.000	339.5	8.22e-23	1.000	340.0	7.66e-23	1.000	340.5	7.43e-23	1.000
341.0	6.83e-23	1.000	341.5	6.72e-23	1.000	342.0	6.04e-23	1.000	342.5	4.78e-23	1.000	343.0	0.00e+00	1.000
							COOH							
210.0	3.12e-19	1.000	215.0	2.09e-19	1.000	220.0	1.54e-19	1.000	225.0	1.22e-19	1.000	230.0	9.62e-20	1.000
235.0	7.61e-20	1.000	240.0	6.05e-20	1.000	245.0	4.88e-20	1.000	250.0	3.98e-20	1.000	255.0	3.23e-20	1.000
260.0	2.56e-20	1.000	265.0	2.11e-20	1.000	270.0	1.70e-20	1.000	275.0	1.39e-20	1.000	280.0	1.09e-20	1.000
285.0	8.63e-21	1.000	290.0	6.91e-21	1.000	295.0	5.51e-21	1.000	300.0	4.13e-21	1.000	305.0	3.13e-21	1.000
310.0	2.39e-21	1.000	315.0	1.82e-21	1.000	320.0	1.37e-21	1.000	325.0	1.05e-21	1.000	330.0	7.90e-22	1.000
335.0	6.10e-22	1.000	340.0	4.70e-22	1.000	345.0	3.50e-22	1.000	350.0	2.70e-22	1.000	355.0	2.10e-22	1.000
360.0	1.60e-22	1.000	365.0	1.20e-22	1.000	370.0	0.00e+00	1.000						
							GLY_R							
230.0	2.87e-21	1.000	235.0	2.87e-21	1.000	240.0	4.30e-21	1.000	245.0	5.73e-21	1.000	250.0	8.60e-21	1.000
255.0	1.15e-20	1.000	260.0	1.43e-20	1.000	265.0	1.86e-20	1.000	270.0	2.29e-20	1.000	275.0	2.58e-20	1.000
280.0	2.87e-20	1.000	285.0	3.30e-20	1.000	290.0	3.15e-20	1.000	295.0	3.30e-20	1.000	300.0	3.58e-20	1.000
305.0	2.72e-20	1.000	310.0	2.72e-20	1.000	312.5	2.87e-20	1.000	315.0	2.29e-20	1.000	320.0	1.43e-20	1.000
325.0	1.15e-20	1.000	327.5	1.43e-20	1.000	330.0	1.15e-20	1.000	335.0	2.87e-21	1.000	340.0	0.00e+00	1.000
345.0	0.00e+00	1.000	350.0	0.00e+00	1.000	355.0	0.00e+00	1.000	360.0	2.29e-21	1.000	365.0	2.87e-21	1.000
370.0	8.03e-21	1.000	375.0	1.00e-20	1.000	380.0	1.72e-20	0.972	382.0	1.58e-20	0.855	384.0	1.49e-20	0.737
386.0	1.49e-20	0.619	388.0	2.87e-20	0.502	390.0	3.15e-20	0.384	391.0	3.24e-20	0.326	392.0	3.04e-20	0.267
393.0	2.23e-20	0.208	394.0	2.63e-20	0.149	395.0	3.04e-20	0.090	396.0	2.63e-20	0.032	397.0	2.43e-20	0.000
398.0	3.24e-20	0.000	399.0	3.04e-20	0.000	400.0	2.84e-20	0.000	401.0	3.24e-20	0.000	402.0	4.46e-20	0.000
403.0	5.27e-20	0.000	404.0	4.26e-20	0.000	405.0	3.04e-20	0.000	406.0	3.04e-20	0.000	407.0	2.84e-20	0.000
408.0	2.43e-20	0.000	409.0	2.84e-20	0.000	410.0	6.08e-20	0.000	411.0	5.07e-20	0.000	411.5	6.08e-20	0.000
412.0	4.86e-20	0.000	413.0	8.31e-20	0.000	413.5	6.48e-20	0.000	414.0	7.50e-20	0.000	414.5	8.11e-20	0.000
415.0	8.11e-20	0.000	415.5	6.89e-20	0.000	416.0	4.26e-20	0.000	417.0	4.86e-20	0.000	418.0	5.88e-20	0.000
							GLY_ABS							
230.0	2.87e-21	1.000	235.0	2.87e-21	1.000	240.0	4.30e-21	1.000	245.0	5.73e-21	1.000	250.0	8.60e-21	1.000
255.0	1.15e-20	1.000	260.0	1.43e-20	1.000	265.0	1.86e-20	1.000	270.0	2.29e-20	1.000	275.0	2.58e-20	1.000
280.0	2.87e-20	1.000	285.0	3.30e-20	1.000	290.0	3.15e-20	1.000	295.0	3.30e-20	1.000	300.0	3.58e-20	1.000
305.0	2.72e-20	1.000	310.0	2.72e-20	1.000	312.5	2.87e-20	1.000	315.0	2.29e-20	1.000	320.0	1.43e-20	1.000
325.0	1.15e-20	1.000	327.5	1.43e-20	1.000	330.0	1.15e-20	1.000	335.0	2.87e-21	1.000	340.0	0.00e+00	1.000
355.0	0.00e+00	1.000	360.0	2.29e-21	1.000	365.0	2.87e-21	1.000	370.0	8.03e-21	1.000	375.0	1.00e-20	1.000
380.0	1.72e-20	1.000	382.0	1.58e-20	1.000	384.0	1.49e-20	1.000	386.0	1.49e-20	1.000	388.0	2.87e-20	1.000
390.0	3.15e-20	1.000	391.0	3.24e-20	1.000	392.0	3.04e-20	1.000	393.0	2.23e-20	1.000	394.0	2.63e-20	1.000
395.0	3.04e-20	1.000	396.0	2.63e-20	1.000	397.0	2.43e-20	1.000	398.0	3.24e-20	1.000	399.0	3.04e-20	1.000
400.0	2.84e-20	1.000	401.0	3.24e-20	1.000	402.0	4.46e-20	1.000	403.0	5.27e-20	1.000	404.0	4.26e-20	1.000
405.0	3.04e-20	1.000	406.0	3.04e-20	1.000	407.0	2.84e-20	1.000	408.0	2.43e-20	1.000	409.0	2.84e-20	1.000
410.0	6.08e-20	1.000	411.0	5.07e-20	1.000	411.5	6.08e-20	1.000	412.0	4.86e-20	1.000	413.0	8.31e-20	1.000
413.5	6.48e-20	1.000	414.0	7.50e-20	1.000	414.5	8.11e-20	1.000	415.0	8.11e-20	1.000	415.5	6.89e-20	1.000
416.0	4.26e-20	1.000	417.0	4.86e-20	1.000	418.0	5.88e-20	1.000	419.0	6.69e-20	1.000	420.0	3.85e-20	1.000
421.0	5.67e-20	1.000	421.5	4.46e-20	1.000	422.0	5.27e-20	1.000	422.5	1.05e-19	1.000	423.0	8.51e-20	1.000
424.0	6.08e-20	1.000	425.0	7.29e-20	1.000	426.0	1.18e-19	1.000	426.5	1.30e-19	1.000	427.0	1.07e-19	1.000
428.0	1.66e-19	1.000	429.0	4.05e-20	1.000	430.0	5.07e-20	1.000	431.0	4.86e-20	1.000	432.0	4.05e-20	1.000
433.0	3.65e-20	1.000	434.0	4.05e-20	1.000	434.5	6.08e-20	1.000	435.0	5.07e-20	1.000	436.0	8.11e-20	1.000

Table A-5 (continued)

WL (nm)	Abs (cm^2)	QY (nm)	WL	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY
436.5	1.13e-19	1.000	437.0	5.27e-20	1.000	438.0	1.01e-19	1.000	438.5	1.38e-19	1.000	439.0	7.70e-20	1.000
440.0	2.47e-19	1.000	441.0	8.11e-20	1.000	442.0	6.08e-20	1.000	443.0	7.50e-20	1.000	444.0	9.32e-20	1.000
445.0	1.13e-19	1.000	446.0	5.27e-20	1.000	447.0	2.43e-20	1.000	448.0	2.84e-20	1.000	449.0	3.85e-20	1.000
450.0	6.08e-20	1.000	451.0	1.09e-19	1.000	451.5	9.32e-20	1.000	452.0	1.22e-19	1.000	453.0	2.39e-19	1.000
454.0	1.70e-19	1.000	455.0	3.40e-19	1.000	455.5	4.05e-19	1.000	456.0	1.01e-19	1.000	457.0	1.62e-20	1.000
458.0	1.22e-20	1.000	458.5	1.42e-20	1.000	459.0	4.05e-21	1.000	460.0	4.05e-21	1.000	460.5	6.08e-21	1.000
461.0	2.03e-21	1.000	462.0	0.00e+00	1.000									
							MGLY_ADJ							
219.0	9.84e-21	1.000	219.5	1.04e-20	1.000	220.0	1.06e-20	1.000	220.5	1.11e-20	1.000	221.0	1.15e-20	1.000
221.5	1.18e-20	1.000	222.0	1.22e-20	1.000	222.5	1.24e-20	1.000	223.0	1.26e-20	1.000	223.5	1.26e-20	1.000
224.0	1.25e-20	1.000	224.5	1.24e-20	1.000	225.0	1.25e-20	1.000	225.5	1.27e-20	1.000	226.0	1.27e-20	1.000
226.5	1.29e-20	1.000	227.0	1.31e-20	1.000	227.5	1.32e-20	1.000	228.0	1.35e-20	1.000	228.5	1.37e-20	1.000
229.0	1.40e-20	1.000	229.5	1.42e-20	1.000	230.0	1.48e-20	1.000	230.5	1.53e-20	1.000	231.0	1.57e-20	1.000
231.5	1.59e-20	1.000	232.0	1.61e-20	1.000	232.5	1.62e-20	1.000	233.0	1.61e-20	1.000	233.5	1.68e-20	1.000
234.0	1.74e-20	1.000	234.5	1.80e-20	1.000	235.0	1.84e-20	1.000	235.5	1.87e-20	1.000	236.0	1.89e-20	1.000
236.5	1.91e-20	1.000	237.0	1.93e-20	1.000	237.5	1.94e-20	1.000	238.0	1.96e-20	1.000	238.5	1.96e-20	1.000
239.0	2.01e-20	1.000	239.5	2.04e-20	1.000	240.0	2.08e-20	1.000	240.5	2.10e-20	1.000	241.0	2.14e-20	1.000
241.5	2.16e-20	1.000	242.0	2.19e-20	1.000	242.5	2.20e-20	1.000	243.0	2.23e-20	1.000	243.5	2.26e-20	1.000
244.0	2.28e-20	1.000	244.5	2.29e-20	1.000	245.0	2.30e-20	1.000	245.5	2.32e-20	1.000	246.0	2.33e-20	1.000
246.5	2.35e-20	1.000	247.0	2.38e-20	1.000	247.5	2.41e-20	1.000	248.0	2.46e-20	1.000	248.5	2.51e-20	1.000
249.0	2.57e-20	1.000	249.5	2.61e-20	1.000	250.0	2.65e-20	1.000	250.5	2.67e-20	1.000	251.0	2.69e-20	1.000
251.5	2.69e-20	1.000	252.0	2.71e-20	1.000	252.5	2.72e-20	1.000	253.0	2.73e-20	1.000	253.5	2.74e-20	1.000
254.0	2.76e-20	1.000	254.5	2.78e-20	1.000	255.0	2.82e-20	1.000	255.5	2.87e-20	1.000	256.0	2.93e-20	1.000
256.5	2.98e-20	1.000	257.0	3.07e-20	1.000	257.5	3.12e-20	1.000	258.0	3.17e-20	1.000	258.5	3.21e-20	1.000
259.0	3.26e-20	1.000	259.5	3.28e-20	1.000	260.0	3.29e-20	1.000	260.5	3.31e-20	1.000	261.0	3.33e-20	1.000
261.5	3.34e-20	1.000	262.0	3.36e-20	1.000	262.5	3.38e-20	1.000	263.0	3.42e-20	1.000	263.5	3.44e-20	1.000
264.0	3.48e-20	1.000	264.5	3.54e-20	1.000	265.0	3.59e-20	1.000	265.5	3.65e-20	1.000	266.0	3.73e-20	1.000
266.5	3.80e-20	1.000	267.0	3.87e-20	1.000	267.5	3.95e-20	1.000	268.0	4.02e-20	1.000	268.5	4.08e-20	1.000
269.0	4.13e-20	1.000	269.5	4.17e-20	1.000	270.0	4.20e-20	1.000	270.5	4.22e-20	1.000	271.0	4.22e-20	1.000
271.5	4.22e-20	1.000	272.0	4.23e-20	1.000	272.5	4.24e-20	1.000	273.0	4.27e-20	1.000	273.5	4.29e-20	1.000
274.0	4.31e-20	1.000	274.5	4.33e-20	1.000	275.0	4.37e-20	1.000	275.5	4.42e-20	1.000	276.0	4.48e-20	1.000
276.5	4.56e-20	1.000	277.0	4.64e-20	1.000	277.5	4.71e-20	1.000	278.0	4.78e-20	1.000	278.5	4.83e-20	1.000
279.0	4.87e-20	1.000	279.5	4.90e-20	1.000	280.0	4.92e-20	1.000	280.5	4.93e-20	1.000	281.0	4.94e-20	1.000
281.5	4.92e-20	1.000	282.0	4.90e-20	1.000	282.5	4.86e-20	1.000	283.0	4.83e-20	1.000	283.5	4.79e-20	1.000
284.0	4.76e-20	1.000	284.5	4.72e-20	1.000	285.0	4.70e-20	1.000	285.5	4.68e-20	1.000	286.0	4.66e-20	1.000
286.5	4.65e-20	1.000	287.0	4.65e-20	1.000	287.5	4.68e-20	1.000	288.0	4.73e-20	1.000	288.5	4.78e-20	1.000
289.0	4.84e-20	1.000	289.5	4.89e-20	1.000	290.0	4.92e-20	1.000	290.5	4.92e-20	1.000	291.0	4.90e-20	1.000
291.5	4.86e-20	1.000	292.0	4.81e-20	1.000	292.5	4.75e-20	1.000	293.0	4.70e-20	1.000	293.5	4.65e-20	1.000
294.0	4.58e-20	1.000	294.5	4.48e-20	1.000	295.0	4.38e-20	1.000	295.5	4.27e-20	1.000	296.0	4.17e-20	1.000
296.5	4.07e-20	1.000	297.0	3.99e-20	1.000	297.5	3.94e-20	1.000	298.0	3.88e-20	1.000	298.5	3.82e-20	1.000
299.0	3.76e-20	1.000	299.5	3.72e-20	1.000	300.0	3.69e-20	1.000	300.5	3.68e-20	1.000	301.0	3.70e-20	1.000
301.5	3.72e-20	1.000	302.0	3.74e-20	1.000	302.5	3.74e-20	1.000	303.0	3.75e-20	1.000	303.5	3.71e-20	1.000
304.0	3.62e-20	1.000	304.5	3.51e-20	1.000	305.0	3.38e-20	1.000	305.5	3.25e-20	1.000	306.0	3.15e-20	1.000
306.5	3.04e-20	1.000	307.0	2.92e-20	1.000	307.5	2.80e-20	1.000	308.0	2.71e-20	1.000	308.5	2.63e-20	1.000
309.0	2.52e-20	1.000	309.5	2.43e-20	1.000	310.0	2.34e-20	1.000	310.5	2.25e-20	1.000	311.0	2.19e-20	1.000
311.5	2.12e-20	1.000	312.0	2.06e-20	1.000	312.5	2.02e-20	1.000	313.0	1.96e-20	1.000	313.5	1.92e-20	1.000
314.0	1.91e-20	1.000	314.5	1.88e-20	1.000	315.0	1.86e-20	1.000	315.5	1.85e-20	1.000	316.0	1.86e-20	1.000
316.5	1.87e-20	1.000	317.0	1.87e-20	1.000	317.5	1.87e-20	1.000	318.0	1.83e-20	1.000	318.5	1.75e-20	1.000
319.0	1.69e-20	1.000	319.5	1.60e-20	1.000	320.0	1.50e-20	1.000	320.5	1.41e-20	1.000	321.0	1.34e-20	1.000
321.5	1.27e-20	1.000	322.0	1.21e-20	1.000	322.5	1.18e-20	1.000	323.0	1.14e-20	1.000	323.5	1.08e-20	1.000
324.0	1.01e-20	1.000	324.5	9.62e-21	1.000	325.0	9.28e-21	1.000	325.5	8.75e-21	1.000	326.0	8.49e-21	1.000

Table A-5 (continued)

WL (nm)	Abs (cm^2)	QY (nm)	WL	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY
326.5	8.21e-21	1.000	327.0	7.71e-21	1.000	327.5	7.38e-21	1.000	328.0	7.18e-21	1.000	328.5	6.86e-21	1.000
329.0	6.71e-21	1.000	329.5	6.63e-21	1.000	330.0	6.46e-21	1.000	330.5	6.29e-21	1.000	331.0	6.21e-21	1.000
331.5	6.18e-21	1.000	332.0	6.20e-21	1.000	332.5	5.49e-21	1.000	333.0	5.21e-21	1.000	333.5	5.38e-21	1.000
334.0	5.35e-21	1.000	334.5	5.04e-21	1.000	335.0	4.94e-21	1.000	335.5	4.90e-21	1.000	336.0	4.52e-21	1.000
336.5	4.26e-21	1.000	337.0	4.11e-21	1.000	337.5	3.76e-21	1.000	338.0	3.61e-21	1.000	338.5	3.58e-21	1.000
339.0	3.47e-21	1.000	339.5	3.32e-21	1.000	340.0	3.22e-21	1.000	340.5	3.10e-21	1.000	341.0	3.00e-21	1.000
341.5	2.94e-21	1.000	342.0	2.89e-21	1.000	342.5	2.86e-21	1.000	343.0	2.88e-21	1.000	343.5	2.88e-21	1.000
344.0	2.89e-21	0.992	344.5	2.91e-21	0.984	345.0	2.95e-21	0.976	345.5	3.00e-21	0.968	346.0	3.08e-21	0.960
346.5	3.18e-21	0.953	347.0	3.25e-21	0.945	347.5	3.30e-21	0.937	348.0	3.39e-21	0.929	348.5	3.51e-21	0.921
349.0	3.63e-21	0.913	349.5	3.73e-21	0.905	350.0	3.85e-21	0.897	350.5	3.99e-21	0.889	351.0	4.27e-21	0.881
351.5	4.47e-21	0.873	352.0	4.63e-21	0.865	352.5	4.78e-21	0.858	353.0	4.92e-21	0.850	353.5	5.07e-21	0.842
354.0	5.23e-21	0.834	354.5	5.39e-21	0.826	355.0	5.56e-21	0.818	355.5	5.77e-21	0.810	356.0	5.97e-21	0.802
356.5	6.15e-21	0.794	357.0	6.35e-21	0.786	357.5	6.56e-21	0.778	358.0	6.76e-21	0.770	358.5	6.95e-21	0.763
359.0	7.20e-21	0.755	359.5	7.44e-21	0.747	360.0	7.64e-21	0.739	360.5	7.89e-21	0.731	361.0	8.15e-21	0.723
361.5	8.43e-21	0.715	362.0	8.71e-21	0.707	362.5	9.02e-21	0.699	363.0	9.33e-21	0.691	363.5	9.65e-21	0.683
364.0	1.00e-20	0.675	364.5	1.04e-20	0.668	365.0	1.08e-20	0.660	365.5	1.11e-20	0.652	366.0	1.15e-20	0.644
366.5	1.19e-20	0.636	367.0	1.23e-20	0.628	367.5	1.27e-20	0.620	368.0	1.31e-20	0.612	368.5	1.35e-20	0.604
369.0	1.40e-20	0.596	369.5	1.44e-20	0.588	370.0	1.47e-20	0.580	370.5	1.51e-20	0.573	371.0	1.55e-20	0.565
371.5	1.59e-20	0.557	372.0	1.64e-20	0.549	372.5	1.70e-20	0.541	373.0	1.73e-20	0.533	373.5	1.77e-20	0.525
374.0	1.81e-20	0.517	374.5	1.86e-20	0.509	375.0	1.90e-20	0.501	375.5	1.96e-20	0.493	376.0	2.02e-20	0.486
376.5	2.06e-20	0.478	377.0	2.10e-20	0.470	377.5	2.14e-20	0.462	378.0	2.18e-20	0.454	378.5	2.24e-20	0.446
379.0	2.30e-20	0.438	379.5	2.37e-20	0.430	380.0	2.42e-20	0.422	380.5	2.47e-20	0.414	381.0	2.54e-20	0.406
381.5	2.62e-20	0.398	382.0	2.69e-20	0.391	382.5	2.79e-20	0.383	383.0	2.88e-20	0.375	383.5	2.96e-20	0.367
384.0	3.02e-20	0.359	384.5	3.10e-20	0.351	385.0	3.20e-20	0.343	385.5	3.29e-20	0.335	386.0	3.39e-20	0.327
386.5	3.51e-20	0.319	387.0	3.62e-20	0.311	387.5	3.69e-20	0.303	388.0	3.70e-20	0.296	388.5	3.77e-20	0.288
389.0	3.88e-20	0.280	389.5	3.97e-20	0.272	390.0	4.03e-20	0.264	390.5	4.12e-20	0.256	391.0	4.22e-20	0.248
391.5	4.29e-20	0.240	392.0	4.30e-20	0.232	392.5	4.38e-20	0.224	393.0	4.47e-20	0.216	393.5	4.55e-20	0.208
394.0	4.56e-20	0.201	394.5	4.59e-20	0.193	395.0	4.67e-20	0.185	395.5	4.80e-20	0.177	396.0	4.87e-20	0.169
396.5	4.96e-20	0.161	397.0	5.08e-20	0.153	397.5	5.19e-20	0.145	398.0	5.23e-20	0.137	398.5	5.39e-20	0.129
399.0	5.46e-20	0.121	399.5	5.54e-20	0.113	400.0	5.59e-20	0.106	400.5	5.77e-20	0.098	401.0	5.91e-20	0.090
401.5	5.99e-20	0.082	402.0	6.06e-20	0.074	402.5	6.20e-20	0.066	403.0	6.35e-20	0.058	403.5	6.52e-20	0.050
404.0	6.54e-20	0.042	404.5	6.64e-20	0.034	405.0	6.93e-20	0.026	405.5	7.15e-20	0.018	406.0	7.19e-20	0.011
406.5	7.32e-20	0.003	407.0	7.58e-20	0.000	407.5	7.88e-20	0.000	408.0	7.97e-20	0.000	408.5	7.91e-20	0.000
409.0	8.11e-20	0.000	409.5	8.41e-20	0.000	410.0	8.53e-20	0.000	410.5	8.59e-20	0.000	411.0	8.60e-20	0.000
411.5	8.80e-20	0.000	412.0	9.04e-20	0.000	412.5	9.45e-20	0.000	413.0	9.34e-20	0.000	413.5	9.37e-20	0.000
414.0	9.63e-20	0.000	414.5	9.71e-20	0.000	415.0	9.70e-20	0.000	415.5	9.65e-20	0.000	416.0	9.69e-20	0.000
416.5	9.89e-20	0.000	417.0	1.00e-19	0.000	417.5	1.02e-19	0.000	418.0	1.00e-19	0.000	418.5	1.02e-19	0.000
419.0	1.01e-19	0.000	419.5	1.01e-19	0.000	420.0	1.03e-19	0.000	420.5	1.01e-19	0.000	421.0	1.04e-19	0.000
BACL_ADJ														
230.0	1.30e-20	1.000	232.5	1.46e-20	1.000	235.0	1.68e-20	1.000	237.5	1.84e-20	1.000	240.0	2.16e-20	1.000
242.5	2.49e-20	1.000	245.0	2.65e-20	1.000	247.5	2.71e-20	1.000	250.0	3.03e-20	1.000	252.5	3.46e-20	1.000
255.0	3.46e-20	1.000	257.5	3.57e-20	1.000	260.0	3.95e-20	1.000	262.5	4.17e-20	1.000	265.0	4.17e-20	1.000
267.5	4.22e-20	1.000	270.0	4.60e-20	1.000	272.5	4.54e-20	1.000	275.0	4.33e-20	1.000	277.5	4.22e-20	1.000
280.0	4.44e-20	1.000	282.5	4.33e-20	1.000	285.0	3.90e-20	1.000	287.5	3.57e-20	1.000	290.0	3.25e-20	1.000
292.5	2.92e-20	1.000	295.0	2.60e-20	1.000	297.5	2.16e-20	1.000	300.0	1.79e-20	1.000	302.5	1.73e-20	1.000
305.0	1.46e-20	1.000	307.5	1.08e-20	1.000	310.0	9.20e-21	1.000	312.5	7.03e-21	1.000	315.0	6.49e-21	1.000
317.5	5.41e-21	1.000	320.0	5.41e-21	1.000	322.5	5.41e-21	1.000	325.0	4.33e-21	1.000	327.5	3.25e-21	1.000
330.0	3.79e-21	1.000	332.5	3.79e-21	1.000	335.0	4.33e-21	1.000	337.5	4.87e-21	1.000	340.0	5.41e-21	1.000
342.5	5.95e-21	1.000	345.0	6.49e-21	1.000	347.5	7.03e-21	1.000	350.0	8.12e-21	0.995	352.5	7.57e-21	0.960
355.0	9.20e-21	0.925	357.5	9.74e-21	0.890	360.0	1.08e-20	0.855	362.5	1.19e-20	0.820	365.0	1.41e-20	0.785
367.5	1.51e-20	0.750	370.0	1.79e-20	0.715	372.5	2.00e-20	0.680	375.0	2.11e-20	0.645	377.5	2.33e-20	0.610

Table A-5 (continued)

WL (nm)	Abs (cm^2)	QY (nm)	WL	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY
380.0	2.60e-20	0.575	382.5	2.81e-20	0.540	385.0	3.14e-20	0.505	387.5	3.46e-20	0.470	390.0	3.90e-20	0.435
392.5	4.11e-20	0.399	395.0	4.33e-20	0.364	397.5	4.38e-20	0.329	400.0	4.65e-20	0.294	402.5	4.81e-20	0.259
405.0	5.19e-20	0.224	407.5	5.84e-20	0.189	410.0	6.06e-20	0.154	412.5	6.49e-20	0.119	415.0	6.92e-20	0.084
417.5	6.87e-20	0.049	420.0	6.82e-20	0.014	422.5	6.71e-20	0.000	425.0	6.49e-20	0.000	427.5	5.95e-20	0.000
430.0	5.73e-20	0.000	432.5	6.28e-20	0.000	435.0	6.01e-20	0.000	437.5	5.84e-20	0.000	440.0	5.95e-20	0.000
442.5	6.49e-20	0.000	445.0	5.95e-20	0.000	447.5	4.98e-20	0.000	450.0	3.79e-20	0.000	452.5	2.81e-20	0.000
455.0	1.73e-20	0.000	457.5	1.08e-20	0.000	460.0	5.41e-21	0.000	462.5	3.79e-21	0.000	465.0	2.16e-21	0.000
467.5	1.08e-21	0.000	470.0	1.08e-21	0.000	472.5	0.00e+00	0.000						
						BZCHO								
299.0	1.78e-19	1.000	304.0	7.40e-20	1.000	306.0	6.91e-20	1.000	309.0	6.41e-20	1.000	313.0	6.91e-20	1.000
314.0	6.91e-20	1.000	318.0	6.41e-20	1.000	325.0	8.39e-20	1.000	332.0	7.65e-20	1.000	338.0	8.88e-20	1.000
342.0	8.88e-20	1.000	346.0	7.89e-20	1.000	349.0	7.89e-20	1.000	354.0	9.13e-20	1.000	355.0	8.14e-20	1.000
364.0	5.67e-20	1.000	368.0	6.66e-20	1.000	369.0	8.39e-20	1.000	370.0	8.39e-20	1.000	372.0	3.45e-20	1.000
374.0	3.21e-20	1.000	376.0	2.47e-20	1.000	377.0	2.47e-20	1.000	380.0	3.58e-20	1.000	382.0	9.90e-21	1.000
386.0	0.00e+00	1.000												
						ACROLEIN								
250.0	1.80e-21	1.000	252.0	2.05e-21	1.000	253.0	2.20e-21	1.000	254.0	2.32e-21	1.000	255.0	2.45e-21	1.000
256.0	2.56e-21	1.000	257.0	2.65e-21	1.000	258.0	2.74e-21	1.000	259.0	2.83e-21	1.000	260.0	2.98e-21	1.000
261.0	3.24e-21	1.000	262.0	3.47e-21	1.000	263.0	3.58e-21	1.000	264.0	3.93e-21	1.000	265.0	4.67e-21	1.000
266.0	5.10e-21	1.000	267.0	5.38e-21	1.000	268.0	5.73e-21	1.000	269.0	6.13e-21	1.000	270.0	6.64e-21	1.000
271.0	7.20e-21	1.000	272.0	7.77e-21	1.000	273.0	8.37e-21	1.000	274.0	8.94e-21	1.000	275.0	9.55e-21	1.000
276.0	1.04e-20	1.000	277.0	1.12e-20	1.000	278.0	1.19e-20	1.000	279.0	1.27e-20	1.000	280.0	1.27e-20	1.000
281.0	1.26e-20	1.000	282.0	1.26e-20	1.000	283.0	1.28e-20	1.000	284.0	1.33e-20	1.000	285.0	1.38e-20	1.000
286.0	1.44e-20	1.000	287.0	1.50e-20	1.000	288.0	1.57e-20	1.000	289.0	1.63e-20	1.000	290.0	1.71e-20	1.000
291.0	1.78e-20	1.000	292.0	1.86e-20	1.000	293.0	1.95e-20	1.000	294.0	2.05e-20	1.000	295.0	2.15e-20	1.000
296.0	2.26e-20	1.000	297.0	2.37e-20	1.000	298.0	2.48e-20	1.000	299.0	2.60e-20	1.000	300.0	2.73e-20	1.000
301.0	2.85e-20	1.000	302.0	2.99e-20	1.000	303.0	3.13e-20	1.000	304.0	3.27e-20	1.000	305.0	3.39e-20	1.000
306.0	3.51e-20	1.000	307.0	3.63e-20	1.000	308.0	3.77e-20	1.000	309.0	3.91e-20	1.000	310.0	4.07e-20	1.000
311.0	4.25e-20	1.000	312.0	4.39e-20	1.000	313.0	4.44e-20	1.000	314.0	4.50e-20	1.000	315.0	4.59e-20	1.000
316.0	4.75e-20	1.000	317.0	4.90e-20	1.000	318.0	5.05e-20	1.000	319.0	5.19e-20	1.000	320.0	5.31e-20	1.000
321.0	5.43e-20	1.000	322.0	5.52e-20	1.000	323.0	5.60e-20	1.000	324.0	5.67e-20	1.000	325.0	5.67e-20	1.000
326.0	5.62e-20	1.000	327.0	5.63e-20	1.000	328.0	5.71e-20	1.000	329.0	5.76e-20	1.000	330.0	5.80e-20	1.000
331.0	5.95e-20	1.000	332.0	6.23e-20	1.000	333.0	6.39e-20	1.000	334.0	6.38e-20	1.000	335.0	6.24e-20	1.000
336.0	6.01e-20	1.000	337.0	5.79e-20	1.000	338.0	5.63e-20	1.000	339.0	5.56e-20	1.000	340.0	5.52e-20	1.000
341.0	5.54e-20	1.000	342.0	5.53e-20	1.000	343.0	5.47e-20	1.000	344.0	5.41e-20	1.000	345.0	5.40e-20	1.000
346.0	5.48e-20	1.000	347.0	5.90e-20	1.000	348.0	6.08e-20	1.000	349.0	6.00e-20	1.000	350.0	5.53e-20	1.000
351.0	5.03e-20	1.000	352.0	4.50e-20	1.000	353.0	4.03e-20	1.000	354.0	3.75e-20	1.000	355.0	3.55e-20	1.000
356.0	3.45e-20	1.000	357.0	3.46e-20	1.000	358.0	3.49e-20	1.000	359.0	3.41e-20	1.000	360.0	3.23e-20	1.000
361.0	2.95e-20	1.000	362.0	2.81e-20	1.000	363.0	2.91e-20	1.000	364.0	3.25e-20	1.000	365.0	3.54e-20	1.000
366.0	3.30e-20	1.000	367.0	2.78e-20	1.000	368.0	2.15e-20	1.000	369.0	1.59e-20	1.000	370.0	1.19e-20	1.000
371.0	8.99e-21	1.000	372.0	7.22e-21	1.000	373.0	5.86e-21	1.000	374.0	4.69e-21	1.000	375.0	3.72e-21	1.000
376.0	3.57e-21	1.000	377.0	3.55e-21	1.000	378.0	2.83e-21	1.000	379.0	1.69e-21	1.000	380.0	8.29e-24	1.000
381.0	0.00e+00	1.000												

Table A-5 (continued)

WL (nm)	Abs (cm^2)	QY (nm)	WL	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY
IC3ONO2														
185.0	1.79e-17	1.000	188.0	1.81e-17	1.000	190.0	1.79e-17	1.000	195.0	1.61e-17	1.000	200.0	1.26e-17	1.000
205.0	8.67e-18	1.000	210.0	4.98e-18	1.000	215.0	2.47e-18	1.000	220.0	1.17e-18	1.000	225.0	5.80e-19	1.000
230.0	3.10e-19	1.000	235.0	1.80e-19	1.000	240.0	1.10e-19	1.000	245.0	7.00e-20	1.000	250.0	5.70e-20	1.000
255.0	5.20e-20	1.000	260.0	4.90e-20	1.000	265.0	4.60e-20	1.000	270.0	4.10e-20	1.000	275.0	3.60e-20	1.000
280.0	2.90e-20	1.000	285.0	2.30e-20	1.000	290.0	1.70e-20	1.000	295.0	1.20e-20	1.000	300.0	8.10e-21	1.000
305.0	5.20e-21	1.000	310.0	3.20e-21	1.000	315.0	1.90e-21	1.000	320.0	1.10e-21	1.000	325.0	6.10e-22	1.000
330.0	3.70e-22	1.000	335.0	0.00e+00	1.000									
MGLY_ABS														
219.0	9.84e-21	1.000	219.5	1.04e-20	1.000	220.0	1.06e-20	1.000	220.5	1.11e-20	1.000	221.0	1.15e-20	1.000
221.5	1.18e-20	1.000	222.0	1.22e-20	1.000	222.5	1.24e-20	1.000	223.0	1.26e-20	1.000	223.5	1.26e-20	1.000
224.0	1.25e-20	1.000	224.5	1.24e-20	1.000	225.0	1.25e-20	1.000	225.5	1.27e-20	1.000	226.0	1.27e-20	1.000
226.5	1.29e-20	1.000	227.0	1.31e-20	1.000	227.5	1.32e-20	1.000	228.0	1.35e-20	1.000	228.5	1.37e-20	1.000
229.0	1.40e-20	1.000	229.5	1.42e-20	1.000	230.0	1.48e-20	1.000	230.5	1.53e-20	1.000	231.0	1.57e-20	1.000
231.5	1.59e-20	1.000	232.0	1.61e-20	1.000	232.5	1.62e-20	1.000	233.0	1.61e-20	1.000	233.5	1.68e-20	1.000
234.0	1.74e-20	1.000	234.5	1.80e-20	1.000	235.0	1.84e-20	1.000	235.5	1.87e-20	1.000	236.0	1.89e-20	1.000
236.5	1.91e-20	1.000	237.0	1.93e-20	1.000	237.5	1.94e-20	1.000	238.0	1.96e-20	1.000	238.5	1.96e-20	1.000
239.0	2.01e-20	1.000	239.5	2.04e-20	1.000	240.0	2.08e-20	1.000	240.5	2.10e-20	1.000	241.0	2.14e-20	1.000
241.5	2.16e-20	1.000	242.0	2.19e-20	1.000	242.5	2.20e-20	1.000	243.0	2.23e-20	1.000	243.5	2.26e-20	1.000
244.0	2.28e-20	1.000	244.5	2.29e-20	1.000	245.0	2.30e-20	1.000	245.5	2.32e-20	1.000	246.0	2.33e-20	1.000
246.5	2.35e-20	1.000	247.0	2.38e-20	1.000	247.5	2.41e-20	1.000	248.0	2.46e-20	1.000	248.5	2.51e-20	1.000
249.0	2.57e-20	1.000	249.5	2.61e-20	1.000	250.0	2.65e-20	1.000	250.5	2.67e-20	1.000	251.0	2.69e-20	1.000
251.5	2.69e-20	1.000	252.0	2.71e-20	1.000	252.5	2.72e-20	1.000	253.0	2.73e-20	1.000	253.5	2.74e-20	1.000
254.0	2.76e-20	1.000	254.5	2.78e-20	1.000	255.0	2.82e-20	1.000	255.5	2.87e-20	1.000	256.0	2.93e-20	1.000
256.5	2.98e-20	1.000	257.0	3.07e-20	1.000	257.5	3.12e-20	1.000	258.0	3.17e-20	1.000	258.5	3.21e-20	1.000
259.0	3.26e-20	1.000	259.5	3.28e-20	1.000	260.0	3.29e-20	1.000	260.5	3.31e-20	1.000	261.0	3.33e-20	1.000
261.5	3.34e-20	1.000	262.0	3.36e-20	1.000	262.5	3.38e-20	1.000	263.0	3.42e-20	1.000	263.5	3.44e-20	1.000
264.0	3.48e-20	1.000	264.5	3.54e-20	1.000	265.0	3.59e-20	1.000	265.5	3.65e-20	1.000	266.0	3.73e-20	1.000
266.5	3.80e-20	1.000	267.0	3.87e-20	1.000	267.5	3.95e-20	1.000	268.0	4.02e-20	1.000	268.5	4.08e-20	1.000
269.0	4.13e-20	1.000	269.5	4.17e-20	1.000	270.0	4.20e-20	1.000	270.5	4.22e-20	1.000	271.0	4.22e-20	1.000
271.5	4.22e-20	1.000	272.0	4.23e-20	1.000	272.5	4.24e-20	1.000	273.0	4.27e-20	1.000	273.5	4.29e-20	1.000
274.0	4.31e-20	1.000	274.5	4.33e-20	1.000	275.0	4.37e-20	1.000	275.5	4.42e-20	1.000	276.0	4.48e-20	1.000
276.5	4.56e-20	1.000	277.0	4.64e-20	1.000	277.5	4.71e-20	1.000	278.0	4.78e-20	1.000	278.5	4.83e-20	1.000
279.0	4.87e-20	1.000	279.5	4.90e-20	1.000	280.0	4.92e-20	1.000	280.5	4.93e-20	1.000	281.0	4.94e-20	1.000
281.5	4.92e-20	1.000	282.0	4.90e-20	1.000	282.5	4.86e-20	1.000	283.0	4.83e-20	1.000	283.5	4.79e-20	1.000
284.0	4.76e-20	1.000	284.5	4.72e-20	1.000	285.0	4.70e-20	1.000	285.5	4.68e-20	1.000	286.0	4.66e-20	1.000
286.5	4.65e-20	1.000	287.0	4.65e-20	1.000	287.5	4.68e-20	1.000	288.0	4.73e-20	1.000	288.5	4.78e-20	1.000
289.0	4.84e-20	1.000	289.5	4.89e-20	1.000	290.0	4.92e-20	1.000	290.5	4.92e-20	1.000	291.0	4.90e-20	1.000
291.5	4.86e-20	1.000	292.0	4.81e-20	1.000	292.5	4.75e-20	1.000	293.0	4.70e-20	1.000	293.5	4.65e-20	1.000
294.0	4.58e-20	1.000	294.5	4.48e-20	1.000	295.0	4.38e-20	1.000	295.5	4.27e-20	1.000	296.0	4.17e-20	1.000
296.5	4.07e-20	1.000	297.0	3.99e-20	1.000	297.5	3.94e-20	1.000	298.0	3.88e-20	1.000	298.5	3.82e-20	1.000
299.0	3.76e-20	1.000	299.5	3.72e-20	1.000	300.0	3.69e-20	1.000	300.5	3.68e-20	1.000	301.0	3.70e-20	1.000
301.5	3.72e-20	1.000	302.0	3.74e-20	1.000	302.5	3.74e-20	1.000	303.0	3.75e-20	1.000	303.5	3.71e-20	1.000
304.0	3.62e-20	1.000	304.5	3.51e-20	1.000	305.0	3.38e-20	1.000	305.5	3.25e-20	1.000	306.0	3.15e-20	1.000
306.5	3.04e-20	1.000	307.0	2.92e-20	1.000	307.5	2.80e-20	1.000	308.0	2.71e-20	1.000	308.5	2.63e-20	1.000
309.0	2.52e-20	1.000	309.5	2.43e-20	1.000	310.0	2.34e-20	1.000	310.5	2.25e-20	1.000	311.0	2.19e-20	1.000
311.5	2.12e-20	1.000	312.0	2.06e-20	1.000	312.5	2.02e-20	1.000	313.0	1.96e-20	1.000	313.5	1.92e-20	1.000
314.0	1.91e-20	1.000	314.5	1.88e-20	1.000	315.0	1.86e-20	1.000	315.5	1.85e-20	1.000	316.0	1.86e-20	1.000
316.5	1.87e-20	1.000	317.0	1.87e-20	1.000	317.5	1.87e-20	1.000	318.0	1.83e-20	1.000	318.5	1.75e-20	1.000
319.0	1.69e-20	1.000	319.5	1.60e-20	1.000	320.0	1.50e-20	1.000	320.5	1.41e-20	1.000	321.0	1.34e-20	1.000
321.5	1.27e-20	1.000	322.0	1.21e-20	1.000	322.5	1.18e-20	1.000	323.0	1.14e-20	1.000	323.5	1.08e-20	1.000

Table A-5 (continued)

WL (nm)	Abs (cm^2)	QY (nm)	WL	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY
324.0	1.01e-20	1.000	324.5	9.62e-21	1.000	325.0	9.28e-21	1.000	325.5	8.75e-21	1.000	326.0	8.49e-21	1.000
326.5	8.21e-21	1.000	327.0	7.71e-21	1.000	327.5	7.38e-21	1.000	328.0	7.18e-21	1.000	328.5	6.86e-21	1.000
329.0	6.71e-21	1.000	329.5	6.63e-21	1.000	330.0	6.46e-21	1.000	330.5	6.29e-21	1.000	331.0	6.21e-21	1.000
331.5	6.18e-21	1.000	332.0	6.20e-21	1.000	332.5	5.49e-21	1.000	333.0	5.21e-21	1.000	333.5	5.38e-21	1.000
334.0	5.35e-21	1.000	334.5	5.04e-21	1.000	335.0	4.94e-21	1.000	335.5	4.90e-21	1.000	336.0	4.52e-21	1.000
336.5	4.26e-21	1.000	337.0	4.11e-21	1.000	337.5	3.76e-21	1.000	338.0	3.61e-21	1.000	338.5	3.58e-21	1.000
339.0	3.47e-21	1.000	339.5	3.32e-21	1.000	340.0	3.22e-21	1.000	340.5	3.10e-21	1.000	341.0	3.00e-21	1.000
341.5	2.94e-21	1.000	342.0	2.89e-21	1.000	342.5	2.86e-21	1.000	343.0	2.88e-21	1.000	343.5	2.88e-21	1.000
344.0	2.89e-21	1.000	344.5	2.91e-21	1.000	345.0	2.95e-21	1.000	345.5	3.00e-21	1.000	346.0	3.08e-21	1.000
346.5	3.18e-21	1.000	347.0	3.25e-21	1.000	347.5	3.30e-21	1.000	348.0	3.39e-21	1.000	348.5	3.51e-21	1.000
349.0	3.63e-21	1.000	349.5	3.73e-21	1.000	350.0	3.85e-21	1.000	350.5	3.99e-21	1.000	351.0	4.27e-21	1.000
351.5	4.47e-21	1.000	352.0	4.63e-21	1.000	352.5	4.78e-21	1.000	353.0	4.92e-21	1.000	353.5	5.07e-21	1.000
354.0	5.23e-21	1.000	354.5	5.39e-21	1.000	355.0	5.56e-21	1.000	355.5	5.77e-21	1.000	356.0	5.97e-21	1.000
356.5	6.15e-21	1.000	357.0	6.35e-21	1.000	357.5	6.56e-21	1.000	358.0	6.76e-21	1.000	358.5	6.95e-21	1.000
359.0	7.20e-21	1.000	359.5	7.44e-21	1.000	360.0	7.64e-21	1.000	360.5	7.89e-21	1.000	361.0	8.15e-21	1.000
361.5	8.43e-21	1.000	362.0	8.71e-21	1.000	362.5	9.02e-21	1.000	363.0	9.33e-21	1.000	363.5	9.65e-21	1.000
364.0	1.00e-20	1.000	364.5	1.04e-20	1.000	365.0	1.08e-20	1.000	365.5	1.11e-20	1.000	366.0	1.15e-20	1.000
366.5	1.19e-20	1.000	367.0	1.23e-20	1.000	367.5	1.27e-20	1.000	368.0	1.31e-20	1.000	368.5	1.35e-20	1.000
369.0	1.40e-20	1.000	369.5	1.44e-20	1.000	370.0	1.47e-20	1.000	370.5	1.51e-20	1.000	371.0	1.55e-20	1.000
371.5	1.59e-20	1.000	372.0	1.64e-20	1.000	372.5	1.70e-20	1.000	373.0	1.73e-20	1.000	373.5	1.77e-20	1.000
374.0	1.81e-20	1.000	374.5	1.86e-20	1.000	375.0	1.90e-20	1.000	375.5	1.96e-20	1.000	376.0	2.02e-20	1.000
376.5	2.06e-20	1.000	377.0	2.10e-20	1.000	377.5	2.14e-20	1.000	378.0	2.18e-20	1.000	378.5	2.24e-20	1.000
379.0	2.30e-20	1.000	379.5	2.37e-20	1.000	380.0	2.42e-20	1.000	380.5	2.47e-20	1.000	381.0	2.54e-20	1.000
381.5	2.62e-20	1.000	382.0	2.69e-20	1.000	382.5	2.79e-20	1.000	383.0	2.88e-20	1.000	383.5	2.96e-20	1.000
384.0	3.02e-20	1.000	384.5	3.10e-20	1.000	385.0	3.20e-20	1.000	385.5	3.29e-20	1.000	386.0	3.39e-20	1.000
386.5	3.51e-20	1.000	387.0	3.62e-20	1.000	387.5	3.69e-20	1.000	388.0	3.70e-20	1.000	388.5	3.77e-20	1.000
389.0	3.88e-20	1.000	389.5	3.97e-20	1.000	390.0	4.03e-20	1.000	390.5	4.12e-20	1.000	391.0	4.22e-20	1.000
391.5	4.29e-20	1.000	392.0	4.30e-20	1.000	392.5	4.38e-20	1.000	393.0	4.47e-20	1.000	393.5	4.55e-20	1.000
394.0	4.56e-20	1.000	394.5	4.59e-20	1.000	395.0	4.67e-20	1.000	395.5	4.80e-20	1.000	396.0	4.87e-20	1.000
396.5	4.96e-20	1.000	397.0	5.08e-20	1.000	397.5	5.19e-20	1.000	398.0	5.23e-20	1.000	398.5	5.39e-20	1.000
399.0	5.46e-20	1.000	399.5	5.54e-20	1.000	400.0	5.59e-20	1.000	400.5	5.77e-20	1.000	401.0	5.91e-20	1.000
401.5	5.99e-20	1.000	402.0	6.06e-20	1.000	402.5	6.20e-20	1.000	403.0	6.35e-20	1.000	403.5	6.52e-20	1.000
404.0	6.54e-20	1.000	404.5	6.64e-20	1.000	405.0	6.93e-20	1.000	405.5	7.15e-20	1.000	406.0	7.19e-20	1.000
406.5	7.32e-20	1.000	407.0	7.58e-20	1.000	407.5	7.88e-20	1.000	408.0	7.97e-20	1.000	408.5	7.91e-20	1.000
409.0	8.11e-20	1.000	409.5	8.41e-20	1.000	410.0	8.53e-20	1.000	410.5	8.59e-20	1.000	411.0	8.60e-20	1.000
411.5	8.80e-20	1.000	412.0	9.04e-20	1.000	412.5	9.45e-20	1.000	413.0	9.34e-20	1.000	413.5	9.37e-20	1.000
414.0	9.63e-20	1.000	414.5	9.71e-20	1.000	415.0	9.70e-20	1.000	415.5	9.65e-20	1.000	416.0	9.69e-20	1.000
416.5	9.89e-20	1.000	417.0	1.00e-19	1.000	417.5	1.02e-19	1.000	418.0	1.00e-19	1.000	418.5	1.02e-19	1.000
419.0	1.01e-19	1.000	419.5	1.01e-19	1.000	420.0	1.03e-19	1.000	420.5	1.01e-19	1.000	421.0	1.04e-19	1.000
421.5	1.05e-19	1.000	422.0	1.06e-19	1.000	422.5	1.04e-19	1.000	423.0	1.05e-19	1.000	423.5	1.05e-19	1.000
424.0	1.01e-19	1.000	424.5	1.01e-19	1.000	425.0	1.05e-19	1.000	425.5	1.03e-19	1.000	426.0	1.02e-19	1.000
426.5	1.01e-19	1.000	427.0	9.77e-20	1.000	427.5	9.81e-20	1.000	428.0	1.00e-19	1.000	428.5	1.02e-19	1.000
429.0	9.89e-20	1.000	429.5	9.85e-20	1.000	430.0	1.04e-19	1.000	430.5	1.08e-19	1.000	431.0	1.05e-19	1.000
431.5	1.02e-19	1.000	432.0	9.64e-20	1.000	432.5	1.01e-19	1.000	433.0	1.06e-19	1.000	433.5	1.09e-19	1.000
434.0	1.04e-19	1.000	434.5	1.03e-19	1.000	435.0	1.07e-19	1.000	435.5	1.16e-19	1.000	436.0	1.09e-19	1.000
436.5	1.11e-19	1.000	437.0	9.81e-20	1.000	437.5	9.71e-20	1.000	438.0	1.06e-19	1.000	438.5	1.16e-19	1.000
439.0	1.08e-19	1.000	439.5	1.05e-19	1.000	440.0	9.70e-20	1.000	440.5	1.01e-19	1.000	441.0	1.04e-19	1.000
441.5	1.07e-19	1.000	442.0	1.02e-19	1.000	442.5	9.68e-20	1.000	443.0	1.00e-19	1.000	443.5	1.14e-19	1.000
444.0	1.13e-19	1.000	444.5	1.03e-19	1.000	445.0	9.74e-20	1.000	445.5	8.46e-20	1.000	446.0	8.70e-20	1.000
446.5	9.97e-20	1.000	447.0	1.01e-19	1.000	447.5	9.15e-20	1.000	448.0	9.41e-20	1.000	448.5	8.99e-20	1.000
449.0	1.10e-19	1.000	449.5	9.12e-20	1.000	450.0	8.56e-20	1.000	450.5	8.28e-20	1.000	451.0	6.15e-20	1.000
451.5	5.56e-20	1.000	452.0	6.47e-20	1.000	452.5	7.27e-20	1.000	453.0	5.75e-20	1.000	453.5	5.08e-20	1.000

Table A-5 (continued)

WL (nm)	Abs (cm^2)	QY (nm)	WL	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY	WL (nm)	Abs (cm^2)	QY
454.0	4.38e-20	1.000	454.5	3.81e-20	1.000	455.0	3.61e-20	1.000	455.5	3.61e-20	1.000	456.0	3.13e-20	1.000
456.5	2.72e-20	1.000	457.0	2.44e-20	1.000	457.5	2.22e-20	1.000	458.0	1.82e-20	1.000	458.5	1.43e-20	1.000
459.0	1.32e-20	1.000	459.5	1.05e-20	1.000	460.0	8.95e-21	1.000	460.5	8.90e-21	1.000	461.0	7.94e-21	1.000
461.5	7.04e-21	1.000	462.0	6.46e-21	1.000	462.5	5.63e-21	1.000	463.0	4.78e-21	1.000	463.5	3.94e-21	1.000
464.0	3.26e-21	1.000	464.5	2.97e-21	1.000	465.0	2.65e-21	1.000	465.5	2.46e-21	1.000	466.0	2.27e-21	1.000
466.5	2.08e-21	1.000	467.0	1.86e-21	1.000	467.5	1.76e-21	1.000	468.0	1.60e-21	1.000	468.5	1.44e-21	1.000
469.0	1.34e-21	1.000	469.5	1.20e-21	1.000	470.0	1.07e-21	1.000	470.5	1.02e-21	1.000	471.0	9.92e-22	1.000
471.5	9.97e-22	1.000	472.0	8.87e-22	1.000	472.5	8.27e-22	1.000	473.0	7.76e-22	1.000	473.5	7.15e-22	1.000
474.0	6.71e-22	1.000	474.5	6.67e-22	1.000	475.0	6.10e-22	1.000	475.5	6.17e-22	1.000	476.0	5.54e-22	1.000
476.5	5.22e-22	1.000	477.0	5.10e-22	1.000	477.5	5.17e-22	1.000	478.0	4.80e-22	1.000	478.5	4.71e-22	1.000
479.0	4.60e-22	1.000	479.5	4.35e-22	1.000	480.0	3.90e-22	1.000	480.5	3.71e-22	1.000	481.0	3.62e-22	1.000
481.5	3.52e-22	1.000	482.0	3.05e-22	1.000	482.5	3.05e-22	1.000	483.0	2.86e-22	1.000	483.5	2.53e-22	1.000
484.0	2.75e-22	1.000	484.5	2.59e-22	1.000	485.0	2.47e-22	1.000	485.5	2.36e-22	1.000	486.0	2.12e-22	1.000
486.5	1.89e-22	1.000	487.0	1.93e-22	1.000	487.5	1.86e-22	1.000	488.0	1.82e-22	1.000	488.5	1.75e-22	1.000
489.0	1.74e-22	1.000	489.5	1.72e-22	1.000	490.0	1.66e-22	1.000	490.5	1.75e-22	1.000	491.0	1.54e-22	1.000
491.5	1.74e-22	1.000	492.0	1.63e-22	1.000	492.5	1.53e-22	1.000	493.0	1.52e-22	1.000	493.5	5.85e-23	1.000
494.0	0.00e+00	1.000												

Table A-6. Listing of the reactions of the individual VOCs that can be represented explicitly, but are not part of the base mechanism.

Compound	Rate Parameters [a]				Reactions and Products [b]
	k(298)	A	Ea	B	
Methane	6.36e-15	2.15e-12	3.448	0.0	METHANE + HO. = C-O2.
Ethane	2.54e-13	1.37e-12	0.990	2.0	ETHANE + HO. = RO2-R. + CCHO
Propane	1.13e-12	1.40e-12	0.121	2.0	PROPANE + HO. = #.965 RO2-R. + #.035 RO2-N. + #.261 RCHO + #.704 ACET + #-0.104 XC
n-Butane	2.44e-12	1.52e-12	-0.288	2.0	N-C4 + HO. = #.922 RO2-R. + #.078 RO2-N. + #.414 R2O2. + #.633 CCHO + #.12 RCHO + #.486 MEK + #-0.036 XC
n-Pentane	4.01e-12	2.20e-12	-0.364	2.0	N-C5 + HO. = #.857 RO2-R. + #.143 RO2-N. + #.651 R2O2. + #.148 CCHO + #.221 RCHO + #.239 MEK + #.398 PROD2 + #-0.156 XC
n-Hexane	5.47e-12	1.38e-12	-0.823	2.0	N-C6 + HO. = #.778 RO2-R. + #.222 RO2-N. + #.788 R2O2. + #.011 CCHO + #.113 RCHO + #.69 PROD2 + #.162 XC
n-Heptane	7.02e-12	1.43e-12	-0.950	2.0	N-C7 + HO. = #.707 RO2-R. + #.293 RO2-N. + #.8 R2O2. + #.055 RCHO + #.661 PROD2 + #1.111 XC
n-Octane	8.70e-12	2.48e-12	-0.751	2.0	N-C8 + HO. = #.648 RO2-R. + #.352 RO2-N. + #.787 R2O2. + #.024 RCHO + #.624 PROD2 + #2.073 XC
n-Nonane	9.99e-12	2.26e-12	-0.888	2.0	N-C9 + HO. = #.604 RO2-R. + #.396 RO2-N. + #.777 R2O2. + #.018 RCHO + #.585 PROD2 + #3.055 XC
n-Decane	1.12e-11	2.82e-12	-0.827	2.0	N-C10 + HO. = #.573 RO2-R. + #.427 RO2-N. + #.773 R2O2. + #.015 RCHO + #.558 PROD2 + #4.045 XC
n-Undecane	1.29e-11	1.29e-11	0.000	0.0	N-C11 + HO. = #.554 RO2-R. + #.446 RO2-N. + #.771 R2O2. + #.013 RCHO + #.541 PROD2 + #5.038 XC
n-Dodecane	1.39e-11	1.39e-11	0.000	0.0	N-C12 + HO. = #.542 RO2-R. + #.458 RO2-N. + #.768 R2O2. + #.011 RCHO + #.531 PROD2 + #6.034 XC
n-Tridecane	1.60e-11	1.60e-11	0.000	0.0	N-C13 + HO. = #.535 RO2-R. + #.465 RO2-N. + #.766 R2O2. + #.01 RCHO + #.525 PROD2 + #7.03 XC
n-Tetradecane	1.80e-11	1.80e-11	0.000	0.0	N-C14 + HO. = #.53 RO2-R. + #.47 RO2-N. + #.765 R2O2. + #.009 RCHO + #.521 PROD2 + #8.027 XC
n-Pentadecane	2.10e-11	2.10e-11	0.000	0.0	N-C15 + HO. = #.527 RO2-R. + #.473 RO2-N. + #.764 R2O2. + #.008 RCHO + #.519 PROD2 + #9.025 XC
n-C16	2.30e-11	2.30e-11	0.000	0.0	N-C16 + HO. = #.525 RO2-R. + #.475 RO2-N. + #.763 R2O2. + #.008 RCHO + #.517 PROD2 + #10.023 XC
Isobutane	2.18e-12	1.04e-12	-0.447	2.0	2-ME-C3 + HO. = #.198 RO2-R. + #.042 RO2-N. + #.833 R2O2. + #.761 TBU-O. + #.073 HCHO + #.128 RCHO + #.07 ACET + #.803 XC
Iso-Pentane	3.70e-12	3.70e-12	0.000	0.0	2-ME-C4 + HO. = #.881 RO2-R. + #.095 RO2-N. + #.903 R2O2. + #.024 C-O2. + #.012 HCHO + #.78 CCHO + #.101 RCHO + #.762 ACET + #.038 MEK + #.094 XC
Neopentane	8.47e-13	1.62e-12	0.376	2.0	22-DM-C3 + HO. = #.021 RO2-R. + #.087 RO2-N. + #1.82 R2O2. + #.892 TBU-O. + #.928 HCHO + #.021 RCHO + #.811 XC
2-Methyl Pentane	5.30e-12	5.30e-12	0.000	0.0	2-ME-C5 + HO. = #.818 RO2-R. + #.182 RO2-N. + #.86 R2O2. + #.004 HCHO + #.011 CCHO + #.663 RCHO + #.346 ACET + #.006 MEK + #.153 PROD2 + #.907 XC
3-Methylpentane	5.40e-12	5.40e-12	0.000	0.0	3-ME-C5 + HO. = #.846 RO2-R. + #.154 RO2-N. + #.991 R2O2. + #.005 HCHO + #.988 CCHO + #.069 RCHO + #.63 MEK + #.036 PROD2 + #.152 XC
2,3-Dimethyl Butane	5.80e-12	1.12e-12	-0.982	2.0	23-DM-C4 + HO. = #.86 RO2-R. + #.14 RO2-N. + #.919 R2O2. + #.028 HCHO + #.023 CCHO + #.078 RCHO + #1.572 ACET + #.001 MEK + #.133 XC
2,2-Dimethyl Butane	2.34e-12	3.22e-11	1.552	0.0	22-DM-C4 + HO. = #.305 RO2-R. + #.174 RO2-N. + #1.584 R2O2. + #.009 C-O2. + #.512 TBU-O. + #.227 HCHO + #.732 CCHO + #.103 RCHO + #.202 ACET + #.009 MEK + #.768 XC

Table A-6 (continued)

Compound	Rate Parameters [a]				Reactions and Products [b]
	k(298)	A	Ea	B	
2,2-Dimethyl Pentane	3.40e-12	3.40e-12	0.000	0.0	22-DM-C5 + HO. = #.441 RO2-R. + #.208 RO2-N. + #1.192 R2O2. + #.351 TBU-O. + #.056 HCHO + #.017 CCHO + #.517 RCHO + #.014 ACET + #.017 MEK + #.257 PROD2 + #1.41 XC
3,3-Dimethyl Pentane	3.00e-12	3.00e-12	0.000	0.0	33-DM-C5 + HO. = #.738 RO2-R. + #.237 RO2-N. + #1.596 R2O2. + #.025 C-O2. + #.163 HCHO + #1.331 CCHO + #.046 RCHO + #.619 ACET + #.097 MEK + #.002 PROD2 + #.339 XC
2,3-Dimethyl Pentane	7.15e-12	7.15e-12	0.000	0.0	23-DM-C5 + HO. = #.785 RO2-R. + #.215 RO2-N. + #1.092 R2O2. + #.015 HCHO + #.454 CCHO + #.061 RCHO + #.734 ACET + #.518 MEK + #.01 PROD2 + #.269 XC
3-Methyl Hexane	7.17e-12	7.17e-12	0.000	0.0	3-ME-C6 + HO. = #.752 RO2-R. + #.248 RO2-N. + #.926 R2O2. + #.002 HCHO + #.208 CCHO + #.464 RCHO + #.256 MEK + #.235 PROD2 + #1.267 XC
2,4-Dimethyl Pentane	5.00e-12	5.00e-12	0.000	0.0	24-DM-C5 + HO. = #.797 RO2-R. + #.203 RO2-N. + #1.324 R2O2. + #.333 HCHO + #.016 CCHO + #.562 RCHO + #.484 ACET + #.013 MEK + #.135 PROD2 + #1.414 XC
2-Methyl Hexane	6.89e-12	6.89e-12	0.000	0.0	2-ME-C6 + HO. = #.733 RO2-R. + #.267 RO2-N. + #.908 R2O2. + #.022 HCHO + #.048 CCHO + #.236 RCHO + #.137 ACET + #.51 PROD2 + #1.103 XC
2,2,3-Trimethyl Butane	4.24e-12	7.61e-13	-1.025	2.0	223TM-C4 + HO. = #.183 RO2-R. + #.19 RO2-N. + #1.635 R2O2. + #.627 TBU-O. + #.161 HCHO + #.022 CCHO + #.065 RCHO + #.872 ACET + #.966 XC
2,2,3,3-Tetrame. Butane	1.05e-12	1.72e-12	0.286	2.0	2233M-C4 + HO. = #.067 RO2-R. + #.313 RO2-N. + #2.112 R2O2. + #.62 TBU-O. + #.762 HCHO + #.059 RCHO + #.661 ACET + #1.338 XC
2,3-Dimethyl Hexane	8.57e-12	8.57e-12	0.000	0.0	23-DM-C6 + HO. = #.702 RO2-R. + #.298 RO2-N. + #1.145 R2O2. + #.014 HCHO + #.128 CCHO + #.184 RCHO + #.562 ACET + #.299 MEK + #.251 PROD2 + #.999 XC
2,2,4-Trimethyl Pentane	3.56e-12	1.87e-12	-0.389	2.0	224TM-C5 + HO. = #.403 RO2-R. + #.226 RO2-N. + #1.961 R2O2. + #.37 TBU-O. + #.717 HCHO + #.002 CCHO + #.388 RCHO + #.38 ACET + #.133 MEK + #.027 PROD2 + #1.81 XC
2,4-Dimethyl Hexane	8.57e-12	8.57e-12	0.000	0.0	24-DM-C6 + HO. = #.654 RO2-R. + #.346 RO2-N. + #1.35 R2O2. + #.16 HCHO + #.336 CCHO + #.307 RCHO + #.096 ACET + #.156 MEK + #.295 PROD2 + #1.491 XC
2,3,4-Trimethyl Pentane	7.10e-12	7.10e-12	0.000	0.0	234TM-C5 + HO. = #.719 RO2-R. + #.281 RO2-N. + #1.286 R2O2. + #.039 HCHO + #.448 CCHO + #.033 RCHO + #1.143 ACET + #.296 MEK + #.662 XC
3-Methyl Heptane	8.59e-12	8.59e-12	0.000	0.0	3-ME-C7 + HO. = #.664 RO2-R. + #.336 RO2-N. + #.944 R2O2. + #.001 HCHO + #.179 CCHO + #.15 RCHO + #.063 MEK + #.523 PROD2 + #1.788 XC
2-Methyl Heptane	8.31e-12	8.31e-12	0.000	0.0	2-ME-C7 + HO. = #.661 RO2-R. + #.339 RO2-N. + #.884 R2O2. + #.016 HCHO + #.025 CCHO + #.156 RCHO + #.024 ACET + #.548 PROD2 + #2.078 XC
2,5-Dimethyl Hexane	8.29e-12	8.29e-12	0.000	0.0	25-DM-C6 + HO. = #.651 RO2-R. + #.349 RO2-N. + #1.534 R2O2. + #.157 HCHO + #.435 RCHO + #.571 ACET + #.226 PROD2 + #1.377 XC
4-Methyl Heptane	8.59e-12	8.59e-12	0.000	0.0	4-ME-C7 + HO. = #.678 RO2-R. + #.322 RO2-N. + #.876 R2O2. + #.002 HCHO + #.004 CCHO + #.378 RCHO + #.115 MEK + #.377 PROD2 + #2.202 XC
2,2-Dimethyl Hexane	4.80e-12	4.80e-12	0.000	0.0	22-DM-C6 + HO. = #.458 RO2-R. + #.288 RO2-N. + #.955 R2O2. + #.254 TBU-O. + #.035 HCHO + #.042 CCHO + #.367 RCHO + #.002 ACET + #.013 MEK + #.342 PROD2 + #2.184 XC

Table A-6 (continued)

Compound	Rate Parameters [a]				Reactions and Products [b]
	k(298)	A	Ea	B	
2,3,5-Trimethyl Hexane	7.90e-12	7.90e-12	0.000	0.0	235TM-C6 + HO. = #.624 RO2-R. + #.376 RO2-N. + #1.358 R2O2. + #.094 HCHO + #.104 CCHO + #.178 RCHO + #.631 ACET + #.017 MEK + #.437 PROD2 + #1.324 XC
3,3-Diethyl Pentane	4.90e-12	4.90e-12	0.000	0.0	33-DE-C5 + HO. = #.649 RO2-R. + #.351 RO2-N. + #1.452 R2O2. + #.054 HCHO + #1.323 CCHO + #.022 RCHO + #.608 MEK + #.018 PROD2 + #1.584 XC
4-Ethyl Heptane	1.04e-11	1.04e-11	0.000	0.0	4-ET-C7 + HO. = #.634 RO2-R. + #.366 RO2-N. + #.863 R2O2. + #.001 HCHO + #.049 CCHO + #.328 RCHO + #.487 PROD2 + #2.8 XC
2-Methyl Octane	1.01e-11	1.01e-11	0.000	0.0	2-ME-C8 + HO. = #.589 RO2-R. + #.411 RO2-N. + #.915 R2O2. + #.002 HCHO + #.064 RCHO + #.014 ACET + #.538 PROD2 + #3.072 XC
2,2,5-Trimethyl Hexane	6.08e-12	6.08e-12	0.000	0.0	225TM-C6 + HO. = #.477 RO2-R. + #.328 RO2-N. + #1.309 R2O2. + #.195 TBU-O. + #.046 HCHO + #.002 CCHO + #.614 RCHO + #.434 ACET + #.004 MEK + #.056 PROD2 + #2.901 XC
4-Methyl Octane	9.70e-12	9.70e-12	0.000	0.0	4-ME-C8 + HO. = #.607 RO2-R. + #.393 RO2-N. + #.891 R2O2. + #.001 HCHO + #.034 CCHO + #.127 RCHO + #.006 MEK + #.563 PROD2 + #2.788 XC
3,5-Dimethyl Heptane	1.03e-11	1.03e-11	0.000	0.0	35-DM-C7 + HO. = #.551 RO2-R. + #.449 RO2-N. + #1.47 R2O2. + #.01 HCHO + #.651 CCHO + #.155 RCHO + #.075 MEK + #.4 PROD2 + #1.826 XC
2,4-Dimethyl Heptane	9.99e-12	9.99e-12	0.000	0.0	24-DM-C7 + HO. = #.6 RO2-R. + #.4 RO2-N. + #1.179 R2O2. + #.105 HCHO + #.013 CCHO + #.411 RCHO + #.049 ACET + #.073 MEK + #.382 PROD2 + #2.5 XC
3-Methyl Nonane	1.14e-11	1.14e-11	0.000	0.0	3-ME-C9 + HO. = #.552 RO2-R. + #.448 RO2-N. + #.929 R2O2. + #.036 CCHO + #.063 RCHO + #.014 MEK + #.503 PROD2 + #3.977 XC
2,6-Dimethyl Octane	1.29e-11	1.29e-11	0.000	0.0	26DM-C8 + HO. = #.568 RO2-R. + #.432 RO2-N. + #1.097 R2O2. + #.108 CCHO + #.309 RCHO + #.146 ACET + #.071 MEK + #.276 PROD2 + #3.887 XC
4-Propyl Heptane	1.18e-11	1.18e-11	0.000	0.0	4-PR-C7 + HO. = #.594 RO2-R. + #.406 RO2-N. + #.835 R2O2. + #.001 HCHO + #.001 CCHO + #.297 RCHO + #.462 PROD2 + #3.899 XC
4-Methyl Nonane	1.14e-11	1.14e-11	0.000	0.0	4-ME-C9 + HO. = #.573 RO2-R. + #.427 RO2-N. + #.877 R2O2. + #.001 HCHO + #.019 CCHO + #.141 RCHO + #.004 MEK + #.521 PROD2 + #3.831 XC
2,4-Dimethyl Octane	1.14e-11	1.14e-11	0.000	0.0	24-DM-C8 + HO. = #.557 RO2-R. + #.443 RO2-N. + #1.061 R2O2. + #.041 HCHO + #.034 CCHO + #.211 RCHO + #.024 ACET + #.007 MEK + #.492 PROD2 + #3.55 XC
2-Methyl Nonane	1.28e-11	1.28e-11	0.000	0.0	2-ME-C9 + HO. = #.552 RO2-R. + #.448 RO2-N. + #.896 R2O2. + #.035 RCHO + #.012 ACET + #.517 PROD2 + #4.066 XC
3,4-Diethyl Hexane	7.40e-12	7.40e-12	0.000	0.0	34-DE-C6 + HO. = #.62 RO2-R. + #.38 RO2-N. + #1.106 R2O2. + #.007 HCHO + #.338 CCHO + #.32 RCHO + #.71 MEK + #.126 PROD2 + #2.482 XC
3-Methyl Decane	1.29e-11	1.29e-11	0.000	0.0	3-ME-C10 + HO. = #.527 RO2-R. + #.473 RO2-N. + #.917 R2O2. + #.029 CCHO + #.039 RCHO + #.012 MEK + #.49 PROD2 + #4.998 XC
4-Methyl Decane	1.29e-11	1.29e-11	0.000	0.0	4-ME-C10 + HO. = #.532 RO2-R. + #.468 RO2-N. + #.908 R2O2. + #.001 CCHO + #.08 RCHO + #.003 MEK + #.501 PROD2 + #4.932 XC

Table A-6 (continued)

Compound	Rate Parameters [a]				Reactions and Products [b]
	k(298)	A	Ea	B	
2,6-Dimethyl Nonane	1.28e-11	1.28e-11	0.000	0.0	26DM-C9 + HO. = #.533 RO2-R. + #.467 RO2-N. + #1.037 R2O2. + #.001 CCHO + #.222 RCHO + #.12 ACET + #.006 MEK + #.377 PROD2 + #4.888 XC
3,5-Diethyl Heptane	1.39e-11	1.39e-11	0.000	0.0	35-DE-C7 + HO. = #.466 RO2-R. + #.534 RO2-N. + #1.312 R2O2. + #.002 HCHO + #.476 CCHO + #.123 RCHO + #.044 MEK + #.372 PROD2 + #4.062 XC
3-Methyl Undecane	1.43e-11	1.43e-11	0.000	0.0	3-ME-C11 + HO. = #.516 RO2-R. + #.484 RO2-N. + #.896 R2O2. + #.025 CCHO + #.033 RCHO + #.011 MEK + #.484 PROD2 + #5.997 XC
5-Methyl Undecane	1.43e-11	1.43e-11	0.000	0.0	5-ME-C11 + HO. = #.524 RO2-R. + #.476 RO2-N. + #.867 R2O2. + #.01 CCHO + #.059 RCHO + #.504 PROD2 + #5.923 XC
3,6-Dimethyl Decane	1.45e-11	1.45e-11	0.000	0.0	36DM-C10 + HO. = #.495 RO2-R. + #.505 RO2-N. + #1.079 R2O2. + #.001 HCHO + #.088 CCHO + #.11 RCHO + #.055 MEK + #.459 PROD2 + #5.487 XC
2,6-Diethyl Octane	1.53e-11	1.53e-11	0.000	0.0	36-DE-C8 + HO. = #.518 RO2-R. + #.482 RO2-N. + #1.156 R2O2. + #.301 CCHO + #.058 RCHO + #.108 MEK + #.473 PROD2 + #5.061 XC
3-Methyl Dodecane	1.57e-11	1.57e-11	0.000	0.0	3-ME-C12 + HO. = #.51 RO2-R. + #.49 RO2-N. + #.881 R2O2. + #.023 CCHO + #.03 RCHO + #.009 MEK + #.482 PROD2 + #6.997 XC
5-Methyl Dodecane	1.57e-11	1.57e-11	0.000	0.0	5-ME-C12 + HO. = #.514 RO2-R. + #.486 RO2-N. + #.863 R2O2. + #.009 CCHO + #.044 RCHO + #.499 PROD2 + #6.942 XC
3,6-Dimethyl Undecane	1.60e-11	1.60e-11	0.000	0.0	36DM-C11 + HO. = #.489 RO2-R. + #.511 RO2-N. + #1.047 R2O2. + #.001 HCHO + #.07 CCHO + #.124 RCHO + #.046 MEK + #.443 PROD2 + #6.579 XC
3,7-Diethyl Nonane	1.68e-11	1.68e-11	0.000	0.0	37-DE-C9 + HO. = #.5 RO2-R. + #.5 RO2-N. + #1.107 R2O2. + #.132 CCHO + #.293 RCHO + #.105 MEK + #.304 PROD2 + #6.607 XC
3-Methyl Tridecane	1.71e-11	1.71e-11	0.000	0.0	3-ME-C13 + HO. = #.507 RO2-R. + #.493 RO2-N. + #.871 R2O2. + #.021 CCHO + #.015 RCHO + #.009 MEK + #.493 PROD2 + #7.958 XC
6-Methyl Tridecane	1.71e-11	1.71e-11	0.000	0.0	6-ME-C13 + HO. = #.512 RO2-R. + #.488 RO2-N. + #.852 R2O2. + #.006 CCHO + #.041 RCHO + #.504 PROD2 + #7.909 XC
3,7-Dimethyl Dodecane	1.74e-11	1.74e-11	0.000	0.0	37DM-C12 + HO. = #.496 RO2-R. + #.504 RO2-N. + #.98 R2O2. + #.055 CCHO + #.11 RCHO + #.03 MEK + #.441 PROD2 + #7.772 XC
3,8-Diethyl Decane	1.82e-11	1.82e-11	0.000	0.0	38DE-C10 + HO. = #.471 RO2-R. + #.529 RO2-N. + #1.03 R2O2. + #.066 CCHO + #.057 RCHO + #.017 MEK + #.428 PROD2 + #7.885 XC
3-Methyl Tetradecane	1.85e-11	1.85e-11	0.000	0.0	3-ME-C14 + HO. = #.505 RO2-R. + #.495 RO2-N. + #.862 R2O2. + #.02 CCHO + #.013 RCHO + #.008 MEK + #.493 PROD2 + #8.961 XC
6-Methyl Tetradecane	1.85e-11	1.85e-11	0.000	0.0	6-ME-C14 + HO. = #.51 RO2-R. + #.49 RO2-N. + #.843 R2O2. + #.006 CCHO + #.037 RCHO + #.503 PROD2 + #8.918 XC
3,7-Dimethyl Tridecane	1.88e-11	1.88e-11	0.000	0.0	37DM-C13 + HO. = #.488 RO2-R. + #.512 RO2-N. + #.98 R2O2. + #.045 CCHO + #.087 RCHO + #.028 MEK + #.441 PROD2 + #8.82 XC
3,9-Diethyl Undecane	1.96e-11	1.96e-11	0.000	0.0	39DE-C11 + HO. = #.474 RO2-R. + #.526 RO2-N. + #.997 R2O2. + #.058 CCHO + #.051 RCHO + #.016 MEK + #.436 PROD2 + #8.899 XC
3-Methyl Pentadecane	2.00e-11	2.00e-11	0.000	0.0	3-ME-C15 + HO. = #.504 RO2-R. + #.496 RO2-N. + #.853 R2O2. + #.018 CCHO + #.012 RCHO + #.008 MEK + #.493 PROD2 + #9.964 XC

Table A-6 (continued)

Compound	Rate Parameters [a]				Reactions and Products [b]
	k(298)	A	Ea	B	
7-Methyl Pentadecane	2.00e-11	2.00e-11	0.000	0.0	7-ME-C15 + HO. = #.503 RO2-R. + #.497 RO2-N. + #.853 R2O2. + #.022 RCHO + #.5 PROD2 + #9.95 XC
4,8-Dimethyl Tetradecane	2.02e-11	2.02e-11	0.000	0.0	48DM-C14 + HO. = #.481 RO2-R. + #.519 RO2-N. + #.962 R2O2. + #.001 CCHO + #.071 RCHO + #.003 MEK + #.473 PROD2 + #9.82 XC
Cyclopropane	8.40e-14	8.40e-14	0.000	0.0	CYCC3 + HO. = #.95 RO2-R. + #.05 RO2-N. + #.95 R2O2. + #.95 RCHO + #-0.151 XC
Cyclobutane	1.50e-12	1.50e-12	0.000	0.0	CYCC4 + HO. = #.115 RO2-N. + #1.806 R2O2. + #.885 RCO-O2. + #.655 XC
Cyclopentane	5.02e-12	2.31e-12	-0.467	2.0	CYCC5 + HO. = #.779 RO2-R. + #.221 RO2-N. + #1.665 R2O2. + #.054 CO + #.759 RCHO + #.02 MEK + #1.263 XC
Isopropyl Cyclopropane	2.70e-12	2.70e-12	0.000	0.0	IPR-CC3 + HO. = #.836 RO2-R. + #.162 RO2-N. + #1.825 R2O2. + #.002 RCO-O2. + #.087 HCHO + #.087 CCHO + #.837 RCHO + #.771 ACET + #-0.066 XC
Methylcyclopentane	5.68e-12	5.68e-12	0.000	0.0	ME-CYCC5 + HO. = #.455 RO2-R. + #.302 RO2-N. + #1.852 R2O2. + #.24 CCO-O2. + #.003 RCO-O2. + #.023 CO + #.017 HCHO + #.692 RCHO + #.003 PROD2 + #1.564 XC
Cyclohexane	7.21e-12	2.59e-12	-0.614	2.0	CYCC6 + HO. = #.801 RO2-R. + #.199 RO2-N. + #.474 R2O2. + #.203 RCHO + #.598 PROD2 + #.61 XC
Cycloheptane	1.30e-11	1.30e-11	0.000	0.0	CYCC7 + HO. = #.511 RO2-R. + #.388 RO2-N. + #1.582 R2O2. + #.101 RCO-O2. + #.494 RCHO + #.017 PROD2 + #2.787 XC
1,3-Dimeth. Cyclopentane	6.82e-12	6.82e-12	0.000	0.0	13DMCYC5 + HO. = #.276 RO2-R. + #.378 RO2-N. + #1.878 R2O2. + #.345 CCO-O2. + #.001 RCO-O2. + #.038 CO + #.028 HCHO + #.002 CCHO + #.586 RCHO + #.035 PROD2 + #2.004 XC
Methylcyclohexane	1.00e-11	1.00e-11	0.000	0.0	ME-CYCC6 + HO. = #.662 RO2-R. + #.338 RO2-N. + #1.149 R2O2. + #.011 HCHO + #.002 CCHO + #.457 RCHO + #.209 PROD2 + #2.335 XC
Ethyl Cyclopentane	7.27e-12	7.27e-12	0.000	0.0	ET-CYCC5 + HO. = #.406 RO2-R. + #.386 RO2-N. + #1.865 R2O2. + #.209 RCO-O2. + #.019 CO + #.007 HCHO + #.132 CCHO + #.593 RCHO + #.003 MEK + #.004 PROD2 + #.01 MGLY + #1.927 XC
Cyclooctane	1.40e-11	1.40e-11	0.000	0.0	CYCC8 + HO. = #.527 RO2-R. + #.473 RO2-N. + #1.478 R2O2. + #.001 CO + #.527 RCHO + #3.581 XC
Propyl Cyclopentane	8.69e-12	8.69e-12	0.000	0.0	PR-CYCC5 + HO. = #.392 RO2-R. + #.455 RO2-N. + #1.743 R2O2. + #.153 RCO-O2. + #.013 CO + #.007 HCHO + #.001 CCHO + #.641 RCHO + #.003 MEK + #.027 PROD2 + #.005 MGLY + #2.682 XC
1,3-Dimethyl Cyclohexane	1.19e-11	1.19e-11	0.000	0.0	13DMCYC6 + HO. = #.556 RO2-R. + #.443 RO2-N. + #1.4 R2O2. + #.001 CCO-O2. + #.009 CO + #.02 HCHO + #.014 CCHO + #.511 RCHO + #.001 MEK + #.059 PROD2 + #3.395 XC
Ethylcyclohexane	1.20e-11	1.20e-11	0.000	0.0	ET-CYCC6 + HO. = #.626 RO2-R. + #.374 RO2-N. + #1.048 R2O2. + #.002 HCHO + #.152 CCHO + #.329 RCHO + #.299 PROD2 + #2.666 XC
1,1,3-Trimethyl Cyclohex.	8.70e-12	8.70e-12	0.000	0.0	113MCYC6 + HO. = #.486 RO2-R. + #.51 RO2-N. + #1.584 R2O2. + #.004 CCO-O2. + #.073 CO + #.133 HCHO + #.107 CCHO + #.474 RCHO + #.042 ACET + #.005 MEK + #.103 PROD2 + #3.32 XC
1-Eth.-4-Meth. Cyclohex.	1.37e-11	1.37e-11	0.000	0.0	1E4MCYC6 + HO. = #.52 RO2-R. + #.479 RO2-N. + #1.341 R2O2. + #.001 CCO-O2. + #.034 HCHO + #.142 CCHO + #.413 RCHO + #.143 PROD2 + #3.706 XC
Propyl Cyclohexane	1.35e-11	1.35e-11	0.000	0.0	C3-CYCC6 + HO. = #.611 RO2-R. + #.388 RO2-N. + #.865 R2O2. + #.001 RCO-O2. + #.001 HCHO + #.364 RCHO + #.389 PROD2 + #3.244 XC

Table A-6 (continued)

Compound	Rate Parameters [a]				Reactions and Products [b]
	k(298)	A	Ea	B	
Butyl Cyclohexane	1.49e-11	1.49e-11	0.000	0.0	C4-CYCC6 + HO. = #.577 RO2-R. + #.422 RO2-N. + #.827 R2O2. + #.025 CCHO + #.18 RCHO + #.468 PROD2 + #4.071 XC
1-Meth.-3-Isopr. Cyclohex.	1.51e-11	1.51e-11	0.000	0.0	1M3IPCY6 + HO. = #.536 RO2-R. + #.459 RO2-N. + #1.205 R2O2. + #.004 RCO-O2. + #.006 CO + #.008 HCHO + #.005 CCHO + #.264 RCHO + #.339 ACET + #.294 PROD2 + #3.635 XC
1,4-Diethyl-Cyclohexane	1.55e-11	1.55e-11	0.000	0.0	14DECYC6 + HO. = #.509 RO2-R. + #.489 RO2-N. + #1.23 R2O2. + #.002 RCO-O2. + #.021 HCHO + #.226 CCHO + #.334 RCHO + #.209 PROD2 + #4.33 XC
1,3-Diethyl-Cyclohexane	1.55e-11	1.55e-11	0.000	0.0	13DECYC6 + HO. = #.491 RO2-R. + #.509 RO2-N. + #1.25 R2O2. + #.004 CO + #.002 HCHO + #.177 CCHO + #.335 RCHO + #.001 MEK + #.166 PROD2 + #4.584 XC
Pentyl Cyclohexane	1.63e-11	1.63e-11	0.000	0.0	C5-CYCC6 + HO. = #.557 RO2-R. + #.442 RO2-N. + #.808 R2O2. + #.016 CCHO + #.147 RCHO + #.456 PROD2 + #5.136 XC
1-Ethyl-2-Propyl Cyclohex.	1.70e-11	1.70e-11	0.000	0.0	1E2PCYC6 + HO. = #.461 RO2-R. + #.538 RO2-N. + #1.2 R2O2. + #.001 RCO-O2. + #.007 HCHO + #.031 CCHO + #.187 RCHO + #.349 PROD2 + #5.045 XC
13-Dieth-5-Me. Cyclohex.	1.72e-11	1.72e-11	0.000	0.0	13E5MCC6 + HO. = #.43 RO2-R. + #.565 RO2-N. + #1.372 R2O2. + #.003 CCO-O2. + #.002 RCO-O2. + #.006 CO + #.02 HCHO + #.168 CCHO + #.355 RCHO + #.009 MEK + #.091 PROD2 + #5.589 XC
1-Meth.-4-Pentyl Cyclohex.	1.80e-11	1.80e-11	0.000	0.0	1M4C5CY6 + HO. = #.482 RO2-R. + #.517 RO2-N. + #1.049 R2O2. + #.001 CCO-O2. + #.001 HCHO + #.015 CCHO + #.21 RCHO + #.327 PROD2 + #6.274 XC
1,3,5-Triethyl Cyclohex.	1.90e-11	1.90e-11	0.000	0.0	135ECYC6 + HO. = #.417 RO2-R. + #.58 RO2-N. + #1.354 R2O2. + #.003 RCO-O2. + #.005 CO + #.014 HCHO + #.222 CCHO + #.315 RCHO + #.008 MEK + #.116 PROD2 + #6.373 XC
Hexyl Cyclohexane	1.78e-11	1.78e-11	0.000	0.0	C6-CYCC6 + HO. = #.527 RO2-R. + #.472 RO2-N. + #.849 R2O2. + #.093 RCHO + #.462 PROD2 + #6.118 XC
1-Meth.-2-Hexyl-Cyclohex.	1.94e-11	1.94e-11	0.000	0.0	1M2C6CC6 + HO. = #.463 RO2-R. + #.537 RO2-N. + #1.081 R2O2. + #.001 RCO-O2. + #.004 HCHO + #.009 CCHO + #.128 RCHO + #.38 PROD2 + #7.093 XC
13-Dieth-5-Pent Cyclohx.	2.05e-11	2.05e-11	0.000	0.0	13E5PCC6 + HO. = #.433 RO2-R. + #.564 RO2-N. + #1.238 R2O2. + #.003 RCO-O2. + #.002 CO + #.01 HCHO + #.132 CCHO + #.342 RCHO + #.002 MEK + #.189 PROD2 + #7.163 XC
Heptyl Cyclohexane	1.91e-11	1.91e-11	0.000	0.0	C7-CYCC6 + HO. = #.515 RO2-R. + #.485 RO2-N. + #.855 R2O2. + #.069 RCHO + #.462 PROD2 + #7.108 XC
1-Meth.-4-Heptyl Cyclohex.	2.08e-11	2.08e-11	0.000	0.0	1M4C7CC6 + HO. = #.456 RO2-R. + #.544 RO2-N. + #1.059 R2O2. + #.001 HCHO + #.131 RCHO + #.35 PROD2 + #8.242 XC
13-Diprop-5-Eth Cyclohx.	2.19e-11	2.19e-11	0.000	0.0	13P5ECC6 + HO. = #.445 RO2-R. + #.553 RO2-N. + #1.158 R2O2. + #.002 RCO-O2. + #.001 CO + #.007 HCHO + #.06 CCHO + #.376 RCHO + #.234 PROD2 + #8.017 XC
Octyl Cyclohexane	2.06e-11	2.06e-11	0.000	0.0	C8-CYCC6 + HO. = #.511 RO2-R. + #.488 RO2-N. + #.847 R2O2. + #.063 RCHO + #.463 PROD2 + #8.099 XC
1-Methyl-2-Octyl Cyclohex.	2.22e-11	2.22e-11	0.000	0.0	1M2C8CC6 + HO. = #.462 RO2-R. + #.537 RO2-N. + #1.035 R2O2. + #.003 HCHO + #.008 CCHO + #.105 RCHO + #.394 PROD2 + #9.08 XC
135-Tripropyl Cyclohex.	2.33e-11	2.33e-11	0.000	0.0	135PCYC6 + HO. = #.453 RO2-R. + #.545 RO2-N. + #1.106 R2O2. + #.002 RCO-O2. + #.001 CO + #.005 HCHO + #.415 RCHO + #.258 PROD2 + #8.923 XC
Nonyl Cyclohexane	2.20e-11	2.20e-11	0.000	0.0	C9-CYCC6 + HO. = #.51 RO2-R. + #.49 RO2-N. + #.839 R2O2. + #.058 RCHO + #.465 PROD2 + #9.091 XC

Table A-6 (continued)

Compound	Rate Parameters [a]				Reactions and Products [b]
	k(298)	A	Ea	B	
1,3-Prop.-5-Butyl Cyclohex.	2.47e-11	2.47e-11	0.000	0.0	13P5BCC6 + HO. = #.461 RO2-R. + #.538 RO2-N. + #1.046 R2O2. + #.001 RCO-O2. + #.001 CO + #.003 HCHO + #.013 CCHO + #.322 RCHO + #.318 PROD2 + #9.863 XC
Decyl Cyclohexane	2.34e-11	2.34e-11	0.000	0.0	C10CYCC6 + HO. = #.508 RO2-R. + #.492 RO2-N. + #.834 R2O2. + #.055 RCHO + #.467 PROD2 + #10.085 XC
1-Methyl-4-Nonyl Cyclohex.	2.37e-11	2.37e-11	0.000	0.0	1M4C9CY6 + HO. = #.458 RO2-R. + #.541 RO2-N. + #1.018 R2O2. + #.001 HCHO + #.113 RCHO + #.367 PROD2 + #10.209 XC
Propene	2.63e-11	4.85e-12	-1.002	0.0	PROPENE + HO. = #.984 RO2-R. + #.016 RO2-N. + #.984 HCHO + #.984 CCHO + #-0.048 XC
	1.01e-17	5.51e-15	3.732	0.0	PROPENE + O3 = #.32 HO. + #.06 HO2. + #.26 C-O2. + #.51 CO + #.135 CO2 + #.5 HCHO + #.5 CCHO + #.185 HCOOH + #.17 CCO-OH + #.07 INERT + #.07 XC
	9.49e-15	4.59e-13	2.297	0.0	PROPENE + NO3 = #.95 RO2-R. + #.05 RO2-N. + #2.699 XC + XN
	3.98e-12	1.18e-11	0.644	0.0	PROPENE + O3P = #.45 RCHO + #.55 MEK + #-0.55 XC
1-Butene	3.14e-11	6.55e-12	-0.928	0.0	1-BUTENE + HO. = #.975 RO2-R. + #.025 RO2-N. + #.006 R2O2. + #.969 HCHO + #.975 RCHO + #-0.045 XC
	9.65e-18	3.36e-15	3.466	0.0	1-BUTENE + O3 = #.116 HO. + #.06 HO2. + #.057 RO2-R. + #.306 CO + #.065 CO2 + #.5 HCHO + #.057 CCHO + #.5 RCHO + #.185 HCOOH + #.444 RCO-OH
	1.35e-14	3.14e-13	1.864	0.0	1-BUTENE + NO3 = #.921 RO2-R. + #.079 RO2-N. + #.075 R2O2. + #.075 CCHO + #.075 RCHO + #.845 RNO3 + #-1.925 XC + #.155 XN
	4.18e-12	1.25e-11	0.648	0.0	1-BUTENE + O3P = #.45 RCHO + #.55 MEK + #.45 XC
3-Methyl-1-Butene	3.18e-11	5.32e-12	-1.059	0.0	3M-1-BUT + HO. = #.929 RO2-R. + #.071 RO2-N. + #.174 R2O2. + #.75 HCHO + #.174 CCHO + #.75 RCHO + #.167 ACET + #.012 PROD2 + #.653 XC
	1.10e-17	3.36e-15	3.388	0.0	3M-1-BUT + O3 = #.101 HO. + #.06 HO2. + #.039 RO2-R. + #.002 RO2-N. + #.291 CO + #.065 CO2 + #.5 HCHO + #.5 RCHO + #.039 ACET + #.185 HCOOH + #.46 RCO-OH + #.953 XC
	1.38e-14	1.38e-14	0.000	0.0	3M-1-BUT + NO3 = #.852 RO2-R. + #.148 RO2-N. + #.828 R2O2. + #.828 RCHO + #.795 ACET + #.057 RNO3 + #-1.099 XC + #.943 XN
	4.14e-12	1.32e-11	0.686	0.0	3M-1-BUT + O3P = #.45 RCHO + #.55 MEK + #1.45 XC
1-Pentene	3.14e-11	5.86e-12	-0.994	0.0	1-PENTEN + HO. = #.928 RO2-R. + #.072 RO2-N. + #.121 R2O2. + #.815 HCHO + #.908 RCHO + #.021 PROD2 + #.908 XC
	1.00e-17	3.36e-15	3.445	0.0	1-PENTEN + O3 = #.101 HO. + #.06 HO2. + #.04 RO2-R. + #.001 RO2-N. + #.291 CO + #.065 CO2 + #.5 HCHO + #.54 RCHO + #.185 HCOOH + #.46 RCO-OH + #.955 XC
	1.38e-14	1.38e-14	0.000	0.0	1-PENTEN + NO3 = #.836 RO2-R. + #.164 RO2-N. + #.783 R2O2. + #.033 RCHO + #.82 RNO3 + #-1.001 XC + #.18 XN
	4.65e-12	1.48e-11	0.686	0.0	1-PENTEN + O3P = #.45 RCHO + #.55 MEK + #1.45 XC
1-Hexene	3.70e-11	6.91e-12	-0.994	0.0	1-HEXENE + HO. = #.905 RO2-R. + #.095 RO2-N. + #.419 R2O2. + #.526 HCHO + #.636 RCHO + #.269 PROD2 + #1.38 XC
	1.10e-17	3.36e-15	3.388	0.0	1-HEXENE + O3 = #.085 HO. + #.041 HO2. + #.042 RO2-R. + #.002 RO2-N. + #.275 CO + #.065 CO2 + #.5 HCHO + #.523 RCHO + #.185 HCOOH + #.475 RCO-OH + #1.97 XC
	1.38e-14	1.38e-14	0.000	0.0	1-HEXENE + NO3 = #.765 RO2-R. + #.235 RO2-N. + #.847 R2O2. + #.765 RNO3 + #.235 XN
	4.65e-12	1.48e-11	0.686	0.0	1-HEXENE + O3P = #.45 RCHO + #.55 MEK + #2.45 XC

Table A-6 (continued)

Compound	Rate Parameters [a]				Reactions and Products [b]
	k(298)	A	Ea	B	
3-Methyl-1-Pentene	3.16e-11	3.16e-11	0.000	0.0	3M1-C5E + HO. = #.891 RO2-R. + #.109 RO2-N. + #.179 R2O2. + #.762 HCHO + #.162 CCHO + #.786 RCHO + #.045 MEK + #.023 PROD2 + #1.583 XC
	4.90e-18	3.36e-15	3.867	0.0	3M1-C5E + O3 = #.085 HO. + #.051 HO2. + #.032 RO2-R. + #.002 RO2-N. + #.275 CO + #.065 CO2 + #.5 HCHO + #.018 CCHO + #.5 RCHO + #.014 MEK + #.185 HCOOH + #.475 RCO-OH + #1.946 XC
	1.38e-14	1.38e-14	0.000	0.0	3M1-C5E + NO3 = #.778 RO2-R. + #.222 RO2-N. + #1.052 R2O2. + #.455 CCHO + #.627 RCHO + #.349 MEK + #.201 RNO3 + #-0.726 XC + #.799 XN
	5.60e-12	5.60e-12	0.000	0.0	3M1-C5E + O3P = #.45 RCHO + #.55 PROD2 + #1.35 XC
3,3-Dimethyl-1-Butene	2.80e-11	5.23e-12	-0.994	0.0	33M1-BUT + HO. = #.373 RO2-R. + #.117 RO2-N. + #1.046 R2O2. + #.51 TBU-O. + #.369 HCHO + #.531 CCHO + #.372 RCHO + #.001 ACET + #1.216 XC
	5.20e-18	3.36e-15	3.832	0.0	33M1-BUT + O3 = #.085 HO. + #.036 HO2. + #.024 RO2-R. + #.001 RO2-N. + #.024 TBU-O. + #.275 CO + #.065 CO2 + #.5 HCHO + #.5 RCHO + #.185 HCOOH + #.475 RCO-OH + #1.972 XC
	1.38e-14	1.38e-14	0.000	0.0	33M1-BUT + NO3 = #.186 RO2-N. + #1.661 R2O2. + #.814 TBU-O. + #.847 RCHO + #-0.098 XC + XN
	4.39e-12	4.39e-12	0.000	0.0	33M1-BUT + O3P = #.45 RCHO + #.55 MEK + #2.45 XC
4-Methyl-1-Pentene	3.16e-11	3.16e-11	0.000	0.0	4M1-C5E + HO. = #.886 RO2-R. + #.114 RO2-N. + #.189 R2O2. + #.718 HCHO + #.001 CCHO + #.847 RCHO + #.001 ACET + #.037 PROD2 + #1.825 XC
	9.20e-18	3.36e-15	3.494	0.0	4M1-C5E + O3 = #.085 HO. + #.051 HO2. + #.032 RO2-R. + #.001 RO2-N. + #.275 CO + #.065 CO2 + #.509 HCHO + #.515 RCHO + #.008 ACET + #.185 HCOOH + #.475 RCO-OH + #1.962 XC
	1.38e-14	1.38e-14	0.000	0.0	4M1-C5E + NO3 = #.771 RO2-R. + #.229 RO2-N. + #.801 R2O2. + #.006 HCHO + #.029 RCHO + #.006 ACET + #.754 RNO3 + #-0.009 XC + #.246 XN
	5.60e-12	5.60e-12	0.000	0.0	4M1-C5E + O3P = #.45 RCHO + #.55 MEK + #2.45 XC
1-Heptene	4.00e-11	7.47e-12	-0.994	0.0	1-HEPTEN + HO. = #.809 RO2-R. + #.191 RO2-N. + #.426 R2O2. + #.44 HCHO + #.537 RCHO + #.272 PROD2 + #2.172 XC
	1.20e-17	3.36e-15	3.337	0.0	1-HEPTEN + O3 = #.06 HO. + #.06 HO2. + #.25 CO + #.065 CO2 + #.5 HCHO + #.5 RCHO + #.185 HCOOH + #.5 RCO-OH + #3 XC
	1.38e-14	1.38e-14	0.000	0.0	1-HEPTEN + NO3 = #.702 RO2-R. + #.298 RO2-N. + #.81 R2O2. + #.702 RNO3 + XC + #.298 XN
	8.53e-12	8.53e-12	0.000	0.0	1-HEPTEN + O3P = #.45 RCHO + #.55 PROD2 + #2.35 XC
1-Octene	3.16e-11	3.16e-11	0.000	0.0	1-OCTENE + HO. = #.756 RO2-R. + #.244 RO2-N. + #.419 R2O2. + #.421 HCHO + #.497 RCHO + #.258 PROD2 + #3.072 XC
	1.40e-17	3.36e-15	3.246	0.0	1-OCTENE + O3 = #.06 HO. + #.06 HO2. + #.25 CO + #.065 CO2 + #.5 HCHO + #.5 RCHO + #.185 HCOOH + #.5 RCO-OH + #4 XC
	1.38e-14	1.38e-14	0.000	0.0	1-OCTENE + NO3 = #.647 RO2-R. + #.353 RO2-N. + #.781 R2O2. + #.647 RNO3 + #2 XC + #.353 XN
	5.60e-12	5.60e-12	0.000	0.0	1-OCTENE + O3P = #.45 RCHO + #.55 PROD2 + #3.35 XC
1-Nonene	3.16e-11	3.16e-11	0.000	0.0	1-C9E + HO. = #.709 RO2-R. + #.291 RO2-N. + #.418 R2O2. + #.404 HCHO + #.471 RCHO + #.238 PROD2 + #4.01 XC
	1.01e-17	1.01e-17	0.000	0.0	1-C9E + O3 = #.06 HO. + #.06 HO2. + #.25 CO + #.065 CO2 + #.5 HCHO + #.5 RCHO + #.185 HCOOH + #.5 RCO-OH + #5 XC
	1.38e-14	1.38e-14	0.000	0.0	1-C9E + NO3 = #.599 RO2-R. + #.401 RO2-N. + #.795 R2O2. + #.599 RNO3 + #3 XC + #.401 XN
	5.60e-12	5.60e-12	0.000	0.0	1-C9E + O3P = #.45 RCHO + #.55 PROD2 + #4.35 XC

Table A-6 (continued)

Compound	Rate Parameters [a]				Reactions and Products [b]
	k(298)	A	Ea	B	
1-Decene	3.16e-11	3.16e-11	0.000	0.0	1-C10E + HO. = #.677 RO2-R. + #.323 RO2-N. + #.408 R2O2. + #.392 HCHO + #.455 RCHO + #.222 PROD2 + #4.974 XC
	9.30e-18	3.36e-15	3.488	0.0	1-C10E + O3 = #.06 HO. + #.06 HO2. + #.25 CO + #.065 CO2 + #.5 HCHO + #.5 RCHO + #.185 HCOOH + #.5 RCO-OH + #6 XC
	1.38e-14	1.38e-14	0.000	0.0	1-C10E + NO3 = #.568 RO2-R. + #.432 RO2-N. + #.791 R2O2. + #.568 RNO3 + #4 XC + #.432 XN
	5.60e-12	5.60e-12	0.000	0.0	1-C10E + O3P = #.45 RCHO + #.55 PROD2 + #5.35 XC
1-Undecene	3.16e-11	3.16e-11	0.000	0.0	1-C11E + HO. = #.657 RO2-R. + #.343 RO2-N. + #.4 R2O2. + #.384 HCHO + #.445 RCHO + #.213 PROD2 + #5.95 XC
	1.01e-17	1.01e-17	0.000	0.0	1-C11E + O3 = #.06 HO. + #.06 HO2. + #.25 CO + #.065 CO2 + #.5 HCHO + #.5 RCHO + #.185 HCOOH + #.5 RCO-OH + #7 XC
	1.38e-14	1.38e-14	0.000	0.0	1-C11E + NO3 = #.55 RO2-R. + #.45 RO2-N. + #.782 R2O2. + #.55 RNO3 + #5 XC + #.45 XN
	5.60e-12	5.60e-12	0.000	0.0	1-C11E + O3P = #.45 RCHO + #.55 PROD2 + #6.35 XC
1-Dodecene	3.16e-11	3.16e-11	0.000	0.0	1-C12E + HO. = #.645 RO2-R. + #.355 RO2-N. + #.395 R2O2. + #.379 HCHO + #.438 RCHO + #.207 PROD2 + #6.936 XC
	1.01e-17	1.01e-17	0.000	0.0	1-C12E + O3 = #.06 HO. + #.06 HO2. + #.25 CO + #.065 CO2 + #.5 HCHO + #.5 RCHO + #.185 HCOOH + #.5 RCO-OH + #8 XC
	1.38e-14	1.38e-14	0.000	0.0	1-C12E + NO3 = #.539 RO2-R. + #.461 RO2-N. + #.779 R2O2. + #.539 RNO3 + #6 XC + #.461 XN
	5.60e-12	5.60e-12	0.000	0.0	1-C12E + O3P = #.45 RCHO + #.55 PROD2 + #7.35 XC
1-Tridecene	3.16e-11	3.16e-11	0.000	0.0	1-C13E + HO. = #.637 RO2-R. + #.363 RO2-N. + #.392 R2O2. + #.376 HCHO + #.434 RCHO + #.203 PROD2 + #7.927 XC
	1.01e-17	1.01e-17	0.000	0.0	1-C13E + O3 = #.06 HO. + #.06 HO2. + #.25 CO + #.065 CO2 + #.5 HCHO + #.5 RCHO + #.185 HCOOH + #.5 RCO-OH + #9 XC
	1.38e-14	1.38e-14	0.000	0.0	1-C13E + NO3 = #.532 RO2-R. + #.468 RO2-N. + #.776 R2O2. + #.532 RNO3 + #7 XC + #.468 XN
	5.60e-12	5.60e-12	0.000	0.0	1-C13E + O3P = #.45 RCHO + #.55 PROD2 + #8.35 XC
1-Tetradecene	3.16e-11	3.16e-11	0.000	0.0	1-C14E + HO. = #.633 RO2-R. + #.367 RO2-N. + #.39 R2O2. + #.374 HCHO + #.432 RCHO + #.201 PROD2 + #8.921 XC
	1.01e-17	1.01e-17	0.000	0.0	1-C14E + O3 = #.06 HO. + #.06 HO2. + #.25 CO + #.065 CO2 + #.5 HCHO + #.5 RCHO + #.185 HCOOH + #.5 RCO-OH + #10 XC
	1.38e-14	1.38e-14	0.000	0.0	1-C14E + NO3 = #.528 RO2-R. + #.472 RO2-N. + #.773 R2O2. + #.528 RNO3 + #8 XC + #.472 XN
	5.60e-12	5.60e-12	0.000	0.0	1-C14E + O3P = #.45 RCHO + #.55 PROD2 + #9.35 XC
1-Pentadecene	3.16e-11	3.16e-11	0.000	0.0	1-C15E + HO. = #.629 RO2-R. + #.371 RO2-N. + #.388 R2O2. + #.372 HCHO + #.43 RCHO + #.2 PROD2 + #9.917 XC
	1.01e-17	1.01e-17	0.000	0.0	1-C15E + O3 = #.06 HO. + #.06 HO2. + #.25 CO + #.065 CO2 + #.5 HCHO + #.5 RCHO + #.185 HCOOH + #.5 RCO-OH + #11 XC
	1.38e-14	1.38e-14	0.000	0.0	1-C15E + NO3 = #.525 RO2-R. + #.475 RO2-N. + #.772 R2O2. + #.525 RNO3 + #9 XC + #.475 XN
	5.60e-12	5.60e-12	0.000	0.0	1-C15E + O3P = #.45 RCHO + #.55 PROD2 + #10.35 XC
Isobutene	5.14e-11	9.47e-12	-1.002	0.0	ISOBUTEN + HO. = #.9 RO2-R. + #.1 RO2-N. + #.9 HCHO + #.9 ACET + #-0.2 XC
	1.13e-17	2.70e-15	3.243	0.0	ISOBUTEN + O3 = #.707 HO. + #.04 RO2-R. + #.627 R2O2. + #.667 CCO-O2. + #.167 CO + #.043 CO2 + #1.333 HCHO + #.333 ACET + #.123 HCOOH
	3.32e-13	3.32e-13	0.000	0.0	ISOBUTEN + NO3 = #.645 NO2 + #.039 RO2-N. + #.961 R2O2. + #.316 C-O2. + #.645 HCHO + #.645 ACET + #.872 XC + #.355 XN
	1.69e-11	1.69e-11	0.000	0.0	ISOBUTEN + O3P = #.4 RCHO + #.6 MEK + #.4 XC

Table A-6 (continued)

Compound	Rate Parameters [a]				Reactions and Products [b]
	k(298)	A	Ea	B	
2-Methyl-1-Butene	6.11e-11	1.14e-11	-0.994	0.0	2M-1-BUT + HO. = #.936 RO2-R. + #.064 RO2-N. + #.936 HCHO + #.936 MEK + #-0.064 XC
	1.60e-17	2.70e-15	3.037	0.0	2M-1-BUT + O3 = #.707 HO. + #.04 RO2-R. + #.026 RO2-N. + #.601 R2O2. + #.558 CCO-O2. + #.083 RCO-O2. + #.167 CO + #.043 CO2 + #.749 HCHO + #.558 CCHO + #.333 MEK + #.123 HCOOH + #-0.052 XC
	3.32e-13	3.32e-13	0.000	0.0	2M-1-BUT + NO3 = #.019 NO2 + #.917 RO2-R. + #.064 RO2-N. + #.936 R2O2. + #.019 HCHO + #.917 CCHO + #.019 MEK + #2.686 XC + #.981 XN
	1.88e-11	1.88e-11	0.000	0.0	2M-1-BUT + O3P = #.4 RCHO + #.6 MEK + #1.4 XC
23-Dimethyl-1-Butene	5.79e-11	5.79e-11	0.000	0.0	23M1-BUT + HO. = #.901 RO2-R. + #.099 RO2-N. + #.074 R2O2. + #.83 HCHO + #.071 ACET + #.904 MEK + #.747 XC
	1.30e-17	2.70e-15	3.160	0.0	23M1-BUT + O3 = #.707 HO. + #.04 RO2-R. + #.043 RO2-N. + #.584 R2O2. + #.582 CCO-O2. + #.042 RCO-O2. + #.167 CO + #.043 CO2 + #.708 HCHO + #.582 ACET + #.333 MEK + #.123 HCOOH + #.333 XC
	3.32e-13	3.32e-13	0.000	0.0	23M1-BUT + NO3 = #.868 RO2-R. + #.132 RO2-N. + #.904 R2O2. + #.868 ACET + #2.603 XC + XN
	1.73e-11	1.73e-11	0.000	0.0	23M1-BUT + O3P = #.4 RCHO + #.6 MEK + #2.4 XC
2-Ethyl-1-Butene	5.79e-11	5.79e-11	0.000	0.0	2E1-BUT + HO. = #.904 RO2-R. + #.096 RO2-N. + #.904 HCHO + #.904 MEK + #.904 XC
	1.30e-17	2.70e-15	3.160	0.0	2E1-BUT + O3 = #.707 HO. + #.04 RO2-R. + #.043 RO2-N. + #.584 R2O2. + #.624 RCO-O2. + #.167 CO + #.043 CO2 + #.667 HCHO + #.624 CCHO + #.333 MEK + #.123 HCOOH + #.291 XC
	3.32e-13	3.32e-13	0.000	0.0	2E1-BUT + NO3 = #.009 NO2 + #.894 RO2-R. + #.096 RO2-N. + #.904 R2O2. + #.009 HCHO + #.894 CCHO + #.009 MEK + #.894 RNO3 + #-1.779 XC + #.096 XN
	1.73e-11	1.73e-11	0.000	0.0	2E1-BUT + O3P = #.4 RCHO + #.6 MEK + #2.4 XC
2-Methyl-1-Pentene	6.32e-11	1.18e-11	-0.994	0.0	2M1-C5E + HO. = #.904 RO2-R. + #.096 RO2-N. + #.904 HCHO + #.904 MEK + #.904 XC
	1.50e-17	2.70e-15	3.075	0.0	2M1-C5E + O3 = #.707 HO. + #.04 RO2-R. + #.043 RO2-N. + #.584 R2O2. + #.557 CCO-O2. + #.067 RCO-O2. + #.167 CO + #.043 CO2 + #.734 HCHO + #.557 RCHO + #.333 MEK + #.123 HCOOH + #.358 XC
	3.32e-13	3.32e-13	0.000	0.0	2M1-C5E + NO3 = #.829 RO2-R. + #.171 RO2-N. + #.904 R2O2. + #.829 RCHO + #2.487 XC + XN
	2.00e-11	2.00e-11	0.000	0.0	2M1-C5E + O3P = #.4 RCHO + #.6 MEK + #2.4 XC
2,3,3-trimethyl-1-Butene	5.79e-11	5.79e-11	0.000	0.0	233M1BUT + HO. = #.083 RO2-R. + #.164 RO2-N. + #1.537 R2O2. + #.753 TBU-O. + #.083 HCHO + #.866 MEK + #.208 XC
	8.30e-18	2.70e-15	3.426	0.0	233M1BUT + O3 = #.707 HO. + #.04 RO2-R. + #.064 RO2-N. + #.562 R2O2. + #.602 RCO-O2. + #.167 CO + #.043 CO2 + #1.269 HCHO + #.333 MEK + #.123 HCOOH + #1.872 XC
	3.32e-13	3.32e-13	0.000	0.0	233M1BUT + NO3 = #.167 RO2-N. + #1.699 R2O2. + #.833 TBU-O. + #3.499 XC + XN
	1.73e-11	1.73e-11	0.000	0.0	233M1BUT + O3P = #.4 RCHO + #.6 MEK + #3.4 XC

Table A-6 (continued)

Compound	Rate Parameters [a]				Reactions and Products [b]
	k(298)	A	Ea	B	
3-Methyl-2-Isopropyl-1-Butene	5.79e-11	5.79e-11	0.000	0.0	3M2I1C4E + HO. = #.823 RO2-R. + #.177 RO2-N. + #.125 R2O2. + #.703 HCHO + #.12 ACET + #.828 PROD2 + #.906 XC
	3.30e-18	2.70e-15	3.972	0.0	3M2I1C4E + O3 = #.707 HO. + #.04 RO2-R. + #.089 RO2-N. + #.538 R2O2. + #.578 RCO-O2. + #.167 CO + #.043 CO2 + #.667 HCHO + #.578 ACET + #.333 PROD2 + #.123 HCOOH + XC
	3.32e-13	3.32e-13	0.000	0.0	3M2I1C4E + NO3 = #.795 RO2-R. + #.205 RO2-N. + #.828 R2O2. + #.795 ACET + #.828 RNO3 + #-0.583 XC + #.172 XN
	1.73e-11	1.73e-11	0.000	0.0	3M2I1C4E + O3P = #.4 RCHO + #.6 PROD2 + #3.2 XC
trans-2-Butene	6.40e-11	1.01e-11	-1.093	0.0	T-2-BUTE + HO. = #.965 RO2-R. + #.035 RO2-N. + #1.93 CCHO + #-0.07 XC
	1.90e-16	6.64e-15	2.104	0.0	T-2-BUTE + O3 = #.52 HO. + #.52 C-O2. + #.52 CO + #.14 CO2 + CCHO + #.34 CCO-OH + #.14 INERT + #.14 XC
	3.91e-13	1.10e-13	-0.759	2.0	T-2-BUTE + NO3 = #.706 NO2 + #.215 RO2-R. + #.079 RO2-N. + #.706 R2O2. + #1.412 CCHO + #.215 RNO3 + #-0.588 XC + #.079 XN
	2.18e-11	2.18e-11	0.000	0.0	T-2-BUTE + O3P = MEK
cis-2-Butene	5.64e-11	1.10e-11	-0.968	0.0	C-2-BUTE + HO. = #.965 RO2-R. + #.035 RO2-N. + #1.93 CCHO + #-0.07 XC
	1.25e-16	3.22e-15	1.924	0.0	C-2-BUTE + O3 = #.52 HO. + #.52 C-O2. + #.52 CO + #.14 CO2 + CCHO + #.34 CCO-OH + #.14 INERT + #.14 XC
	3.51e-13	1.10e-13	-0.687	0.0	C-2-BUTE + NO3 = #.706 NO2 + #.215 RO2-R. + #.079 RO2-N. + #.706 R2O2. + #1.412 CCHO + #.215 RNO3 + #-0.588 XC + #.079 XN
	1.76e-11	1.76e-11	0.000	0.0	C-2-BUTE + O3P = MEK
2-Methyl-2-Butene	8.69e-11	1.92e-11	-0.894	0.0	2M-2-BUT + HO. = #.936 RO2-R. + #.064 RO2-N. + #.936 CCHO + #.936 ACET + #-0.064 XC
	4.03e-16	2.87e-15	1.162	0.0	2M-2-BUT + O3 = #.856 HO. + #.7 R2O2. + #.156 C-O2. + #.7 CCO-O2. + #.156 CO + #.042 CO2 + #.7 HCHO + #.7 CCHO + #.3 ACET + #.102 CCO-OH + #.042 INERT + #.042 XC
	9.37e-12	9.37e-12	0.000	0.0	2M-2-BUT + NO3 = #.936 NO2 + #.064 RO2-N. + #.936 R2O2. + #.936 CCHO + #.936 ACET + #-0.064 XC + #.064 XN
	5.10e-11	5.10e-11	0.000	0.0	2M-2-BUT + O3P = MEK + XC
trans-2-Pentene	6.70e-11	1.25e-11	-0.994	0.0	T-2-PENT + HO. = #.936 RO2-R. + #.064 RO2-N. + #.936 CCHO + #.936 RCHO + #-0.064 XC
	1.15e-16	1.15e-16	0.000	0.0	T-2-PENT + O3 = #.317 HO. + #.057 RO2-R. + #.26 C-O2. + #.317 CO + #.07 CO2 + #.556 CCHO + #.5 RCHO + #.17 CCO-OH + #.444 RCO-OH + #.07 INERT + #.07 XC
	3.70e-13	3.70e-13	0.000	0.0	T-2-PENT + NO3 = #.472 NO2 + #.396 RO2-R. + #.132 RO2-N. + #.754 R2O2. + #.481 CCHO + #.481 RCHO + #.387 RNO3 + #-0.519 XC + #.141 XN
	2.23e-11	2.23e-11	0.000	0.0	T-2-PENT + O3P = MEK + XC
cis-2-Pentene	6.48e-11	1.21e-11	-0.994	0.0	C-2-PENT + HO. = #.936 RO2-R. + #.064 RO2-N. + #.936 CCHO + #.936 RCHO + #-0.064 XC
	1.15e-16	1.15e-16	0.000	0.0	C-2-PENT + O3 = #.317 HO. + #.057 RO2-R. + #.26 C-O2. + #.317 CO + #.07 CO2 + #.556 CCHO + #.5 RCHO + #.17 CCO-OH + #.444 RCO-OH + #.07 INERT + #.07 XC
	3.70e-13	3.70e-13	0.000	0.0	C-2-PENT + NO3 = #.472 NO2 + #.396 RO2-R. + #.132 RO2-N. + #.754 R2O2. + #.481 CCHO + #.481 RCHO + #.387 RNO3 + #-0.519 XC + #.141 XN
	1.70e-11	1.70e-11	0.000	0.0	C-2-PENT + O3P = MEK + XC

Table A-6 (continued)

Compound	Rate Parameters [a]				Reactions and Products [b]
	k(298)	A	Ea	B	
2,3-Dimethyl-2-Butene	1.10e-10	2.05e-11	-0.994	0.0	23M2-BUT + HO. = #.904 RO2-R. + #.096 RO2-N. + #1.807 ACET
	1.13e-15	3.03e-15	0.584	0.0	23M2-BUT + O3 = HO. + R2O2. + CCO-O2. + HCHO + ACET
	5.72e-11	5.72e-11	0.000	0.0	23M2-BUT + NO3 = #.904 NO2 + #.096 RO2-N. + #.904 R2O2. + #1.807 ACET + #.096 XN
	7.64e-11	7.64e-11	0.000	0.0	23M2-BUT + O3P = MEK + #2 XC
Cis-3-Methyl-2-Hexene	8.71e-11	8.71e-11	0.000	0.0	C3M2-C5E + HO. = #.904 RO2-R. + #.096 RO2-N. + #.904 CCHO + #.904 MEK
	4.51e-16	2.87e-15	1.096	0.0	C3M2-C5E + O3 = #.856 HO. + #.027 RO2-N. + #.673 R2O2. + #.156 C-O2. + #.586 CCO-O2. + #.087 RCO-O2. + #.156 CO + #.042 CO2 + #.087 HCHO + #1.286 CCHO + #.3 MEK + #.102 CCO-OH + #.042 INERT + #-0.012 XC
	9.37e-12	9.37e-12	0.000	0.0	C3M2-C5E + NO3 = #.874 NO2 + #.03 RO2-R. + #.096 RO2-N. + #.904 R2O2. + #.904 CCHO + #.874 MEK + #.03 RNO3 + #-0.06 XC + #.096 XN
	3.71e-11	3.71e-11	0.000	0.0	C3M2-C5E + O3P = #.6 MEK + #.4 PROD2 + #1.2 XC
Trans 3-Methyl-2-Hexene	8.71e-11	8.71e-11	0.000	0.0	T3M2-C5E + HO. = #.904 RO2-R. + #.096 RO2-N. + #.904 CCHO + #.904 MEK
	5.61e-16	2.87e-15	0.967	0.0	T3M2-C5E + O3 = #.856 HO. + #.027 RO2-N. + #.673 R2O2. + #.156 C-O2. + #.586 CCO-O2. + #.087 RCO-O2. + #.156 CO + #.042 CO2 + #.087 HCHO + #1.286 CCHO + #.3 MEK + #.102 CCO-OH + #.042 INERT + #-0.012 XC
	9.37e-12	9.37e-12	0.000	0.0	T3M2-C5E + NO3 = #.874 NO2 + #.03 RO2-R. + #.096 RO2-N. + #.904 R2O2. + #.904 CCHO + #.874 MEK + #.03 RNO3 + #-0.06 XC + #.096 XN
	3.71e-11	3.71e-11	0.000	0.0	T3M2-C5E + O3P = #.6 MEK + #.4 PROD2 + #1.2 XC
Trans 4-Methyl-2-Hexene	6.11e-11	1.14e-11	-0.994	0.0	T4M2-C5E + HO. = #.903 RO2-R. + #.097 RO2-N. + #.017 R2O2. + #.887 CCHO + #.904 RCHO + #.016 ACET + #.885 XC
	1.15e-16	1.15e-16	0.000	0.0	T4M2-C5E + O3 = #.301 HO. + #.039 RO2-R. + #.002 RO2-N. + #.26 C-O2. + #.301 CO + #.07 CO2 + #.5 CCHO + #.5 RCHO + #.039 ACET + #.17 CCO-OH + #.46 RCO-OH + #.07 INERT + #1.023 XC
	3.70e-13	3.70e-13	0.000	0.0	T4M2-C5E + NO3 = #.198 NO2 + #.612 RO2-R. + #.19 RO2-N. + #.808 R2O2. + #.198 CCHO + #.586 RCHO + #.373 ACET + #.239 RNO3 + #.151 XC + #.563 XN
	1.88e-11	1.88e-11	0.000	0.0	T4M2-C5E + O3P = #.88 MEK + #.12 PROD2 + #1.76 XC
Trans-2-Hexene	6.34e-11	6.34e-11	0.000	0.0	T-2-C6E + HO. = #.904 RO2-R. + #.096 RO2-N. + #.904 CCHO + #.904 RCHO + #.904 XC
	1.15e-16	1.15e-16	0.000	0.0	T-2-C6E + O3 = #.301 HO. + #.04 RO2-R. + #.001 RO2-N. + #.26 C-O2. + #.301 CO + #.07 CO2 + #.5 CCHO + #.54 RCHO + #.17 CCO-OH + #.46 RCO-OH + #.07 INERT + #1.025 XC
	3.70e-13	3.70e-13	0.000	0.0	T-2-C6E + NO3 = #.12 NO2 + #.661 RO2-R. + #.219 RO2-N. + #.808 R2O2. + #.12 CCHO + #.134 RCHO + #.654 RNO3 + #.12 XC + #.226 XN
	2.05e-11	2.05e-11	0.000	0.0	T-2-C6E + O3P = #.76 MEK + #.24 PROD2 + #1.52 XC
Trans-3-Hexene	6.34e-11	6.34e-11	0.000	0.0	T-3-C6E + HO. = #.904 RO2-R. + #.096 RO2-N. + #1.807 RCHO
	1.70e-16	6.64e-15	2.170	0.0	T-3-C6E + O3 = #.113 HO. + #.113 RO2-R. + #.113 CO + #.113 CCHO + RCHO + #.887 RCO-OH
	3.70e-13	3.70e-13	0.000	0.0	T-3-C6E + NO3 = #.284 NO2 + #.515 RO2-R. + #.2 RO2-N. + #.775 R2O2. + #.568 RCHO + #.515 RNO3 + #.2 XN
	2.05e-11	2.05e-11	0.000	0.0	T-3-C6E + O3P = #.76 MEK + #.24 PROD2 + #1.52 XC

Table A-6 (continued)

Compound	Rate Parameters [a]				Reactions and Products [b]
	k(298)	A	Ea	B	
Cis-2-Hexene	6.34e-11	6.34e-11	0.000	0.0	C-2-C6E + HO. = #.904 RO2-R. + #.096 RO2-N. + #.904 CCHO + #.904 RCHO + #.904 XC
	1.15e-16	1.15e-16	0.000	0.0	C-2-C6E + O3 = #.301 HO. + #.04 RO2-R. + #.001 RO2-N. + #.26 C-O2. + #.301 CO + #.07 CO2 + #.5 CCHO + #.54 RCHO + #.17 CCO-OH + #.46 RCO-OH + #.07 INERT + #1.025 XC
	3.70e-13	3.70e-13	0.000	0.0	C-2-C6E + NO3 = #.12 NO2 + #.661 RO2-R. + #.219 RO2-N. + #.808 R2O2. + #.12 CCHO + #.134 RCHO + #.654 RNO3 + #.12 XC + #.226 XN
	2.05e-11	2.05e-11	0.000	0.0	C-2-C6E + O3P = #.76 MEK + #.24 PROD2 + #1.52 XC
2-Methyl-2-Pentene	8.89e-11	1.66e-11	-0.994	0.0	2M-2-C5E + HO. = #.904 RO2-R. + #.096 RO2-N. + #.904 RCHO + #.904 ACET
	3.48e-16	3.48e-16	0.000	0.0	2M-2-C5E + O3 = #.734 HO. + #.034 RO2-R. + #.7 R2O2. + #.7 CCO-O2. + #.034 CO + #.7 HCHO + #.034 CCHO + #.7 RCHO + #.3 ACET + #.266 RCO-OH
	9.37e-12	9.37e-12	0.000	0.0	2M-2-C5E + NO3 = #.392 NO2 + #.462 RO2-R. + #.147 RO2-N. + #.922 R2O2. + #.016 HCHO + #.847 RCHO + #.392 ACET + #.006 RNO3 + #1.35 XC + #.602 XN
	3.78e-11	3.78e-11	0.000	0.0	2M-2-C5E + O3P = MEK + #2 XC
Cis-3-Hexene	6.34e-11	6.34e-11	0.000	0.0	C-3-C6E + HO. = #.904 RO2-R. + #.096 RO2-N. + #1.807 RCHO
	1.50e-16	3.22e-15	1.816	0.0	C-3-C6E + O3 = #.113 HO. + #.113 RO2-R. + #.113 CO + #.113 CCHO + RCHO + #.887 RCO-OH
	3.70e-13	3.70e-13	0.000	0.0	C-3-C6E + NO3 = #.284 NO2 + #.515 RO2-R. + #.2 RO2-N. + #.775 R2O2. + #.568 RCHO + #.515 RNO3 + #.2 XN
	2.05e-11	2.05e-11	0.000	0.0	C-3-C6E + O3P = #.76 MEK + #.24 PROD2 + #1.52 XC
2,3-Dimethyl-2-Hexene	1.03e-10	1.92e-11	-0.994	0.0	23M2-C5E + HO. = #.866 RO2-R. + #.134 RO2-N. + #.866 ACET + #.866 MEK + #.134 XC
	6.74e-16	6.74e-16	0.000	0.0	23M2-C5E + O3 = HO. + #.019 RO2-N. + #.981 R2O2. + #.919 CCO-O2. + #.062 RCO-O2. + #.562 HCHO + #.419 CCHO + #.5 ACET + #.5 MEK + #-0.039 XC
	5.72e-11	5.72e-11	0.000	0.0	23M2-C5E + NO3 = #.866 NO2 + #.134 RO2-N. + #.866 R2O2. + #.866 ACET + #.866 MEK + #.134 XC + #.134 XN
	4.95e-11	4.95e-11	0.000	0.0	23M2-C5E + O3P = MEK + #3 XC
Trans 4,4-dimethyl-2-Hexene	5.52e-11	1.03e-11	-0.994	0.0	T44M2C5E + HO. = #.517 RO2-R. + #.147 RO2-N. + #.685 R2O2. + #.336 TBU-O. + #.517 CCHO + #.866 RCHO + #1.477 XC
	1.15e-16	1.15e-16	0.000	0.0	T44M2C5E + O3 = #.285 HO. + #.001 RO2-N. + #.024 R2O2. + #.26 C-O2. + #.024 TBU-O. + #.285 CO + #.07 CO2 + #.5 CCHO + #.5 RCHO + #.17 CCO-OH + #.475 RCO-OH + #.07 INERT + #2.042 XC
	3.70e-13	3.70e-13	0.000	0.0	T44M2C5E + NO3 = #.164 NO2 + #.205 RO2-R. + #.242 RO2-N. + #1.237 R2O2. + #.389 TBU-O. + #.026 HCHO + #.142 CCHO + #.57 RCHO + #.022 ACET + #.204 RNO3 + #1.071 XC + #.632 XN
	1.55e-11	1.55e-11	0.000	0.0	T44M2C5E + O3P = MEK + #3 XC
Cis-3-Heptene	6.34e-11	6.34e-11	0.000	0.0	C-3-C7E + HO. = #.866 RO2-R. + #.134 RO2-N. + #1.733 RCHO + XC
	1.15e-16	1.15e-16	0.000	0.0	C-3-C7E + O3 = #.098 HO. + #.097 RO2-R. + #.001 RO2-N. + #.098 CO + #.057 CCHO + #1.04 RCHO + #.903 RCO-OH + #.955 XC
	3.70e-13	3.70e-13	0.000	0.0	C-3-C7E + NO3 = #.082 NO2 + #.634 RO2-R. + #.284 RO2-N. + #.788 R2O2. + #.163 RCHO + #.634 RNO3 + XC + #.284 XN
	2.05e-11	2.05e-11	0.000	0.0	C-3-C7E + O3P = PROD2 + XC

Table A-6 (continued)

Compound	Rate Parameters [a]				Reactions and Products [b]
	k(298)	A	Ea	B	
Trans-3-Heptene	6.34e-11	6.34e-11	0.000	0.0	T-3-C7E + HO. = #.866 RO2-R. + #.134 RO2-N. + #1.733 RCHO + XC
	1.15e-16	1.15e-16	0.000	0.0	T-3-C7E + O3 = #.098 HO. + #.097 RO2-R. + #.001 RO2-N. + #.098 CO + #.057 CCHO + #1.04 RCHO + #.903 RCO-OH + #.955 XC
	3.70e-13	3.70e-13	0.000	0.0	T-3-C7E + NO3 = #.082 NO2 + #.634 RO2-R. + #.284 RO2-N. + #.788 R2O2. + #.163 RCHO + #.634 RNO3 + XC + #.284 XN
	2.05e-11	2.05e-11	0.000	0.0	T-3-C7E + O3P = PROD2 + XC
Trans-2-Heptene	6.80e-11	1.27e-11	-0.994	0.0	T-2-C7E + HO. = #.866 RO2-R. + #.134 RO2-N. + #.005 R2O2. + #.861 CCHO + #.861 RCHO + #.005 PROD2 + #1.861 XC
	1.15e-16	1.15e-16	0.000	0.0	T-2-C7E + O3 = #.285 HO. + #.023 RO2-R. + #.002 RO2-N. + #.019 R2O2. + #.26 C-O2. + #.285 CO + #.07 CO2 + #.5 CCHO + #.523 RCHO + #.17 CCO-OH + #.475 RCO-OH + #.07 INERT + #2.04 XC
	3.70e-13	3.70e-13	0.000	0.0	T-2-C7E + NO3 = #.013 NO2 + #.691 RO2-R. + #.296 RO2-N. + #.81 R2O2. + #.013 CCHO + #.013 RCHO + #.691 RNO3 + #1.013 XC + #.296 XN
	2.29e-11	2.29e-11	0.000	0.0	T-2-C7E + O3P = PROD2 + XC
Trans-3-Octene	6.34e-11	6.34e-11	0.000	0.0	T-3-C8E + HO. = #.827 RO2-R. + #.173 RO2-N. + #.004 R2O2. + #1.647 RCHO + #.004 PROD2 + #2 XC
	1.15e-16	1.15e-16	0.000	0.0	T-3-C8E + O3 = #.082 HO. + #.08 RO2-R. + #.002 RO2-N. + #.019 R2O2. + #.082 CO + #.057 CCHO + #1.023 RCHO + #.918 RCO-OH + #1.97 XC
	3.70e-13	3.70e-13	0.000	0.0	T-3-C8E + NO3 = #.014 NO2 + #.636 RO2-R. + #.351 RO2-N. + #.781 R2O2. + #.027 RCHO + #.636 RNO3 + #2 XC + #.351 XN
	2.05e-11	2.05e-11	0.000	0.0	T-3-C8E + O3P = PROD2 + #2 XC
Cis-4-Octene	6.34e-11	6.34e-11	0.000	0.0	C-4-C8E + HO. = #.828 RO2-R. + #.172 RO2-N. + #1.656 RCHO + #2 XC
	9.51e-17	3.22e-15	2.086	0.0	C-4-C8E + O3 = #.082 HO. + #.08 RO2-R. + #.002 RO2-N. + #.082 CO + #1.08 RCHO + #.919 RCO-OH + #1.91 XC
	3.70e-13	3.70e-13	0.000	0.0	C-4-C8E + NO3 = #.014 NO2 + #.635 RO2-R. + #.351 RO2-N. + #.781 R2O2. + #.028 RCHO + #.635 RNO3 + #2 XC + #.351 XN
	2.05e-11	2.05e-11	0.000	0.0	C-4-C8E + O3P = PROD2 + #2 XC
Trans-4-Octene	6.91e-11	1.29e-11	-0.994	0.0	T-4-C8E + HO. = #.828 RO2-R. + #.172 RO2-N. + #1.656 RCHO + #2 XC
	1.40e-16	6.64e-15	2.285	0.0	T-4-C8E + O3 = #.082 HO. + #.08 RO2-R. + #.002 RO2-N. + #.082 CO + #1.08 RCHO + #.919 RCO-OH + #1.91 XC
	3.70e-13	3.70e-13	0.000	0.0	T-4-C8E + NO3 = #.014 NO2 + #.635 RO2-R. + #.351 RO2-N. + #.781 R2O2. + #.028 RCHO + #.635 RNO3 + #2 XC + #.351 XN
	2.36e-11	2.36e-11	0.000	0.0	T-4-C8E + O3P = PROD2 + #2 XC
Trans 2,5-Dimethyl 3-Hexene	6.34e-11	6.34e-11	0.000	0.0	T25M3C6E + HO. = #.828 RO2-R. + #.172 RO2-N. + #1.656 RCHO + #2 XC
	4.10e-17	6.64e-15	3.013	0.0	T25M3C6E + O3 = #.082 HO. + #.079 RO2-R. + #.003 RO2-N. + #.082 CO + RCHO + #.079 ACET + #.919 RCO-OH + #1.905 XC
	3.70e-13	3.70e-13	0.000	0.0	T25M3C6E + NO3 = #.168 NO2 + #.551 RO2-R. + #.281 RO2-N. + #.763 R2O2. + #.636 RCHO + #.288 ACET + #.262 RNO3 + #1.964 XC + #.57 XN
	2.05e-11	2.05e-11	0.000	0.0	T25M3C6E + O3P = PROD2 + #2 XC

Table A-6 (continued)

Compound	Rate Parameters [a]				Reactions and Products [b]
	k(298)	A	Ea	B	
Trans 2,2-Dimethyl 3-Hexene	6.34e-11	6.34e-11	0.000	0.0	T22M3C6E + HO. = #.433 RO2-R. + #.187 RO2-N. + #.775 R2O2. + #.38 TBU-O. + #1.261 RCHO + #1.954 XC
	4.20e-17	6.64e-15	2.998	0.0	T22M3C6E + O3 = #.082 HO. + #.057 RO2-R. + #.001 RO2-N. + #.024 R2O2. + #.024 TBU-O. + #.082 CO + #.057 CCHO + RCHO + #.918 RCO-OH + #1.972 XC
	3.70e-13	3.70e-13	0.000	0.0	T22M3C6E + NO3 = #.154 NO2 + #.194 RO2-R. + #.277 RO2-N. + #1.177 R2O2. + #.376 TBU-O. + #.017 HCHO + #.011 CCHO + #.707 RCHO + #.002 ACET + #.183 RNO3 + #1.949 XC + #.663 XN
	2.05e-11	2.05e-11	0.000	0.0	T22M3C6E + O3P = #.88 MEK + #.12 PROD2 + #3.76 XC
2,4,4-trimethyl-2-Pentene	8.71e-11	8.71e-11	0.000	0.0	244M2C5E + HO. = #.785 RO2-R. + #.215 RO2-N. + #.056 R2O2. + #.025 CCHO + #.785 RCHO + #.785 ACET + #2.95 XC
	1.40e-16	2.87e-15	1.788	0.0	244M2C5E + O3 = #.7 HO. + #.7 R2O2. + #.7 CCO-O2. + #.7 HCHO + #.7 RCHO + #.3 ACET + #.3 RCO-OH + #3 XC
	9.37e-12	9.37e-12	0.000	0.0	244M2C5E + NO3 = #.526 NO2 + #.036 RO2-R. + #.438 RO2-N. + #1.865 R2O2. + #.077 HCHO + #.532 CCHO + #.527 RCHO + #.494 ACET + #.032 MEK + #.035 RNO3 + #1.829 XC + #.439 XN
	3.71e-11	3.71e-11	0.000	0.0	244M2C5E + O3P = #.6 MEK + #.4 PROD2 + #4.2 XC
Trans-4-Nonene	6.34e-11	6.34e-11	0.000	0.0	T-4-C9E + HO. = #.794 RO2-R. + #.206 RO2-N. + #.005 R2O2. + #1.579 RCHO + #.004 PROD2 + #3 XC
	1.15e-16	1.15e-16	0.000	0.0	T-4-C9E + O3 = #.066 HO. + #.063 RO2-R. + #.003 RO2-N. + #.019 R2O2. + #.066 CO + #1.063 RCHO + #.935 RCO-OH + #2.925 XC
	3.70e-13	3.70e-13	0.000	0.0	T-4-C9E + NO3 = #.005 NO2 + #.601 RO2-R. + #.393 RO2-N. + #.762 R2O2. + #.01 RCHO + #.601 RNO3 + #3 XC + #.393 XN
	2.05e-11	2.05e-11	0.000	0.0	T-4-C9E + O3P = PROD2 + #3 XC
3,4-Diethyl-2-Hexene	8.71e-11	8.71e-11	0.000	0.0	34E2-C6E + HO. = #.771 RO2-R. + #.229 RO2-N. + #.771 CCHO + #.771 PROD2 + #2.459 XC
	4.21e-18	2.87e-15	3.864	0.0	34E2-C6E + O3 = #.856 HO. + #.12 RO2-N. + #.58 R2O2. + #.156 C-O2. + #.58 RCO-O2. + #.156 CO + #.042 CO2 + #.841 CCHO + #.439 MEK + #.3 PROD2 + #.102 CCO-OH + #.042 INERT + #1.744 XC
	9.37e-12	9.37e-12	0.000	0.0	34E2-C6E + NO3 = #.049 NO2 + #.631 RO2-R. + #.321 RO2-N. + #1.058 R2O2. + #.315 CCHO + #.275 RCHO + #.354 MEK + #.049 PROD2 + #.699 RNO3 + #.715 XC + #.252 XN
	3.71e-11	3.71e-11	0.000	0.0	34E2-C6E + O3P = PROD2 + #4 XC
Cis-5-Decene	6.34e-11	6.34e-11	0.000	0.0	C-5-C10E + HO. = #.768 RO2-R. + #.232 RO2-N. + #.01 R2O2. + #1.521 RCHO + #.008 PROD2 + #4 XC
	1.20e-16	3.22e-15	1.948	0.0	C-5-C10E + O3 = #.05 HO. + #.047 RO2-R. + #.003 RO2-N. + #.038 R2O2. + #.05 CO + #1.047 RCHO + #.95 RCO-OH + #3.94 XC
	3.70e-13	3.70e-13	0.000	0.0	C-5-C10E + NO3 = #.578 RO2-R. + #.422 RO2-N. + #.75 R2O2. + #.578 RNO3 + #4 XC + #.422 XN
	2.05e-11	2.05e-11	0.000	0.0	C-5-C10E + O3P = PROD2 + #4 XC
Trans-4-Decene	6.34e-11	6.34e-11	0.000	0.0	T-4-C10E + HO. = #.768 RO2-R. + #.232 RO2-N. + #.01 R2O2. + #1.521 RCHO + #.008 PROD2 + #4 XC
	1.15e-16	1.15e-16	0.000	0.0	T-4-C10E + O3 = #.041 HO. + #.04 RO2-R. + #.001 RO2-N. + #.041 CO + #1.04 RCHO + #.96 RCO-OH + #3.955 XC
	3.70e-13	3.70e-13	0.000	0.0	T-4-C10E + NO3 = #.005 NO2 + #.574 RO2-R. + #.421 RO2-N. + #.75 R2O2. + #.01 RCHO + #.574 RNO3 + #4 XC + #.421 XN
	2.05e-11	2.05e-11	0.000	0.0	T-4-C10E + O3P = PROD2 + #4 XC

Table A-6 (continued)

Compound	Rate Parameters [a]				Reactions and Products [b]
	k(298)	A	Ea	B	
Trans-5-Undecene	6.34e-11	6.34e-11	0.000	0.0	T-5-C11E + HO. = #.751 RO2-R. + #.249 RO2-N. + #.015 R2O2. + #1.48 RCHO + #.011 PROD2 + #5 XC
	1.15e-16	1.15e-16	0.000	0.0	T-5-C11E + O3 = #.025 HO. + #.023 RO2-R. + #.002 RO2-N. + #.019 R2O2. + #.025 CO + #1.023 RCHO + #.975 RCO-OH + #4.97 XC
	3.70e-13	3.70e-13	0.000	0.0	T-5-C11E + NO3 = #.56 RO2-R. + #.44 RO2-N. + #.742 R2O2. + #.56 RNO3 + #5 XC + #.44 XN
	2.05e-11	2.05e-11	0.000	0.0	T-5-C11E + O3P = PROD2 + #5 XC
Trans-5-Dodecene	6.34e-11	6.34e-11	0.000	0.0	T-5-C12E + HO. = #.742 RO2-R. + #.258 RO2-N. + #.015 R2O2. + #1.461 RCHO + #.011 PROD2 + #6 XC
	1.15e-16	1.15e-16	0.000	0.0	T-5-C12E + O3 = #.025 HO. + #.023 RO2-R. + #.002 RO2-N. + #.019 R2O2. + #.025 CO + #1.023 RCHO + #.975 RCO-OH + #5.97 XC
	3.70e-13	3.70e-13	0.000	0.0	T-5-C12E + NO3 = #.547 RO2-R. + #.453 RO2-N. + #.746 R2O2. + #.547 RNO3 + #6 XC + #.453 XN
	2.05e-11	2.05e-11	0.000	0.0	T-5-C12E + O3P = PROD2 + #6 XC
Trans-5-Tridecene	6.34e-11	6.34e-11	0.000	0.0	T-5-C13E + HO. = #.735 RO2-R. + #.265 RO2-N. + #.015 R2O2. + #1.45 RCHO + #.011 PROD2 + #7 XC
	1.15e-16	1.15e-16	0.000	0.0	T-5-C13E + O3 = #.025 HO. + #.023 RO2-R. + #.002 RO2-N. + #.019 R2O2. + #.025 CO + #1.023 RCHO + #.975 RCO-OH + #6.97 XC
	3.70e-13	3.70e-13	0.000	0.0	T-5-C13E + NO3 = #.538 RO2-R. + #.462 RO2-N. + #.753 R2O2. + #.538 RNO3 + #7 XC + #.462 XN
	2.05e-11	2.05e-11	0.000	0.0	T-5-C13E + O3P = PROD2 + #7 XC
Trans-5-Tetradecene	6.34e-11	6.34e-11	0.000	0.0	T-5-C14E + HO. = #.732 RO2-R. + #.268 RO2-N. + #.015 R2O2. + #1.442 RCHO + #.011 PROD2 + #8 XC
	1.15e-16	1.15e-16	0.000	0.0	T-5-C14E + O3 = #.025 HO. + #.023 RO2-R. + #.002 RO2-N. + #.019 R2O2. + #.025 CO + #1.023 RCHO + #.975 RCO-OH + #7.97 XC
	3.70e-13	3.70e-13	0.000	0.0	T-5-C14E + NO3 = #.533 RO2-R. + #.467 RO2-N. + #.753 R2O2. + #.533 RNO3 + #8 XC + #.467 XN
	2.05e-11	2.05e-11	0.000	0.0	T-5-C14E + O3P = PROD2 + #8 XC
Trans-5-Tetradecene	6.34e-11	6.34e-11	0.000	0.0	T-5-C15E + HO. = #.729 RO2-R. + #.271 RO2-N. + #.015 R2O2. + #1.437 RCHO + #.01 PROD2 + #9 XC
	1.15e-16	1.15e-16	0.000	0.0	T-5-C15E + O3 = #.025 HO. + #.023 RO2-R. + #.002 RO2-N. + #.019 R2O2. + #.025 CO + #1.023 RCHO + #.975 RCO-OH + #8.97 XC
	3.70e-13	3.70e-13	0.000	0.0	T-5-C15E + NO3 = #.53 RO2-R. + #.47 RO2-N. + #.752 R2O2. + #.53 RNO3 + #9 XC + #.47 XN
	2.05e-11	2.05e-11	0.000	0.0	T-5-C15E + O3P = PROD2 + #9 XC
1,3-Butadiene	6.65e-11	1.48e-11	-0.890	0.0	13-BUTDE + HO. = #.961 RO2-R. + #.039 RO2-N. + #.481 HCHO + #.481 METHACRO + #.481 ISOPROD + #-1.039 XC
	6.31e-18	1.34e-14	4.537	0.0	13-BUTDE + O3 = #.06 HO. + #.06 HO2. + #.25 CO + #.19 CO2 + #.5 HCHO + #.125 PROD2 + #.5 METHACRO + #.185 HCOOH + #.375 RCO-OH + #-1 XC
	1.00e-13	1.00e-13	0.000	0.0	13-BUTDE + NO3 = #.921 RO2-R. + #.079 RO2-N. + #.921 MVK + #-0.159 XC + XN
	1.98e-11	1.98e-11	0.000	0.0	13-BUTDE + O3P = #.25 HO2. + #.23 RO2-R. + #.02 RO2-N. + #.23 CO + #.75 PROD2 + #.23 METHACRO + #-1.77 XC

Table A-6 (continued)

Compound	Rate Parameters [a]				Reactions and Products [b]
	k(298)	A	Ea	B	
Cyclopentene	6.70e-11	1.25e-11	-0.994	0.0	CYC-PNTE + HO. = #.936 RO2-R. + #.064 RO2-N. + #.936 RCHO + #1.809 XC
	5.56e-16	1.80e-15	0.696	0.0	CYC-PNTE + O3 = #.05 HO. + #.002 RO2-N. + #.048 R2O2. + #.048 RCO-O2. + #.05 CO + #.95 RCHO + #1.944 XC
	5.30e-13	5.30e-13	0.000	0.0	CYC-PNTE + NO3 = #.813 NO2 + #.064 RO2-R. + #.123 RO2-N. + #.951 R2O2. + #.788 RCHO + #.077 MGLY + #.012 RNO3 + #1.595 XC + #.175 XN
	2.10e-11	2.10e-11	0.000	0.0	CYC-PNTE + O3P = #.24 MEK + #.76 PROD2 + #-0.52 XC
1-Methyl cyclohexene	8.71e-11	8.71e-11	0.000	0.0	1M-CC5E + HO. = #.904 RO2-R. + #.096 RO2-N. + #.904 RCHO + #2.711 XC
	6.70e-16	2.70e-15	0.825	0.0	1M-CC5E + O3 = #.7 HO. + #.067 RO2-N. + #.633 R2O2. + #.565 CCO-O2. + #.068 RCO-O2. + #.068 HCHO + #.565 RCHO + #.3 RCO-OH + #1.601 XC
	9.37e-12	9.37e-12	0.000	0.0	1M-CC5E + NO3 = #.838 NO2 + #.052 RO2-R. + #.11 RO2-N. + #.981 R2O2. + #.813 RCHO + #.077 BACL + #2.593 XC + #.162 XN
	3.71e-11	3.71e-11	0.000	0.0	1M-CC5E + O3P = PROD2
Cyclohexene	6.75e-11	1.26e-11	-0.994	0.0	CYC-HEXE + HO. = #.904 RO2-R. + #.096 RO2-N. + #.904 RCHO + #2.711 XC
	8.14e-17	2.88e-15	2.112	0.0	CYC-HEXE + O3 = RCHO + #3 XC
	5.85e-13	1.05e-12	0.346	0.0	CYC-HEXE + NO3 = #.297 NO2 + #.54 RO2-R. + #.163 RO2-N. + #.402 R2O2. + #.342 RCHO + #.495 RNO3 + #1.026 XC + #.209 XN
	2.00e-11	2.00e-11	0.000	0.0	CYC-HEXE + O3P = PROD2
1-Methyl Cyclohexene	8.71e-11	8.71e-11	0.000	0.0	1M-CC6E + HO. = #.866 RO2-R. + #.134 RO2-N. + #.866 RCHO + #3.599 XC
	1.65e-16	2.87e-15	1.690	0.0	1M-CC6E + O3 = #.7 HO. + #.094 RO2-N. + #.606 R2O2. + #.541 CCO-O2. + #.065 RCO-O2. + #.065 HCHO + #.541 RCHO + #.3 RCO-OH + #2.572 XC
	9.37e-12	9.37e-12	0.000	0.0	1M-CC6E + NO3 = #.73 NO2 + #.103 RO2-R. + #.168 RO2-N. + #.985 R2O2. + #.832 RCHO + #3.497 XC + #.27 XN
	9.00e-11	9.00e-11	0.000	0.0	1M-CC6E + O3P = PROD2 + XC
4-Methyl Cyclohexene	6.34e-11	6.34e-11	0.000	0.0	4M-CC6E + HO. = #.866 RO2-R. + #.134 RO2-N. + #.866 RCHO + #3.599 XC
	8.21e-17	2.88e-15	2.107	0.0	4M-CC6E + O3 = RCHO + #4 XC
	3.70e-13	3.70e-13	0.000	0.0	4M-CC6E + NO3 = #.264 NO2 + #.52 RO2-R. + #.216 RO2-N. + #.469 R2O2. + #.003 HCHO + #.003 CCHO + #.343 RCHO + #.003 PROD2 + #.441 RNO3 + #2.002 XC + #.295 XN
	2.05e-11	2.05e-11	0.000	0.0	4M-CC6E + O3P = PROD2 + XC
1,2-Dimethyl Cyclohexene	1.05e-10	1.05e-10	0.000	0.0	12M-CC6E + HO. = #.828 RO2-R. + #.172 RO2-N. + #.828 PROD2 + #2 XC
	2.07e-16	3.03e-15	1.589	0.0	12M-CC6E + O3 = HO. + #.172 RO2-N. + #.828 R2O2. + #.739 CCO-O2. + #.089 RCO-O2. + #.089 HCHO + #.739 RCHO + #2.917 XC
	5.72e-11	5.72e-11	0.000	0.0	12M-CC6E + NO3 = #.828 NO2 + #.172 RO2-N. + #.828 R2O2. + #.828 PROD2 + #2 XC + #.172 XN
	5.29e-11	5.29e-11	0.000	0.0	12M-CC6E + O3P = PROD2 + #2 XC

Table A-6 (continued)

Compound	Rate Parameters [a]				Reactions and Products [b]
	k(298)	A	Ea	B	
a-Pinene	5.37e-11	1.21e-11	-0.882	0.0	A-PINENE + HO. = #.75 RO2-R. + #.25 RO2-N. + #.5 R2O2. + #.75 RCHO + #6.5 XC
	8.65e-17	1.01e-15	1.455	0.0	A-PINENE + O3 = #.7 HO. + #.081 RO2-R. + #.321 RO2-N. + #1.375 R2O2. + #.298 RCO-O2. + #.051 CO + #.339 HCHO + #.218 RCHO + #.345 ACET + #.002 GLY + #.081 BACL + #.3 RCO-OH + #3.875 XC
	6.16e-12	1.19e-12	-0.974	0.0	A-PINENE + NO3 = #.75 NO2 + #.25 RO2-N. + #.75 R2O2. + #.75 RCHO + #6.25 XC + #.25 XN
	3.20e-11	3.20e-11	0.000	0.0	A-PINENE + O3P = PROD2 + #4 XC
b-Pinene	7.88e-11	2.38e-11	-0.709	0.0	B-PINENE + HO. = #.75 RO2-R. + #.25 RO2-N. + #.5 R2O2. + #.75 HCHO + #.75 PROD2 + #3.25 XC
	1.50e-17	1.01e-15	2.493	0.0	B-PINENE + O3 = #.34 HO. + #.09 HO2. + #.05 RO2-N. + #.2 R2O2. + #.2 RCO-O2. + #.375 CO + #.1 CO2 + #.25 HCHO + #.75 PROD2 + #.28 HCOOH + #3.595 XC
	2.51e-12	2.51e-12	0.000	0.0	B-PINENE + NO3 = #.75 RO2-R. + #.25 RO2-N. + #.75 R2O2. + #.75 RNO3 + #4 XC + #.25 XN
	2.70e-11	2.70e-11	0.000	0.0	B-PINENE + O3P = #.4 RCHO + #.6 PROD2 + #5.2 XC
3-Carene	8.79e-11	1.64e-11	-0.994	0.0	3-CARENE + HO. = #.75 RO2-R. + #.25 RO2-N. + #.5 R2O2. + #.75 RCHO + #6.25 XC
	3.70e-17	1.01e-15	1.958	0.0	3-CARENE + O3 = #.7 HO. + #.161 RO2-N. + #.539 R2O2. + #.482 CCO-O2. + #.058 RCO-O2. + #.058 HCHO + #.482 RCHO + #.3 RCO-OH + #5.492 XC
	9.10e-12	9.10e-12	0.000	0.0	3-CARENE + NO3 = #.75 NO2 + #.25 RO2-N. + #.75 R2O2. + #.75 RCHO + #6.25 XC + #.25 XN
	3.20e-11	3.20e-11	0.000	0.0	3-CARENE + O3P = PROD2 + #4 XC
Sabinene	1.17e-10	2.19e-11	-0.994	0.0	SABINENE + HO. = #.75 RO2-R. + #.25 RO2-N. + #.5 R2O2. + #.75 HCHO + #.75 PROD2 + #3.25 XC
	8.60e-17	1.01e-15	1.459	0.0	SABINENE + O3 = #.34 HO. + #.09 HO2. + #.05 RO2-N. + #.2 R2O2. + #.2 RCO-O2. + #.375 CO + #.1 CO2 + #.25 HCHO + #.75 PROD2 + #.28 HCOOH + #3.595 XC
	1.00e-11	1.00e-11	0.000	0.0	SABINENE + NO3 = #.75 RO2-R. + #.25 RO2-N. + #.75 R2O2. + #.75 RNO3 + #4 XC + #.25 XN
	1.69e-11	1.69e-11	0.000	0.0	SABINENE + O3P = #.4 RCHO + #.6 PROD2 + #5.2 XC
d-Limonene	1.71e-10	3.19e-11	-0.994	0.0	D-LIMONE + HO. = #.75 RO2-R. + #.25 RO2-N. + #.5 R2O2. + #.75 RCHO + #6.25 XC
	2.00e-16	3.71e-15	1.729	0.0	D-LIMONE + O3 = #.7 HO. + #.161 RO2-N. + #.539 R2O2. + #.482 CCO-O2. + #.058 RCO-O2. + #.058 HCHO + #.482 RCHO + #.3 RCO-OH + #5.492 XC
	1.22e-11	1.22e-11	0.000	0.0	D-LIMONE + NO3 = #.75 NO2 + #.25 RO2-N. + #.75 R2O2. + #.75 RCHO + #6.25 XC + #.25 XN
	7.20e-11	7.20e-11	0.000	0.0	D-LIMONE + O3P = PROD2 + #4 XC
Benzene	1.23e-12	2.47e-12	0.411	0.0	BENZENE + HO. = #.236 HO2. + #.764 RO2-R. + #.207 GLY + #.236 PHEN + #.764 DCB1 + #1.114 XC
Toluene	5.95e-12	1.81e-12	-0.705	0.0	TOLUENE + HO. = #.234 HO2. + #.758 RO2-R. + #.008 RO2-N. + #.116 GLY + #.135 MGLY + #.234 CRES + #.085 BALD + #.46 DCB1 + #.156 DCB2 + #.057 DCB3 + #1.178 XC
Ethyl Benzene	7.10e-12	7.10e-12	0.000	0.0	C2-BENZ + HO. = #.19 HO2. + #.786 RO2-R. + #.024 RO2-N. + #.239 PROD2 + #.094 GLY + #.109 MGLY + #.19 CRES + #.498 DCB1 + #.049 DCB3 + #2.338 XC

Table A-6 (continued)

Compound	Rate Parameters [a]				Reactions and Products [b]
	k(298)	A	Ea	B	
n-Propyl Benzene	6.00e-12	6.00e-12	0.000	0.0	N-C3-BEN + HO. = #.19 HO2. + #.786 RO2-R. + #.024 RO2-N. + #.239 PROD2 + #.094 GLY + #.109 MGLY + #.19 CRES + #.498 DCB1 + #.049 DCB3 + #3.338 XC
Isopropyl Benzene (cumene)	6.50e-12	6.50e-12	0.000	0.0	I-C3-BEN + HO. = #.19 HO2. + #.786 RO2-R. + #.024 RO2-N. + #.239 PROD2 + #.094 GLY + #.109 MGLY + #.19 CRES + #.498 DCB1 + #.049 DCB3 + #3.338 XC
s-Butyl Benzene	6.00e-12	6.00e-12	0.000	0.0	S-C4-BEN + HO. = #.19 HO2. + #.786 RO2-R. + #.024 RO2-N. + #.239 PROD2 + #.094 GLY + #.109 MGLY + #.19 CRES + #.498 DCB1 + #.049 DCB3 + #4.338 XC
m-Xylene	2.36e-11	2.36e-11	0.000	0.0	M-XYLENE + HO. = #.21 HO2. + #.782 RO2-R. + #.008 RO2-N. + #.107 GLY + #.335 MGLY + #.21 CRES + #.037 BALD + #.347 DCB1 + #.29 DCB2 + #.108 DCB3 + #1.628 XC
o-Xylene	1.37e-11	1.37e-11	0.000	0.0	O-XYLENE + HO. = #.161 HO2. + #.831 RO2-R. + #.008 RO2-N. + #.084 GLY + #.238 MGLY + #.139 BACL + #.161 CRES + #.054 BALD + #.572 DCB1 + #.06 DCB2 + #.145 DCB3 + #1.697 XC
p-Xylene	1.43e-11	1.43e-11	0.000	0.0	P-XYLENE + HO. = #.188 HO2. + #.804 RO2-R. + #.008 RO2-N. + #.195 GLY + #.112 MGLY + #.188 CRES + #.083 BALD + #.709 DCB1 + #.012 DCB3 + #2.432 XC
1,2,4-Trimethyl Benzene	3.25e-11	3.25e-11	0.000	0.0	124-TMB + HO. = #.186 HO2. + #.804 RO2-R. + #.01 RO2-N. + #.063 GLY + #.364 MGLY + #.079 BACL + #.186 CRES + #.044 BALD + #.733 DCB1 + #.027 DCB3 + #2.73 XC
1,3,5-Trimethyl Benzene	5.75e-11	5.75e-11	0.000	0.0	135-TMB + HO. = #.186 HO2. + #.804 RO2-R. + #.01 RO2-N. + #.621 MGLY + #.186 CRES + #.025 BALD + #.569 DCB1 + #.097 DCB2 + #.114 DCB3 + #2.273 XC
1,2,3-Trimethyl Benzene	3.27e-11	3.27e-11	0.000	0.0	123-TMB + HO. = #.186 HO2. + #.804 RO2-R. + #.01 RO2-N. + #.065 GLY + #.166 MGLY + #.383 BACL + #.186 CRES + #.044 BALD + #.533 DCB1 + #.077 DCB2 + #.149 DCB3 + #1.904 XC
Naphthalene	2.16e-11	1.07e-12	-1.779	0.0	NAPHTHAL + HO. = #.236 HO2. + #.215 RO2-R. + #.07 RO2-N. + #.479 RCO-O2. + #.084 GLY + #.236 PHEN + #.117 DCB1 + #.049 DCB2 + #.049 DCB3 + #5.601 XC
Tetralin	3.43e-11	3.43e-11	0.000	0.0	TETRALIN + HO. = #.6 HO2. + #.108 RO2-R. + #.129 RO2-N. + #.163 RCO-O2. + #.084 GLY + #.6 PHEN + #.016 DCB1 + #.046 DCB2 + #.046 DCB3 + #4.446 XC
Methyl Naphthalenes	5.20e-11	5.20e-11	0.000	0.0	ME-NAPH + HO. = #.236 HO2. + #.155 RO2-R. + #.07 RO2-N. + #.539 RCO-O2. + #.084 GLY + #.038 MGLY + #.236 CRES + #.003 DCB1 + #.076 DCB2 + #.076 DCB3 + #6.259 XC
2,3-Dimethyl Naphth.	7.68e-11	7.68e-11	0.000	0.0	23-DMN + HO. = #.236 HO2. + #.094 RO2-R. + #.07 RO2-N. + #.6 RCO-O2. + #.084 GLY + #.076 MGLY + #.236 CRES + #.103 DCB2 + #.103 DCB3 + #6.709 XC
Styrene	5.80e-11	5.80e-11	0.000	0.0	STYRENE + HO. = #.87 RO2-R. + #.13 RO2-N. + #.87 HCHO + #.87 BALD + #.26 XC
	1.71e-17	1.71e-17	0.000	0.0	STYRENE + O3 = #.4 HCHO + #.6 BALD + #.6 HCOOH + #.4 RCO-OH + #1.6 XC
	1.51e-13	1.51e-13	0.000	0.0	STYRENE + NO3 = #.22 NO2 + #.65 RO2-R. + #.13 RO2-N. + #.22 R2O2. + #.22 HCHO + #.22 BALD + #.65 RNO3 + #1.56 XC + #.13 XN
	1.76e-11	1.76e-11	0.000	0.0	STYRENE + O3P = PROD2 + #2 XC
Acetylene	8.97e-13	9.40e-12	1.391	0.0	ACETYLEN + HO. = #.603 HO. + #.297 HO2. + #.1 RO2-R. + #.393 CO + #.096 HCHO + #.607 GLY + #.297 HCOOH
	7.80e-21	2.00e-14	8.739	0.0	ACETYLEN + O3 = #.5 HO. + #1.5 HO2. + #1.5 CO + #.5 CO2

Table A-6 (continued)

Compound	Rate Parameters [a]				Reactions and Products [b]
	k(298)	A	Ea	B	
Methyl Acetylene	5.90e-12	5.90e-12	0.000	0.0	ME-ACTYL + HO. = #.67 HO. + #.33 CCO-O2. + #.67 MGLY + #.33 HCOOH
	1.43e-20	1.00e-14	7.970	0.0	ME-ACTYL + O3 = HO. + R2O2. + RCO-O2. + HCHO + #-1 XC
Ethyl Acetylene	8.00e-12	8.00e-12	0.000	0.0	ET-ACTYL + HO. = #.67 HO. + #.33 RCO-O2. + #.67 MGLY + #.33 HCOOH + #.67 XC
	1.97e-20	1.00e-14	7.780	0.0	ET-ACTYL + O3 = HO. + #.039 RO2-N. + #.961 R2O2. + #.961 RCO-O2. + #.961 CCHO + #-1.039 XC
2-Butyne	2.74e-11	1.00e-11	-0.596	0.0	2-BUTYNE + HO. = #.67 HO. + #.33 CCO-O2. + #.67 BACL + #.33 CCO-OH
	1.97e-20	1.00e-14	7.780	0.0	2-BUTYNE + O3 = HO. + #.039 RO2-N. + #.961 R2O2. + #.961 RCO-O2. + #.961 HCHO + #-0.077 XC
Methanol	9.27e-13	3.10e-12	0.715	0.0	MEOH + HO. = HO2. + HCHO
Ethanol	3.31e-12	5.56e-13	-1.057	0.0	ETOH + HO. = #.95 HO2. + #.05 RO2-R. + #.081 HCHO + #.96 CCHO
Isopropyl Alcohol	5.39e-12	6.49e-13	-1.254	0.0	I-C3-OH + HO. = #.953 HO2. + #.046 RO2-R. + #.001 RO2-N. + #.046 HCHO + #.046 CCHO + #.953 ACET + #-0.003 XC
n-Propyl Alcohol	5.53e-12	5.53e-12	0.000	0.0	N-C3-OH + HO. = #.759 HO2. + #.238 RO2-R. + #.003 RO2-N. + #.208 HCHO + #.207 CCHO + #.79 RCHO + #-0.009 XC
t-Butyl Alcohol	1.14e-12	3.86e-13	-0.640	0.0	T-C4-OH + HO. = #.693 RO2-R. + #.052 RO2-N. + #.254 TBU-O. + #.693 HCHO + #.693 ACET + #.15 XC
n-Butyl Alcohol	8.57e-12	8.57e-12	0.000	0.0	N-C4-OH + HO. = #.517 HO2. + #.47 RO2-R. + #.013 RO2-N. + #.308 HCHO + #.08 CCHO + #.827 RCHO + #.093 PROD2 + #.414 XC
Isobutyl Alcohol	6.91e-12	6.91e-12	0.000	0.0	I-C4-OH + HO. = #.56 HO2. + #.403 RO2-R. + #.037 RO2-N. + #.393 HCHO + #.036 CCHO + #.607 RCHO + #.319 ACET + #.531 XC
s-Butyl Alcohol	9.95e-12	9.95e-12	0.000	0.0	S-C4-OH + HO. = #.829 HO2. + #.165 RO2-R. + #.006 RO2-N. + #.016 HCHO + #.238 CCHO + #.033 RCHO + #.843 MEK + #.005 XC
Cyclopentanol	1.07e-11	1.07e-11	0.000	0.0	CC5-OH + HO. = #.398 HO2. + #.563 RO2-R. + #.038 RO2-N. + #.004 CO + #.102 HCHO + #.331 RCHO + #.631 MEK + #1.148 XC
Pentyl Alcohol	1.11e-11	1.11e-11	0.000	0.0	C5OH + HO. = #.375 HO2. + #.591 RO2-R. + #.035 RO2-N. + #.263 HCHO + #.027 CCHO + #.882 RCHO + #.084 PROD2 + #1.327 XC
2-Pentanol	1.18e-11	1.18e-11	0.000	0.0	2-C5OH + HO. = #.643 HO2. + #.335 RO2-R. + #.022 RO2-N. + #.034 HCHO + #.146 CCHO + #.141 RCHO + #.73 MEK + #.093 PROD2 + #.642 XC
3-Pentanol	1.22e-11	1.22e-11	0.000	0.0	3-C5OH + HO. = #.765 HO2. + #.22 RO2-R. + #.015 RO2-N. + #.174 CCHO + #.195 RCHO + #.79 MEK + #.818 XC
Cyclohexanol	1.74e-11	1.74e-11	0.000	0.0	CC6-OH + HO. = #.439 HO2. + #.507 RO2-R. + #.054 RO2-N. + #.04 HCHO + #.246 RCHO + #.705 PROD2 + #.666 XC
2-Hexanol	1.21e-11	1.21e-11	0.000	0.0	2-C6OH + HO. = #.543 HO2. + #.415 RO2-R. + #.042 RO2-N. + #.032 HCHO + #.13 CCHO + #.15 RCHO + #.808 PROD2 + #.156 XC
1-Hexanol	1.25e-11	1.25e-11	0.000	0.0	1-C6OH + HO. = #.107 HO2. + #.815 RO2-R. + #.077 RO2-N. + #.098 HCHO + #.002 CCHO + #.675 RCHO + #.254 PROD2 + #1.886 XC
1-Heptanol	1.37e-11	1.37e-11	0.000	0.0	1-C7OH + HO. = #.863 RO2-R. + #.137 RO2-N. + #.025 R2O2. + #.054 HCHO + #.547 RCHO + #.316 PROD2 + #2.588 XC
1-Octanol	2.02e-11	2.02e-11	0.000	0.0	1-C8-OH + HO. = #.773 RO2-R. + #.227 RO2-N. + #.321 R2O2. + #.054 HCHO + #.388 RCHO + #.385 PROD2 + #3.109 XC

Table A-6 (continued)

Compound	Rate Parameters [a]				Reactions and Products [b]
	k(298)	A	Ea	B	
2-Octanol	2.52e-11	2.52e-11	0.000	0.0	2-C8-OH + HO. = #.062 HO2. + #.777 RO2-R. + #.161 RO2-N. + #.008 HCHO + #.183 CCHO + #.198 RCHO + #.64 PROD2 + #2.22 XC
3-Octanol	3.14e-11	3.14e-11	0.000	0.0	3-C8-OH + HO. = #.225 HO2. + #.642 RO2-R. + #.133 RO2-N. + #.142 CCHO + #.356 RCHO + #.61 PROD2 + #2.19 XC
4-Octanol	2.87e-11	2.87e-11	0.000	0.0	4-C8-OH + HO. = #.161 HO2. + #.695 RO2-R. + #.144 RO2-N. + #.717 RCHO + #.497 PROD2 + #2.002 XC
2-Ethyl-1-Hexanol	1.33e-11	1.33e-11	0.000	0.0	2-ETC6OH + HO. = #.005 HO2. + #.842 RO2-R. + #.152 RO2-N. + #.34 HCHO + #.04 CCHO + #.605 RCHO + #.328 PROD2 + #2.884 XC
Ethylene Glycol	1.47e-11	1.47e-11	0.000	0.0	ET-GLYCL + HO. = HO2. + #.067 HCHO + #.966 CCHO
Propylene Glycol	2.15e-11	2.15e-11	0.000	0.0	PR-GLYCL + HO. = #.987 HO2. + #.013 RO2-R. + #.039 HCHO + #.039 CCHO + #.315 RCHO + #.646 MEK + #-0.646 XC
Glycerol	1.87e-11	1.87e-11	0.000	0.0	GLYCERL + HO. = HO2. + #.017 HCHO + #.017 CCHO + #.435 RCHO + #.548 PROD2 + #-1.645 XC
1,2-Butandiol	1.59e-11	1.59e-11	0.000	0.0	12-C4OH2 + HO. = #.916 HO2. + #.081 RO2-R. + #.003 RO2-N. + #.022 HCHO + #.14 CCHO + #.285 RCHO + #.641 MEK + #.257 XC
1,2-Dihydroxy Hexane	1.87e-11	1.87e-11	0.000	0.0	C6-GLYCL + HO. = #.779 HO2. + #.2 RO2-R. + #.021 RO2-N. + #.069 CCHO + #.361 RCHO + #.618 PROD2 + #.943 XC
Dimethyl Ether	2.99e-12	1.04e-11	0.739	0.0	ME-O-ME + HO. = RO2-R. + #.079 HCHO + #.961 INERT + #.961 XC
Trimethylene Oxide	1.03e-11	1.03e-11	0.000	0.0	TME-OX + HO. = #.138 RO2-R. + #1.862 R2O2. + #.862 RCO-O2. + #.003 CO + #.006 HCHO + #.135 RCHO
Dimethoxy methane	4.90e-12	4.90e-12	0.000	0.0	METHYLAL + HO. = RO2-R. + #.086 HCHO + #.639 PROD2 + #.359 INERT + #-1.282 XC
	4.90e-12	4.90e-12	0.000	0.0	METHYLAL + HO. = RO2-R. + #.086 HCHO + #.639 PROD2 + #.359 INERT + #-1.282 XC
Tetrahydrofuran	1.61e-11	1.61e-11	0.000	0.0	THF + HO. = #.913 RO2-R. + #.078 RO2-N. + #1.033 R2O2. + #.009 RCO-O2. + #.05 CO + #.013 HCHO + #.863 RCHO + #.05 PROD2 + #.554 XC
Diethyl Ether	1.33e-11	8.02e-13	-1.663	0.0	ET-O-ET + HO. = #.131 RO2-R. + #.039 RO2-N. + #.848 R2O2. + #.83 C-O2. + #.006 HCHO + #.168 CCHO + #.006 RCHO + #.859 MEK + #.01 PROD2 + #-0.923 XC
Alpha-Methyltetrahydrofuran	2.23e-11	2.52e-12	-1.292	0.0	AM-THF + HO. = #.819 RO2-R. + #.139 RO2-N. + #1.222 R2O2. + #.04 C-O2. + #.003 RCO-O2. + #.01 CO + #.025 HCHO + #.008 CCHO + #.849 RCHO + #.007 PROD2 + #1.478 XC
Tetrahydropyran	1.38e-11	1.38e-11	0.000	0.0	THP + HO. = #.835 RO2-R. + #.164 RO2-N. + #1.6 R2O2. + #.001 RCO-O2. + #.025 CO + #.026 HCHO + #.704 RCHO + #.13 PROD2 + #.001 GLY + #1.062 XC
Methyl n-Butyl Ether	1.48e-11	1.48e-11	0.000	0.0	MNBE + HO. = #.92 RO2-R. + #.08 RO2-N. + #.784 R2O2. + #.006 HCHO + #.038 CCHO + #.72 RCHO + #.068 MEK + #.131 PROD2 + #.694 INERT + #.522 XC
Methyl t-Butyl Ether	2.98e-12	5.89e-13	-0.960	0.0	MTBE + HO. = #.743 RO2-R. + #.078 RO2-N. + #.381 R2O2. + #.162 C-O2. + #.016 TBU-O. + #.234 HCHO + #.024 ACET + #.719 MEK + #.007 PROD2 + #.155 INERT + #.94 XC
Ethyl Isopropyl Ether	2.44e-11	2.44e-11	0.000	0.0	ET-O-IPR + HO. = #.246 RO2-R. + #.064 RO2-N. + #.702 R2O2. + #.689 C-O2. + #.008 HCHO + #.221 CCHO + #.002 RCHO + #.219 ACET + #.71 MEK + #.004 PROD2 + #-0.051 XC
Ethyl t-Butyl Ether	8.84e-12	8.84e-12	0.000	0.0	ETBE + HO. = #.143 RO2-R. + #.1 RO2-N. + #.812 R2O2. + #.645 C-O2. + #.112 TBU-O. + #.055 HCHO + #.128 CCHO + #.018 RCHO + #.016 ACET + #.645 MEK + #.109 INERT + #1.319 XC

Table A-6 (continued)

Compound	Rate Parameters [a]				Reactions and Products [b]
	k(298)	A	Ea	B	
Di n-Propyl Ether	1.88e-11	1.18e-12	-1.639	0.0	PR-O-PR + HO. = #.895 RO2-R. + #.105 RO2-N. + #.962 R2O2. + #.875 CCHO + #.014 RCHO + #.796 MEK + #.085 PROD2 + #-0.116 XC
Ethyl n-Butyl Ether	2.13e-11	2.13e-11	0.000	0.0	ENBE + HO. = #.59 RO2-R. + #.115 RO2-N. + #.884 R2O2. + #.295 C-O2. + #.011 HCHO + #.086 CCHO + #.492 RCHO + #.722 MEK + #.104 PROD2 + #-0.154 XC
Methyl t-Amyl Ether	7.91e-12	7.91e-12	0.000	0.0	MTAE + HO. = #.536 RO2-R. + #.128 RO2-N. + #1.078 R2O2. + #.336 C-O2. + #.22 HCHO + #.513 CCHO + #.028 RCHO + #.055 ACET + #.33 MEK + #.026 PROD2 + #.001 HCOOH + #.433 INERT + #1.492 XC
2-Butyl Tetrahydrofuran	2.76e-11	2.76e-11	0.000	0.0	2BU-THF + HO. = #.644 RO2-R. + #.354 RO2-N. + #1.179 R2O2. + #.002 RCO-O2. + #.001 CO + #.034 HCHO + #.735 RCHO + #.001 MEK + #.003 PROD2 + #.002 HCOOH + #3.61 XC
Di-n-butyl Ether	2.88e-11	2.88e-11	0.000	0.0	BU-O-BU + HO. = #.79 RO2-R. + #.21 RO2-N. + #.905 R2O2. + #.032 CCHO + #.738 RCHO + #.653 MEK + #.147 PROD2 + #.967 XC
Di-Isobutyl Ether	2.60e-11	2.60e-11	0.000	0.0	IBU2-O + HO. = #.768 RO2-R. + #.232 RO2-N. + #.963 R2O2. + #.019 HCHO + #.006 RCHO + #.765 ACET + #.78 MEK + #.013 PROD2 + #1.081 XC
Di-n-Pentyl Ether	3.47e-11	3.47e-11	0.000	0.0	C5-O-C5 + HO. = #.681 RO2-R. + #.319 RO2-N. + #1.293 R2O2. + #.007 CCHO + #.606 RCHO + #.705 PROD2 + #2.027 XC
2-Methoxyethanol	1.34e-11	4.50e-12	-0.646	0.0	MEO-ETOH + HO. = #.278 HO2. + #.722 RO2-R. + #.648 HCHO + #.307 RCHO + #.048 PROD2 + #.642 INERT + #.497 XC
1-Methoxy-2-Propanol	2.00e-11	2.00e-11	0.000	0.0	MEOC3OH + HO. = #.39 HO2. + #.6 RO2-R. + #.01 RO2-N. + #.001 HCHO + #.571 CCHO + #.419 PROD2 + #.571 INERT + #-0.287 XC
2-Methoxy-1-Propanol	2.53e-11	2.53e-11	0.000	0.0	2MEOC3OH + HO. = #.161 HO2. + #.806 RO2-R. + #.032 RO2-N. + #.763 HCHO + #.001 CCHO + #.178 RCHO + #.027 PROD2 + #.762 INERT + #1.583 XC
2-Ethoxyethanol	1.87e-11	1.87e-11	0.000	0.0	ETO-ETOH + HO. = #.015 HO2. + #.792 RO2-R. + #.02 RO2-N. + #.173 C-O2. + #.549 HCHO + #.083 CCHO + #.268 RCHO + #.437 MEK + #.206 PROD2 + #-0.793 XC
Diethylene Glycol	2.75e-11	2.75e-11	0.000	0.0	DET-GLCL + HO. = #.293 HO2. + #.68 RO2-R. + #.027 RO2-N. + #.68 HCHO + #.293 RCHO + #.68 PROD2 + #-1.802 XC
3-Ethoxy-1-Propanol	2.20e-11	2.20e-11	0.000	0.0	3ETOC3OH + HO. = #.707 RO2-R. + #.054 RO2-N. + #.476 R2O2. + #.239 C-O2. + #.691 HCHO + #.127 CCHO + #.28 RCHO + #.393 MEK + #.272 PROD2 + #-0.551 XC
3-Methoxy-1-Butanol	2.36e-12	2.36e-12	0.000	0.0	3MEOC4OH + HO. = #.933 RO2-R. + #.054 RO2-N. + #.582 R2O2. + #.012 C-O2. + #1.172 HCHO + #.155 CCHO + #.19 RCHO + #.001 MEK + #.037 PROD2 + #.715 INERT + #1.667 XC
2-Propoxyethanol	2.47e-11	2.47e-11	0.000	0.0	2PROETOH + HO. = #.944 RO2-R. + #.056 RO2-N. + #.245 R2O2. + #.407 HCHO + #.37 CCHO + #.165 RCHO + #.369 MEK + #.41 PROD2 + #-0.912 XC
1-Ethoxy-2-Propanol	2.62e-11	2.62e-11	0.000	0.0	ETOC3OH + HO. = #.163 HO2. + #.634 RO2-R. + #.043 RO2-N. + #.16 C-O2. + #.033 HCHO + #.416 CCHO + #.35 MEK + #.574 PROD2 + #-1.127 XC
2-(2-Methoxyethoxy) Ethanol	3.41e-11	3.41e-11	0.000	0.0	MOEOETOH + HO. = #.942 RO2-R. + #.058 RO2-N. + #.453 R2O2. + #.307 HCHO + #.001 CCHO + #.216 RCHO + #.019 MEK + #.718 PROD2 + #.001 HCOOH + #.519 INERT + #-1.211 XC
2-Butoxyethanol	2.57e-11	2.57e-11	0.000	0.0	BUO-ETOH + HO. = #.889 RO2-R. + #.111 RO2-N. + #.133 R2O2. + #.55 HCHO + #.013 CCHO + #.318 RCHO + #.508 MEK + #.26 PROD2 + #.21 XC

Table A-6 (continued)

Compound	Rate Parameters [a]				Reactions and Products [b]
	k(298)	A	Ea	B	
3 methoxy -3 methyl-Butanol	7.10e-12	7.10e-12	0.000	0.0	3MOMC4OH + HO. = #.126 HO2. + #.656 RO2-R. + #.053 RO2-N. + #.165 C-O2. + #.11 HCHO + #.202 CCHO + #.599 RCHO + #.026 ACET + #.141 PROD2 + #.001 HCOOH + #.181 INERT + #2.101 XC
Dipropylene Glycol	3.64e-11	3.64e-11	0.000	0.0	DPR-GLCL + HO. = #.464 HO2. + #.485 RO2-R. + #.052 RO2-N. + #.485 CCHO + #.948 PROD2 + #-0.969 XC
2-(2-Ethoxyethoxy) EtOH	5.08e-11	5.08e-11	0.000	0.0	CARBITOL + HO. = #.803 RO2-R. + #.117 RO2-N. + #.538 R2O2. + #.08 C-O2. + #.249 HCHO + #.027 CCHO + #.177 RCHO + #.405 MEK + #.757 PROD2 + #.003 HCOOH + #-1.781 XC
2-tert-Butoxy-1-Propanol	2.46e-11	2.46e-11	0.000	0.0	PG-2TB-E + HO. = #.131 HO2. + #.74 RO2-R. + #.113 RO2-N. + #.016 C-O2. + #.724 HCHO + #.166 RCHO + #.016 PROD2 + #.705 INERT + #4.283 XC
1-tert-Butoxy-2-Propanol	1.87e-11	1.87e-11	0.000	0.0	PG-1TB-E + HO. = #.407 HO2. + #.498 RO2-R. + #.076 RO2-N. + #.02 C-O2. + #.025 HCHO + #.453 CCHO + #.001 ACET + #.452 MEK + #.472 PROD2 + #.956 XC
n-Butoxy-2-Propanol	3.05e-11	3.05e-11	0.000	0.0	BUOC3OH + HO. = #.891 RO2-R. + #.109 RO2-N. + #.065 R2O2. + #.334 CCHO + #.273 RCHO + #.276 MEK + #.619 PROD2 + #.039 XC
Dipropylene Glycol Methyl Ether	4.89e-11	4.89e-11	0.000	0.0	DPRGOME + HO. = #.786 RO2-R. + #.124 RO2-N. + #.476 R2O2. + #.09 C-O2. + #.047 HCHO + #.209 CCHO + #.014 MEK + #.857 PROD2 + #.001 HCOOH + #.512 INERT + #-0.012 XC
2-(2-Butoxyethoxy)-EtOH	4.52e-11	4.52e-11	0.000	0.0	C8-CELSV + HO. = #.821 RO2-R. + #.179 RO2-N. + #.531 R2O2. + #.199 HCHO + #.01 CCHO + #.345 RCHO + #.317 MEK + #.71 PROD2 + #.146 XC
Tripropylene Glycol Monomethyl Ether	7.83e-11	7.83e-11	0.000	0.0	TPRGOME + HO. = #.573 RO2-R. + #.258 RO2-N. + #.995 R2O2. + #.169 C-O2. + #.029 HCHO + #.144 CCHO + #.098 MEK + #.947 PROD2 + #.021 HCOOH + #.403 INERT + #1.464 XC
Methyl Formate	2.27e-13	2.27e-13	0.000	0.0	ME-FORM + HO. = RO2-R. + #.914 CO + #.01 CO2 + #.01 HCHO + #.914 HCOOH + #.076 INERT + #.076 XC
Ethyl Formate	1.02e-12	1.02e-12	0.000	0.0	ET-FORM + HO. = #.138 RO2-R. + #.862 R2O2. + #.708 CCO-O2. + #.154 RCO-O2. + #.09 CO2 + #.09 CCHO + #.014 RCHO + #.708 HCOOH + #.035 INERT + #.069 XC
Methyl Acetate	3.47e-13	8.30e-13	0.517	0.0	ME-ACET + HO. = #.985 RO2-R. + #.015 RO2-N. + #.909 CO + #.909 CCO-OH + #.076 INERT + #.106 XC
Methyl Propionate	1.03e-12	1.03e-12	0.000	0.0	ME-PRAT + HO. = #.926 RO2-R. + #.042 RO2-N. + #.113 R2O2. + #.032 RCO-O2. + #.354 CO + #.032 CCHO + #.239 RCHO + #.292 MEK + #.067 PROD2 + #.304 BACL + #.024 INERT + #-0.294 XC
n-Propyl Formate	2.38e-12	2.38e-12	0.000	0.0	C3-FORM + HO. = #.173 RO2-R. + #.039 RO2-N. + #.789 R2O2. + #.788 RCO-O2. + #.053 CO2 + #.001 HCHO + #.121 RCHO + #.033 MEK + #.351 HCOOH + #.019 INERT + #.483 XC
Ethyl Acetate	1.60e-12	1.60e-12	0.000	0.0	ET-ACET + HO. = #.154 RO2-R. + #.04 RO2-N. + #.812 R2O2. + #.806 CCO-O2. + #.096 RCHO + #.006 MEK + #.018 MGLY + #.801 CCO-OH + #.039 INERT + #.141 XC
Ethyl Propionate	2.14e-12	2.14e-12	0.000	0.0	ET-PRAT + HO. = #.208 RO2-R. + #.071 RO2-N. + #.831 R2O2. + #.719 CCO-O2. + #.002 RCO-O2. + #.002 CCHO + #.15 RCHO + #.662 MEK + #.092 PROD2 + #.023 BACL + #-0.616 XC
n-Butyl Formate	3.12e-12	3.12e-12	0.000	0.0	C4-FORM + HO. = #.354 RO2-R. + #.072 RO2-N. + #.827 R2O2. + #.574 RCO-O2. + #.017 CO2 + #.119 CCHO + #.066 RCHO + #.201 MEK + #.087 PROD2 + #.14 HCOOH + #.927 XC

Table A-6 (continued)

Compound	Rate Parameters [a]				Reactions and Products [b]
	k(298)	A	Ea	B	
Methyl Butyrate	3.04e-12	3.04e-12	0.000	0.0	ME-BUAT + HO. = #.919 RO2-R. + #.066 RO2-N. + #.165 R2O2. + #.015 RCO-O2. + #.144 CO + #.001 HCHO + #.096 CCHO + #.099 RCHO + #.601 MEK + #.026 PROD2 + #.076 MGLY + #.132 BACL + #.609 XC
Propyl Acetate	3.40e-12	3.40e-12	0.000	0.0	PR-ACET + HO. = #.434 RO2-R. + #.065 RO2-N. + #.552 R2O2. + #.501 RCO-O2. + #.017 CO + #.001 HCHO + #.039 CCHO + #.05 RCHO + #.354 MEK + #.002 MGLY + #.509 CCO-OH + #.021 INERT + #.404 XC
Isopropyl Acetate	3.40e-12	3.40e-12	0.000	0.0	IPR-ACET + HO. = #.143 RO2-R. + #.073 RO2-N. + #.955 R2O2. + #.731 C-O2. + #.053 CCO-O2. + #.175 CO2 + #.058 HCHO + #.034 RCHO + #.175 ACET + #.106 MGLY + #.053 CCO-OH + #.558 INERT + #1.879 XC
Methyl Isobutyrate	1.73e-12	1.73e-12	0.000	0.0	ME-IBUAT + HO. = #.379 RO2-R. + #.075 RO2-N. + #.763 R2O2. + #.546 RCO-O2. + #.205 CO + #.106 HCHO + #.008 CCHO + #.081 RCHO + #.538 ACET + #.206 MEK + #.017 PROD2 + #.075 BACL + #-0.497 XC
t-Butyl Acetate	4.25e-13	4.25e-13	0.000	0.0	TBU-ACET + HO. = #.156 RO2-R. + #.178 RO2-N. + #1.571 R2O2. + #.667 C-O2. + #.16 CO2 + #.811 HCHO + #.16 ACET + #.156 MGLY + #.507 INERT + #1.843 XC
s-Butyl Acetate	5.50e-12	5.50e-12	0.000	0.0	SBU-ACET + HO. = #.716 RO2-R. + #.108 RO2-N. + #1.06 R2O2. + #.17 CCO-O2. + #.005 RCO-O2. + #.006 HCHO + #.835 CCHO + #.048 RCHO + #.011 MEK + #.175 CCO-OH + #.657 INERT + #2.122 XC
n-Propyl Propionate	4.02e-12	4.02e-12	0.000	0.0	PR-PRAT + HO. = #.426 RO2-R. + #.103 RO2-N. + #.571 R2O2. + #.471 RCO-O2. + #.014 CO + #.001 HCHO + #.036 CCHO + #.085 RCHO + #.732 MEK + #.05 PROD2 + #.011 BACL + #.018 INERT + #.336 XC
Ethyl Butyrate	4.94e-12	4.94e-12	0.000	0.0	ET-BUAT + HO. = #.431 RO2-R. + #.107 RO2-N. + #.61 R2O2. + #.461 CCO-O2. + #.002 RCO-O2. + #.001 HCHO + #.053 CCHO + #.093 RCHO + #.677 MEK + #.065 PROD2 + #.038 MGLY + #.02 BACL + #.757 XC
Isobutyl Acetate	4.61e-12	4.61e-12	0.000	0.0	IBU-ACET + HO. = #.817 RO2-R. + #.119 RO2-N. + #.892 R2O2. + #.008 C-O2. + #.055 RCO-O2. + #.424 CO + #.053 HCHO + #.003 CCHO + #.015 RCHO + #.76 ACET + #.055 MEK + #.479 CCO-OH + #.344 INERT + #.782 XC
n-Butyl Acetate	4.20e-12	4.20e-12	0.000	0.0	BU-ACET + HO. = #.677 RO2-R. + #.12 RO2-N. + #.516 R2O2. + #.203 RCO-O2. + #.014 CO + #.116 CCHO + #.172 RCHO + #.252 MEK + #.253 PROD2 + #.217 CCO-OH + #.016 INERT + #.932 XC
2-Ethoxyethyl Acetate	1.94e-11	1.94e-11	0.000	0.0	CSV-ACET + HO. = #.561 RO2-R. + #.108 RO2-N. + #.839 R2O2. + #.283 C-O2. + #.047 RCO-O2. + #.41 CO + #.002 HCHO + #.057 CCHO + #.055 RCHO + #.746 MEK + #.048 PROD2 + #.457 CCO-OH + #.039 INERT + #.01 XC
n-Propyl Butyrate	7.41e-12	7.41e-12	0.000	0.0	PR-BUAT + HO. = #.487 RO2-R. + #.146 RO2-N. + #.515 R2O2. + #.367 RCO-O2. + #.01 CO + #.001 HCHO + #.061 CCHO + #.062 RCHO + #.736 MEK + #.041 PROD2 + #.004 MGLY + #.011 BACL + #1.456 XC
Amyl Acetate	6.06e-12	6.06e-12	0.000	0.0	AM-ACET + HO. = #.765 RO2-R. + #.22 RO2-N. + #.742 R2O2. + #.015 RCO-O2. + #.019 CCHO + #.215 RCHO + #.639 PROD2 + #.015 CCO-OH + #1.088 XC

Table A-6 (continued)

Compound	Rate Parameters [a]				Reactions and Products [b]
	k(298)	A	Ea	B	
Butyl Propionate	5.06e-12	5.06e-12	0.000	0.0	BU-PRAT + HO. = #.634 RO2-R. + #.167 RO2-N. + #.533 R2O2. + #.199 RCO-O2. + #.012 CO + #.102 CCHO + #.178 RCHO + #.412 MEK + #.25 PROD2 + #.007 BACL + #.014 INERT + #1.465 XC
Ethyl 3-Ethoxy Propionate	1.96e-11	1.96e-11	0.000	0.0	E3EOC3OH + HO. = #.407 RO2-R. + #.157 RO2-N. + #.987 R2O2. + #.279 C-O2. + #.157 CCO-O2. + #.002 HCHO + #.058 CCHO + #.056 RCHO + #.823 MEK + #.079 PROD2 + #.316 MGLY + #.001 BACL + #.464 XC
n-Butyl Butyrate	1.06e-11	1.06e-11	0.000	0.0	BU-BUAT + HO. = #.621 RO2-R. + #.213 RO2-N. + #.486 R2O2. + #.166 RCO-O2. + #.009 CO + #.104 CCHO + #.136 RCHO + #.465 MEK + #.199 PROD2 + #.003 MGLY + #.007 BACL + #2.511 XC
Isobutyl Isobutyrate	5.52e-12	5.52e-12	0.000	0.0	IBU-IBTR + HO. = #.692 RO2-R. + #.233 RO2-N. + #.906 R2O2. + #.006 C-O2. + #.069 RCO-O2. + #.302 CO + #.069 HCHO + #.002 CCHO + #.034 RCHO + #.658 ACET + #.726 MEK + #.003 PROD2 + #.003 BACL + #1.007 XC
Isoamyl Isobutyrate	6.94e-12	6.94e-12	0.000	0.0	IC5IBUAT + HO. = #.588 RO2-R. + #.294 RO2-N. + #.844 R2O2. + #.118 RCO-O2. + #.028 HCHO + #.457 RCHO + #.435 ACET + #.135 MEK + #.118 PROD2 + #.002 BACL + #2.919 XC
2-Ethyl-Hexyl Acetate	1.10e-11	1.10e-11	0.000	0.0	2ETHXACT + HO. = #.582 RO2-R. + #.414 RO2-N. + #.934 R2O2. + #.004 RCO-O2. + #.004 CO + #.096 CCHO + #.127 RCHO + #.075 MEK + #.478 PROD2 + #.008 CCO-OH + #.062 INERT + #3.686 XC
Propylene Carbonate	6.90e-13	6.90e-13	0.000	0.0	PC + HO. = #.63 RO2-R. + #.021 RO2-N. + #1.507 R2O2. + #.349 CCO-O2. + #.527 CO + #.213 HCHO + #.034 RCHO + #.945 INERT + #1.39 XC
Methyl Lactate	2.76e-12	2.76e-12	0.000	0.0	ME-LACT + HO. = #.835 HO2. + #.154 RO2-R. + #.006 RO2-N. + #.005 RCO-O2. + #.08 CO + #.061 HCHO + #.005 CCHO + #.007 MEK + #.08 PROD2 + #.061 MGLY + #.841 BACL + #-0.256 XC
Ethyl Lactate	3.91e-12	3.91e-12	0.000	0.0	ET-LACT + HO. = #.182 HO2. + #.453 RO2-R. + #.031 RO2-N. + #.334 CCO-O2. + #.001 RCO-O2. + #.039 HCHO + #.001 CCHO + #.039 RCHO + #.016 MEK + #.334 PROD2 + #.039 MGLY + #.541 BACL + #-0.358 XC
1-Methoxy-2-Propyl Acetate	1.44e-11	1.44e-11	0.000	0.0	PGME-ACT + HO. = #.327 RO2-R. + #.126 RO2-N. + #1.399 R2O2. + #.539 CCO-O2. + #.008 RCO-O2. + #.031 HCHO + #.003 RCHO + #.049 MEK + #.05 PROD2 + #.547 CCO-OH + #1.005 INERT + #1.512 XC
2-Methyoxy-1-propyl Acetate	2.30e-11	2.30e-11	0.000	0.0	2PGMEACT + HO. = #.828 RO2-R. + #.109 RO2-N. + #.93 R2O2. + #.059 C-O2. + #.005 RCO-O2. + #.714 CO + #.011 HCHO + #.011 CCHO + #.043 MEK + #.001 PROD2 + #.001 HCOOH + #.718 CCO-OH + #.978 INERT + #1.937 XC
Dimethyl Succinate	1.50e-12	1.50e-12	0.000	0.0	DBE-4 + HO. = #.879 RO2-R. + #.121 RO2-N. + #.513 R2O2. + #.722 CO + #.383 MEK + #.398 PROD2 + #.098 BACL + #.24 XC
Diisopropyl Carbonate	6.88e-12	6.88e-12	0.000	0.0	DIPR-CB + HO. = #.252 RO2-R. + #.137 RO2-N. + #.648 R2O2. + #.578 C-O2. + #.032 CCO-O2. + #.202 CO2 + #.038 HCHO + #.049 RCHO + #.404 ACET + #.612 MEK + #1.487 XC
Dimethyl Glutarate	3.50e-12	3.50e-12	0.000	0.0	DBE-5 + HO. = #.829 RO2-R. + #.171 RO2-N. + #.153 R2O2. + #.417 CO + #.384 MEK + #.417 PROD2 + #.028 BACL + #1.407 XC
Dimethyl Adipate	8.80e-12	8.80e-12	0.000	0.0	DBE-6 + HO. = #.785 RO2-R. + #.215 RO2-N. + #.616 R2O2. + #.089 CO + #.881 RCHO + #.138 MEK + #.085 PROD2 + #.019 MGLY + #.124 BACL + #2.368 XC
2-Butoxyethyl Acetate	2.38e-11	2.38e-11	0.000	0.0	2BUETACT + HO. = #.769 RO2-R. + #.202 RO2-N. + #.89 R2O2. + #.03 RCO-O2. + #.351 CO + #.017 CCHO + #.359 RCHO + #.675 MEK + #.105 PROD2 + #.38 CCO-OH + #.031 INERT + #1.116 XC

Table A-6 (continued)

Compound	Rate Parameters [a]				Reactions and Products [b]
	k(298)	A	Ea	B	
Ethylene Oxide	7.60e-14	7.60e-14	0.000	0.0	ETOX + HO. = RO2-R. + R2O2. + #.914 CO + #.01 CO2 + #.01 HCHO + #.914 HCOOH + #.076 INERT + #.076 XC
Propylene Oxide	5.20e-13	5.20e-13	0.000	0.0	PROX + HO. = #.777 RO2-R. + #.008 RO2-N. + #1.429 R2O2. + #.215 CCO-O2. + #.675 CO + #.03 CO2 + #.222 HCHO + #.027 CCHO + #.006 RCHO + #.416 HCOOH + #.474 CCO-OH + #.067 INERT + #.093 XC
1,2-Epoxybutane	1.91e-12	1.91e-12	0.000	0.0	12BUOX + HO. = #.805 RO2-R. + #.057 RO2-N. + #1.733 R2O2. + #.138 RCO-O2. + #.713 CO + #.025 CO2 + #.006 HCHO + #.555 CCHO + #.019 RCHO + #.21 MEK + #.645 HCOOH + #.063 INERT + #-0.216 XC
Formic Acid	4.50e-13	4.50e-13	0.000	0.0	FORMACID + HO. = HO2. + CO2
Acetic Acid	8.00e-13	8.00e-13	0.000	0.0	ACETACID + HO. = #.491 RO2-R. + #.509 C-O2. + #.509 CO2 + #.491 MGLY + #-0.491 XC
Propionic Acid	1.16e-12	1.16e-12	0.000	0.0	PROPACID + HO. = RO2-R. + #.142 CO2 + #.142 CCHO + #.4 RCHO + #.457 BACL + #-0.457 XC
Methyl Acrylate	3.16e-11	3.16e-11	0.000	0.0	ME-ACRYL + HO. = #.942 RO2-R. + #.039 RO2-N. + #.02 R2O2. + #.02 RCO-O2. + #.862 HCHO + #.079 RCHO + #.02 CCO-OH + #.862 INERT + #1.707 XC
	1.01e-17	1.01e-17	0.000	0.0	ME-ACRYL + O3 = #.06 HO. + #.06 HO2. + #.25 CO + #.065 CO2 + #.5 HCHO + #.185 HCOOH + #.5 INERT + #2.5 XC
	1.38e-14	1.38e-14	0.000	0.0	ME-ACRYL + NO3 = #.032 RO2-R. + #.039 RO2-N. + #.929 R2O2. + #.929 RCO-O2. + #.929 CCO-OH + #-0.878 XC + XN
	5.60e-12	5.60e-12	0.000	0.0	ME-ACRYL + O3P = #.45 RCHO + #.55 MEK + #.45 XC
Vinyl Acetate	3.16e-11	3.16e-11	0.000	0.0	VIN-ACET + HO. = #.949 RO2-R. + #.042 RO2-N. + #.085 R2O2. + #.01 RCO-O2. + #.061 CO + #.682 HCHO + #.01 CCHO + #.066 PROD2 + #.682 MGLY + #.201 BACL + #-0.286 XC
	1.01e-17	1.01e-17	0.000	0.0	VIN-ACET + O3 = #.06 HO. + #.06 HO2. + #.25 CO + #.065 CO2 + #.5 HCHO + #.5 MGLY + #.185 HCOOH + #1.5 XC
	1.38e-14	1.38e-14	0.000	0.0	VIN-ACET + NO3 = #.917 RO2-R. + #.049 RO2-N. + #.292 R2O2. + #.034 RCO-O2. + #.209 CO + #.034 RCHO + #.691 BACL + #.227 RNO3 + #-0.828 XC + #.773 XN
	5.60e-12	5.60e-12	0.000	0.0	VIN-ACET + O3P = #.45 RCHO + #.55 MEK + #.45 XC
Ethyl Acrylate	3.16e-11	3.16e-11	0.000	0.0	ET-ACRYL + HO. = #.523 RO2-R. + #.094 RO2-N. + #.854 R2O2. + #.383 CCO-O2. + #.416 HCHO + #.402 PROD2 + #.416 MGLY + #.088 BACL + #-0.758 XC
	1.01e-17	1.01e-17	0.000	0.0	ET-ACRYL + O3 = #.06 HO. + #.06 HO2. + #.25 CO + #.065 CO2 + #.5 HCHO + #.5 MGLY + #.185 HCOOH + #2.5 XC
	1.38e-14	1.38e-14	0.000	0.0	ET-ACRYL + NO3 = #.193 RO2-R. + #.118 RO2-N. + #1.536 R2O2. + #.689 CCO-O2. + #.159 BACL + #.723 RNO3 + #-2.06 XC + #.277 XN
	5.60e-12	5.60e-12	0.000	0.0	ET-ACRYL + O3P = #.45 RCHO + #.55 MEK + #1.45 XC
2-Methylpropanal	2.63e-11	6.61e-12	-0.817	0.0	2MEC3AL + HO. = #.082 RO2-R. + #.004 RO2-N. + #.011 R2O2. + #.914 RCO-O2. + #.078 CO + #.011 HCHO + #.011 CCHO + #.004 RCHO + #.067 ACET + #.91 XC
	2.84e-15	2.84e-15	0.000	0.0	2MEC3AL + NO3 = RCO-O2. + XC + XN
	Phot Set = C2CHO				2MEC3AL + HV = HO2. + #.96 RO2-R. + #.04 RO2-N. + CO + #.96 ACET + #-0.12 XC

Table A-6 (continued)

Compound	Rate Parameters [a]				Reactions and Products [b]
	k(298)	A	Ea	B	
Butanal	2.35e-11	5.26e-12	-0.886	0.0	1C4RCHO + HO. = #.088 RO2-R. + #.008 RO2-N. + #.015 R2O2. + #.905 RCO-O2. + #.052 CO + #.014 HCHO + #.015 CCHO + #.073 RCHO + #.001 GLY + #.925 XC
	2.84e-15	2.84e-15	0.000	0.0	1C4RCHO + NO3 = RCO-O2. + XC + XN
		Phot Set = C2CHO			1C4RCHO + HV = HO2. + #.98 RO2-R. + #.02 RO2-N. + CO + #.98 RCHO + #-0.06 XC
Pentanal	2.85e-11	6.34e-12	-0.890	0.0	1C5RCHO + HO. = #.089 RO2-R. + #.018 RO2-N. + #.08 R2O2. + #.893 RCO-O2. + #.043 CO + #.011 HCHO + #.021 CCHO + #.087 RCHO + #.002 MGLY + #1.851 XC
	2.84e-15	2.84e-15	0.000	0.0	1C5RCHO + NO3 = RCO-O2. + #2 XC + XN
		Phot Set = C2CHO			1C5RCHO + HV = #.244 HO2. + #1.688 RO2-R. + #.068 RO2-N. + CO + #.932 RCHO + #.796 XC
2,2-Dimethylpropanal (pivaldehyde)	2.66e-11	6.82e-12	-0.805	0.0	22DMC3AL + HO. = #.023 RO2-R. + #.003 RO2-N. + #.024 R2O2. + #.974 RCO-O2. + #.023 CO + #.024 HCHO + #.001 RCHO + #.023 ACET + #1.946 XC
	2.84e-15	2.84e-15	0.000	0.0	22DMC3AL + NO3 = RCO-O2. + #2 XC + XN
		Phot Set = C2CHO			22DMC3AL + HV = #.039 HO2. + #.961 RO2-R. + #.039 RO2-N. + #.961 TBU-O. + CO + #.884 XC
3-Methylbutanal	2.74e-11	2.74e-11	0.000	0.0	3MC4RCHO + HO. = #.13 RO2-R. + #.012 RO2-N. + #.112 R2O2. + #.002 C-O2. + #.856 RCO-O2. + #.125 CO + #.092 HCHO + #.036 RCHO + #.096 ACET + #.004 GLY + #1.736 XC
	2.84e-15	2.84e-15	0.000	0.0	3MC4RCHO + NO3 = RCO-O2. + #2 XC + XN
		Phot Set = C2CHO			3MC4RCHO + HV = #.652 HO2. + #1.295 RO2-R. + #.053 RO2-N. + CO + #.348 HCHO + #.614 RCHO + #.334 ACET + #.494 XC
Glutaraldehyde	4.16e-11	4.16e-11	0.000	0.0	GLTRALD + HO. = #.04 RO2-R. + #.009 RO2-N. + #.051 R2O2. + #.951 RCO-O2. + #.033 CO + #.023 HCHO + #.04 RCHO + #.001 GLY + #1.916 XC
	5.68e-15	5.68e-15	0.000	0.0	GLTRALD + NO3 = RCO-O2. + #2 XC + XN
		Phot Set = C2CHO			GLTRALD + HV = #.039 HO2. + #.961 RO2-R. + #.039 RO2-N. + #.961 RCO-O2. + CO + #.884 XC
Hexanal	2.43e-11	2.43e-11	0.000	0.0	1C6RCHO + HO. = #.112 RO2-R. + #.04 RO2-N. + #.154 R2O2. + #.848 RCO-O2. + #.014 CO + #.002 HCHO + #.103 RCHO + #.018 MGLY + #2.835 XC
	2.84e-15	2.84e-15	0.000	0.0	1C6RCHO + NO3 = RCO-O2. + #3 XC + XN
		Phot Set = C2CHO			1C6RCHO + HV = #.064 HO2. + #1.813 RO2-R. + #.124 RO2-N. + CO + #.876 RCHO + #1.629 XC
Heptanal	2.57e-11	2.57e-11	0.000	0.0	1C7RCHO + HO. = #.136 RO2-R. + #.066 RO2-N. + #.192 R2O2. + #.797 RCO-O2. + #.009 CO + #.119 RCHO + #.017 MGLY + #3.792 XC
	2.84e-15	2.84e-15	0.000	0.0	1C7RCHO + NO3 = RCO-O2. + #4 XC + XN
		Phot Set = C2CHO			1C7RCHO + HV = #.096 HO2. + #1.72 RO2-R. + #.183 RO2-N. + CO + #.817 RCHO + #2.45 XC
Octanal	2.71e-11	2.71e-11	0.000	0.0	1C8RCHO + HO. = #.164 RO2-R. + #.096 RO2-N. + #.219 R2O2. + #.74 RCO-O2. + #.008 CO + #.149 RCHO + #.015 MGLY + #4.705 XC
	2.84e-15	2.84e-15	0.000	0.0	1C8RCHO + NO3 = RCO-O2. + #5 XC + XN
	2.84e-15	2.84e-15	0.000	0.0	1C8RCHO + NO3 = RCO-O2. + #5 XC + XN

Table A-6 (continued)

Compound	Rate Parameters [a]				Reactions and Products [b]
	k(298)	A	Ea	B	
Acrolein	1.99e-11	1.99e-11	0.000	0.0	ACROLEIN + HO. = #.25 RO2-R. + #.75 MA-RCO3. + #.167 CO + #.083 HCHO + #.167 CCHO + #.083 GLY + #-0.75 XC
	2.90e-19	1.36e-15	5.006	0.0	ACROLEIN + O3 = #.31 HO. + #.81 HO2. + CO + #.315 CO2 + #.5 HCHO + #.5 GLY + #.185 HCOOH
	2.94e-15	2.94e-15	0.000	0.0	ACROLEIN + NO3 = #.031 RO2-R. + #.002 RO2-N. + #.967 MA-RCO3. + #.031 CO + #.031 RCHO + #-1.003 XC + XN
	2.37e-12	2.37e-12	0.000	0.0	ACROLEIN + O3P = RCHO
	Phot Set = ACROLEIN, QY =			2.0e-3	ACROLEIN + HV = #.172 HO. + #1.01 HO2. + #.172 C-O2. + #.33 MA-RCO3. + #1.182 CO + #.046 CO2 + #.34 HCHO + #.112 CCO-OH + #.046 INERT + #-0.284 XC
Crotonaldehyde	3.64e-11	3.64e-11	0.000	0.0	CROTALD + HO. = #.529 RO2-R. + #.021 RO2-N. + #.45 MA-RCO3. + #.032 CO + #.497 CCHO + #.032 RCHO + #.497 GLY + #-0.043 XC
	9.00e-19	9.00e-19	0.000	0.0	CROTALD + O3 = #.51 HO. + #.75 HO2. + #.26 C-O2. + #1.01 CO + #.32 CO2 + #.5 CCHO + #.5 GLY + #.17 CCO-OH + #.07 INERT + #.07 XC
	5.12e-15	5.12e-15	0.000	0.0	CROTALD + NO3 = #.13 NO2 + #.377 RO2-R. + #.044 RO2-N. + #.13 R2O2. + #.45 MA-RCO3. + #.253 CO + #.45 HNO3 + #.13 CCHO + #.377 RCHO + #.13 GLY + #.036 XC + #.42 XN
	7.29e-12	7.29e-12	0.000	0.0	CROTALD + O3P = #.88 RCHO + #.12 MGLY + XC
	Phot Set = ACROLEIN, QY =			2.1e-3	CROTALD + HV = #2 HO2. + #2 CO + CCHO
Hydroxy Methacrolein	4.30e-11	4.30e-11	0.000	0.0	HOMACR + HO. = #.596 RO2-R. + #.024 RO2-N. + #.38 MA-RCO3. + #.445 CO + #.151 HCHO + #.445 PROD2 + #.151 MGLY + #-1.382 XC
	1.13e-18	1.36e-15	4.200	0.0	HOMACR + O3 = #.208 HO. + #.208 HO2. + #.45 CO + #.117 CO2 + #.1 HCHO + MGLY + #.333 HCOOH
	4.58e-15	1.50e-12	3.430	0.0	HOMACR + NO3 = #.481 RO2-R. + #.019 RO2-N. + #.5 MA-RCO3. + #.453 CO + #.5 HNO3 + #.028 HCHO + #.028 MGLY + #.453 RNO3 + #-1.397 XC + #.047 XN
	9.95e-12	9.95e-12	0.000	0.0	HOMACR + O3P = RCHO + XC
	Phot Set = ACROLEIN, QY =			2.1e-3	HOMACR + HV = HO2. + RCO-O2. + CO + HCHO + #-1 XC
Cyclobutanone	8.70e-13	8.70e-13	0.000	0.0	CC4-KET + HO. = #.072 RO2-N. + #1.784 R2O2. + #.928 RCO-O2. + #.823 HCHO + #-0.038 XC
	Phot Set = KETONE, QY =			1.5e-1	CC4-KET + HV = #4 XC
Methyl Ethyl Ketone	1.19e-12	1.30e-12	0.050	0.0	MEK + HO. = #.376 RO2-R. + #.039 RO2-N. + #.592 R2O2. + #.511 CCO-O2. + #.074 RCO-O2. + #.088 HCHO + #.504 CCHO + #.376 RCHO + #.299 XC
	Phot Set = KETONE, QY =			1.5e-1	MEK + HV = RO2-R. + CCO-O2. + CCHO
Cyclopentanone	2.94e-12	2.94e-12	0.000	0.0	CC5-KET + HO. = #.626 RO2-R. + #.116 RO2-N. + #1.074 R2O2. + #.258 RCO-O2. + #.077 HCHO + #.626 RCHO + #.029 GLY + #1.518 XC
	Phot Set = KETONE, QY =			1.0e-1	CC5-KET + HV = #5 XC
3-Pentanone	2.00e-12	2.00e-12	0.000	0.0	DEK + HO. = #.375 RO2-R. + #.066 RO2-N. + #.589 R2O2. + #.559 RCO-O2. + #.559 CCHO + #.375 RCHO + #.684 XC
	Phot Set = KETONE, QY =			1.0e-1	DEK + HV = RO2-R. + RCO-O2. + CCHO
2-Pentanone	4.56e-12	4.56e-12	0.000	0.0	MPK + HO. = #.154 RO2-R. + #.064 RO2-N. + #1.374 R2O2. + #.762 CCO-O2. + #.02 RCO-O2. + #.613 HCHO + #.592 CCHO + #.204 RCHO + #.121 MEK + #.144 XC
	Phot Set = KETONE, QY =			1.0e-1	MPK + HV = #.98 RO2-R. + #.02 RO2-N. + CCO-O2. + #.98 RCHO + #-0.06 XC

Table A-6 (continued)

Compound	Rate Parameters [a]				Reactions and Products [b]
	k(298)	A	Ea	B	
Cyclohexanone	6.39e-12	6.39e-12	0.000	0.0	CC6-KET + HO. = #.387 RO2-R. + #.177 RO2-N. + #.722 R2O2. + #.436 RCO-O2. + #.059 HCHO + #.194 RCHO + #.197 PROD2 + #1.803 XC
	Phot Set = KETONE, QY =			5.0e-2	CC6-KET + HV = #6 XC
Methyl t-Butyl Ketone	1.21e-12	1.21e-12	0.000	0.0	MTBK + HO. = #.021 RO2-R. + #.149 RO2-N. + #1.657 R2O2. + #.774 CCO-O2. + #.055 RCO-O2. + #.882 HCHO + #.021 RCHO + #.774 ACET + #.122 XC
	Phot Set = KETONE, QY =			5.0e-2	MTBK + HV = #.039 RO2-N. + #.961 R2O2. + CCO-O2. + #.961 TBU-O. + #.884 XC
4-Methyl-2-Pentanone	1.41e-11	1.41e-11	0.000	0.0	MIBK + HO. = #.012 RO2-R. + #.098 RO2-N. + #1.708 R2O2. + #.879 CCO-O2. + #.011 RCO-O2. + #.829 HCHO + #.021 CCHO + #.096 RCHO + #.769 ACET + #.004 MEK + #.135 XC
	Phot Set = KETONE, QY =			5.0e-2	MIBK + HV = #.947 RO2-R. + #.053 RO2-N. + #.348 R2O2. + CCO-O2. + #.348 HCHO + #.614 RCHO + #.334 ACET + #.494 XC
Methyl n-Butyl Ketone	9.10e-12	9.10e-12	0.000	0.0	MNBK + HO. = #.425 RO2-R. + #.101 RO2-N. + #1.016 R2O2. + #.46 CCO-O2. + #.014 RCO-O2. + #.339 HCHO + #.195 CCHO + #.651 RCHO + #.145 MEK + #.088 PROD2 + #.642 XC
	Phot Set = KETONE, QY =			5.0e-2	MNBK + HV = #.932 RO2-R. + #.068 RO2-N. + #.756 R2O2. + CCO-O2. + #.932 RCHO + #.796 XC
Di-Isopropyl Ketone	5.38e-12	5.38e-12	0.000	0.0	DIPK + HO. = #.095 RO2-R. + #.16 RO2-N. + #1.017 R2O2. + #.745 RCO-O2. + #.26 HCHO + #.235 CCHO + #.095 RCHO + #.51 ACET + #1.26 XC
	Phot Set = KETONE, QY =			2.0e-2	DIPK + HV = #.96 RO2-R. + #.04 RO2-N. + RCO-O2. + #.96 ACET + #.88 XC
2-Methyl-3-Hexanone	7.21e-12	7.21e-12	0.000	0.0	2M-3-HXO + HO. = #.298 RO2-R. + #.161 RO2-N. + #.829 R2O2. + #.54 RCO-O2. + #.19 HCHO + #.188 CCHO + #.161 RCHO + #.252 ACET + #.244 MEK + #1.629 XC
	Phot Set = KETONE, QY =			2.0e-2	2M-3-HXO + HV = #.98 RO2-R. + #.02 RO2-N. + RCO-O2. + #.98 RCHO + #.94 XC
2-Heptanone	1.17e-11	1.17e-11	0.000	0.0	C7-KET-2 + HO. = #.514 RO2-R. + #.191 RO2-N. + #.938 R2O2. + #.284 CCO-O2. + #.011 RCO-O2. + #.099 HCHO + #.013 CCHO + #.591 RCHO + #.348 PROD2 + #1.266 XC
	Phot Set = KETONE, QY =			2.0e-2	C7-KET-2 + HV = #.876 RO2-R. + #.124 RO2-N. + #.936 R2O2. + CCO-O2. + #.876 RCHO + #1.629 XC
2-Octanone	1.10e-11	1.10e-11	0.000	0.0	C8-KET-2 + HO. = #.517 RO2-R. + #.294 RO2-N. + #.916 R2O2. + #.18 CCO-O2. + #.009 RCO-O2. + #.014 HCHO + #.226 RCHO + #.488 PROD2 + #2.228 XC
	Phot Set = KETONE, QY =			1.0e-2	C8-KET-2 + HV = #.817 RO2-R. + #.183 RO2-N. + #.904 R2O2. + CCO-O2. + #.817 RCHO + #2.45 XC
2-Nonanone	1.22e-11	1.22e-11	0.000	0.0	C9-KET-2 + HO. = #.504 RO2-R. + #.355 RO2-N. + #.872 R2O2. + #.14 CCO-O2. + #.149 RCHO + #.495 PROD2 + #3.167 XC
Di-isobutyl ketone (2,6-dimethyl-4-heptanone)	2.75e-11	2.75e-11	0.000	0.0	DIBK + HO. = #.019 RO2-R. + #.28 RO2-N. + #1.404 R2O2. + #.014 C-O2. + #.687 RCO-O2. + #.595 HCHO + #.005 CCHO + #.123 RCHO + #.626 ACET + #.026 PROD2 + #2.233 XC
2-Decanone	1.32e-11	1.32e-11	0.000	0.0	C10-K-2 + HO. = #.521 RO2-R. + #.395 RO2-N. + #.807 R2O2. + #.083 CCO-O2. + #.087 RCHO + #.518 PROD2 + #4.095 XC
Hydroxy Acetone	3.02e-12	3.02e-12	0.000	0.0	HOACET + HO. = #.756 HO2. + #.034 RO2-R. + #.177 CCO-O2. + #.034 RCO-O2. + #.211 HCHO + #.789 MGLY + #-0.034 XC
	Phot Set = KETONE, QY =			1.5e-1	HOACET + HV = HO2. + CCO-O2. + HCHO

Table A-6 (continued)

Compound	Rate Parameters [a]				Reactions and Products [b]
	k(298)	A	Ea	B	
Methoxy Acetone	6.77e-12	6.77e-12	0.000	0.0	MEOACET + HO. = #.148 RO2-R. + #.039 RO2-N. + #.813 R2O2. + #.799 CCO-O2. + #.014 RCO-O2. + #.028 HCHO + #.148 MEK + #.792 INERT + #.714 XC
	Phot Set = KETONE, QY =			1.0e-1	MEOACET + HV = RO2-R. + CCO-O2. + #.079 HCHO + #.961 INERT + #.961 XC
Diacetone Alcohol	1.49e-12	1.49e-12	0.000	0.0	DIACTALC + HO. = #.233 RO2-R. + #.085 RO2-N. + #.682 R2O2. + #.619 CCO-O2. + #.063 RCO-O2. + #.388 HCHO + #.501 RCHO + #.143 ACET + #.207 MEK + #.026 MGLY + #.835 XC
	Phot Set = KETONE, QY =			2.0e-2	DIACTALC + HV = #.93 RO2-R. + #.07 RO2-N. + CCO-O2. + #.93 HCHO + #.93 ACET + #-0.14 XC
Nitrobenzene	1.50e-13	1.50e-13	0.000	0.0	NO2-BENZ + HO. = #.236 HO2. + #.764 RO2-R. + #.207 GLY + #.236 PHEN + #.764 DCB1 + #1.114 XC
Toluene Diisocyanate	7.40e-12	7.40e-12	0.000	0.0	TDI + HO. = #.5 HO. + CRES
Para Toluene Isocyanate	5.90e-12	5.90e-12	0.000	0.0	P-TI + HO. = #.2 HO. + #.7 HO2. + #.15 MGLY + CRES
Methylene Diphenylene Diisocyanate	1.18e-11	1.18e-11	0.000	0.0	MDI + HO. = #.2 HO. + #.7 HO2. + #.15 MGLY + CRES
	1.18e-11	1.18e-11	0.000	0.0	MDI + HO. = #.2 HO. + #.7 HO2. + #.15 MGLY + CRES
Ethyl Amine	2.77e-11	1.47e-11	-0.376	0.0	ET-AMINE + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
Dimethyl Amine	6.62e-11	2.89e-11	-0.491	0.0	DM-AMINE + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
Trimethyl Amine	6.11e-11	2.62e-11	-0.501	0.0	TM-AMINE + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
Ethanolamine	3.15e-11	3.15e-11	0.000	0.0	ETOH-NH2 + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
Diethanol Amine	9.37e-11	9.37e-11	0.000	0.0	ETOH2-NH + HO. = #.96 RO2-R. + #.04 RO2-N. + #.5 HCHO + #.5 RCHO
Triethanolamine	1.16e-10	1.16e-10	0.000	0.0	ETOH3-N + HO. = #.905 RO2-R. + #.095 RO2-N. + #.5 HCHO + #.5 RCHO
N-Methyl-2-Pyrrolidone	2.15e-11	2.15e-11	0.000	0.0	NMP + HO. = #.92 HO2. + #.08 RO2-N. + #.46 RCHO + #.46 PROD2 + #.38 XC + XN
	1.26e-13	1.26e-13	0.000	0.0	NMP + NO3 = #.92 HO2. + #.08 RO2-N. + #.92 PROD2 + #-1 XC + XN
Methyl Chloride	4.36e-14	3.15e-13	1.163	2.0	CH3-CL + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
Dichloromethane	1.42e-13	7.69e-13	0.994	2.0	CL2-ME + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
Methyl Bromide	4.02e-14	2.34e-13	1.035	2.0	ME-BR + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
Chloroform	1.03e-13	5.67e-13	1.002	2.0	CHCL3 + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
Vinyl Chloride	6.97e-12	1.69e-12	-0.839	0.0	CL-ETHE + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
Ethyl Chloride	4.11e-13	6.94e-13	0.302	2.0	C2-CL + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
1,1-Dichloroethane	2.60e-13	2.60e-13	0.000	0.0	11CL2-C2 + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
1,2-Dichloroethane	2.48e-13	9.90e-13	0.813	2.0	12CL2-C2 + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
Ethyl Bromide	2.99e-13	2.72e-11	2.671	0.0	C2-BR + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
1,1,2-Trichloroethane	1.97e-13	4.00e-13	0.413	2.0	112CL3C2 + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
1,1,1-Trichloroethane	1.19e-14	5.33e-13	2.244	2.0	111-TCE + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
1,2-Dibromoethane	2.22e-13	9.27e-13	0.839	2.0	11BR2-C2 + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
n-Propyl Bromide	1.18e-12	1.18e-12	0.000	0.0	C3-BR + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
n-Butyl Bromide	2.46e-12	2.46e-12	0.000	0.0	C4-BR + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
Trans-1,2-Dichloroethene	2.34e-12	1.01e-12	-0.497	0.0	T-12-DCE + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
Trichloroethylene	2.36e-12	5.63e-13	-0.849	0.0	CL3-ETHE + HO. = RO2-R. + #.5 HCHO + #.5 RCHO

Table A-6 (continued)

Compound	Rate Parameters [a]				Reactions and Products [b]
	k(298)	A	Ea	B	
Perchloroethylene	1.67e-13	9.64e-12	2.403	0.0	CL4-ETHE + HO. = RO2-R. + #.5 HCHO + #.5 RCHO
2-(Cl-methyl)-3-Cl-Propene	3.16e-11	3.16e-11	0.000	0.0	CL2IBUTE + HO. = #.481 RO2-R. + #.039 RO2-N. + #.961 R2O2. + #.481 Cl. + #.961 HCHO + #.961 MEK + #-1.039 XC
	3.90e-19	3.90e-19	0.000	0.0	CL2IBUTE + O3 = #.707 HO. + #.04 RO2-R. + #.627 R2O2. + #.667 Cl. + #.167 CO + #.043 CO2 + #.667 HCHO + #.333 MEK + #.667 MGLY + #.123 HCOOH + #-0.333 XC
	1.00e-15	1.00e-15	0.000	0.0	CL2IBUTE + NO3 = #.039 RO2-N. + #1.923 R2O2. + #.961 Cl. + #.961 HCHO + #2.807 XC + XN
	5.60e-12	5.60e-12	0.000	0.0	CL2IBUTE + O3P = #.4 RCHO + #.6 MEK + #.4 XC
Monochlorobenzene	7.70e-13	7.70e-13	0.000	0.0	CL-BEN + HO. = #.236 HO2. + #.764 RO2-R. + #.207 GLY + #.236 PHEN + #.764 DCB1 + #1.114 XC
p-Dichlorobenzene	5.55e-13	5.55e-13	0.000	0.0	CL2-BEN + HO. = #.236 HO2. + #.764 RO2-R. + #.207 GLY + #.236 PHEN + #.764 DCB1 + #1.114 XC
Benzotrifluoride	4.60e-13	4.60e-13	0.000	0.0	CF3-BEN + HO. = #.234 HO2. + #.758 RO2-R. + #.008 RO2-N. + #.116 GLY + #.135 MGLY + #.234 CRES + #.085 BALD + #.46 DCB1 + #.156 DCB2 + #.057 DCB3 + #1.178 XC
p-Trifluoromethyl-Cl-Benzene	2.40e-13	2.40e-13	0.000	0.0	PCBTF + HO. = #.234 HO2. + #.758 RO2-R. + #.008 RO2-N. + #.116 GLY + #.135 MGLY + #.234 CRES + #.085 BALD + #.46 DCB1 + #.156 DCB2 + #.057 DCB3 + #1.178 XC
Species Used to Derive Lumped Parameter Model Species in the Base Mechanism					
Isoprene Product #1	7.00e-11	7.00e-11	0.000	0.0	IP-MHY1 + HO. = #.702 RO2-R. + #.048 RO2-N. + #.25 MA-RCO3. + #.426 CO + #.276 CCHO + #.426 PROD2 + #.276 MGLY + #-0.65 XC
	1.00e-17	1.00e-17	0.000	0.0	IP-MHY1 + O3 = #.202 HO. + #.002 HO2. + #.1 RO2-R. + #.1 RCO-O2. + #.102 CO + #.202 HCHO + #.1 CCHO + #.9 MGLY + #.798 RCO-OH + #-0.898 XC
	1.00e-13	1.00e-13	0.000	0.0	IP-MHY1 + NO3 = #.936 RO2-R. + #.064 RO2-N. + #.936 CO + #.936 RNO3 + #-1.936 XC + #.064 XN
	2.47e-11	2.47e-11	0.000	0.0	IP-MHY1 + O3P = RCHO + #2 XC
	Phot Set = ACROLEIN, QY =			4.1e-3	IP-MHY1 + HV = HO2. + CCO-O2. + CO + CCHO
Isoprene Product #2	7.00e-11	7.00e-11	0.000	0.0	IP-MHY2 + HO. = #.702 RO2-R. + #.048 RO2-N. + #.25 MA-RCO3. + #.426 CO + #.276 CCHO + #.426 PROD2 + #.276 MGLY + #-0.65 XC
	1.00e-17	1.00e-17	0.000	0.0	IP-MHY2 + O3 = #.202 HO. + #.002 HO2. + #.1 RO2-R. + #.1 RCO-O2. + #.102 CO + #.202 HCHO + #.1 CCHO + #.9 MGLY + #.798 RCO-OH + #-0.898 XC
	1.00e-13	1.00e-13	0.000	0.0	IP-MHY2 + NO3 = #.936 RO2-R. + #.064 RO2-N. + #.936 CO + #.936 RNO3 + #-1.936 XC + #.064 XN
	2.47e-11	2.47e-11	0.000	0.0	IP-MHY2 + O3P = RCHO + #2 XC
	Phot Set = ACROLEIN, QY =			2.1e-3	IP-MHY2 + HV = HO2. + CCO-O2. + CO + CCHO
Isoprene Product #3	7.00e-11	7.00e-11	0.000	0.0	IP-HMY + HO. = #.702 RO2-R. + #.048 RO2-N. + #.25 MA-RCO3. + #.016 CO + #.042 HCHO + #.058 RCHO + #.645 MEK + #.645 GLY + #-0.385 XC
	1.00e-17	1.00e-17	0.000	0.0	IP-HMY + O3 = #.55 HO. + #1.442 HO2. + #.004 RO2-R. + #.004 RCO-O2. + #1.35 CO + #.45 CO2 + #.004 HCHO + #.9 MEK + #.1 GLY + #.096 MGLY + #-0.904 XC
	1.00e-13	1.00e-13	0.000	0.0	IP-HMY + NO3 = #.936 RO2-R. + #.064 RO2-N. + #.936 HCHO + #.936 RCHO + #.872 XC + XN
	2.47e-11	2.47e-11	0.000	0.0	IP-HMY + O3P = #.6 RCHO + #.4 MGLY + #2 XC
	Phot Set = ACROLEIN, QY =			2.1e-3	IP-HMY + HV = #2 HO2. + #2 CO + MEK + #-1 XC

Table A-6 (continued)

Compound	Rate Parameters [a]				Reactions and Products [b]
	k(298)	A	Ea	B	
PROD2 Species #1	9.63e-12	9.63e-12	0.000	0.0	PROD2-1 + HO. = #.34 HO2. + #.529 RO2-R. + #.036 RO2-N. + #.084 CCO-O2. + #.01 RCO-O2. + #.445 HCHO + #.954 RCHO + #1.278 XC
	Phot Set = KETONE, QY =			0.050	PROD2-1 + HV = RO2-R. + #.013 R2O2. + CCO-O2. + #.033 HCHO + #.002 CCHO + #.987 RCHO
PROD2 Species #2	1.46e-11	1.46e-11	0.000	0.0	PROD2-2 + HO. = #.201 HO2. + #.667 RO2-R. + #.07 RO2-N. + #.062 CCO-O2. + #.613 HCHO + #.007 CCHO + #.345 RCHO + #.578 MEK + #1.484 XC
	Phot Set = KETONE, QY =			0.020	PROD2-2 + HV = #.95 RO2-R. + #.05 RO2-N. + #.748 R2O2. + CCO-O2. + #1.485 HCHO + #.737 CCHO + #.213 RCHO + #.102 XC
PROD2 Species #3	1.52e-11	1.52e-11	0.000	0.0	PROD2-3 + HO. = #.451 HO2. + #.394 RO2-R. + #.06 RO2-N. + #.095 RCO-O2. + #.008 HCHO + #.3 CCHO + #.348 RCHO + #.551 PROD2 + #1.397 XC
	Phot Set = KETONE, QY =			0.010	PROD2-3 + HV = #.931 RO2-R. + #.069 RO2-N. + #.786 R2O2. + RCO-O2. + #.931 RCHO + #.793 XC
PROD2 Species #4	1.83e-11	1.83e-11	0.000	0.0	PROD2-4 + HO. = #.491 HO2. + #.36 RO2-R. + #.075 RO2-N. + #.075 RCO-O2. + #.086 CCHO + #.531 RCHO + #.568 PROD2 + #2.154 XC
PROD2 Species #5	1.97e-11	1.97e-11	0.000	0.0	PROD2-5 + HO. = #.41 HO2. + #.416 RO2-R. + #.107 RO2-N. + #.066 RCO-O2. + #.029 CCHO + #.615 RCHO + #.527 PROD2 + #3.089 XC
	1.97e-11	1.97e-11	0.000	0.0	PROD2-5 + HO. = #.41 HO2. + #.416 RO2-R. + #.107 RO2-N. + #.066 RCO-O2. + #.029 CCHO + #.615 RCHO + #.527 PROD2 + #3.089 XC
RNO3 Species #1	1.60e-12	1.60e-12	0.000		RNO3-1 + HO. = #.573 NO2 + #.355 RO2-R. + #.072 RO2-N. + #.685 R2O2. + #1.023 CCHO + #.199 RCHO + #.061 MEK + #.156 RNO3 + #-0.257 XC + #.272 XN
	Phot Set = IC3ONO2				RNO3-1 + HV = NO2 + #.606 HO2. + #.394 RO2-R. + #.789 CCHO + #.606 MEK
RNO3 Species #2	1.15e-11	1.15e-11	0.000		RNO3-2 + HO. = #.008 NO2 + #.611 HO2. + #.357 RO2-R. + #.024 RO2-N. + #.007 HCHO + #.124 CCHO + #.145 RCHO + #.831 RNO3 + #-0.82 XC + #.161 XN
	Phot Set = IC3ONO2				RNO3-2 + HV = NO2 + HO2. + PROD2 + #-1 XC
RNO3 Species #3	4.70e-12	4.70e-12	0.000		RNO3-3 + HO. = #.732 NO2 + #.134 RO2-R. + #.133 RO2-N. + #1.031 R2O2. + #.012 HCHO + #1.082 CCHO + #.072 RCHO + #.545 MEK + #.03 PROD2 + #.071 RNO3 + #.022 XC + #.197 XN
	Phot Set = IC3ONO2				RNO3-3 + HV = NO2 + #.92 RO2-R. + #.08 RO2-N. + #.308 R2O2. + #1.536 CCHO + #.496 MEK + #.101 PROD2 + #-0.141 XC
RNO3 Species #4	9.90e-12	9.90e-12	0.000		RNO3-4 + HO. = #.103 NO2 + #.065 HO2. + #.722 RO2-R. + #.11 RO2-N. + #.006 CCHO + #.576 RCHO + #.102 PROD2 + #.218 RNO3 + #2.68 XC + #.679 XN
	Phot Set = IC3ONO2				RNO3-4 + HV = NO2 + #.441 HO2. + #.484 RO2-R. + #.075 RO2-N. + #.441 HCHO + #.441 RCHO + #.484 PROD2 + #1.882 XC
RNO3 Species #5	5.64e-12	5.64e-12	0.000		RNO3-5 + HO. = #.599 NO2 + #.126 RO2-R. + #.276 RO2-N. + #1.11 R2O2. + #.041 HCHO + #.402 CCHO + #.269 RCHO + #.035 ACET + #.455 MEK + #.143 PROD2 + #.039 RNO3 + #1.674 XC + #.362 XN
	Phot Set = IC3ONO2				RNO3-5 + HV = NO2 + #.828 RO2-R. + #.172 RO2-N. + #.564 R2O2. + #.362 HCHO + #.262 CCHO + #.44 RCHO + #.119 ACET + #.358 MEK + #.269 PROD2 + #1.36 XC

Table A-6 (continued)

Compound	Rate Parameters [a]				Reactions and Products [b]
	k(298)	A	Ea	B	
RNO3 Species #6	9.87e-12	9.87e-12	0.000		RNO3-6 + HO. = #.018 NO2 + #.564 RO2-R. + #.419 RO2-N. + #.756 R2O2. + #.001 CCHO + #.021 RCHO + #.015 PROD2 + #.547 RNO3 + #4.052 XC + #.436 XN
	Phot Set = IC3ONO2				RNO3-6 + HV = NO2 + #.761 RO2-R. + #.239 RO2-N. + #.042 R2O2. + #.761 PROD2 + #4 XC

[a] See footnotes to Table 50.

[b] Documentation text is in Table A-4.

APPENDIX B.

EVALUATION TABULATIONS AND FIGURES

This Appendix contains the table and figures giving the results of the evaluation of the mechanism against the individual environmental chamber experiments. Table B-1 lists all the environmental chamber experiments that were simulated in this study, and summarizes their major characteristics and selected experimental and calculated $\Delta(O_3\text{-}NO)$ results. Percentage differences between experimental and calculated data are also shown. Figure B-1 through Figure B-90 contain plots of the experimental and calculated data, or distribution plots of the errors in the simulations of the $\Delta(O_3\text{-}NO)$ data, for the various types of experiments that were modeled. The methods of procedure and the results of this evaluation are discussed in Section V of this report.

Table B-1. Summary of environmental chamber experiments used for mechanism evaluation.

Run	Run Type or VOC [a]	Rct'y Type [a]	Chr Set [b]	NOx (ppm)	Pr.Eq. (ppm) [c]	k1 (min^{-1}) [d]	T (K) [e]	Ref [f]	Δ (O3-NO) Results (pphm)								
									2 Hour			4 Hour			6 Hour		
									Expt	Calc	Δ%	Expt	Calc	Δ%	Expt	Calc	Δ%
Characterization Runs																	
ETC458	Pure Air		3			0.35	301	1	-	2		-	5		-	7	
ETC485	Pure Air		3		0.00	0.35	300	1	-	2		-	5		-	7	
DTC049A	Pure Air		1			0.39	301	1	-	1		-	3		-	5	
ITC1009	Acetald - Air		11		0.42	0.35	302	1	-	2		-	4		-	7	
ITC627	Acetald - Air		5		0.23	0.35	300	1	-	2		-	4		-	7	
ITC892	Acetald - Air		9		0.19	0.35	299	1	-	2		-	4		-		
ITC957	Acetald - Air		10		0.46	0.35	301	1	1	2	48	3	4	28	5	7	23
ETC319	Acetald - Air		2		0.30	0.35	298	1	-	1		-	3		-	5	
ETC382	Acetald - Air		3		0.21	0.35	301	1	-	2		-	4		-	8	
CTC019	Acetald - Air		1		0.34	0.20	304	2	-	0		-	2		-	3	
EC253	Acetald - Air		1		0.33	0.29	303	1	-	3		-	9		-	14	
CTC031	CO - NOx (RS)		1	0.26	0.03	0.20	300	2	5	4	-26	10	8	-18	14	12	-17
CTC061	CO - NOx (RS)		2	0.23	0.03	0.19	300	2	4	4	13	7	9	15	-	12	
CTC090A	CO - NOx (RS)		4	0.26	0.03	0.19	294	2	-	4		8	8	1	-	11	
CTC090B	CO - NOx (RS)		4	0.26	0.03	0.19	294	2	-	4		9	8	-22	12	11	-12
ITC507	n-C4 - NOx (RS)		2	0.09	0.37	0.37	301	1	10	10	-3	16	17	9	23	27	18
ITC533	n-C4 - NOx (RS)		3	0.10	0.29	0.36	303	1	8	8	0	14	15	2	21	23	9
ITC939	n-C4 - NOx (RS)		10	0.53	0.48	0.35	301	1	5	4	-17	7	7	0	10	10	2
ITC948	n-C4 - NOx (RS)		10	0.26	0.46	0.35	301	1	7	6	-10	12	11	-3	17	16	-2
ETC214	n-C4 - NOx (RS)		2	0.49	0.39	0.35	299	1	1	4	84	3	8	62	7	13	48
ETC318	n-C4 - NOx (RS)		2	0.52	0.42	0.35	298	1	1	3	61	3	6	48	6	9	36
DTC058A	n-C4 - NOx (RS)		1	0.24	0.38	0.39	301	1	4	4	-6	9	9	-6	14	13	-7
DTC058B	n-C4 - NOx (RS)		1	0.24	0.39	0.39	301	1	4	4	6	8	9	12	12	13	8
DTC145A	n-C4 - NOx (RS)		3	0.65	0.43	0.26	298	2	8	5	-38	13	11	-21	19	16	-18
DTC145B	n-C4 - NOx (RS)		3	0.66	0.43	0.26	298	2	6	7	16	13	14	8	20	20	2
DTC171A	n-C4 - NOx (RS)		3	0.59	0.51	0.24	298	2	9	7	-26	18	16	-17	-	23	
DTC171B	n-C4 - NOx (RS)		3	0.58	0.49	0.24	298	2	10	9	-11	21	19	-12	-	27	
DTC215A	n-C4 - NOx (RS)		3	0.54	0.44	0.23	299	2	4	6	28	-	13		-	20	
DTC215B	n-C4 - NOx (RS)		3	0.56	0.45	0.23	299	2	6	8	21	14	17	15	22	24	8
DTC228A	n-C4 - NOx (RS)		10	0.28	0.19	0.23	297	3	2	2	4	4	4	12	6	6	14
DTC228B	n-C4 - NOx (RS)		10	0.28	0.20	0.23	297	3	2	2	14	4	4	18	5	6	19
DTC236A	n-C4 - NOx (RS)		10	0.26	0.38	0.23	296	3	4	3	-22	7	6	-21	11	8	-27
DTC253A	n-C4 - NOx (RS)		10	0.27	0.41	0.23	297	3	3	3	-8	6	6	0	10	10	-3
DTC253B	n-C4 - NOx (RS)		10	0.27	0.41	0.23	297	3	3	3	4	6	6	6	9	10	6
DTC285A	n-C4 - NOx (RS)		10	0.25	0.42	0.22	298	4	4	3	-20	8	6	-21	12	10	-22
DTC285B	n-C4 - NOx (RS)		10	0.25	0.41	0.22	298	4	3	3	-8	7	6	-7	11	10	-11
DTC299A	n-C4 - NOx (RS)		10	0.26	0.43	0.22	297	4	3	3	7	6	7	7	10	10	4
DTC299B	n-C4 - NOx (RS)		10	0.26	0.42	0.22	297	4	3	3	19	5	6	23	7	10	23
XTC085	n-C4 - NOx (RS)		1	0.55	0.39	0.26	302	1	4	4	-4	8	7	-10	11	11	-3
XTC098	n-C4 - NOx (RS)		1	0.57	0.42	0.25	303	1	4	4	5	8	8	1	-	12	
CTC013	n-C4 - NOx (RS)		1	0.45	0.30	0.20	303	2	2	3	40	3	5	39	-	8	
CTC020	n-C4 - NOx (RS)		1	0.26	0.40	0.20	304	2	2	3	32	4	6	32	7	9	29
CTC028	n-C4 - NOx (RS)		1	0.27	0.38	0.20	304	2	2	3	19	5	6	22	-	10	
CTC042	n-C4 - NOx (RS)		2	0.26	0.38	0.20	301	2	5	3	-60	9	6	-49	-	10	
CTC045	n-C4 - NOx (RS)		2	0.46	0.37	0.20	301	2	-	3		6	6	-10	8	8	0
CTC058	n-C4 - NOx (RS)		2	0.26	0.37	0.19	299	2	4	3	-33	8	6	-36	-	9	

Table B-1 (continued)

Run	Run Type or VOC [a]	Rct'y Type [a]	Chr Set [b]	NOx (ppm)	Pr.Eq. (ppm) [c]	k1 (min^{-1}) [d]	T (K) [e]	Ref [f]	Δ (O3-NO) Results (pphm)								
									2 Hour			4 Hour			6 Hour		
									Expt	Calc	Δ%	Expt	Calc	Δ%	Expt	Calc	Δ%
CTC074	n-C4 - NOx (RS)		3	0.25	0.38	0.19	297	2	2	3	17	6	6	-3	-	10	
CTC084A	n-C4 - NOx (RS)		4	0.25	0.41	0.19	299	2	2	3	19	5	6	21	-	9	
CTC084B	n-C4 - NOx (RS)		4	0.25	0.41	0.19	299	2	2	3	13	5	6	22	8	9	11
CTC099A	n-C4 - NOx (RS)		4	0.27	0.36	0.19	295	2	3	2	-19	5	5	-5	-	8	
CTC099B	n-C4 - NOx (RS)		4	0.27	0.37	0.19	295	2	4	2	-64	8	5	-51	-	8	
CTC114A	n-C4 - NOx (RS)		5	0.24	0.38	0.19	296	2	3	2	-18	5	5	-5	-	8	
CTC114B	n-C4 - NOx (RS)		5	0.24	0.38	0.19	296	2	3	2	-18	5	5	-5	-	8	
CTC120A	n-C4 - NOx (RS)		5	0.26	0.37	0.19	294	2	2	2	27	4	5	28	-	8	
CTC120B	n-C4 - NOx (RS)		5	0.25	0.37	0.19	294	2	3	2	-1	5	5	12	-	8	
CTC135A	n-C4 - NOx (RS)		6	0.26	0.35	0.18	294	2	3	2	-14	5	5	-3	-	8	
CTC135B	n-C4 - NOx (RS)		6	0.26	0.35	0.18	294	2	3	2	-19	6	5	-11	-	8	
CTC241A	n-C4 - NOx (RS)		9	0.27	0.53	0.13	302	5	3	3	-9	8	7	-8	-	11	
CTC241B	n-C4 - NOx (RS)		9	0.27	0.53	0.13	302	5	3	3	2	7	7	-4	12	11	-11
CTC244A	n-C4 - NOx (RS)		9	0.26	0.60	0.13	293	6	4	3	-39	8	7	-24	15	11	-31
CTC244B	n-C4 - NOx (RS)		9	0.26	0.59	0.13	293	6	4	3	-26	8	7	-16	13	11	-18
CTC252A	n-C4 - NOx (RS)		9	0.25	0.61	0.13	293	6	3	3	12	6	7	15	11	12	10
CTC252B	n-C4 - NOx (RS)		9	0.25	0.58	0.13	293	6	3	3	-1	6	7	13	9	11	12
EC162	n-C4 - NOx (RS)		1	0.54	0.20	0.34	301	1	21	16	-34	36	27	-30	44	37	-17
EC178	n-C4 - NOx (RS)		1	0.10	0.19	0.34	304	1	20	19	-6	36	38	6	45	52	13
EC304	n-C4 - NOx (RS)		1	0.51	0.42	0.40	302	1	29	30	2	49	52	5	63	73	14
EC305	n-C4 - NOx (RS)		1	0.11	0.42	0.41	302	1	28	31	10	43	55	22	48	66	28
EC307	n-C4 - NOx (RS)		1	0.11	0.63	0.41	302	1	30	37	18	46	62	27	50	72	30
EC355	n-C4 - NOx (RS)		1	0.50	0.41	0.35	302	1	20	27	26	33	44	24	46	60	24
EC356	n-C4 - NOx (RS)		1	0.50	0.43	0.35	302	1	20	27	28	33	44	25	45	61	27
OTC296A	n-C4 - NOx (RS)		11	0.53	0.46	0.00	310	7	8	7	-11	23	20	-12	-	31	
OTC296B	n-C4 - NOx (RS)		11	0.52	0.51	0.00	310	7	6	7	17	19	22	17	31	35	11
OTC303A	n-C4 - NOx (RS)		12	0.54	0.40	0.00	313	7	-	6		27	19	-39	-	28	
OTC303B	n-C4 - NOx (RS)		12	0.52	0.39	0.00	313	7	7	6	-22	20	19	-1	-	29	
OTC307A	n-C4 - NOx (RS)		12	0.46	0.38	0.00	319	7	14	12	-20	35	33	-9	-	43	
OTC307B	n-C4 - NOx (RS)		12	0.48	0.38	0.00	319	7	13	12	-4	32	34	4	44	45	1
Single VOC - NOx Runs																	
ITC1555	ETHENE		12	0.45	0.68	0.35	301	1	33	41	19	94	112	16	132	126	-5
ITC926	ETHENE		10	0.53	1.28	0.35	301	1	94	115	18	130	133	3	112	110	-1
ITC936	ETHENE		10	0.52	0.63	0.35	301	1	29	33	13	70	95	26	119	135	12
ETC220	ETHENE		2	0.51	0.20	0.35	299	1	5	5	8	12	13	14	20	23	11
ETC221	ETHENE		2	0.51	1.31	0.35	299	1	98	104	6	151	154	2	-	140	
ETC381	ETHENE		3	0.52	0.67	0.35	301	1	33	35	7	95	99	4	151	150	-1
ETC439	ETHENE		3	0.66	0.63	0.35	300	1	26	23	-17	66	61	-8	130	115	-13
ETC464	ETHENE		3	0.38	0.48	0.35	301	1	23	25	9	63	71	11	116	117	0
ETC466	ETHENE		3	0.41	0.48	0.35	300	1	22	23	4	55	63	12	108	112	3
ETC467	ETHENE		3	0.52	0.48	0.35	300	1	17	19	12	41	50	18	73	90	19
ETC469	ETHENE		3	0.46	0.58	0.35	301	1	22	29	25	58	82	30	114	133	15
ETC471	ETHENE		3	0.45	0.58	0.35	302	1	25	30	18	70	86	19	127	135	6
ETC473	ETHENE		3	0.46	0.61	0.35	301	1	25	31	21	66	89	26	123	138	10
ETC476	ETHENE		3	0.43	0.55	0.35	300	1	20	26	26	52	77	32	104	126	17
ETC479	ETHENE		3	0.42	0.57	0.35	301	1	22	30	26	59	86	31	115	131	12
ETC482	ETHENE		3	0.41	0.51	0.35	301	1	25	26	5	61	73	16	114	121	6
ETC486	ETHENE		3	0.44	0.51	0.35	301	1	20	24	17	54	67	19	108	118	9

Table B-1 (continued)

Run	Run Type or VOC [a]	Rct'y Type [a]	Chr Set [b]	NOx (ppm)	Pr.Eq. (ppm) [c]	k1 (min^{-1}) [d]	T (K) [e]	Ref [f]	Δ (O3-NO) Results (pphm) 2 Hour Expt	2 Hour Calc	2 Hour Δ%	4 Hour Expt	4 Hour Calc	4 Hour Δ%	6 Hour Expt	6 Hour Calc	6 Hour Δ%
ETC497	ETHENE		3	0.45	0.57	0.35	301	1	22	27	20	61	80	23	118	131	9
ETC505	ETHENE		3	0.40	0.53	0.35	300	1	23	25	10	59	75	21	108	122	11
DTC041B	ETHENE		1	0.17	0.57	0.39	300	1	30	48	36	79	88	10	88	92	4
DTC043A	ETHENE		1	0.47	0.55	0.39	300	1	17	23	24	49	65	26	101	123	18
DTC044B	ETHENE		1	0.16	0.59	0.39	300	1	33	50	35	81	88	8	89	91	2
DTC045A	ETHENE		1	0.48	0.57	0.39	301	1	19	24	22	54	70	24	113	130	13
DTC046B	ETHENE		1	0.17	0.57	0.19	300	1	10	14	33	36	48	24	58	64	10
DTC047A	ETHENE		1	0.48	0.59	0.39	301	1	20	24	16	55	71	22	113	131	14
DTC048B	ETHENE		1	0.17	0.59	0.39	301	1	35	49	28	82	88	7	89	92	3
DTC050A	ETHENE		1	0.16	0.59	0.39	301	1	34	50	33	80	87	9	86	90	4
DTC051A	ETHENE		1	0.48	0.59	0.39	301	1	20	25	20	56	74	24	117	135	13
DTC072B	ETHENE		1	0.47	0.56	0.39	302	1	18	24	24	49	65	24	102	118	13
XTC105	ETHENE		1	0.24	0.60	0.25	301	1	20	17	-16	71	58	-24	99	85	-16
XTC112	ETHENE		1	0.52	0.87	0.25	302	1	24	24	-3	74	72	-4	134	125	-7
EC142	ETHENE		1	0.49	0.31	0.31	301	1	40	32	-24	80	62	-29	109	92	-18
EC143	ETHENE		1	0.50	0.66	0.31	300	1	109	74	-48	145	124	-16	123	120	-2
EC156	ETHENE		1	0.47	0.65	0.33	301	1	110	75	-47	139	124	-11	117	121	3
EC285	ETHENE		1	1.01	0.63	0.38	302	1	66	77	15	115	153	25	165	194	15
EC286	ETHENE		1	0.97	1.22	0.38	302	1	144	173	17	169	192	12	141	162	13
EC287	ETHENE		1	0.54	1.30	0.37	302	1	137	148	8	116	133	13	97	109	12
OTC278B	ETHENE		11	0.46	0.25	0.00	313	7,8	12	8	-51	38	30	-27	62	48	-28
OTC279A	ETHENE		11	0.53	0.37	0.00	313	7,8	23	15	-49	87	56	-55	-	94	
OTC280B	ETHENE		11	0.54	0.39	0.00	312	7,8	23	19	-18	82	57	-44	-	86	
OTC297A	ETHENE		11	0.63	0.37	0.00	309	7	17	9	-96	60	39	-55	-	70	
OTC297B	ETHENE		11	0.28	0.37	0.00	309	7	24	18	-34	-	83		111	110	0
OTC304A	ETHENE		12	0.60	0.36	0.00	316	7	18	14	-29	63	51	-23	-	79	
OTC304B	ETHENE		12	0.23	0.36	0.00	316	7	-	32		91	93	3	-	104	
ITC1550	PROPENE		12	0.49	0.98	0.35	301	1	70	71	2	106	106	0	-		
ITC1556	PROPENE		12	0.49	0.99	0.35	301	1	53	67	21	104	109	5	114	110	-3
ITC484	PROPENE		2	0.45	0.46	0.39	300	1	14	21	37	32	46	30	40	68	41
ITC510	PROPENE		2	0.59	0.95	0.53	302	1	57	70	18	107	135	21	127	156	19
ITC532	PROPENE		3	0.56	0.91	0.36	302	1	32	45	28	76	104	27	100	125	20
ITC569	PROPENE		4	0.48	0.94	0.36	299	1	44	53	18	96	109	12	-	117	
ITC693	PROPENE		6	0.48	1.07	0.35	301	1	62	74	16	110	117	6	115	118	2
ITC716	PROPENE		6	0.53	1.01	0.35	300	1	59	55	-8	101	115	13	108	124	13
ITC728	PROPENE		6	0.49	1.02	0.35	299	1	51	62	18	94	114	18	101	116	13
ITC736	PROPENE		7	0.49	0.50	0.35	299	1	21	19	-13	40	41	2	58	61	6
ITC754	PROPENE		7	0.57	0.95	0.35	299	1	56	43	-29	-	102		-	124	
ITC791	PROPENE		7	0.53	0.92	0.35	299	1	58	44	-31	103	102	-1	117	120	2
ITC792	PROPENE		8	0.50	0.95	0.35	296	1	50	50	-1	95	104	8	110	113	2
ITC810	PROPENE		8	0.52	0.90	0.35	298	1	52	43	-20	104	99	-5	122	117	-4
ITC860	PROPENE		9	0.52	0.98	0.35	298	1	42	51	17	86	109	22	99	120	17
ITC925	PROPENE		10	0.56	1.06	0.35	302	1	45	64	30	90	118	23	109	123	11
ITC938	PROPENE		10	0.54	0.81	0.35	301	1	43	36	-17	90	87	-3	105	110	5
ITC947	PROPENE		10	0.54	0.60	0.35	301	1	40	20	-96	81	49	-64	99	76	-30
ETC321	PROPENE		2	0.44	1.02	0.35	299	1	48	51	6	114	112	-2	117	116	0
ETC440	PROPENE		3	0.60	1.16	0.35	300	1	51	48	-6	123	123	0	133	138	4
ETC449	PROPENE		3	0.25	0.91	0.35	300	1	71	73	3	76	81	6	75	80	6

Table B-1 (continued)

Run	Run Type or VOC [a]	Rct'y Type [a]	Chr Set [b]	NOx (ppm)	Pr.Eq. (ppm) [c]	k1 (min^{-1}) [d]	T (K) [e]	Ref [f]	Δ (O3-NO) Results (pphm) 2 Hour Expt	2 Hour Calc	2 Hour Δ%	4 Hour Expt	4 Hour Calc	4 Hour Δ%	6 Hour Expt	6 Hour Calc	6 Hour Δ%
ETC475	PROPENE		3	0.26	0.89	0.35	300	1	79	73	-8	73	84	14	71	83	15
DTC026A	PROPENE		1	0.49	1.15	0.39	302	1	100	77	-29	126	128	1	125	128	3
DTC026B	PROPENE		1	0.49	1.16	0.39	302	1	98	78	-25	127	129	1	125	129	4
DTC052A	PROPENE		1	0.30	0.94	0.39	301	1	84	82	-2	83	92	10	82	92	10
DTC054A	PROPENE		1	0.29	0.98	0.39	301	1	80	83	3	80	88	10	79	88	10
DTC060A	PROPENE		1	0.24	0.93	0.39	301	1	75	76	2	73	84	13	-		
DTC060B	PROPENE		1	0.51	0.97	0.39	301	1	52	41	-27	118	111	-6	-		
DTC128A	PROPENE		3	0.48	0.89	0.29	299	2	45	36	-26	100	88	-13	110	106	-4
DTC128B	PROPENE		3	0.49	0.87	0.29	299	2	47	35	-34	101	82	-24	110	99	-11
DTC129A	PROPENE		3	0.47	0.96	0.29	299	2	51	42	-20	103	98	-5	-	109	
DTC129B	PROPENE		3	0.47	0.94	0.29	299	2	51	41	-25	102	91	-12	-	101	
DTC146A	PROPENE		3	0.51	1.06	0.26	298	2	36	36	0	95	98	2	110	113	3
DTC146B	PROPENE		3	0.52	1.05	0.26	298	2	38	36	-4	95	92	-3	108	107	0
DTC153A	PROPENE		3	0.51	1.12	0.25	297	2	41	36	-15	104	101	-3	110	112	2
DTC155B	PROPENE		3	0.10	0.43	0.25	298	2	18	23	24	37	40	7	38	42	9
DTC158B	PROPENE		3	0.51	0.78	0.25	298	2	48	21	-128	108	50	-117	109	77	-42
DTC159A	PROPENE		3	0.51	0.73	0.25	298	2	50	18	-172	109	46	-140	109	74	-48
DTC168A	PROPENE		3	0.52	1.20	0.24	299	2	49	39	-26	109	107	-2	110	113	2
DTC169A	PROPENE		3	0.55	1.20	0.24	299	2	44	37	-20	110	106	-3	114	117	2
DTC170B	PROPENE		3	0.51	1.13	0.24	299	2	53	34	-55	-	95		107	108	0
DTC179B	PROPENE		3	0.50	1.22	0.24	299	2	50	41	-23	106	104	-3	106	105	0
DTC187A	PROPENE		3	0.57	1.13	0.23	299	2	35	32	-12	101	94	-7	119	117	-2
DTC187B	PROPENE		3	0.59	1.08	0.23	299	2	38	30	-29	102	79	-29	117	107	-9
DTC190A	PROPENE		3	0.57	1.20	0.23	299	2	47	35	-33	113	103	-9	115	116	1
DTC205A	PROPENE		3	0.57	1.10	0.23	299	2	41	30	-38	105	88	-19	-	114	
DTC205B	PROPENE		3	0.60	1.15	0.23	299	2	45	32	-43	107	88	-21	116	111	-4
DTC246A	PROPENE		10	0.48	0.95	0.23	297	3	20	22	10	58	71	18	87	101	14
DTC288A	PROPENE		10	0.54	1.04	0.22	298	4	28	31	11	76	86	12	91	99	8
DTC288B	PROPENE		10	0.54	1.02	0.22	298	4	28	29	5	78	86	9	95	102	6
DTC301A	PROPENE		11	0.52	1.04	0.21	296	4	23	28	19	69	84	17	96	100	4
DTC301B	PROPENE		11	0.51	1.03	0.21	296	4	22	28	21	69	84	17	99	100	1
DTC331A	PROPENE		11	0.55	1.07	0.21	296	9	24	27	13	72	83	14	97	100	3
DTC331B	PROPENE		11	0.54	1.06	0.21	296	9	23	27	13	71	83	14	100	101	2
DTC346A	PROPENE		11	0.58	1.01	0.20	299	10	29	24	-24	82	72	-14	98	100	2
DTC346B	PROPENE		11	0.59	1.02	0.20	299	10	30	23	-30	83	71	-17	99	100	1
DTC371A	PROPENE		11	0.57	0.64	0.20	299	10	28	11	-156	82	26	-213	100	44	-126
DTC371B	PROPENE		11	0.57	0.64	0.20	299	10	28	11	-153	82	26	-214	101	44	-128
DTC393A	PROPENE		11	0.57	0.92	0.19	296	11	23	18	-27	62	49	-27	94	84	-11
DTC393B	PROPENE		11	0.56	0.91	0.19	296	11	23	18	-29	62	49	-26	91	84	-9
DTC405A	PROPENE		11	0.56	0.99	0.19	299	10	29	21	-43	83	65	-28	103	98	-5
DTC405B	PROPENE		11	0.56	0.98	0.19	299	10	30	20	-46	82	63	-31	102	96	-6
DTC417A	PROPENE		11	0.53	1.19	0.19	297	10	27	29	7	83	92	10	105	100	-4
DTC417B	PROPENE		11	0.53	1.23	0.19	297	10	28	32	12	84	93	11	105	98	-7
DTC431A	PROPENE		11	0.56	1.11	0.18	297	12	31	25	-24	90	78	-15	104	98	-6
DTC431B	PROPENE		11	0.56	1.11	0.18	297	12	32	25	-28	91	78	-17	108	98	-10
DTC443A	PROPENE		11	0.53	1.20	0.17	297	13	26	29	9	83	90	7	103	96	-7
DTC443B	PROPENE		11	0.53	1.21	0.17	297	13	27	29	7	84	89	6	103	95	-9
DTC458A	PROPENE		12	0.53	1.19	0.16	298	14	34	32	-5	87	90	3	-	95	

Table B-1 (continued)

Run	Run Type or VOC [a]	Rct'y Type [a]	Chr Set [b]	NOx (ppm)	Pr.Eq. (ppm) [c]	k1 (min^{-1}) [d]	T (K) [e]	Ref [f]	Δ (O3-NO) Results (pphm)								
									2 Hour			4 Hour			6 Hour		
									Expt	Calc	Δ%	Expt	Calc	Δ%	Expt	Calc	Δ%
DTC458B	PROPENE		11	0.53	1.23	0.16	298	14	26	27	4	80	86	8	-	93	
DTC472A	PROPENE		14	0.51	1.05	0.23	298	13	38	31	-21	99	90	-9	109	104	-5
DTC472B	PROPENE		15	0.51	1.05	0.23	298	13	37	30	-21	99	89	-11	110	104	-6
DTC483A	PROPENE		14	0.49	1.17	0.22	298	13	43	44	1	103	99	-4	108	99	-10
DTC483B	PROPENE		15	0.49	1.17	0.22	298	13	41	44	6	102	100	-2	108	100	-8
DTC503A	PROPENE		14	0.52	1.09	0.22	299	15	38	31	-23	102	93	-10	114	105	-8
DTC503B	PROPENE		15	0.51	1.09	0.22	299	15	36	30	-18	101	93	-8	113	105	-7
DTC526A	PROPENE		14	0.51	1.10	0.21	300	10	42	31	-32	104	94	-11	112	102	-9
DTC526B	PROPENE		15	0.51	1.11	0.21	300	10	41	31	-34	104	94	-10	112	103	-8
DTC578A	PROPENE		14	0.49	1.19	0.20	298	16	29	34	14	91	94	3	105	96	-9
DTC578B	PROPENE		15	0.49	1.19	0.20	298	16	27	33	18	89	96	7	104	98	-6
DTC597A	PROPENE		14	0.49	1.16	0.19	298	16	23	29	22	74	92	20	99	99	0
DTC597B	PROPENE		15	0.49	1.15	0.19	298	16	21	28	27	69	91	25	98	99	1
XTC081	PROPENE		1	0.56	1.10	0.26	302	1	43	27	-55	122	94	-30	134	121	-11
XTC082	PROPENE		1	0.54	1.06	0.26	302	1	45	27	-69	122	89	-37	131	116	-13
XTC097	PROPENE		1	0.56	1.20	0.25	302	1	42	29	-45	122	105	-16	131	125	-5
XTC113	PROPENE		1	0.53	1.19	0.25	302	1	44	27	-64	118	92	-28	123	113	-9
CTC012	PROPENE		1	0.42	0.79	0.20	302	2	18	15	-17	57	48	-20	-	80	
CTC018	PROPENE		1	0.47	1.00	0.20	303	2	25	20	-25	86	76	-13	105	99	-6
CTC023	PROPENE		1	0.50	1.14	0.20	301	2	32	25	-31	100	89	-13	110	102	-8
CTC049	PROPENE		2	0.50	1.18	0.20	301	2	38	25	-54	99	92	-8	-	102	
CTC059	PROPENE		2	0.49	1.07	0.19	300	2	26	21	-25	86	75	-15	-	99	
CTC078	PROPENE		3	0.47	1.16	0.19	298	2	30	22	-36	92	83	-11	-	98	
CTC083A	PROPENE		4	0.51	1.25	0.19	298	2	26	23	-12	83	79	-5	106	99	-7
CTC083B	PROPENE		4	0.51	1.23	0.19	298	2	28	22	-26	87	73	-19	-	98	
CTC086A	PROPENE		4	0.44	1.22	0.19	295	2	28	25	-10	88	83	-7	105	91	-15
CTC086B	PROPENE		4	0.44	1.23	0.19	295	2	30	26	-16	92	87	-6	105	93	-13
CTC102A	PROPENE		5	0.49	1.13	0.19	295	2	25	19	-31	77	67	-16	-	98	
CTC102B	PROPENE		5	0.49	1.14	0.19	295	2	27	19	-38	78	69	-13	-	99	
CTC115A	PROPENE		5	0.47	1.15	0.19	295	2	23	20	-16	73	71	-3	-	96	
CTC115B	PROPENE		5	0.47	1.14	0.19	295	2	24	20	-21	75	71	-5	-	96	
CTC132A	PROPENE		6	0.49	1.16	0.18	293	2	26	19	-41	80	61	-30	-	95	
CTC132B	PROPENE		6	0.49	1.15	0.18	293	2	27	19	-45	80	63	-26	-	96	
CTC147A	PROPENE		6	0.53	1.32	0.18	299	4	37	29	-27	102	95	-8	-	98	
CTC147B	PROPENE		6	0.53	1.32	0.18	299	4	36	29	-24	102	94	-9	107	97	-11
CTC153A	PROPENE		6	0.54	1.28	0.18	301	4	42	25	-69	107	94	-13	-	102	
CTC153B	PROPENE		6	0.54	1.26	0.18	301	4	43	24	-75	107	92	-16	-	102	
CTC163A	PROPENE		7	0.50		0.18	299	0	32	23	-41	99	87	-14	-	99	
CTC163B	PROPENE		7	0.50	1.25	0.18	299	0	33	23	-45	100	88	-14	-	98	
CTC170A	PROPENE		7	0.54		0.17	299	5	35	22	-57	105	86	-21	-	99	
CTC170B	PROPENE		7	0.53	1.32	0.17	299	5	36	23	-55	104	90	-16	-	98	
CTC191A	PROPENE		7	0.48	1.26	0.16	298	17	29	21	-42	95	79	-21	-	90	
CTC191B	PROPENE		7	0.47	1.25	0.16	298	17	29	20	-43	96	80	-20	105	90	-17
CTC203A	PROPENE		8	0.48	1.35	0.15	298	18	30	22	-37	96	82	-17	-	88	
CTC203B	PROPENE		8	0.47	1.39	0.15	298	18	30	23	-28	96	83	-16	100	86	-16
CTC219A	PROPENE		8	0.49	1.23	0.14	297	19	31	17	-84	94	62	-52	-	89	
CTC219B	PROPENE		8	0.48	1.22	0.14	297	19	28	18	-61	93	69	-34	100	88	-14
CTC234A	PROPENE		9	0.51	1.53	0.14	302	5	25	25	0	90	88	-3	-	85	

Table B-1 (continued)

Run	Run Type or VOC [a]	Rct'y Type [a]	Chr Set [b]	NOx (ppm)	Pr.Eq. (ppm) [c]	k1 (min^{-1}) [d]	T (K) [e]	Ref [f]	Δ (O3-NO) Results (pphm)								
									2 Hour			4 Hour			6 Hour		
									Expt	Calc	Δ%	Expt	Calc	Δ%	Expt	Calc	Δ%
CTC234B	PROPENE		9	0.51	1.54	0.14	302	5	25	26	6	90	87	-3	96	83	-15
CTC245A	PROPENE		9	0.49	1.52	0.13	295	6	25	17	-44	90	75	-19	108	89	-21
CTC245B	PROPENE		9	0.49	1.51	0.13	295	6	25	17	-41	89	70	-27	109	90	-21
CTC264A	PROPENE		10	0.50	1.39	0.12	294	20	21	12	-75	78	40	-95	100	88	-13
CTC264B	PROPENE		10	0.50	1.42	0.12	294	20	20	13	-58	74	41	-81	99	86	-16
EC121	PROPENE		1	0.51	0.48	0.27	302	1	64	37	-71	86	65	-32	90	80	-12
EC177	PROPENE		1	0.50	0.49	0.33	305	1	47	47	-1	74	85	13	89	105	16
EC216	PROPENE		1	0.52	0.50	0.43	301	1	50	55	9	77	87	12	93	103	10
EC230	PROPENE		1	0.50	0.55	0.29	302	1	35	44	21	55	73	25	67	88	24
EC256	PROPENE		1	0.53	0.11	0.29	303	1	11	10	-10	21	21	0	28	28	1
EC276	PROPENE		1	0.52	0.54	0.35	302	1	40	50	20	63	81	22	78	97	20
EC277	PROPENE		1	0.11	0.56	0.36	302	1	40	49	19	39	48	19	39	48	19
EC278	PROPENE		1	0.50	1.02	0.36	302	1	86	104	17	97	109	12	93	104	11
EC279	PROPENE		1	0.98	1.15	0.36	302	1	77	96	19	123	146	16	141	159	11
EC314	PROPENE		1	0.98	1.06	0.46	302	1	87	103	16	127	152	17	144	168	14
EC317	PROPENE		1	0.57	0.49	0.53	303	1	49	57	15	74	86	14	87	102	15
EC665	PROPENE		1	0.44	0.48	0.38	303	1	37	34	-7	50	55	9	57	67	15
EC684	PROPENE		1	0.44	1.13	0.38	303	1	66	92	28	72	107	33	69	105	35
EC687	PROPENE		1	0.47	1.04	0.37	303	1	64	82	22	95	107	12	89	110	19
EC691	PROPENE		1	0.49	1.08	0.37	304	1	63	87	27	90	111	19	86	113	24
EC863	PROPENE		1	0.57	0.52	0.22	302	1	33	25	-33	49	41	-20	56	52	-7
EC870	PROPENE		1	0.54	1.04	0.33	302	1	78	68	-14	91	101	10	84	107	21
EC885	PROPENE		1	0.52	0.93	0.29	301	1	61	53	-15	88	86	-2	87	93	7
EC899	PROPENE		1	0.48	1.06	0.27	302	1	60	63	6	83	95	12	77	96	20
OTC272A	PROPENE		11	0.54	1.08	0.00	311	7	134	88	-52	158	149	-6	158	153	-3
OTC272B	PROPENE		11	0.53	1.07	0.00	311	7	125	90	-39	152	149	-2	-	155	
OTC295A	PROPENE		11	0.54	1.51	0.00	313	7	135	129	-5	154	150	-3	-	153	
OTC295B	PROPENE		11	0.52	1.49	0.00	313	7	124	127	3	145	149	3	-	153	
OTC298A	PROPENE		11	0.58	1.29	0.00	311	7	136	92	-48	156	156	0	153	160	4
OTC298B	PROPENE		11	0.57	1.35	0.00	311	7	121	103	-18	151	155	3	-	159	
ITC927	1-BUTENE		10	0.54	1.27	0.35	301	1	38	41	8	81	84	4	98	105	7
ITC928	1-BUTENE		10	1.05	0.01	0.35	301	1	-2			13	16	19	42	54	23
ITC930	1-BUTENE		10	0.53	3.33	0.35	302	1	103	99	-4	88	76	-15	85	76	-12
ITC935	1-BUTENE		10	1.09	3.42	0.35	301	1	66	100	34	142	162	12	154	153	-1
EC122	1-BUTENE		1	0.51	0.26	0.27	301	1	29	21	-40	45	37	-22	56	48	-18
EC123	1-BUTENE		1	0.51	0.48	0.27	300	1	48	35	-39	70	56	-26	86	69	-25
EC124	1-BUTENE		1	1.00	0.51	0.27	301	1	26	32	20	46	53	14	60	67	10
ITC929	1-HEXENE		10	0.52	1.19	0.35	302	1	13	14	11	34	38	11	60	65	8
ITC931	1-HEXENE		10	0.51	2.40	0.35	301	1	28	34	16	89	99	10	80	103	22
ITC934	1-HEXENE		10	1.07	2.27	0.35	303	1	20	15	-31	46	47	3	79	85	7
ITC937	1-HEXENE		10	1.08	0.01	0.35	301	1	-3			7	9	25	19	25	26
ITC694	ISOBUTEN		6	0.50	1.98	0.35	301	1	109	103	-6	126	142	11	126	144	12
DTC052B	ISOBUTEN		1	0.30	1.06	0.39	301	1	64	67	6	85	96	11	92	103	11
EC146	T-2-BUTE		1	0.51	0.56	0.32	301	1	41	43	5	52	53	2	60	60	0
EC147	T-2-BUTE		1	0.96	1.01	0.32	301	1	66	72	9	79	86	8	89	95	7
EC157	T-2-BUTE		1	0.56	0.52	0.33	301	1	41	41	-1	50	51	1	58	57	-2
ITC511	ISOPRENE		2	0.60	3.83	0.53	300	1	135	148	9	125	136	9	-		
ITC811	ISOPRENE		8	0.46	2.42	0.35	297	1	121	92	-32	130	111	-17	-		

Table B-1 (continued)

Run	Run Type or VOC [a]	Rct'y Type [a]	Chr Set [b]	NOx (ppm)	Pr.Eq. (ppm) [c]	k1 (min^{-1}) [d]	T (K) [e]	Ref [f]	Δ (O3-NO) Results (pphm)								
									2 Hour			4 Hour			6 Hour		
									Expt	Calc	Δ%	Expt	Calc	Δ%	Expt	Calc	Δ%
ITC812	ISOPRENE		8	0.53	1.28	0.35	297	1	59	33	-82	96	59	-63	114	76	-50
DTC053A	ISOPRENE		1	0.15	1.16	0.39	301	1	37	41	11	55	53	-2	56	53	-6
DTC053B	ISOPRENE		1	0.24	1.17	0.39	301	1	29	32	9	64	70	8	79	80	2
DTC056A	ISOPRENE		1	0.47	2.73	0.39	301	1	102	113	10	125	115	-9	122	112	-9
DTC056B	ISOPRENE		1	0.47	1.48	0.39	301	1	38	41	7	77	82	6	97	105	7
XTC093	ISOPRENE		1	0.16	1.07	0.25	301	1	20	16	-24	46	43	-7	-	46	
XTC101	ISOPRENE		1	0.53	1.55	0.25	302	1	28	27	-3	65	61	-7	89	90	2
EC520	ISOPRENE		1	0.49	1.69	0.31	302	1	63	68	8	86	94	8	89	99	11
EC522	ISOPRENE		1	0.96	1.72	0.32	304	1	66	69	4	89	95	6	102	111	8
EC524	ISOPRENE		1	1.00	3.34	0.33	302	1	133	146	9	157	169	7	148	164	10
EC527	ISOPRENE		1	0.53	1.61	0.34	301	1	65	63	-3	89	91	2	91	102	11
EC669	ISOPRENE		1	0.47	1.82	0.38	303	1	56	70	20	66	99	33	70	107	35
OTC309A	ISOPRENE		12	0.21	0.99	0.00	318	0	45	50	10	79	88	11	-	97	
OTC309B	ISOPRENE		12	0.37	0.99	0.00	318	0	40	40	1	90	96	6	-	112	
OTC316A	ISOPRENE		12	0.42	0.86	0.00	310	0	31	25	-23	65	55	-18	77	66	-16
OTC316B	ISOPRENE		12	0.42	1.70	0.00	310	0	74	74	1	120	116	-4	124	116	-7
ETC420	A-PINENE		3	0.29	0.54	0.35	299	1	36	39	6	51	50	-2	57	56	-1
ETC443	A-PINENE		3	0.26	0.57	0.35	300	1	41	46	10	54	55	2	61	62	2
ETC444	A-PINENE		3	0.30	0.56	0.35	300	1	40	44	9	51	52	2	58	59	2
ETC446	A-PINENE		3	0.53	0.56	0.35	300	1	19	20	4	43	44	2	55	54	-2
ETC447	A-PINENE		3	0.13	0.56	0.35	300	1	36	38	5	39	41	5	41	45	8
XTC095	A-PINENE		1	0.24	0.59	0.25	302	1	39	39	0	45	45	0	-	47	
OTC318A	A-PINENE		12	0.26	0.43	0.00	310	0	20	21	3	48	48	1	-	56	
ETC421	B-PINENE		3	0.25	0.82	0.35	299	1	7	5	-48	13	14	12	24	41	42
ETC433	B-PINENE		3	0.27	0.80	0.35	300	1	4	5	15	11	13	20	21	32	34
ETC434	B-PINENE		3	0.29	2.92	0.35	300	1	16	11	-44	52	72	27	44	64	31
ETC435	B-PINENE		3	0.14	0.84	0.35	301	1	5	6	22	19	37	49	37	48	24
ETC442	B-PINENE		3	0.29	0.82	0.35	301	1	4	5	14	11	13	15	22	29	24
XTC099	B-PINENE		1	0.23	1.59	0.25	304	1	9	4	-101	33	17	-96	46	59	22
OTC318B	B-PINENE		12	0.26	0.53	0.00	310	0	17	5	-233	49	15	-222	-	26	
ETC424	3-CARENE		3	0.25	0.99	0.35	299	1	19	19	4	52	42	-24	57	49	-15
ETC456	3-CARENE		3	0.23	0.83	0.35	300	1	17	15	-7	48	36	-32	54	44	-24
ETC457	3-CARENE		3	0.16	0.88	0.35	301	1	29	24	-22	41	41	2	42	48	14
ETC459	3-CARENE		3	0.50	0.76	0.35	301	1	11	8	-37	30	19	-55	51	30	-72
ETC423	SABINENE		3	0.25	1.15	0.35	299	1	16	22	29	47	49	4	53	55	4
ETC436	SABINENE		3	0.29	1.14	0.35	300	1	12	18	36	43	47	8	51	53	5
ETC437	SABINENE		3	0.58	1.14	0.35	300	1	13	12	-13	34	28	-20	46	39	-19
ETC438	SABINENE		3	0.14	0.59	0.35	300	1	7	12	40	25	27	7	31	31	2
ETC425	D-LIMONE		3	0.25	1.97	0.35	299	1	48	49	1	56	57	1	62	63	3
ETC450	D-LIMONE		3	0.24	1.77	0.35	301	1	49	45	-8	57	54	-7	63	61	-4
ETC451	D-LIMONE		3	0.57	1.69	0.35	301	1	34	40	16	52	48	-8	58	51	-13
ETC452	D-LIMONE		3	0.16	1.76	0.35	301	1	45	43	-4	50	51	3	51	57	10
ITC560	BENZENE		3	0.11	2.84	0.36	301	1	38	46	17	-			-		
ITC561	BENZENE		3	0.11	0.34	0.36	301	1	35	34	-2	-			-		
ITC562	BENZENE		3	0.57	0.36	0.36	301	1	35	8	-337	75	19	-294	80	32	-147
ITC698	BENZENE		6	0.49	0.70	0.35	301	1	34	24	-43	76	62	-23	-		
ITC710	BENZENE		6	0.53	0.70	0.35	300	1	32	20	-57	71	51	-39	73	100	26
ITC831	BENZENE		8	1.01	0.01	0.35	298	1	-1	2		4	5	21	8	8	-4

Table B-1 (continued)

Run	Run Type or VOC [a]	Rct'y Type [a]	Chr Set [b]	NOx (ppm)	Pr.Eq. (ppm) [c]	k1 (min^{-1}) [d]	T (K) [e]	Ref [f]	Δ (O3-NO) Results (pphm) 2 Hour Expt	2 Hour Calc	2 Hour Δ%	4 Hour Expt	4 Hour Calc	4 Hour Δ%	6 Hour Expt	6 Hour Calc	6 Hour Δ%
CTC159A	BENZENE		6	0.26	1.74	0.18	303	0	31	31	-1	56	53	-5	-	49	
CTC159B	BENZENE		6	0.26	0.86	0.18	303	0	13	11	-19	50	38	-33	-	51	
CTC160A	BENZENE		6	0.49	0.96	0.18	302	0	4	8	50	16	22	30	-	45	
CTC160B	BENZENE		6	0.49	1.74	0.18	302	0	8	19	60	38	66	42	-	73	
ITC534	TOLUENE		3	0.53	0.49	0.36	302	1	61	58	-5	87	101	13	-		
ITC699	TOLUENE		6	0.49	0.37	0.35	300	1	59	41	-44	83	85	2	-		
ITC828	TOLUENE		8	1.01	0.01	0.35	297	1	-1	2		5	7	25	13	13	-1
DTC042A	TOLUENE		1	0.99	0.24	0.39	300	1	4	5	25	19	20	7	45	41	-10
DTC042B	TOLUENE		1	0.10	0.13	0.39	300	1	32	27	-19	35	37	7	34	38	9
DTC151A	TOLUENE		3	0.32	0.43	0.25	298	2	36	39	8	65	67	2	59	65	10
DTC155A	TOLUENE		3	0.10	0.16	0.25	298	2	25	21	-22	28	32	13	27	33	18
DTC158A	TOLUENE		3	0.50	0.57	0.25	298	2	41	45	10	87	86	-1	79	90	12
DTC170A	TOLUENE		3	0.49	0.58	0.24	299	2	42	45	8	89	86	-4	81	89	9
XTC106	TOLUENE		1	0.25	0.47	0.25	301	1	57	56	-2	58	61	5	-	60	
CTC026	TOLUENE		1	0.27	0.50	0.20	302	2	45	47	4	54	58	7	-	58	
CTC034	TOLUENE		1	0.52	0.50	0.20	305	2	36	41	14	83	88	6	-	92	
CTC048	TOLUENE		2	0.25	0.22	0.20	301	2	17	19	9	49	46	-6	48	53	9
CTC065	TOLUENE		2	0.66	0.23	0.19	300	2	5	6	6	22	23	4	-	46	
CTC079	TOLUENE		3	0.26	0.12	0.19	298	2	4	5	16	19	20	4	-	32	
EC264	TOLUENE		1	0.44	0.26	0.34	303	1	53	68	23	79	87	9	-		
EC266	TOLUENE		1	0.44	0.27	0.34	302	1	52	68	24	78	86	9	73	80	9
EC269	TOLUENE		1	0.48	0.13	0.34	302	1	32	34	6	51	60	16	69	84	18
EC270	TOLUENE		1	0.47	0.20	0.35	302	1	44	52	16	67	84	19	78	89	12
EC271	TOLUENE		1	0.21	0.26	0.35	302	1	47	57	18	42	53	21	40	50	20
EC273	TOLUENE		1	0.11	0.13	0.40	303	1	30	40	25	29	39	26	28	38	26
EC293	TOLUENE		1	0.49	0.24	0.40	302	1	74	70	-6	77	92	17	72	86	16
EC327	TOLUENE		1	0.49	0.13	0.41	302	1	33	40	17	57	70	18	76	89	15
EC340	TOLUENE		1	0.49	0.12	0.36	302	1	35	34	-3	57	59	4	-		
OTC299A	TOLUENE		11	0.51	0.28	0.00	312	7	56	50	-12	98	111	11	-	114	
OTC299B	TOLUENE		11	0.50	0.12	0.00	312	7	-	9		37	41	11	-	62	
OTC300A	TOLUENE		11	0.52	0.12	0.00	312	7	14	12	-13	54	48	-12	-	71	
OTC300B	TOLUENE		11	0.22	0.12	0.00	312	7	27	30	10	61	64	4	-	67	
DTC223A	C2-BENZ		3	0.26	0.43	0.22	299	2	19	24	24	49	51	3	-	58	
DTC223B	C2-BENZ		3	0.27	0.22	0.22	299	2	9	12	25	26	25	-7	42	35	-19
DTC224A	C2-BENZ		3	0.53	0.45	0.22	298	2	15	15	-3	41	37	-10	-	55	
DTC224B	C2-BENZ		3	0.55	0.20	0.22	298	2	7	7	2	20	17	-12	-	27	
CTC057	C2-BENZ		2	0.27	0.55	0.20	300	2	16	17	7	48	47	-1	50	57	11
CTC092A	C2-BENZ		4	0.27	0.29	0.19	295	2	7	5	-24	23	18	-28	-	29	
CTC092B	C2-BENZ		4	0.27	0.54	0.19	295	2	16	14	-10	43	39	-10	51	57	10
CTC098B	C2-BENZ		4	0.49	0.51	0.19	295	2	5	8	29	20	25	21	-	43	
DTC073A	M-XYLENE		1	0.48	0.11	0.39	302	1	10	9	-12	31	27	-14	43	39	-10
DTC188A	M-XYLENE		3	0.55	0.12	0.23	299	2	7	7	0	22	21	-7	35	32	-8
DTC188B	M-XYLENE		3	0.57	0.22	0.23	299	2	24	18	-31	53	42	-25	67	55	-21
DTC189A	M-XYLENE		3	0.25	0.24	0.23	299	2	34	30	-11	56	51	-10	58	57	-3
DTC189B	M-XYLENE		3	0.26	0.11	0.23	299	2	16	13	-26	31	25	-24	40	33	-21
DTC191A	M-XYLENE		3	0.57	0.49	0.23	298	2	57	50	-13	96	87	-11	98	104	5
DTC191B	M-XYLENE		3	0.59	1.01	0.23	298	2	97	94	-4	97	99	3	85	94	9
DTC192A	M-XYLENE		3	0.30	0.49	0.23	298	2	61	56	-9	63	63	0	-	62	

Table B-1 (continued)

Run	Run Type or VOC [a]	Rct'y Type [a]	Chr Set [b]	NOx (ppm)	Pr.Eq. (ppm) [c]	k1 (min^{-1}) [d]	T (K) [e]	Ref [f]	Δ (O3-NO) Results (pphm) 2 Hour			4 Hour			6 Hour		
									Expt	Calc	Δ%	Expt	Calc	Δ%	Expt	Calc	Δ%
DTC192B	M-XYLENE		3	0.15	0.49	0.23	298	2	40	43	8	37	42	12	35	40	13
DTC193A	M-XYLENE		3	0.13	0.27	0.23	299	2	36	35	-1	37	38	3	35	38	7
DTC193B	M-XYLENE		3	0.13	0.15	0.23	299	2	27	22	-19	39	34	-13	40	35	-13
CTC029	M-XYLENE		1	0.27	0.33	0.20	300	2	38	46	17	62	64	3	63	65	3
CTC035	M-XYLENE		1	0.28	0.15	0.20	301	2	20	18	-10	43	39	-8	57	54	-5
CTC036	M-XYLENE		1	0.51	0.15	0.20	302	2	7	8	15	30	29	-1	45	43	-3
CTC066	M-XYLENE		2	0.56	0.30	0.19	300	2	19	32	41	57	65	13	77	87	12
CTC080	M-XYLENE		3	0.51	0.48	0.19	298	2	52	64	18	93	97	4	92	98	6
CTC094A	M-XYLENE		4	0.49	0.51	0.19	294	2	41	62	33	77	93	18	-	93	
CTC094B	M-XYLENE		4	0.49	0.52	0.19	294	2	44	62	30	78	93	16	-	92	
DTC207A	O-XYLENE		3	0.28	0.17	0.23	299	2	21	24	12	47	43	-9	62	60	-4
DTC207B	O-XYLENE		3	0.30	0.36	0.23	299	2	48	54	12	65	67	4	-	65	
DTC208A	O-XYLENE		3	0.52	0.31	0.23	300	2	35	41	15	76	71	-7	-	98	
DTC208B	O-XYLENE		3	0.56	0.16	0.23	300	2	13	13	3	39	34	-14	53	47	-13
DTC209A	O-XYLENE		3	0.12	0.15	0.23	299	2	27	28	2	-	37		-	38	
DTC209B	O-XYLENE		3	0.13	0.09	0.23	299	2	15	16	11	-	28		-	35	
CTC038	O-XYLENE		1	0.25	0.16	0.20	301	2	16	16	0	47	40	-18	59	57	-4
CTC039	O-XYLENE		1	0.48	0.08	0.20	301	2	3	3	-20	11	10	-10	-	20	
CTC046	O-XYLENE		2	0.50	0.16	0.20	303	2	3	6	48	18	24	26	-	43	
CTC068	O-XYLENE		2	0.26	0.34	0.19	302	2	39	44	12	58	62	6	57	63	9
CTC081	O-XYLENE		3	0.26	0.29	0.19	298	2	35	34	-4	57	60	5	-	62	
CTC091A	O-XYLENE		4	0.28	0.25	0.19	295	2	23	25	7	54	52	-4	-	64	
EC288	O-XYLENE		1	0.50	0.10	0.38	302	1	42	33	-26	59	55	-7	69	69	0
EC291	O-XYLENE		1	0.49	0.32	0.39	302	1	84	101	16	91	109	16	91	104	12
DTC198A	P-XYLENE		3	0.26	0.24	0.23	299	2	7	10	25	23	23	2	-	36	
DTC198B	P-XYLENE		3	0.27	0.47	0.23	299	2	15	20	26	-	46		-	57	
DTC199A	P-XYLENE		3	0.55	0.47	0.23	299	2	10	12	18	34	32	-6	-	50	
DTC199B	P-XYLENE		3	0.55	0.25	0.23	299	2	8	8	1	23	18	-25	41	29	-40
DTC200A	P-XYLENE		3	0.13	0.22	0.23	299	2	12	14	14	-	30		-	36	
DTC200B	P-XYLENE		3	0.13	0.12	0.23	299	2	8	8	8	19	16	-14	30	24	-26
CTC041	P-XYLENE		1	0.26	0.21	0.20	300	2	5	4	-36	17	13	-32	32	23	-41
CTC043	P-XYLENE		2	0.25	0.11	0.20	301	2	2	2	-17	7	5	-26	14	10	-40
CTC044	P-XYLENE		2	0.51	0.22	0.20	301	2	1	3	50	6	7	21	13	13	3
CTC047	P-XYLENE		2	0.28	0.54	0.20	301	2	9	12	26	37	39	5	-	59	
CTC069	P-XYLENE		2	0.24	1.11	0.19	302	2	17	35	52	57	56	-1	57	53	-8
CTC070	P-XYLENE		2	0.50	1.12	0.19	301	2	10	22	53	50	70	29	93	94	1
DTC201A	124-TMB		3	0.25	0.23	0.23	299	2	13	14	11	31	29	-6	-	42	
DTC203A	124-TMB		3	0.51	0.44	0.23	298	2	15	18	21	44	45	2	-	63	
DTC203B	124-TMB		3	0.54	0.23	0.23	298	2	10	9	-9	29	24	-18	44	36	-22
DTC204A	124-TMB		3	0.12	0.22	0.23	298	2	14	18	21	31	32	5	39	34	-13
DTC204B	124-TMB		3	0.12	0.13	0.23	298	2	9	11	15	20	20	-1	-	27	
CTC056	124-TMB		2	0.25	0.28	0.20	300	2	8	10	18	32	29	-9	50	45	-12
CTC091B	124-TMB		4	0.28	0.58	0.19	295	2	19	23	19	47	52	9	-	59	
CTC093A	124-TMB		4	0.48	0.60	0.19	294	2	13	15	11	43	42	-2	-	64	
CTC093B	124-TMB		4	0.49	1.42	0.19	294	2	35	48	27	74	86	15	-	83	
ITC703	135-TMB		6	0.49	1.23	0.35	301	1	107	105	-3	106	102	-3	-		
ITC706	135-TMB		6	0.47	0.61	0.35	300	1	70	78	11	94	101	7	101	104	3
ITC709	135-TMB		6	0.97	1.10	0.35	301	1	108	124	13	139	170	18	154	173	11

Table B-1 (continued)

Run	Run Type	Rct'y	Chr	NOx	Pr.Eq.	k1	T	Ref	Δ (O3-NO) Results (pphm)								
	or VOC	Type	Set	(ppm)	(ppm)	(min^{-1})	(K)		2 Hour			4 Hour			6 Hour		
	[a]	[a]	[b]		[c]	[d]	[e]	[f]	Expt	Calc	Δ%	Expt	Calc	Δ%	Expt	Calc	Δ%
ITC742	135-TMB		7	0.52	1.09	0.35	300	1	-	107		-	106		-		
ITC826	135-TMB		8	0.90	0.01	0.35	297	1	-2	2		19	17	-13	35	34	-5
DTC194A	135-TMB		3	0.26	0.38	0.23	299	2	38	37	-4	57	54	-6	62	59	-5
DTC194B	135-TMB		3	0.28	0.76	0.23	299	2	58	58	1	57	57	-1	-	54	
DTC195A	135-TMB		3	0.55	0.77	0.23	300	2	60	59	-2	91	91	1	93	97	4
DTC195B	135-TMB		3	0.56	0.38	0.23	300	2	33	25	-30	53	43	-21	63	55	-16
DTC196A	135-TMB		3	0.13	0.38	0.23	300	2	36	37	3	38	38	0	39	38	-1
DTC196B	135-TMB		3	0.14	0.19	0.23	300	2	27	23	-16	37	32	-14	-	37	
DTC206A	135-TMB		3	0.27	0.32	0.23	299	2	38	33	-18	58	48	-20	63	58	-7
XTC103	135-TMB		1	0.50	0.67	0.25	301	1	77	73	-5	107	102	-4	109	108	-1
CTC030	135-TMB		1	0.52	0.71	0.20	300	2	-	62		-	95		-	103	
CTC050	135-TMB		2	0.27	0.43	0.20	303	2	44	41	-7	56	60	7	-	66	
CTC071	135-TMB		2	0.52	0.73	0.19	300	2	64	62	-3	96	95	-1	-	102	
CTC073	135-TMB		3	0.26	0.39	0.19	297	2	32	36	10	52	55	5	56	60	6
CTC098A	135-TMB		4	0.48	0.44	0.19	295	2	32	32	0	58	55	-6	-	69	
EC901	135-TMB		1	0.49	0.68	0.27	303	1	67	82	19	74	94	21	63	92	32
EC903	135-TMB		1	1.01	1.21	0.27	302	1	111	131	16	127	153	17	124	148	16
DTC211A	123-TMB		3	0.25	0.17	0.23	299	2	28	26	-8	47	41	-15	-	52	
DTC211B	123-TMB		3	0.26	0.39	0.23	299	2	52	52	-1	63	55	-15	-	53	
DTC212A	123-TMB		3	0.51	0.40	0.23	299	2	49	50	1	-	78		-	94	
DTC212B	123-TMB		3	0.54	0.22	0.23	299	2	24	23	-4	49	45	-8	59	56	-5
DTC213A	123-TMB		3	0.11	0.19	0.23	299	2	31	30	-2	-	33		-	34	
DTC213B	123-TMB		3	0.11	0.12	0.23	299	2	18	21	15	30	31	3	35	32	-10
CTC054	123-TMB		2	0.23	0.27	0.20	302	2	35	37	6	53	53	1	54	56	3
CTC075	123-TMB		3	0.52	0.29	0.19	298	2	22	25	10	53	55	3	68	72	6
CTC076	123-TMB		3	0.26	0.23	0.19	297	2	29	27	-6	49	48	-3	58	56	-3
ITC751	NAPHTHAL		7	0.54	0.62	0.35	299	1	15	17	8	32	34	6	44	47	6
ITC755	NAPHTHAL		7	0.27	1.18	0.35	299	1	18	24	24	40	40	1	-	53	
ITC756	NAPHTHAL		7	0.25	2.28	0.35	299	1	28	26	-10	45	43	-4	-		
ITC798	NAPHTHAL		8	0.60	1.62	0.35	298	1	20	30	35	46	53	13	65	69	7
ITC802	NAPHTHAL		8	0.59	0.71	0.35	296	1	18	17	-6	39	35	-11	54	48	-11
ITC739	TETRALIN		7	0.54	0.36	0.35	299	1	8	6	-44	14	13	-9	18	20	6
ITC747	TETRALIN		7	0.54	15.10	0.35	299	1	29	37	22	63	72	13	90	82	-9
ITC748	TETRALIN		7	0.23	13.61	0.35	299	1	31	26	-23	52	47	-10	-		
ITC750	TETRALIN		7	0.54	7.12	0.35	299	1	25	32	22	50	65	23	88	80	-10
ITC832	TETRALIN		8	0.99	0.01	0.35	298	1	10	2	-332	29	49	40	65	98	34
ITC771	23-DMN		7	0.25	1.18	0.35	299	1	31	33	7	48	49	2	-		
ITC774	23-DMN		7	0.56	0.99	0.35	299	1	33	45	26	60	64	7	77	82	5
ITC775	23-DMN		7	0.26	0.42	0.35	299	1	21	22	7	38	35	-10	49	45	-10
ITC806	23-DMN		8	0.38	1.45	0.35	297	1	36	39	8	60	59	0	63	63	1
ITC1000	ACETYLEN		11	0.10	0.01	0.35	302	1	2	2	-24	42	49	14	54	58	6
ITC1006	ACETYLEN		11	0.27	1.78	0.35	302	1	111	113	2	105	106	1	-		
ITC1007	ACETYLEN		11	0.23	1.92	0.35	301	1	104	106	2	96	98	2	-		
CTC188A	ACETYLEN		7	0.13	0.36	0.16	298	17	4	6	27	20	27	28	46	47	1
CTC188B	ACETYLEN		7	0.13	0.65	0.16	298	17	17	19	11	55	50	-10	-	59	
ITC1549	FORMALD		12	0.37	0.02	0.35	301	1	-1			12	18	33	19	26	26
ITC1554	FORMALD		12	0.44	0.38	0.35	300	1	26	42	39	37	57	34	-		
ITC864	FORMALD		9	0.54	0.01	0.35	299	1	1	1	39	18	25	29	-		

Table B-1 (continued)

Run	Run Type or VOC [a]	Rct'y Type [a]	Chr Set [b]	NOx (ppm)	Pr.Eq. (ppm) [c]	k1 (min^{-1}) [d]	T (K) [e]	Ref [f]	Δ (O3-NO) Results (pphm)								
									2 Hour			4 Hour			6 Hour		
									Expt	Calc	Δ%	Expt	Calc	Δ%	Expt	Calc	Δ%
ETC378	FORMALD		3	0.24	0.08	0.35	301	1	5	9	37	9	12	26	11	13	20
ETC441	FORMALD		3	0.27	0.17	0.35	301	1	17	20	15	24	26	9	27	29	6
DTC149A	FORMALD		3	0.32	0.20	0.25	298	2	22	21	-6	32	30	-6	37	35	-6
DTC149B	FORMALD		3	0.34	0.21	0.25	298	2	23	22	-6	33	31	-8	38	35	-8
DTC218A	FORMALD		3	0.28	0.17	0.23	299	2	17	16	-7	26	23	-11	30	27	-11
DTC218B	FORMALD		3	0.29	0.19	0.23	299	2	18	18	-3	-	25		32	29	-10
DTC270A	FORMALD		10	0.28	0.14	0.22	298	3	14	12	-21	20	17	-18	24	21	-16
DTC270B	FORMALD		10	0.27	0.14	0.22	298	3	14	12	-15	20	18	-12	24	22	-10
DTC387A	FORMALD		11	0.26	0.20	0.19	299	11	19	18	-6	28	26	-6	34	32	-7
XTC086	FORMALD		1	0.16	0.21	0.26	302	1	23	23	1	36	36	1	45	45	-1
CTC016	FORMALD		1	0.24	0.34	0.20	303	2	26	29	11	40	44	9	51	54	6
CTC024	FORMALD		1	0.17	0.17	0.20	302	2	13	14	3	21	21	2	26	26	0
CTC077	FORMALD		3	0.16	0.15	0.19	299	2	12	10	-15	19	17	-13	24	21	-13
CTC095A	FORMALD		4	0.26	0.19	0.19	294	2	12	13	9	20	21	7	-	26	
CTC095B	FORMALD		4	0.26	0.19	0.19	294	2	12	13	5	20	21	4	-	26	
CTC116A	FORMALD		5	0.24	0.16	0.19	296	2	12	11	-9	18	17	-7	-	21	
CTC116B	FORMALD		5	0.26	0.16	0.19	296	2	12	10	-18	18	16	-12	-	21	
CTC133A	FORMALD		6	0.26	0.18	0.18	296	2	13	12	-13	20	19	-9	-	23	
CTC133B	FORMALD		6	0.25	0.18	0.18	296	2	13	11	-17	21	18	-12	-	23	
CTC176A	FORMALD		7	0.25	0.18	0.16	299	10	11	9	-20	18	16	-16	-	20	
CTC176B	FORMALD		7	0.25	0.18	0.16	299	10	11	9	-22	19	16	-18	-	21	
DTC055B	ACETALD		1	0.14	0.79	0.39	301	1	18	23	19	32	39	18	43	52	17
DTC150A	ACETALD		3	0.14	1.05	0.25	298	2	15	18	14	25	29	13	33	38	13
DTC150B	ACETALD		3	0.15	1.03	0.25	298	2	16	18	9	26	28	7	34	36	5
DTC152B	ACETALD		3	0.20	0.99	0.25	301	2	28	21	-34	49	33	-48	60	42	-42
DTC387B	ACETALD		11	0.26	0.30	0.19	299	11	8	10	15	15	17	10	21	23	8
XTC083	ACETALD		1	0.25	0.62	0.26	302	1	24	26	7	37	39	5	49	51	4
XTC092	ACETALD		1	0.25	0.69	0.25	301	1	20	22	8	31	34	9	41	46	10
CTC014	ACETALD		1	0.23	0.58	0.20	303	2	13	18	29	22	29	23	-	37	
CTC015	ACETALD		1	0.24	0.57	0.20	303	2	12	17	30	20	27	26	-	36	
CTC032	ACETALD		1	0.28	0.70	0.20	301	2	16	19	14	26	29	12	33	37	12
CTC072	ACETALD		3	0.26	0.66	0.19	298	2	15	17	14	24	27	12	-	34	
EC164	ACETALD		1	0.54	0.21	0.35	305	1	23	23	-1	35	36	5	41	46	11
EC254	ACETALD		1	0.11	0.28	0.29	303	1	16	17	7	26	28	7	34	37	8
OTC273B	ACETALD		11	0.30	0.72	0.00	315	7,8	50	53	6	100	109	8	113	126	10
OTC274A	ACETALD		11	0.28	0.69	0.00	308	7,8	49	40	-22	86	75	-15	-	95	
OTC305A	ACETALD		12	0.28	0.90	0.00	316	7	58	58	0	104	107	3	-	115	
OTC317B	ACETALD		12	0.26	0.78	0.00	305	0	27	28	4	47	46	-1	-	49	
ITC941	ACROLEIN		10	0.55	0.51	0.35	301	1	15	16	6	28	31	11	37	43	12
ITC944	ACROLEIN		10	0.27	1.24	0.35	301	1	25	23	-8	45	40	-12	65	58	-13
ITC945	ACROLEIN		10	0.52	0.01	0.35	301	1	1	3	61	17	20	16	-		
ITC946	ACROLEIN		10	0.54	1.20	0.35	302	1	68	37	-85	110	78	-41	107	105	-2
ITC513	METHACRO		2	0.57	3.22	0.53	301	1	68	82	17	111	116	4	105	110	4
ITC819	METHACRO		8	0.48	2.21	0.35	298	1	44	45	2	78	74	-5	110	95	-16
ITC823	METHACRO		8	0.51	41.39	0.35	298	1	64	60	-7	108	91	-19	98	80	-23
ETC386	METHACRO		3	0.56	2.83	0.35	301	1	56	57	2	105	97	-8	100	106	6
DTC075A	METHACRO		1	0.50	5.69	0.39	302	1	64	79	19	97	79	-23	85	73	-16
DTC075B	METHACRO		1	0.26	3.09	0.39	302	1	32	51	37	64	58	-10	63	56	-14

Table B-1 (continued)

Run	Run Type or VOC [a]	Rct'y Type [a]	Chr Set [b]	NOx (ppm)	Pr.Eq. (ppm) [c]	k1 (min^{-1}) [d]	T (K) [e]	Ref [f]	Δ (O3-NO) Results (pphm)								
									2 Hour			4 Hour			6 Hour		
									Expt	Calc	Δ%	Expt	Calc	Δ%	Expt	Calc	Δ%
XTC094	METHACRO		1	0.49	5.06	0.25	302	1	51	46	-11	85	70	-21	-	70	
XTC102	METHACRO		1	0.24	2.00	0.25	301	1	31	24	-27	55	41	-32	-	57	
EC530	METHACRO		1	0.43	0.96	0.34	301	1	37	40	7	56	60	7	69	77	10
EC651	METHACRO		1	0.45	1.85	0.34	302	1	48	48	1	59	76	23	59	91	35
EC652	METHACRO		1	0.45	1.01	0.34	302	1	44	43	-2	55	64	14	62	83	26
EC655	METHACRO		1	0.80	1.88	0.34	302	1	67	72	7	88	99	10	104	125	17
OTC317A	METHACRO		12	0.25	0.64	0.00	305	0	24	17	-46	44	31	-41	51	36	-42
ETC445	ACETONE		3	0.14	0.08	0.35	300	1	13	15	15	23	28	18	33	41	21
DTC054B	ACETONE		1	0.29	0.13	0.39	301	1	15	20	22	27	35	23	39	51	24
DTC055A	ACETONE		1	0.15	0.17	0.39	301	1	20	25	19	36	46	21	50	61	18
XTC084	ACETONE		1	0.24	0.12	0.26	302	1	24	18	-34	40	31	-29	-	44	
XTC090	ACETONE		1	0.19	0.13	0.25	302	1	20	18	-8	34	31	-9	-	44	
OTC273A	ACETONE		11	0.30	0.14	0.00	315	7,8	51	42	-20	107	96	-12	-	120	
OTC274B	ACETONE		11	0.27	0.12	0.00	308	7,8	34	30	-11	71	64	-11	90	89	-1
DTC337A	MEK		11	0.29	0.39	0.21	296	10	26	27	5	39	42	6	51	56	8
DTC337B	MEK		11	0.11	0.39	0.21	296	10	19	20	8	-	33		-	38	
DTC361A	MEK		11	0.10	0.45	0.20	298	10	21	22	4	33	34	3	36	38	5
DTC361B	MEK		11	0.23	0.47	0.20	298	10	27	29	7	43	45	4	59	59	1
CTC178A	MEK		7	0.24	0.44	0.16	298	10	24	23	-5	36	34	-6	-	44	
CTC178B	MEK		7	0.09	0.44	0.16	298	10	17	16	-7	28	26	-7	-	33	
CTC256A	MPK		10	0.20		0.13	296	20	11	12	8	19	19	1	-	24	
CTC256B	C7-KET-2		10	0.20		0.13	296	20	4	4	2	8	8	0	13	12	-7
ITC512	MVK		2	0.60	1.44	0.53	301	1	69	82	16	-	106		100	105	5
ITC815	MVK		8	0.52	1.33	0.35	298	1	53	52	-2	100	93	-7	-		
ITC816	MVK		8	0.51	0.63	0.35	297	1	37	31	-19	64	58	-9	97	88	-10
EC529	MVK		1	0.48	0.70	0.34	301	1	44	52	16	77	87	12	91	96	6
EC644	MVK		1	0.49	0.42	0.34	303	1	54	44	-23	72	71	-1	-		
EC648	MVK		1	0.83	0.65	0.34	303	1	73	66	-11	103	102	-1	104	133	22
EC649	MVK		1	0.46	0.01	0.34	302	1	6	3	-88	51	58	12	62	90	31
EC281	O-CRESOL		1	0.49	0.64	0.37	302	1	18	15	-20	35	37	5	46	50	7
EC289	M-CRESOL		1	0.47	0.48	0.40	302	1	39	16	-137	49	34	-46	51	42	-20
EC290	P-CRESOL		1	0.50	0.59	0.39	302	1	17	18	5	32	38	14	41	46	11
<u>Incermental Reactivity Runs -- VOC Added to Base Case Surrogate</u>																	
ETC483	CO	MRE	3	0.42	1.95	0.35	300	1	45	42	-7	120	116	-3	148	153	3
ETC487	CO	MRE	3	0.46	1.52	0.35	301	1	41	38	-8	112	109	-2	143	152	6
ETC416	CO	MR3	3	0.62	1.82	0.35	299	1	31	27	-14	68	66	-4	115	116	1
ETC418	CO	MR3	3	0.52	1.39	0.35	299	1	29	28	-2	66	69	3	114	121	6
DTC014A	CO	MR8	1	0.48	1.83	0.39	301	1	91	79	-14	130	121	-8	146	147	1
DTC015B	CO	MR8	1	0.50	1.89	0.39	301	1	102	80	-28	142	122	-17	153	149	-3
DTC016A	CO	MR8	1	0.48	1.08	0.39	300	1	65	56	-17	99	85	-17	122	111	-10
DTC020B	CO	MR8	1	0.50	1.33	0.39	300	1	66	49	-33	100	81	-23	125	111	-13
DTC029A	CO	R8	1	0.17	1.21	0.39	301	1	74	73	0	84	86	2	84	88	5
CTC105B	CO	MR3	5	0.30	0.45	0.19	296	2	18	21	14	44	53	17	69	80	14
CTC123A	CO	MR8	5	0.40	0.54	0.18	293	2	53	52	0	76	83	8	91	99	8
ETC506	ETHANE	MRE	3	0.41	1.03	0.35	300	1	32	36	13	83	92	10	121	128	5
ETC092	ETHANE	MR3	2	0.51	0.54	0.36	301	1	13	18	27	34	45	23	58	73	20
ETC099	ETHANE	MR3	2	0.50	0.53	0.36	300	1	14	17	17	35	43	19	56	69	19
ETC235	ETHANE	MR3	2	0.49	0.87	0.35	301	1	24	27	11	58	63	8	98	106	7

Table B-1 (continued)

Run	Run Type or VOC [a]	Rct'y Type [a]	Chr Set [b]	NOx (ppm)	Pr.Eq. (ppm) [c]	k1 (min^{-1}) [d]	T (K) [e]	Ref [f]	Δ (O3-NO) Results (pphm) 2 Hour Expt	2 Hour Calc	2 Hour Δ%	4 Hour Expt	4 Hour Calc	4 Hour Δ%	6 Hour Expt	6 Hour Calc	6 Hour Δ%
DTC242A	ETHANE	MR3	10	0.32	0.59	0.23	296	3	15	18	20	36	45	20	59	75	21
ETC226	PROPANE	MR3	2	0.48	0.92	0.35	299	1	14	20	29	40	55	27	71	100	29
ETC230	PROPANE	MR3	2	0.51	1.67	0.35	300	1	25	25	1	63	66	5	114	124	8
ETC305	PROPANE	MR3	2	0.54	1.27	0.35	301	1	19	19	-2	53	50	-5	100	92	-8
ETC484	N-C4	MRE	3	0.46	2.04	0.35	300	1	45	28	-64	121	89	-35	139	143	2
ETC488	N-C4	MRE	3	0.42	1.53	0.35	300	1	32	26	-23	95	79	-20	132	131	-1
ETC094	N-C4	MR3	2	0.48	1.02	0.36	301	1	13	16	23	33	42	22	57	73	21
ETC097	N-C4	MR3	2	0.50	0.94	0.36	301	1	14	16	11	35	42	17	62	72	14
ETC135	N-C4	MR3	2	0.52	0.89	0.35	301	1	11	13	17	31	36	12	53	60	12
ETC224	N-C4	MR3	2	0.50	1.41	0.35	300	1	20	18	-6	52	51	-2	93	94	1
ETC389	N-C4	R3	3	0.16	0.72	0.35	301	1	20	23	14	55	59	6	72	76	5
ETC393	N-C4	R3	3	0.16	0.69	0.35	300	1	19	22	12	56	57	1	74	76	2
DTC019B	N-C4	MR8	1	0.46	1.00	0.39	300	1	72	67	-6	107	103	-4	130	132	2
DTC031A	N-C4	R8	1	0.17	0.93	0.39	301	1	70	72	2	80	83	3	79	83	5
ETC201	N-C6	MR3	2	0.50		0.35	300	1	11	10	-8	30	29	-4	55	53	-4
ETC209	N-C6	MR3	2	0.51	0.74	0.35	299	1	-	9		25	27	8	47	49	4
DTC072A	N-C6	MRE	1	0.47	1.16	0.39	302	1	14	12	-22	41	34	-20	91	75	-23
ETC237	N-C8	MR3	2	0.48	0.95	0.35	301	1	6	5	-11	18	14	-23	34	27	-28
ETC239	N-C8	MR3	2	0.53	0.92	0.35	301	1	6	6	-5	18	15	-15	34	28	-20
DTC024B	N-C8	MR8	1	0.50	0.75	0.39	301	1	41	35	-16	72	63	-14	100	86	-16
DTC070A	N-C8	MR8	1	0.49	0.63	0.39	301	1	38	36	-6	66	63	-4	87	87	-1
DTC037B	N-C8	R8	1	0.18	0.77	0.39	301	1	54	55	2	66	73	9	67	76	12
DTC071B	N-C8	R8	1	0.18	0.56	0.39	302	1	52	49	-6	65	69	7	65	74	12
CTC110B	N-C8	MR3	5	0.30	0.57	0.19	296	2	8	9	12	26	30	14	-	55	
CTC131A	N-C8	MR8	5	0.39	0.87	0.18	293	2	32	26	-22	56	59	6	70	77	9
DTC271B	N-C12	MR3	10	0.30	0.57	0.22	298	4	7	7	3	23	23	3	38	44	14
DTC273A	N-C12	MR3	10	0.31	0.52	0.22	298	4	9	9	-4	28	26	-5	49	49	0
DTC283B	N-C12	MR3	10	0.32	0.61	0.22	297	4	6	7	19	18	22	18	34	42	19
DTC272A	N-C12	MR8	10	0.14	0.42	0.22	298	4	24	28	16	36	42	14	26	48	45
DTC274B	N-C12	MR8	10	0.16	0.40	0.22	298	4	28	30	5	42	44	5	47	51	7
DTC284A	N-C12	MR8	10	0.15	0.48	0.22	298	4	28	32	13	42	45	8	47	49	6
DTC293A	N-C12	R8	10	0.08	0.50	0.22	297	4	26	29	9	31	31	0	31	30	-2
CTC150B	N-C12	MR8	6	0.42	0.68	0.18	299	4	30	25	-24	58	55	-4	74	73	-1
CTC154A	N-C12	MR8	6	0.42	0.87	0.18	301	4	32	22	-49	61	56	-9	77	75	-2
DTC275A	N-C14	MR3	10	0.32	0.58	0.22	298	4	6	6	-7	19	18	-5	35	35	-1
DTC277B	N-C14	MR3	10	0.31	0.57	0.22	298	4	7	12	41	23	35	35	42	65	35
DTC289B	N-C14	MR3	10	0.35	0.67	0.22	297	4	5	5	13	14	15	10	26	29	11
DTC276B	N-C14	MR8	10	0.17	0.48	0.22	298	4	29	29	1	44	45	3	50	53	5
DTC278A	N-C14	MR8	10	0.16	0.44	0.22	298	4	29	35	18	43	48	10	49	51	4
DTC290A	N-C14	MR8	10	0.17	0.48	0.22	298	4	24	31	21	39	46	15	45	52	15
CTC151A	N-C14	MR8	6	0.50	0.71	0.18	303	4	34	28	-22	55	54	-2	68	68	1
CTC158A	N-C14	MR8	6	0.36	0.92	0.18	304	4	22	18	-22	52	53	2	68	72	5
DTC279B	N-C15	MR3	10	0.32	0.64	0.22	298	4	4	6	31	15	19	22	31	37	18
DTC280A	N-C15	MR8	10	0.16	0.43	0.22	298	4	26	33	21	40	47	14	46	51	11
DTC282A	N-C16	MR3	10	0.33	0.56	0.22	299	4	8	10	22	23	29	22	40	52	24
DTC291B	N-C16	MR3	10	0.33	0.70	0.22	297	4	5	5	-3	14	14	-4	28	27	-2
DTC281B	N-C16	MR8	10	0.16	0.49	0.22	298	4	26	29	8	41	45	9	48	52	8
CTC152B	N-C16	MR8	6	0.37	0.65	0.18	301	4	22	17	-28	43	43	0	-	55	

Table B-1 (continued)

Run	Run Type or VOC [a]	Rct'y Type [a]	Chr Set [b]	NOx (ppm)	Pr.Eq. (ppm) [c]	k1 (min^{-1}) [d]	T (K) [e]	Ref [f]	Δ (O3-NO) Results (pphm)								
									2 Hour			4 Hour			6 Hour		
									Expt	Calc	Δ%	Expt	Calc	Δ%	Expt	Calc	Δ%
CTC156B	N-C16	MR8	6	0.41	0.88	0.18	303	4	25	16	-51	52	49	-6	65	67	4
ETC228	2-ME-C3	MR3	2	0.51	0.67	0.35	300	1	14	18	23	41	50	18	72	91	21
ETC232	2-ME-C3	MR3	2	0.51	2.31	0.35	299	1	21	20	-6	63	53	-18	133	117	-14
ETC241	2-ME-C3	MR3	2	0.48	1.32	0.35	301	1	17	20	14	54	55	2	119	117	-1
ETC303	2-ME-C3	MR3	2	0.45	0.96	0.35	300	1	13	18	30	41	50	18	88	102	13
ETC291	224TM-C5	MR3	2	0.50	1.81	0.35	303	1	13	13	2	43	41	-5	102	96	-6
ETC293	224TM-C5	MR3	2	0.49	1.92	0.35	302	1	12	12	-4	42	39	-7	99	91	-9
DTC733A	26DM-C8	MR4	18	0.30	0.53	0.16	296	21	4	3	-36	12	7	-74	23	12	-80
DTC749A	26DM-C8	MR4	18	0.38	0.55	0.16	298	21	6	5	-38	20	12	-70	36	22	-67
DTC738B	26DM-C8	MR8	18	0.31	0.41	0.16	293	21	18	13	-40	42	36	-18	55	50	-11
DTC747A	26DM-C8	MR8	18	0.29	0.42	0.16	299	21	16	13	-21	44	43	-3	59	58	-2
DTC739A	26DM-C8	R8	18	0.10	0.39	0.16	295	21	27	29	8	31	34	10	30	35	13
DTC734B	2-ME-C9	MR3	18	0.40	0.50	0.16	295	21	5	3	-70	13	6	-115	24	10	-132
DTC741A	2-ME-C9	MR3	18	0.38	0.48	0.16	295	21	5	4	-26	14	9	-51	27	17	-62
DTC737A	2-ME-C9	MR8	18	0.32	0.43	0.16	294	21	17	12	-36	42	36	-15	55	51	-6
DTC746B	2-ME-C9	MR8	18	0.30	0.44	0.16	298	21	13	12	-8	39	39	0	53	55	4
DTC740B	2-ME-C9	R8	18	0.10	0.39	0.16	295	21	24	27	10	28	33	14	28	34	19
DTC725A	34-DE-C6	MR4	18		0.51	0.16	295	21	9	8	-13	29	22	-28	47	37	-27
DTC730A	34-DE-C6	MR4	18	0.30	0.51	0.16	296	21	6	4	-49	18	11	-68	32	20	-54
DTC726B	34-DE-C6	MR8	18	0.29	0.43	0.16	294	21	22	22	2	42	42	0	54	53	-2
DTC729B	34-DE-C6	MR8	18	0.24	0.40	0.16	294	21	15	15	-2	39	43	9	52	55	6
DTC732B	34-DE-C6	R8	18	0.08	0.41	0.16	296	21	-	26		30	30	2	29	30	5
DTC748B	34-DE-C6	R8	18	0.09	0.41	0.16	297	21	25	28	12	28	33	17	27	34	21
DTC541A	CYCC6	MR3	14	0.38	0.76	0.21	299	10	8	9	14	24	26	6	45	47	5
DTC551A	CYCC6	MR3	14	0.38	0.93	0.20	300	10	8	7	-8	21	18	-11	37	33	-11
DTC543B	CYCC6	MR8	15	0.30	0.96	0.21	299	10	42	40	-5	65	64	-2	81	79	-2
DTC552B	CYCC6	MR8	15	0.31	0.73	0.20	300	10	36	26	-36	64	54	-18	81	71	-14
DTC544A	CYCC6	R8	14	0.13	0.63	0.21	299	10	40	39	-3	49	48	-2	52	51	-2
DTC553A	CYCC6	R8	14	0.13	0.78	0.20	300	10	41	40	-3	51	50	-2	54	54	-1
DTC315B	C6-CYCC6	MR3	11	0.33	0.62	0.21	298	5	8	6	-19	21	19	-11	36	34	-4
DTC318B	C6-CYCC6	MR3	11	0.33	0.57	0.21	297	5	7	8	13	21	24	13	37	43	16
DTC317A	C6-CYCC6	MR8	11	0.17	0.54	0.21	297	5	27	28	4	41	44	6	46	52	11
DTC319B	C6-CYCC6	MR8	11	0.18	0.57	0.21	297	5	20	21	3	37	40	5	45	51	11
CTC167A	C6-CYCC6	MR8	7	0.41	0.95	0.18	300	5	28	22	-27	58	58	0	-	76	
CTC233A	C6-CYCC6	R8	9	0.17	0.85	0.14	299	5	37	39	5	44	46	5	-	47	
DTC324A	C8-CYCC6	MR3	11	0.32	0.59	0.21	298	5	9	10	19	25	30	17	44	56	22
DTC325B	C8-CYCC6	R8	11	0.18	0.68	0.21	299	5	25	29	13	40	47	15	46	55	16
CTC231A	C8-CYCC6	MR3	9	0.27	0.70	0.14	303	5	4	5	26	12	13	12	24	25	3
CTC168B	C8-CYCC6	MR8	7	0.41	0.96	0.18	300	5	27	22	-23	55	59	7	-	78	
CTC232B	C8-CYCC6	MR8	9	0.46	0.81	0.14	301	5	14	15	5	38	44	13	54	63	14
CTC239B	C8-CYCC6	MR8	9	0.44	1.01	0.13	301	5	18	16	-12	48	49	2	61	67	9
CTC240A	C8-CYCC6	R8	9	0.17	1.01	0.13	300	5	33	36	7	41	44	8	43	46	7
ETC199	ETHENE	MR3	2		0.52	0.35	301	1	23	23	-2	65	61	-6	120	108	-11
ETC203	ETHENE	MR3	2	0.52	0.46	0.35	301	1	20	20	-2	54	53	-2	96	91	-6
DTC017A	ETHENE	MR8	1	0.48	0.56	0.39	300	1	56	54	-5	94	89	-6	119	118	-1
DTC038A	ETHENE	R8	1	0.17	0.57	0.39	301	1	63	65	3	65	69	5	62	66	6
ETC496	PROPENE	MRE	3	0.38	0.82	0.35	301	1	45	57	21	111	117	5	123	121	-2
ETC500	PROPENE	MRE	3	0.42	0.76	0.35	300	1	35	43	19	100	113	11	127	131	3

Table B-1 (continued)

Run	Run Type or VOC [a]	Rct'y Type [a]	Chr Set [b]	NOx (ppm)	Pr.Eq. (ppm) [c]	k1 (min^{-1}) [d]	T (K) [e]	Ref [f]	Δ (O3-NO) Results (pphm)								
									2 Hour			4 Hour			6 Hour		
									Expt	Calc	Δ%	Expt	Calc	Δ%	Expt	Calc	Δ%
ETC106	PROPENE	MR3	2	0.52	0.44	0.36	300	1	14	17	16	39	45	13	65	74	11
ETC108	PROPENE	MR3	2	0.52	0.45	0.36	300	1	14	16	12	37	44	16	59	71	17
ETC110	PROPENE	MR3	2	0.52	0.42	0.36	300	1	13	15	12	36	41	12	62	67	8
ETC118	PROPENE	MR3	2	0.50	0.49	0.36	302	1	14	20	28	39	53	26	70	91	23
DTC018A	PROPENE	MR8	1	0.48	0.71	0.39	301	1	73	65	-12	109	104	-6	117	124	6
DTC032B	PROPENE	R8	1	0.17	0.66	0.39	300	1	61	63	4	59	64	7	59	64	8
CTC142B	PROPENE	MR3	6	0.37	0.49	0.18	295	2	9	10	10	26	31	16	-	55	
CTC130B	PROPENE	MR8	5	0.39	0.86	0.18	293	2	52	53	3	79	83	5	84	87	4
ETC253	ISOBUTEN	MR3	2	0.48	0.81	0.35	301	1	29	26	-14	81	82	1	122	125	2
ETC255	ISOBUTEN	MR3	2	0.48	0.79	0.35	302	1	29	27	-10	80	84	5	121	128	5
ETC257	ISOBUTEN	MR3	2	0.48	0.62	0.35	301	1	22	20	-9	57	57	1	97	102	5
ETC493	T-2-BUTE	MRE	3	0.42	0.93	0.35	301	1	93	95	1	122	127	4	123	127	3
ETC501	T-2-BUTE	MRE	3	0.42	0.72	0.35	300	1	64	67	5	110	118	7	127	133	4
ETC307	T-2-BUTE	MR3	2	0.54	0.60	0.35	300	1	52	46	-12	81	73	-10	109	102	-7
ETC309	T-2-BUTE	MR3	2	0.52	0.53	0.35	301	1	44	37	-18	75	66	-14	105	93	-13
DTC043B	T-2-BUTE	MRE	1	0.47	0.79	0.39	300	1	72	73	2	122	125	2	141	146	3
DTC021B	T-2-BUTE	MR8	1	0.49	1.06	0.39	300	1	90	87	-3	107	110	3	112	124	10
DTC069A	T-2-BUTE	MR8	1	0.48	0.72	0.39	302	1	69	66	-5	89	91	1	106	112	6
DTC041A	T-2-BUTE	RE	1	0.17	0.79	0.39	300	1	71	75	5	76	82	7	70	76	8
DTC033A	T-2-BUTE	R8	1	0.17	0.65	0.39	300	1	55	58	4	58	61	5	59	63	6
ETC495	ISOPRENE	MRE	3	0.42	1.28	0.35	300	1	42	56	25	106	120	12	131	126	-4
ETC503	ISOPRENE	MRE	3	0.42	1.61	0.35	301	1	65	81	20	119	120	1	126	114	-11
ETC510	ISOPRENE	MRE	3	0.41	1.43	0.35	300	1	45	65	31	109	119	9	127	119	-7
ETC271	ISOPRENE	MR3	2	0.49	0.98	0.35	299	1	31	32	2	78	74	-5	118	116	-2
ETC273	ISOPRENE	MR3	2	0.49	0.92	0.35	301	1	31	32	2	80	75	-7	121	116	-4
ETC275	ISOPRENE	MR3	2	0.49	0.79	0.35	302	1	29	28	-3	73	65	-13	117	107	-10
ETC277	ISOPRENE	MR3	2	0.50	0.67	0.35	302	1	26	25	-6	68	59	-15	113	98	-15
DTC047B	ISOPRENE	MRE	1	0.48	1.02	0.39	301	1	36	40	8	102	107	5	145	146	1
DTC046A	ISOPRENE	RE	1	0.17	1.04	0.19	300	1	14	18	23	48	53	10	55	55	0
DTC050B	ISOPRENE	RE	1	0.16	0.99	0.39	301	1	50	56	11	78	77	-1	76	72	-6
ETC508	A-PINENE	MRE	3	0.41	0.82	0.35	301	1	54	66	19	103	111	8	121	124	2
DTC045B	A-PINENE	MRE	1	0.48	0.79	0.39	301	1	40	48	17	105	111	6	140	146	4
DTC044A	A-PINENE	RE	1	0.16	0.79	0.39	300	1	58	65	10	73	77	5	70	73	5
DTC034B	A-PINENE	R8	1	0.16	0.93	0.39	301	1	49	49	1	48	49	3	46	50	8
DTC051B	B-PINENE	MRE	1	0.48	0.92	0.39	301	1	16	18	9	52	73	29	118	134	12
DTC048A	B-PINENE	RE	1	0.17	0.91	0.39	301	1	18	36	50	66	78	15	70	80	12
ETC263	BENZENE	MR3	2	0.48	0.73	0.35	303	1	24	30	20	82	92	11	91	110	17
ETC265	BENZENE	MR3	2	0.49	0.69	0.35	300	1	23	26	11	67	76	13	96	114	16
DTC039B	BENZENE	R8	1	0.18	0.76	0.39	301	1	53	60	13	50	57	13	47	54	13
ETC101	TOLUENE	MR3	2	0.50	0.38	0.36	300	1	13	16	20	39	43	8	65	71	9
ETC103	TOLUENE	MR3	2	0.52	0.38	0.36	301	1	14	15	6	40	42	6	68	71	4
DTC023A	TOLUENE	MR8	1	0.47	0.52	0.39	301	1	60	57	-6	100	94	-7	108	114	6
DTC030B	TOLUENE	R8	1	0.17	0.64	0.39	300	1	50	55	9	48	54	10	47	53	11
CTC108B	TOLUENE	MR3	5	0.31	0.54	0.19	295	2	19	24	21	53	60	12	-	76	
CTC127B	TOLUENE	MR8	5	0.39	0.65	0.18	293	2	46	49	7	68	78	12	-	83	
ETC311	C2-BENZ	MR3	2	0.52	0.42	0.35	297	1	11	12	10	36	38	5	61	62	2
ETC313	C2-BENZ	MR3	2	0.53	0.40	0.35	298	1	13	12	-7	38	35	-7	64	58	-10
ETC315	C2-BENZ	MR3	2	0.53	0.44	0.35	298	1	14	14	3	45	42	-6	78	70	-12

Table B-1 (continued)

Run	Run Type or VOC [a]	Rct'y Type [a]	Chr Set [b]	NOx (ppm)	Pr.Eq. (ppm) [c]	k1 (min^{-1}) [d]	T (K) [e]	Ref [f]	Δ (O3-NO) Results (pphm)								
									2 Hour			4 Hour			6 Hour		
									Expt	Calc	Δ%	Expt	Calc	Δ%	Expt	Calc	Δ%
ETC196	M-XYLENE	MR3	2	0.48		0.35	300	1	19	24	24	54	61	11	92	102	9
ETC207	M-XYLENE	MR3	2	0.51		0.35	299	1	21	23	10	59	59	0	98	96	-2
ETC301	M-XYLENE	MR3	2	0.46	0.43	0.35	300	1	19	23	17	56	58	4	97	98	1
DTC025A	M-XYLENE	MR8	1	0.47	0.50	0.39	302	1	57	56	-1	91	91	0	114	116	2
DTC068B	M-XYLENE	MR8	1	0.48	0.43	0.39	301	1	47	47	0	75	75	0	100	102	2
DTC035A	M-XYLENE	R8	1	0.17	0.49	0.39	301	1	54	55	2	55	56	2	56	57	2
DTC067B	M-XYLENE	R8	1	0.17	0.52	0.39	301	1	54	55	4	54	56	4	53	56	5
CTC109A	M-XYLENE	MR3	5	0.31	0.51	0.19	295	2	37	25	-44	49	61	20	-	78	
CTC128A	M-XYLENE	MR8	5	0.41	0.64	0.18	294	2	43	49	11	66	76	12	-	87	
ETC259	O-XYLENE	MR3	2	0.49	0.44	0.35	300	1	22	20	-6	56	54	-3	95	94	-1
ETC261	O-XYLENE	MR3	2	0.48	0.44	0.35	301	1	21	22	2	57	57	0	100	100	0
ETC348	P-XYLENE	MR3	2	0.52	0.49	0.35	303	1	23	24	1	63	61	-4	107	104	-3
ETC267	124-TMB	MR3	2	0.49	0.45	0.35	300	1	21	18	-15	54	49	-8	93	86	-9
ETC269	124-TMB	MR3	2	0.48	0.45	0.35	302	1	23	20	-10	59	54	-9	102	93	-10
ETC249	135-TMB	MR3	2	0.49	0.57	0.35	301	1	35	35	1	85	83	-2	126	126	0
ETC297	123-TMB	MR3	2	0.46	0.45	0.35	301	1	34	32	-8	86	73	-17	122	114	-7
ETC299	123-TMB	MR3	2	0.48	0.44	0.35	301	1	29	27	-8	76	65	-16	117	105	-11
CTC246A	STYRENE	MR3	9	0.25	1.60	0.13	295	6	5	4	-19	15	12	-27	30	23	-31
CTC250B	STYRENE	MR3	9	0.23	0.96	0.13	296	6	4	5	20	15	16	5	29	29	-1
CTC248B	STYRENE	MR8	9	0.31	1.72	0.13	292	6	37	42	12	54	60	10	61	61	-1
CTC251A	STYRENE	MR8	9	0.35	2.22	0.13	294	6	37	42	11	52	62	17	58	61	5
CTC249A	STYRENE	R8	9	0.16	1.74	0.13	295	6	32	33	2	31	30	-2	28	27	-4
CTC253B	STYRENE	R8	9	0.16	1.30	0.13	295	6	35	35	0	38	36	-5	36	33	-8
CTC184B	ACETYLEN	MR3	7	0.23	0.91	0.16	298	17	34	28	-23	74	66	-13	81	72	-11
CTC185A	ACETYLEN	MR3	7	0.27	0.95	0.16	301	17	42	31	-34	85	74	-16	92	82	-12
CTC192A	ACETYLEN	MR3	7	0.22	0.67	0.16	298	17	20	17	-17	61	52	-17	77	67	-15
CTC186B	ACETYLEN	MR8	7	0.37	0.77	0.16	298	17	41	42	1	74	74	0	89	85	-5
CTC193B	ACETYLEN	MR8	7	0.37	0.92	0.16	298	17	51	48	-5	85	81	-4	93	89	-5
CTC187A	ACETYLEN	R8	7	0.15	0.85	0.16	298	17	43	41	-5	47	44	-7	46	42	-8
CTC194A	ACETYLEN	R8	8	0.15	1.06	0.16	297	17	44	43	-4	48	45	-6	47	43	-9
ETC285	MEOH	MR3	2	0.52	0.66	0.35	303	1	24	24	0	71	66	-7	127	120	-5
ETC287	MEOH	MR3	2	0.51	0.41	0.35	303	1	17	17	2	48	46	-4	85	77	-11
ETC289	MEOH	MR3	2	0.50	0.47	0.35	304	1	20	20	1	58	54	-9	105	93	-13
ETC131	ETOH	MR3	2	0.54	0.70	0.35	302	1	14	15	8	37	41	9	60	65	7
ETC133	ETOH	MR3	2	0.53	0.66	0.35	302	1	13	15	12	38	39	5	60	62	4
ETC138	ETOH	MR3	2	0.54	0.70	0.35	300	1	13	14	10	35	38	9	56	60	8
ETC148	I-C3-OH	MR3	2	0.51	1.19	0.35	302	1	19	20	8	47	49	3	82	81	0
ETC155	I-C3-OH	MR3	2	0.50	0.67	0.35	300	1	22	20	-12	55	50	-8	93	85	-9
ETC157	I-C3-OH	MR3	2	0.51	0.60	0.35	300	1	19	18	-7	46	47	2	78	79	2
ETC159	I-C3-OH	MR3	2	0.50	0.65	0.35	301	1	18	19	3	47	50	5	81	85	5
DTC395A	I-C3-OH	MR3	11	0.40	2.39	0.19	299	10	25	25	-2	64	57	-12	96	93	-3
DTC398B	I-C3-OH	MR3	11	0.43	0.98	0.19	297	10	19	15	-30	47	36	-29	80	61	-32
DTC396B	I-C3-OH	MR8	11	0.29	2.52	0.19	299	10	63	70	10	81	91	11	77	100	23
DTC399A	I-C3-OH	MR8	11	0.27	0.75	0.19	298	10	40	37	-9	62	55	-11	72	68	-6
DTC397A	I-C3-OH	R8	11	0.13	1.36	0.19	298	10	45	45	1	50	55	10	47	59	20
DTC400B	I-C3-OH	R8	11	0.11	0.79	0.19	298	10	39	37	-4	44	44	0	43	46	7
DTC233A	T-C4-OH	MR3	10	0.30	0.75	0.23	296	3	15	18	15	40	49	18	69	83	17
DTC241B	T-C4-OH	MR3	10	0.32	0.95	0.23	295	3	16	15	-7	39	41	7	68	79	14

Table B-1 (continued)

Run	Run Type or VOC [a]	Rct'y Type [a]	Chr Set [b]	NOx (ppm)	Pr.Eq. (ppm) [c]	k1 (min^{-1}) [d]	T (K) [e]	Ref [f]	Δ (O3-NO) Results (pphm)								
									2 Hour			4 Hour			6 Hour		
									Expt	Calc	Δ%	Expt	Calc	Δ%	Expt	Calc	Δ%
DTC249A	T-C4-OH	MR8	10	0.25	0.82	0.23	297	3	40	54	26	61	80	24	72	91	20
DTC256A	T-C4-OH	MR8	10	0.26	0.62	0.23	297	3	33	42	22	51	67	25	54	82	34
DTC259A	T-C4-OH	R8	10	0.16	0.70	0.23	297	3	39	48	19	51	62	19	54	67	19
DTC268A	T-C4-OH	R8	10	0.16	0.59	0.22	299	3	39	46	14	52	60	14	54	64	15
DTC269A	T-C4-OH	R8	10	0.17	0.75	0.22	299	3	45	51	12	57	66	13	59	70	15
DTC508B	1-C8-OH	MR3	15	0.37	0.93	0.22	299	10	5	6	8	15	15	1	30	29	-4
DTC529A	1-C8-OH	MR3	14	0.36	0.54	0.21	299	10	9	10	6	27	26	-1	49	47	-6
DTC509A	1-C8-OH	MR8	14	0.30	0.50	0.22	299	10	32	26	-22	55	49	-13	70	64	-10
DTC519B	1-C8-OH	R8	15	0.12	0.60	0.21	298	10	35	36	4	43	45	4	45	47	5
DTC517A	2-C8-OH	MR3	14	0.37		0.21	299	10	10	11	8	32	31	-4	60	55	-9
DTC521B	2-C8-OH	MR8	15	0.30		0.21	299	10	34	31	-9	59	57	-3	74	73	-1
DTC524B	2-C8-OH	R8	15	0.13		0.21	299	10	38	38	-1	45	46	1	46	48	4
DTC514B	3-C8-OH	MR3	15	0.38		0.21	299	10	9	10	10	28	28	-1	52	50	-5
DTC516B	3-C8-OH	MR8	15	0.32		0.21	299	10	34	33	-2	55	54	-2	70	69	-1
DTC520A	3-C8-OH	R8	14	0.13		0.21	299	10	38	39	0	46	47	3	46	49	7
DTC385A	PR-GLYCL	MR3	11	0.39	2.50	0.19	298	11	27	28	1	64	58	-11	94	86	-9
DTC389B	PR-GLYCL	MR3	11	0.36	1.31	0.19	299	11	20	21	3	48	46	-5	78	73	-6
DTC386B	PR-GLYCL	MR8	11	0.29	1.17	0.19	298	11	49	45	-9	69	62	-10	76	74	-3
DTC390A	PR-GLYCL	MR8	11	0.28	1.01	0.19	297	11	43	42	-3	64	60	-6	75	72	-4
DTC388A	PR-GLYCL	R8	11	0.11	1.26	0.19	298	11	39	38	-2	45	45	0	43	45	4
DTC391B	PR-GLYCL	R8	11	0.11	0.80	0.19	297	11	37	34	-8	42	40	-6	41	40	-2
ETC279	ME-O-ME	MR3	2	0.50	0.85	0.35	303	1	28	27	-5	75	68	-11	132	122	-8
ETC281	ME-O-ME	MR3	2	0.51	0.77	0.35	303	1	25	25	2	66	64	-4	121	115	-6
ETC283	ME-O-ME	MR3	2	0.51	0.63	0.35	303	1	24	23	-3	65	59	-11	117	104	-12
ETC295	ME-O-ME	MR3	2	0.48	0.62	0.35	301	1	21	24	12	56	59	4	102	103	1
DTC510B	ET-O-ET	MR3	15	0.39	0.84	0.22	299	10	19	21	12	53	56	5	99	98	-2
DTC522A	ET-O-ET	MR3	14	0.37	1.34	0.21	299	10	23	29	19	73	80	9	116	115	-1
DTC511A	ET-O-ET	MR8	14	0.31	1.30	0.21	299	10	78	88	11	107	114	6	109	120	10
DTC515A	ET-O-ET	MR8	14	0.31	0.65	0.21	299	10	57	49	-16	87	76	-15	101	93	-8
DTC513A	ET-O-ET	R8	14	0.13	0.72	0.21	298	10	49	50	2	57	59	3	57	60	6
DTC525A	ET-O-ET	R8	14	0.13	0.56	0.21	299	10	46	45	-3	53	53	-1	54	54	0
ETC120	MTBE	MR3	2	0.53		0.35	301	1	12	14	12	33	38	15	56	66	16
ETC123	MTBE	MR3	2	0.52		0.35	305	1	16	17	6	44	46	6	81	85	5
ETC125	MTBE	MR3	2	0.51		0.35	302	1	10	14	27	31	40	21	55	70	21
ETC127	MTBE	MR3	2	0.53		0.35	302	1	12	13	8	34	37	9	58	64	10
DTC489A	MEOC3OH	MR3	14	0.38	2.05	0.22	298	15	31	29	-10	71	64	-11	104	96	-8
DTC495A	MEOC3OH	MR3	14	0.38	1.33	0.22	299	15	25	25	0	59	57	-3	94	90	-4
DTC492A	MEOC3OH	MR8	14	0.31	1.39	0.22	298	15	58	62	6	80	83	4	91	93	3
DTC500A	MEOC3OH	MR8	14	0.30	0.93	0.22	298	15	49	52	6	70	73	4	82	84	3
DTC496B	MEOC3OH	R8	15	0.12	1.13	0.22	299	15	47	46	-2	53	53	1	52	54	4
DTC501B	MEOC3OH	R8	15	0.13	0.85	0.22	299	15	45	44	-2	51	51	1	51	52	3
ETC163	ETO-ETOH	MR3	2	0.49		0.35	302	1	27	35	22	80	91	11	143	141	-2
ETC171	ETO-ETOH	MR3	2	0.49	1.03	0.35	301	1	21	27	20	62	70	12	122	121	0
ETC175	ETO-ETOH	MR3	2	0.50		0.35	298	1	18	21	15	49	57	14	91	99	8
DTC491B	BUO-ETOH	MR3	15	0.38	1.44	0.22	298	15	15	11	-32	42	35	-21	85	74	-16
DTC498B	BUO-ETOH	MR3	15	0.38	0.93	0.22	299	15	9	8	-13	24	23	-7	42	42	1
DTC505B	BUO-ETOH	MR3	15	0.38	1.07	0.22	298	15	12	12	0	35	34	0	69	69	0
DTC493B	BUO-ETOH	MR8	15	0.30	0.99	0.22	297	15	57	59	5	85	87	2	97	98	2

Table B-1 (continued)

Run	Run Type or VOC [a]	Rct'y Type [a]	Chr Set [b]	NOx (ppm)	Pr.Eq. (ppm) [c]	k1 (min^{-1}) [d]	T (K) [e]	Ref [f]	Δ (O3-NO) Results (pphm)								
									2 Hour			4 Hour			6 Hour		
									Expt	Calc	Δ%	Expt	Calc	Δ%	Expt	Calc	Δ%
DTC502A	BUO-ETOH	MR8	14	0.30	0.67	0.22	299	15	52	47	-10	78	73	-7	91	87	-4
DTC497A	BUO-ETOH	R8	14	0.13	0.87	0.22	299	15	48	48	-2	57	57	0	57	59	3
DTC506A	BUO-ETOH	R8	14	0.12	0.70	0.22	298	15	44	43	-3	52	51	-2	53	52	-1
ETC166	CARBITOL	MR3	2	0.51	1.43	0.35	304	1	19	19	-1	56	55	0	112	107	-4
ETC169	CARBITOL	MR3	2	0.51	1.21	0.35	300	1	16	15	-11	44	44	-1	82	80	-2
ETC173	CARBITOL	MR3	2	0.51	2.29	0.35	300	1	15	14	-4	42	45	6	87	96	9
DTC327A	ME-ACET	MR3	11	0.34	0.64	0.21	297	9	15	18	19	40	45	11	67	76	12
DTC328B	ME-ACET	MR3	11	0.32	0.72	0.21	297	9	13	19	30	37	47	21	66	79	16
DTC336A	ME-ACET	MR3	11	0.32	0.77	0.21	296	9	17	18	9	42	46	10	69	77	11
DTC332A	ME-ACET	MR8	11	0.57	0.52	0.21	297	9	19	20	3	37	37	2	46	48	4
DTC335B	ME-ACET	MR8	11	0.42	0.55	0.21	297	9	26	30	12	45	50	11	57	66	13
DTC329A	ME-ACET	R8	11	0.17	0.64	0.21	296	9	41	47	13	55	59	6	59	63	6
DTC330B	ME-ACET	R8	11	0.17	0.55	0.21	296	9	38	44	12	53	56	6	58	60	4
DTC358A	ET-ACET	MR3	11	0.33	0.88	0.20	298	10	13	13	0	28	29	4	40	42	6
DTC362B	ET-ACET	MR3	11	0.30	0.79	0.20	298	10	11	13	14	25	29	13	39	45	13
DTC364B	ET-ACET	MR3	11	0.32	0.78	0.20	298	10	12	13	3	28	28	3	41	43	5
DTC359B	ET-ACET	MR8	11	0.27	0.78	0.20	298	10	28	30	6	42	46	9	51	58	11
DTC408B	ET-ACET	MR8	11	0.28	1.03	0.19	298	10	32	28	-12	45	43	-4	55	54	-1
DTC415B	ET-ACET	R3	11	0.20	0.76	0.19	297	10	12	11	-11	26	23	-13	42	37	-12
DTC394A	ET-ACET	R8	11	0.11	0.75	0.19	296	10	25	24	-1	31	33	5	33	36	8
DTC409A	ET-ACET	R8	11	0.11	0.94	0.19	298	10	25	23	-6	31	32	3	33	36	7
CTC195B	ET-ACET	R8	8	0.14	0.85	0.15	297	10	34	31	-9	40	37	-9	42	38	-8
DTC688B	IPR-ACET	MR3	18	0.43	1.40	0.17	294	20	19	16	-16	51	43	-18	95	78	-22
DTC689A	IPR-ACET	MR8	18	0.32	1.06	0.16	294	20	70	65	-8	101	93	-8	114	104	-10
DTC697A	IPR-ACET	MR8	18	0.32	0.66	0.16	296	20	46	41	-12	75	67	-11	91	83	-10
DTC528B	ME-IBUAT	MR3	15	0.38	0.88	0.21	299	10	10	13	23	29	30	5	49	46	-5
DTC533A	ME-IBUAT	MR3	14	0.36	0.74	0.21	299	10	10	14	30	31	34	9	53	53	0
DTC530B	ME-IBUAT	MR8	15	0.31	0.76	0.21	299	10	33	32	-2	54	50	-9	71	64	-11
DTC534B	ME-IBUAT	MR8	15	0.29	0.94	0.21	299	10	32	34	8	56	53	-5	73	67	-9
DTC531A	ME-IBUAT	R8	14	0.12	0.77	0.21	299	10	34	33	-5	44	40	-9	47	42	-11
DTC539A	ME-IBUAT	R8	14	0.13	0.92	0.21	299	10	34	33	-1	44	42	-4	47	44	-6
DTC548A	ME-IBUAT	R8	14	0.13	1.09	0.20	299	10	34	32	-7	44	42	-5	48	46	-4
CTC216B	TBU-ACET	MR3	8	0.23		0.14	298	19	9	8	-19	30	27	-9	56	53	-5
CTC221A	TBU-ACET	MR3	8	0.24	0.80	0.14	299	19	8	7	-14	27	24	-10	54	51	-7
CTC217A	TBU-ACET	MR8	8	0.42	0.86	0.14	297	19	44	39	-12	77	82	6	96	100	4
CTC222B	TBU-ACET	MR8	8	0.43	0.71	0.14	299	19	39	31	-24	70	69	-1	89	88	0
CTC220B	TBU-ACET	R8	8	0.16	0.82	0.14	298	19	46	46	-1	54	54	-1	55	55	-1
CTC223A	TBU-ACET	R8	8	0.16	0.90	0.14	298	19	49	48	-2	57	57	-1	59	58	-2
DTC365A	BU-ACET	MR3	11		1.45	0.20	298	10	9	9	2	20	21	5	33	36	7
DTC368B	BU-ACET	MR3	11		1.53	0.20	299	10	8	9	8	19	21	9	32	35	10
DTC402B	BU-ACET	MR3	11		1.10	0.19	299	10	9	10	5	24	24	1	39	39	0
DTC403A	BU-ACET	MR8	11	0.29	1.25	0.19	299	10	37	40	8	58	63	7	70	77	9
DTC410B	BU-ACET	MR8	11	0.26	1.63	0.19	298	10	41	39	-4	61	60	0	71	73	3
DTC406A	BU-ACET	R8	11	0.12	1.00	0.19	299	10	35	36	3	42	44	3	44	46	4
DTC411A	BU-ACET	R8	11	0.11	1.63	0.19	297	10	34	34	1	41	43	5	43	47	7
DTC235B	PC	MR3	10	0.30	0.51	0.23	297	3	13	17	25	33	41	20	57	70	19
DTC239B	PC	MR3	10	0.31	0.68	0.23	297	3	14	17	22	32	37	13	56	60	7
DTC243A	PC	MR3	10	0.32	1.09	0.23	296	3	20	16	-28	37	34	-9	59	58	-1

Table B-1 (continued)

Run	Run Type	Rct'y	Chr	NOx	Pr.Eq.	k1	T	Ref	Δ (O3-NO) Results (pphm)								
	or VOC	Type	Set	(ppm)	(ppm)	(min^{-1})	(K)		2 Hour			4 Hour			6 Hour		
	[a]	[a]	[b]		[c]	[d]	[e]	[f]	Expt	Calc	Δ%	Expt	Calc	Δ%	Expt	Calc	Δ%
DTC264B	PC	MR3	10	0.30	0.68	0.22	298	3	13	17	22	32	39	17	54	67	19
DTC250B	PC	MR8	10	0.26	0.70	0.23	297	3	39	44	12	56	66	15	67	82	18
DTC260B	PC	R8	10	0.17	0.55	0.22	297	3	37	43	14	49	58	16	53	65	18
DTC266A	PC	R8	10	0.16	0.65	0.22	298	3	36	44	20	47	60	23	51	67	25
DTC532B	PGME-ACT	MR3	15	0.36	0.98	0.21	299	10	10	10	5	25	25	-1	40	39	-4
DTC537A	PGME-ACT	MR3	14	0.35	0.73	0.21	299	10	11	11	3	29	27	-7	48	44	-10
DTC549B	PGME-ACT	MR3	15	0.37	1.06	0.20	300	10	12	10	-17	28	24	-19	45	37	-22
DTC538B	PGME-ACT	MR8	15	0.29	0.94	0.21	299	10	36	35	-4	54	54	-1	68	69	1
DTC547B	PGME-ACT	MR8	15	0.30	1.24	0.20	300	10	39	35	-11	58	55	-5	72	70	-3
CTC197B	DBE-4	MR3	8	0.25		0.15	297	18	9	8	-18	27	24	-16	51	46	-10
CTC211B	DBE-4	MR3	8	0.22	0.96	0.15	298	18	8	8	5	26	27	1	50	49	-1
CTC198A	DBE-4	MR8	8	0.39	1.52	0.15	298	18	57	64	10	93	93	0	109	102	-7
CTC208A	DBE-4	MR8	8	0.43	1.14	0.15	298	18	47	54	14	80	87	8	99	98	-1
CTC199B	DBE-4	R8	8	0.15	1.07	0.15	298	18	48	45	-5	56	52	-7	56	52	-7
CTC210A	DBE-4	R8	8	0.16	1.36	0.15	298	18	50	47	-6	59	55	-8	59	56	-7
CTC201A	DBE-5	MR3	8	0.25	1.60	0.15	298	18	4	3	-16	11	9	-20	22	18	-22
CTC209B	DBE-5	MR3	8	0.25	1.03	0.15	298	18	6	5	-17	18	15	-19	33	29	-13
CTC204A	DBE-5	MR8	8	0.44	1.21	0.15	298	18	37	34	-8	70	76	8	88	91	4
CTC212B	DBE-5	MR8	8			0.15	298	18	33	39	16	64	79	19	81	96	15
CTC205B	DBE-5	R8	8	0.16	1.20	0.15	298	18	45	44	-2	53	52	-2	54	54	-1
CTC215A	DBE-5	R8	8	0.18	1.46	0.15	297	18	48	46	-5	57	55	-4	58	57	-2
ETC470	FORMALD	MRE	3	0.39	0.63	0.35	301	1	56	81	30	119	130	8	137	137	0
ETC489	FORMALD	MRE	3	0.42	0.64	0.35	301	1	51	81	37	118	133	11	138	141	3
ETC352	FORMALD	MR3	2	0.53	0.46	0.35	303	1	35	39	10	71	75	5	111	113	2
ETC357	FORMALD	MR3	2	0.53	0.52	0.35	303	1	46	56	18	86	102	16	120	136	12
DTC022B	FORMALD	MR8	1	0.51	0.56	0.39	300	1	62	66	7	89	96	7	108	118	8
DTC036A	FORMALD	R8	1	0.18	0.53	0.39	300	1	60	63	5	64	68	5	64	68	7
CTC138B	FORMALD	MR8	6	0.40	0.60	0.18	293	2	42	42	1	61	65	6	75	81	7
CTC140A	FORMALD	MR8	6	0.36	0.62	0.18	294	2	39	46	15	58	68	14	73	81	10
ETC335	ACETALD	MR3	2	0.54	0.80	0.35	303	1	41	41	-1	71	70	-1	103	101	-2
ETC338	ACETALD	MR3	2	0.52	1.14	0.35	303	1	46	46	1	74	75	2	102	105	2
DTC065A	ACETALD	MR8	1	0.45	1.31	0.39	301	1	54	58	6	79	87	10	98	109	10
DTC066B	ACETALD	R8	1	0.18	1.37	0.39	302	1	43	47	8	51	57	11	55	62	13
CTC107A	ACETALD	MR3	5	0.31	0.78	0.19	295	2	18	20	10	31	33	5	-	44	
CTC266A	BENZALD	MR4	10	0.23	0.53	0.12	299	6	4	2	-82	16	7	-131	30	14	-108
CTC267B	BENZALD	R8	10	0.16	0.65	0.12	300	6	31	30	-2	35	35	1	35	36	3
ETC480	ACETONE	MRE	3	0.42	0.58	0.35	301	1	28	41	33	72	100	29	120	133	10
ETC481	ACETONE	MRE	3	0.42	0.57	0.35	301	1	31	45	30	72	101	28	119	132	10
ETC490	ACETONE	MRE	3	0.42	0.58	0.35	301	1	37	48	22	89	103	13	125	131	4
ETC243	ACETONE	MR3	2	0.49	0.38	0.35	301	1	17	18	2	47	45	-3	78	73	-6
ETC245	ACETONE	MR3	2	0.50	0.40	0.35	302	1	22	23	6	51	53	3	86	85	-1
ETC247	ACETONE	MR3	2	0.49	0.40	0.35	301	1	25	27	5	56	57	2	92	91	-2
DTC028A	ACETONE	MR8	1	0.48	0.49	0.39	301	1	51	55	8	78	86	9	103	114	9
DTC064B	ACETONE	MR8	1	0.49	0.52	0.39	302	1	59	63	5	90	100	10	115	130	11
OTC275A	ACETONE	R8	11	0.56	0.53	0.00	319	7,8	133	122	-9	170	175	3	159	178	11
OTC276B	ACETONE	R8	11	0.57	0.47	0.00	315	7,8	95	91	-4	150	151	1	-	166	
DTC338A	MEK	MR8	11	0.29	0.57	0.21	297	10	38	41	7	54	58	7	64	70	8
DTC345B	MEK	MRX	11	0.34	0.56	0.20	300	10	26	27	3	52	52	1	75	76	2

Table B-1 (continued)

Run	Run Type or VOC [a]	Rct'y Type [a]	Chr Set [b]	NOx (ppm)	Pr.Eq. (ppm) [c]	k1 (min^{-1}) [d]	T (K) [e]	Ref [f]	Δ (O3-NO) Results (pphm)								
									2 Hour			4 Hour			6 Hour		
									Expt	Calc	Δ%	Expt	Calc	Δ%	Expt	Calc	Δ%
DTC363A	MEK	MRX	11	0.32	0.60	0.20	298	10	30	30	0	54	54	1	75	75	1
CTC181A	MEK	MR3	7	0.23	0.56	0.16	298	10	24	22	-10	47	40	-16	62	56	-12
CTC180B	MEK	MR8	7	0.39	0.75	0.16	298	10	47	46	-2	67	66	-3	82	79	-4
CTC255A	MPK	MR3	9	0.22	0.44	0.13	296	20	11	13	15	25	25	1	39	35	-9
CTC260B	MPK	MR8	10	0.38	0.66	0.12	295	20	38	40	5	57	61	6	71	71	1
CTC263B	MPK	MR8	10	0.16	0.60	0.12	294	20	36	33	-8	41	39	-4	40	39	-4
CTC258B	MPK	R8	10	0.17		0.13	296	20	38	35	-8	43	41	-5	-	42	
DTC554B	CC6-KET	MR3	15	0.37		0.20	299	10	9	8	-20	22	19	-12	33	32	-5
DTC558A	CC6-KET	MR3	14	0.34		0.20	300	10	10	9	-6	23	23	-2	38	38	0
DTC556A	CC6-KET	MR8	14	0.28		0.20	300	10	26	32	18	44	51	14	56	64	13
DTC559A	CC6-KET	MR8	14	0.29	0.42	0.20	299	10	28	32	13	46	49	6	60	62	3
DTC557B	CC6-KET	R8	15	0.12		0.20	300	10	28	32	13	37	40	8	39	42	8
CTC235A	CC6-KET	R8	9	0.16		0.14	301	10	31	35	11	38	41	8	-	42	
CTC238A	CC6-KET	R8	9	0.17		0.13	301	10	36	37	3	43	43	0	-	44	
DTC366B	MIBK	MR3	11	0.32		0.20	298	10	17	19	9	32	33	2	47	45	-2
DTC369A	MIBK	MR3	11	0.35		0.20	298	10	19	21	8	35	36	2	50	49	-3
DTC370B	MIBK	MR8	11	0.29		0.20	298	10	32	34	5	50	52	5	63	67	6
DTC414A	MIBK	MR8	11	0.27		0.19	298	10	37	36	-3	56	54	-4	67	68	2
DTC412B	MIBK	R8	11	0.11		0.19	297	10	27	26	-1	29	34	16	30	36	18
DTC418A	MIBK	R8	11	0.11		0.19	298	10	27	27	-1	32	34	5	33	36	6
CTC183A	MIBK	MR3	7	0.23		0.16	298	10	11	10	-8	22	19	-12	32	27	-20
CTC182B	MIBK	MR8	7	0.38		0.16	298	10	42	38	-10	63	60	-4	78	75	-4
CTC257A	C7-KET-2	MR3	10	0.24	0.45	0.13	297	20	4	4	4	11	10	-8	20	17	-17
CTC262A	C7-KET-2	MR8	10	0.38	0.60	0.12	294	20	29	26	-12	58	61	5	73	74	1
CTC259A	C7-KET-2	R8	10	0.17	0.64	0.12	295	20	38	38	0	45	45	1	44	46	5
DTC447A	TDI	MR3	12	0.42	0.99	0.17	297	14	2	4	46	7	9	17	15	15	0
DTC450A	TDI	MR3	12	0.37	0.64	0.17	297	14	8	8	4	25	21	-17	42	34	-24
DTC456A	TDI	MR8	12	0.28	0.53	0.17	297	14	15	14	-6	31	28	-9	39	35	-12
DTC459A	TDI	MR8	12	0.30	0.43	0.16	298	14	19	21	6	37	36	-2	46	45	-1
DTC453A	TDI	R8	12	0.16	0.86	0.17	295	14	9	8	-7	18	15	-17	21	20	-8
DTC454A	TDI	R8	12	0.13	0.51	0.17	297	14	20	22	9	26	26	0	26	25	-2
DTC462B	TDI	R8	13	0.14	0.54	0.16	299	14	19	23	15	28	27	-2	29	26	-9
DTC467A	TDI2	MR3	12	0.37	0.61	0.16	294	14	5	6	19	15	16	9	28	27	-5
DTC466A	TDI2	R8	12	0.15	0.46	0.16	297	14	21	21	0	-	27		27	27	-2
DTC601A	P-TI	MR3	16	0.39	0.58	0.19	298	22	11	16	27	33	37	11	57	57	1
DTC602A	P-TI	MR3	16	0.45	1.37	0.19	298	22	8	11	25	27	29	7	50	47	-6
DTC618A	P-TI	MR3	16	0.56	2.81	0.18	297	22	7	9	18	22	23	3	41	38	-8
DTC610A	P-TI	MR8	16	0.31	2.80	0.19	297	22	25	33	24	47	51	8	53	49	-8
DTC604B	P-TI	R8	17	0.20	1.24	0.19	298	22	31	31	1	33	33	0	32	32	1
DTC608A	P-TI	R8	16	0.15	2.05	0.19	297	22	29	34	14	32	33	3	30	32	5
DTC240A	NMP	MR3	10	0.31		0.23	296	3	9	8	-18	23	26	10	63	71	10
DTC244B	NMP	MR3	10	0.38		0.23	295	3	9	9	-8	24	30	20	-	76	
DTC252A	NMP	MR8	10	0.26		0.23	297	3	48	56	13	53	63	16	50	60	17
DTC255B	NMP	MR8	10	0.27		0.23	297	3	30	30	-1	55	60	8	54	61	11
DTC261A	NMP	R8	10	0.16		0.22	296	3	33	37	10	40	46	12	39	45	13
DTC267B	NMP	R8	10	0.16		0.22	299	3	39	42	7	43	47	7	41	45	9
DTC421A	C3-BR	MR3	11	0.38	0.81	0.19	297	12	18	17	-2	65	43	-49	66	74	10
DTC433A	C3-BR	MR3	11	0.39	0.60	0.18	297	12	17	14	-23	55	35	-55	82	59	-39

Table B-1 (continued)

Run	Run Type or VOC [a]	Rct'y Type [a]	Chr Set [b]	NOx (ppm)	Pr.Eq. (ppm) [c]	k1 (min^{-1}) [d]	T (K) [e]	Ref [f]	Δ (O3-NO) Results (pphm) 2 Hour Expt	Calc	Δ%	4 Hour Expt	Calc	Δ%	6 Hour Expt	Calc	Δ%
DTC423B	C3-BR	MR8	11	0.29	0.65	0.19	297	12	32	48	33	53	68	23	57	76	25
DTC427A	C3-BR	MR8	11	0.26	0.72	0.18	298	12	36	51	30	58	71	18	50	78	36
DTC424A	C3-BR	R8	11	0.10	0.55	0.18	297	12	31	32	5	30	34	13	28	34	18
DTC428B	C3-BR	R8	11	0.11	0.73	0.18	298	12	31	38	20	29	43	34	26	43	39
DTC401A	C4-BR	MR3	11	0.35	1.65	0.19	298	10	17	35	51	68	77	12	52	100	48
DTC426B	C4-BR	MR3	11	0.34	1.15	0.18	297	12	15	27	46	63	64	2	68	90	25
DTC419B	C4-BR	MR8	11	0.28	1.14	0.19	297	12	43	67	35	61	85	28	49	90	46
DTC430A	C4-BR	MR8	11	0.24	0.94	0.18	297	12	39	58	34	60	75	20	49	81	40
DTC420B	C4-BR	R8	11	0.11	1.16	0.19	297	12	32	42	22	29	48	39	26	48	47
DTC432B	C4-BR	R8	11	0.12	1.54	0.18	297	12	33	45	27	29	53	45	26	55	53
DTC303B	CL3-ETHE	MR3	11	0.33		0.21	298	23	24	35	31	91	79	-15	87	101	14
DTC305A	CL3-ETHE	MR3	11	0.33		0.21	299	23	12	21	43	39	51	23	76	81	6
DTC308B	CL3-ETHE	MR8	11	0.17		0.21	301	23	37	39	5	47	53	12	46	58	20
DTC311B	CL3-ETHE	MR8	11	0.29		0.21	298	23	33	35	8	60	55	-8	66	70	6
DTC320A	CL3-ETHE	MR8	11	0.30		0.21	297	23	28	32	11	48	49	3	59	64	8
DTC309A	CL3-ETHE	R8	11	0.17		0.21	299	23	46	50	9	45	57	21	43	57	26
DTC321B	CL3-ETHE	R8	11	0.11		0.21	298	23	33	37	9	34	42	19	33	43	23
DTC312A	CL3-ETHE	RX	11	0.32		0.21	299	23	18	17	-3	48	45	-8	76	74	-3
DTC692B	DMC	MR3	18	0.44	0.82	0.16	298	0	18	14	-29	46	34	-34	77	57	-36
DTC703B	DMC	MR3	18	0.42	1.04	0.16	296	0	18	16	-7	46	40	-16	79	68	-15
DTC693A	DMC	MR8	18	0.31	0.71	0.16	298	0	46	48	4	71	70	-2	86	82	-5
DTC705A	DMC	MR8	18	0.29	0.64	0.16	296	0	37	41	10	-	62		78	74	-5
DTC698B	DMC	R8	18	0.10	0.69	0.16	295	0	36	34	-4	41	40	-4	42	41	-1
DTC763B	DMC	R8	18	0.09		0.16	299	0	28	32	10	32	35	10	32	36	10
DTC750B	MIPR-CB	MR3	18	0.35		0.16	300	0	17	16	-11	44	41	-7	74	73	-1
DTC759A	MIPR-CB	MR3	18	0.37		0.16	299	0	12	14	12	37	36	-2	70	67	-4
DTC755A	MIPR-CB	MR8	18	0.29		0.16	299	0	50	51	2	77	74	-4	88	84	-4
DTC762A	MIPR-CB	MR8	18	0.30		0.16	299	0	39	37	-6	65	61	-6	78	75	-3
DTC758B	MIPR-CB	R8	18	0.09		0.16	299	0	35	35	0	40	40	0	40	40	1
DTC763B	MIPR-CB	R8	18	0.09		0.16	299	0	28	32	10	32	35	10	32	36	10
DTC694A	ME-PVAT	MR3	18	0.40	0.81	0.16	298	0	8	8	3	22	20	-13	38	32	-20
DTC701B	ME-PVAT	MR3	18	0.39	0.95	0.16	296	0	7	7	-1	18	16	-15	31	26	-21
DTC695B	ME-PVAT	MR8	18	0.31	0.81	0.16	299	0	28	31	8	54	57	5	69	71	2
DTC702A	ME-PVAT	MR8	18	0.32	1.01	0.16	297	0	27	27	0	54	53	-1	71	68	-5
DTC700A	ME-PVAT	R8	18	0.11	0.96	0.16	296	0	30	29	-1	36	35	-5	39	35	-9
DTC707B	ME-PVAT	R8	18	0.11	1.21	0.16	297	0	27	28	5	35	36	2	38	38	1
DTC442A	MS-A	MR3	11	0.34		0.17	294	13	5	7	20	16	20	20	31	36	14
DTC486A	MS-A	MR8	14	0.30		0.22	298	13	33	26	-30	57	49	-15	72	66	-9
DTC487B	MS-A	R8	15	0.13		0.22	298	13	36	36	1	42	42	0	43	42	-1
DTC441B	MS-B	MR3	11	0.35		0.18	294	13	6	6	6	15	17	10	26	29	11
DTC480A	MS-B	MR8	14	0.29		0.22	298	13	27	22	-22	50	46	-9	66	62	-6
DTC481B	MS-B	R8	15	0.13		0.22	298	13	34	35	3	42	43	3	42	44	3
DTC440A	MS-C	MR3	11	0.36		0.18	296	13	6	7	10	18	19	6	32	34	4
DTC478A	MS-C	MR8	14	0.30		0.22	297	13	30	27	-11	52	51	-3	66	67	0
DTC479B	MS-C	R8	15	0.14		0.22	297	13	36	38	5	45	46	3	46	47	2
DTC439B	MS-D	MR3	11	0.35		0.18	297	13	7	6	-8	21	19	-10	36	34	-8
DTC476A	MS-D	MR8	14	0.31		0.22	298	13	30	23	-29	53	47	-13	68	62	-10
DTC477B	MS-D	R8	15	0.13		0.22	297	13	36	38	5	43	44	3	43	44	3

Table B-1 (continued)

Run	Run Type or VOC [a]	Rct'y Type [a]	Chr Set [b]	NOx (ppm)	Pr.Eq. (ppm) [c]	k1 (min^{-1}) [d]	T (K) [e]	Ref [f]	Δ (O3-NO) Results (pphm) 2 Hour Expt	2 Hour Calc	2 Hour Δ%	4 Hour Expt	4 Hour Calc	4 Hour Δ%	6 Hour Expt	6 Hour Calc	6 Hour Δ%
<u>VOC Mixture - NOx Runs (Including Base Case Reactivity Experiments)</u>																	
EC166	MIX-A		1	0.11	0.25	0.35	301	1	26	18	-42	44	34	-32	53	46	-17
EC172	MIX-A		1	0.10	0.08	0.37	301	1	14	12	-23	23	20	-16	33	27	-20
EC144	MIX-E		1	0.51	0.88	0.31	301	1	130	95	-37	136	125	-9	116	113	-3
EC145	MIX-E		1	1.00	0.77	0.31	301	1	65	61	-7	107	104	-3	151	138	-10
EC149	MIX-E		1	1.00	0.89	0.31	301	1	77	65	-18	94	90	-4	107	103	-4
EC150	MIX-E		1	1.02	0.90	0.32	301	1	78	72	-8	116	108	-7	157	137	-15
EC151	MIX-E		1	2.06	1.47	0.31	301	1	91	94	3	128	136	6	152	161	5
EC152	MIX-E		1	0.51	0.96	0.32	301	1	93	87	-7	117	112	-4	108	109	1
EC153	MIX-E		1	0.99	1.70	0.33	302	1	153	140	-9	174	172	-1	157	159	1
EC160	MIX-E		1	1.01	0.73	0.34	301	1	75	57	-31	117	95	-23	163	126	-29
EC161	MIX-E		1	0.54	0.83	0.34	301	1	96	75	-28	123	105	-17	-		
XTC111	MIX-AE		1	0.22	1.14	0.25	303	1	7	5	-29	26	16	-63	65	40	-62
EC163	MIX-AO		1	0.51	0.47	0.34	300	1	40	33	-19	61	51	-20	80	63	-25
EC217	MIX-EO		1	0.48	0.19	0.43	301	1	12	20	41	19	32	40	26	41	37
EC257	MIX-EO		1	0.52	0.25	0.29	303	1	33	33	-1	46	47	3	52	54	4
EC272	MIX-RO		1	0.48	0.35	0.34	302	1	43	47	9	65	75	14	81	92	12
EC335	MIX-RO		1	0.50	0.42	0.38	302	1	54	63	15	77	96	19	73	92	21
EC336	MIX-RO		1	0.49	0.34	0.38	302	1	67	87	23	70	94	25	63	87	27
EC337	MIX-RO		1	0.51	0.30	0.38	302	1	34	35	2	66	73	9	62	77	19
EC338	MIX-RO		1	0.50	0.42	0.37	302	1	61	64	5	86	107	20	78	104	25
EC339	MIX-RO		1	0.50	0.21	0.37	302	1	19	16	-20	41	37	-13	60	55	-9
DTC073B	MIX-AR		1	0.49	0.44	0.39	302	1	5	6	21	12	13	7	23	22	-7
DTC076A	MIX-AR		1	0.48	0.31	0.39	302	1	6	9	38	18	23	21	33	35	7
EC328	MIX-AR		1	0.50	0.33	0.42	303	1	46	50	9	74	91	19	89	112	20
EC331	MIX-AR		1	0.52	0.65	0.41	302	1	91	110	18	81	102	21	73	93	21
ETC218	MIX-ER		2	0.47	0.61	0.35	299	1	79	75	-4	114	108	-6	106	101	-5
EC329	MIX-ER		1	0.50	0.22	0.41	302	1	42	46	10	69	81	15	76	94	19
EC330	MIX-ER		1	0.32	0.22	0.42	302	1	45	51	13	53	68	22	49	64	24
EC334	MIX-ER		1	0.50	0.32	0.39	302	1	63	71	11	75	96	22	69	90	23
ITC437	SURG-4		2	0.08	0.35	0.46	305	1	37	41	10	42	45	5	46	47	3
ITC438	SURG-4		2	0.08	0.37	0.46	302	1	30	40	25	33	43	22	36	45	21
ITC440	SURG-4		2	0.08	0.17	0.45	302	1	20	30	32	31	41	24	37	45	19
ITC442	SURG-4		2	0.14	0.34	0.45	303	1	37	49	26	55	61	11	60	65	8
ITC444	SURG-4		2	0.14	0.16	0.44	303	1	15	24	37	29	43	34	41	56	28
ITC446	SURG-4		2	0.07	0.39	0.44	302	1	29	36	20	29	37	20	30	36	17
ITC450	SURG-4		2	0.08	0.35	0.43	302	1	33	39	17	38	42	9	40	44	8
ITC452	SURG-4		2	0.08	0.33	0.43	302	1	31	39	21	38	43	11	40	45	11
ITC456	SURG-4		2	0.08	0.41	0.42	301	1	31	41	25	37	44	17	39	46	14
ITC459	SURG-4		2	0.08	0.35	0.42	301	1	31	38	19	37	40	7	39	41	7
ITC461	SURG-4		2	0.09	0.35	0.41	302	1	30	40	23	37	42	12	39	44	11
ITC465	SURG-4		2	0.09	0.33	0.41	301	1	32	40	21	39	44	12	40	46	13
ITC467	SURG-4		2	0.09	0.33	0.40	302	1	29	41	30	36	45	20	38	47	20
ITC471	SURG-4		2	0.09	0.33	0.40	302	1	29	39	28	36	43	17	37	45	19
ITC483	SURG-4		2	0.08	0.34	0.39	302	1	30	38	22	35	41	14	39	43	8
ITC488	SURG-4		2	0.08	0.39	0.38	303	1	28	39	28	34	42	18	35	43	18
ITC489	SURG-4		2	0.09	0.35	0.38	302	1	28	38	27	34	41	17	36	43	16
ITC497	SURG-4		2	0.09	0.34	0.38	301	1	27	38	29	34	41	17	36	42	15

Table B-1 (continued)

Run	Run Type or VOC [a]	Rct'y Type [a]	Chr Set [b]	NOx (ppm)	Pr.Eq. (ppm) [c]	k1 (min^{-1}) [d]	T (K) [e]	Ref [f]	Δ (O3-NO) Results (pphm) 2 Hour Expt	2 Hour Calc	2 Hour Δ%	4 Hour Expt	4 Hour Calc	4 Hour Δ%	6 Hour Expt	6 Hour Calc	6 Hour Δ%
ITC501	SURG-4		2	0.09	0.34	0.38	302	1	30	39	23	37	42	12	39	44	12
ITC503	SURG-4		2	0.09	0.34	0.37	302	1	27	40	32	33	44	23	35	45	22
ITC571	SURG-4		4	0.11	0.33	0.36	298	1	28	39	28	39	46	16	-	47	
ITC572	SURG-4		4	0.12	0.34	0.36	299	1	34	40	15	40	48	16	45	49	8
ITC574	SURG-4		4	0.09	0.33	0.36	301	1	33	38	14	39	44	12	41	45	10
ITC578	SURG-4		4	0.09	0.32	0.36	299	1	30	36	18	38	40	5	42	41	-1
ITC580	SURG-4		4	0.09	0.33	0.36	299	1	31	38	18	42	42	1	44	43	-1
ITC581	SURG-4		4	0.09	0.48	0.35	300	1	37	41	10	41	41	1	43	42	-3
ITC584	SURG-4		4	0.09	0.36	0.35	300	1	34	38	12	43	42	-3	45	43	-4
ITC586	SURG-4		4	0.08	0.34	0.35	301	1	34	36	6	40	39	-3	43	41	-7
ITC590	SURG-4		4	0.09	0.33	0.35	302	1	31	37	17	40	41	3	44	43	-2
ITC598	SURG-4		4	0.10	0.37	0.35	300	1	34	40	14	42	43	3	44	45	1
ITC603	SURG-4		4	0.09	0.34	0.35	300	1	31	38	18	39	41	5	41	42	3
ITC607	SURG-4		4	0.10	0.37	0.35	302	1	34	40	15	43	44	2	45	46	1
ITC609	SURG-4		4	0.09	0.37	0.35	301	1	32	39	18	41	42	4	44	44	0
ITC613	SURG-4		4	0.08	0.37	0.35	301	1	31	37	17	38	40	5	40	41	3
EC676	SURG-4		1	0.09	0.40	0.37	301	1	20	38	47	19	39	50	16	41	61
ITC573	SURG-4R		4	0.11	0.18	0.36	300	1	24	26	7	-	40		43	47	8
EC231	SURG-7		1	0.68	0.97	0.29	302	1	78	106	27	104	132	21	96	118	18
EC232	SURG-7		1	0.48	0.47	0.29	302	1	37	33	-10	60	66	10	75	92	19
EC233	SURG-7		1	0.09	0.48	0.29	302	1	36	42	15	41	50	17	41	50	17
EC237	SURG-7		1	0.46	0.84	0.29	302	1	74	94	21	101	112	10	94	102	8
EC238	SURG-7		1	0.91	0.82	0.29	303	1	61	83	26	97	137	29	128	159	19
EC241	SURG-7		1	0.47	0.40	0.28	302	1	34	43	21	56	74	24	76	97	22
EC242	SURG-7		1	0.46	1.47	0.29	302	1	102	107	4	83	85	2	77	75	-2
EC243	SURG-7		1	0.47		0.29	302	1	107	111	4	-			-		
EC245	SURG-7		1	0.94	1.47	0.29	302	1	136	164	17	151	150	-1	133	130	-2
EC246	SURG-7		1	0.48	0.44	0.29	302	1	35	37	5	55	63	13	73	86	15
EC247	SURG-7		1	0.48	0.72	0.29	302	1	77	95	19	100	106	5	-		
ITC626	SURG-8S		5	0.29	0.51	0.35	296	1	26	29	11	53	69	24	73	87	16
ITC630	SURG-8S		5	0.31	0.25	0.35	298	1	13	11	-16	22	23	5	31	35	12
ITC631	SURG-8S		5	0.32	0.14	0.35	300	1	8	5	-56	12	10	-18	17	15	-13
ITC633	SURG-8S		5	0.61	0.51	0.35	299	1	17	14	-19	31	35	9	42	53	21
ITC635	SURG-8S		5	1.19	0.52	0.35	300	1	13	8	-68	23	20	-18	31	32	4
ITC637	SURG-8S		5	0.30	0.51	0.35	299	1	28	29	2	54	68	21	71	89	20
ITC865	SURG-8S		9	0.31	0.63	0.35	296	1	30	33	11	62	79	22	80	95	16
ITC867	SURG-8S		9	0.28	0.52	0.35	297	1	29	47	40	52	81	36	68	93	27
ITC868	SURG-8S		9	0.37	0.39	0.35	296	1	28	13	-117	47	29	-64	61	44	-38
ITC871	SURG-8S		9	0.37	0.29	0.35	296	1	16	10	-66	29	21	-39	40	31	-30
ITC872	SURG-8S		9	0.36	0.25	0.35	297	1	16	16	-3	26	26	-1	34	34	-1
ITC873	SURG-8S		9	0.37	0.19	0.35	296	1	12	5	-117	20	11	-74	27	17	-61
ITC874	SURG-8S		9	0.36	0.22	0.35	296	1	11	6	-95	21	12	-72	28	18	-51
ITC877	SURG-8S		9	0.38	0.26	0.35	296	1	16	17	3	27	28	5	34	36	7
ITC880	SURG-8S		9	0.66	0.31	0.35	295	1	10	6	-70	20	14	-45	28	21	-30
ITC881	SURG-8S		9	0.67	0.25	0.35	296	1	10	10	5	18	18	1	25	24	-4
ITC885	SURG-8S		9	0.64	0.19	0.35	295	1	6	4	-58	11	7	-44	16	12	-37
ITC888	SURG-8S		9	0.32	0.40	0.35	296	1	19	11	-77	40	24	-63	57	38	-48
ITC891	SURG-8S		9	0.32	0.57	0.35	296	1	31	27	-16	64	66	4	81	89	10

Table B-1 (continued)

Run	Run Type or VOC [a]	Rct'y Type [a]	Chr Set [b]	NOx (ppm)	Pr.Eq. (ppm) [c]	k1 (min^{-1}) [d]	T (K) [e]	Ref [f]	Δ (O3-NO) Results (pphm)								
									2 Hour			4 Hour			6 Hour		
									Expt	Calc	Δ%	Expt	Calc	Δ%	Expt	Calc	Δ%
DTC312B	SURG-X		11	0.31	0.68	0.21	299	23	21	18	-16	49	44	-11	77	72	-6
DTC345A	SURG-X		11	0.34	0.49	0.20	300	10	14	15	5	38	38	-1	65	65	-1
DTC363B	SURG-X		11	0.32	0.49	0.20	298	10	14	14	1	37	36	-1	62	62	1
DTC568B	SURG-X		15	0.46	0.51	0.20	298	16	8	13	41	25	35	27	44	54	19
DTC569B	SURG-X		15	0.36	0.49	0.20	298	16	9	14	40	-	40		58	66	13
DTC572B	SURG-X		15	0.38	0.44	0.20	298	16	7	10	30	25	29	12	46	48	4
DTC573B	SURG-X		15	0.13	0.38	0.20	297	16	32	33	4	40	40	1	41	42	1
DTC576B	SURG-X		15	0.41	0.49	0.20	299	16	8	12	29	28	33	13	50	55	9
DTC577B	SURG-X		15	0.33	0.37	0.20	298	16	22	23	8	40	40	1	51	51	0
DTC581B	SURG-X		15	0.40	0.50	0.20	298	16	7	13	45	25	35	28	43	58	25
DTC583B	SURG-X		15	0.35	0.51	0.19	298	16	-	13		26	33	24	46	58	21
DTC586B	SURG-X		15	0.32	0.43	0.19	297	16	22	30	26	41	47	13	52	59	12
DTC589B	SURG-X		15	0.42	0.53	0.19	298	16	6	12	46	21	30	33	37	53	31
DTC591B	SURG-X		15	0.35	0.42	0.19	296	16	20	27	24	40	45	12	50	57	12
DTC593B	SURG-X		15	0.45	0.52	0.19	297	16	6	12	45	22	32	31	40	53	24
DTC594B	SURG-X		15	0.32	0.42	0.19	298	16	-	29		42	46	9	54	58	8
DTC596B	SURG-X		15	0.29	0.52	0.19	297	16	9	15	36	29	38	25	55	65	16
DTC598A	SURG-X		14	0.03	0.15	0.19	298	16	11	12	15	12	15	16	13	15	18
DTC598B	SURG-X		15	0.14	0.15	0.19	298	16	8	10	23	15	18	14	21	23	12
DTC615B	SURG-X		17	0.72	0.41	0.19	298	22	23	13	-74	36	26	-36	43	36	-21
DTC719B	SURG-X		18	0.41	0.53	0.16	294	0	11	10	-10	32	27	-19	51	42	-23
ETC090	SURG-3M		2	0.55	0.37	0.36	301	1	9	13	31	27	37	27	46	60	23
ETC091	SURG-3M		2	0.51	0.33	0.36	301	1	9	12	27	27	34	22	43	55	21
ETC093	SURG-3M		2	0.51	0.34	0.36	301	1	11	13	17	30	36	18	47	58	19
ETC095	SURG-3M		2	0.51	0.35	0.36	301	1	9	13	28	28	36	24	46	59	22
ETC098	SURG-3M		2	0.51	0.33	0.36	301	1	10	12	17	29	34	15	44	54	18
ETC100	SURG-3M		2	0.51	0.34	0.36	300	1	9	12	24	27	34	21	45	55	19
ETC102	SURG-3M		2	0.51	0.34	0.36	300	1	12	12	0	29	34	14	48	55	12
ETC104	SURG-3M		2	0.50	0.34	0.36	300	1	10	12	20	27	34	21	44	54	20
ETC107	SURG-3M		2	0.50	0.36	0.36	300	1	12	13	5	31	37	17	47	59	20
ETC109	SURG-3M		2	0.52	0.34	0.36	300	1	8	12	32	24	33	28	41	53	24
ETC113	SURG-3M		2	0.51	0.35	0.36	300	1	9	12	28	26	34	25	42	55	24
ETC114	SURG-3M		2	0.49	0.34	0.36	300	1	8	12	33	26	34	25	41	55	25
ETC115	SURG-3M		2	0.53	0.33	0.36	300	1	8	11	31	24	32	25	40	51	21
ETC116	SURG-3M		2	0.51	0.37	0.36	301	1	12	15	24	34	42	20	56	69	18
ETC117	SURG-3M		2	0.52	0.33	0.36	301	1	9	12	25	27	34	21	43	55	21
ETC119	SURG-3M		2	0.52	0.35	0.35	302	1	11	13	20	31	37	16	50	60	16
ETC122	SURG-3M		2	0.53	0.31	0.35	304	1	9	11	18	28	33	14	48	53	11
ETC124	SURG-3M		2	0.50	0.31	0.35	303	1	8	11	25	27	33	17	45	54	16
ETC126	SURG-3M		2	0.52	0.31	0.35	302	1	8	11	26	27	32	18	43	52	18
ETC128	SURG-3M		2	0.53	0.31	0.35	301	1	8	10	20	24	30	19	40	49	17
ETC129	SURG-3M		2	0.53	0.31	0.35	301	1	7	10	28	24	30	19	41	49	17
ETC130	SURG-3M		2	0.52	0.30	0.35	302	1	8	10	21	26	31	17	43	50	15
ETC132	SURG-3M		2	0.54	0.31	0.35	302	1	8	10	26	24	30	18	43	48	11
ETC134	SURG-3M		2	0.53	0.31	0.35	303	1	8	11	30	25	32	20	43	51	15
ETC137	SURG-3M		2	0.52	0.29	0.35	300	1	8	9	11	23	27	14	39	44	12
ETC139	SURG-3M		2	0.53	0.31	0.35	301	1	9	10	11	25	30	16	42	48	14
ETC143	SURG-3M		2		0.29	0.35	301	1	11	11	0	30	33	8	48	51	5

Table B-1 (continued)

Run	Run Type or VOC [a]	Rct'y Type [a]	Chr Set [b]	NOx (ppm)	Pr.Eq. (ppm) [c]	k1 (min^{-1}) [d]	T (K) [e]	Ref [f]	Δ (O3-NO) Results (pphm)								
									2 Hour			4 Hour			6 Hour		
									Expt	Calc	Δ%	Expt	Calc	Δ%	Expt	Calc	Δ%
ETC145	SURG-3M		2	0.51	0.28	0.35	301	1	8	10	20	23	28	19	39	45	14
ETC147	SURG-3M		2	0.50	0.28	0.35	301	1	8	10	15	23	28	16	38	44	13
ETC149	SURG-3M		2	0.51	0.28	0.35	302	1	8	10	22	24	28	14	41	45	10
ETC156	SURG-3M		2	0.51	0.40	0.35	300	1	16	16	-1	43	44	3	69	72	4
ETC158	SURG-3M		2	0.50	0.40	0.35	300	1	14	16	11	37	43	14	60	70	14
ETC160	SURG-3M		2	0.50	0.44	0.35	300	1	16	18	13	42	49	15	68	82	18
ETC161	SURG-3M		2	0.52	0.43	0.35	301	1	16	18	12	43	48	11	70	79	13
ETC162	SURG-3M		2	0.50	0.43	0.35	301	1	15	18	17	43	49	11	70	80	13
ETC165	SURG-3M		2	0.50	0.43	0.35	303	1	16	18	11	45	50	9	79	85	6
ETC168	SURG-3M		2	0.52	0.39	0.35	301	1	16	15	-6	44	43	-4	73	68	-7
ETC170	SURG-3M		2	0.51	0.40	0.35	301	1	16	16	3	43	44	4	72	72	0
ETC172	SURG-3M		2	0.50	0.41	0.35	300	1	14	16	11	40	44	10	68	73	7
ETC174	SURG-3M		2	0.50	0.44	0.35	299	1	13	16	20	40	47	15	67	79	15
ETC186	SURG-3M		2	0.40	0.08	0.35	299	1	13	3	-350	39	6	-556	67	9	-674
ETC188	SURG-3M		2		0.18	0.35	300	1	16	5	-197	44	18	-146	78	31	-152
ETC197	SURG-3M		2		0.17	0.35	300	1	28	5	-486	54	16	-234	84	28	-202
ETC208	SURG-3M		2	0.49	0.40	0.35	299	1	14	16	10	45	44	-2	-	72	
ETC210	SURG-3M		2	0.50	0.41	0.35	299	1	13	15	13	40	43	7	66	71	7
ETC215	SURG-3M		2	0.48	0.39	0.35	300	1	13	16	18	39	43	11	64	70	8
ETC223	SURG-3M		2	0.50	0.40	0.35	300	1	17	16	-6	44	44	0	71	72	1
ETC225	SURG-3M		2	0.50	0.40	0.35	299	1	11	15	23	34	41	19	55	68	19
ETC227	SURG-3M		2	0.50	0.43	0.35	300	1	12	17	26	37	46	19	62	77	20
ETC229	SURG-3M		2	0.51	0.43	0.35	300	1	12	16	24	38	45	17	63	75	17
ETC231	SURG-3M		2	0.50	0.42	0.35	299	1	13	16	14	39	43	11	63	72	12
ETC234	SURG-3M		2	0.50	0.39	0.35	302	1	14	15	11	41	42	4	70	70	1
ETC236	SURG-3M		2	0.50	0.38	0.35	301	1	14	15	3	41	41	1	69	68	-2
ETC238	SURG-3M		2	0.47	0.37	0.35	301	1	13	15	8	39	41	5	67	68	1
ETC240	SURG-3M		2	0.48	0.37	0.35	300	1	12	14	16	36	39	9	62	65	4
ETC242	SURG-3M		2	0.48	0.38	0.35	301	1	15	15	2	41	42	2	72	70	-4
ETC244	SURG-3M		2	0.47	0.37	0.35	302	1	13	15	14	40	42	5	69	69	1
ETC246	SURG-3M		2	0.49	0.38	0.35	302	1	14	16	10	41	44	6	72	73	2
ETC248	SURG-3M		2	0.49	0.42	0.35	301	1	16	17	5	46	47	1	83	80	-4
ETC250	SURG-3M		2	0.50	0.44	0.35	299	1	14	15	8	42	44	4	73	74	2
ETC252	SURG-3M		2	0.50	0.41	0.35	300	1	13	16	16	39	45	14	67	75	11
ETC254	SURG-3M		2	0.42	0.37	0.35	299	1	12	14	18	34	40	14	59	67	13
ETC256	SURG-3M		2	0.49	0.41	0.35	302	1	17	16	-8	44	44	-1	77	75	-2
ETC258	SURG-3M		2	0.48	0.41	0.35	301	1	16	16	-3	44	44	1	76	76	0
ETC260	SURG-3M		2	0.49	0.41	0.35	300	1	15	15	2	41	42	3	70	72	3
ETC262	SURG-3M		2	0.47	0.40	0.35	302	1	17	17	2	44	46	5	75	79	5
ETC264	SURG-3M		2	0.49	0.41	0.35	301	1	17	15	-14	45	44	-4	75	74	-1
ETC266	SURG-3M		2	0.48	0.40	0.35	300	1	17	15	-16	44	42	-4	74	71	-3
ETC268	SURG-3M		2	0.48	0.39	0.35	302	1	19	17	-15	49	45	-8	83	76	-9
ETC270	SURG-3M		2	0.49	0.39	0.35	301	1	16	15	-6	44	42	-3	74	70	-6
ETC272	SURG-3M		2	0.48	0.40	0.35	301	1	16	16	-3	45	43	-3	76	72	-5
ETC274	SURG-3M		2	0.52	0.39	0.35	302	1	16	16	-1	49	45	-7	83	74	-13
ETC276	SURG-3M		2	0.49	0.38	0.35	302	1	16	16	0	46	44	-4	80	73	-10
ETC278	SURG-3M		2	0.51	0.38	0.35	302	1	15	15	1	45	43	-5	80	71	-14
ETC280	SURG-3M		2	0.50	0.38	0.35	303	1	16	16	2	47	45	-4	84	75	-12

Table B-1 (continued)

Run	Run Type or VOC [a]	Rct'y Type [a]	Chr Set [b]	NOx (ppm)	Pr.Eq. (ppm) [c]	k1 (min^{-1}) [d]	T (K) [e]	Ref [f]	Δ (O3-NO) Results (pphm): 2 Hour			4 Hour			6 Hour		
									Expt	Calc	Δ%	Expt	Calc	Δ%	Expt	Calc	Δ%
ETC282	SURG-3M		2	0.50	0.37	0.35	302	1	16	16	1	46	44	-5	81	72	-13
ETC284	SURG-3M		2	0.49	0.38	0.35	302	1	16	17	5	46	46	-2	83	76	-10
ETC286	SURG-3M		2	0.48	0.39	0.35	303	1	15	18	14	46	48	3	84	80	-5
ETC288	SURG-3M		2	0.49	0.37	0.35	303	1	16	17	5	48	46	-5	88	76	-15
ETC290	SURG-3M		2	0.49	0.39	0.35	304	1	17	18	4	51	48	-6	90	80	-12
ETC292	SURG-3M		2	0.49	0.38	0.35	301	1	16	16	2	46	45	-4	79	73	-8
ETC294	SURG-3M		2	0.48	0.38	0.35	301	1	15	17	10	45	45	-1	79	74	-7
ETC296	SURG-3M		2	0.47	0.37	0.35	301	1	16	16	2	47	44	-7	83	73	-13
ETC298	SURG-3M		2	0.49	0.40	0.35	302	1	18	20	8	51	51	-1	89	84	-6
ETC300	SURG-3M		2	0.48	0.40	0.35	300	1	16	18	9	47	48	3	80	79	-1
ETC302	SURG-3M		2	0.46	0.38	0.35	300	1	10	13	23	33	38	14	57	63	10
ETC304	SURG-3M		2	0.49	0.37	0.35	300	1	11	14	23	35	40	13	60	64	7
ETC306	SURG-3M		2	0.54	0.37	0.35	301	1	11	11	2	36	33	-9	61	55	-12
ETC308	SURG-3M		2	0.53	0.37	0.35	301	1	12	12	1	38	35	-6	65	59	-10
ETC310	SURG-3M		2	0.53	0.37	0.35	299	1	11	12	7	34	35	2	58	57	-2
ETC312	SURG-3M		2	0.52	0.38	0.35	297	1	10	11	10	32	33	3	55	55	1
ETC314	SURG-3M		2	0.53	0.37	0.35	298	1	11	11	-2	35	33	-5	59	54	-8
ETC316	SURG-3M		2	0.50	0.36	0.35	298	1	12	12	1	36	35	-4	60	56	-6
ETC323	SURG-3M		2	0.54	0.43	0.35	304	1	24	22	-6	59	55	-8	101	90	-13
ETC324	SURG-3M		2	0.62	0.42	0.35	302	1	15	16	6	43	45	5	68	70	3
ETC325	SURG-3M		2	0.53	0.42	0.35	302	1	18	19	3	49	49	0	81	80	-1
ETC326	SURG-3M		2	0.53	0.42	0.35	302	1	21	19	-11	52	50	-5	85	81	-6
ETC327	SURG-3M		2	0.49	0.44	0.35	302	1	19	21	8	51	54	5	88	92	4
ETC328	SURG-3M		2	0.52	0.42	0.35	303	1	18	20	9	49	50	2	80	81	1
ETC329	SURG-3M		2	0.52	0.41	0.35	303	1	19	19	4	51	50	-2	84	81	-4
ETC330	SURG-3M		2	0.50	0.41	0.35	303	1	20	20	-1	53	51	-4	88	83	-6
ETC331	SURG-3M		2	0.51	0.40	0.35	303	1	18	18	-1	49	47	-3	82	77	-6
ETC334	SURG-3M		2	0.52	0.41	0.35	303	1	19	19	-1	50	49	-1	84	81	-4
ETC336	SURG-3M		2	0.53	0.43	0.35	303	1	20	21	4	52	53	2	87	87	0
ETC339	SURG-3M		2	0.52	0.45	0.35	303	1	22	21	-3	55	54	-3	93	90	-3
ETC345	SURG-3M		2	0.52	0.44	0.35	303	1	21	21	-1	56	54	-3	91	89	-2
ETC347	SURG-3M		2	0.52	0.43	0.35	303	1	20	21	3	53	53	0	87	87	1
ETC349	SURG-3M		2	0.51	0.42	0.35	304	1	22	20	-7	56	52	-9	92	86	-7
ETC351	SURG-3M		2	0.57	0.42	0.35	303	1	18	18	0	49	49	-2	78	77	-2
ETC353	SURG-3M		2	0.51	0.42	0.35	303	1	18	19	3	49	49	0	84	81	-3
ETC356	SURG-3M		2	0.51	0.39	0.35	302	1	17	15	-15	47	41	-16	77	67	-16
ETC376	SURG-3M		3	0.50	0.41	0.35	302	1	17	19	11	46	48	4	78	79	2
ETC408	SURG-3M		3	0.53	0.41	0.35	300	1	17	16	-8	43	43	2	67	68	2
ETC411	SURG-3M		3	0.52	0.43	0.35	300	1	16	18	11	43	47	9	69	76	10
ETC413	SURG-3M		3	0.54	0.42	0.35	299	1	16	15	-7	42	42	1	66	68	3
ETC415	SURG-3M		3	0.53	0.42	0.35	298	1	12	16	23	37	44	17	60	70	14
ETC419	SURG-3M		3	0.54	0.45	0.35	299	1	15	18	18	42	49	15	66	78	16
DTC233B	SURG-3M		10	0.30	0.49	0.23	296	3	13	17	28	34	43	23	58	72	20
DTC235A	SURG-3M		10	0.31	0.46	0.23	297	3	13	16	20	34	40	14	59	68	14
DTC237B	SURG-3M		10	0.30	0.47	0.23	298	3	12	17	32	33	43	23	58	71	18
DTC239A	SURG-3M		10	0.33	0.49	0.23	297	3	13	17	22	34	40	14	59	66	11
DTC240B	SURG-3M		10	0.31	0.49	0.23	296	3	12	16	29	33	42	22	56	71	21
DTC241A	SURG-3M		10	0.33	0.48	0.23	295	3	14	15	9	33	38	14	54	66	18

Table B-1 (continued)

Run	Run Type	Rct'y	Chr	NOx	Pr.Eq.	k1	T	Ref	Δ (O3-NO) Results (pphm)								
	or VOC	Type	Set	(ppm)	(ppm)	(min^{-1})	(K)		2 Hour			4 Hour			6 Hour		
	[a]	[a]	[b]		[c]	[d]	[e]	[f]	Expt	Calc	Δ%	Expt	Calc	Δ%	Expt	Calc	Δ%
DTC242B	SURG-3M		10	0.32	0.48	0.23	296	3	13	16	21	34	41	18	57	70	19
DTC243B	SURG-3M		10	0.31	0.47	0.23	296	3	12	14	17	31	37	17	52	65	19
DTC244A	SURG-3M		10	0.33	0.47	0.23	295	3	11	16	29	30	38	22	49	66	26
DTC264A	SURG-3M		10	0.31	0.47	0.22	298	3	11	16	31	32	40	22	53	69	23
DTC271A	SURG-3M		10	0.30	0.47	0.22	298	4	12	15	15	34	38	12	55	67	18
DTC273B	SURG-3M		10	0.31	0.48	0.22	298	4	14	14	5	37	38	2	63	66	5
DTC275B	SURG-3M		10	0.31	0.46	0.22	298	4	12	14	13	34	37	8	60	65	7
DTC277A	SURG-3M		10	0.33	0.51	0.22	298	4	13	22	42	35	52	32	61	80	24
DTC279A	SURG-3M		10	0.32	0.49	0.22	298	4	9	18	49	31	44	30	56	73	23
DTC282B	SURG-3M		10	0.34	0.48	0.22	299	4	15	16	5	39	40	3	68	68	1
DTC283A	SURG-3M		10	0.31	0.50	0.22	297	4	12	17	34	33	44	25	58	73	21
DTC289A	SURG-3M		10	0.35	0.50	0.22	297	4	12	16	28	33	40	19	55	69	20
DTC291A	SURG-3M		10	0.33	0.51	0.22	297	4	12	16	28	33	42	21	57	71	20
DTC302A	SURG-3M		11	0.35	0.47	0.21	297	23	8	14	42	27	36	25	46	60	24
DTC302B	SURG-3M		11	0.35	0.47	0.21	297	23	7	14	47	26	36	26	48	61	22
DTC303A	SURG-3M		11	0.33	0.51	0.21	298	23	11	16	35	33	41	20	59	71	17
DTC305B	SURG-3M		11	0.33	0.49	0.21	299	23	12	16	27	37	40	8	66	69	4
DTC315A	SURG-3M		11	0.33	0.47	0.21	298	5	15	15	-5	38	37	-2	62	63	3
DTC324B	SURG-3M		11	0.31	0.49	0.21	298	5	16	19	19	41	47	14	68	75	9
DTC327B	SURG-3M		11	0.33	0.51	0.21	297	9	12	16	25	34	40	15	60	69	14
DTC328A	SURG-3M		11	0.32	0.51	0.21	297	9	11	16	28	33	40	17	56	68	17
DTC336B	SURG-3M		11	0.32	0.50	0.21	296	9	13	15	16	33	38	13	57	66	13
DTC352B	SURG-3M		11	0.34	0.50	0.20	298	10	14	15	9	38	39	3	65	66	2
DTC358B	SURG-3M		11	0.33	0.50	0.20	298	10	15	16	4	39	40	4	64	67	4
DTC375B	SURG-3M		11	0.35	0.46	0.20	300	16	14	13	-6	34	34	1	57	59	3
DTC377A	SURG-3M		11	0.36	0.47	0.20	297	16	12	13	10	32	35	7	52	57	9
DTC380A	SURG-3M		11	0.37	0.47	0.20	298	16	11	10	-14	31	27	-14	52	46	-14
DTC385B	SURG-3M		11	0.39	0.44	0.19	298	11	11	11	-1	31	29	-6	50	47	-6
DTC389A	SURG-3M		11	0.37	0.45	0.19	299	11	13	12	-9	34	31	-11	56	51	-11
DTC395B	SURG-3M		11	0.41	0.45	0.19	299	10	14	11	-28	37	30	-24	61	49	-26
DTC398A	SURG-3M		11	0.43	0.47	0.19	297	10	13	11	-19	35	29	-18	57	48	-20
DTC401B	SURG-3M		11	0.36	0.44	0.19	298	10	11	12	2	32	31	-3	54	51	-5
DTC402A	SURG-3M		11	0.37	0.49	0.19	299	10	13	14	6	37	37	1	61	63	2
DTC426A	SURG-3M		11	0.36	0.53	0.18	297	12	10	14	25	33	36	10	56	62	10
DTC433B	SURG-3M		11	0.47	0.48	0.18	297	12	14	9	-59	39	24	-62	66	40	-66
DTC438B	SURG-3M		11	0.36	0.49	0.18	296	13	10	11	7	30	29	-4	50	47	-8
DTC439A	SURG-3M		11	0.35	0.48	0.18	297	13	11	11	8	31	31	1	51	51	-1
DTC440B	SURG-3M		11	0.35	0.48	0.18	296	13	10	12	13	30	31	2	50	49	-2
DTC441A	SURG-3M		11	0.35	0.48	0.18	294	13	9	10	14	25	27	6	40	44	8
DTC442B	SURG-3M		11	0.35	0.50	0.17	294	13	7	10	33	22	28	21	40	48	16
DTC447B	SURG-3M		11	0.39	0.51	0.17	297	14	11	11	1	32	29	-11	48	48	-1
DTC449A	SURG-3M		12	0.35	0.48	0.17	297	14	17	17	2	41	38	-6	64	61	-4
DTC449B	SURG-3M		11	0.35	0.48	0.17	297	14	13	11	-23	35	29	-19	55	48	-16
DTC450B	SURG-3M		11	0.37	0.52	0.17	297	14	12	11	-7	35	30	-15	57	50	-14
DTC467B	SURG-3M		13	0.36	0.48	0.16	294	14	9	12	20	26	27	2	39	43	9
DTC489B	SURG-3M		15	0.38		0.22	298	15	15	16	5	42	41	-3	74	70	-4
DTC491A	SURG-3M		14	0.38	0.52	0.22	298	15	17	17	-1	46	43	-7	81	74	-9
DTC495B	SURG-3M		15	0.38	0.51	0.22	299	15	15	17	12	42	43	1	75	74	-1

Table B-1 (continued)

Run	Run Type or VOC [a]	Rct'y Type [a]	Chr Set [b]	NOx (ppm)	Pr.Eq. (ppm) [c]	k1 (min^{-1}) [d]	T (K) [e]	Ref [f]	Δ (O3-NO) Results (pphm) 2 Hour Expt	Calc	Δ%	4 Hour Expt	Calc	Δ%	6 Hour Expt	Calc	Δ%
DTC498A	SURG-3M		14	0.38	0.31	0.22	299	15	8	8	1	26	23	-11	42	37	-11
DTC505A	SURG-3M		14	0.39	0.48	0.22	298	15	13	16	19	40	40	0	70	67	-5
DTC508A	SURG-3M		14	0.37	0.48	0.22	299	10	13	16	18	40	40	1	71	69	-3
DTC510A	SURG-3M		14	0.39	0.50	0.22	299	10	17	16	-5	46	40	-14	79	68	-16
DTC512A	SURG-3M		14	0.38	0.47	0.21	299	10	14	14	7	40	37	-9	70	62	-14
DTC514A	SURG-3M		14	0.39	0.48	0.21	299	10	13	15	11	39	37	-6	71	62	-14
DTC517B	SURG-3M		15	0.37	0.49	0.21	299	10	12	14	16	37	38	1	68	65	-3
DTC522B	SURG-3M		15	0.37	0.48	0.21	299	10	12	14	11	36	36	-1	65	62	-5
DTC528A	SURG-3M		14	0.38	0.49	0.21	299	10	14	14	2	40	37	-9	71	62	-13
DTC529B	SURG-3M		15	0.36	0.45	0.21	299	10	12	12	0	34	31	-11	63	54	-16
DTC532A	SURG-3M		14	0.36	0.49	0.21	299	10	11	14	24	34	37	7	64	65	2
DTC533B	SURG-3M		15	0.36	0.48	0.21	299	10	11	14	20	36	38	5	64	64	1
DTC537B	SURG-3M		15	0.35	0.46	0.21	299	10	10	13	20	33	34	2	61	59	-3
DTC541B	SURG-3M		15	0.38	0.49	0.21	299	10	11	13	18	35	34	0	62	59	-5
DTC549A	SURG-3M		14	0.37	0.45	0.20	300	10	14	13	-7	39	33	-17	70	57	-22
DTC551B	SURG-3M		15	0.38	0.44	0.20	300	10	12	11	-3	35	29	-20	63	48	-30
DTC554A	SURG-3M		14	0.38	0.47	0.20	299	10	13	14	6	37	35	-4	66	60	-9
DTC558B	SURG-3M		15	0.34	0.49	0.20	300	10	11	14	19	33	36	8	61	63	4
DTC565B	SURG-3M		15	0.40	0.47	0.20	299	16	9	12	21	26	32	18	44	53	18
DTC570A	SURG-3M		14	0.37	0.51	0.20	298	16	11	14	18	34	36	5	59	61	3
DTC570B	SURG-3M		15	0.37	0.51	0.20	298	16	10	13	22	32	35	8	56	59	6
DTC590A	SURG-3M		14	0.42	0.56	0.19	297	16	10	15	33	31	38	18	52	63	18
DTC590B	SURG-3M		15	0.42	0.56	0.19	297	16	8	14	43	27	37	27	46	61	24
DTC600A	SURG-3M		14	0.37	0.49	0.19	298	22	10	13	23	31	33	7	54	55	2
DTC600B	SURG-3M		15	0.37	0.49	0.19	298	22	9	12	28	28	32	12	50	53	7
DTC601B	SURG-3M		15	0.38	0.49	0.19	298	22	-	12		30	31	5	52	53	1
DTC602B	SURG-3M		15	0.39	0.51	0.19	298	22	10	12	17	30	31	5	54	54	1
DTC603A	SURG-3M		16	0.38	0.49	0.19	298	22	14	17	18	36	39	7	62	65	4
DTC603B	SURG-3M		15	0.37	0.50	0.19	298	22	8	12	30	27	31	14	50	54	9
DTC618B	SURG-3M		17	0.42	0.50	0.18	297	22	8	9	2	27	25	-5	48	44	-9
DTC688A	SURG-3M		18	0.42	0.52	0.17	294	20	13	10	-29	37	29	-28	60	47	-28
DTC692A	SURG-3M		18	0.44	0.53	0.16	298	0	13	11	-20	38	29	-33	64	47	-37
DTC694B	SURG-3M		18	0.41	0.54	0.16	298	0	11	11	7	32	30	-9	55	47	-16
DTC701A	SURG-3M		18	0.40	0.49	0.16	296	0	11	9	-17	33	25	-32	56	40	-38
DTC703A	SURG-3M		18	0.43	0.52	0.16	296	0	10	10	-2	33	27	-23	57	44	-31
DTC724A	SURG-3M		18	0.34	0.46	0.16	294	0	7	10	29	27	28	7	47	47	1
DTC734A	SURG-3M		18	0.39	0.50	0.16	295	21	10	10	0	32	29	-11	54	47	-16
DTC741B	SURG-3M		18	0.38	0.48	0.16	295	21	9	9	-2	29	25	-15	47	41	-16
DTC750A	SURG-3M		18	0.36	0.51	0.16	300	0	13	11	-20	34	29	-16	55	49	-13
DTC753B	SURG-3M		18	0.41	0.47	0.16	299	0	8	9	9	29	26	-10	48	42	-13
DTC757B	SURG-3M		18	0.38	0.47	0.16	299	0	10	9	-4	31	26	-16	51	43	-18
DTC759B	SURG-3M		18	0.37	0.47	0.16	299	0	9	10	7	29	26	-10	49	43	-13
DTC760A	SURG-3M		18	0.39	0.49	0.16	298	0	15	9	-60	33	23	-44	54	40	-37
DTC766B	SURG-3M		18	0.37	0.52	0.16	300	0	8	11	25	29	31	5	53	52	-2
DTC773B	SURG-3M		18	0.38	0.50	0.16	300	0	10	11	4	31	29	-4	51	49	-5
DTC783A	SURG-3M		18	0.40	0.55	0.16	300	0	13	12	-9	35	32	-10	55	54	-1
XTC104	SURG-3M		1	0.51	0.33	0.25	301	1	11	12	8	37	36	0	58	55	-4
CTC100A	SURG-3M		4	0.45	0.35	0.19	295	2	5	6	26	16	22	27	-	37	

Table B-1 (continued)

Run	Run Type or VOC [a]	Rct'y Type [a]	Chr Set [b]	NOx (ppm)	Pr.Eq. (ppm) [c]	k1 (min^{-1}) [d]	T (K) [e]	Ref [f]	Δ (O3-NO) Results (pphm) 2 Hour Expt	2 Hour Calc	2 Hour Δ%	4 Hour Expt	4 Hour Calc	4 Hour Δ%	6 Hour Expt	6 Hour Calc	6 Hour Δ%
CTC100B	SURG-3M		4	0.45	0.36	0.19	295	2	5	7	28	18	24	25	-	40	
CTC101A	SURG-3M		4	0.36	0.44	0.19	295	2	8	12	34	26	36	26	43	58	26
CTC101B	SURG-3M		4	0.35	0.44	0.19	295	2	8	12	30	28	36	21	45	59	24
CTC103A	SURG-3M		5	0.30	0.46	0.19	295	2	10	16	34	30	41	28	-	66	
CTC103B	SURG-3M		5	0.30	0.46	0.19	295	2	11	16	35	31	44	30	-	70	
CTC104B	SURG-3M		5	0.29	0.45	0.19	295	2	11	15	29	31	42	26	52	68	24
CTC105A	SURG-3M		5	0.30	0.45	0.19	296	2	11	16	33	32	42	24	53	66	20
CTC107B	SURG-3M		5	0.30	0.44	0.19	295	2	10	15	29	32	40	20	-	66	
CTC108A	SURG-3M		5	0.31	0.44	0.19	295	2	10	13	29	30	38	21	-	63	
CTC109B	SURG-3M		5	0.31	0.43	0.19	295	2	11	14	16	33	39	15	-	64	
CTC110A	SURG-3M		5	0.30	0.46	0.19	296	2	11	15	26	34	43	21	-	69	
CTC112B	SURG-3M		5	0.29	0.43	0.19	296	2	11	14	22	31	39	21	-	64	
CTC113A	SURG-3M		5	0.30	0.20	0.19	297	2	13	6	-117	34	21	-61	-	33	
CTC113B	SURG-3M		5	0.30	0.21	0.19	297	2	12	6	-92	34	23	-46	-	35	
CTC119A	SURG-3M		5	0.31	0.43	0.19	294	2	12	13	7	30	35	12	-	57	
CTC121B	SURG-3M		5	0.31	0.42	0.19	292	2	9	12	26	27	34	21	-		
CTC142A	SURG-3M		6	0.37	0.34	0.18	295	2	6	6	10	18	21	16	-	35	
CTC172A	SURG-3M		7	0.32	0.44	0.17	294	10	7	9	23	26	28	9	-	50	
CTC172B	SURG-3M		7	0.32	0.44	0.17	294	10	8	9	13	27	28	4	-	51	
CTC181B	SURG-3M		7	0.23	0.43	0.16	298	10	13	11	-18	39	33	-17	63	54	-15
CTC183B	SURG-3M		7	0.23	0.43	0.16	298	10	12	11	-7	37	34	-9	61	55	-11
CTC184A	SURG-3M		7	0.23	0.43	0.16	298	17	11	10	-8	35	32	-11	60	53	-14
CTC185B	SURG-3M		7	0.28	0.43	0.16	301	17	12	11	-8	36	34	-5	60	56	-8
CTC192B	SURG-3M		7	0.22	0.41	0.16	298	17	9	9	-3	32	28	-15	57	49	-18
CTC196B	SURG-3M		8	0.22	0.42	0.15	297	10	10	11	5	34	33	-2	-	53	
CTC197A	SURG-3M		8	0.25		0.15	297	18	10	10	4	33	31	-6	57	52	-10
CTC201B	SURG-3M		8	0.24	0.54	0.15	298	18	9	8	-22	29	26	-13	51	47	-7
CTC209A	SURG-3M		8	0.25	0.45	0.15	298	18	10	10	6	32	31	-2	55	52	-5
CTC211A	SURG-3M		8	0.23	0.46	0.15	298	18	8	11	24	30	33	7	54	53	-3
CTC216A	SURG-3M		8	0.24	0.44	0.14	298	19	10	10	-5	33	30	-10	57	50	-13
CTC221B	SURG-3M		8	0.24	0.42	0.14	299	19	9	9	-5	32	29	-10	55	49	-13
CTC231B	SURG-3M		9	0.27	0.51	0.14	303	5	8	13	43	27	37	27	-	56	
CTC246B	SURG-3M		9	0.25	0.48	0.13	295	6	6	9	28	30	28	-4	53	47	-14
CTC250A	SURG-3M		9	0.24	0.45	0.13	296	6	7	8	21	27	27	0	50	45	-11
CTC255B	SURG-3M		9	0.22	0.44	0.13	296	20	7	8	22	26	27	6	48	45	-6
CTC257B	SURG-3M		10	0.24	0.46	0.13	297	20	7	7	5	26	25	-2	47	43	-9
DTC725B	SURG-4M		18		0.51	0.16	295	21	10	10	5	30	27	-13	48	42	-15
DTC730B	SURG-4M		18	0.31	0.52	0.16	296	21	9	12	26	26	29	11	44	48	9
DTC733B	SURG-4M		18	0.30	0.53	0.16	296	21	9	12	29	27	30	10	47	50	8
DTC749B	SURG-4M		18	0.38	0.54	0.16	298	21	12	12	-1	34	30	-13	54	48	-12
CTC266B	SURG-4M		10	0.24	0.46	0.12	299	6	10	6	-74	33	21	-61	53	36	-46
ETC217	SURG-3		2	0.26	0.39	0.35	299	1	18	23	21	55	60	7	84	87	3
ETC219	SURG-3		2	0.25	0.38	0.35	300	1	20	22	11	58	59	1	85	85	0
ETC387	SURG-3		3	0.15	0.28	0.35	301	1	21	22	2	52	51	-1	62	65	5
ETC388	SURG-3		3	0.15	0.34	0.35	301	1	25	27	7	58	59	2	65	67	4
ETC390	SURG-3		3	0.14	0.34	0.35	300	1	23	26	15	56	57	3	64	65	2
ETC392	SURG-3		3	0.15	0.32	0.35	300	1	24	23	-4	58	55	-6	68	69	2
ETC395	SURG-3		3	0.14	0.34	0.35	299	1	24	26	10	57	57	-1	66	64	-2

Table B-1 (continued)

Run	Run Type or VOC [a]	Rct'y Type [a]	Chr Set [b]	NOx (ppm)	Pr.Eq. (ppm) [c]	k1 (min^{-1}) [d]	T (K) [e]	Ref [f]	Δ (O3-NO) Results (pphm)								
									2 Hour			4 Hour			6 Hour		
									Expt	Calc	Δ%	Expt	Calc	Δ%	Expt	Calc	Δ%
ETC399	SURG-3		3	0.15	0.35	0.35	300	1	23	28	18	54	60	9	60	68	11
ETC401	SURG-3		3	0.15	0.35	0.35	300	1	20	28	27	53	59	10	60	66	9
ETC403	SURG-3		3	0.15	0.31	0.35	299	1	19	22	15	50	53	6	62	65	5
ETC405	SURG-3		3	0.13	0.33	0.35	299	1	21	26	17	53	55	5	61	63	2
ETC407	SURG-3		3	0.16	0.34	0.35	300	1	23	27	17	56	60	7	67	70	4
DTC318A	SURG-3		11	0.34	0.49	0.21	297	5	12	14	13	32	36	10	55	62	12
DTC360A	SURG-3		11	0.25	0.52	0.20	297	10	12	18	35	32	45	29	57	67	15
DTC360B	SURG-3		11	0.24	0.52	0.20	297	10	11	18	40	31	45	31	57	67	15
DTC362A	SURG-3		11	0.30	0.50	0.20	298	10	12	15	19	34	39	14	60	67	10
DTC364A	SURG-3		11	0.32	0.48	0.20	298	10	14	14	-4	37	36	-4	63	62	-1
DTC365B	SURG-3		11	0.32	0.49	0.20	298	10	13	15	13	35	38	6	61	65	6
DTC366A	SURG-3		11	0.33	0.50	0.20	298	10	13	15	16	35	39	10	60	67	11
DTC368A	SURG-3		11	0.35	0.49	0.20	299	10	13	14	6	35	35	1	61	60	0
DTC369B	SURG-3		11	0.35	0.49	0.20	298	10	12	14	11	34	35	3	59	60	2
DTC415A	SURG-3		11	0.20	0.48	0.19	297	10	15	16	5	42	41	-4	61	58	-5
DTC421B	SURG-3		11	0.39	0.52	0.19	297	12	13	12	-11	37	32	-17	64	53	-20
DTC011A	SURG-8M		1	0.52	0.39	0.39	301	1	38	35	-8	60	55	-8	-	71	
DTC011B	SURG-8M		1	0.52	0.38	0.39	301	1	39	35	-9	61	55	-11	78	69	-13
DTC012A	SURG-8M		1	0.52	0.41	0.39	301	1	42	37	-14	63	57	-11	81	73	-11
DTC012B	SURG-8M		1	0.51	0.41	0.39	301	1	42	38	-12	64	58	-11	-	74	
DTC013A	SURG-8M		1	0.45	0.40	0.39	300	1	40	38	-5	61	58	-4	79	76	-4
DTC013B	SURG-8M		1	0.45	0.40	0.39	300	1	41	37	-8	62	58	-8	-	74	
DTC014B	SURG-8M		1	0.48	0.39	0.39	301	1	41	37	-11	62	57	-10	80	72	-11
DTC015A	SURG-8M		1	0.50	0.41	0.39	301	1	43	37	-16	66	58	-13	-	76	
DTC016B	SURG-8M		1	0.48	0.38	0.39	300	1	40	35	-14	62	55	-13	78	69	-13
DTC017B	SURG-8M		1	0.48	0.38	0.39	300	1	40	36	-11	61	55	-10	78	71	-10
DTC018B	SURG-8M		1	0.48	0.41	0.39	301	1	44	39	-13	66	59	-10	84	77	-9
DTC019A	SURG-8M		1	0.46	0.40	0.39	300	1	39	38	-3	60	59	-2	77	77	-1
DTC020A	SURG-8M		1	0.50	0.38	0.39	300	1	32	26	-24	53	48	-11	68	63	-8
DTC021A	SURG-8M		1	0.49	0.42	0.39	300	1	41	40	-2	61	61	-1	77	78	1
DTC022A	SURG-8M		1	0.50	0.40	0.39	300	1	40	37	-7	61	58	-6	77	74	-4
DTC023B	SURG-8M		1	0.47	0.40	0.39	301	1	40	39	-1	61	60	-2	80	78	-2
DTC024A	SURG-8M		1	0.50	0.41	0.39	301	1	41	38	-6	63	59	-6	82	77	-6
DTC025B	SURG-8M		1	0.47	0.42	0.39	302	1	40	41	1	64	64	1	85	85	0
DTC028B	SURG-8M		1	0.49	0.41	0.39	301	1	39	40	3	61	62	1	80	81	1
DTC064A	SURG-8M		1	0.49	0.40	0.39	302	1	38	38	0	60	59	-1	77	78	2
DTC065B	SURG-8M		1	0.48	0.40	0.39	301	1	37	38	4	58	60	3	75	79	5
DTC068A	SURG-8M		1	0.48	0.38	0.39	301	1	34	36	4	56	56	1	72	74	2
DTC069B	SURG-8M		1	0.48	0.36	0.39	302	1	37	35	-5	58	56	-5	75	73	-3
DTC070B	SURG-8M		1	0.49	0.40	0.39	301	1	37	38	2	58	60	3	74	79	6
DTC249B	SURG-8M		10	0.26	0.36	0.23	297	3	24	28	16	36	44	17	47	57	18
DTC250A	SURG-8M		10	0.27	0.34	0.23	297	3	23	25	8	36	41	12	45	54	16
DTC251A	SURG-8M		10	0.26	0.34	0.23	297	3	24	26	9	37	41	10	46	53	13
DTC251B	SURG-8M		10	0.26	0.35	0.23	297	3	24	26	10	37	41	11	46	54	14
DTC252B	SURG-8M		10	0.26	0.37	0.23	297	3	25	29	13	38	45	16	48	59	19
DTC255A	SURG-8M		10	0.27	0.34	0.23	297	3	22	25	14	33	40	16	42	52	20
DTC256B	SURG-8M		10	0.27	0.36	0.23	297	3	24	27	12	35	43	17	46	56	17
DTC272B	SURG-8M		10	0.14	0.33	0.22	298	4	26	30	14	37	42	11	11	46	75

Table B-1 (continued)

Run	Run Type or VOC [a]	Rct'y Type [a]	Chr Set [b]	NOx (ppm)	Pr.Eq. (ppm) [c]	k1 (min^{-1}) [d]	T (K) [e]	Ref [f]	Δ (O3-NO) Results (pphm)								
									2 Hour			4 Hour			6 Hour		
									Expt	Calc	Δ%	Expt	Calc	Δ%	Expt	Calc	Δ%
DTC274A	SURG-8M		10	0.16	0.35	0.22	298	4	30	31	5	43	45	5	47	50	6
DTC276A	SURG-8M		10	0.17	0.36	0.22	298	4	33	33	0	47	47	-1	51	52	2
DTC278B	SURG-8M		10	0.16	0.39	0.22	298	4	32	36	11	46	47	3	51	50	-2
DTC280B	SURG-8M		10	0.17	0.37	0.22	298	4	32	34	8	45	48	5	50	51	2
DTC281A	SURG-8M		10	0.16	0.37	0.22	298	4	30	34	11	44	46	6	48	50	5
DTC284B	SURG-8M		10	0.15	0.37	0.22	298	4	31	34	10	44	45	2	49	48	-3
DTC290B	SURG-8M		10	0.17	0.37	0.22	298	4	31	33	8	44	47	5	49	51	5
DTC292B	SURG-8M		10	0.16	0.56	0.22	297	4	23	27	13	38	44	14	46	51	11
DTC311A	SURG-8M		11	0.29	0.37	0.21	298	23	26	26	2	42	42	1	52	55	5
DTC317B	SURG-8M		11	0.18	0.37	0.21	297	5	30	33	8	43	46	7	48	52	8
DTC319A	SURG-8M		11	0.18	0.34	0.21	297	5	27	29	8	40	43	6	-	50	
DTC320B	SURG-8M		11	0.30	0.38	0.21	297	23	25	27	5	41	43	4	52	56	6
DTC332B	SURG-8M		11	0.57	0.38	0.21	297	9	15	16	10	29	31	8	37	40	8
DTC335A	SURG-8M		11	0.43	0.40	0.21	297	9	21	22	9	37	40	6	46	50	8
DTC338B	SURG-8M		11	0.29	0.39	0.21	297	10	24	28	15	40	44	10	50	57	11
DTC359A	SURG-8M		11	0.28	0.39	0.20	298	10	26	29	8	43	45	6	54	58	8
DTC370A	SURG-8M		11	0.28	0.36	0.20	298	10	24	24	2	40	40	1	50	52	3
DTC378A	SURG-8M		11	0.26	0.55	0.20	298	16	44	42	-6	63	63	0	71	74	4
DTC381B	SURG-8M		11	0.27	0.34	0.20	298	16	26	24	-7	41	38	-7	51	49	-4
DTC390B	SURG-8M		11	0.28	0.36	0.19	297	11	25	24	-6	41	39	-5	52	51	-2
DTC396A	SURG-8M		11	0.29	0.35	0.19	299	10	28	22	-26	44	38	-18	56	49	-14
DTC399B	SURG-8M		11	0.27	0.37	0.19	298	10	27	25	-6	42	40	-7	53	51	-4
DTC403B	SURG-8M		11	0.30	0.39	0.19	299	10	27	28	3	44	45	2	55	58	5
DTC408A	SURG-8M		11	0.28	0.36	0.19	298	10	30	24	-23	46	39	-18	57	51	-13
DTC410A	SURG-8M		11	0.28	0.37	0.19	298	10	29	26	-12	45	41	-9	56	53	-5
DTC414B	SURG-8M		11	0.27	0.39	0.19	298	10	28	27	-4	45	42	-6	56	53	-5
DTC419A	SURG-8M		11	0.29	0.45	0.19	297	12	31	32	2	47	50	5	58	63	8
DTC423A	SURG-8M		11	0.29	0.50	0.19	297	12	27	36	25	44	55	19	56	67	17
DTC427B	SURG-8M		11	0.26	0.47	0.18	298	12	28	36	21	47	54	13	59	64	8
DTC430B	SURG-8M		11	0.25	0.40	0.18	297	12	29	28	-4	46	43	-7	58	54	-6
DTC455A	SURG-8M		12	0.25	0.40	0.17	297	14	27	28	3	43	42	-1	52	53	2
DTC455B	SURG-8M		11	0.25	0.41	0.17	297	14	25	25	0	42	40	-4	52	51	-2
DTC456B	SURG-8M		11	0.28	0.40	0.17	297	14	26	25	-3	41	41	-2	50	51	3
DTC459B	SURG-8M		11	0.29	0.41	0.16	298	14	24	24	1	41	40	-1	51	50	0
DTC474A	SURG-8M		14	0.31	0.39	0.23	298	13	33	30	-11	51	46	-11	66	60	-10
DTC474B	SURG-8M		15	0.30	0.40	0.23	298	13	32	30	-8	51	46	-10	65	60	-9
DTC476B	SURG-8M		15	0.31	0.41	0.22	298	13	33	31	-8	52	48	-9	66	62	-6
DTC478B	SURG-8M		15	0.31	0.44	0.22	297	13	34	34	0	53	52	-2	67	66	-1
DTC480B	SURG-8M		15	0.30	0.41	0.22	298	13	33	31	-5	51	48	-7	66	63	-5
DTC486B	SURG-8M		15	0.30	0.41	0.22	298	13	33	31	-6	51	48	-8	66	62	-6
DTC488A	SURG-8M		14	0.30	0.38	0.22	298	13	32	23	-42	51	40	-26	66	53	-23
DTC488B	SURG-8M		15	0.30	0.38	0.22	298	13	32	22	-43	50	40	-25	64	53	-22
DTC492B	SURG-8M		15	0.30	0.38	0.22	298	15	29	28	-3	46	44	-4	59	58	-3
DTC493A	SURG-8M		14	0.30	0.38	0.22	297	15	29	28	-4	47	44	-5	61	58	-5
DTC500B	SURG-8M		15	0.30	0.42	0.22	298	15	32	32	0	50	49	-1	64	63	-1
DTC502B	SURG-8M		15	0.30	0.39	0.22	299	15	32	29	-10	50	46	-9	64	59	-7
DTC509B	SURG-8M		15	0.30	0.38	0.22	299	10	32	27	-18	50	44	-15	64	57	-13
DTC511B	SURG-8M		15	0.31	0.39	0.21	299	10	32	28	-16	51	45	-13	65	59	-11

Table B-1 (continued)

Run	Run Type or VOC [a]	Rct'y Type [a]	Chr Set [b]	NOx (ppm)	Pr.Eq. (ppm) [c]	k1 (min^{-1}) [d]	T (K) [e]	Ref [f]	Δ (O3-NO) Results (pphm)								
									2 Hour			4 Hour			6 Hour		
									Expt	Calc	Δ%	Expt	Calc	Δ%	Expt	Calc	Δ%
DTC515B	SURG-8M		15	0.31	0.37	0.21	299	10	31	25	-24	49	41	-19	63	54	-18
DTC516A	SURG-8M		14	0.32	0.40	0.21	299	10	31	28	-9	49	45	-10	64	59	-8
DTC521A	SURG-8M		14	0.30	0.39	0.21	299	10	32	28	-13	50	45	-11	64	58	-10
DTC530A	SURG-8M		14	0.31	0.37	0.21	299	10	29	26	-14	47	41	-13	60	55	-11
DTC534A	SURG-8M		14	0.29	0.38	0.21	299	10	29	27	-7	48	44	-8	62	57	-8
DTC538A	SURG-8M		14	0.29	0.37	0.21	299	10	28	27	-3	46	43	-6	59	57	-5
DTC547A	SURG-8M		14	0.31	0.36	0.20	300	10	31	25	-20	49	41	-18	63	54	-16
DTC552A	SURG-8M		14	0.31	0.37	0.20	300	10	32	26	-26	52	43	-21	67	56	-19
DTC556B	SURG-8M		15	0.28	0.42	0.20	300	10	26	33	20	44	50	12	58	64	9
DTC610B	SURG-8M		17	0.31	0.43	0.19	297	22	26	30	13	43	46	7	54	58	7
DTC616A	SURG-8M		16	0.81	0.37	0.19	297	22	9	11	18	19	22	14	26	30	13
DTC616B	SURG-8M		17	0.80	0.38	0.19	297	22	8	10	16	16	19	15	23	27	16
DTC689B	SURG-8M		18	0.33	0.44	0.16	294	20	27	25	-10	46	41	-12	58	50	-15
DTC693B	SURG-8M		18	0.31	0.45	0.16	298	0	29	29	1	48	46	-2	60	58	-3
DTC695A	SURG-8M		18	0.32	0.50	0.16	299	0	29	32	9	49	50	3	63	63	1
DTC697B	SURG-8M		18	0.32	0.42	0.16	296	20	30	24	-22	49	41	-17	60	52	-16
DTC702B	SURG-8M		18	0.32	0.44	0.16	297	0	26	25	-3	45	43	-6	57	54	-6
DTC705B	SURG-8M		18	0.29	0.45	0.16	296	0	25	27	9	42	44	4	56	55	-2
DTC720A	SURG-8M		18	0.33	0.40	0.16	296	0	28	21	-34	46	39	-18	58	50	-17
DTC726A	SURG-8M		18	0.29	0.42	0.16	294	21	24	24	1	43	42	-1	55	53	-3
DTC729A	SURG-8M		18	0.24	0.40	0.16	294	21	18	25	30	36	41	13	47	52	10
DTC737B	SURG-8M		18	0.32	0.43	0.16	294	21	24	22	-7	41	40	-5	51	49	-5
DTC738A	SURG-8M		18	0.31	0.42	0.16	293	21	25	23	-11	43	41	-4	54	52	-4
DTC746A	SURG-8M		18	0.30	0.44	0.16	298	21	25	28	11	42	45	6	54	57	6
DTC747B	SURG-8M		18	0.29	0.43	0.16	299	21	24	27	12	42	44	6	52	56	6
DTC754A	SURG-8M		18	0.31	0.43	0.16	299	0	26	27	5	44	44	1	56	56	0
DTC755B	SURG-8M		18	0.29	0.43	0.16	299	0	26	27	4	44	43	-1	55	54	-1
DTC762B	SURG-8M		18	0.30	0.42	0.16	299	0	25	25	-3	44	42	-3	54	53	-1
DTC769B	SURG-8M		18	0.28	0.43	0.16	299	0	19	28	32	39	45	13	50	57	11
DTC771B	SURG-8M		18	0.29	0.44	0.16	299	0	24	29	19	42	46	8	53	58	9
DTC772A	SURG-8M		18	0.30	0.44	0.16	299	0	26	27	4	45	44	-1	56	56	-1
DTC776B	SURG-8M		18	0.30	0.40	0.16	300	0	24	24	-3	43	42	-3	54	54	0
DTC780A	SURG-8M		18	0.30	0.42	0.16	300	0	25	24	-5	44	42	-5	56	53	-5
DTC786B	SURG-8M		18	0.30	0.47	0.16	300	0	23	30	24	39	47	16	47	58	19
CTC123B	SURG-8M		5	0.40	0.53	0.18	293	2	35	34	0	52	58	10	64	74	13
CTC124A	SURG-8M		5	0.39	0.51	0.18	293	2	33	33	0	49	54	9	-	69	
CTC126B	SURG-8M		5	0.38	0.51	0.18	294	2	32	33	2	50	54	9	-		
CTC127A	SURG-8M		5	0.39	0.51	0.18	293	2	33	31	-6	50	53	6	-	67	
CTC128B	SURG-8M		5	0.40	0.55	0.18	294	2	35	36	2	53	58	9	-	75	
CTC130A	SURG-8M		5	0.39	0.53	0.18	293	2	32	33	2	50	55	8	63	70	10
CTC131B	SURG-8M		5	0.40	0.54	0.18	293	2	33	34	3	51	56	9	64	72	12
CTC138A	SURG-8M		6	0.40	0.55	0.18	293	2	34	35	3	51	56	9	64	71	11
CTC140B	SURG-8M		6	0.37	0.55	0.18	294	2	30	37	18	49	59	18	-	74	
CTC149A	SURG-8M		6	0.42	0.47	0.18	299	4	25	23	-8	42	42	-1	-	51	
CTC149B	SURG-8M		6	0.42	0.46	0.18	299	4	25	22	-12	42	41	-2	-	52	
CTC150A	SURG-8M		6	0.43	0.54	0.18	299	4	36	33	-9	59	57	-3	75	73	-3
CTC151B	SURG-8M		6	0.51	0.54	0.18	303	4	37	33	-11	57	55	-4	71	68	-4
CTC152A	SURG-8M		6	0.38	0.45	0.18	301	4	27	25	-6	43	42	-3	52	51	-2

Table B-1 (continued)

Run	Run Type or VOC [a]	Rct'y Type [a]	Chr Set [b]	NOx (ppm)	Pr.Eq. (ppm) [c]	k1 (min^{-1}) [d]	T (K) [e]	Ref [f]	Δ (O3-NO) Results (pphm)								
									2 Hour			4 Hour			6 Hour		
									Expt	Calc	Δ%	Expt	Calc	Δ%	Expt	Calc	Δ%
CTC154B	SURG-8M		6	0.42	0.54	0.18	301	4	41	35	-15	62	60	-4	78	77	-1
CTC156A	SURG-8M		6	0.41	0.52	0.18	303	4	36	34	-6	58	58	0	-	74	
CTC158B	SURG-8M		6	0.36	0.52	0.18	304	4	35	39	11	60	64	7	-	79	
CTC165A	SURG-8M		7	0.57	0.57	0.18	305	5	31	36	15	51	61	16	-	80	
CTC165B	SURG-8M		7	0.57	0.58	0.18	305	5	32	36	10	51	60	15	-	80	
CTC167B	SURG-8M		7	0.41	0.57	0.18	300	5	36	39	8	58	63	9	-	80	
CTC168A	SURG-8M		7	0.41	0.58	0.18	300	5	37	40	9	59	64	9	-	80	
CTC171A	SURG-8M		7	0.39	0.56	0.17	300	5	38	36	-4	61	60	-2	-	73	
CTC171B	SURG-8M		7	0.39	0.55	0.17	300	5	37	35	-6	61	59	-3	-	74	
CTC180A	SURG-8M		7	0.39	0.57	0.16	298	10	35	35	0	57	57	-1	72	71	-2
CTC182A	SURG-8M		7	0.39	0.57	0.16	298	10	36	34	-7	58	56	-4	74	70	-6
CTC186A	SURG-8M		7	0.38	0.53	0.16	298	17	32	30	-7	54	52	-4	70	66	-5
CTC193A	SURG-8M		7	0.37	0.55	0.16	298	17	35	31	-14	57	53	-8	72	66	-10
CTC198B	SURG-8M		8	0.39	0.58	0.15	298	18	34	32	-7	56	56	0	71	71	-1
CTC204B	SURG-8M		8	0.44	0.60	0.15	298	18	32	30	-9	56	56	0	71	71	1
CTC208B	SURG-8M		8	0.43	0.61	0.15	298	18	32	32	0	56	58	4	70	73	4
CTC212A	SURG-8M		8			0.15	298	18	29	35	16	52	58	10	66	73	9
CTC217B	SURG-8M		8	0.43	0.58	0.14	297	19	31	26	-19	55	52	-6	70	66	-5
CTC222A	SURG-8M		8	0.45	0.55	0.14	299	19	32	24	-31	56	49	-14	71	62	-15
CTC232A	SURG-8M		9	0.46	0.57	0.14	301	5	20	25	22	42	49	14	-	63	
CTC239A	SURG-8M		9	0.44	0.59	0.13	301	5	28	28	1	52	54	4	-	67	
CTC248A	SURG-8M		9	0.32	0.60	0.13	292	6	32	39	17	54	60	10	66	68	3
CTC251B	SURG-8M		9	0.34	0.63	0.13	294	6	32	34	6	52	56	6	66	66	1
CTC260A	SURG-8M		10	0.40	0.65	0.12	295	20	28	29	4	50	55	10	63	67	7
CTC262B	SURG-8M		10	0.38	0.60	0.12	294	20	29	26	-11	50	51	1	64	62	-4
DTC027A	SURG-8		1	0.15	0.40	0.39	302	1	52	49	-6	61	59	-4	63	61	-3
DTC027B	SURG-8		1	0.15	0.41	0.39	302	1	52	50	-4	61	59	-4	63	61	-3
DTC029B	SURG-8		1	0.17	0.43	0.39	301	1	54	53	-2	63	64	2	64	66	3
DTC030A	SURG-8		1	0.17	0.40	0.39	300	1	50	50	0	59	62	4	60	64	6
DTC031B	SURG-8		1	0.17	0.43	0.39	301	1	52	53	2	61	63	4	62	66	5
DTC032A	SURG-8		1	0.17	0.42	0.39	300	1	51	52	3	60	63	5	61	65	7
DTC033B	SURG-8		1	0.17	0.41	0.39	300	1	51	51	0	60	62	2	62	64	4
DTC034A	SURG-8		1	0.16	0.41	0.39	301	1	50	50	0	60	62	4	60	64	7
DTC035B	SURG-8		1	0.17	0.40	0.39	301	1	51	49	-3	60	62	4	61	65	6
DTC036B	SURG-8		1	0.18	0.44	0.39	300	1	54	53	-2	-	65		63	67	6
DTC037A	SURG-8		1	0.17	0.42	0.39	301	1	51	52	1	61	64	5	61	66	7
DTC038B	SURG-8		1	0.17	0.39	0.39	301	1	51	49	-4	59	62	4	61	64	6
DTC039A	SURG-8		1	0.18	0.41	0.39	301	1	52	51	-3	61	64	6	61	67	9
DTC066A	SURG-8		1	0.17	0.37	0.39	302	1	49	47	-4	59	63	5	60	66	9
DTC067A	SURG-8		1	0.17	0.38	0.39	301	1	48	48	-1	59	62	6	60	65	9
DTC071A	SURG-8		1	0.18	0.39	0.39	302	1	49	49	0	60	64	7	61	68	11
DTC258A	SURG-8		10	0.14	0.36	0.23	297	3	28	33	15	35	43	17	36	44	19
DTC258B	SURG-8		10	0.13	0.36	0.23	297	3	29	33	14	36	42	16	-	44	
DTC259B	SURG-8		10	0.16	0.35	0.23	297	3	27	32	16	37	44	16	41	49	16
DTC260A	SURG-8		10	0.17	0.36	0.22	297	3	28	32	14	39	46	16	42	52	18
DTC261B	SURG-8		10	0.16	0.34	0.22	296	3	25	31	18	36	44	19	39	48	19
DTC266B	SURG-8		10	0.16	0.34	0.22	298	3	25	31	18	36	45	20	39	50	21
DTC267A	SURG-8		10	0.16	0.36	0.22	299	3	29	33	13	40	46	13	43	51	16

Table B-1 (continued)

Run	Run Type or VOC [a]	Rct'y Type [a]	Chr Set [b]	NOx (ppm)	Pr.Eq. (ppm) [c]	k1 (min^{-1}) [d]	T (K) [e]	Ref [f]	Δ (O3-NO) Results (pphm)								
									2 Hour			4 Hour			6 Hour		
									Expt	Calc	Δ%	Expt	Calc	Δ%	Expt	Calc	Δ%
DTC268B	SURG-8		10	0.16	0.47	0.22	299	3	34	40	15	46	54	14	49	58	15
DTC269B	SURG-8		10	0.17	0.36	0.22	299	3	30	33	8	42	46	9	45	52	13
DTC293B	SURG-8		10	0.08	0.39	0.22	297	4	28	29	4	32	30	-4	32	30	-6
DTC298A	SURG-8		10	0.09	0.38	0.22	298	4	29	30	4	31	31	0	31	31	1
DTC308A	SURG-8		11	0.17	0.37	0.21	301	23	32	34	4	45	48	6	48	54	11
DTC309B	SURG-8		11	0.17	0.53	0.21	299	23	42	45	6	49	52	6	49	53	6
DTC321A	SURG-8		11	0.11	0.38	0.21	298	23	30	32	7	33	37	9	32	37	12
DTC325A	SURG-8		11	0.18	0.42	0.21	299	5	31	38	17	44	50	13	47	54	13
DTC329B	SURG-8		11	0.18	0.39	0.21	296	9	29	34	13	43	47	8	49	51	5
DTC330A	SURG-8		11	0.17	0.39	0.21	296	9	30	34	12	43	46	6	48	49	4
DTC386A	SURG-8		11	0.29	0.34	0.19	298	11	26	20	-30	41	34	-21	52	44	-18
DTC388B	SURG-8		11	0.11	0.37	0.19	298	11	29	30	3	34	34	-1	34	34	0
DTC391A	SURG-8		11	0.11	0.36	0.19	297	11	30	29	-2	35	34	-3	35	34	-3
DTC394B	SURG-8		11	0.11	0.36	0.19	296	10	29	30	2	34	35	2	34	36	5
DTC397B	SURG-8		11	0.13	0.36	0.19	298	10	32	31	-3	38	39	3	38	41	8
DTC400A	SURG-8		11	0.12	0.36	0.19	298	10	31	30	-3	36	37	1	36	38	5
DTC406B	SURG-8		11	0.13	0.39	0.19	299	10	32	33	3	37	38	3	37	38	4
DTC409B	SURG-8		11	0.11	0.36	0.19	298	10	31	30	-3	35	36	2	34	37	7
DTC411B	SURG-8		11	0.11	0.36	0.19	297	10	30	29	-3	35	35	1	34	35	4
DTC412A	SURG-8		11	0.11	0.36	0.19	297	10	30	32	4	35	36	5	35	37	6
DTC418B	SURG-8		11	0.10	0.38	0.19	298	10	30	30	0	34	34	-2	34	34	0
DTC420A	SURG-8		11	0.10	0.47	0.19	297	12	32	31	-3	35	32	-12	34	31	-10
DTC424B	SURG-8		11	0.10	0.44	0.18	297	12	31	30	-5	35	30	-15	34	30	-14
DTC428A	SURG-8		11	0.12	0.42	0.18	298	12	32	32	1	36	37	3	35	37	6
DTC432A	SURG-8		11	0.09	0.42	0.18	297	12	33	28	-18	37	29	-28	36	28	-27
DTC451A	SURG-8		12	0.10	0.43	0.17	297	14	31	30	-4	36	33	-9	36	33	-8
DTC451B	SURG-8		11	0.10	0.44	0.17	297	14	32	29	-8	37	31	-17	36	31	-17
DTC453B	SURG-8		11	0.14	0.40	0.17	295	14	29	30	4	35	37	5	35	38	10
DTC454B	SURG-8		11	0.12	0.40	0.17	297	14	29	29	1	34	34	-1	33	34	1
DTC462A	SURG-8		12	0.13	0.40	0.16	299	14	30	31	4	36	37	3	35	38	7
DTC466B	SURG-8		13	0.13	0.38	0.16	297	14	30	29	-5	-	34		34	35	2
DTC477A	SURG-8		14	0.13	0.46	0.22	297	13	38	38	-1	43	42	-2	43	42	-2
DTC479A	SURG-8		14	0.14	0.44	0.22	297	13	37	38	2	44	44	1	44	44	0
DTC481A	SURG-8		14	0.13	0.41	0.22	298	13	37	36	-2	42	41	-2	42	42	-2
DTC487A	SURG-8		14	0.13	0.40	0.22	298	13	37	35	-3	42	41	-4	43	41	-4
DTC496A	SURG-8		14	0.13	0.41	0.22	299	15	37	36	-3	43	41	-4	44	42	-5
DTC497B	SURG-8		15	0.13	0.41	0.22	299	15	37	36	-2	43	42	-3	44	43	-3
DTC501A	SURG-8		14	0.13	0.40	0.22	299	15	37	35	-6	43	41	-5	44	42	-5
DTC506B	SURG-8		15	0.12	0.39	0.22	298	15	35	34	-2	41	40	-2	41	40	-2
DTC513B	SURG-8		15	0.13	0.36	0.21	298	10	35	33	-7	42	40	-4	43	42	-2
DTC519A	SURG-8		14	0.13	0.34	0.21	298	10	35	32	-7	41	39	-6	42	40	-5
DTC520B	SURG-8		15	0.12	0.39	0.21	299	10	35	34	-4	41	40	-2	42	41	-2
DTC524A	SURG-8		14	0.13	0.39	0.21	299	10	36	34	-6	42	40	-5	43	41	-4
DTC525B	SURG-8		15	0.13	0.38	0.21	299	10	37	34	-8	44	42	-6	45	43	-4
DTC531B	SURG-8		15	0.12	0.37	0.21	299	10	35	33	-7	42	39	-7	43	40	-6
DTC539B	SURG-8		15	0.13	0.38	0.21	299	10	34	34	-2	41	41	-1	42	42	0
DTC540A	SURG-8		14	0.12	0.37	0.21	299	10	35	33	-6	40	40	-2	42	41	-1
DTC543A	SURG-8		14	0.30	0.40	0.21	299	10	31	29	-5	48	45	-7	62	58	-7

Table B-1 (continued)

Run	Run Type or VOC [a]	Rct'y Type [a]	Chr Set [b]	NOx (ppm)	Pr.Eq. (ppm) [c]	k1 (min^{-1}) [d]	T (K) [e]	Ref [f]	Δ (O3-NO) Results (pphm) 2 Hour Expt	2 Hour Calc	2 Hour Δ%	4 Hour Expt	4 Hour Calc	4 Hour Δ%	6 Hour Expt	6 Hour Calc	6 Hour Δ%
DTC544B	SURG-8		15	0.13	0.38	0.21	299	10	36	34	-7	43	41	-3	44	43	-2
DTC548B	SURG-8		15	0.13	0.37	0.20	299	10	35	32	-8	42	41	-3	43	43	0
DTC553B	SURG-8		15	0.13	0.37	0.20	300	10	36	33	-7	43	42	-3	44	44	-1
DTC557A	SURG-8		14	0.12	0.42	0.20	300	10	35	35	0	42	40	-5	43	41	-6
DTC559B	SURG-8		15	0.28		0.20	299	10	26	32	17	43	50	15	54	64	15
DTC560B	SURG-8		15	0.12	0.41	0.20	299	16	30	33	11	37	37	2	38	37	-2
DTC604A	SURG-8		16	0.14	0.38	0.19	298	22	35	33	-6	40	41	4	41	43	5
DTC608B	SURG-8		17	0.15	0.43	0.19	297	22	32	35	9	40	43	7	41	44	7
DTC609A	SURG-8		16	0.14	0.42	0.19	298	22	31	35	10	37	41	10	-	42	
DTC609B	SURG-8		17	0.13	0.42	0.19	298	22	31	34	9	37	41	8	-	41	
DTC698A	SURG-8		18	0.10	0.43	0.16	295	0	30	29	-3	33	32	-1	33	32	-4
DTC700B	SURG-8		18	0.10	0.44	0.16	296	0	30	30	-2	33	32	-2	33	32	-2
DTC707A	SURG-8		18	0.10	0.41	0.16	297	0	30	28	-7	35	32	-8	35	32	-8
DTC723B	SURG-8		18	0.11	0.42	0.16	295	0	30	29	-1	33	33	-1	33	33	-1
DTC732A	SURG-8		18	0.08	0.42	0.16	296	21	26	25	-3	29	26	-9	29	26	-9
DTC739B	SURG-8		18	0.10	0.40	0.16	295	21	26	28	7	28	31	8	28	30	9
DTC740A	SURG-8		18	0.10	0.40	0.16	295	21	26	28	7	29	31	6	28	31	8
DTC748A	SURG-8		18	0.09	0.43	0.16	297	21	25	27	7	27	28	6	26	28	7
DTC758A	SURG-8		18	0.09	0.44	0.16	299	0	27	28	2	29	30	3	28	30	4
DTC763A	SURG-8		18	0.09	0.42	0.16	299	0	25	27	9	27	29	10	26	30	11
DTC763A	SURG-8		18	0.09	0.42	0.16	299	0	25	27	9	27	29	10	26	30	11
DTC770A	SURG-8		18	0.08	0.42	0.16	299	0	22	26	17	24	28	16	23	28	18
DTC778B	SURG-8		18	0.09	0.43	0.16	300	0	27	28	3	-	30		29	31	6
DTC782B	SURG-8		18	0.09	0.46	0.16	300	0	26	28	7	27	29	9	26	29	12
DTC787A	SURG-8		18	0.10	0.44	0.16	299	0	25	29	14	27	32	16	-		
XTC109	SURG-8		1	0.24	0.38	0.25	302	1	41	39	-7	63	60	-6	-	72	
XTC116	SURG-8		1	0.22	0.42	0.25	301	1	45	42	-6	64	62	-3	69	71	2
CTC187B	SURG-8		7	0.15	0.58	0.16	298	17	39	38	-3	44	42	-6	44	42	-5
CTC194B	SURG-8		8	0.15	0.58	0.16	297	17	39	38	-4	44	42	-6	44	42	-5
CTC195A	SURG-8		8	0.14	0.52	0.15	297	10	39	36	-10	44	41	-7	44	41	-6
CTC199A	SURG-8		8	0.16	0.58	0.15	298	18	39	39	-1	44	44	-1	44	44	-1
CTC205A	SURG-8		8	0.17	0.59	0.15	298	18	41	40	-3	46	45	-3	46	45	-3
CTC210B	SURG-8		8	0.16	0.60	0.15	298	18	40	38	-3	44	43	-4	44	43	-3
CTC215B	SURG-8		8	0.18	0.56	0.15	297	18	41	39	-6	47	46	-4	47	47	-1
CTC220A	SURG-8		8	0.16	0.55	0.14	298	19	40	37	-6	46	44	-4	46	44	-4
CTC223B	SURG-8		8	0.17	0.56	0.14	298	19	40	38	-4	46	44	-3	46	45	-1
CTC233B	SURG-8		9	0.17	0.62	0.14	299	5	38	39	3	43	44	2	43	44	4
CTC235B	SURG-8		9	0.15	0.60	0.14	301	10	36	36	1	40	41	1	41	41	2
CTC238B	SURG-8		9	0.16	0.58	0.13	301	10	37	38	1	43	43	2	43	44	4
CTC240B	SURG-8		9	0.16	0.60	0.13	300	5	37	38	3	42	43	1	-	44	
CTC249B	SURG-8		9	0.16	0.63	0.13	295	6	37	37	0	42	41	-1	42	41	-2
CTC253A	SURG-8		9	0.16	0.63	0.13	295	6	39	38	-4	45	43	-5	45	43	-5
CTC258A	SURG-8		10	0.17	0.59	0.13	296	20	39	37	-5	44	43	-3	43	44	3
CTC259B	SURG-8		10	0.17	0.64	0.12	295	20	37	38	1	43	43	0	43	43	0
CTC263A	SURG-8		10	0.16	0.62	0.12	294	20	37	36	-3	42	41	-2	41	42	2
CTC267A	SURG-8		10	0.16	0.59	0.12	300	6	36	36	-2	40	41	3	39	42	6
OTC275B	SURG-8		11	0.63	0.44	0.00	319	7,8	84	75	-11	148	137	-8	-	158	
OTC276A	SURG-8		11	0.58	0.44	0.00	315	7,8	80	69	-15	135	120	-12	144	144	0

Table B-1 (continued)

Run	Run Type or VOC [a]	Rct'y Type [a]	Chr Set [b]	NOx (ppm)	Pr.Eq. (ppm) [c]	k1 (min^{-1}) [d]	T (K) [e]	Ref [f]	Δ (O3-NO) Results (pphm)								
									2 Hour			4 Hour			6 Hour		
									Expt	Calc	Δ%	Expt	Calc	Δ%	Expt	Calc	Δ%
OTC277A	SURG-8		11	0.51	0.40	0.00	312	7,8	67	61	-10	121	109	-12	-	131	
OTC277B	SURG-8		11	0.52	0.39	0.00	312	7,8	63	60	-5	115	109	-6	133	132	-1

[a] See Table 45 for the definitions of the codes used to designate run type and incremental reactivity experiment category.

[b] Characterization set. Runs with the same chamber and characterization set number are assumed to have the same chamber effects and (for CTC runs) light spectrum.

[c] "Propene equivalent" for all VOCs injected in experiment. Sum of measured initial VOC concentration times OH rate constant, divided by the OH rate constant for propene.

[d] NO2 photolysis rate assigned for this experiment.

[e] Average measured temperature for this experiment.

[f] References for reports describing chamber experiments. These reports are available at http://cert.ucr.edu/~carter/bycarter.htm.

0 Unpublished results from this laboratory.
1 Carter et al. (1995d)
2 Carter et al. (1997a)
3 Carter et al. (1996c)
4 Carter et al. (1996a)
5 Carter et al. (1999b)
6 Carter et al. (1999c)
7 Carter et al. (1995c)
8 Carter et al. (1993b)
9 Carter et al. (1996b)
10 Carter et al. (1999a)
11 Carter et al. (1997b)
12 Carter et al. (1997d)
13 Carter et al. (1997f)
14 Carter et al. (1997i)
15 Carter et al. (1999f)
16 Carter et al. (1999h)
17 Carter et al. (1997c)
18 Carter et al. (1997e)
19 Carter et al. (1997g)
20 Carter et al. (1999e)
21 Carter et al. (1999d)
22 Carter et al. (1999g)
23 Carter et al. (1996d)

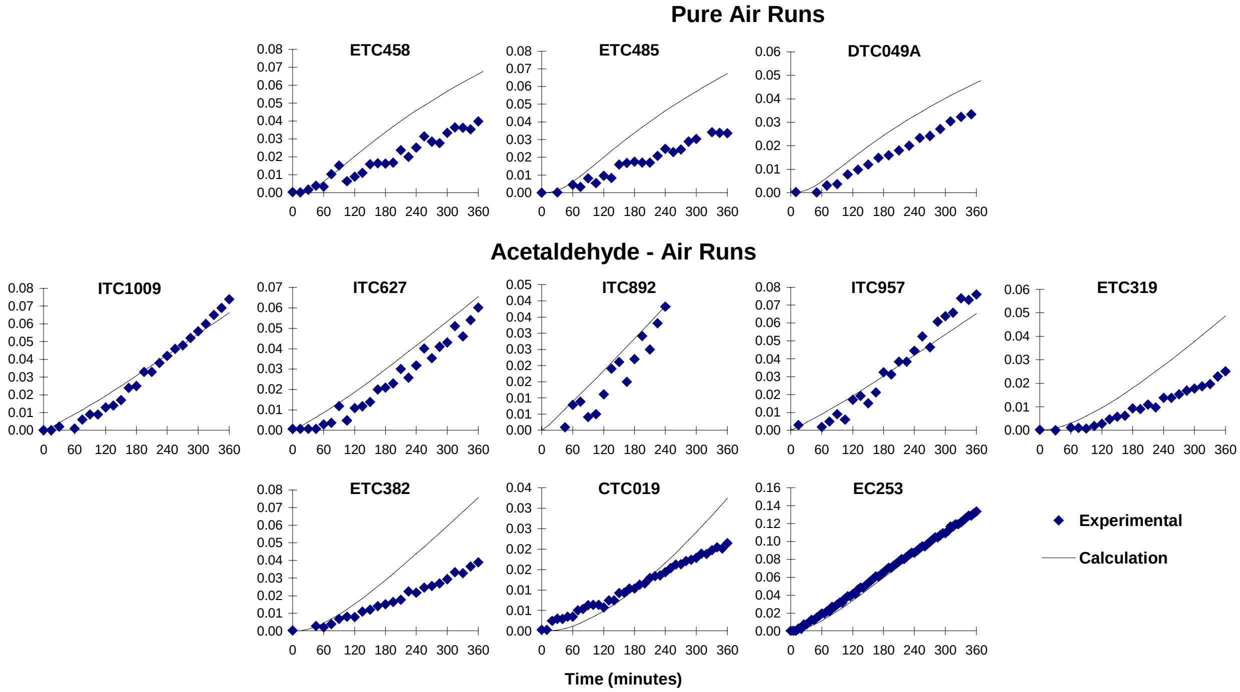


Figure B-1. Plots of experimental and calculated ozone data for the pure air and acetaldehyde - air runs.

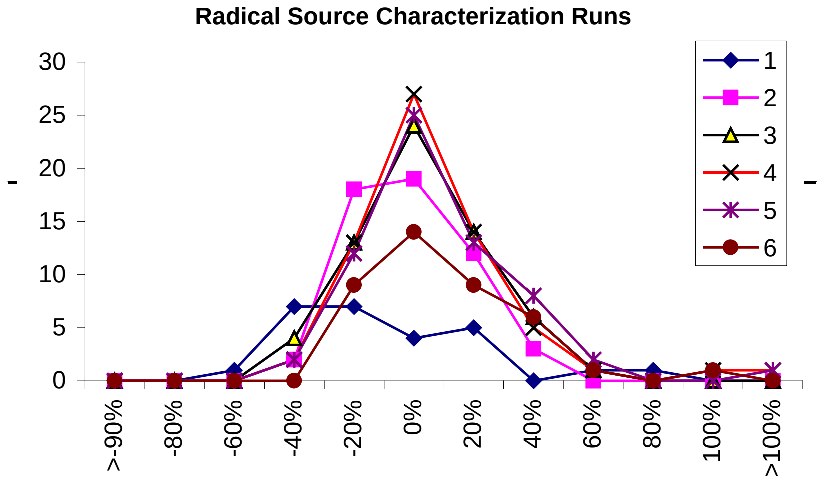


Figure B-2. Distribution plots of percentage errors of fits of calculated to experimental hourly Δ($[O_3]$-[NO]) data for the radical source characterization (CO - NO_x and n-butane - NO_x) runs.

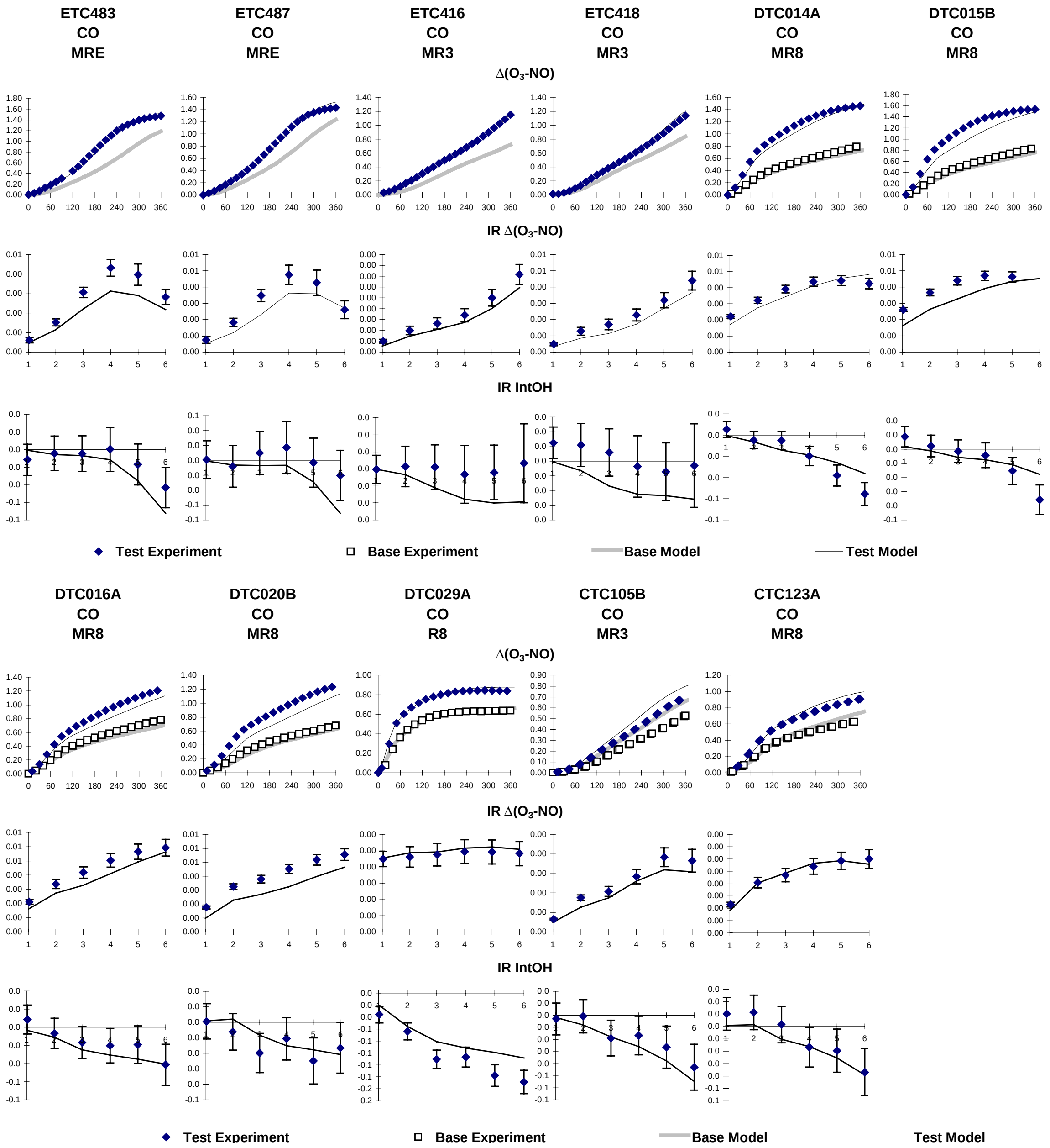


Figure B-3. Plots of experimental and calculated results of the incremental reactivity experiments with CO.

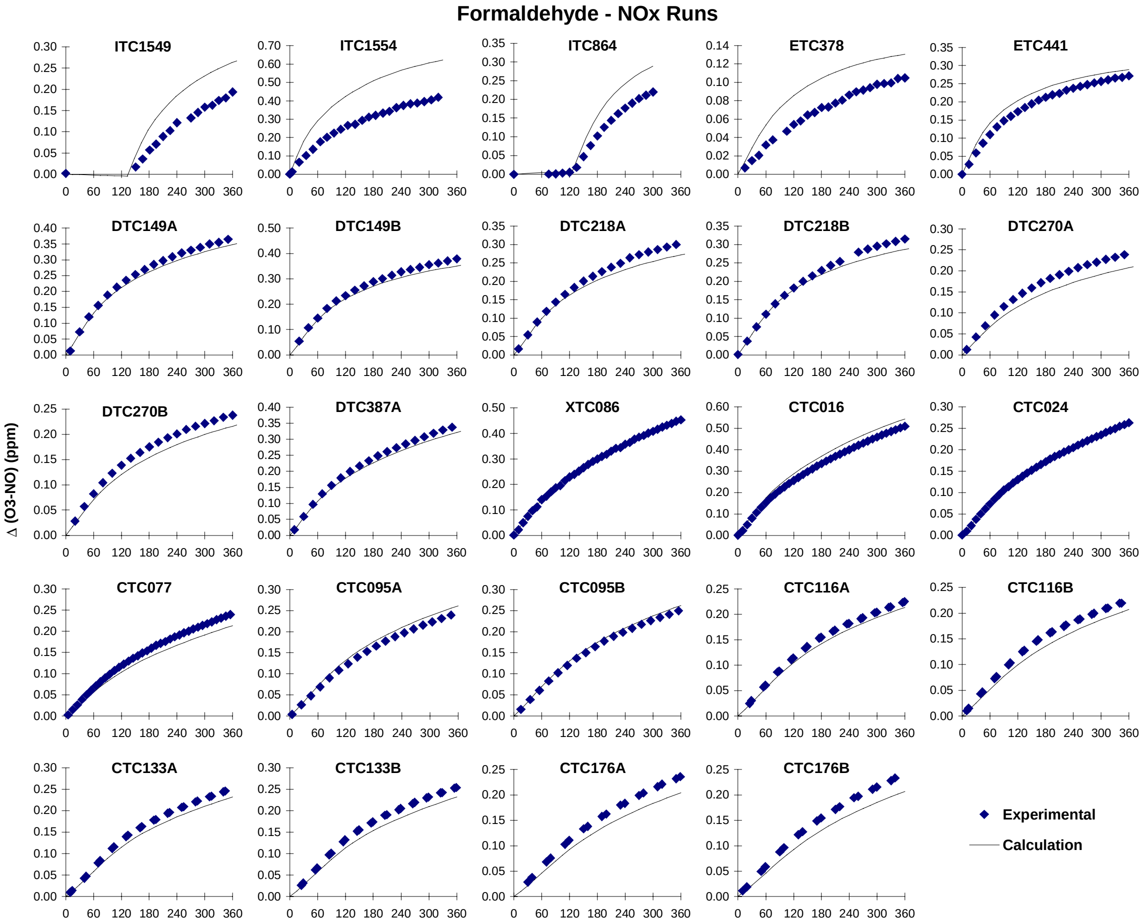


Figure B-4. Plots of experimental and calculated $\Delta([O_3]-[NO])$ data for the formaldehyde - NO_x experiments.

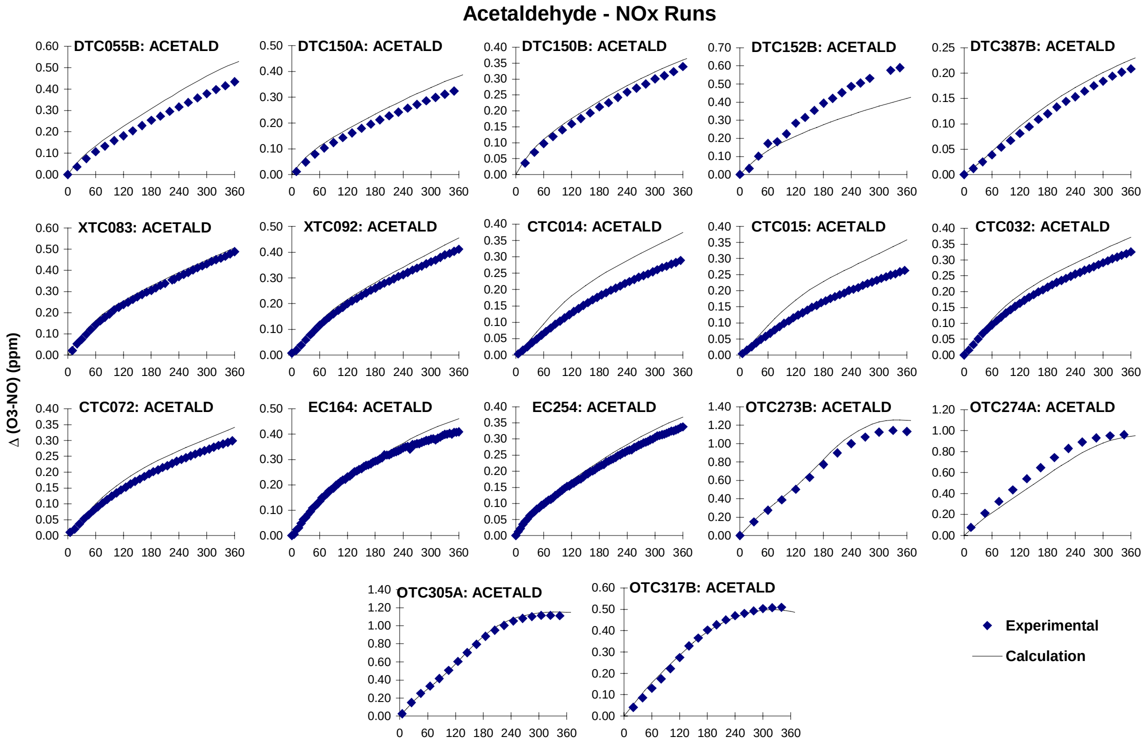


Figure B-5. Plots of experimental and calculated $\Delta([O_3]-[NO])$ data for the acetaldehyde - NO_x experiments.

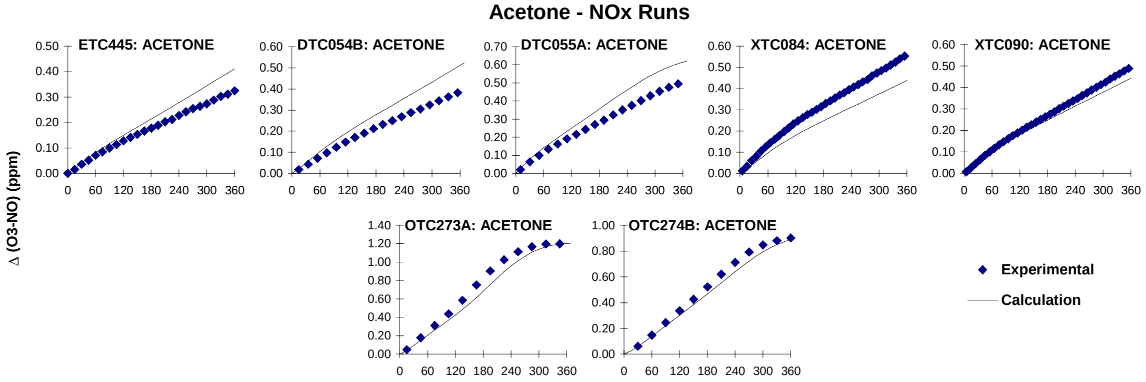
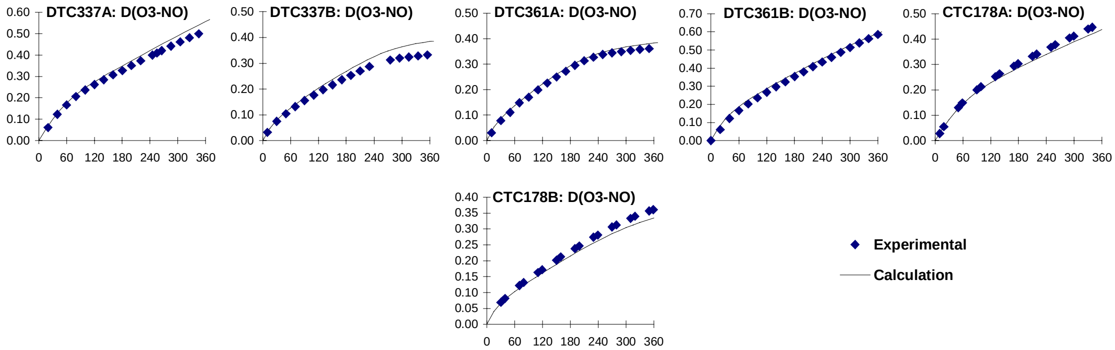
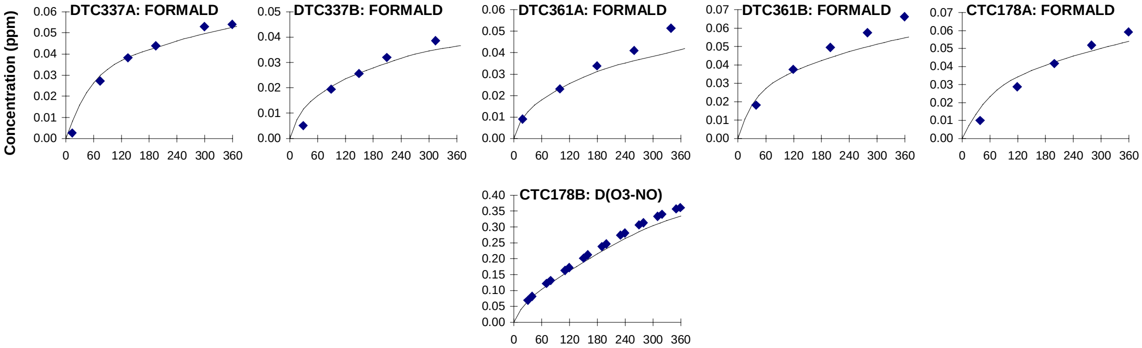


Figure B-6. Plots of experimental and calculated $\Delta([O_3]-[NO])$ data for the acetone - NO_x experiments.

MEK - NOx Runs -- Δ (O3-NO) data



MEK - NOx Runs -- Formaldehyde data



MEK - NOx Runs -- Acetaldehyde data

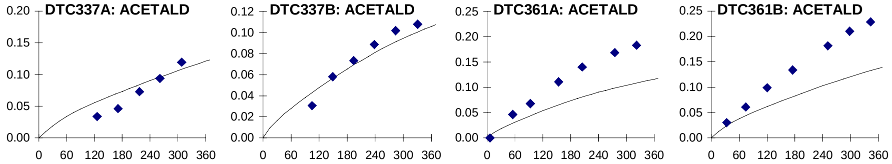


Figure B-7. Plots of experimental and calculated $\Delta([O_3]-[NO])$, formaldehyde, and acetaldehyde data for the methyl ethyl ketone (MEK) - NO_x experiments.

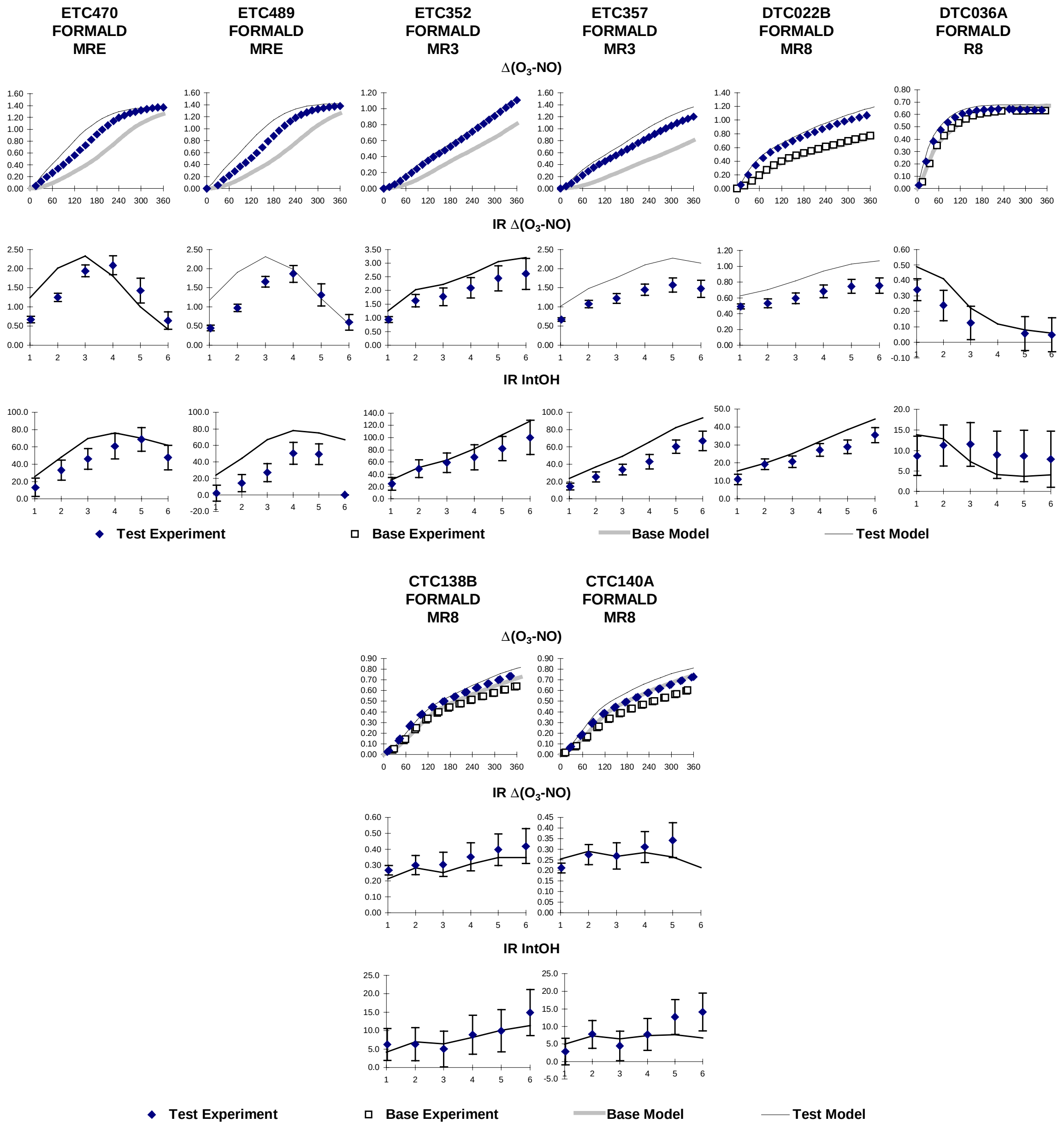


Figure B-8. Plots of experimental and calculated results of the incremental reactivity experiments with formaldehyde.

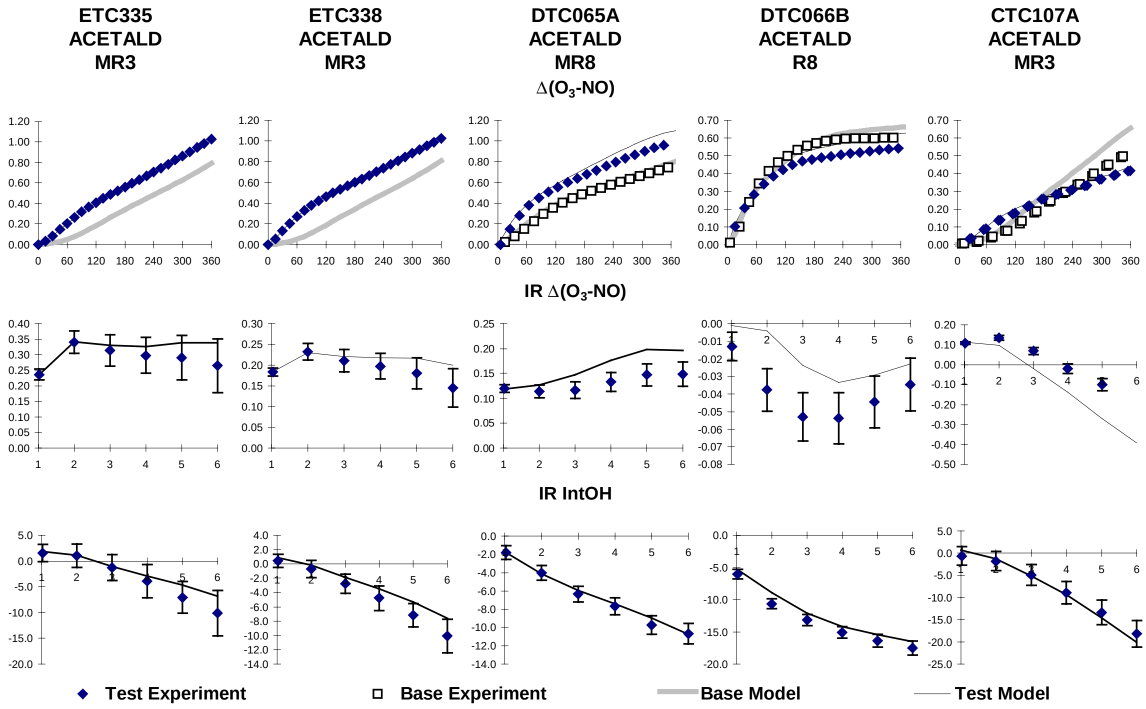


Figure B-9. Plots of experimental and calculated results of the incremental reactivity experiments with acetaldehyde.

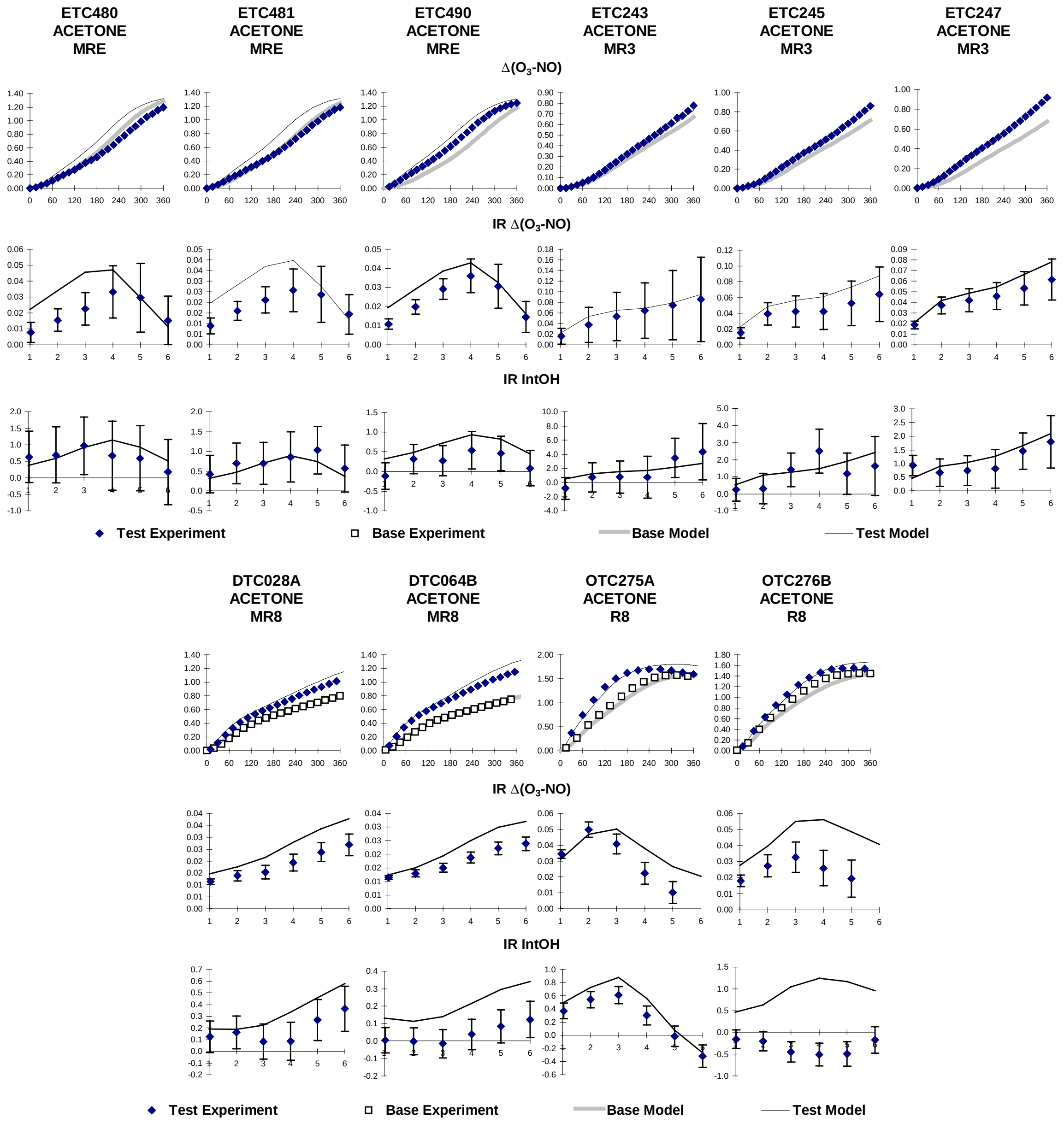


Figure B-10. Plots of experimental and calculated results of the incremental reactivity experiments with acetone.

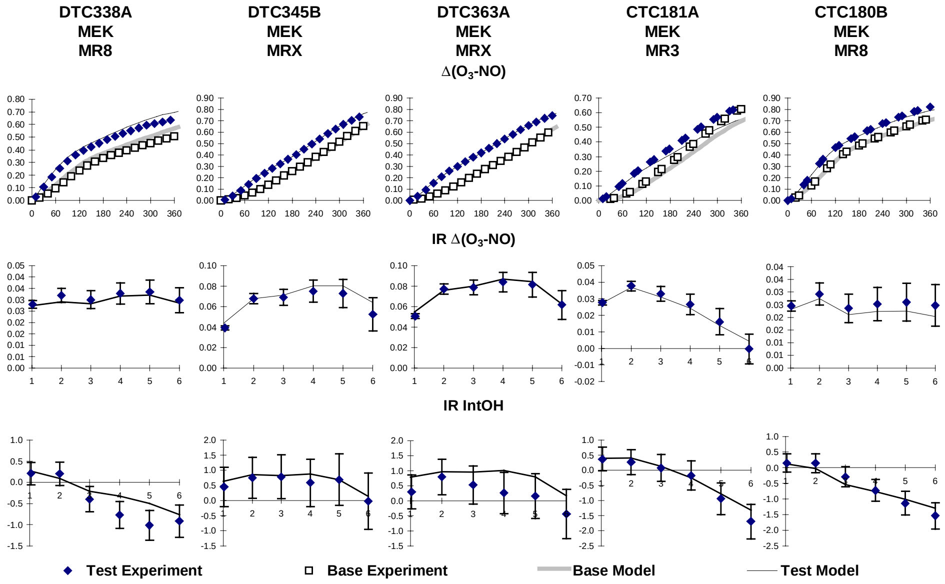


Figure B-11. Plots of experimental and calculated results of the incremental reactivity experiments with methyl ethyl ketone.

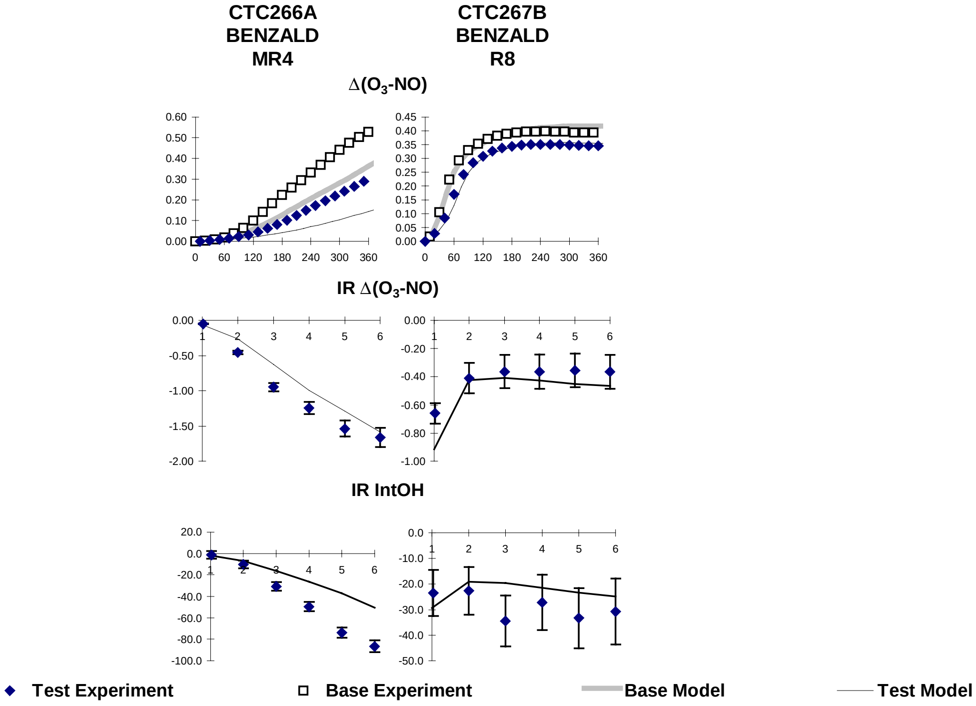


Figure B-12. Plots of experimental and calculated results of the incremental reactivity experiments with benzaldehyde.

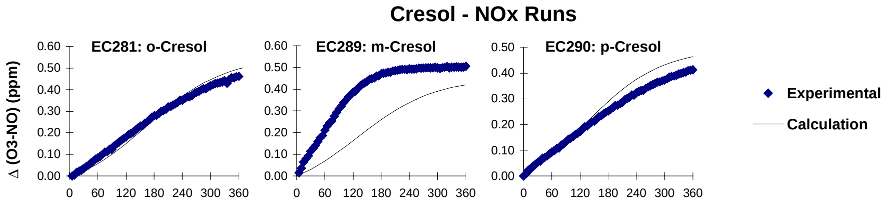


Figure B-13. Plots of experimental and calculated Δ([O$_3$]-[NO]) data for the cresol - NO$_x$ experiments.

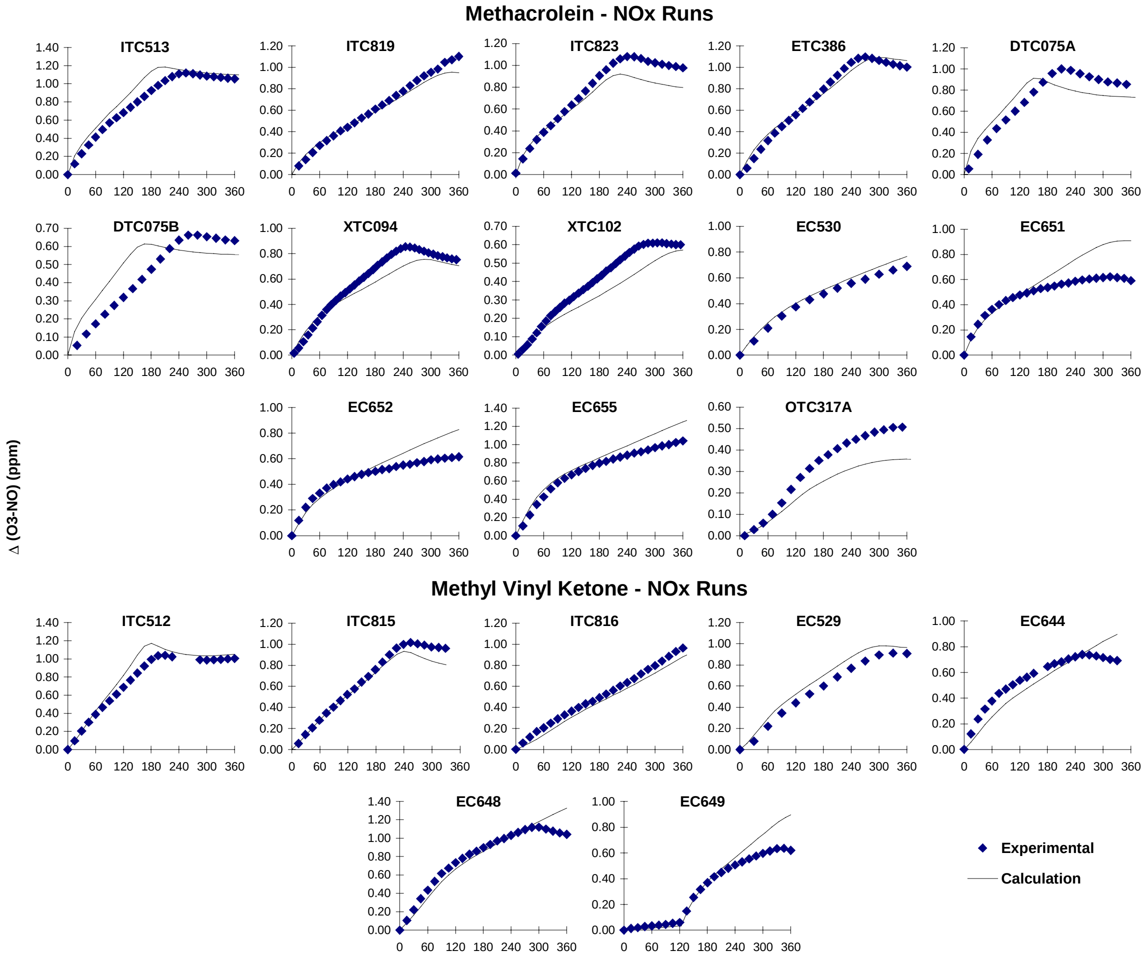


Figure B-14. Plots of experimental and calculated Δ([O$_3$]-[NO]) data for the methacrolein - NO$_x$ and the methyl vinyl ketone - NO$_x$ experiments.

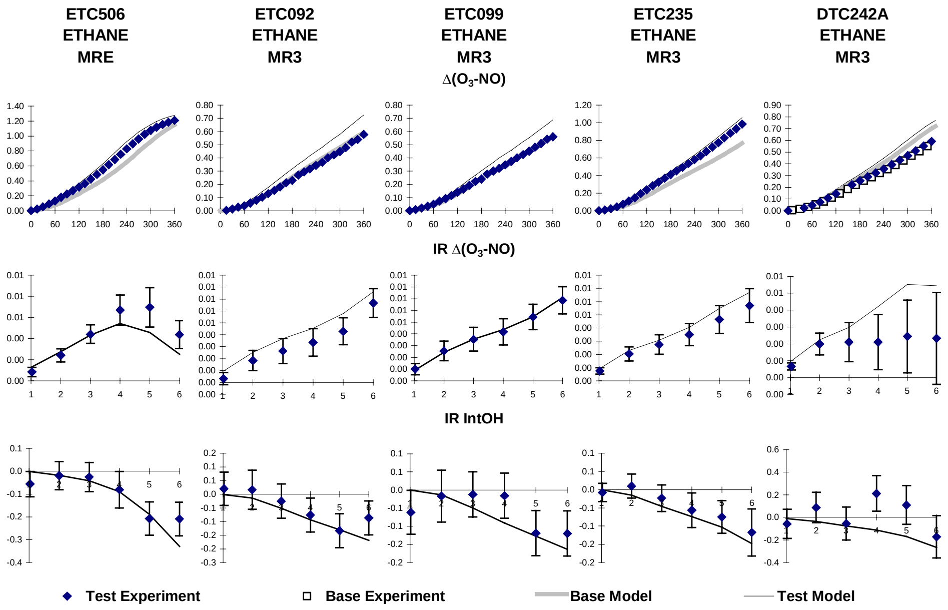


Figure B-15. Plots of experimental and calculated results of the incremental reactivity experiments with ethane

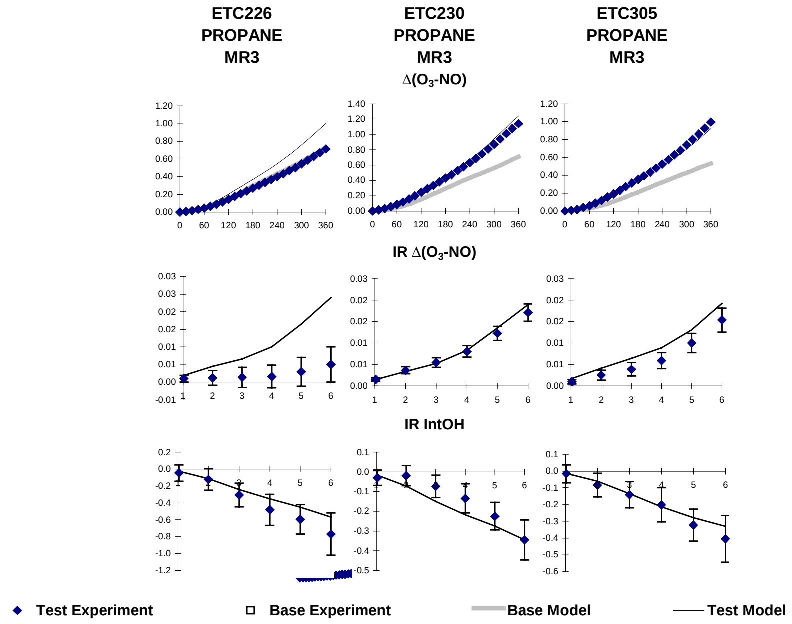


Figure B-16. Plots of experimental and calculated results of the incremental reactivity experiments with propane

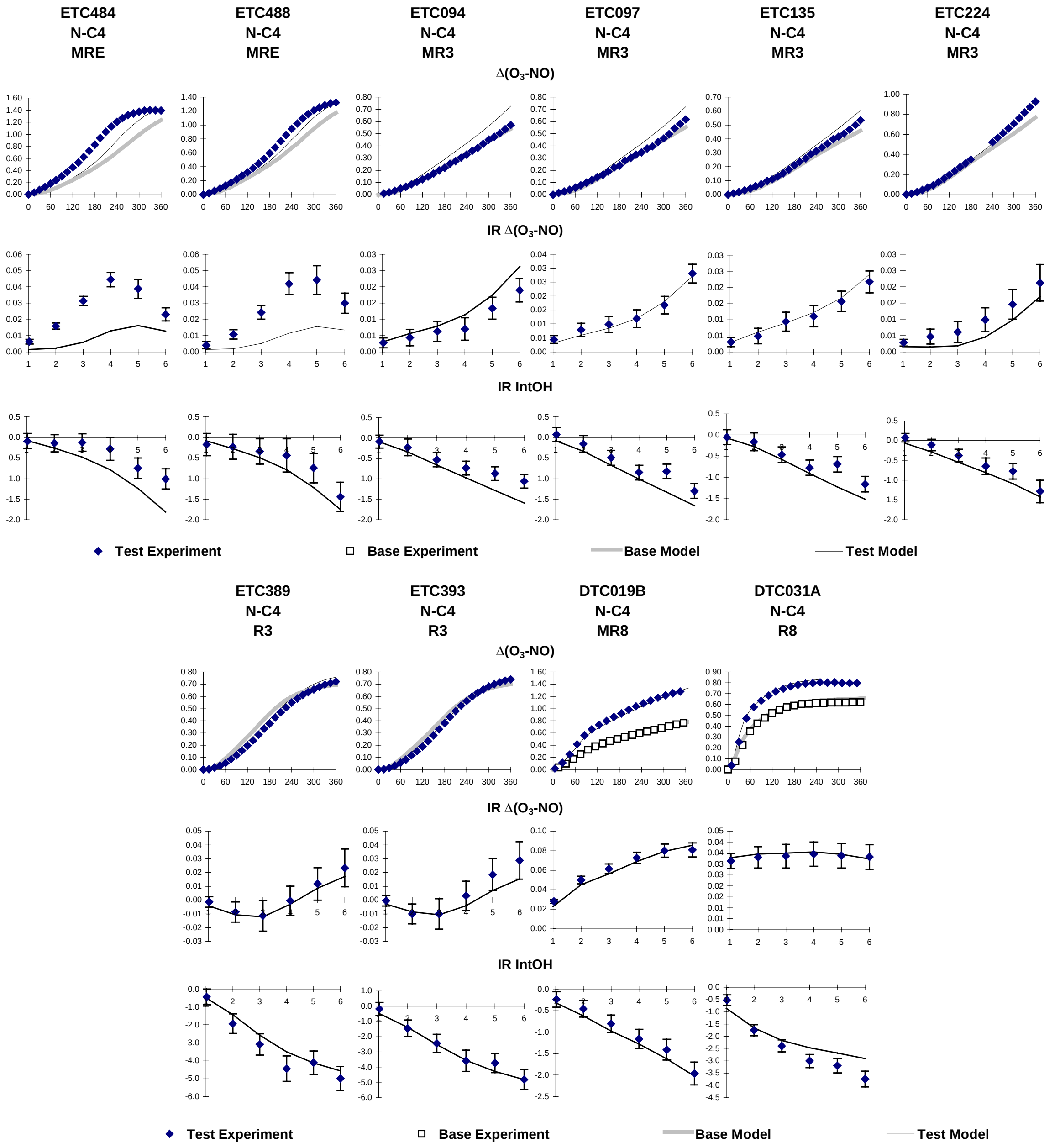


Figure B-17. Plots of experimental and calculated results of the incremental reactivity experiments with n-butane.

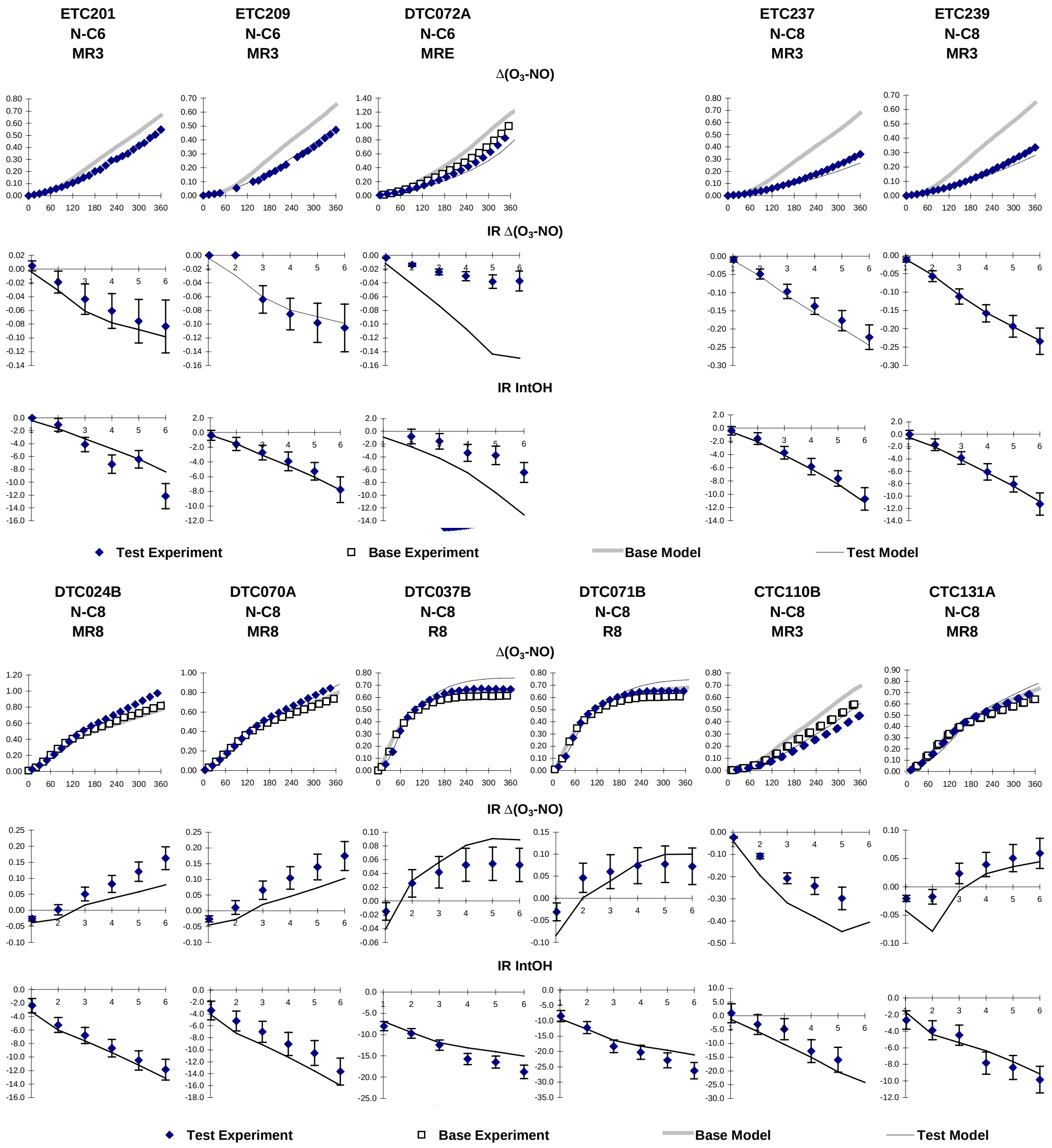


Figure B-18. Plots of experimental and calculated results of the incremental reactivity experiments with n-hexane and n-octane.

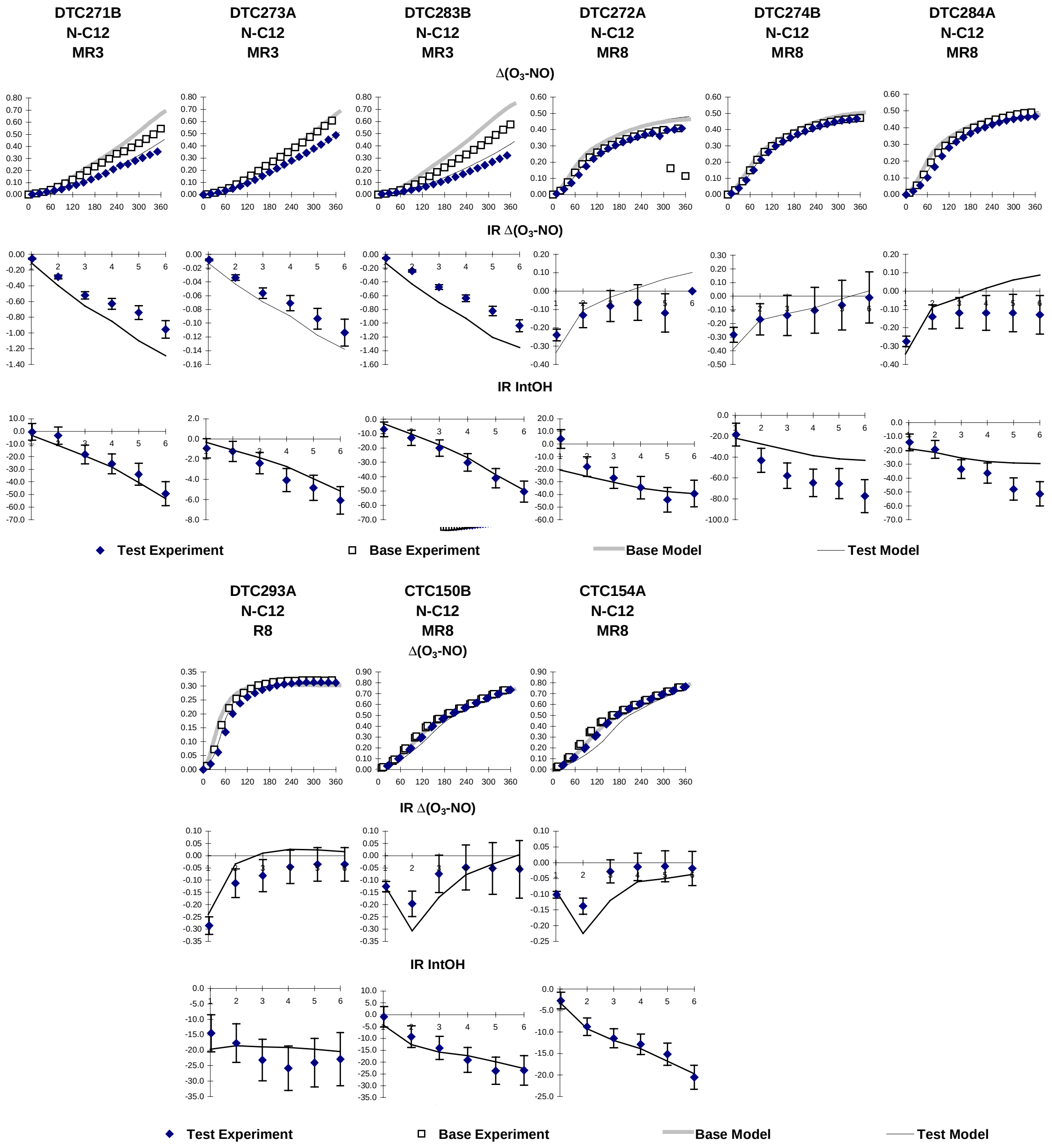


Figure B-19. Plots of experimental and calculated results of the incremental reactivity experiments with n-dodecane.

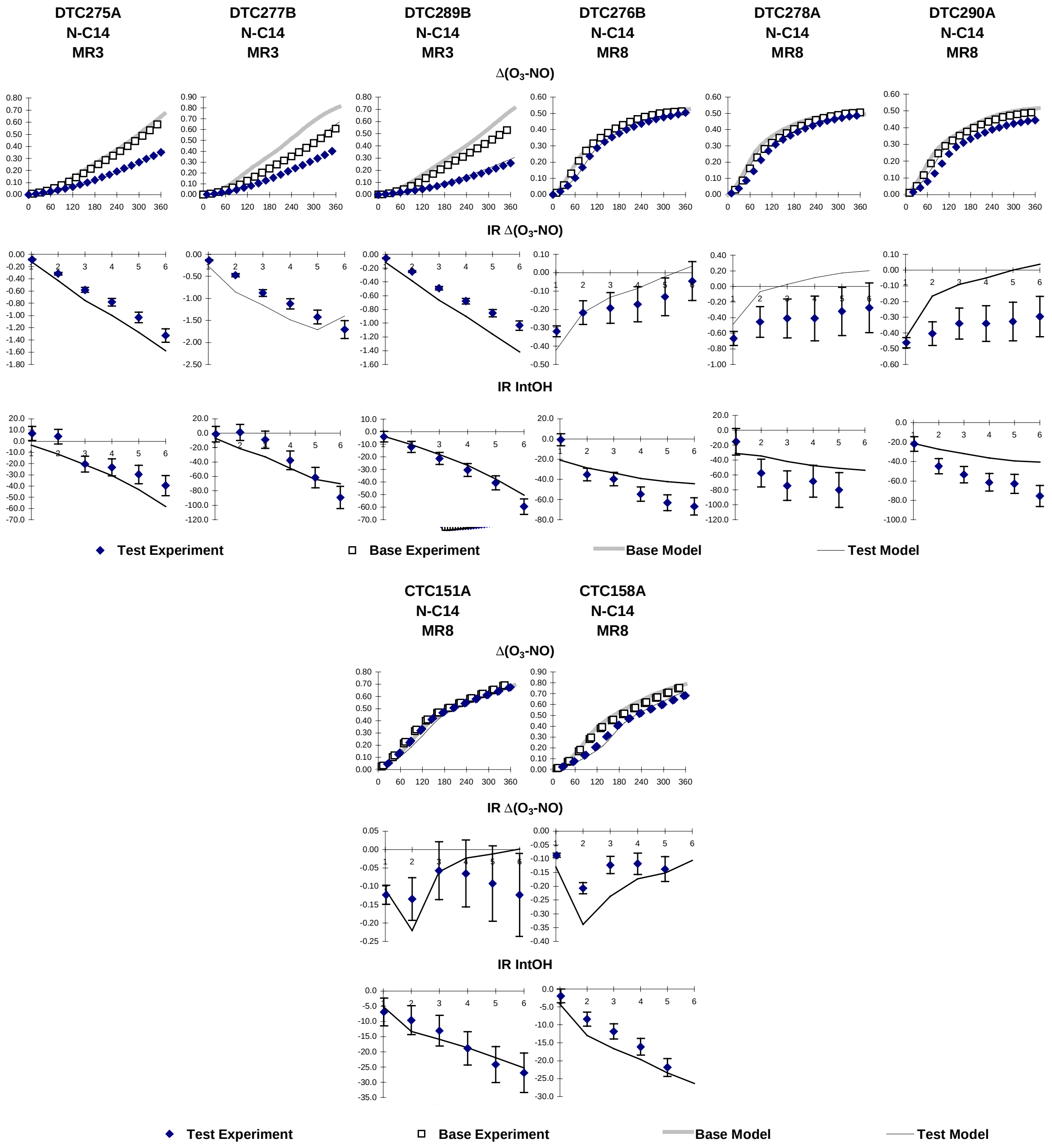


Figure B-20. Plots of experimental and calculated results of the incremental reactivity experiments with n-tetradecane.

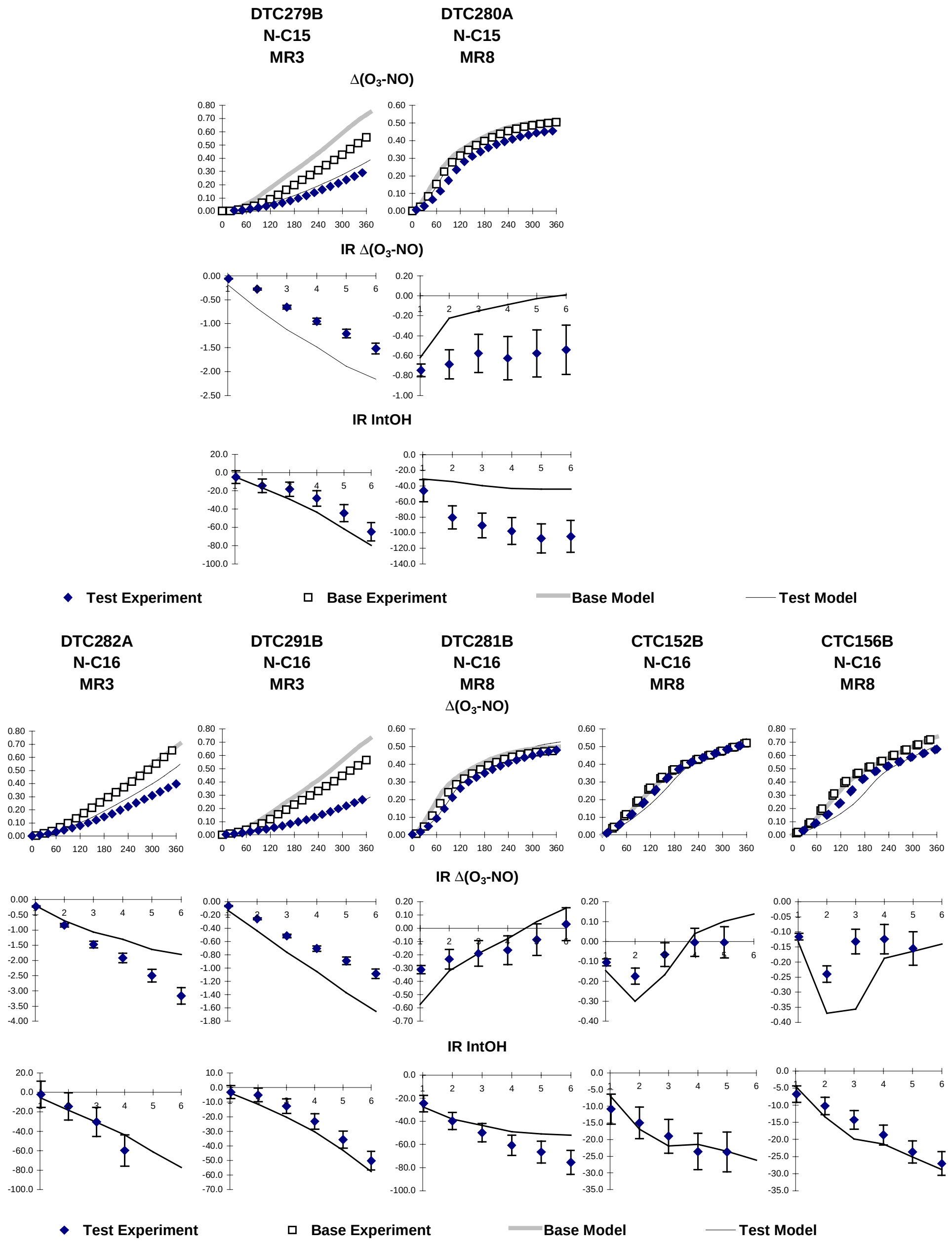


Figure B-21. Plots of experimental and calculated results of the incremental reactivity experiments with n-pentadecane and n-hexadecane.

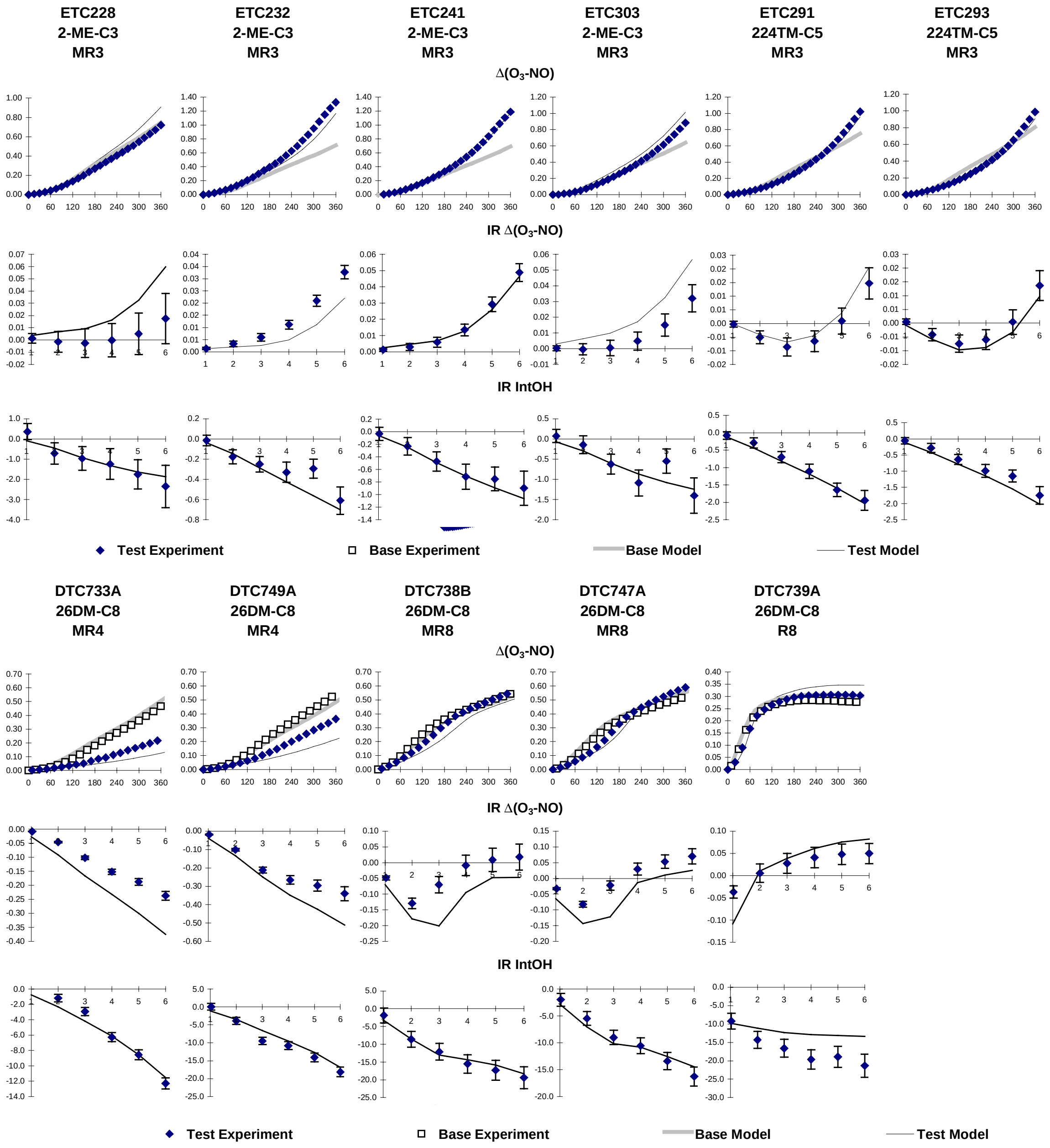


Figure B-22. Plots of experimental and calculated results of the incremental reactivity experiments with 2-methyl propene, 2,2,4-trimethyl butane and 2,5-dimethyl octane.

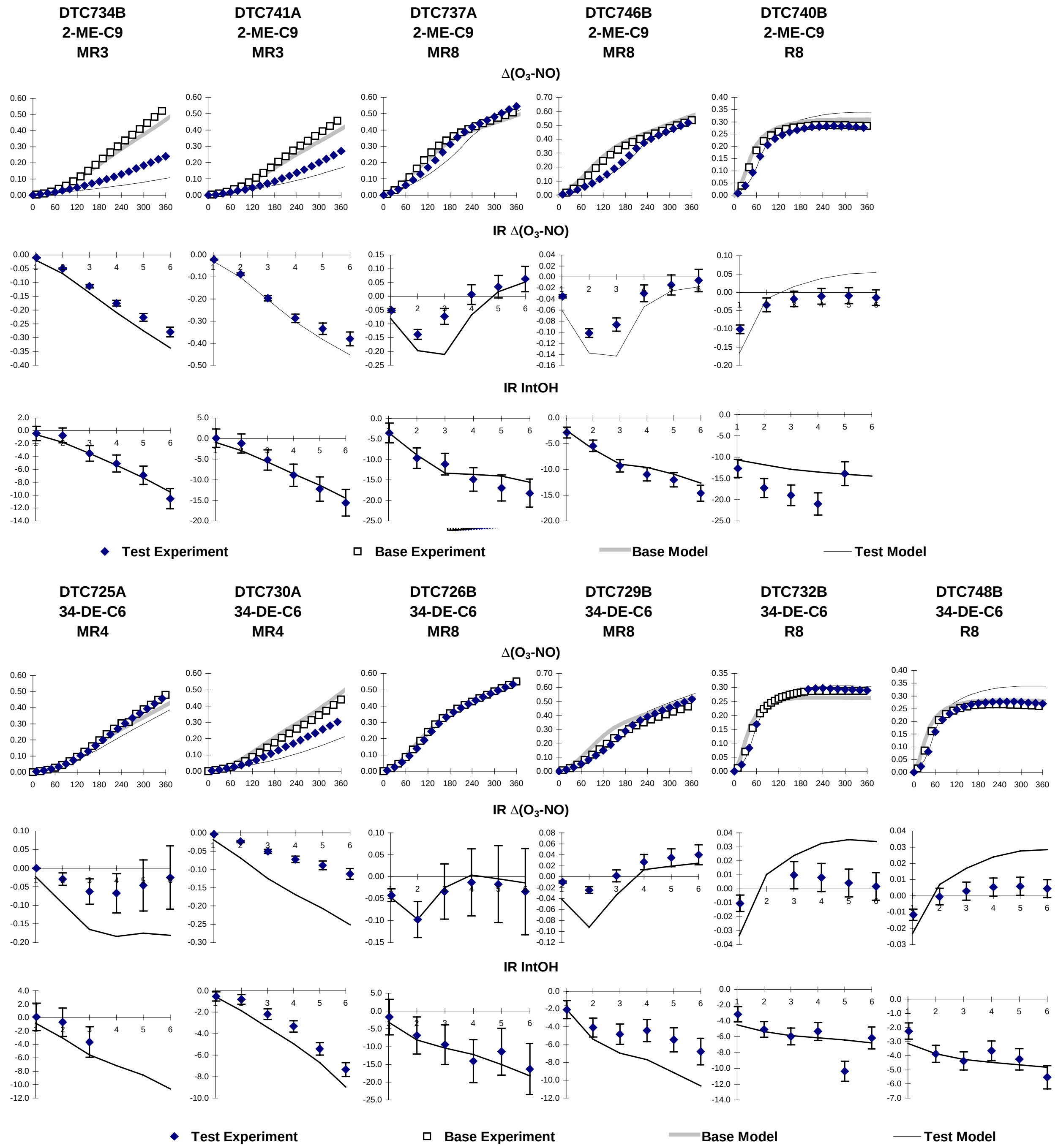


Figure B-23. Plots of experimental and calculated results of the incremental reactivity experiments with 2-methyl nonane and 3,4-diethyl hexane.

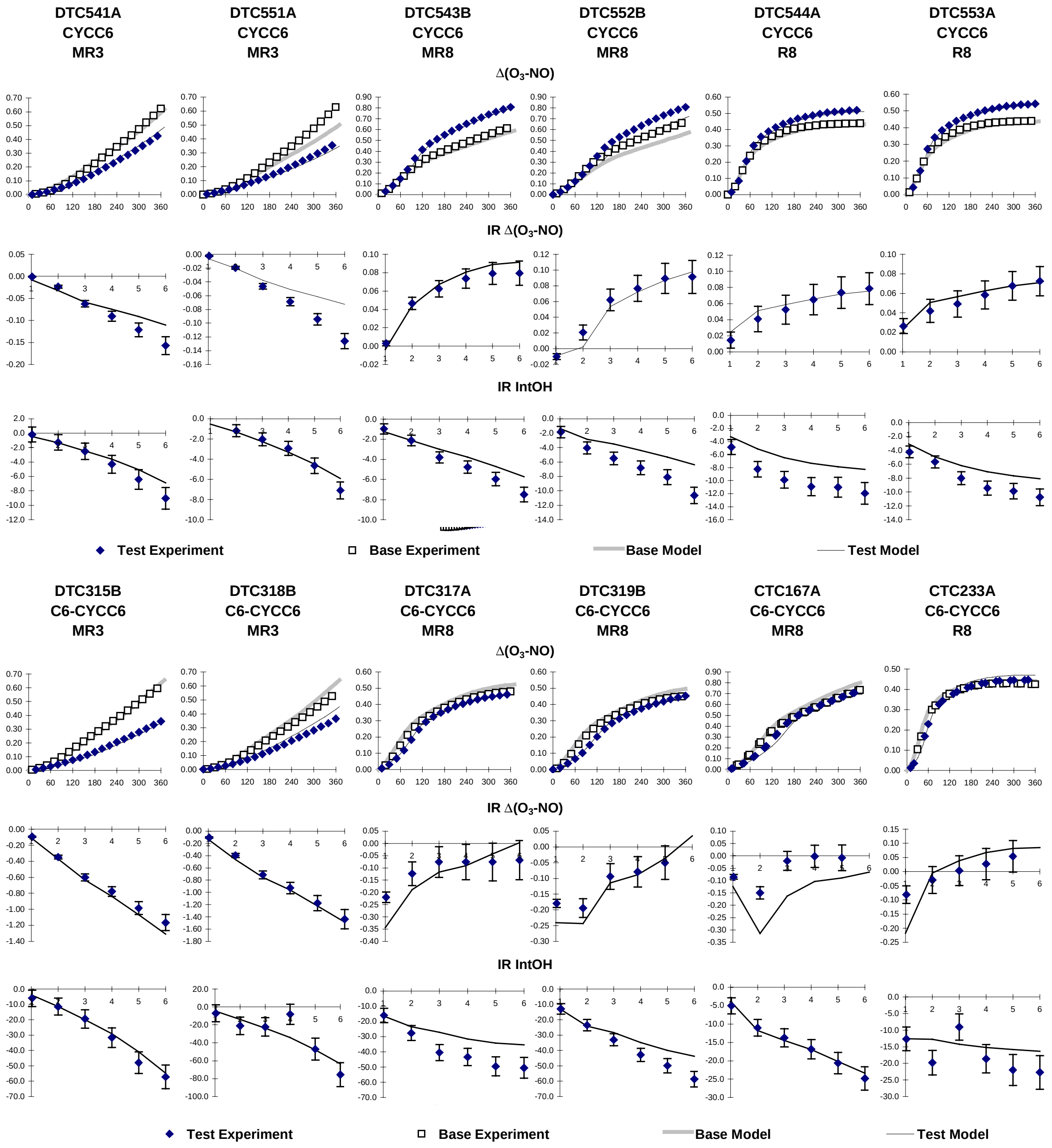


Figure B-24. Plots of experimental and calculated results of the incremental reactivity experiments with cyclohexane and n-hexyl cyclohexane.

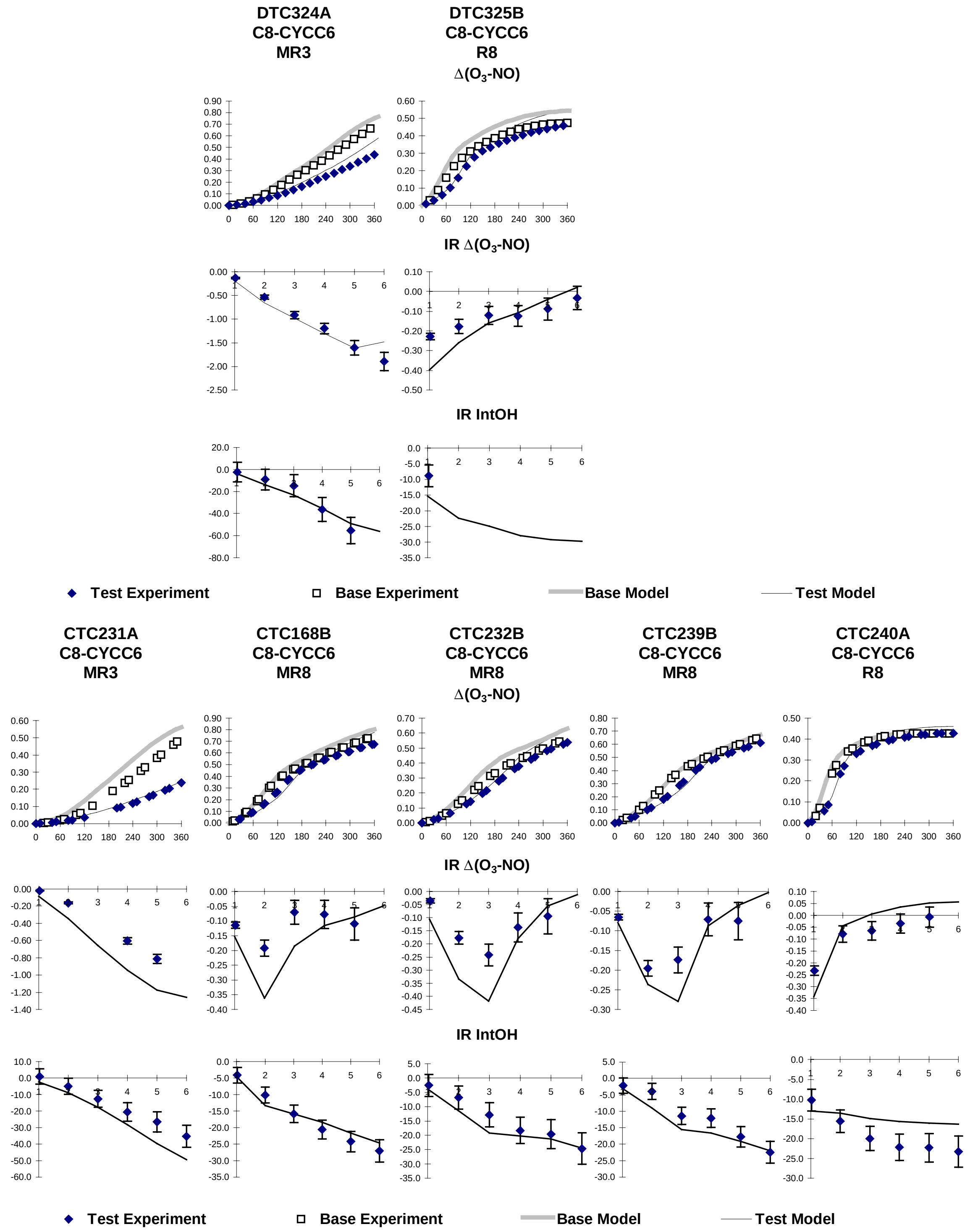


Figure B-25. Plots of experimental and calculated results of the incremental reactivity experiments with n-octyl cyclohexane.

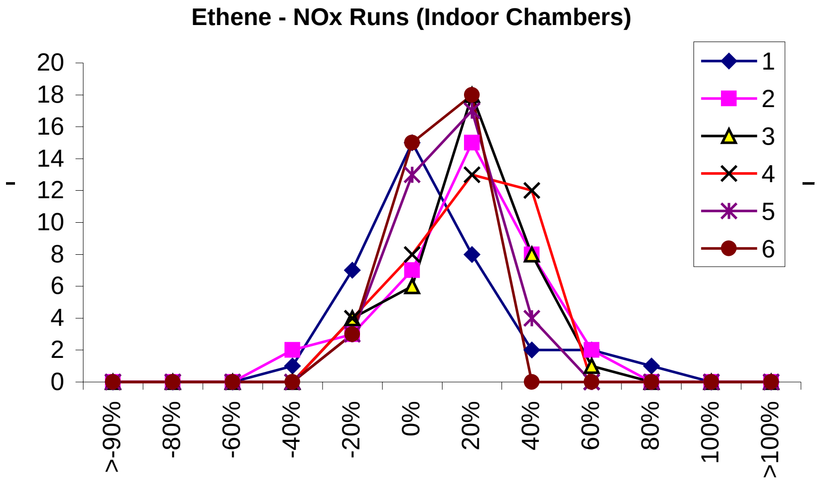


Figure B-26. Distribution plots of percentage errors of fits of calculated to experimental hourly Δ([O_3]-[NO]) data for the ethene - NO_x runs carried out in indoor chambers.

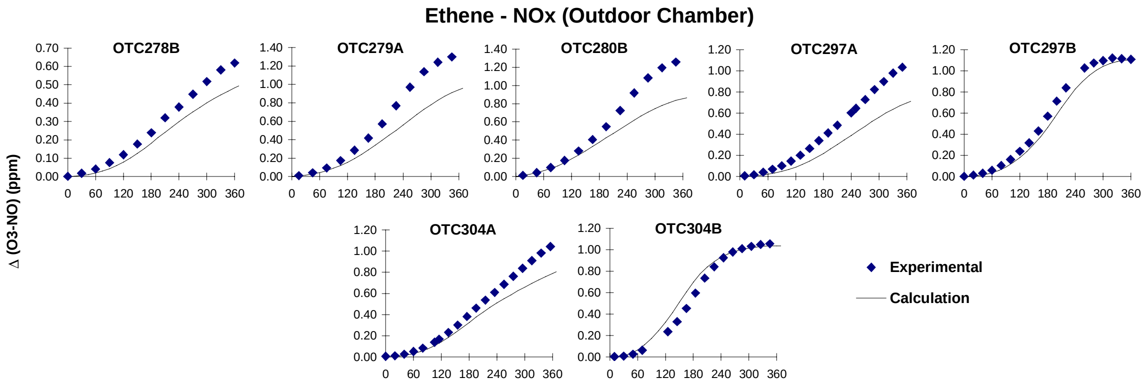


Figure B-27. Plots of experimental and calculated Δ([O_3]-[NO]) data for the ethene - NO_x runs carried out in the SAPRC outdoor chamber (OTC).

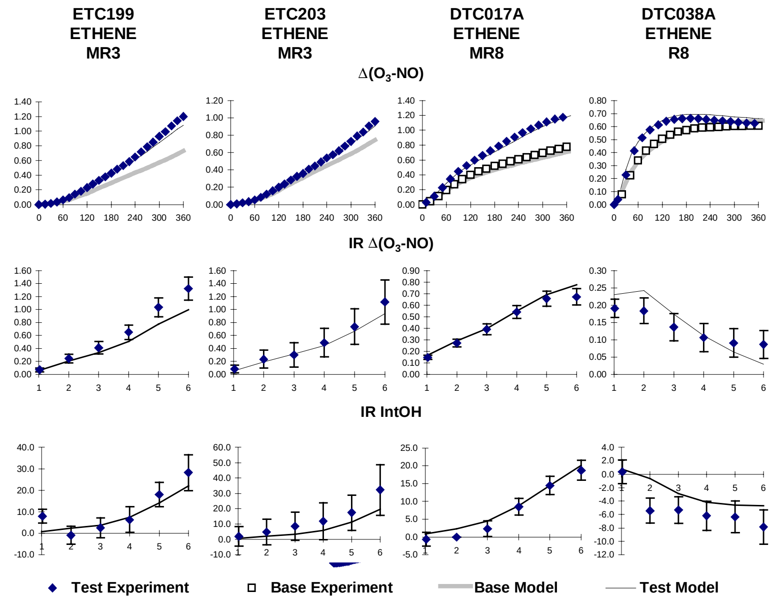


Figure B-28. Plots of experimental and calculated results of the incremental reactivity experiments with ethene.

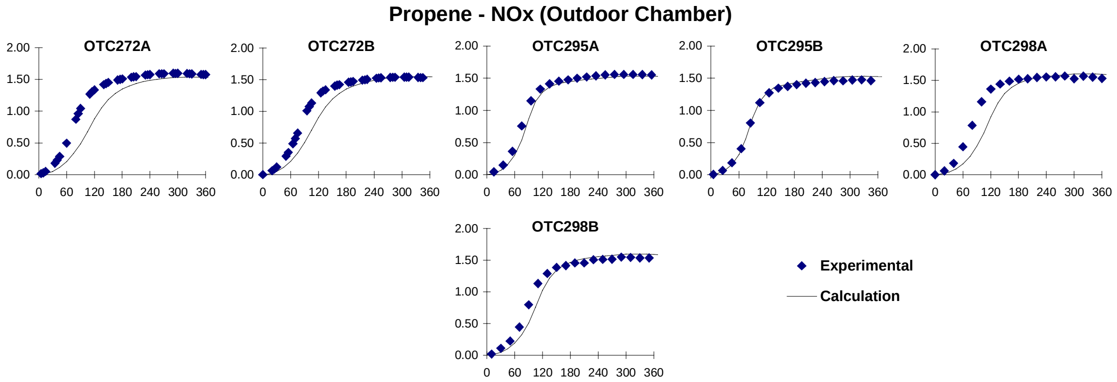


Figure B-29. Plots of experimental and calculated $\Delta([O_3]-[NO])$ data for the propene - NO_x runs using the SAPRC outdoor chamber.

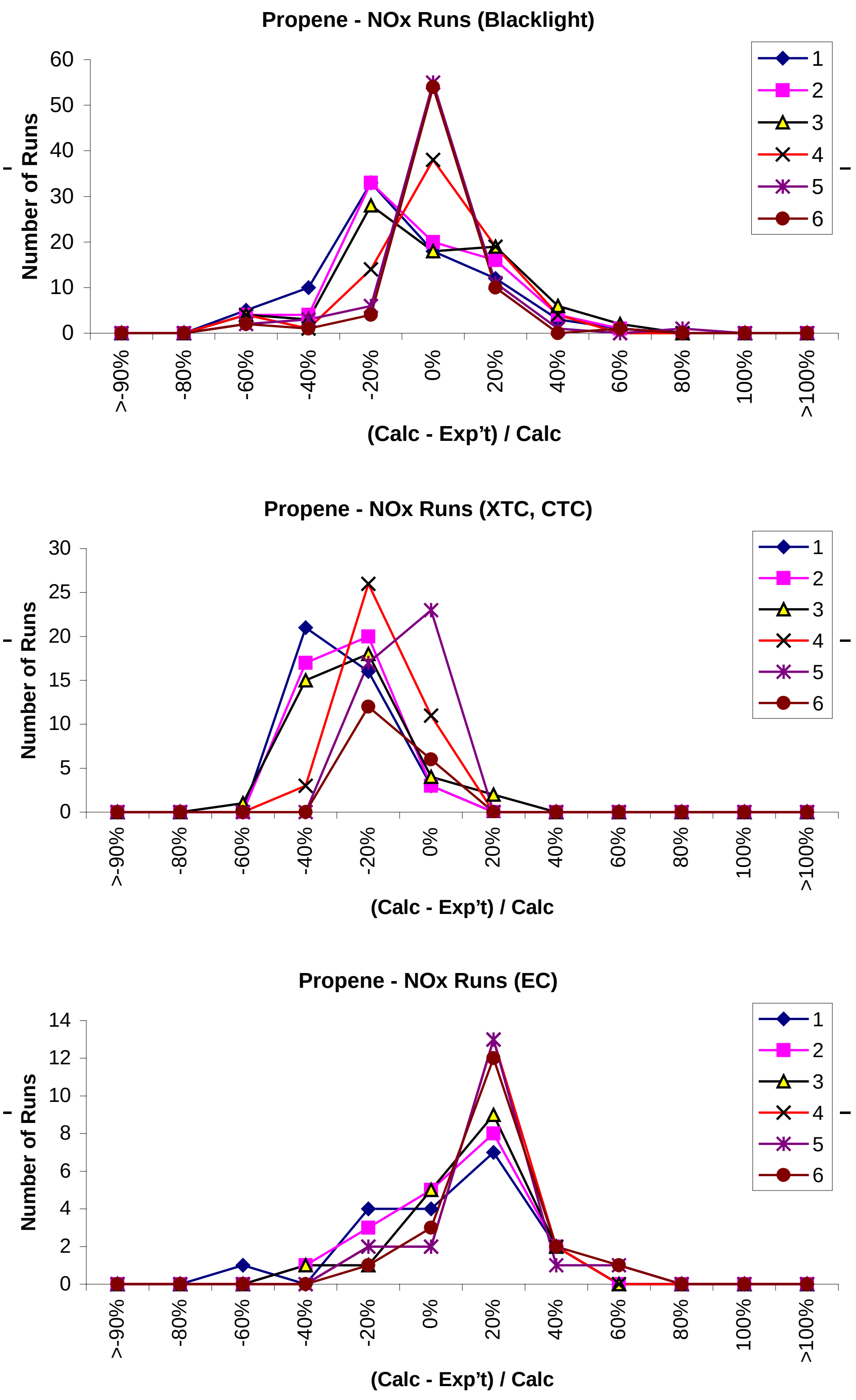


Figure B-30. Distribution plots of percentage errors of fits of calculated to experimental hourly $\Delta([O_3]-[NO])$ data for the propene - NO_x runs carried out using various chambers.

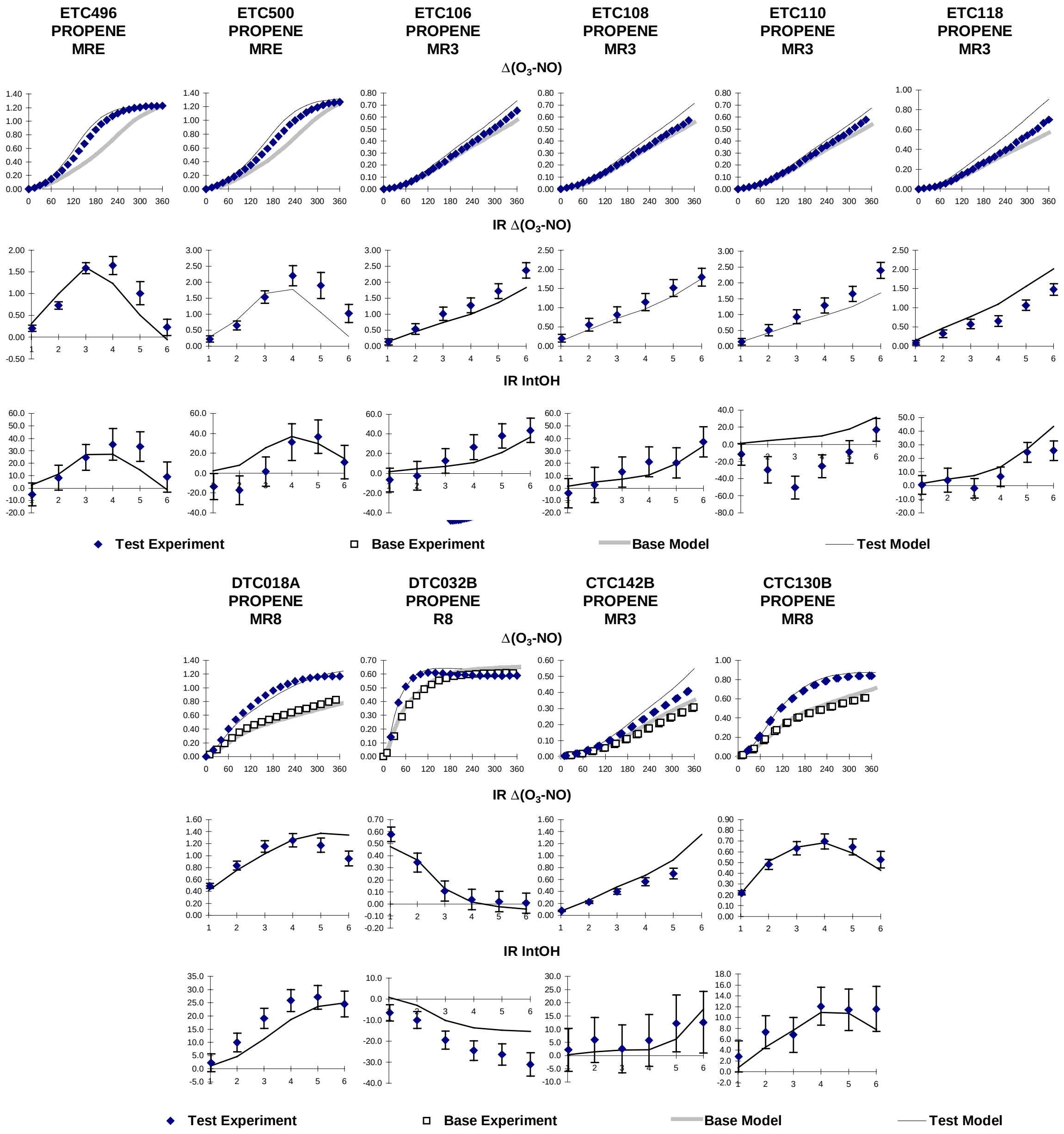


Figure B-31. Plots of experimental and calculated results of the incremental reactivity experiments with propene.

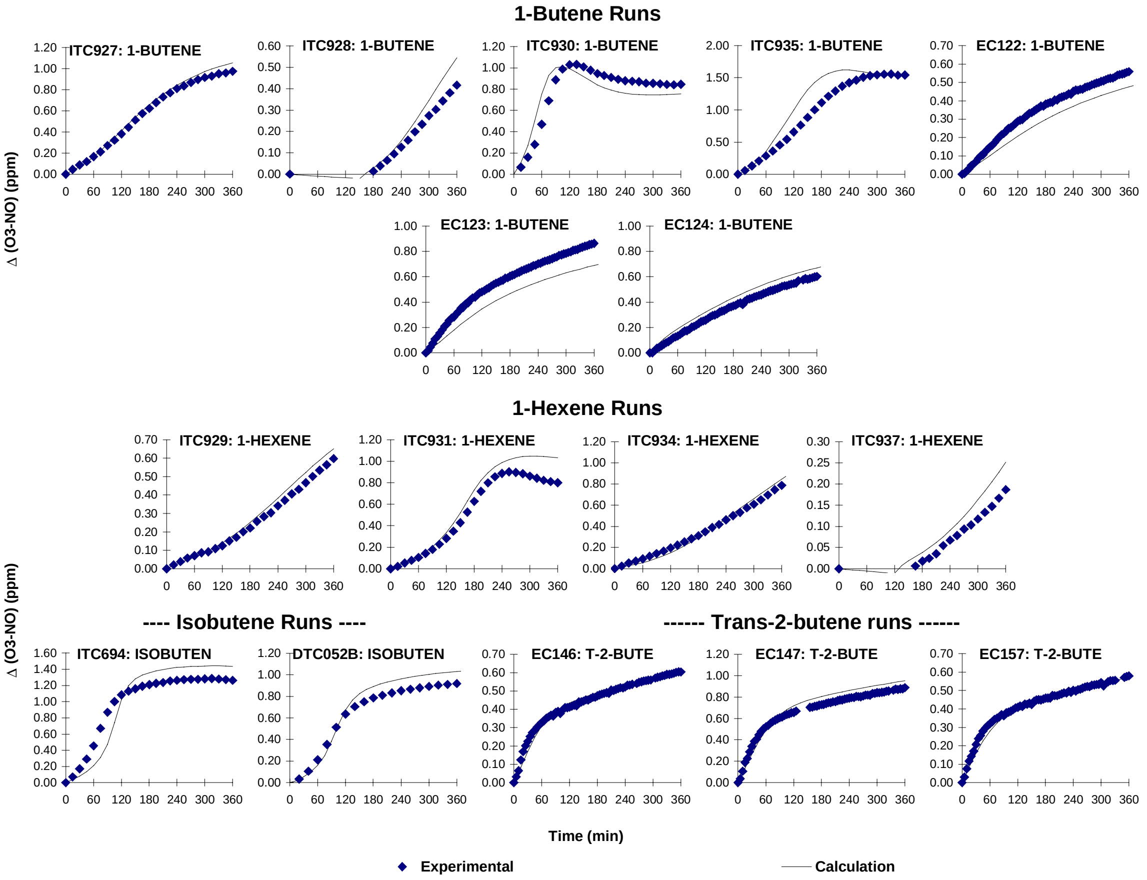


Figure B-32. Plots of experimental and calculated $\Delta([O_3]-[NO])$ data for the 1-butene, 1-hexene, isobutene, and trans-2-butene - NO_x experiments.

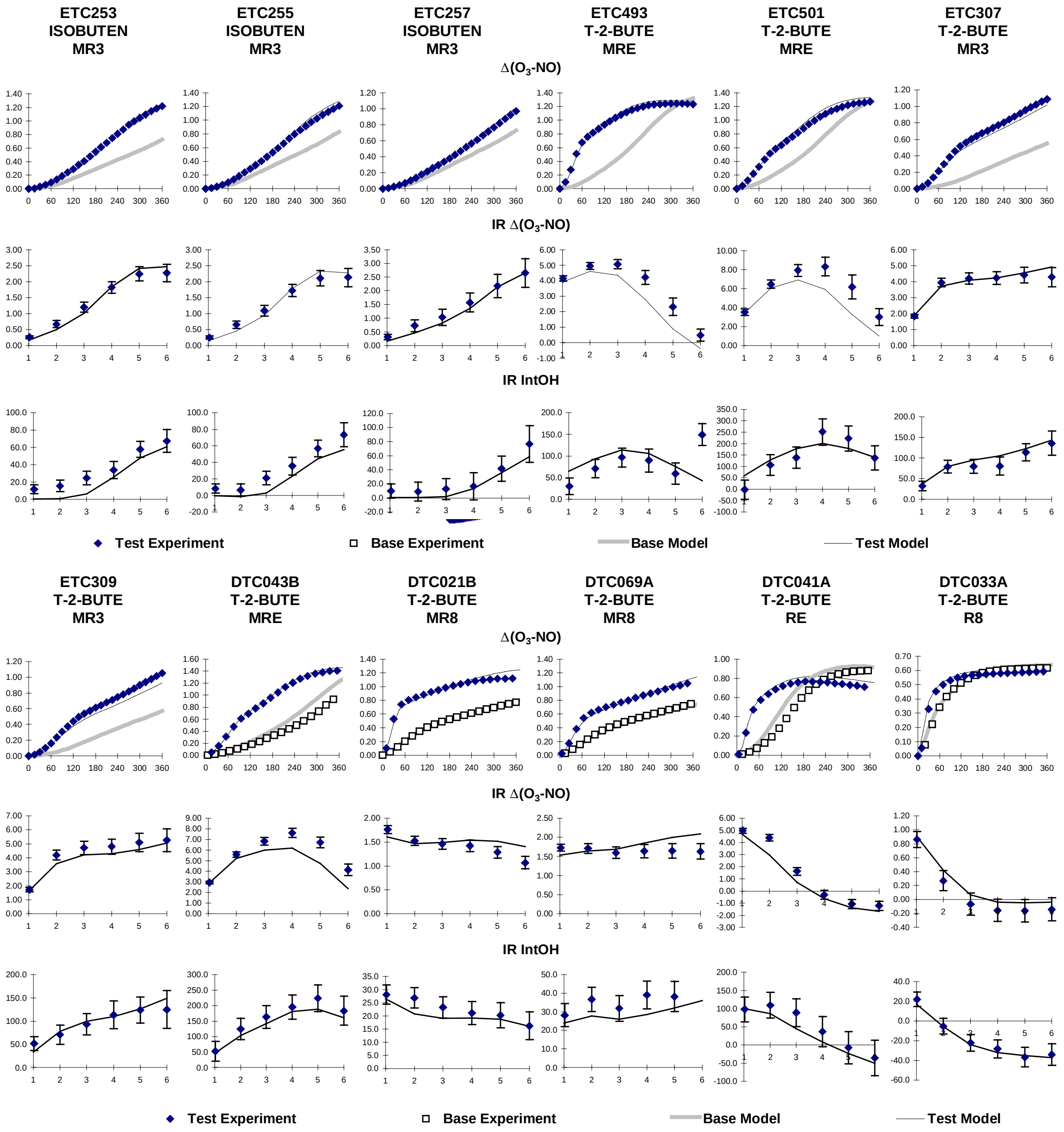


Figure B-33. Plots of experimental and calculated results of the incremental reactivity experiments with isobutene and trans-2-butene.

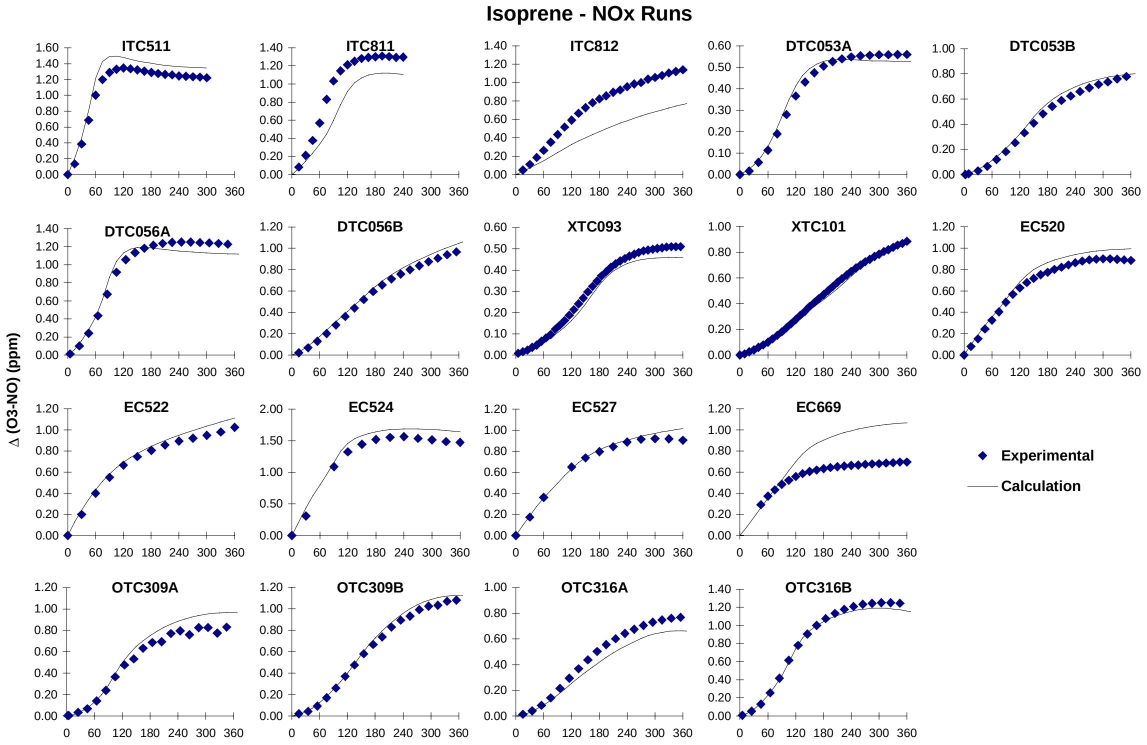


Figure B-34. Plots of experimental and calculated Δ([O_3]-[NO]) data for the isoprene - NO_x experiments.

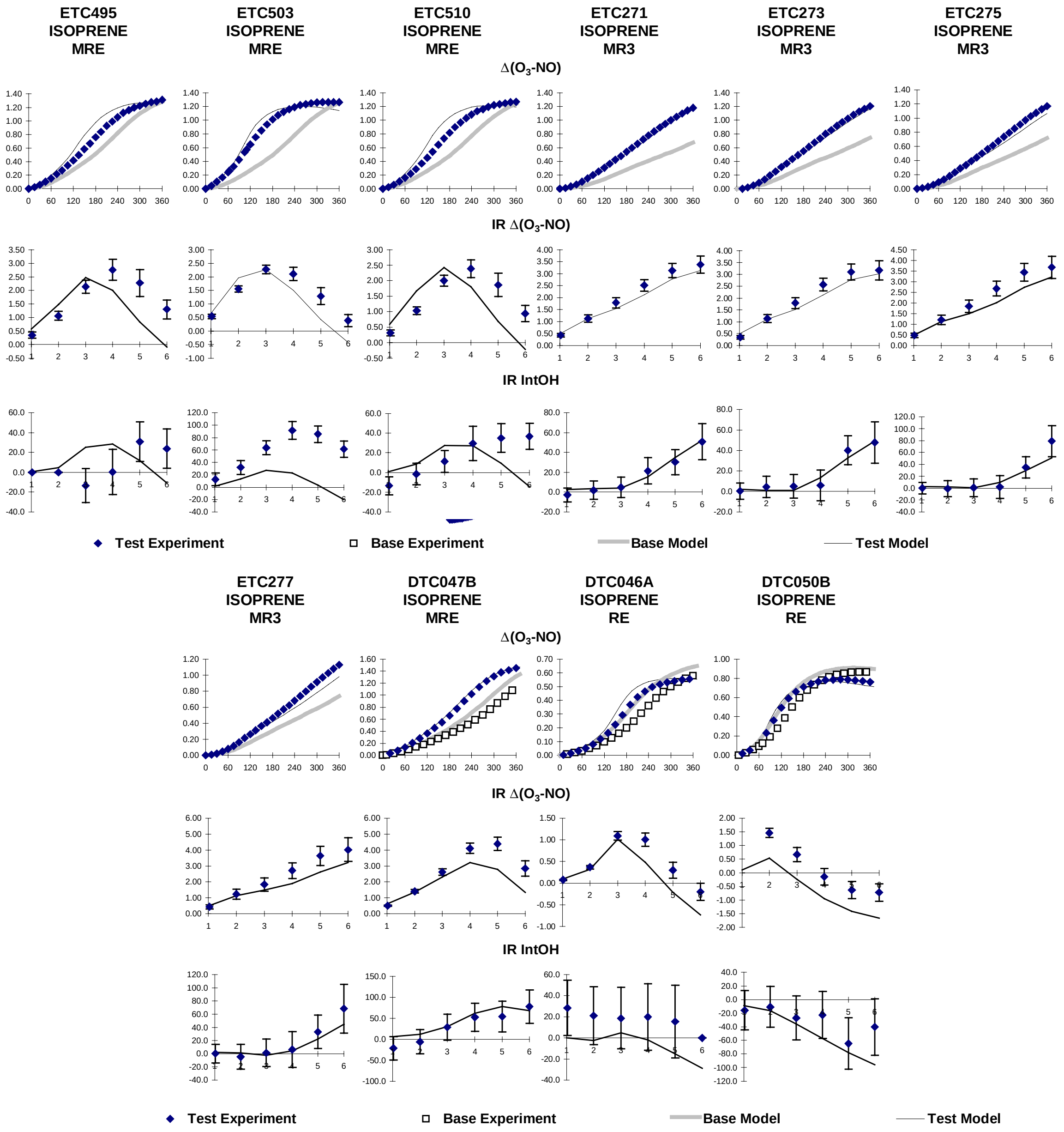


Figure B-35. Plots of experimental and calculated results of the incremental reactivity experiments with isoprene.

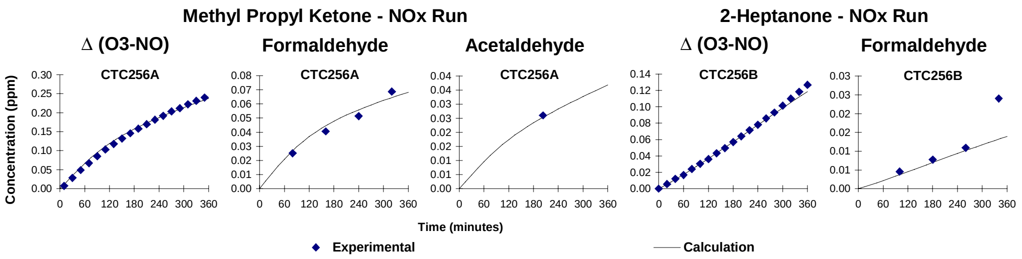


Figure B-36. Plots of experimental and calculated $\Delta([O_3]-[NO])$ data for the methyl propyl ketone - NO_x and 2-heptanone - NO_x experiments.

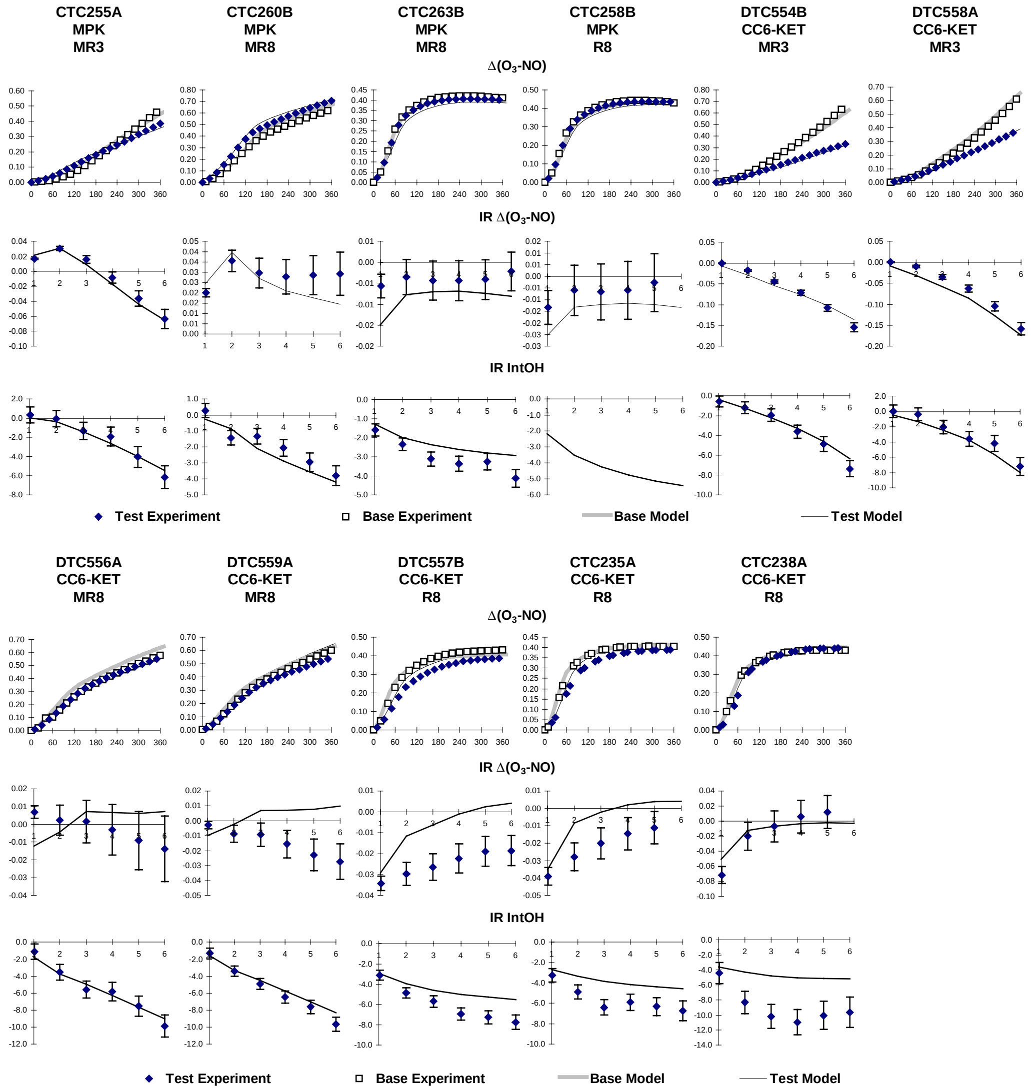


Figure B-37. Plots of experimental and calculated results of the incremental reactivity experiments with methyl propyl ketone and cyclohexanone.

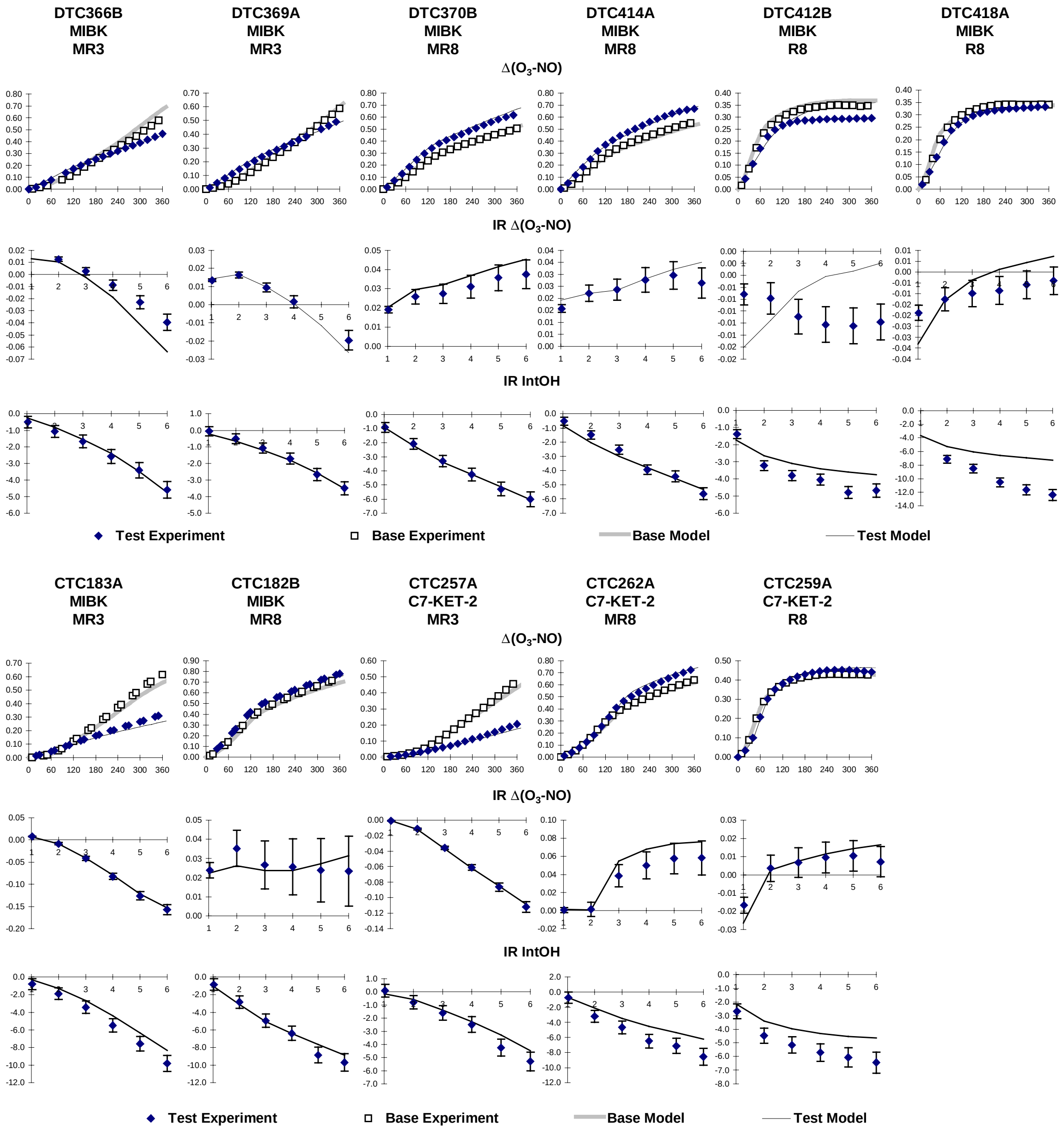


Figure B-38. Plots of experimental and calculated results of the incremental reactivity experiments with methyl isobutyl ketone and 2-heptanone.

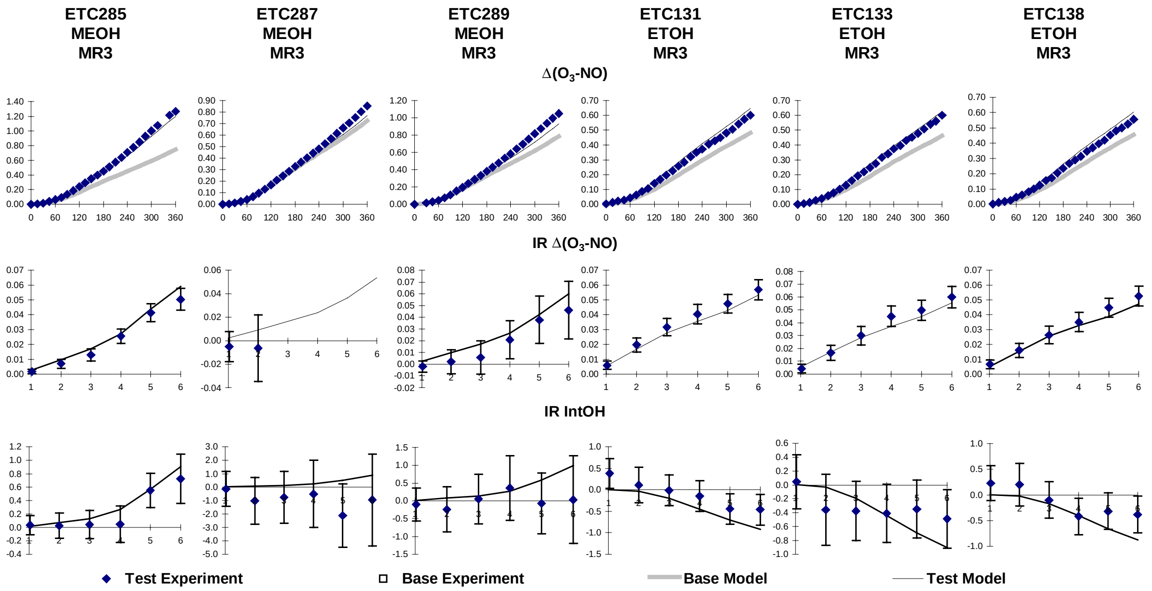


Figure B-39. Plots of experimental and calculated results of the incremental reactivity experiments with methanol and ethanol.

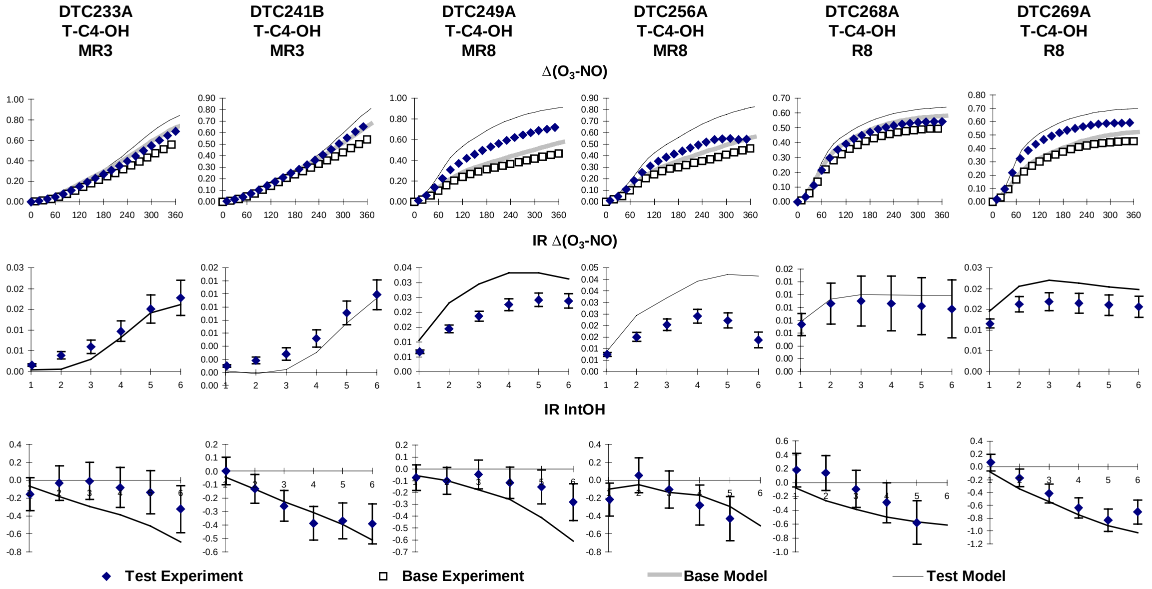


Figure B-40. Plots of experimental and calculated results of the incremental reactivity experiments with t-butyl alcohol. (Run DTC259A, whose results are very similar to those for run DTC269A, is not shown.)

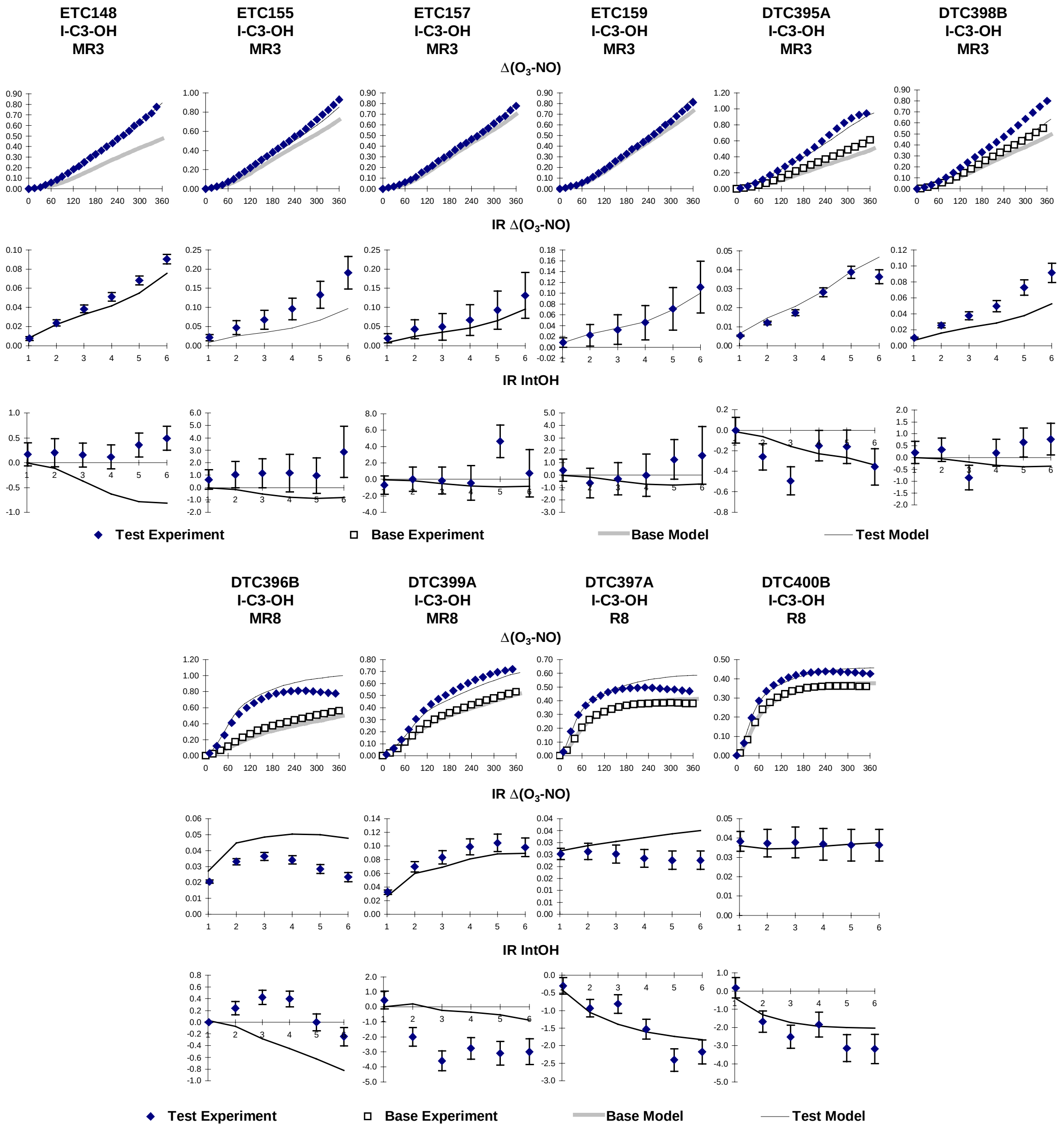


Figure B-41. Plots of experimental and calculated results of the incremental reactivity experiments with isopropyl alcohol.

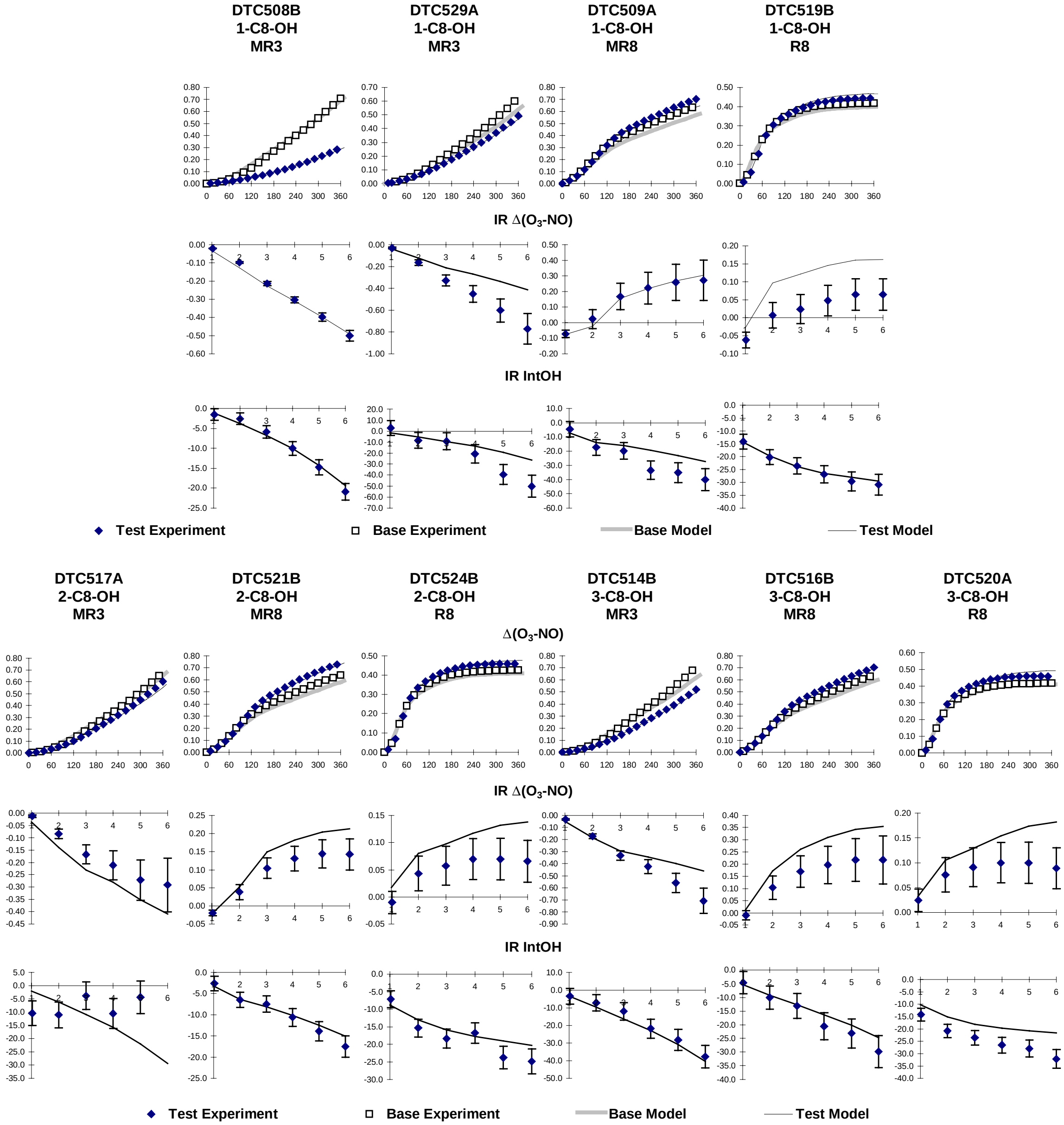


Figure B-42. Plots of experimental and calculated results of the incremental reactivity experiments with 1-, 2-, and 3-octanols.

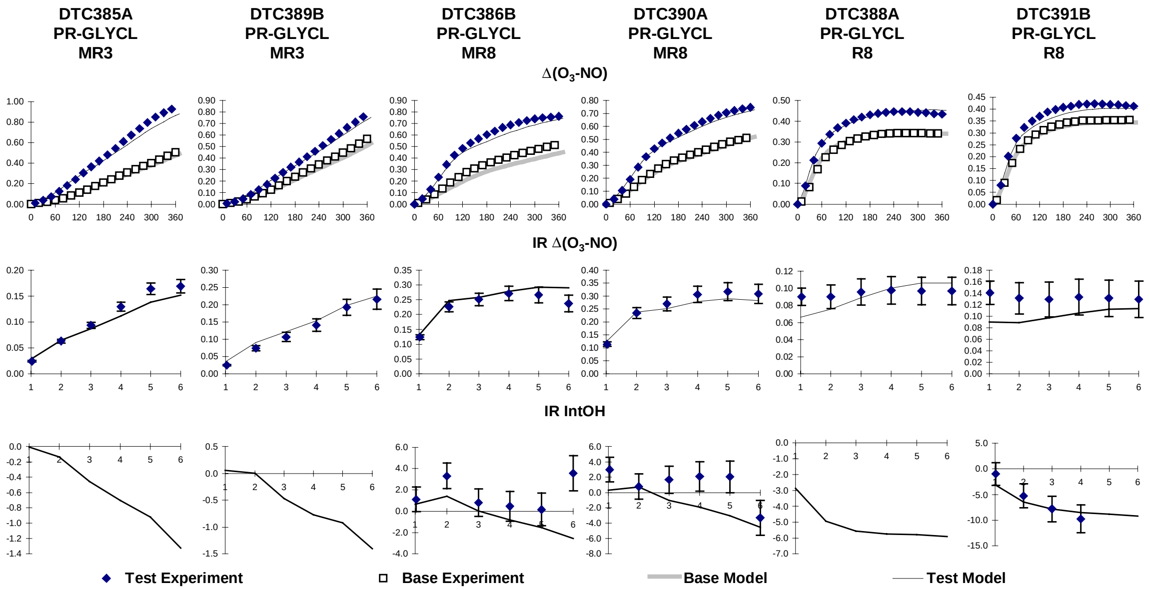


Figure B-43. Plots of experimental and calculated results of the incremental reactivity experiments with propylene glycol.

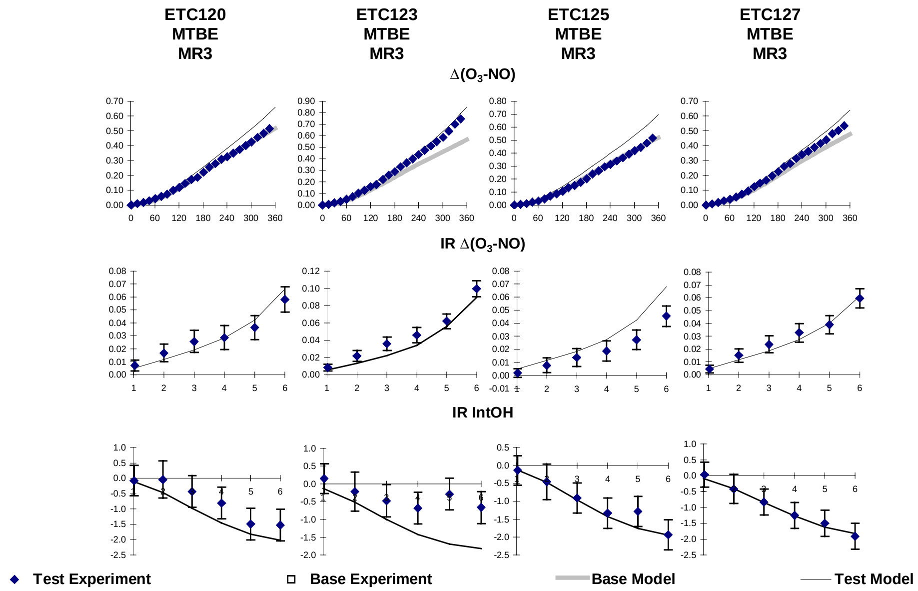


Figure B-44. Plots of experimental and calculated results of the incremental reactivity experiments with methyl t-butyl ether.

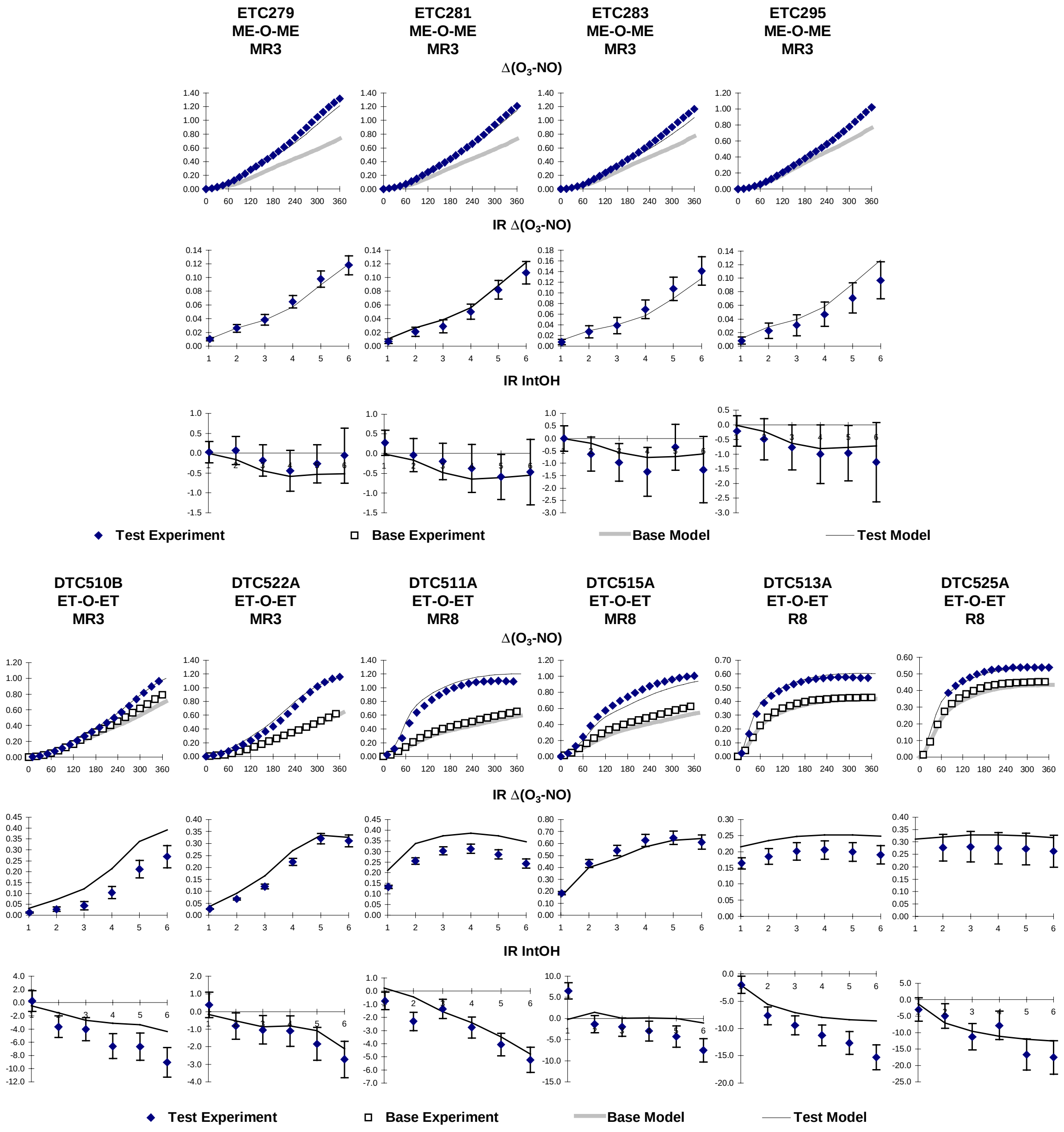


Figure B-45. Plots of experimental and calculated results of the incremental reactivity experiments with dimethyl ether and diethyl ether.

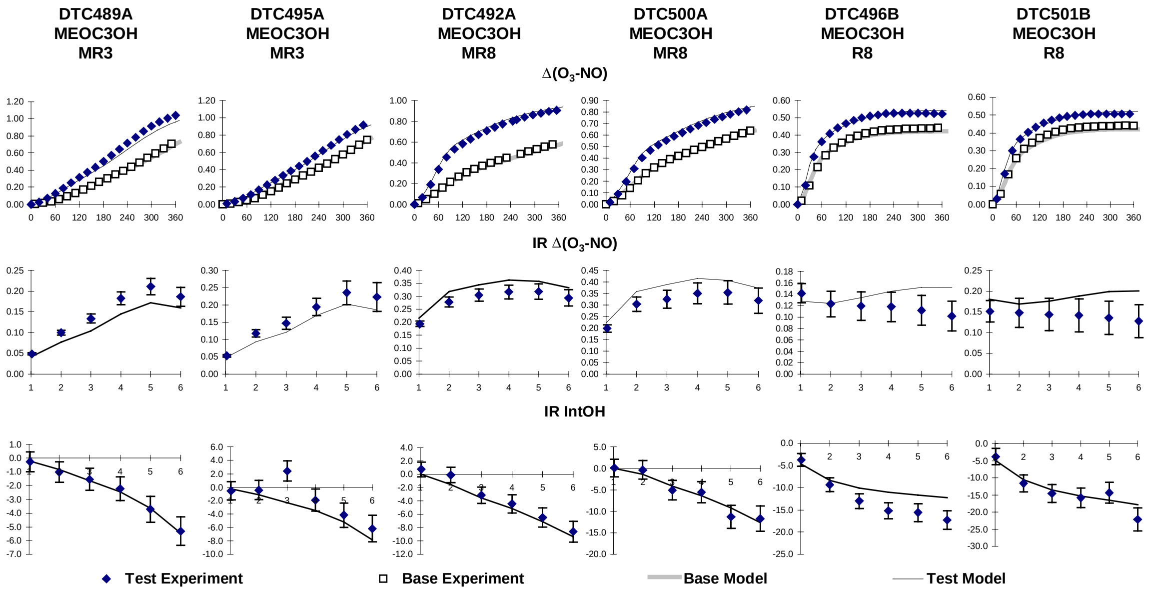


Figure B-46. Plots of experimental and calculated results of the incremental reactivity experiments with 1-Methoxy-2-Propanol

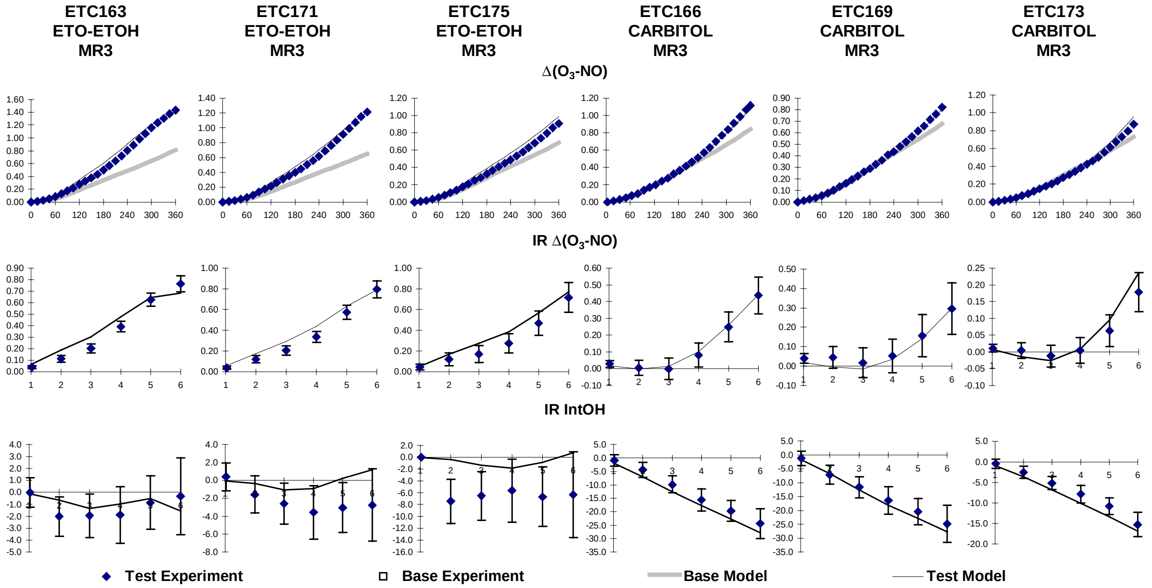


Figure B-47. Plots of experimental and calculated results of the incremental reactivity experiments with ethoxy ethanol and carbitol.

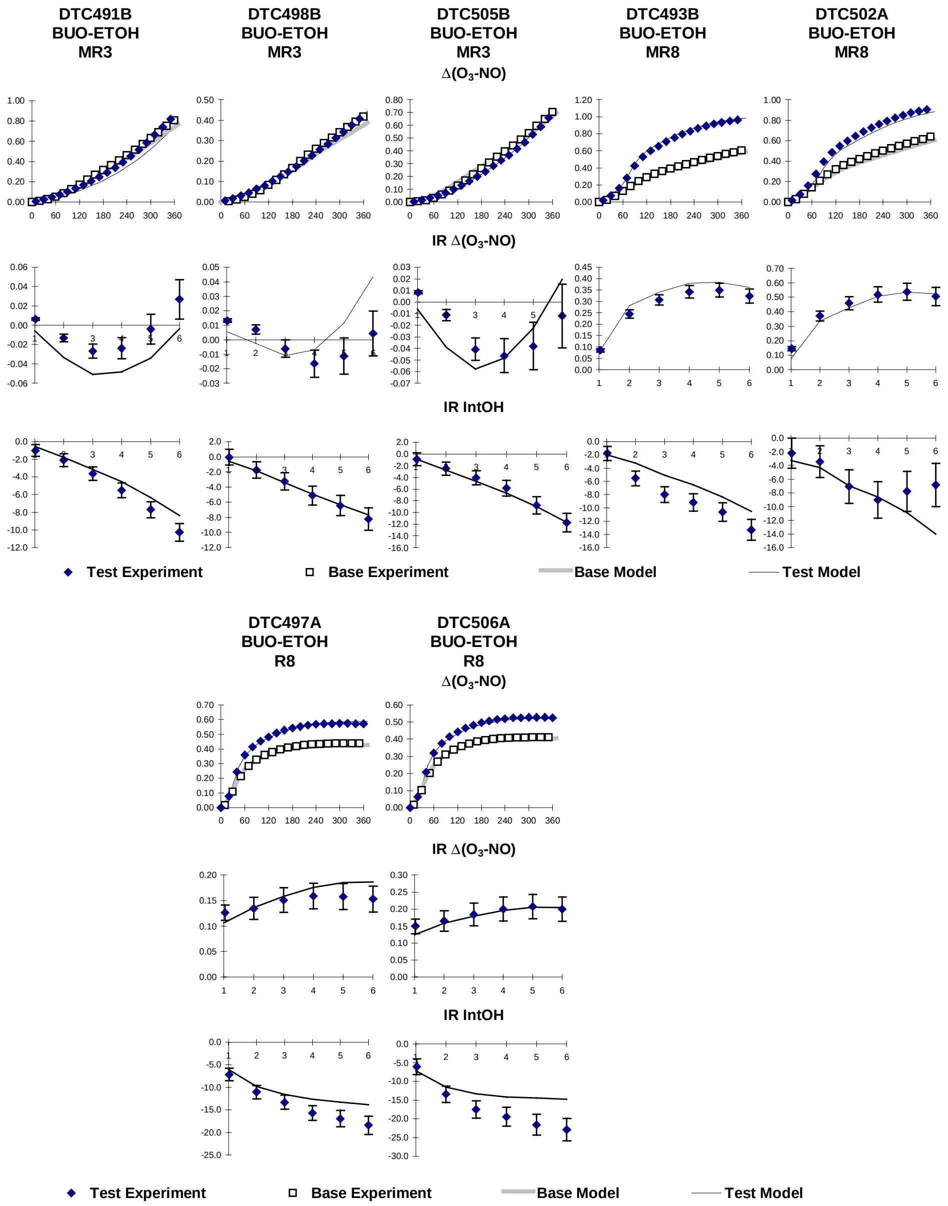


Figure B-48. Plots of experimental and calculated results of the incremental reactivity experiments with butoxy ethanol.

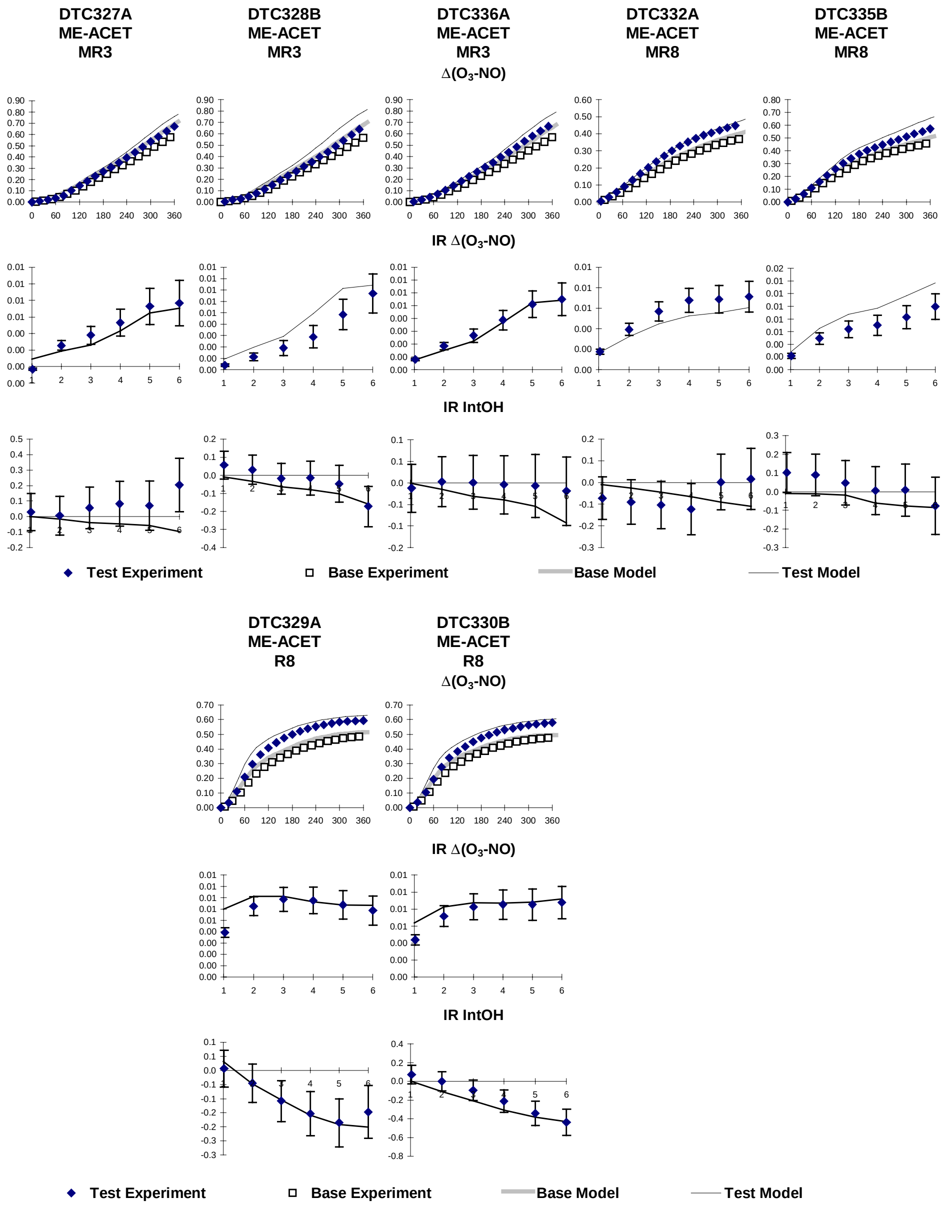


Figure B-49. Plots of experimental and calculated results of the incremental reactivity experiments with methyl acetate.

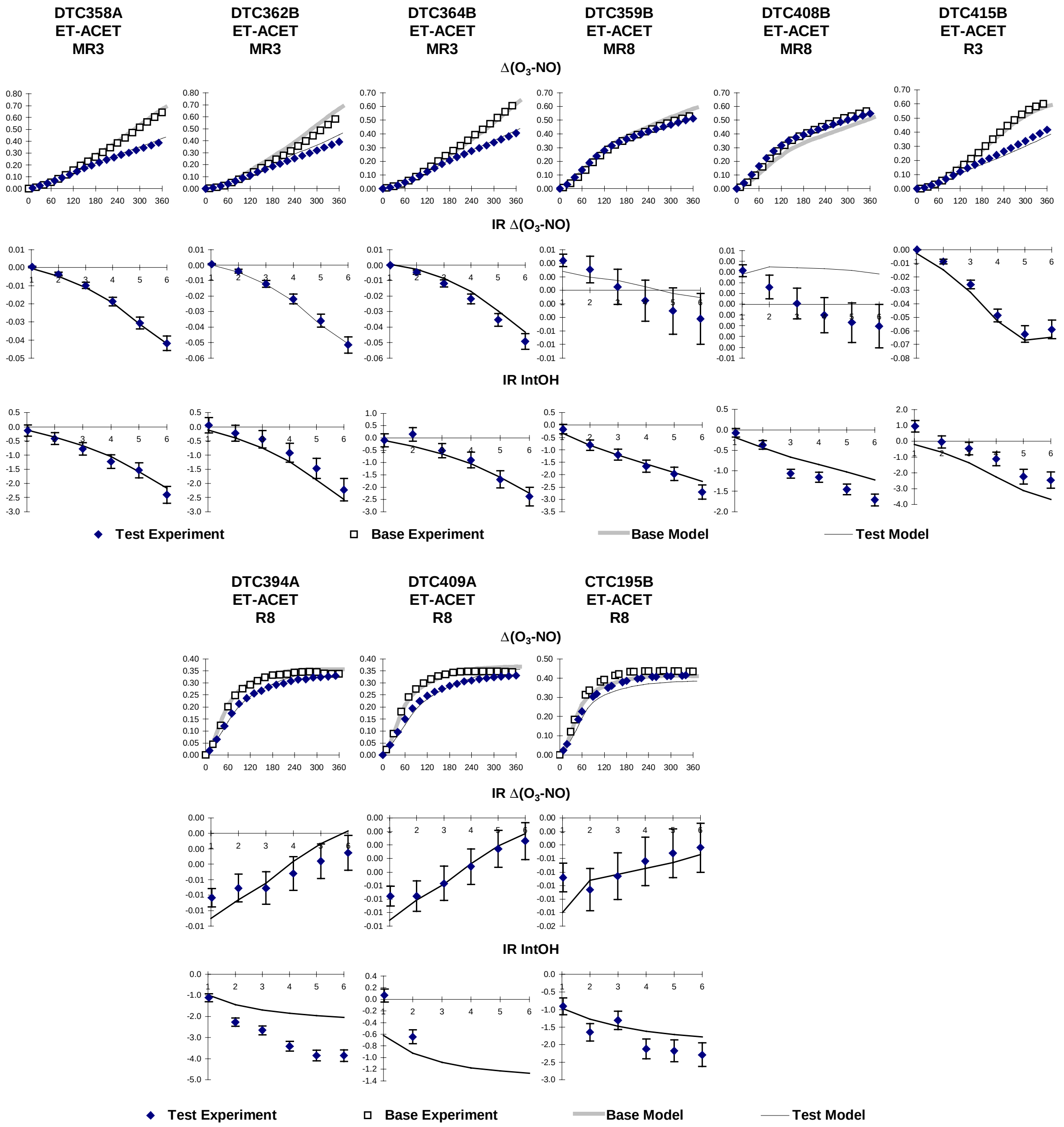


Figure B-50. Plots of experimental and calculated results of the incremental reactivity experiments with ethyl acetate.

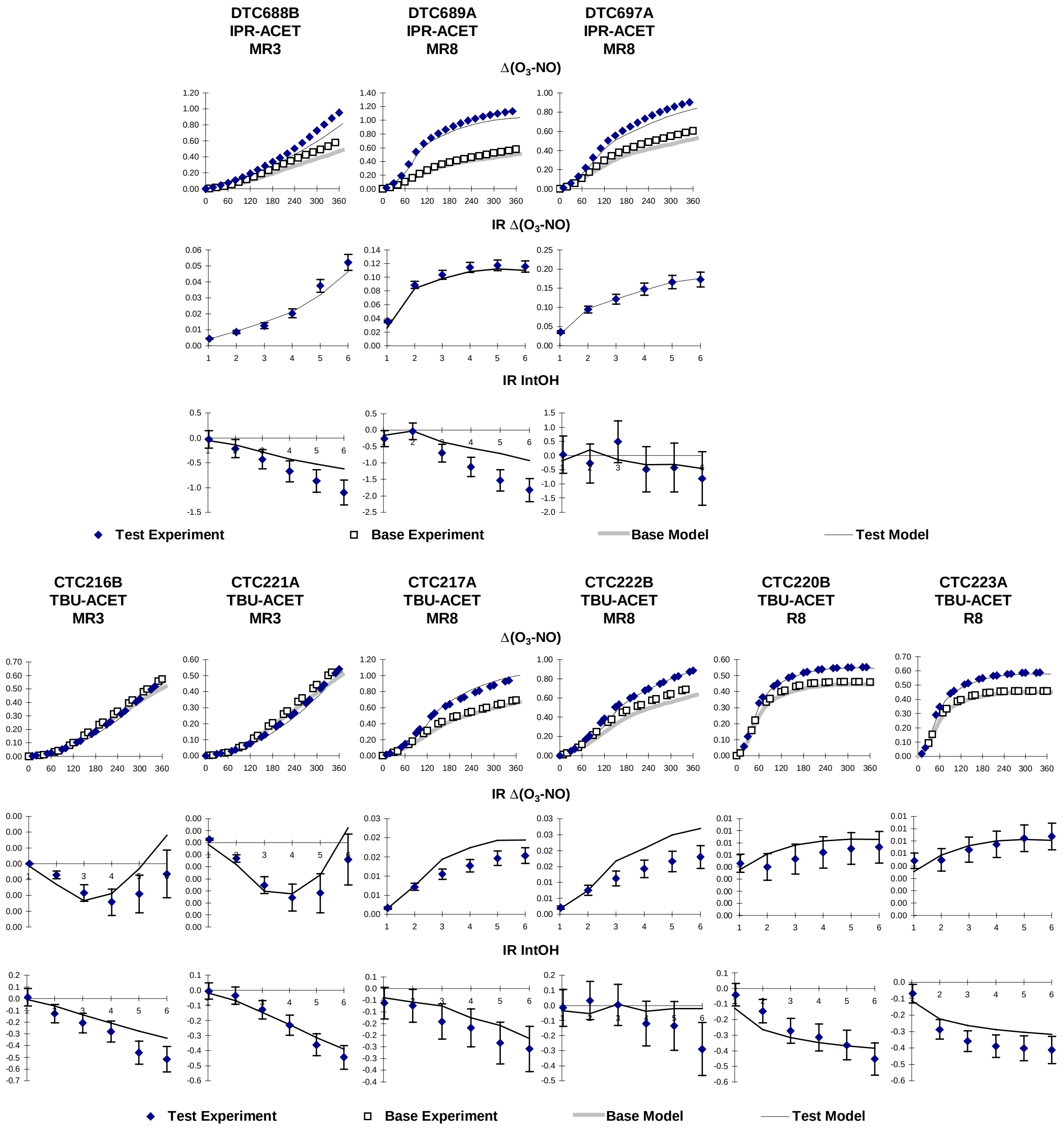


Figure B-51. Plots of experimental and calculated results of the incremental reactivity experiments with isopropyl and t-butyl acetates.

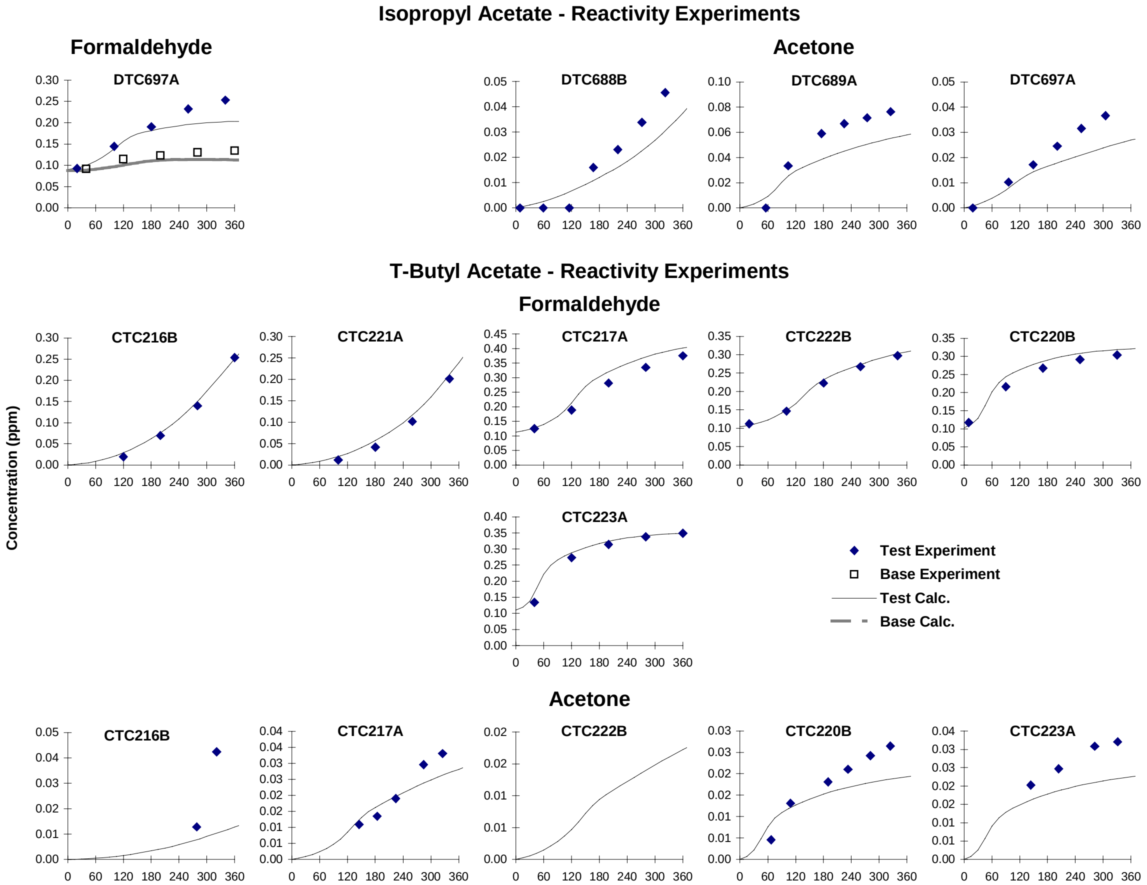


Figure B-52. Plots of experimental and calculated formaldehyde and acetone data for the isopropyl acetate and t-butyl acetate incremental reactivity experiments.

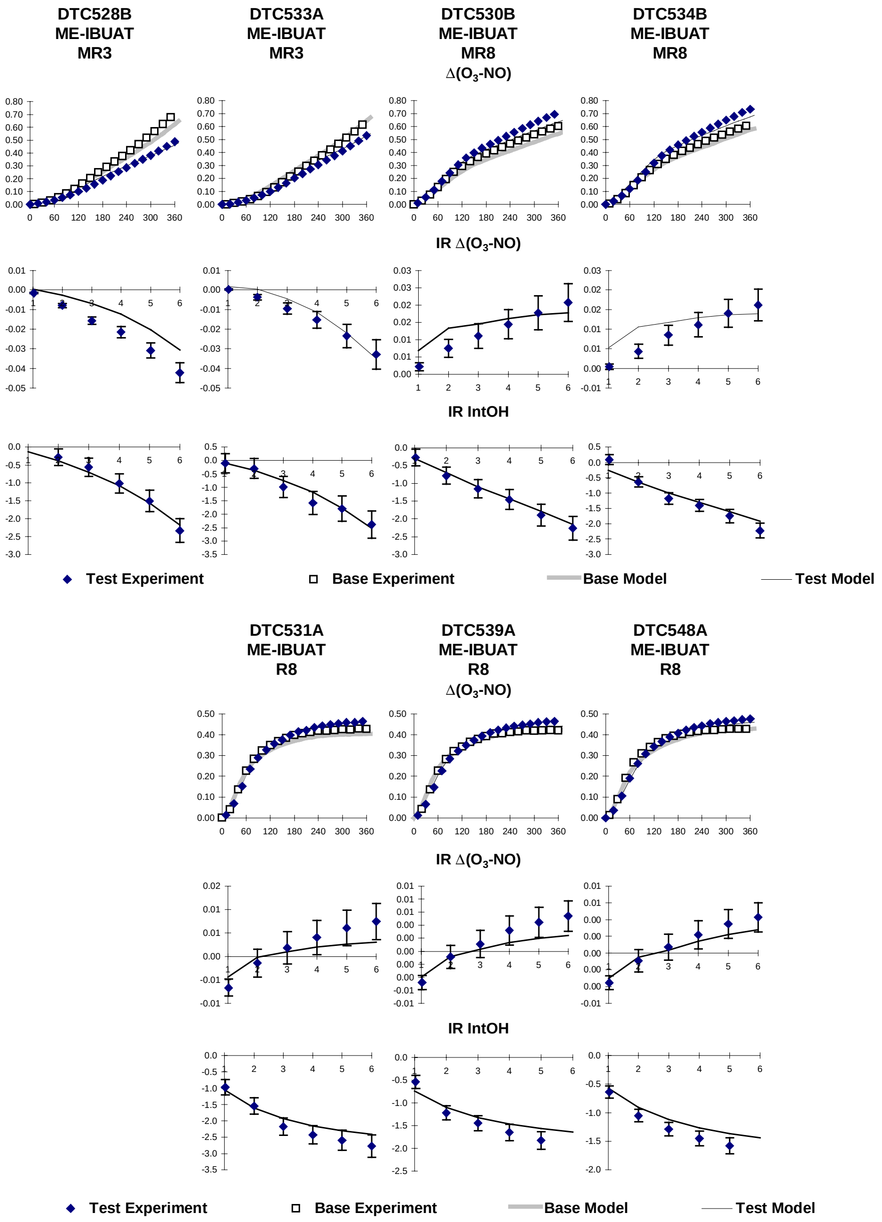


Figure B-53. Plots of experimental and calculated results of the incremental reactivity experiments with methyl isobutyrate.

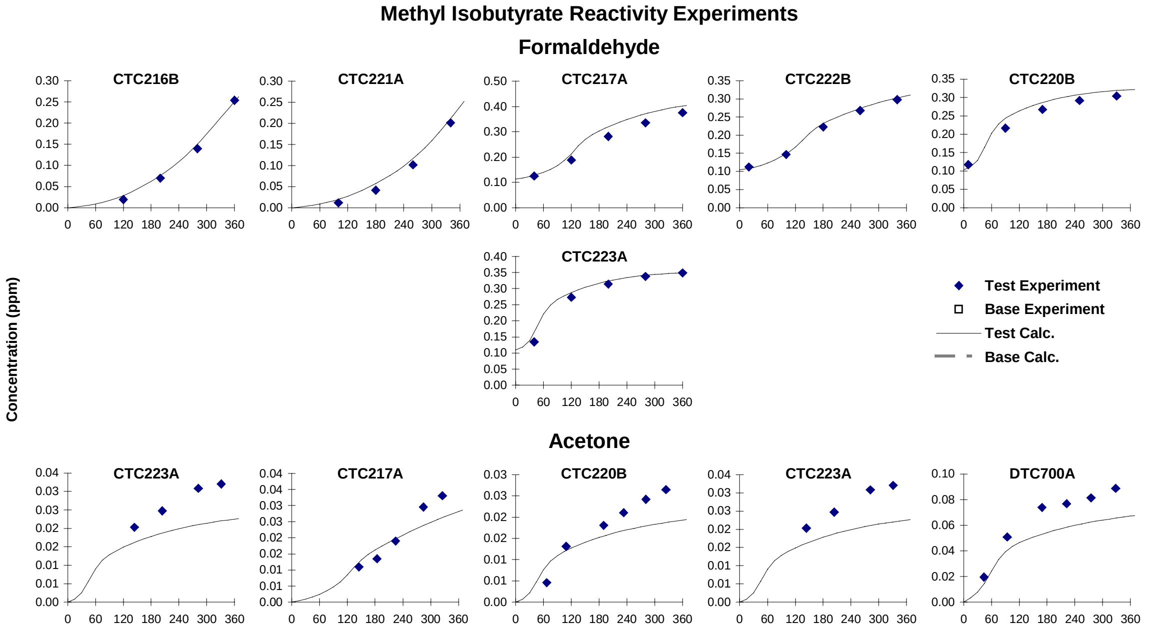


Figure B-54. Plots of experimental and calculated formaldehyde and acetone data for the methyl isobutyrate incremental reactivity experiments.

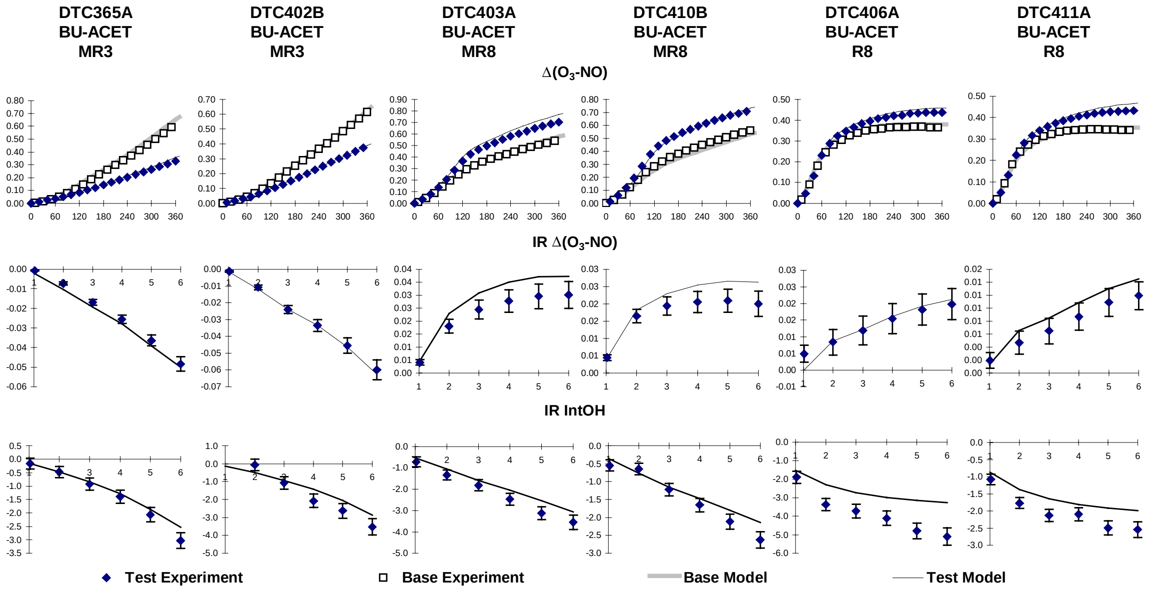


Figure B-55. Plots of experimental and calculated results of the incremental reactivity experiments with butyl acetate. (Run DTC368B, whose results are very similar to those for the other mini-surrogate runs, is not shown.)

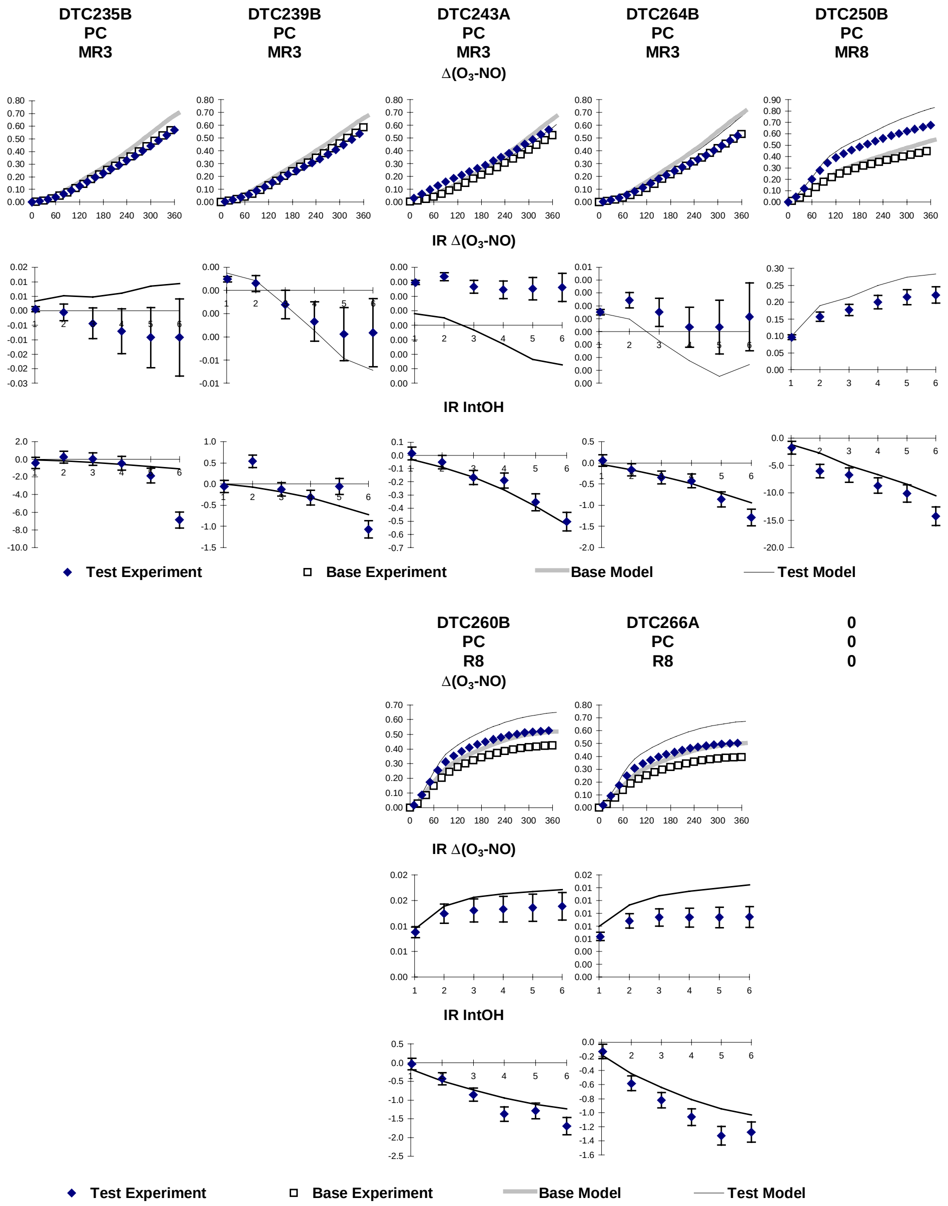


Figure B-56. Plots of experimental and calculated results of the incremental reactivity experiments with propylene carbonate.

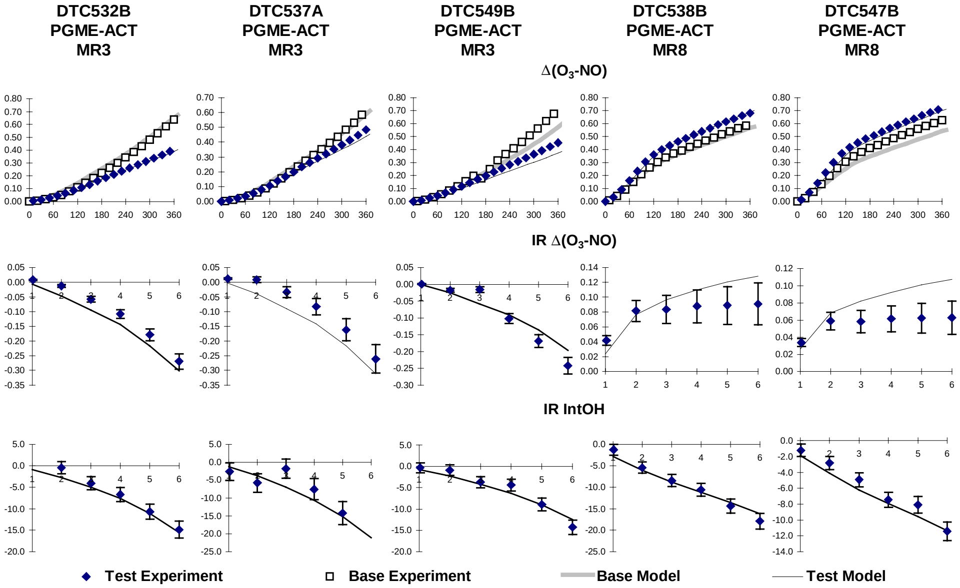


Figure B-57. Plots of experimental and calculated results of the incremental reactivity experiments with propylene glycol methyl ether acetate.

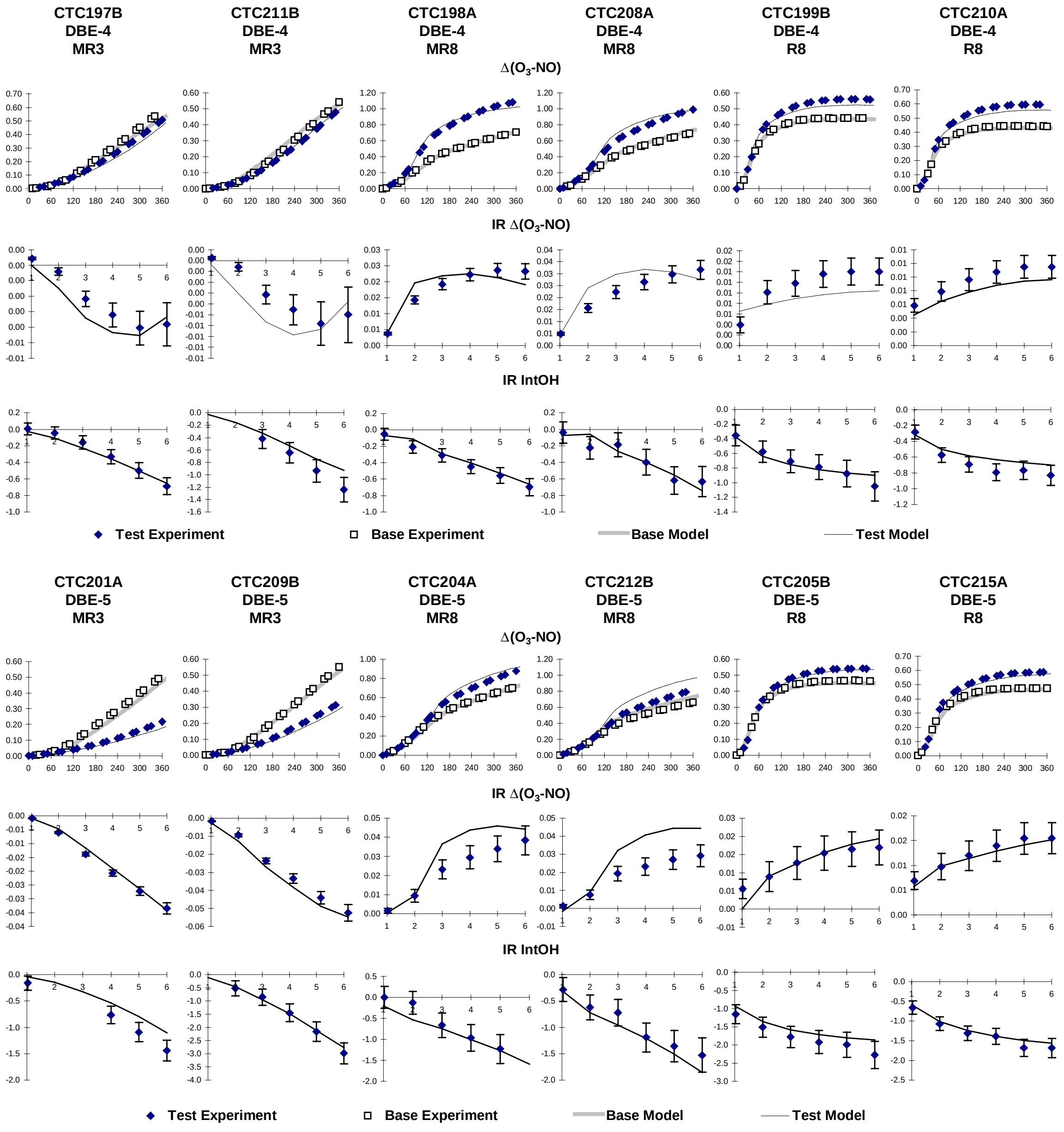


Figure B-58. Plots of experimental and calculated results of the incremental reactivity experiments with the dibasic esters Dimethyl Glutarate and Dimethyl Adipate.

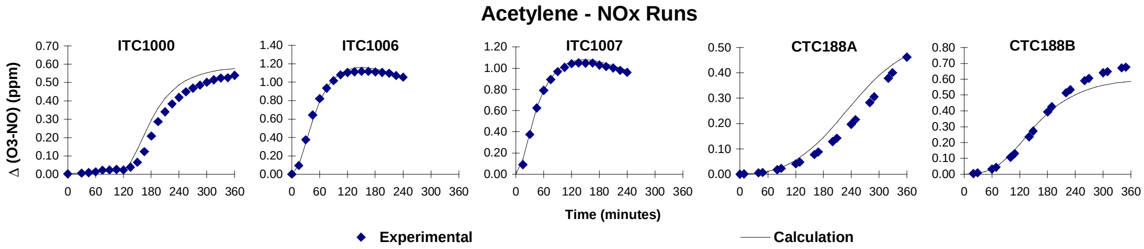


Figure B-59. Plots of experimental and calculated $\Delta([O_3]-[NO])$ data for the acetylene - NO_x experiments.

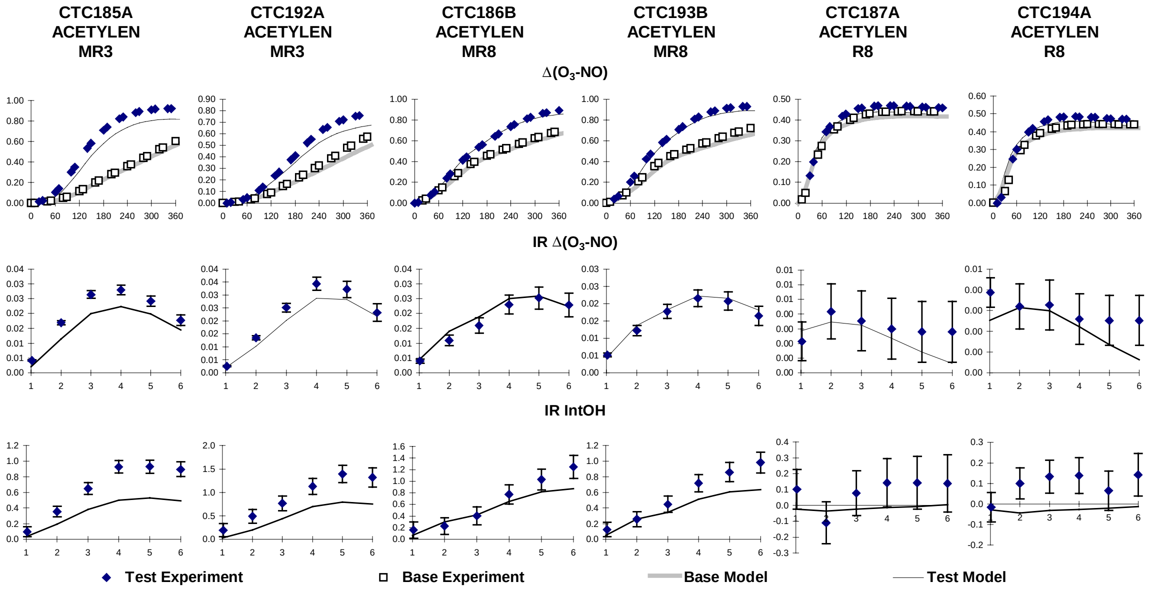


Figure B-60. Plots of experimental and calculated results of the incremental reactivity experiments with acetylene. (Run CTC184B, which has similar results as run CTC185A, is not shown.)

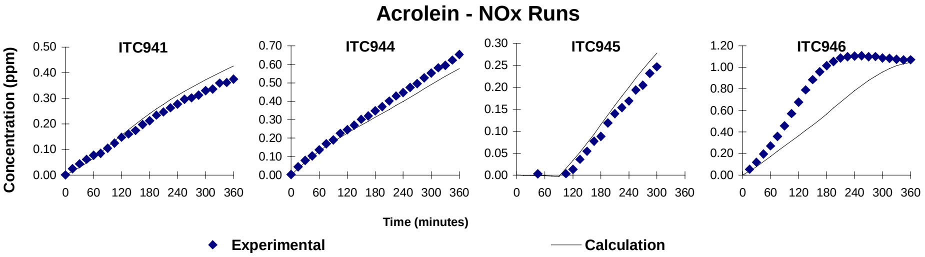


Figure B-61. Plots of experimental and calculated $\Delta([O_3]-[NO])$ data for the acrolein - NO_x experiments.

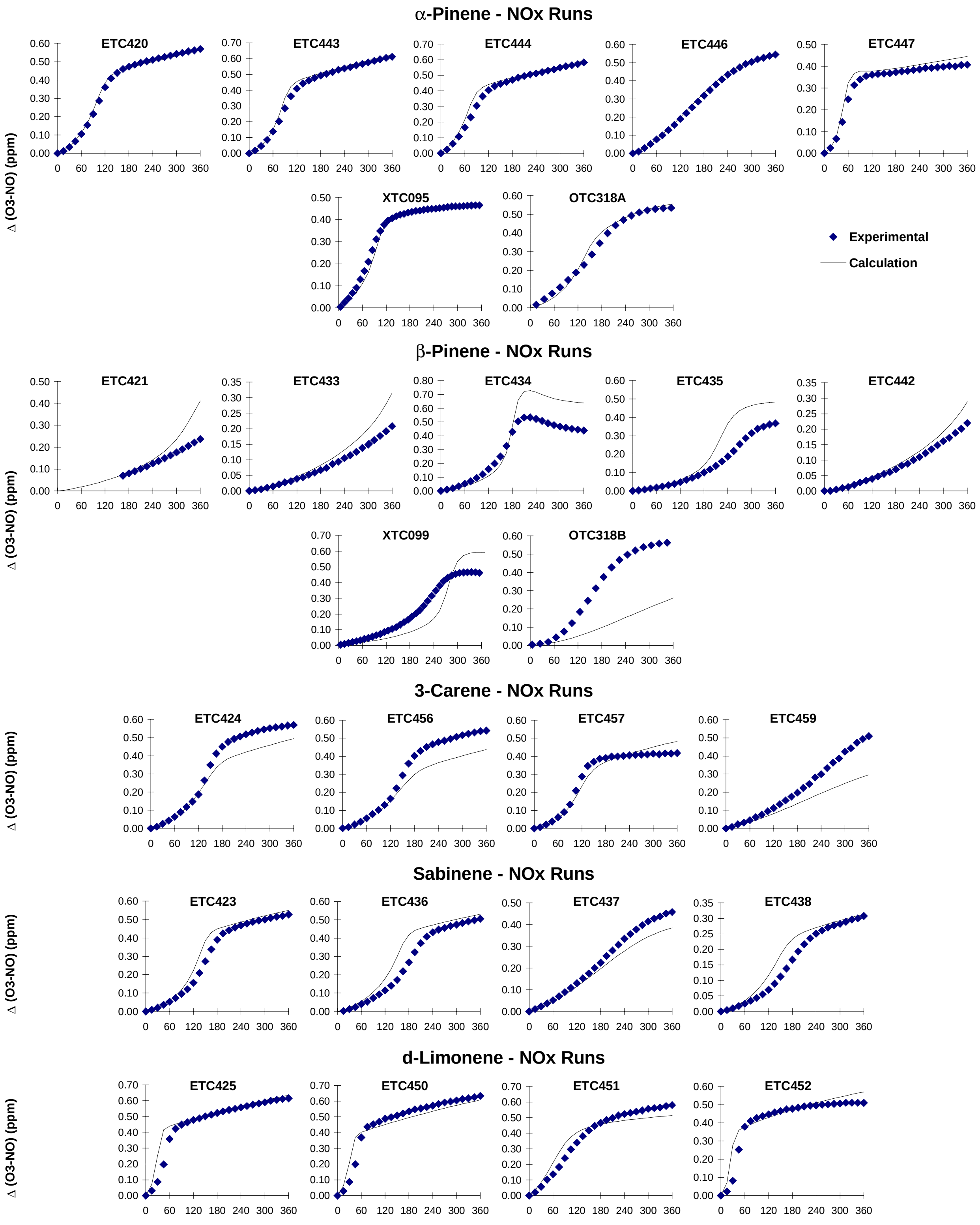


Figure B-62. Plots of experimental and calculated $\Delta([O_3]-[NO])$ data for the terpene - NO_x experiments.

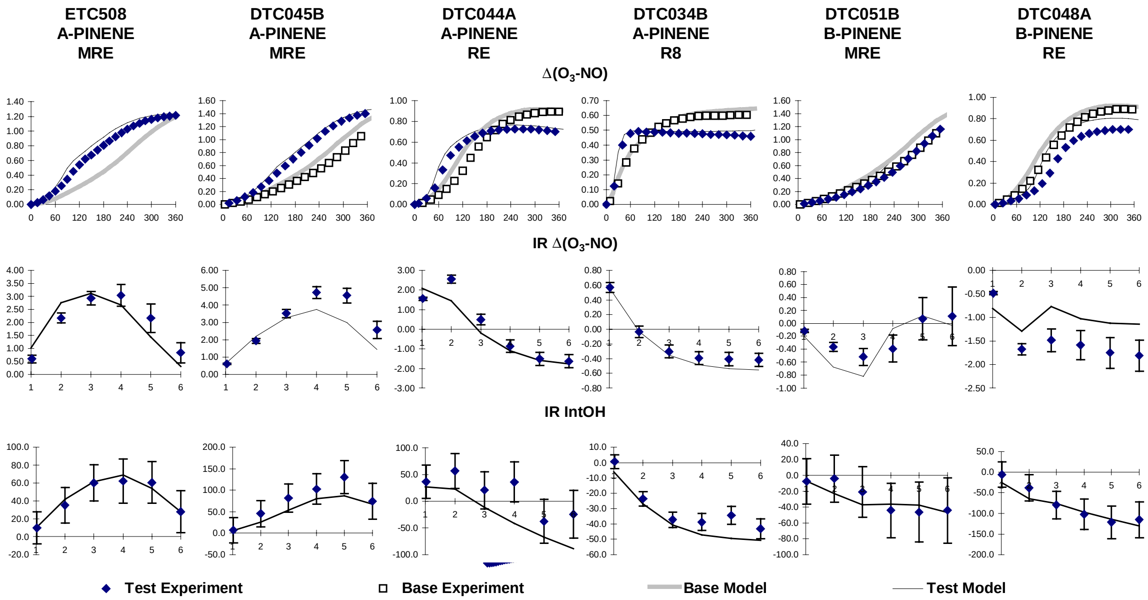


Figure B-63. Plots of experimental and calculated results of the incremental reactivity experiments with α- and β-pinenes.

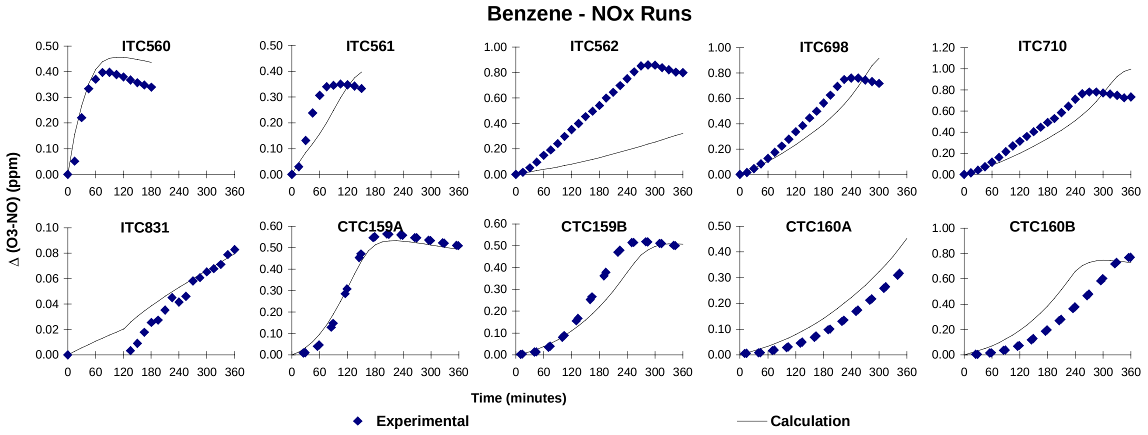


Figure B-64. Plots of experimental and calculated Δ([O$_3$]-[NO]) data for the benzene - NO$_2$ experiments.

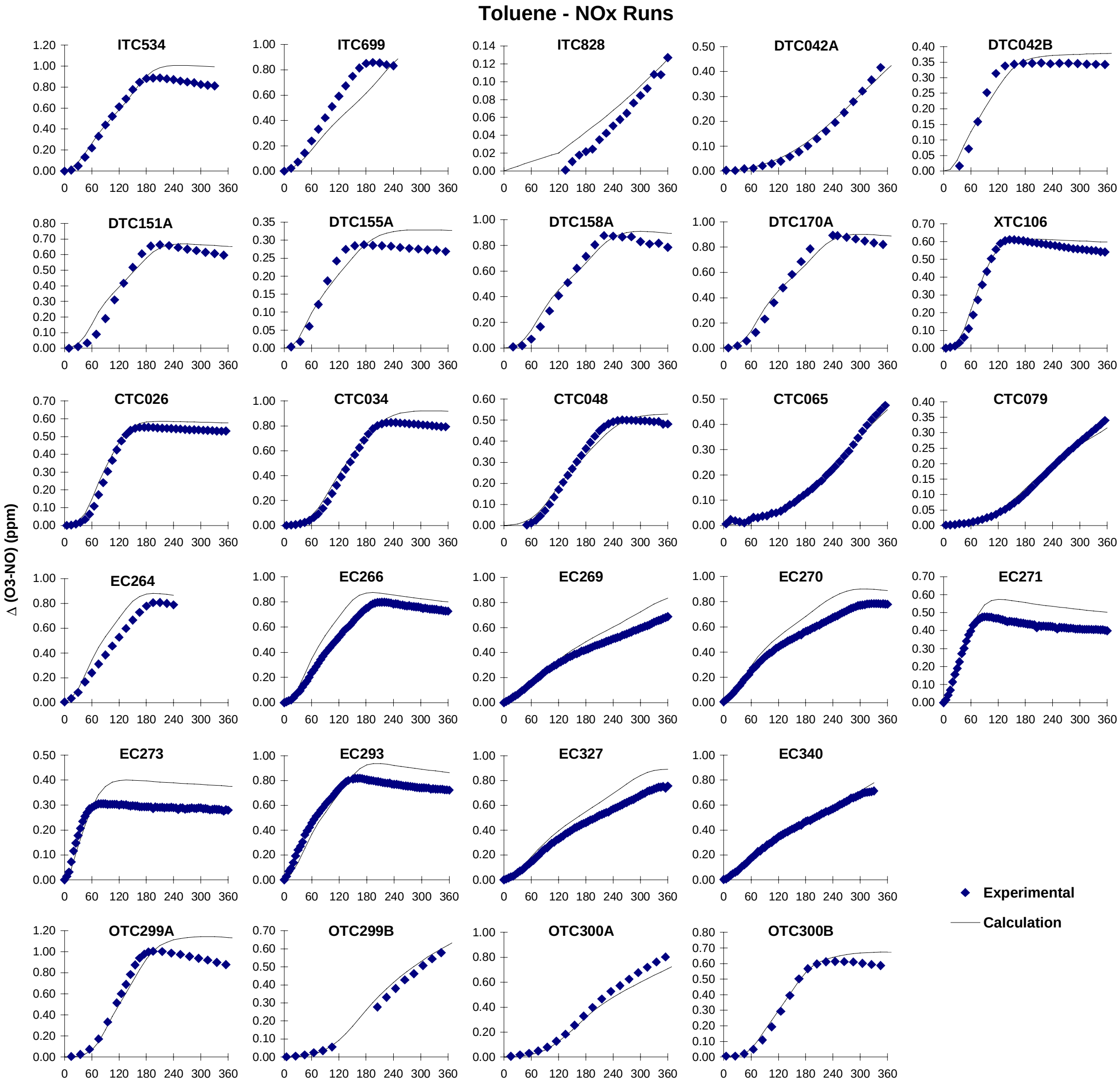


Figure B-65. Plots of experimental and calculated Δ([O$_3$]-[NO]) data for the toluene - NO$_x$ experiments.

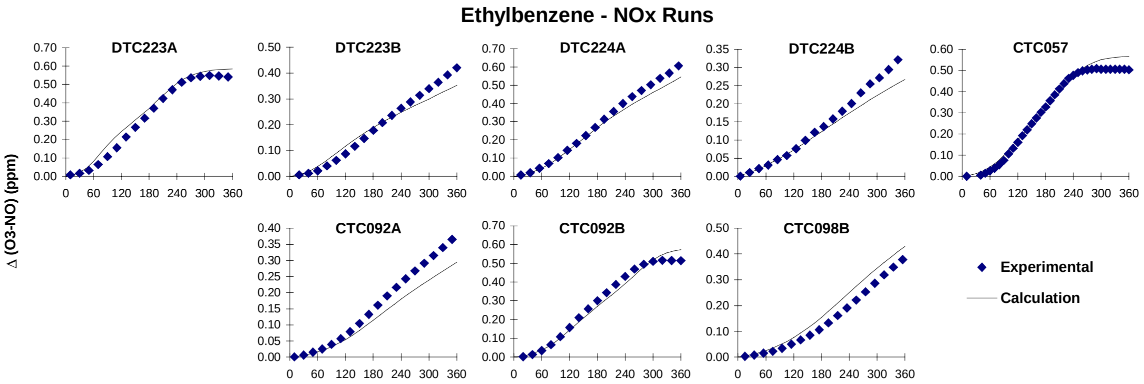


Figure B-66. Plots of experimental and calculated $\Delta([O_3]-[NO])$ data for the ethylbenzene - NO_x experiments.

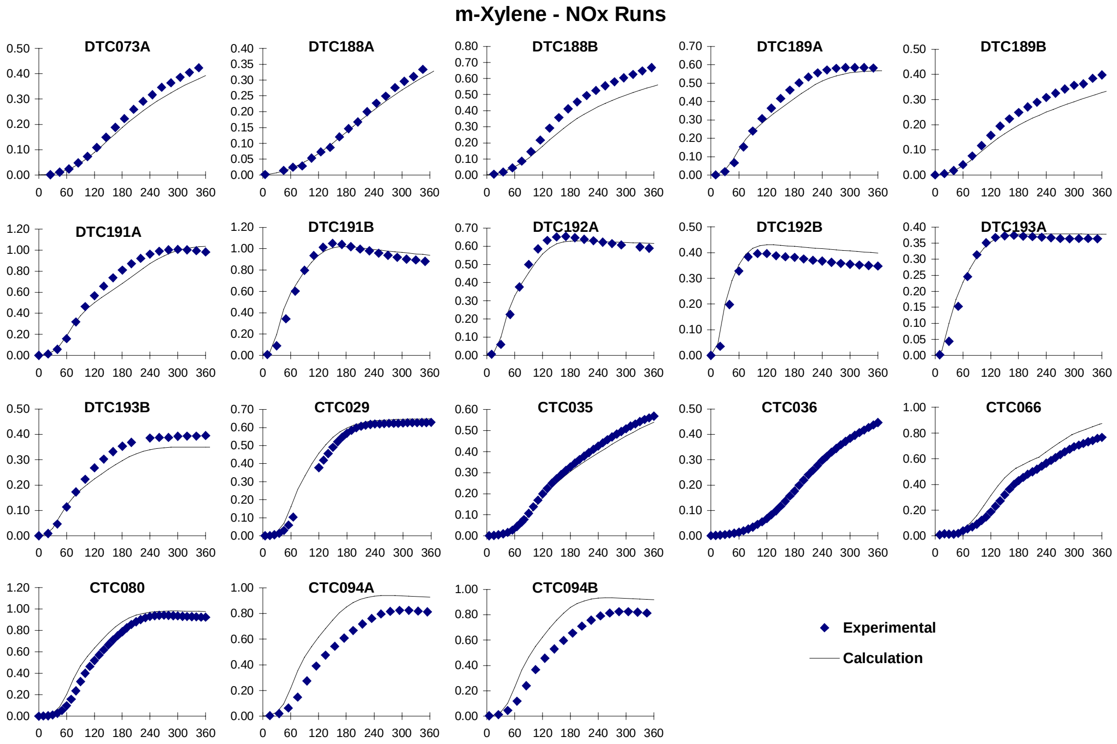


Figure B-67. Plots of experimental and calculated $\Delta([O_3]-[NO])$ data for the m-xylene - NO_2 experiments.

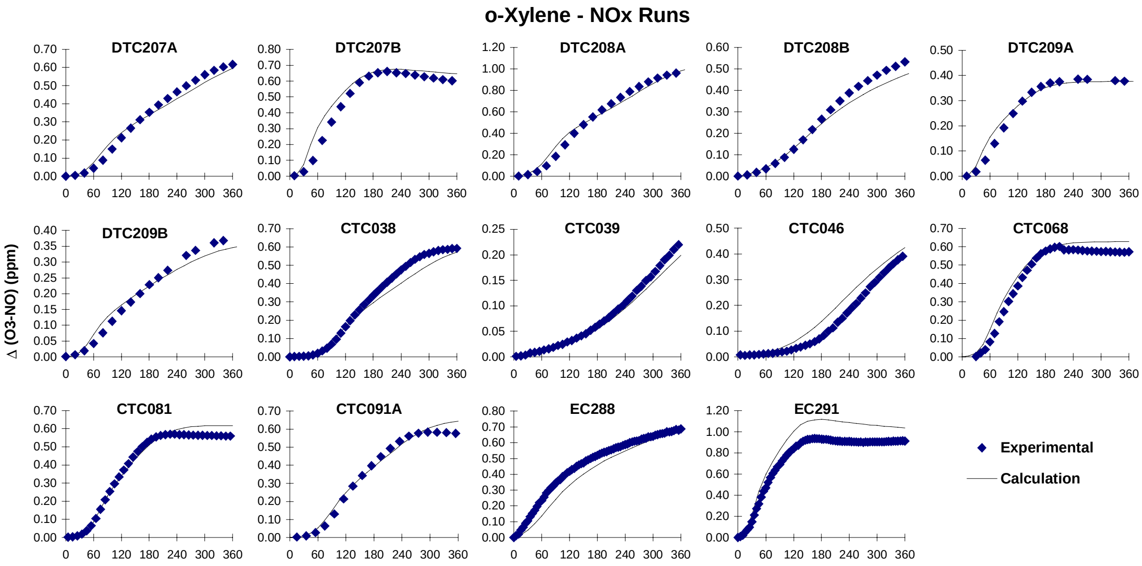


Figure B-68. Plots of experimental and calculated Δ([O_3]-[NO]) data for the o-xylene - NO_2 experiments.

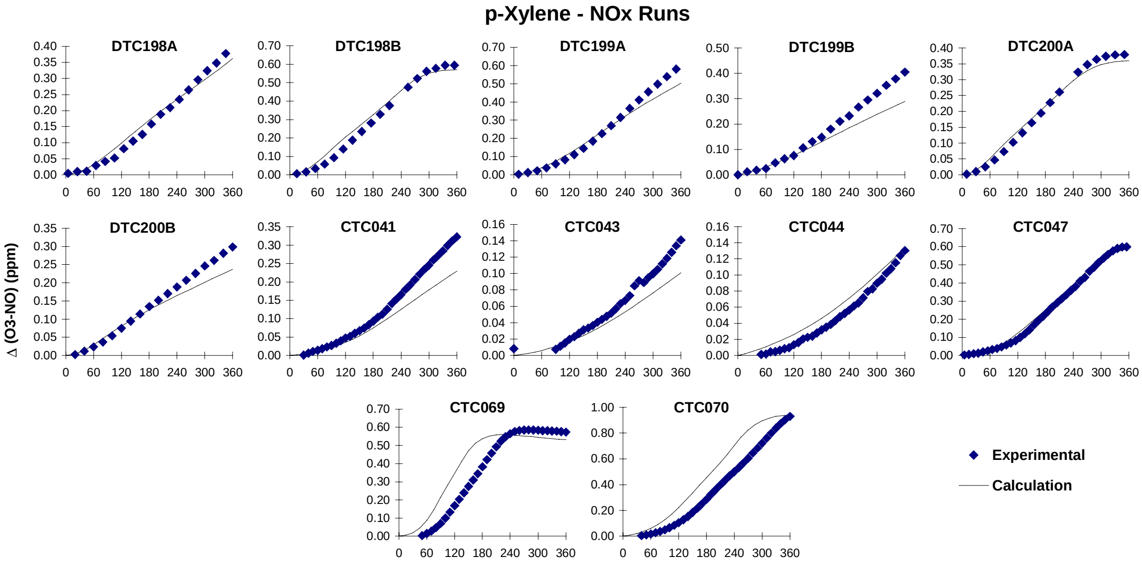


Figure B-69. Plots of experimental and calculated Δ([O_3]-[NO]) data for the p-xylene - NO_x experiments.

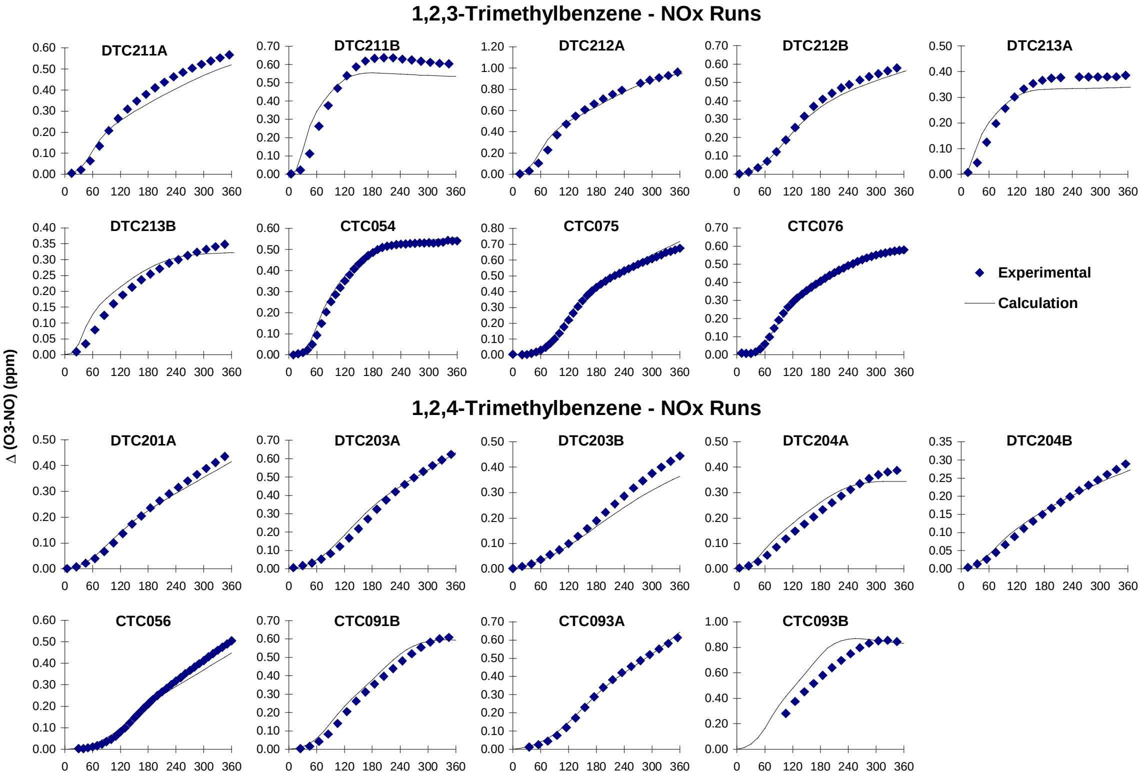


Figure B-70. Plots of experimental and calculated $\Delta([O_3]-[NO])$ data for the 1,2,3-trimethylbenzene and 1,2,4-trimethylbenzene - NO_x experiments.

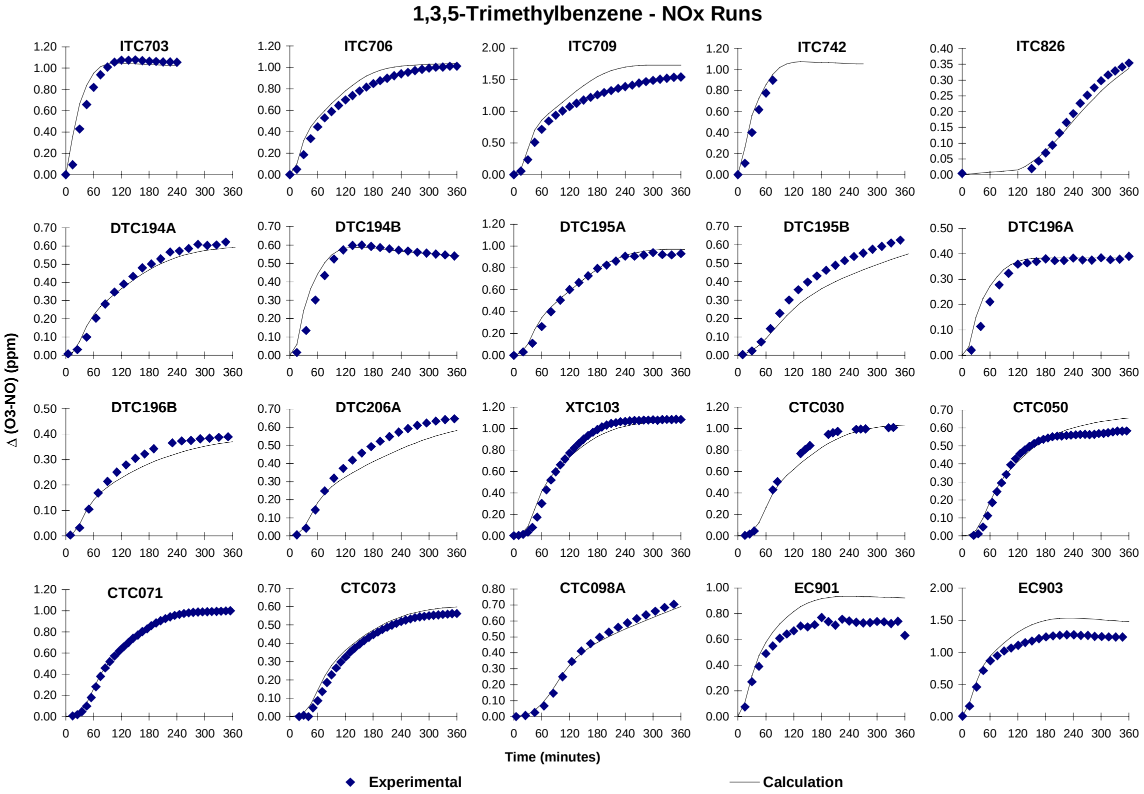


Figure B-71. Plots of experimental and calculated $\Delta([O_3]-[NO])$ data for the 1,3,5-trimethylbenzene - NO_x experiments.

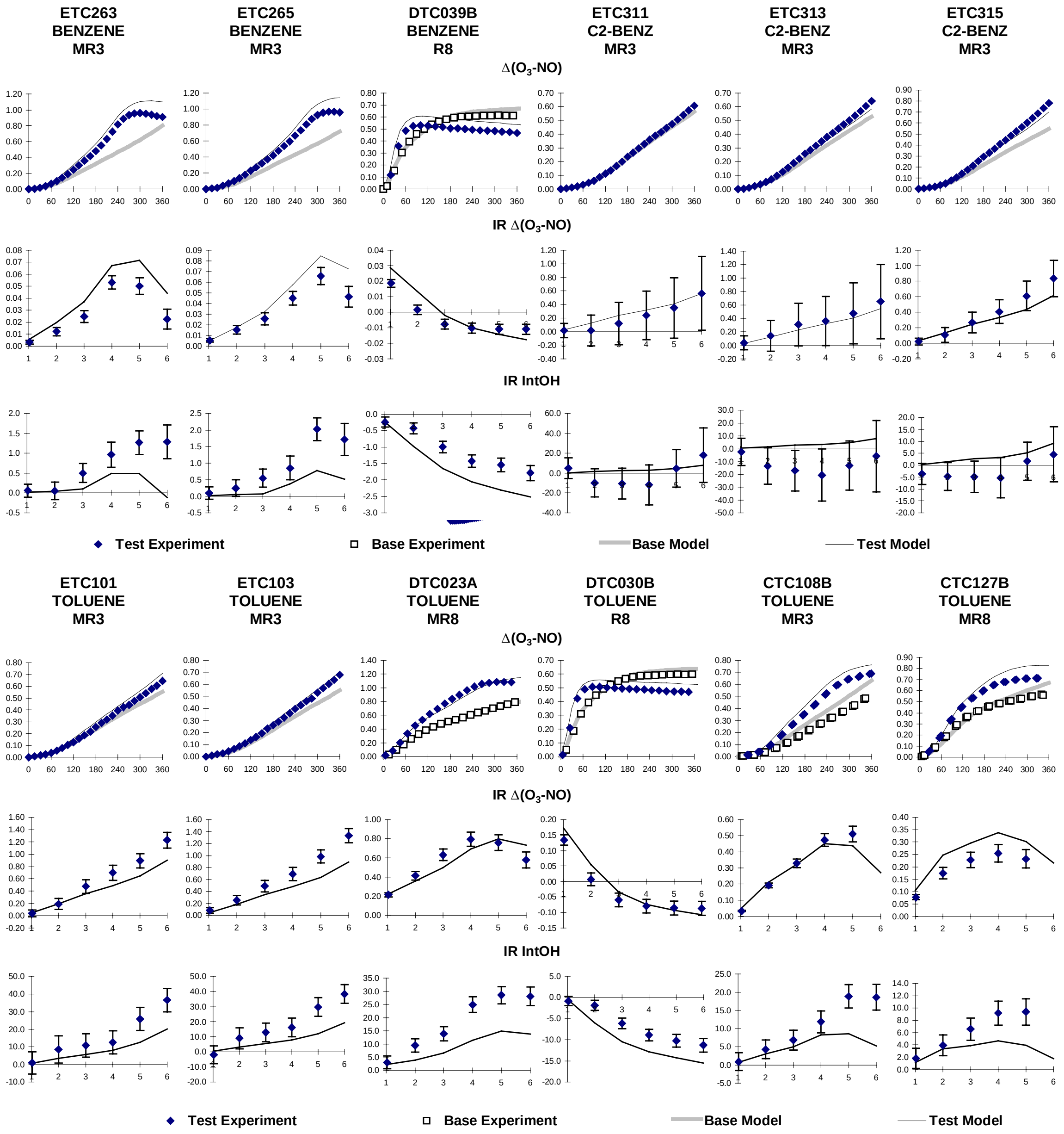


Figure B-72. Plots of experimental and calculated results of the incremental reactivity experiments with benzene, toluene, and ethylbenzene.

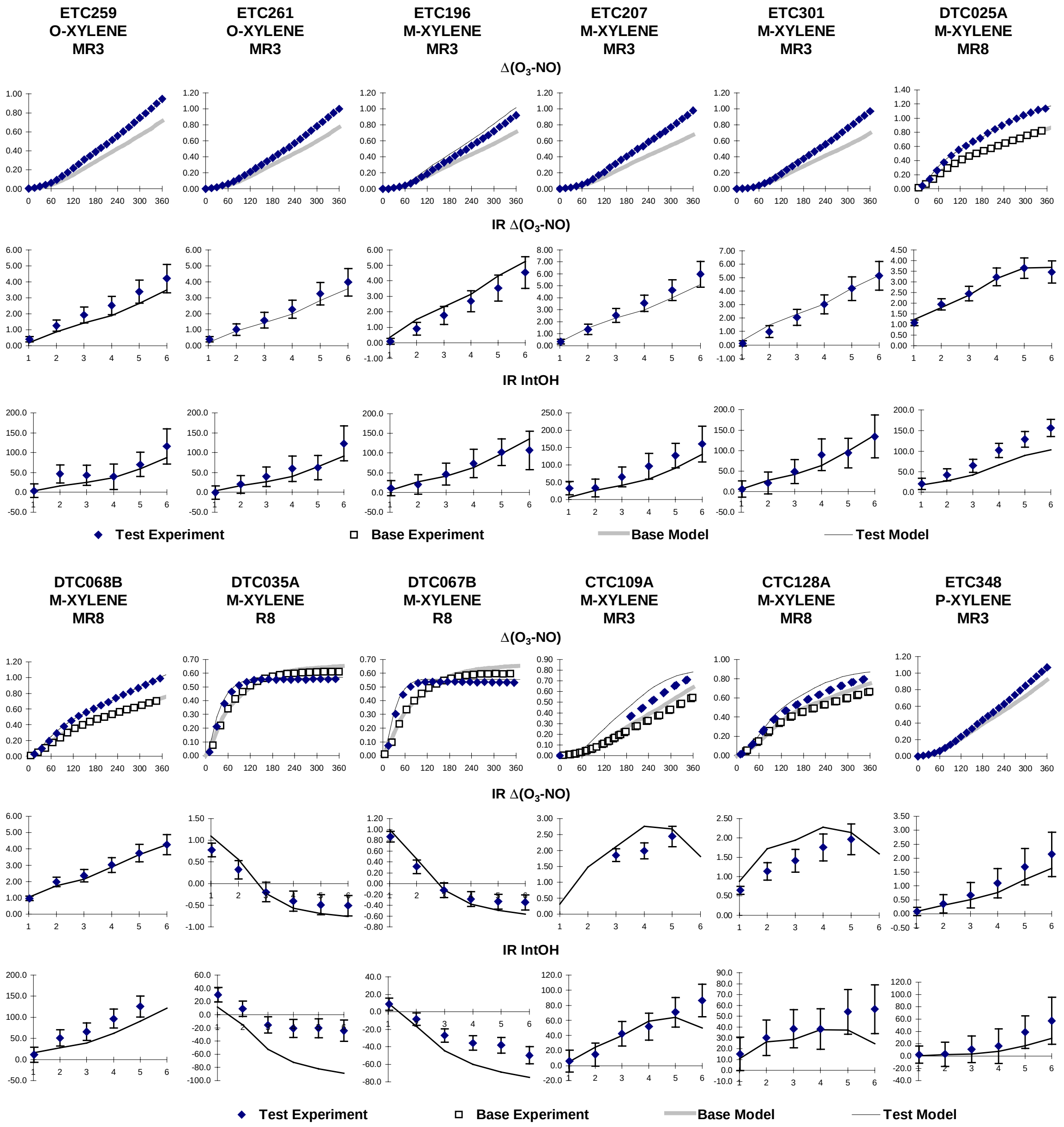


Figure B-73. Plots of experimental and calculated results of the incremental reactivity experiments with o-, m-, and p-xylenes.

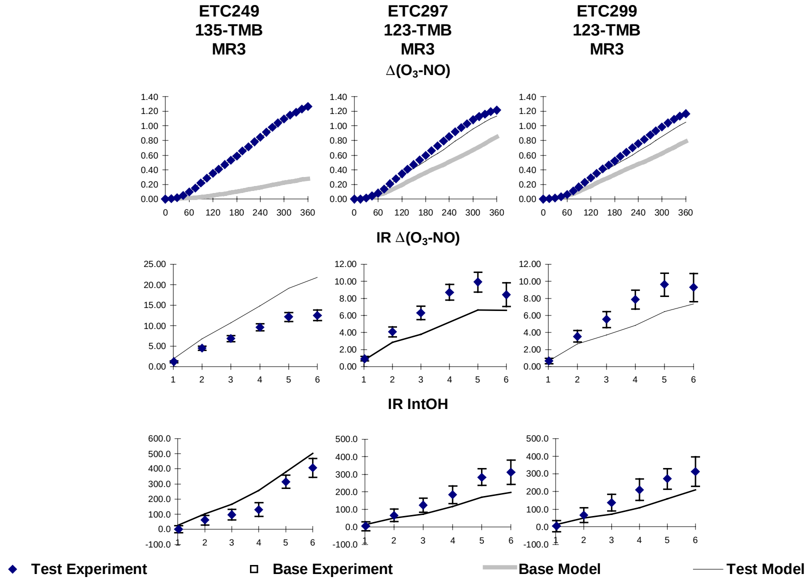


Figure B-74. Plots of experimental and calculated results of the incremental reactivity experiments with the trimethyl benzenes.

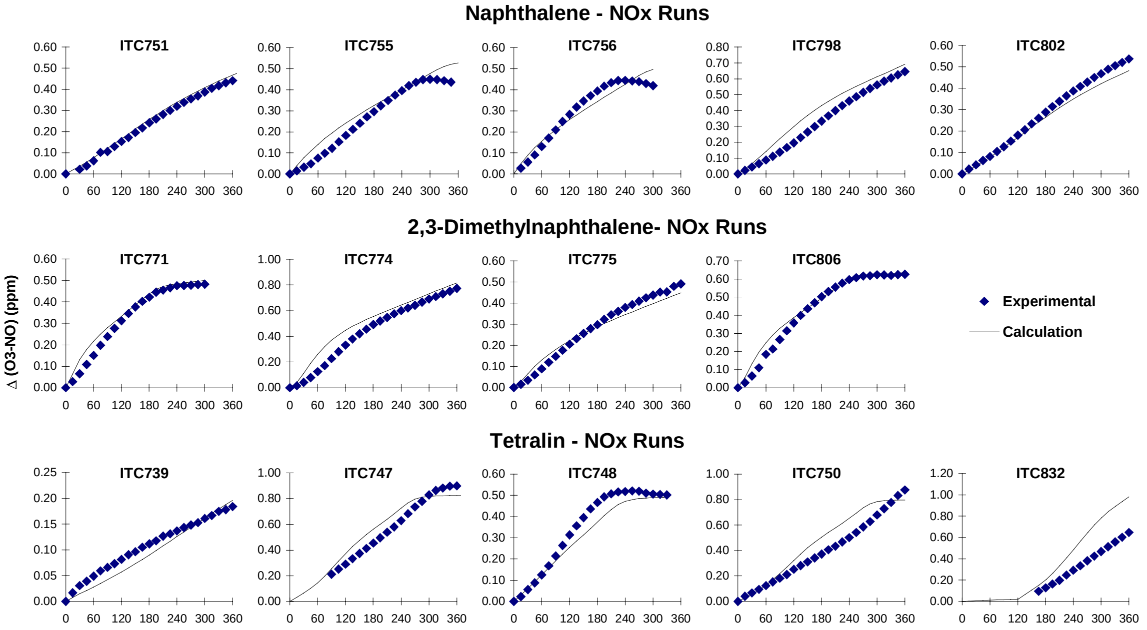


Figure B-75. Plots of experimental and calculated Δ([O_3]-[NO]) data for the naphthalene - NO_x, 2,3-dimethylnaphthalene - NO_x and tetralin - NO_x experiments.

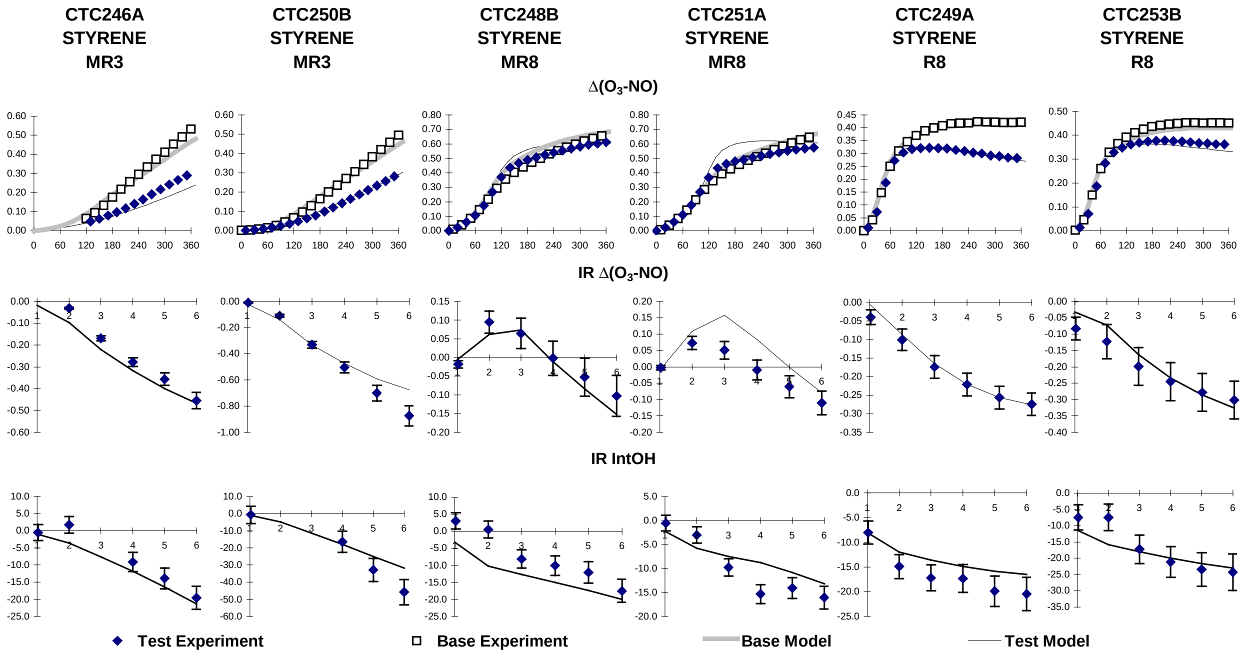


Figure B-76. Plots of experimental and calculated results of the incremental reactivity experiments with styrene.

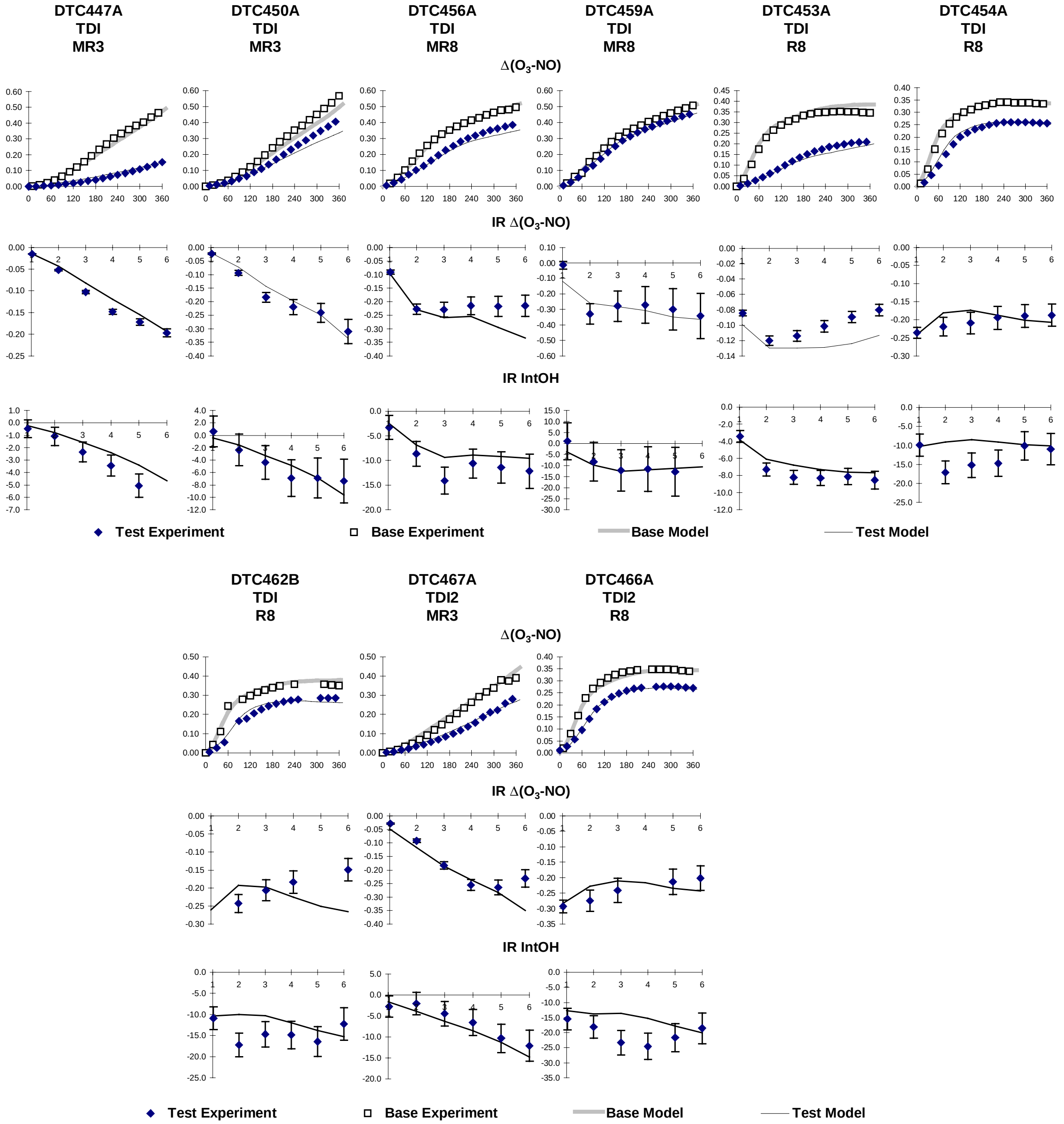


Figure B-77. Plots of experimental and calculated results of the incremental reactivity experiments with the toluene diisocyanate isomers (TDI and TDI2)

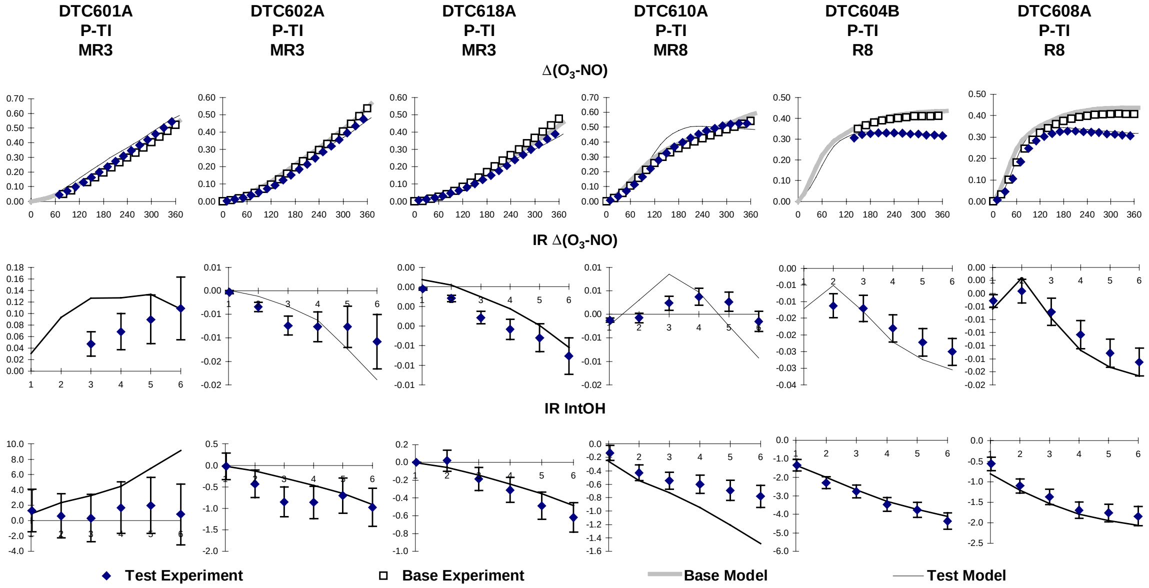


Figure B-78. Plots of experimental and calculated results of the incremental reactivity experiments with para toluene isocyanate.

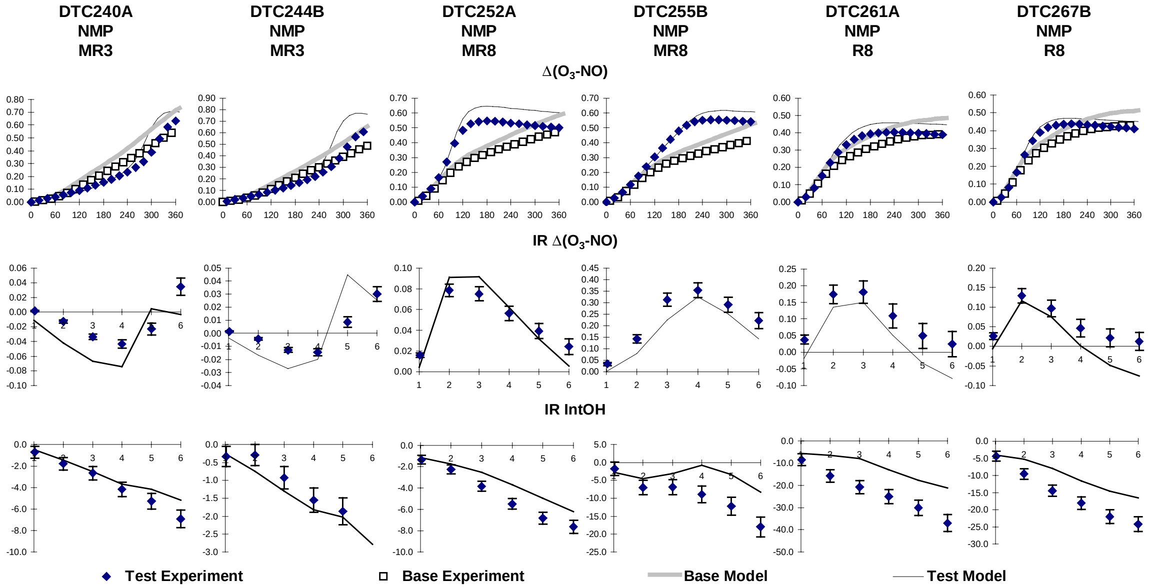


Figure B-79. Plots of experimental and calculated results of the incremental reactivity experiments with N-Methyl-2-Pyrrolidone.

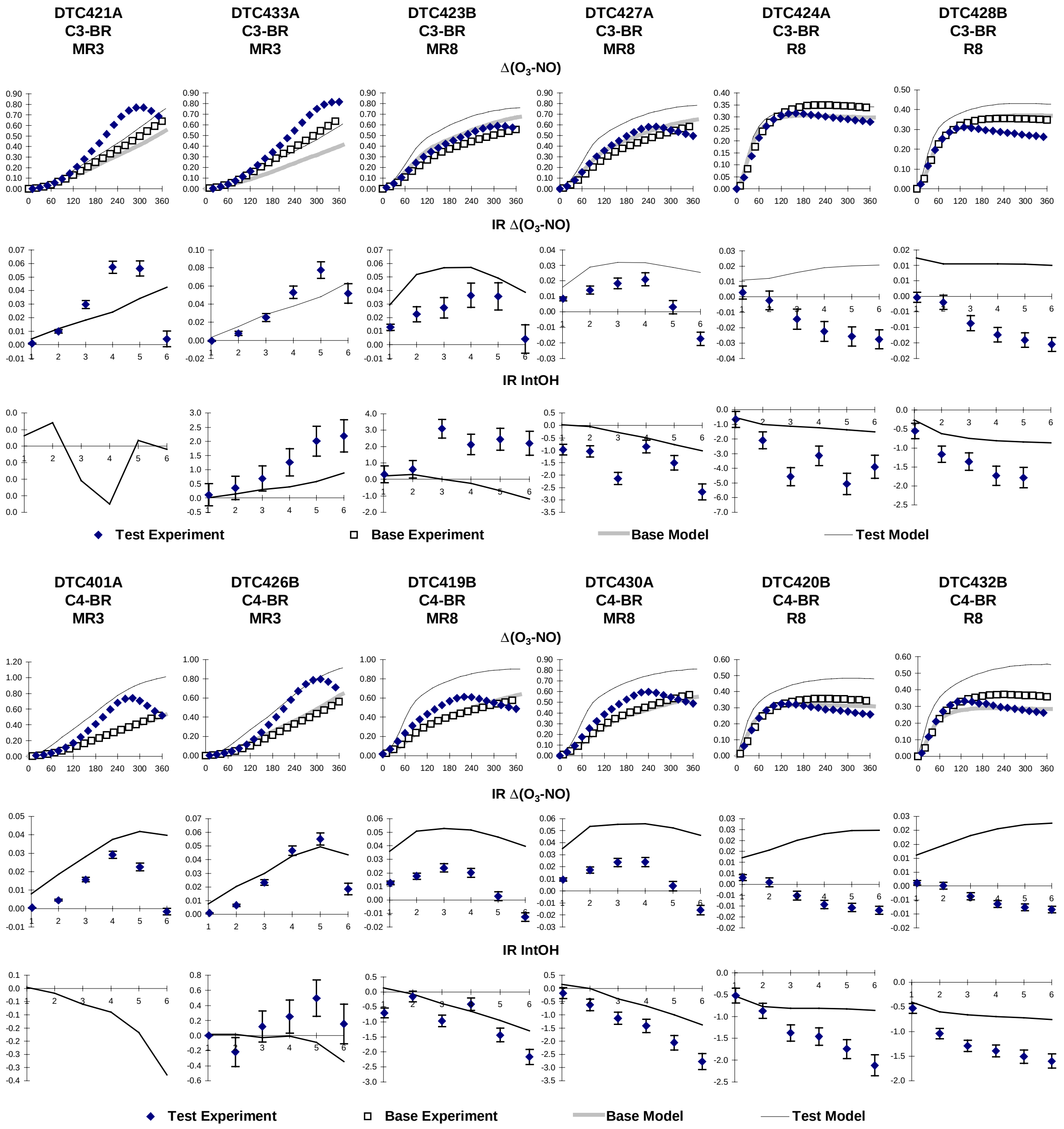


Figure B-80. Plots of experimental and calculated results of the incremental reactivity experiments with propyl and n-butyl bromides.

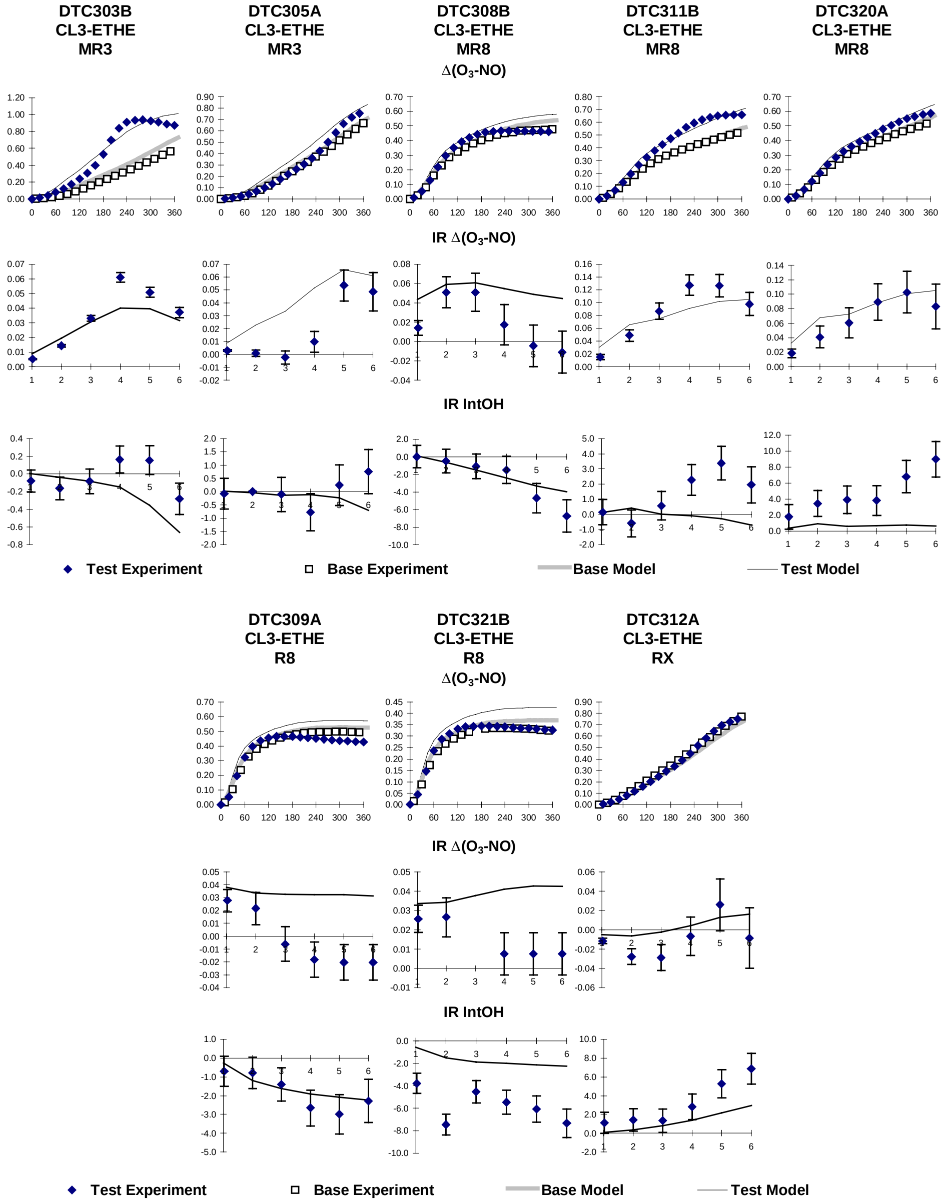


Figure B-81. Plots of experimental and calculated results of the incremental reactivity experiments with trichloroethylene.

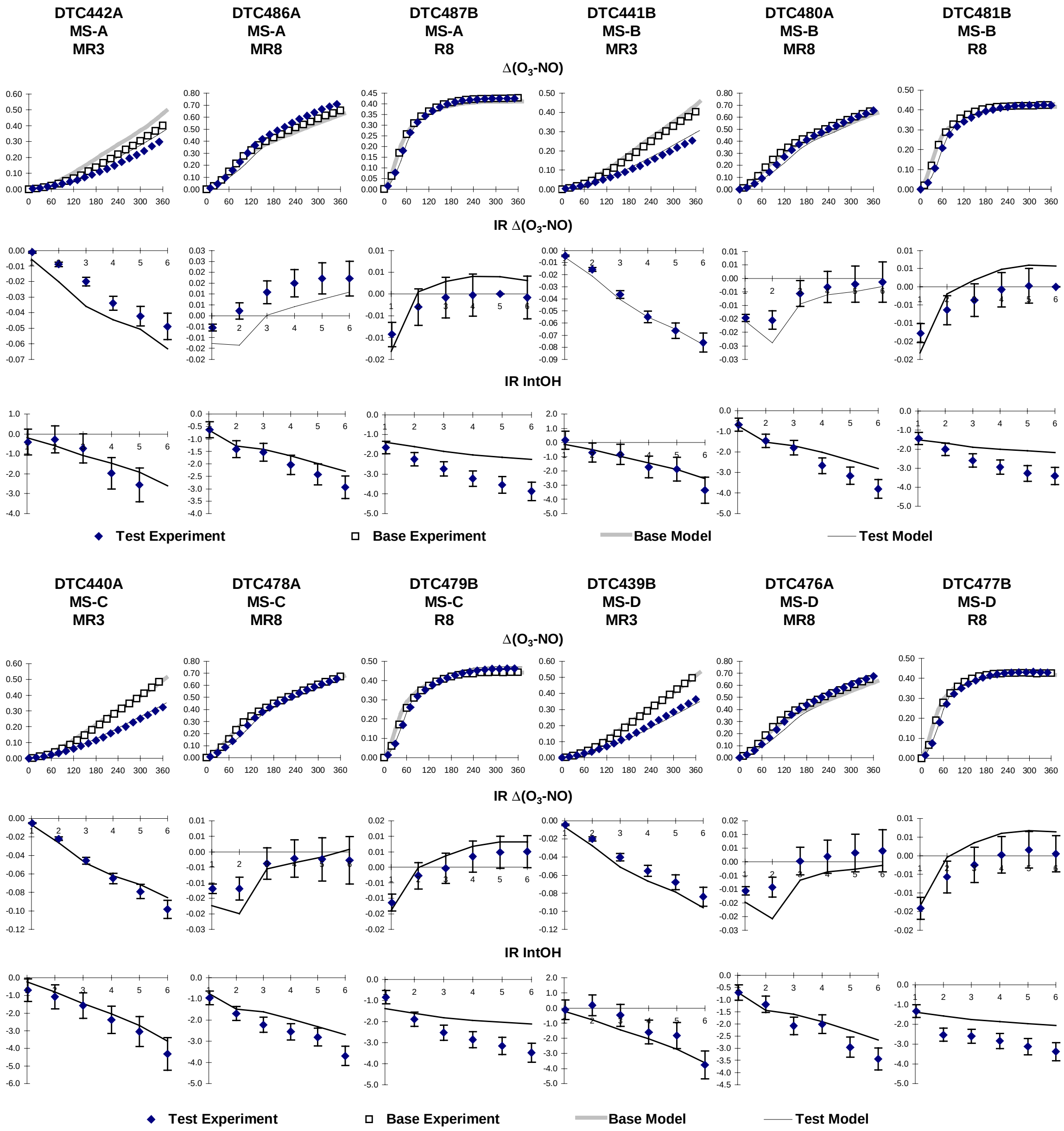


Figure B-82. Plots of experimental and calculated results of the incremental reactivity experiments with the mineral spirits samples used in the Safety-Kleen study (Carter et al, 1997f).

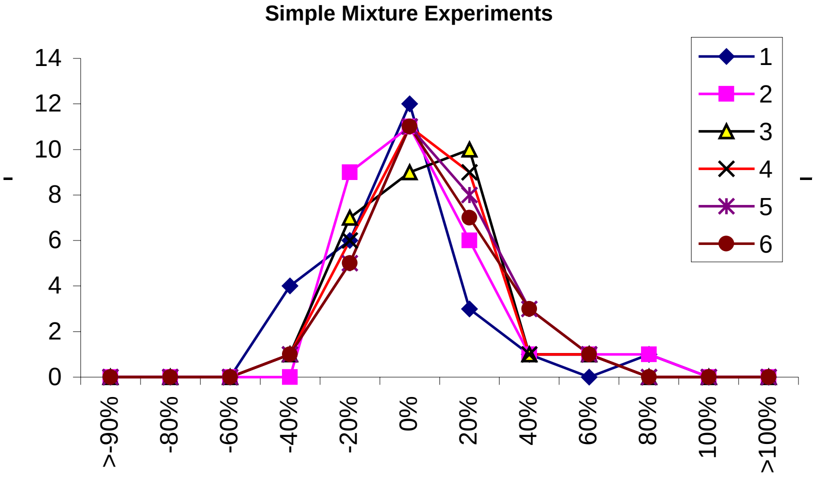


Figure B-83. Distribution plots of percentage errors of fits of calculated to experimental hourly Δ([O_3]-[NO]) data for the simple mixture experiments (most carried out in the SAPRC EC).

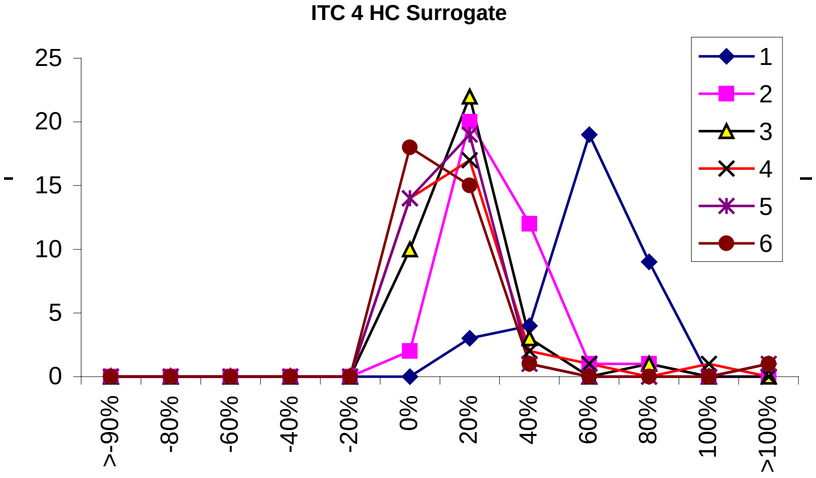


Figure B-84. Distribution plots of percentage errors of fits of calculated to experimental hourly Δ([O_3]-[NO]) data for the four hydrocarbon surrogate experiments carried out in the ITC.

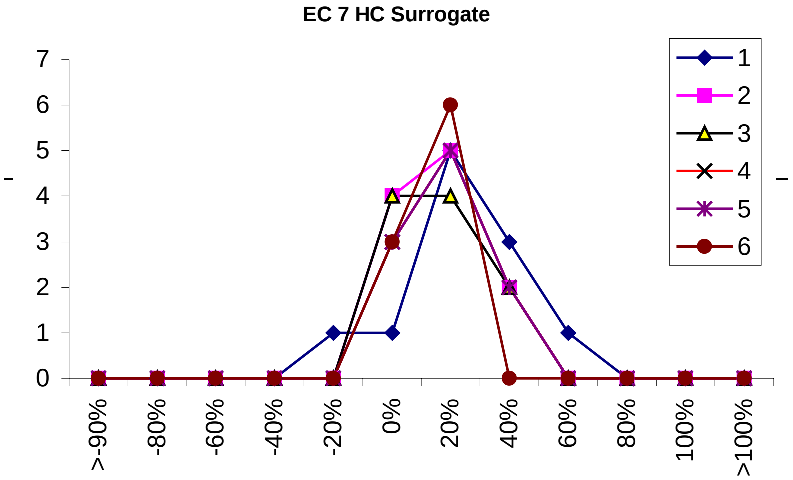


Figure B-85. Distribution plots of percentage errors of fits of calculated to experimental hourly $\Delta([O_3]-[NO])$ data for the seven hydrocarbon surrogate experiments carried out in the SAPRC EC.

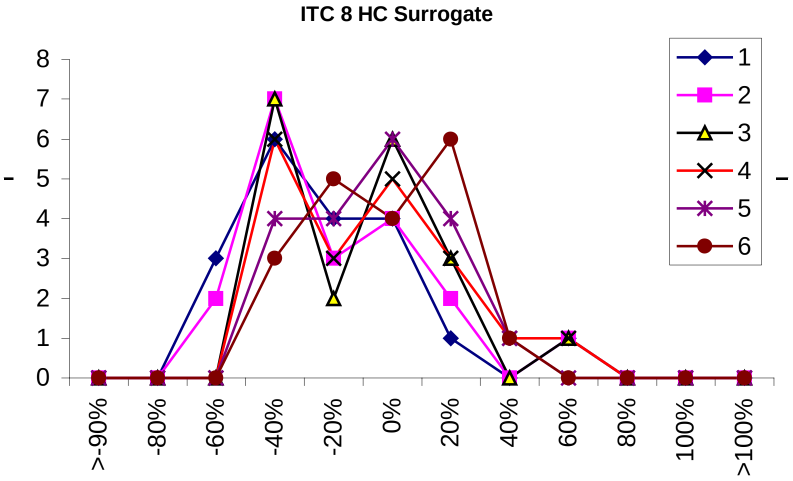
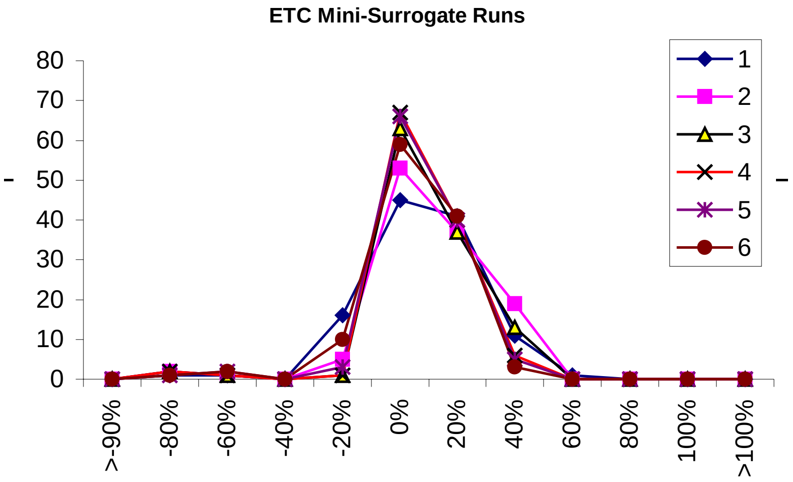
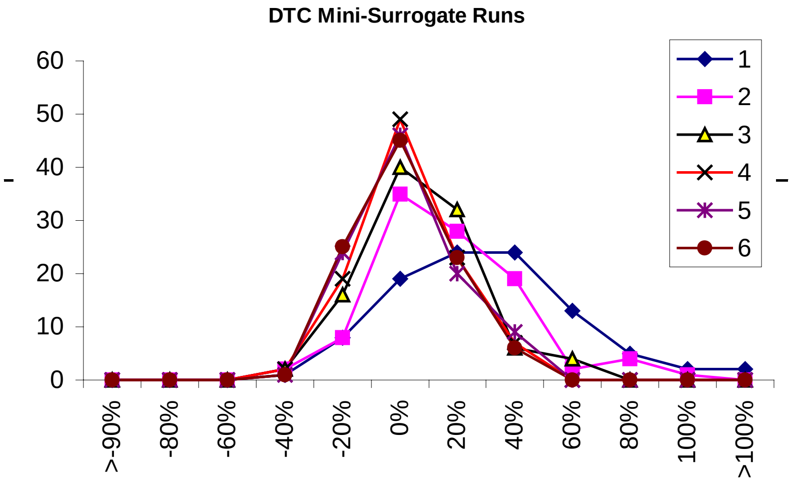


Figure B-86. Distribution plots of percentage errors of fits of calculated to experimental hourly $\Delta([O_3]-[NO])$ data for the eight hydrocarbon surrogate experiments carried out in the ITC.





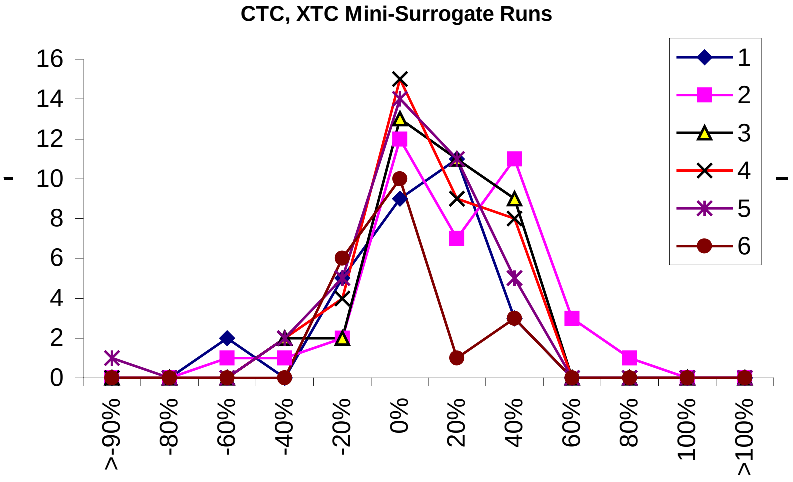


Figure B-87. Distribution plots of percentage errors of fits of calculated to experimental hourly $\Delta([O_3]-[NO])$ data for the base-case mini-surrogate experiments carried out in various chambers.

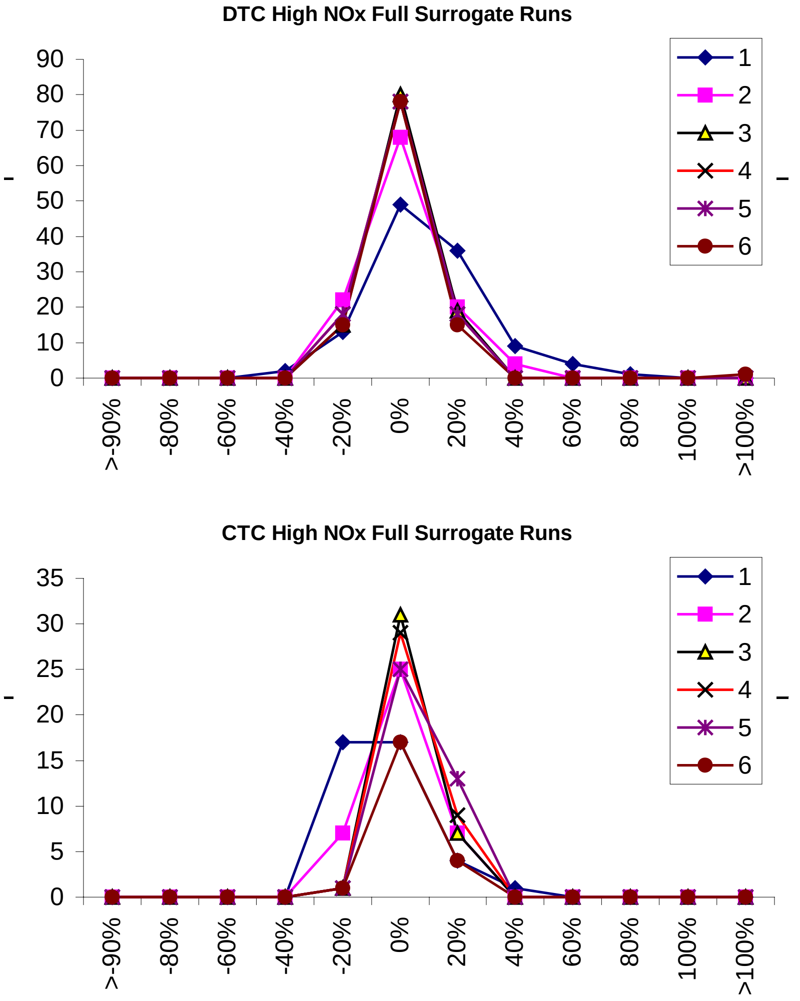
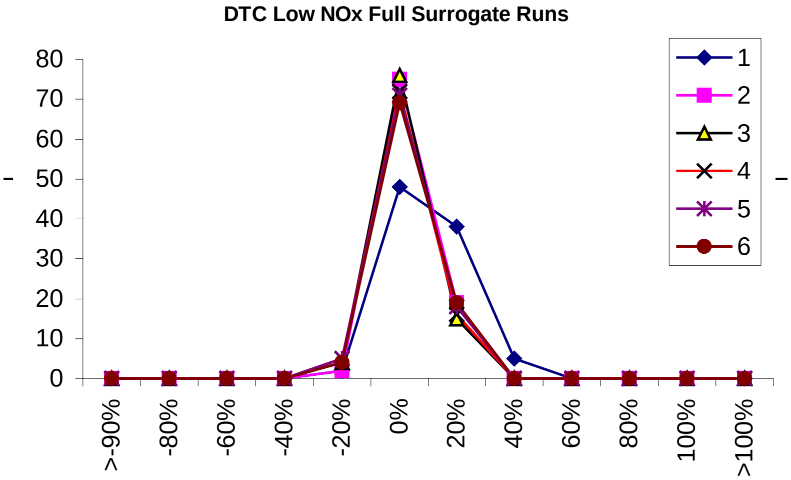


Figure B-88. Distribution plots of percentage errors of fits of calculated to experimental hourly Δ([O_3]-[NO]) data for the base-case high NO_x full surrogate experiments carried out in various chambers.



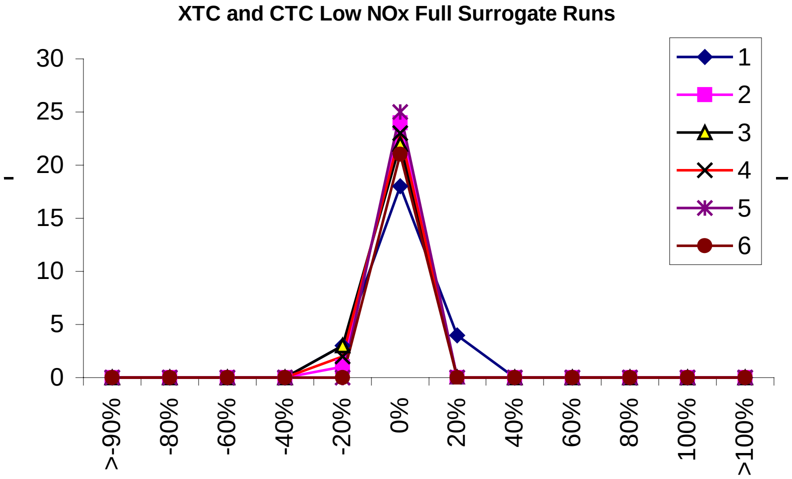


Figure B-89. Distribution plots of percentage errors of fits of calculated to experimental hourly $\Delta([O_3]-[NO])$ data for the base-case low NO_x full surrogate experiments.

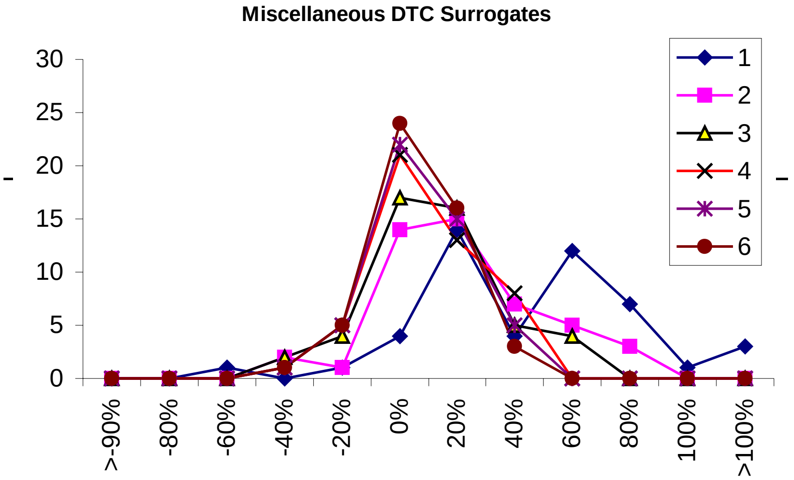


Figure B-90. Distribution plots of percentage errors of fits of calculated to experimental hourly Δ([O_3]-[NO]) data for the miscellaneous non-standard surrogates used in various incremental reactivity experiments in the DTC.

APPENDIX C.

LISTING OF DETAILED MODEL SPECIES AND REACTIVITIES

This Appendix contains a complete listing and summary of all the detailed model species that are represented in the current mechanism, and gives the calculated reactivity results and the uncertainty assignments. Table C-1 lists all the detailed model species, indicates how they are represented in the model, gives their uncertainty classification and experimental availability codes, and other documentation notes and comments. It also gives the updated MIR values, calculated as discussed in Section VII, and the upper limit MIR values, derived as discussed in Appendix D. The uncertainty codes used in this table are defined in Table C-2, the experimental availability codes are defined in Table C-3, and the text for the comments footnotes is given in Table C-4.

A summary of incremental and reactivity results using various scales in addition to MIR are given in Table C-5. The derivations of these scales are given in Section VII. This table includes averages of base case and adjusted NO_x reactivities calculated for the various 39 urban areas as discussed in Section VII. The reactivities calculated for the individual urban areas are given in Table C-6 and Table C-7, where the former has the O_3 yield reactivity data, and the latter has the reactivities relative to the maximum 8-hour average. Because of their length, they are not included with the printed (or PDF) version of this report, but are available as supplementary material as Excel-97 files. They can be downloaded from a FTP site linked to http://cert.ucr.edu/~carter/reactdat.htm

Table C-1 Listing of detailed model species, their representation in the model, atmospheric reactivity estimates, and uncertainty assignments.

Name	Desctiption	MWt	Unc [a]	Exp [b]	Notes [c]	MIR [d]	UL MIR [e]	Representation in Model [f]		Lump Gp. [g]
CO	Carbon Monoxide	28.01	1	1	1,2	0.066	(0.42)	Expl		CO
METHANE	Methane	16.04	1	4	1	0.0153	(0.024)	Asn'd		CH4
ETHANE	Ethane	30.07	1	2	1,2	0.35	(0.97)	Gen'd	CH3-CH3	ALK1
PROPANE	Propane	44.10	1	2	1,2,3	0.64	(2.95)	Gen'd	CH3-CH2-CH3	ALK2
N-C4	n-Butane	58.12	1	1	1,2,3	1.48	(4.49)	Gen'd	CH3-CH2-CH2-CH3	ALK3
N-C5	n-Pentane	72.15	1	7	3	1.77	(5.39)	Gen'd	CH3-CH2-CH2-CH2-CH3	ALK4
N-C6	n-Hexane	86.18	2	2	2,3	1.71	(5.65)	Gen'd	CH3-CH2-CH2-CH2-CH2-CH3	ALK4
N-C7	n-Heptane	100.21	2	-	3	1.48	(5.77)	Gen'd	CH3-CH2-CH2-CH2-CH2-CH2-CH3	ALK5
N-C8	n-Octane	114.23	2	1	2,3	1.28	(5.75)	Gen'd	CH3-CH2-CH2-CH2-CH2-CH2-CH2-CH3	ALK5
N-C9	n-Nonane	128.26	3a	7	3	1.10	(5.52)	Gen'd	CH3-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH3	ALK5
N-C10	n-Decane	142.29	3a	-	3	0.97	(5.26)	Gen'd	CH3-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH3	ALK5
N-C11	n-Undecane	156.31	3a	-	3	0.88	(5.10)	Gen'd	CH3-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH3	ALK5
N-C12	n-Dodecane	170.34	3a	1	2,3	0.81	(4.84)	Gen'd	CH3-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH3	ALK5
N-C13	n-Tridecane	184.37	3a	-	3	0.77	(4.74)	Gen'd	CH3-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH3	ALK5
N-C14	n-Tetradecane	198.40	3a	1	2,3	0.73	(4.61)	Gen'd	CH3-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH3	ALK5
N-C15	n-Pentadecane	212.42	3a	1	2,3	0.70	(4.54)	Gen'd	CH3-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH3	ALK5
N-C16	n-C16	226.45	3a	1	2,3	0.67	(4.38)	Gen'd	CH3-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH3	ALK5
N-C17	n-C17	240.46	3a			0.63	(4.11)	L.Mol	N-C16	
N-C18	n-C18	254.49	3a			0.59	(3.90)	L.Mol	N-C16	
N-C19	n-C19	268.51	3a			0.56	(3.70)	L.Mol	N-C16	
N-C20	n-C20	282.54	3a			0.54	(3.50)	L.Mol	N-C16	
N-C21	n-C21	296.57	3a			0.51	(3.34)	L.Mol	N-C16	
N-C22	n-C22	310.59	3a			0.49	(3.19)	L.Mol	N-C16	
2-ME-C3	Isobutane	58.12	1	2	2,3,4	1.48	(4.06)	Gen'd	CH3-CH(CH3)-CH3	ALK3
2-ME-C4	Iso-Pentane	72.15	2	7	3	1.87	(5.02)	Gen'd	CH3-CH(CH3)-CH2-CH3	ALK4
22-DM-C3	Neopentane	72.15	2	7	3	0.77	(1.39)	Gen'd	CH3-C(CH3)(CH3)-CH3	ALK2
2-ME-C5	2-Methyl Pentane	86.18	2	-	3	2.02	(5.51)	Gen'd	CH3-CH(CH3)-CH2-CH2-CH3	ALK4
3-ME-C5	3-Methylpentane	86.18	2	-	3	2.33	(5.61)	Gen'd	CH3-CH2-CH(CH3)-CH2-CH3	ALK4
23-DM-C4	2,3-Dimethyl Butane	86.18	2	7	3	1.28	(5.88)	Gen'd	CH3-CH(CH3)-CH(CH3)-CH3	ALK4
22-DM-C4	2,2-Dimethyl Butane	86.18	2	-	3	1.45	(2.93)	Gen'd	CH3-C(CH3)(CH3)-CH2-CH3	ALK3
22-DM-C5	2,2-Dimethyl Pentane	100.21	2	-	3	1.45	(3.39)	Gen'd	CH3-C(CH3)(CH3)-CH2-CH2-CH3	ALK3

Table C-1 (continued)

Name	Desctiption	MWt	Unc [a]	Exp [b]	Notes [c]	MIR [d]	UL MIR [e]		Representation [f]	Lump Gp. [g]
33-DM-C5	3,3-Dimethyl Pentane	100.21	2	-	3	1.51	(5.16)	Gen'd	CH3-CH2-C(CH3)(CH3)-CH2-CH3	ALK3
23-DM-C5	2,3-Dimethyl Pentane	100.21	2	-	3	1.75	(8.35)	Gen'd	CH3-CH(CH3)-CH(CH3)-CH2-CH3	ALK5
3-ME-C6	3-Methyl Hexane	100.21	2	-	3	2.10	(8.35)	Gen'd	CH3-CH2-CH(CH3)-CH2-CH2-CH3	ALK5
24-DM-C5	2,4-Dimethyl Pentane	100.21	2	-	3	1.90	(4.56)	Gen'd	CH3-CH(CH3)-CH2-CH(CH3)-CH3	ALK4
2-ME-C6	2-Methyl Hexane	100.21	2	-	3	1.74	(8.22)	Gen'd	CH3-CH(CH3)-CH2-CH2-CH2-CH3	ALK5
223TM-C4	2,2,3-Trimethyl Butane	100.21	2	-	3	1.47	(4.06)	Gen'd	CH3-C(CH3)(CH3)-CH(CH3)-CH3	ALK4
2233M-C4	2,2,3,3-Tetrame. Butane	114.23	3	-	3	0.49	(1.07)	Gen'd	CH3-C(CH3)(CH3)-C(CH3)(CH3)-CH3	ALK2
23-DM-C6	2,3-Dimethyl Hexane	114.23	3	-	3	1.62	(7.87)	Gen'd	CH3-CH(CH3)-CH(CH3)-CH2-CH2-CH3	ALK5
224TM-C5	2,2,4-Trimethyl Pentane	114.23	1	2	2,3,4	1.59	(3.11)	Gen'd	CH3-C(CH3)(CH3)-CH2-CH(CH3)-CH3	ALK4
24-DM-C6	2,4-Dimethyl Hexane	114.23	3	-	3	2.13	(7.87)	Gen'd	CH3-CH(CH3)-CH2-CH(CH3)-CH2-CH3	ALK5
234TM-C5	2,3,4-Trimethyl Pentane	114.23	3	-	3	1.42	(5.08)	Gen'd	CH3-CH(CH3)-CH(CH3)-CH(CH3)-CH3	ALK5
3-ME-C7	3-Methyl Heptane	114.23	3	-	3	1.66	(7.87)	Gen'd	CH3-CH2-CH(CH3)-CH2-CH2-CH2-CH3	ALK5
2-ME-C7	2-Methyl Heptane	114.23	3	-	3	1.46	(7.77)	Gen'd	CH3-CH(CH3)-CH2-CH2-CH2-CH2-CH3	ALK5
25-DM-C6	2,5-Dimethyl Hexane	114.23	3	-	3	1.90	(7.77)	Gen'd	CH3-CH(CH3)-CH2-CH2-CH(CH3)-CH3	ALK5
4-ME-C7	4-Methyl Heptane	114.23	3	-	3	1.67	(7.87)	Gen'd	CH3-CH2-CH2-CH(CH3)-CH2-CH2-CH3	ALK5
22-DM-C6	2,2-Dimethyl Hexane	114.23	3	-	3	1.34	(3.87)	Gen'd	CH3-C(CH3)(CH3)-CH2-CH2-CH2-CH3	ALK4
235TM-C6	2,3,5-Trimethyl Hexane	128.26	3	-	3	1.47	(4.82)	Gen'd	CH3-CH(CH3)-CH(CH3)-CH2-CH(CH3)-CH3	ALK5
33-DE-C5	3,3-Diethyl Pentane	128.26	3	-	3	1.55	(3.50)	Gen'd	CH3-CH2-C(CH2-CH3)(CH2-CH3)-CH2-CH3	ALK4
4-ET-C7	4-Ethyl Heptane	128.26	3	-	3	1.63	(7.48)	Gen'd	CH3-CH2-CH2-CH(CH2-CH3)-CH2-CH2-CH3	ALK5
2-ME-C8	2-Methyl Octane	128.26	3	-	3	1.15	(5.52)	Gen'd	CH3-CH(CH3)-CH2-CH2-CH2-CH2-CH2-CH3	ALK5
225TM-C6	2,2,5-Trimethyl Hexane	128.26	3	-	3	1.47	(6.06)	Gen'd	CH3-C(CH3)(CH3)-CH2-CH2-CH(CH3)-CH3	ALK4
4-ME-C8	4-Methyl Octane	128.26	3	-	3	1.31	(5.42)	Gen'd	CH3-CH2-CH2-CH(CH3)-CH2-CH2-CH2-CH3	ALK5
35-DM-C7	3,5-Dimethyl Heptane	128.26	3	-	3	2.03	(7.44)	Gen'd	CH3-CH2-CH(CH3)-CH2-CH(CH3)-CH2-CH3	ALK5
24-DM-C7	2,4-Dimethyl Heptane	128.26	3	-	3	1.75	(7.38)	Gen'd	CH3-CH(CH3)-CH2-CH(CH3)-CH2-CH2-CH3	ALK5
3-ME-C9	3-Methyl Nonane	142.29	3	-	3	1.05	(6.95)	Gen'd	CH3-CH2-CH(CH3)-CH2-CH2-CH2-CH2-CH2-CH3	ALK5
26DM-C8	2,6-Dimethyl Octane	142.29	1	1	2,3	1.44	(5.63)	Gen'd	CH3-CH(CH3)-CH2-CH2-CH2-CH(CH3)-CH2-CH3	ALK5
4-PR-C7	4-Propyl Heptane	142.29	3	-	3	1.37	(7.02)	Gen'd	CH3-CH2-CH2-CH(CH2-CH2-CH3)-CH2-CH2-CH3	ALK5
4-ME-C9	4-Methyl Nonane	142.29	3	-	3	1.18	(6.95)	Gen'd	CH3-CH2-CH2-CH(CH3)-CH2-CH2-CH2-CH2-CH3	ALK5
24-DM-C8	2,4-Dimethyl Octane	142.29	3	-	3	1.35	(6.95)	Gen'd	CH3-CH(CH3)-CH2-CH(CH3)-CH2-CH2-CH2-CH3	ALK5
2-ME-C9	2-Methyl Nonane	142.29	1	1	2,3	1.02	(5.60)	Gen'd	CH3-CH(CH3)-CH2-CH2-CH2-CH2-CH2-CH2-CH3	ALK5
34-DE-C6	3,4-Diethyl Hexane	142.29	2	1a	2,3	1.36	(4.18)	Gen'd	CH3-CH2-CH(CH2-CH3)-CH(CH2-CH3)-CH2-CH3	ALK5
3-ME-C10	3-Methyl Decane	156.31	3	-	3	0.91	(6.55)	Gen'd	CH3-CH2-CH(CH3)-CH2-CH2-CH2-CH2-CH2-CH2-CH3	ALK5

Table C-1 (continued)

Name	Desctiption	MWt	Unc [a]	Exp [b]	Notes [c]	MIR [d]	UL MIR [e]		Representation [f]	Lump Gp. [g]
4-ME-C10	4-Methyl Decane	156.31	3	-	3	0.95	(6.55)	Gen’d	CH3-CH2-CH2-CH(CH3)-CH2-CH2-CH2-CH2-CH2-CH3	ALK5
26DM-C9	2,6-Dimethyl Nonane	156.31	3	-	3	1.09	(6.55)	Gen’d	CH3-CH(CH3)-CH2-CH2-CH2-CH(CH3)-CH2-CH2-CH3	ALK5
35-DE-C7	3,5-Diethyl Heptane	156.31	3	-	3	1.46	(6.69)	Gen’d	CH3-CH2-CH(CH2-CH3)-CH2-CH(CH2-CH3)-CH2-CH3	ALK5
3-ME-C11	3-Methyl Undecane	170.34	3	-	3	0.83	(6.19)	Gen’d	CH3-CH2-CH(CH3)-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH3	ALK5
5-ME-C11	5-Methyl Undecane	170.34	3	-	3	0.87	(6.19)	Gen’d	CH3-CH2-CH2-CH2-CH(CH3)-CH2-CH2-CH2-CH2-CH2-CH3	ALK5
36DM-C10	3,6-Dimethyl Decane	170.34	3	-	3	1.03	(6.22)	Gen’d	CH3-CH2-CH(CH3)-CH2-CH2-CH(CH3)-CH2-CH2-CH2-CH3	ALK5
36-DE-C8	2,6-Diethyl Octane	170.34	3	-	3	1.28	(6.29)	Gen’d	CH3-CH2-CH(CH2-CH3)-CH2-CH2-CH(CH2-CH3)-CH2-CH3	ALK5
3-ME-C12	3-Methyl Dodecane	184.37	3	-	3	0.77	(5.86)	Gen’d	CH3-CH2-CH(CH3)-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH3	ALK5
5-ME-C12	5-Methyl Dodecane	184.37	3	-	3	0.79	(5.86)	Gen’d	CH3-CH2-CH2-CH2-CH(CH3)-CH2-CH2-CH2-CH2-CH2-CH2-CH3	ALK5
36DM-C11	3,6-Dimethyl Undecane	184.37	3	-	3	0.95	(5.89)	Gen’d	CH3-CH2-CH(CH3)-CH2-CH2-CH(CH3)-CH2-CH2-CH2-CH2-CH3	ALK5
37-DE-C9	3,7-Diethyl Nonane	184.37	3	-	3	1.17	(5.96)	Gen’d	CH3-CH2-CH(CH2-CH3)-CH2-CH2-CH2-CH(CH2-CH3)-CH2-CH3	ALK5
3-ME-C13	3-Methyl Tridecane	198.40	3	-	3	0.72	(5.56)	Gen’d	CH3-CH2-CH(CH3)-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH3	ALK5
6-ME-C13	6-Methyl Tridecane	198.40	3	-	3	0.75	(5.56)	Gen’d	CH3-CH2-CH2-CH2-CH2-CH(CH3)-CH2-CH2-CH2-CH2-CH2-CH2-CH3	ALK5
37DM-C12	3,7-Dimethyl Dodecane	198.40	3	-	3	0.86	(5.59)	Gen’d	CH3-CH2-CH(CH3)-CH2-CH2-CH2-CH(CH3)-CH2-CH2-CH2-CH2-CH3	ALK5
38DE-C10	3,8-Diethyl Decane	198.40	3	-	3	0.77	(5.66)	Gen’d	CH3-CH2-CH(CH2-CH3)-CH2-CH2-CH2-CH2-CH(CH2-CH3)-CH2-CH3	ALK5
3-ME-C14	3-Methyl Tetradecane	212.42	3	-	3	0.68	(5.29)	Gen’d	CH3-CH2-CH(CH3)-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH3	ALK5
6-ME-C14	6-Methyl Tetradecane	212.42	3	-	3	0.71	(5.29)	Gen’d	CH3-CH2-CH2-CH2-CH2-CH(CH3)-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH3	ALK5
37DM-C13	3,7-Dimethyl Tridecane	212.42	3	-	3	0.77	(5.32)	Gen’d	CH3-CH2-CH(CH3)-CH2-CH2-CH2-CH(CH3)-CH2-CH2-CH2-CH2-CH2-CH3	ALK5
39DE-C11	3,9-Diethyl Undecane	212.42	3	-	3	0.72	(5.39)	Gen’d	CH3-CH2-CH(CH2-CH3)-CH2-CH2-CH2-CH2-CH2-CH(CH2-CH3)-CH2-CH3	ALK5
3-ME-C15	3-Methyl Pentadecane	226.45	3	-	3	0.64	(5.05)	Gen’d	CH3-CH2-CH(CH3)-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH3	ALK5
7-ME-C15	7-Methyl Pentadecane	226.45	3	-	3	0.65	(5.05)	Gen’d	CH3-CH2-CH2-CH2-CH2-CH2-CH(CH3)-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH3	ALK5
48DM-C14	4,8-Dimethyl Tetradecane	226.45	3	-	3	0.69	(5.09)	Gen’d	CH3-CH2-CH2-CH(CH3)-CH2-CH2-CH2-CH(CH3)-CH2-CH2-CH2-CH2-CH2-CH3	ALK5
BR-C5	Branched C5 Alkanes	72.15	3	-	5	1.87	(5.02)	L.Mol	2-ME-C4	
BR-C6	Branched C6 Alkanes	86.18	3	6	5	1.73	(5.72)	L.Mol	0.5 23-DM-C4 +0.25 3-ME-C5 +0.25 2-ME-C5	
BR-C7	Branched C7 Alkanes	100.21	3	-	5	1.91	(6.40)	L.Mol	0.5 24-DM-C5 +0.25 3-ME-C6 +0.25 2-ME-C6	
BR-C8	Branched C8 Alkanes	114.23	3	-	5	1.85	(7.83)	L.Mol	0.5 24-DM-C6 +0.25 4-ME-C7 +0.25 2-ME-C7	
BR-C9	Branched C9 Alkanes	128.26	3	-	5	1.49	(6.43)	L.Mol	0.5 24-DM-C7 +0.25 4-ME-C8 +0.25 2-ME-C8	
BR-C10	Branched C10 Alkanes	142.29	3	6	5,6	1.27	(5.94)	L.Mol	0.5 26DM-C8 +0.25 4-ME-C9 +0.25 2-ME-C9	
BR-C11	Branched C11 alkanes	156.31	3	-	5,6	1.01	(6.55)	L.Mol	0.5 26DM-C9 +0.25 4-ME-C10 +0.25 3-ME-C10	
BR-C12	Branched C12 Alkanes	170.34	3	-	5,6	0.94	(6.22)	L.Mol	0.5 36DM-C10 +0.25 5-ME-C11 +0.25 3-ME-C11	
BR-C13	Branched C13 Alkanes	184.37	3	-	5,6	0.86	(5.89)	L.Mol	0.5 36DM-C11 +0.25 5-ME-C12 +0.25 3-ME-C12	
BR-C14	Branched C14 Alkanes	198.39	3	-	5,6	0.80	(5.59)	L.Mol	0.5 37DM-C12 +0.25 6-ME-C13 +0.25 3-ME-C13	

Table C-1 (continued)

Name	Desctiption	MWt	Unc [a]	Exp [b]	Notes [c]	MIR [d]	UL MIR [e]		Representation [f]	Lump Gp. [g]
BR-C15	Branched C15 Alkanes	212.42	3	-	5,6	0.73	(5.32)	L.Mol	0.5 37DM-C13 +0.25 6-ME-C14 +0.25 3-ME-C14	
BR-C16	Branched C16 Alkanes	226.44	3	-	5	0.67	(5.09)	L.Mol	0.5 48DM-C14 +0.25 7-ME-C15 +0.25 3-ME-C15	
BR-C17	Branched C17 Alkanes	240.46	3	-	5	0.63	(4.79)	L.Mol	BR-C16	
BR-C18	Branched C18 Alkanes	254.49	3	-	5	0.59	(4.52)	L.Mol	BR-C16	
CYCC3	Cyclopropane	42.08	3	-	3	0.112	(0.24)	Gen’d	*CH2-CH2-CH2-*	ALK1
CYCC4	Cyclobutane	56.11	3	-	3	1.21	(2.98)	Gen’d	*CH2-CH2-CH2-CH2-*	ALK2
CYCC5	Cyclopentane	70.14	2	-	3	2.65	(6.57)	Gen’d	*CH2-CH2-CH2-CH2-CH2-*	ALK4
IPR-CC3	Isopropyl Cyclopropane	84.16	3	-	3	1.66	(3.34)	Gen’d	*CH(CH(CH3)-CH3)-CH2-CH2-*	ALK3
ME-CYCC5	Methylcyclopentane	84.16	2	-	3	2.46	(8.97)	Gen’d	*CH(CH3)-CH2-CH2-CH2-CH2-*	ALK4
CYCC6	Cyclohexane	84.16	1	1	2,3	2.02	(6.98)	Gen’d	*CH2-CH2-CH2-CH2-CH2-CH2-*	ALK5
CYCC7	Cycloheptane	98.19	3	-	3	2.40	(8.18)	Gen’d	*CH2-CH2-CH2-CH2-CH2-CH2-CH2-*	ALK5
13DMCYC5	1,3-Dimeth. Cyclopentane	98.19	3	-	3	2.24	(8.35)	Gen’d	*CH(CH3)-CH2-CH(CH3)-CH2-CH2-*	ALK5
ME-CYCC6	Methylcyclohexane	98.19	3	7	3	2.09	(7.19)	Gen’d	*CH(CH3)-CH2-CH2-CH2-CH2-CH2-*	ALK5
ET-CYCC5	Ethyl Cyclopentane	98.19	3	-	3	2.36	(8.59)	Gen’d	*CH(CH2-CH3)-CH2-CH2-CH2-CH2-*	ALK5
CYCC8	Cyclooctane	112.22	3	-	3	1.83	(7.39)	Gen’d	*CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-*	ALK5
PR-CYCC5	Propyl Cyclopentane	112.22	3	-	3	2.00	(8.04)	Gen’d	*CH(CH2-CH2-CH3)-CH2-CH2-CH2-CH2-*	ALK5
13DMCYC6	1,3-Dimethyl Cyclohexane	112.22	3	-	3	1.82	(8.93)	Gen’d	*CH(CH3)-CH2-CH(CH3)-CH2-CH2-CH2-*	ALK5
ET-CYCC6	Ethylcyclohexane	112.22	3	-	3	1.95	(8.93)	Gen’d	*CH(CH2-CH3)-CH2-CH2-CH2-CH2-CH2-*	ALK5
113MCYC6	1,1,3-Trimethyl Cyclohex.	126.24	3	-	3	1.53	(5.20)	Gen’d	*C(CH3)(CH3)-CH2-CH(CH3)-CH2-CH2-CH2-*	ALK5
1E4MCYC6	1-Eth.-4-Meth. Cyclohex.	126.24	3	-	3	1.74	(8.25)	Gen’d	*CH(CH2-CH3)-CH2-CH2-CH(CH3)-CH2-CH2-*	ALK5
C3-CYCC6	Propyl Cyclohexane	126.24	3	-	3	1.71	(8.21)	Gen’d	*CH(CH2-CH2-CH3)-CH2-CH2-CH2-CH2-CH2-*	ALK5
C4-CYCC6	Butyl Cyclohexane	140.27	3	-	3	1.33	(7.60)	Gen’d	*CH(CH2-CH2-CH2-CH3)-CH2-CH2-CH2-CH2-CH2-*	ALK5
1M3IPCY6	1-Meth.-3-Isopr. Cyclohex.	140.27	3	-	3	1.38	(7.63)	Gen’d	*CH(CH(CH3)-CH3)-CH2-CH(CH3)-CH2-CH2-CH2-*	ALK5
14DECYC6	1,4-Diethyl-Cyclohexane	140.27	3	-	3	1.62	(7.70)	Gen’d	*CH(CH2-CH3)-CH2-CH2-CH(CH2-CH3)-CH2-CH2-*	ALK5
13DECYC6	1,3-Diethyl-Cyclohexane	140.27	3	-	3	1.45	(7.70)	Gen’d	*CH(CH2-CH3)-CH2-CH(CH2-CH3)-CH2-CH2-CH2-*	ALK5
C5-CYCC6	Pentyl Cyclohexane	154.30	3	-	3	1.14	(7.08)	Gen’d	*CH(CH2-CH2-CH2-CH2-CH3)-CH2-CH2-CH2-CH2-CH2-*	ALK5
1E2PCYC6	1-Ethyl-2-Propyl Cyclohex.	154.30	3	-	3	1.11	(7.15)	Gen’d	*CH(CH2-CH3)-CH(CH2-CH2-CH3)-CH2-CH2-CH2-CH2-*	ALK5
13E5MCC6	13-Dieth-5-Me. Cyclohex.	154.30	3	-	3	1.28	(7.19)	Gen’d	*CH(CH2-CH3)-CH2-CH(CH2-CH3)-CH2-CH(CH3)-CH2-*	ALK5
1M4C5CY6	1-Meth.-4-Pentyl Cyclohex.	168.33	3	-	3	1.00	(6.64)	Gen’d	*CH(CH2-CH2-CH2-CH2-CH3)-CH2-CH2-CH(CH3)-CH2-CH2-*	ALK5
135ECYC6	1,3,5-Triethyl Cyclohex.	168.33	3	-	3	1.20	(6.74)	Gen’d	*CH(CH2-CH3)-CH2-CH(CH2-CH3)-CH2-CH(CH2-CH3)-CH2-*	ALK5
C6-CYCC6	Hexyl Cyclohexane	168.33	1	1	2,3	0.94	(5.41)	Gen’d	*CH(CH2-CH2-CH2-CH2-CH2-CH3)-CH2-CH2-CH2-CH2-CH2-*	ALK5
1M2C6CC6	1-Meth.-2-Hexyl-Cyclohex.	182.35	3	-	3	0.86	(6.26)	Gen’d	*CH(CH2-CH2-CH2-CH2-CH2-CH3)-CH(CH3)-CH2-CH2-CH2-CH2-*	ALK5

Table C-1 (continued)

Name	Desctiption	MWt	Unc [a]	Exp [b]	Notes [c]	MIR [d]	UL MIR [e]		Representation [f]	Lump Gp. [g]
13E5PCC6	13-Dieth-5-Pent Cyclohx.	182.35	3	-	3	1.14	(6.33)	Gen'd	*CH(CH2-CH2-CH3)-CH2-CH(CH2-CH3)-CH2-CH(CH2-CH3)-CH2-*	ALK5
C7-CYCC6	Heptyl Cyclohexane	182.35	3	-	3	0.84	(6.23)	Gen'd	*CH(CH2-CH2-CH2-CH2-CH2-CH2-CH3)-CH2-CH2-CH2-CH2-CH2-*	ALK5
1M4C7CC6	1-Meth.-4-Heptyl Cyclohex.	196.38	3	-	3	0.75	(5.89)	Gen'd	*CH(CH2-CH2-CH2-CH2-CH2-CH2-CH3)-CH2-CH2-CH(CH3)-CH2-CH2-*	ALK5
13P5ECC6	13-Diprop-5-Eth Cyclohx.	196.38	3	-	3	1.09	(5.95)	Gen'd	*CH(CH2-CH3)-CH2-CH(CH2-CH2-CH3)-CH2-CH(CH2-CH2-CH3)-CH2-*	ALK5
C8-CYCC6	Octyl Cyclohexane	196.38	1	1	2,3	0.78	(5.89)	Gen'd	*CH(CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH3)-CH2-CH2-CH2-CH2-CH2-*	ALK5
1M2C8CC6	1-Methyl-2-Octyl Cyclohex.	210.41	3	-	3	0.73	(5.58)	Gen'd	*CH(CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH3)-CH(CH3)-CH2-CH2-CH2-CH2-*	ALK5
135PCYC6	135-Tripropyl Cyclohex.	210.41	3	-	3	1.05	(5.65)	Gen'd	*CH(CH2-CH2-CH3)-CH2-CH(CH2-CH2-CH3)-CH2-CH(CH2-CH2-CH3)-CH2-*	ALK5
C9-CYCC6	Nonyl Cyclohexane	210.41	3	-	3	0.73	(5.58)	Gen'd	*CH(CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH3)-CH2-CH2-CH2-CH2-CH2-*	ALK5
13P5BCC6	1,3-Prop.-5-Butyl Cyclohex.	224.43	3	-	3	0.93	(5.34)	Gen'd	*CH(CH2-CH2-CH2-CH3)-CH2-CH(CH2-CH2-CH3)-CH2-CH(CH2-CH2-CH3)-CH2-*	ALK5
C10CYCC6	Decyl Cyclohexane	224.43	3	-	3	0.69	(5.27)	Gen'd	*CH(CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH3)-CH2-CH2-CH2-CH2-CH2-*	ALK5
1M4C9CY6	1-Methyl-4-Nonyl Cyclohex.	224.43	3	-	3	0.66	(5.30)	Gen'd	*CH(CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH3)-CH2-CH2-CH(CH3)-CH2-CH2-*	ALK5
CYC-C6	C6 Cycloalkanes	84.16	1	6	5	2.02	(6.98)	L.Mol	CYCC6	
CYC-C7	C7 Cycloalkanes	98.19	3	-	5	2.09	(7.19)	L.Mol	ME-CYCC6	
CYC-C8	C8 Cycloalkanes	112.22	3	-	5	1.95	(8.93)	L.Mol	ET-CYCC6	
BCYC-C9	C9 Bicycloalkanes	124.23	3	-	5	1.75	(8.38)	L.Mol	0.5 C3-CYCC6 +0.5 1E4MCYC6	
CYC-C9	C9 Cycloalkanes	126.24	3	-	5	1.72	(8.25)	L.Mol	0.5 C3-CYCC6 +0.5 1E4MCYC6	
BCYC-C10	C10 Bicycloalkanes	138.25	3	-	5	1.46	(7.74)	L.Mol	0.34 C4-CYCC6 +0.33 1M3IPCY6 +0.33 14DECYC6	
CYC-C10	C10 Cycloalkanes	140.27	3	?	5,6	1.44	(7.63)	L.Mol	0.34 C4-CYCC6 +0.33 1M3IPCY6 +0.33 14DECYC6	
BCYC-C11	C11 Bicycloalkanes	152.28	3	-	5	1.19	(7.21)	L.Mol	0.34 C5-CYCC6 +0.33 13E5MCC6 +0.33 1E2PCYC6	
CYC-C11	C11 Cycloalkanes	154.30	3	-	5,6	1.18	(7.12)	L.Mol	0.34 C5-CYCC6 +0.33 13E5MCC6 +0.33 1E2PCYC6	
BCYC-C12	C12 Bicycloalkanes	166.30	3	-	5	1.06	(6.34)	L.Mol	0.34 C6-CYCC6 +0.33 135ECYC6 +0.33 1M4C5CY6	
CYC-C12	C12 Cycloalkanes	168.32	3	6	5,6	1.05	(6.26)	L.Mol	0.34 C6-CYCC6 +0.33 135ECYC6 +0.33 1M4C5CY6	
BCYC-C13	C13 Bicycloalkanes	180.33	3	-	5	0.96	(6.33)	L.Mol	0.34 C7-CYCC6 +0.33 13E5PCC6 +0.33 1M2C6CC6	
CYC-C13	C13 Cycloalkanes	182.35	3	-	5,6	0.95	(6.26)	L.Mol	0.34 C7-CYCC6 +0.33 13E5PCC6 +0.33 1M2C6CC6	
BCYC-C14	C14 Bicycloalkanes	194.36	3	6	5	0.88	(5.98)	L.Mol	0.34 C8-CYCC6 +0.33 13P5ECC6 +0.33 1M4C7CC6	
CYC-C14	C14 Cycloalkanes	196.38	3	-	5,6	0.87	(5.92)	L.Mol	0.34 C8-CYCC6 +0.33 13P5ECC6 +0.33 1M4C7CC6	
BCYC-C15	C15 Bicycloalkanes	208.39	3	-	5	0.85	(5.63)	L.Mol	0.34 C9-CYCC6 +0.33 135PCYC6 +0.33 1M2C8CC6	
CYC-C15	C15 Cycloalkanes	210.41	3	6	5,6	0.84	(5.58)	L.Mol	0.34 C9-CYCC6 +0.33 135PCYC6 +0.33 1M2C8CC6	
ETHENE	Ethene	28.05	1	1a	2,3	9.53	(17.21)	Gen'd	CH2=CH2	ETHE
PROPENE	Propene	42.08	1	1	2,3,4	12.19	(20.50)	Gen'd	CH2=CH-CH3	OLE1
1-BUTENE	1-Butene	56.11	2	3	2,3,4	10.91	(20.50)	Gen'd	CH2=CH-CH2-CH3	OLE1
3M-1-BUT	3-Methyl-1-Butene	70.14	3	-	3	7.72	(20.53)	Gen'd	CH2=CH-CH(CH3)-CH3	OLE1

Table C-1 (continued)

Name	Desctiption	MWt	Unc [a]	Exp [b]	Notes [c]	MIR [d]	UL MIR [e]		Representation [f]	Lump Gp. [g]
1-PENTEN	1-Pentene	70.14	2	-	3	8.00	(20.50)	Gen'd	CH2=CH-CH2-CH2-CH3	OLE1
1-HEXENE	1-Hexene	84.16	2	3	2,3,4	6.09	(18.24)	Gen'd	CH2=CH-CH2-CH2-CH2-CH3	OLE1
3M1-C5E	3-Methyl-1-Pentene	84.16	3	-	3	6.55	(18.24)	Gen'd	CH2=CH-CH(CH3)-CH2-CH3	OLE1
33M1-BUT	3,3-Dimethyl-1-Butene	84.16	3	-	3	6.46	(18.21)	Gen'd	CH2=CH-C(CH3)(CH3)-CH3	OLE1
4M1-C5E	4-Methyl-1-Pentene	84.16	3	-	3	6.21	(18.24)	Gen'd	CH2=CH-CH2-CH(CH3)-CH3	OLE1
1-HEPTEN	1-Heptene	98.19	3	-	3	4.49	(15.64)	Gen'd	CH2=CH-CH2-CH2-CH2-CH2-CH3	OLE1
1-OCTENE	1-Octene	112.22	4	-	3	3.42	13.69	Gen'd	CH2=CH-CH2-CH2-CH2-CH2-CH2-CH3	OLE1
1-C9E	1-Nonene	126.24	4	-	3	2.82	12.18	Gen'd	CH2=CH-CH2-CH2-CH2-CH2-CH2-CH2-CH3	OLE1
1-C10E	1-Decene	140.27	4	-	3	2.39	10.95	Gen'd	CH2=CH-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH3	OLE1
1-C11E	1-Undecene	154.30	4	-	3	2.09	9.96	Gen'd	CH2=CH-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH3	OLE1
1-C12E	1-Dodecene	168.33	4	-	3	1.87	9.14	Gen'd	CH2=CH-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH3	OLE1
1-C13E	1-Tridecene	182.35	4	-	3	1.70	8.42	Gen'd	CH2=CH-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH3	OLE1
1-C14E	1-Tetradecene	196.38	4	-	3	1.56	7.84	Gen'd	CH2=CH-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH3	OLE1
1-C15E	1-Pentadecene	210.41	4	-	3	1.45	7.29	Gen'd	CH2=CH-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH3	OLE1
C4-OLE1	C4 Terminal Alkenes	56.11	2			10.91	(20.50)	L.Mol	1-BUTENE	
C5-OLE1	C5 Terminal Alkenes	70.14	2			8.00	(20.50)	L.Mol	1-PENTEN	
C6-OLE1	C6 Terminal Alkenes	84.16	3			6.09	(18.24)	L.Mol	1-HEXENE	
C7-OLE1	C7 Terminal Alkenes	98.19	3			4.49	(15.64)	L.Mol	1-HEPTEN	
C8-OLE1	C8 Terminal Alkenes	112.22	4			3.42	13.69	L.Mol	1-OCTENE	
C9-OLE1	C9 Terminal Alkenes	126.24	4			2.82	12.18	L.Mol	1-C9E	
C10-OLE1	C10 Terminal Alkenes	140.27	4			2.39	10.95	L.Mol	1-C10E	
C11-OLE1	C11 Terminal Alkenes	154.30	4			2.09	9.96	L.Mol	1-C11E	
C12-OLE1	C12 Terminal Alkenes	168.32	4			1.87	9.14	L.Mol	1-C12E	
C13-OLE1	C13 Terminal Alkenes	182.35	4			1.70	8.42	L.Mol	1-C13E	
C14-OLE1	C14 Terminal Alkenes	196.38	4			1.56	7.84	L.Mol	1-C14E	
C15-OLE1	C15 Terminal Alkenes	210.41	4			1.45	7.29	L.Mol	1-C15E	
ISOBUTEN	Isobutene	56.11	1	2	2,3,4	6.59	(20.53)	Gen'd	CH2=C(CH3)-CH3	OLE2
2M-1-BUT	2-Methyl-1-Butene	70.14	3	-	3	6.78	(20.53)	Gen'd	CH2=C(CH3)-CH2-CH3	OLE2
23M1-BUT	23-Dimethyl-1-Butene	84.16	3	-	3	5.02	(18.24)	Gen'd	CH2=C(CH3)-CH(CH3)-CH3	OLE2
2E1-BUT	2-Ethyl-1-Butene	84.16	3	-	3	5.28	(18.24)	Gen'd	CH2=C(CH2-CH3)-CH2-CH3	OLE2
2M1-C5E	2-Methyl-1-Pentene	84.16	3	-	3	5.41	(18.24)	Gen'd	CH2=C(CH3)-CH2-CH2-CH3	OLE2
233M1BUT	2,3,3-trimethyl-1-Butene	98.19	3	-	3	4.94	(15.64)	Gen'd	CH2=C(CH3)-C(CH3)(CH3)-CH3	OLE2

Table C-1 (continued)

Name	Desctiption	MWt	Unc [a]	Exp [b]	Notes [c]	MIR [d]	UL MIR [e]		Representation [f]	Lump Gp. [g]
3M2I1C4E	3-Methyl-2-Isopropyl-1-Butene	112.22	4	-	3	4.29	13.69	Gen'd	CH2=C(CH(CH3)-CH3)-CH(CH3)-CH3	OLE2
T-2-BUTE	trans-2-Butene	56.11	1	1	2,3	14.51	(20.53)	Gen'd	CH3-CH=CH(CH3)	OLE2
C-2-BUTE	cis-2-Butene	56.11	1	7	3	13.81	(20.53)	Gen'd	CH3-CH=CH-CH3	OLE2
2M-2-BUT	2-Methyl-2-Butene	70.14	2	-	3	14.97	(20.53)	Gen'd	CH3-C(CH3)=CH-CH3	OLE2
T-2-PENT	trans-2-Pentene	70.14	2	-	3	10.86	(20.53)	Gen'd	CH3-CH=CH(CH2-CH3)	OLE2
C-2-PENT	cis-2-Pentene	70.14	2	-	3	10.86	(20.53)	Gen'd	CH3-CH=CH-CH2-CH3	OLE2
23M2-BUT	2,3-Dimethyl-2-Butene	84.16	3	-	3	13.90	(18.24)	Gen'd	CH3-C(CH3)=C{CH3}-CH3	OLE2
C3M2-C5E	Cis-3-Methyl-2-Hexene	84.16	3	-	3	13.40	(18.24)	Gen'd	CH3-CH=C(CH3)-CH2-CH3	OLE2
T3M2-C5E	Trans 3-Methyl-2-Hexene	84.16	3	-	3	14.13	(18.24)	Gen'd	CH3-CH=C{CH3}-CH2-CH3	OLE2
T4M2-C5E	Trans 4-Methyl-2-Hexene	84.16	3	-	3	8.57	(18.24)	Gen'd	CH3-CH(CH3)-CH=CH-CH3	OLE2
T-2-C6E	Trans-2-Hexene	84.16	3	-	3	8.69	(18.24)	Gen'd	CH3-CH=CH(CH2-CH2-CH3)	OLE2
T-3-C6E	Trans-3-Hexene	84.16	3	-	3	8.68	(18.24)	Gen'd	CH3-CH2-CH=CH(CH2-CH3)	OLE2
C-2-C6E	Cis-2-Hexene	84.16	3	-	3	8.69	(18.24)	Gen'd	CH3-CH=CH-CH2-CH2-CH3	OLE2
2M-2-C5E	2-Methyl-2-Pentene	84.16	3	-	3	12.40	(18.24)	Gen'd	CH3-C(CH3)=CH-CH2-CH3	OLE2
C-3-C6E	Cis-3-Hexene	84.16	3	-	3	8.74	(18.24)	Gen'd	CH3-CH2-CH=CH-CH2-CH3	OLE2
23M2-C5E	2,3-Dimethyl-2-Hexene	98.19	4	-	3	10.88	15.64	Gen'd	CH3-C(CH3)=C(CH3)-CH2-CH3	OLE2
T44M2C5E	Trans 4,4-dimethyl-2-Hexene	98.19	4	-	3	7.16	15.64	Gen'd	CH3-C(CH3)(CH3)-CH=CH-CH3	OLE2
C-3-C7E	Cis-3-Heptene	98.19	4	-	3	7.26	15.64	Gen'd	CH3-CH2-CH=CH-CH2-CH2-CH3	OLE2
T-3-C7E	Trans-3-Heptene	98.19	4	-	3	7.26	15.64	Gen'd	CH3-CH2-CH=CH(CH2-CH2-CH3)	OLE2
T-2-C7E	Trans-2-Heptene	98.19	4	-	3	7.10	15.64	Gen'd	CH3-CH=CH(CH2-CH2-CH2-CH3)	OLE2
T-3-C8E	Trans-3-Octene	112.22	4	-	3	5.97	13.69	Gen'd	CH3-CH2-CH=CH(CH2-CH2-CH2-CH3)	OLE2
C-4-C8E	Cis-4-Octene	112.22	4	-	3	6.06	13.69	Gen'd	CH3-CH2-CH2-CH=CH-CH2-CH2-CH3	OLE2
T-4-C8E	Trans-4-Octene	112.22	4	-	3	6.02	13.69	Gen'd	CH3-CH2-CH2-CH=CH(CH2-CH2-CH3)	OLE2
T25M3C6E	Trans 2,5-Dimethyl 3-Hexene	112.22	4	-	3	6.22	13.69	Gen'd	CH3-CH(CH3)-CH=CH(CH(CH3)-CH3)	OLE2
T22M3C6E	Trans 2,2-Dimethyl 3-Hexene	112.22	4	-	3	6.04	13.69	Gen'd	CH3-C(CH3)(CH3)-CH=CH(CH2-CH3)	OLE2
244M2C5E	2,4,4-trimethyl-2-Pentene	126.24	4	-	3	5.98	12.17	Gen'd	CH3-C(CH3)=CH-C(CH3)(CH3)-CH2-CH3	OLE2
T-4-C9E	Trans-4-Nonene	128.26	4	-	3	4.96	11.99	Gen'd	CH3-CH2-CH2-CH=CH(CH2-CH2-CH2-CH3)	OLE2
34E2-C6E	3,4-Diethyl-2-Hexene	140.27	4	-	3	3.86	10.95	Gen'd	CH3-CH=C(CH2-CH3)-CH(CH2-CH3)-CH2-CH3	OLE2

Table C-1 (continued)

Name	Desctiption	MWt	Unc [a]	Exp [b]	Notes [c]	MIR [d]	UL MIR [e]		Representation [f]	Lump Gp. [g]
C-5-C10E	Cis-5-Decene	140.27	4	-	3	4.30	10.95	Gen’d	CH3-CH2-CH2-CH2-CH=CH-CH2-CH2-CH2-CH3	OLE2
T-4-C10E	Trans-4-Decene	140.27	4	-	3	4.27	10.95	Gen’d	CH3-CH2-CH2-CH=CH(CH2-CH2-CH2-CH2-CH3)	OLE2
T-5-C11E	Trans-5-Undecene	154.30	4	-	3	3.73	9.96	Gen’d	CH3-CH2-CH2-CH2-CH=CH(CH2-CH2-CH2-CH2-CH3)	OLE2
T-5-C12E	Trans-5-Dodecene	168.33	4	-	3	3.37	9.14	Gen’d	CH3-CH2-CH2-CH2-CH=CH(CH2-CH2-CH2-CH2-CH2-CH3)	OLE2
T-5-C13E	Trans-5-Tridecene	182.35	4	-	3	3.09	8.42	Gen’d	CH3-CH2-CH2-CH2-CH=CH(CH2-CH2-CH2-CH2-CH2-CH2-CH3)	OLE2
T-5-C14E	Trans-5-Tetradecene	196.38	4	-	3	2.85	7.84	Gen’d	CH3-CH2-CH2-CH2-CH=CH(CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH3)	OLE2
T-5-C15E	Trans-5-Tetradecene	210.41	4	-	3	2.65	7.29	Gen’d	CH3-CH2-CH2-CH2-CH=CH(CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH3)	OLE2
2-C5-OLE	2-Pentenes	70.14	2			10.86	(20.53)	L.Mol	0.5 C-2-PENT +0.5 T-2-PENT	
2-C6-OLE	2-Hexenes	84.16	3			8.69	(18.24)	L.Mol	0.5 C-2-C6E +0.5 T-2-C6E	
2-C7-OLE	2-Heptenes	98.19	3			7.26	(15.64)	L.Mol	0.5 T-3-C7E +0.5 C-3-C7E	
3-C8-OLE	3-Octenes	112.22	4			5.97	13.69	L.Mol	T-3-C8E	
3-C9-OLE	3-Nonenes	126.24	4			5.04	12.18	L.Mol	T-4-C9E	
3C10-OLE	C10 3-Alkenes	140.27	4			4.27	10.95	L.Mol	T-4-C10E	
3C11-OLE	C11 3-Alkenes	154.30	4			3.73	9.96	L.Mol	T-5-C11E	
2C12-OLE	C12 2-Alkenes	168.32	4			3.37	9.14	L.Mol	T-5-C12E	
3C12-OLE	C12 3-Alkenes	168.32	4			3.37	9.14	L.Mol	T-5-C12E	
3C13-OLE	C13 3-Alkenes	182.35	4			3.09	8.42	L.Mol	T-5-C13E	
3C14-OLE	C14 3-Alkenes	196.38	4			2.85	7.84	L.Mol	T-5-C14E	
3C15-OLE	C15 3-Alkenes	210.41	4			2.65	7.29	L.Mol	T-5-C15E	
C4-OLE2	C4 Internal Alkenes	56.11	1			14.16	(20.53)	L.Mol	0.5 T-2-BUTE +0.5 C-2-BUTE	
C5-OLE2	C5 Internal Alkenes	70.14	3			10.86	(20.53)	L.Mol	0.5 C-2-PENT +0.5 T-2-PENT	
C6-OLE2	C6 Internal Alkenes	84.16	3			8.69	(18.24)	L.Mol	0.5 C-2-C6E +0.5 T-2-C6E	
C7-OLE2	C7 Internal Alkenes	98.19	3			7.26	(15.64)	L.Mol	T-3-C7E	
C8-OLE2	C8 Internal Alkenes	112.22	4			6.02	13.69	L.Mol	T-4-C8E	
C9-OLE2	C9 Internal Alkenes	126.24	4			5.04	12.18	L.Mol	T-4-C9E	
C10-OLE2	C10 Internal Alkenes	140.27	4			4.27	10.95	L.Mol	T-4-C10E	
C11-OLE2	C11 Internal Alkenes	154.30	4			3.73	9.96	L.Mol	T-5-C11E	
C12-OLE2	C12 Internal Alkenes	168.32	4			3.37	9.14	L.Mol	T-5-C12E	
C13-OLE2	C13 Internal Alkenes	182.35	4			3.09	8.42	L.Mol	T-5-C13E	
C14-OLE2	C14 Internal Alkenes	196.38	4			2.85	7.84	L.Mol	T-5-C14E	
C15-OLE2	C15 Internal Alkenes	210.41	4			2.65	7.29	L.Mol	T-5-C15E	
13-BUTDE	1,3-Butadiene	54.09	3	-	3	12.88	(21.30)	Gen’d	CH2=CH-CH=CH2	OLE2

Table C-1 (continued)

Name	Desctiption	MWt	Unc [a]	Exp [b]	Notes [c]	MIR [d]	UL MIR [e]		Representation [f]	Lump Gp. [g]
ISOPRENE	Isoprene	68.12	1	1	2,3,4	11.48	(21.14)	Gen'd	CH2=CH-C(CH3)=CH2	ISOP
CYC-PNTE	Cyclopentene	68.12	4	-	3	7.04	21.14	Gen'd	*CH=CH-CH2-CH2-CH2-*	OLE2
1M-CC5E	1-Methyl cyclohexene	82.15	4	-	3	12.33	17.53	Gen'd	*C(CH3)=CH-CH2-CH2-CH2-*	OLE2
CYC-HEXE	Cyclohexene	82.15	4	-	3	5.47	18.69	Gen'd	*CH=CH-CH2-CH2-CH2-CH2-*	OLE2
1M-CC6E	1-Methyl Cyclohexene	96.17	4	-	3	7.35	15.97	Gen'd	*C(CH3)=CH-CH2-CH2-CH2-CH2-*	OLE2
4M-CC6E	4-Methyl Cyclohexene	96.17	4	-	3	4.39	15.97	Gen'd	*CH(CH3)-CH2-CH=CH-CH2-CH2-*	OLE2
12M-CC6E	1,2-Dimethyl Cyclohexene	110.20	4	-	3	6.58	13.94	Gen'd	*C(CH3)=C(CH3)-CH2-CH2-CH2-CH2-*	OLE2
CYC-PNDE	Cyclopentadiene	66.10	5	-	7	7.25	21.79	L.Mol	CYC-PNTE	
C6-OL2D	C6 Cyclic or di-olefins	82.15	5b	-	5,7	8.90	18.69	L.Mol	0.5 C-2-C6E +0.5 T-2-C6E	
C7-OL2D	C7 Cyclic or di-olefins	96.18	5b	-	5,7	7.25	15.97	L.Mol	T-2-C7E	
C8-OL2D	C8 Cyclic or di-olefins	110.20	5b	-	5,7	6.13	13.94	L.Mol	T-4-C8E	
C9-OL2D	C9 Cyclic or di-olefins	124.23	5b	-	5,7	5.12	12.38	L.Mol	T-4-C9E	
C10-OL2D	C10 Cyclic or di-olefins	138.26	5b	-	5,7	4.34	11.11	L.Mol	T-4-C10E	
C11-OL2D	C11 Cyclic or di-olefins	152.29	5b	-	5,7	3.78	10.09	L.Mol	T-5-C11E	
C12-OL2D	C12 Cyclic or di-olefins	166.31	5b	-	5,7	3.41	9.25	L.Mol	T-5-C12E	
C13-OL2D	C13 Cyclic or di-olefins	180.34	5b	-	5,7	3.12	8.51	L.Mol	T-5-C13E	
C14-OL2D	C14 Cyclic or di-olefins	194.37	5b	-	5,7	2.88	7.92	L.Mol	T-5-C14E	
C15-OL2D	C15 Cyclic or di-olefins	208.39	5b	-	5,7	2.68	7.36	L.Mol	T-5-C15E	
A-PINENE	a-Pinene	136.24	2c	1	2,8	4.51	(11.27)	Trp		TRP1
B-PINENE	b-Pinene	136.24	3c	1a	2,8	3.58	(11.27)	Trp		TRP1
3-CARENE	3-Carene	136.24	2c	3	2,8	3.47	(11.27)	Trp		TRP1
SABINENE	Sabinene	136.24	2c	3	2,8	3.96	(11.27)	Trp		TRP1
D-LIMONE	d-Limonene	136.24	2c	3	2,8	4.25	(11.27)	Trp		TRP1
BENZENE	Benzene	78.11	3c	2	2,8	0.91	(4.31)	Asn'd		ARO1
TOLUENE	Toluene	92.14	2c	1	2,8	4.24	(11.56)	Asn'd		ARO1
C2-BENZ	Ethyl Benzene	106.17	2c	1	2,8	3.03	(10.96)	Asn'd		ARO1
N-C3-BEN	n-Propyl Benzene	120.20	3c	-	7	2.40	(8.91)	Asn'd		ARO1
I-C3-BEN	Isopropyl Benzene (cumene)	120.20	3c	-	7	2.53	(9.31)	Asn'd		ARO1
S-C4-BEN	s-Butyl Benzene	134.22	3c	-	7	2.15	(8.01)	Asn'd		ARO1
N-C4-BEN	n-Butyl Benzene	134.22	3c	-	7	2.15	(8.01)	L.Mol	N-C3-BEN	
M-XYLENE	m-Xylene	106.17	2c	1	2,8	11.04	(14.32)	Asn'd		ARO2

Table C-1 (continued)

Name	Desctiption	MWt	Unc [a]	Exp [b]	Notes [c]	MIR [d]	UL MIR [e]		Representation [f]	Lump Gp. [g]
O-XYLENE	o-Xylene	106.17	2c	1	2,8	7.87	(13.53)	Asn'd		ARO2
P-XYLENE	p-Xylene	106.17	2c	1	2,8	4.56	(13.64)	Asn'd		ARO2
124-TMB	1,2,4-Trimethyl Benzene	120.20	2c	2	2,8	7.57	(12.76)	Asn'd		ARO2
135-TMB	1,3,5-Trimethyl Benzene	120.20	2c	2	2,8	11.76	(12.79)	Asn'd		ARO2
123-TMB	1,2,3-Trimethyl Benzene	120.20	2c	2	2,8	11.74	(12.76)	Asn'd		ARO2
C9-BEN1	C9 Monosub. Benzenes	120.20	3c	-	7	2.40	(8.91)	L.Mol	N-C3-BEN	
C10-BEN1	C10 Monosub. Benzenes	134.22	3c	-	7	2.15	(8.01)	L.Mol	N-C3-BEN	
C11-BEN1	C11 Monosub. Benzenes	148.25	3c	-	7	1.94	(7.23)	L.Mol	N-C3-BEN	
C12-BEN1	C12 Monosub. Benzenes	162.28	3c	-	7	1.78	(6.60)	L.Mol	N-C3-BEN	
C13-BEN1	C13 Monosub. Benzenes	176.30	3c	-	7	1.63	(6.09)	L.Mol	N-C3-BEN	
C8-BEN2	C8 Disub. Benzenes	106.17	3b	6	5	7.86	(13.85)	L.Mol	0.34 M-XYLENE +0.33 O-XYLENE +0.33 P-XYLENE	
C9-BEN2	C9 Disub. Benzenes	120.20	3b	-	5	6.94	(12.22)	L.Mol	0.34 M-XYLENE +0.33 O-XYLENE +0.33 P-XYLENE	
C10-BEN2	C10 Disub. Benzenes	134.22	3b	-	5	6.22	(10.94)	L.Mol	0.34 M-XYLENE +0.33 O-XYLENE +0.33 P-XYLENE	
C11-BEN2	C11 Disub. Benzenes	148.25	3b	-	5	5.63	(9.90)	L.Mol	0.34 M-XYLENE +0.33 O-XYLENE +0.33 P-XYLENE	
C12-BEN2	C12 Disub. Benzenes	162.28	3b	-	5	5.14	(9.05)	L.Mol	0.34 M-XYLENE +0.33 O-XYLENE +0.33 P-XYLENE	
C13-BEN2	C13 Disub. Benzenes	176.30	3b	-	5	4.73	(8.32)	L.Mol	0.34 M-XYLENE +0.33 O-XYLENE +0.33 P-XYLENE	
C9-BEN3	C9 Trisub. Benzenes	120.20	3b	6	5	10.37	(12.76)	L.Mol	0.34 135-TMB +0.33 123-TMB +0.33 124-TMB	
C10-BEN3	C10 Trisub. Benzenes	134.22	3b	-	5	9.29	(11.44)	L.Mol	0.34 135-TMB +0.33 123-TMB +0.33 124-TMB	
C11-BEN3	C11 Trisub. Benzenes	148.25	3b	-	5	8.41	(10.36)	L.Mol	0.34 135-TMB +0.33 123-TMB +0.33 124-TMB	
C12-BEN3	C12 Trisub. Benzenes	162.28	3b	-	5	7.68	(9.44)	L.Mol	0.34 135-TMB +0.33 123-TMB +0.33 124-TMB	
C13-BEN3	C13 Trisub. Benzenes	176.30	3b	-	5	7.07	(8.71)	L.Mol	0.34 135-TMB +0.33 123-TMB +0.33 124-TMB	
C10-BEN4	C10 Tetrasub. Benzenes	134.22	4b	-	5	9.29	11.44	L.Mol	0.34 135-TMB +0.33 123-TMB +0.33 124-TMB	
C11-BEN4	C11 Tetrasub. Benzenes	148.25	4b	-	5	8.41	10.36	L.Mol	0.34 135-TMB +0.33 123-TMB +0.33 124-TMB	
C12-BEN4	C12 Tetrasub. Benzenes	162.28	4b	-	5	7.68	9.44	L.Mol	0.34 135-TMB +0.33 123-TMB +0.33 124-TMB	
C11-BEN5	C11 Pentasub. Benzenes	148.25	4b	-	5	8.41	10.36	L.Mol	0.34 135-TMB +0.33 123-TMB +0.33 124-TMB	
C12-BEN5	C11 Pentasub. Benzenes	162.28	4b	-	5	7.68	9.44	L.Mol	0.34 135-TMB +0.33 123-TMB +0.33 124-TMB	
C12-BEN6	C12 Hexaasub. Benzenes	162.28	4b	-	5	7.68	9.44	L.Mol	0.34 135-TMB +0.33 123-TMB +0.33 124-TMB	
NAPHTHAL	Naphthalene	128.17	3c	3b	2,8	3.49	(11.80)	Asn'd		ARO2
TETRALIN	Tetralin	132.21	3c	3b	2,8	3.01	(11.62)	Asn'd		ARO2
ME-NAPH	Methyl Naphthalenes	142.20	3c	-b	8	4.89	(10.81)	Asn'd		ARO2
1ME-NAPH	1-Methyl Naphthalene	142.20	3c	-	8	4.89	(10.81)	L.Mol	ME-NAPH	ARO2
2ME-NAPH	2-Methyl Naphthalene	142.20	3c,h	-	8	4.89	(10.81)	L.Mol	ME-NAPH	ARO2

Table C-1 (continued)

Name	Desctiption	MWt	Unc [a]	Exp [b]	Notes [c]	MIR [d]	UL MIR [e]		Representation [f]	Lump Gp. [g]
23-DMN	2,3-Dimethyl Naphth.	156.23	3c	3	2,8	5.85	(9.84)	Asn’d		ARO2
INDAN	Indan	118.18	5c	-	7	3.36	12.98	L.Mol	TETRALIN	ARO1
DM-NAPH	Dimethyl Naphthalenes	156.23	3c	-	7	5.85	(9.84)	L.Mol	23-DMN	
C12-NAP1	C12 Monosub. Naphth.	156.23	3c	-	7	4.44	(9.84)	L.Mol	ME-NAPH	
C12-NAP2	C12 Disub. Naphthalenes	156.23	3c	-	7	5.85	(9.84)	L.Mol	23-DMN	
C13-NAP1	C13 Monosub. Naphth.	170.26	4c	-	7	4.08	9.02	L.Mol	ME-NAPH	
C13-NAP2	C13 Disub. Naphthalenes	170.26	4c	-	7	5.37	9.02	L.Mol	23-DMN	
C13-NAP3	C13 Trisub. Naphthalenes	170.26	4c	-	7	5.37	9.02	L.Mol	23-DMN	
C11-TET	C11 Tetralin or Indane	146.24	5c	-	7	2.72	10.51	L.Mol	TETRALIN	
STYRENE	Styrene	104.15	2	-	9	2.17	(14.75)	Asn’d		OLE2
AME-STYR	a-Methyl Styrene	118.18	4	-	7	1.91	13.01	L.Mol	STYRENE	
C9-STYR	C9 Styrenes	118.18	4	-	7	1.91	13.01	L.Mol	STYRENE	
C10-STYR	C10 Styrenes	132.21	4	-	7	1.71	11.62	L.Mol	STYRENE	
ACETYLEN	Acetylene	26.04	2	1	2,3.4	1.31	(3.69)	Gen’d	HC::CH	ALK2
ME-ACTYL	Methyl Acetylene	40.07	4	-	3	6.70	14.95	Gen’d	HC::C-CH3	ALK4
ET-ACTYL	Ethyl Acetylene	54.09	4	-	3	6.23	17.00	Gen’d	HC::C-CH2-CH3	ALK5
2-BUTYNE	2-Butyne	54.09	4	-	3	16.86	21.19	Gen’d	CH3-C::C-CH3	ALK5
MEOH	Methanol	32.04	1	2	2,3	0.77	(1.53)	Gen’d	CH3-OH	ALK2
ETOH	Ethanol	46.07	1	2	2,3	1.88	(6.00)	Gen’d	CH3-CH2-OH	ALK3
I-C3-OH	Isopropyl Alcohol	60.10	1	1	2,3	0.80	(7.93)	Gen’d	CH3-CH(OH)-CH3	ALK4
N-C3-OH	n-Propyl Alcohol	60.10	2	-	3	3.00	(8.17)	Gen’d	CH3-CH2-CH2-OH	ALK4
T-C4-OH	t-Butyl Alcohol	74.12	3	1a	2,3,4	0.50	(1.74)	Gen’d	CH3-C(CH3)(OH)-CH3	ALK2
N-C4-OH	n-Butyl Alcohol	74.12	3	-	3	3.57	(8.76)	Gen’d	CH3-CH2-CH2-CH2-OH	ALK5
I-C4-OH	Isobutyl Alcohol	74.12	3	-	3	2.50	(11.11)	Gen’d	CH3-CH(CH3)-CH2-OH	ALK5
S-C4-OH	s-Butyl Alcohol	74.12	3	-	3	1.77	(12.77)	Gen’d	CH3-CH(OH)-CH2-CH3	ALK5
CC5-OH	Cyclopentanol	86.13	3	-	3	2.07	(8.50)	Gen’d	*CH(OH)-CH2-CH2-CH2-CH2-*	ALK5
C5OH	Pentyl Alcohol	88.15	3	-	3	3.48	(8.44)	Gen’d	CH3-CH2-CH2-CH2-CH2-OH	ALK5
2-C5OH	2-Pentanol	88.15	3	-	3	1.94	(8.71)	Gen’d	CH3-CH(OH)-CH2-CH2-CH3	ALK5
3-C5OH	3-Pentanol	88.15	3	-	3	1.92	(8.85)	Gen’d	CH3-CH2-CH(OH)-CH2-CH3	ALK5
CC6-OH	Cyclohexanol	100.16	3	-	3	2.84	(11.07)	Gen’d	*CH(OH)-CH2-CH2-CH2-CH2-CH2-*	ALK5
2-C6OH	2-Hexanol	102.18	3	-	3	2.48	(7.61)	Gen’d	CH3-CH(OH)-CH2-CH2-CH2-CH3	ALK5
1-C6OH	1-Hexanol	102.18	3	-	3	2.81	(7.72)	Gen’d	CH3-CH2-CH2-CH2-CH2-CH2-OH	ALK5

Table C-1 (continued)

Name	Desctiption	MWt	Unc [a]	Exp [b]	Notes [c]	MIR [d]	UL MIR [e]		Representation [f]	Lump Gp. [g]
1-C7OH	1-Heptanol	116.20	3	-	3	2.31	(7.06)	Gen'd	CH3-CH2-CH2-CH2-CH2-CH2-CH2-OH	ALK5
1-C8-OH	1-Octanol	130.23	2	1	2,3	2.13	(7.28)	Gen'd	CH3-CH2-CH2-CH2-CH2-CH2-CH2-CH2-OH	ALK5
2-C8-OH	2-Octanol	130.23	2	1	2,3	2.46	(7.81)	Gen'd	CH3-CH(OH)-CH2-CH2-CH2-CH2-CH2-CH3	ALK5
3-C8-OH	3-Octanol	130.23	2	1	2,3	2.87	(8.32)	Gen'd	CH3-CH2-CH(OH)-CH2-CH2-CH2-CH2-CH3	ALK5
4-C8-OH	4-Octanol	130.23	3	-	3	3.27	(8.11)	Gen'd	CH3-CH2-CH2-CH(OH)-CH2-CH2-CH2-CH3	ALK5
2-ETC6OH	2-Ethyl-1-Hexanol	130.23	3	-	3	2.44	(7.93)	Gen'd	CH3-CH2-CH(CH2-OH)-CH2-CH2-CH2-CH3	ALK5
ET-GLYCL	Ethylene Glycol	62.07	2	-	3	3.64	(8.79)	Gen'd	HO-CH2-CH2-OH	ALK5
PR-GLYCL	Propylene Glycol	76.10	1	1	2,3	2.77	(11.20)	Gen'd	CH3-CH(OH)-CH2-OH	ALK5
GLYCERL	Glycerol	92.10	2	-	3	3.20	(9.38)	Gen'd	HO-CH2-CH(OH)-CH2-OH	ALK5
12-C4OH2	1,2-Butandiol	90.12	2	-	3	2.19	(12.04)	Gen'd	CH3-CH2-CH(OH)-CH2-OH	ALK5
C6-GLYCL	1,2-Dihydroxy Hexane	118.18	3	-	3	2.56	(9.55)	Gen'd	CH3-CH2-CH2-CH2-CH(OH)-CH2-OH	ALK5
ME-O-ME	Dimethyl Ether	46.07	1	2	2,3	1.05	(5.65)	Gen'd	CH3-O-CH3	ALK3
TME-OX	Trimethylene Oxide	58.08	3	-	3	5.81	(12.35)	Gen'd	*CH2-CH2-CH2-O-*	ALK5
METHYLAL	Dimethoxy methane	76.10	1	-	3	1.66	(5.92)	Gen'd	CH3-O-CH2-O-CH3	ALK4
THF	Tetrahydrofuran	72.11	3	-	3	5.39	(12.17)	Gen'd	*CH2-CH2-CH2-CH2-O-*	ALK5
ET-O-ET	Diethyl Ether	74.12	1	1	2,3	4.35	(10.85)	Gen'd	CH3-CH2-O-CH2-CH3	ALK5
AM-THF	Alpha-Methyltetrahydrofuran	86.13	3	-	3	4.95	(11.34)	Gen'd	*CH(CH3)-CH2-CH2-CH2-O-*	ALK5
THP	Tetrahydropyran	86.13	3	-	3	4.08	(9.56)	Gen'd	*CH2-CH2-CH2-CH2-CH2-O-*	ALK5
MNBE	Methyl n-Butyl Ether	88.15	3	-	3	3.94	(9.61)	Gen'd	CH3-CH2-CH2-CH2-O-CH3	ALK5
MTBE	Methyl t-Butyl Ether	88.15	1	2	2,3,4	0.88	(3.43)	Gen'd	CH3-C(CH3)(CH3)-O-CH3	ALK3
ET-O-IPR	Ethyl Isopropyl Ether	88.15	3	-	3	4.17	(13.56)	Gen'd	CH3-CH(CH3)-O-CH2-CH3	ALK5
ETBE	Ethyl t-Butyl Ether	102.18	3	8	3	2.32	(6.45)	Gen'd	CH3-C(CH3)(CH3)-O-CH2-CH3	ALK5
PR-O-PR	Di n-Propyl Ether	102.18	3	-	3	3.72	(9.02)	Gen'd	CH3-CH2-CH2-O-CH2-CH2-CH3	ALK5
ENBE	Ethyl n-Butyl Ether	102.18	3	-	3	4.14	(9.47)	Gen'd	CH3-CH2-CH2-CH2-O-CH2-CH3	ALK5
MTAE	Methyl t-Amyl Ether	102.18	3	-	3	2.38	(6.06)	Gen'd	CH3-CH2-C(CH3)(CH3)-O-CH3	ALK5
2BU-THF	2-Butyl Tetrahydrofuran	128.22	3	-	3	2.68	(9.55)	Gen'd	*CH(CH2-CH2-CH2-CH3)-CH2-CH2-CH2-O-*	ALK5
BU-O-BU	Di-n-butyl Ether	130.23	3	-	3	3.50	(8.11)	Gen'd	CH3-CH2-CH2-CH2-O-CH2-CH2-CH2-CH3	ALK5
IBU2-O	Di-Isobutyl Ether	130.23	3	-	3	1.51	(7.87)	Gen'd	CH3-CH(CH3)-CH2-O-CH2-CH(CH3)-CH3	ALK5
C5-O-C5	Di-n-Pentyl Ether	158.29	3	-	3	3.17	(7.01)	Gen'd	CH3-CH2-CH2-CH2-CH2-O-CH2-CH2-CH2-CH2-CH3	ALK5
MEO-ETOH	2-Methoxyethanol	76.10	3	-	3	3.34	(10.56)	Gen'd	CH3-O-CH2-CH2-OH	ALK5
MEOC3OH	1-Methoxy-2-Propanol	90.12	1	1	2,3,4	3.22	(10.50)	Gen'd	CH3-CH(OH)-CH2-O-CH3	ALK5

Table C-1 (continued)

Name	Desctiption	MWt	Unc [a]	Exp [b]	Notes [c]	MIR [d]	UL MIR [e]		Representation [f]	Lump Gp. [g]
2MEOC3OH	2-Methoxy-1-Propanol	90.12	3	-	3	3.30	(12.78)	Gen’d	CH3-O-CH(CH3)-CH2-OH	ALK5
ETO-ETOH	2-Ethoxyethanol	90.12	2	2	2,3,4	4.20	(10.27)	Gen’d	CH3-CH2-O-CH2-CH2-OH	ALK5
DET-GLCL	Diethylene Glycol	106.12	3	-	3	4.45	(10.86)	Gen’d	HO-CH2-CH2-O-CH2-CH2-OH	ALK5
3ETOC3OH	3-Ethoxy-1-Propanol	104.15	3	-	3	4.61	(9.38)	Gen’d	CH3-CH2-O-CH2-CH2-CH2-OH	ALK5
3MEOC4OH	3-Methoxy-1-Butanol	104.15	3	-	3	1.05	(9.59)	Gen’d	CH3-O-CH(CH3)-CH2-CH2-OH	ALK5
2PROETOH	2-Propoxyethanol	104.15	3	-	3	4.21	(11.52)	Gen’d	CH3-CH2-CH2-O-CH2-CH2-OH	ALK5
ETOC3OH	1-Ethoxy-2-Propanol	104.15	3	-	3	3.66	(11.64)	Gen’d	CH3-CH(OH)-CH2-O-CH2-CH3	ALK5
MOEOETOH	2-(2-Methoxyethoxy) Ethanol	120.15	3	-	3	3.79	(10.53)	Gen’d	CH3-O-CH2-CH2-O-CH2-CH2-OH	ALK5
BUO-ETOH	2-Butoxyethanol	118.18	1	1	2,3,4	3.34	(8.65)	Gen’d	CH3-CH2-CH2-CH2-O-CH2-CH2-OH	ALK5
3MOMC4OH	3 methoxy -3 methyl-Butanol	118.18	3	-	3	1.89	(7.07)	Gen’d	CH3-O-C(CH3)(CH3)-CH2-CH2-OH	ALK5
DPR-GLCL	Dipropylene Glycol	134.18	3	-	3	3.26	(9.51)	Gen’d	CH3-CH(OH)-CH2-O-CH2-CH(OH)-CH3	ALK5
CARBITOL	2-(2-Ethoxyethoxy) EtOH	134.18	3	2	2,3,4	3.86	(8.97)	Gen’d	CH3-CH2-O-CH2-CH2-O-CH2-CH2-OH	ALK5
PG-2TB-E	2-tert-Butoxy-1-Propanol	132.20	3	-	3	2.00	(9.07)	Gen’d	CH3-C(CH3)(CH3)-O-CH(CH3)-CH2-OH	ALK5
PG-1TB-E	1-tert-Butoxy-2-Propanol	132.20	3	-	3	2.18	(8.54)	Gen’d	CH3-C(CH3)(CH3)-O-CH2-CH(OH)-CH3	ALK5
BUOC3OH	n-Butoxy-2-Propanol	132.20	3	-	3	3.29	(9.40)	Gen’d	CH3-CH(OH)-CH2-O-CH2-CH2-CH2-CH3	ALK5
DPRGOME	Dipropylene Glycol Methyl Ether	148.20	3	-	3	2.96	(8.84)	Gen’d	CH3-CH(OH)-CH2-O-CH(CH3)-CH2-O-CH3	ALK5
C8-CELSV	2-(2-Butoxyethoxy)-EtOH	162.23	3	-	3	3.06	(8.05)	Gen’d	CH3-CH2-CH2-CH2-O-CH2-CH2-O-CH2-CH2-OH	ALK5
TPRGOME	Tripropylene Glycol Monomethyl Ether	206.28	3	-	3	2.32	(6.47)	Gen’d	CH3-CH(OH)-CH2-O-CH(CH3)-CH2-O-CH(CH3)-CH2-O-CH3	ALK5
ME-FORM	Methyl Formate	60.05	3	-	3	0.072	(0.43)	Gen’d	CH3-O-CHO	ALK1
ET-FORM	Ethyl Formate	74.08	3	-	3	0.58	(2.14)	Gen’d	CH3-CH2-O-CHO	ALK2
ME-ACET	Methyl Acetate	74.08	1	1	2,3,4	0.085	(0.76)	Gen’d	CH3-O-CO-CH3	ALK2
ME-PRAT	Methyl Propionate	88.11	3	-	3	0.76	(1.81)	Gen’d	CH3-CH2-CO-O-CH3	ALK2
C3-FORM	n-Propyl Formate	88.11	3	-	3	1.05	(3.86)	Gen’d	CH3-CH2-CH2-O-CHO	ALK3
ET-ACET	Ethyl Acetate	88.11	1	1	2,3,4	0.72	(2.72)	Gen’d	CH3-CH2-O-CO-CH3	ALK2
ET-PRAT	Ethyl Propionate	102.13	3	-	3	0.94	(3.03)	Gen’d	CH3-CH2-O-CO-CH2-CH3	ALK3
C4-FORM	n-Butyl Formate	102.13	3	-	3	1.10	(4.18)	Gen’d	CH3-CH2-CH2-CH2-O-CHO	ALK3
ME-BUAT	Methyl Butyrate	102.13	3	-	3	1.25	(4.11)	Gen’d	CH3-CH2-CH2-CO-O-CH3	ALK3
PR-ACET	Propyl Acetate	102.13	3	-	3	0.99	(4.49)	Gen’d	CH3-CH2-CH2-O-CO-CH3	ALK3

Table C-1 (continued)

Name	Desctiption	MWt	Unc [a]	Exp [b]	Notes [c]	MIR [d]	UL MIR [e]		Representation [f]	Lump Gp. [g]
IPR-ACET	Isopropyl Acetate	102.13	3	2	2,3	1.33	(4.49)	Gen'd	CH3-CH(CH3)-O-CO-CH3	ALK3
ME-IBUAT	Methyl Isobutyrate	102.13	2	1	2,3,4	0.78	(2.51)	Gen'd	CH3-CH(CH3)-CO-O-CH3	ALK3
TBU-ACET	t-Butyl Acetate	116.16	2	1	2,3,4	0.24	(0.59)	Gen'd	CH3-C(CH3)(CH3)-O-CO-CH3	ALK2
SBU-ACET	s-Butyl Acetate	116.16	3	-	3	1.61	(5.70)	Gen'd	CH3-CH2-CH(CH3)-O-CO-CH3	ALK4
PR-PRAT	n-Propyl Propionate	116.16	3	-	3	1.11	(4.51)	Gen'd	CH3-CH2-CH2-O-CO-CH2-CH3	ALK4
ET-BUAT	Ethyl Butyrate	116.16	3	-	3	1.40	(5.28)	Gen'd	CH3-CH2-CH2-CO-O-CH2-CH3	ALK4
IBU-ACET	Isobutyl Acetate	116.16	3	-	3	0.78	(7.91)	Gen'd	CH3-CH(CH3)-CH2-O-CO-CH3	ALK4
BU-ACET	n-Butyl Acetate	116.16	2	1	2,3,4	1.08	(4.69)	Gen'd	CH3-CH2-CH2-CH2-O-CO-CH3	ALK4
CSV-ACET	2-Ethoxyethyl Acetate	132.16	3	-	3	2.10	(11.62)	Gen'd	CH3-CH2-O-CH2-CH2-O-CO-CH3	ALK5
PR-BUAT	n-Propyl Butyrate	130.19	3	-	3	1.36	(6.22)	Gen'd	CH3-CH2-CH2-O-CO-CH2-CH2-CH3	ALK5
AM-ACET	Amyl Acetate	130.19	3	-	3	1.29	(8.13)	Gen'd	CH3-CH2-CH2-CH2-CH2-O-CO-CH3	ALK4
BU-PRAT	Butyl Propionate	130.19	3	-	3	1.11	(7.43)	Gen'd	CH3-CH2-CH2-CH2-O-CO-CH2-CH3	ALK4
E3EOC3OH	Ethyl 3-Ethoxy Propionate	146.19	3	-	3	3.48	(10.50)	Gen'd	CH3-CH2-O-CH2-CH2-CO-O-CH2-CH3	ALK5
BU-BUAT	n-Butyl Butyrate	144.22	3	-	3	1.40	(6.87)	Gen'd	CH3-CH2-CH2-CH2-O-CO-CH2-CH2-CH3	ALK5
IBU-IBTR	Isobutyl Isobutyrate	144.22	3	-	3	0.77	(7.03)	Gen'd	CH3-CH(CH3)-CH2-O-CO-CH(CH3)-CH3	ALK4
IC5IBUAT	Isoamyl Isobutyrate	158.24	3	-	3	1.10	(7.13)	Gen'd	CH3-CH(CH3)-CH2-CH2-O-CO-CH(CH3)-CH3	ALK5
2ETHXACT	2-Ethyl-Hexyl Acetate	172.27	3	-	3	1.02	(7.80)	Gen'd	CH3-CH2-CH2-CH2-CH(CH2-CH3)-CH2-O-CO-CH3	ALK5
PC	Propylene Carbonate	102.09	2	1	2,3,4	0.28	(1.07)	Gen'd	*CH(CH3)-CH2-O-CO-O-*	ALK2
ME-LACT	Methyl Lactate	104.11	3	-	3	2.84	(3.71)	Gen'd	CH3-CH(OH)-CO-O-CH3	ALK3
ET-LACT	Ethyl Lactate	118.13	3	-	3	2.73	(4.35)	Gen'd	CH3-CH(OH)-CO-O-CH2-CH3	ALK4
PGME-ACT	1-Methoxy-2-Propyl Acetate	132.16	2	1	2,3	1.92	(8.67)	Gen'd	CH3-O-CH2-CH(CH3)-O-CO-CH3	ALK5
2PGMEACT	2-Methyoxy-1-propyl Acetate	132.16	3	-	3	1.29	(11.62)	Gen'd	CH3-O-CH(CH3)-CH2-O-CO-CH3	ALK5
DBE-4	Dimethyl Succinate	146.14	2	1	2,3,4	0.41	(1.55)	Gen'd	CH3-O-CO-CH2-CH2-CO-O-CH3	ALK2
DIPR-CB	Diisopropyl Carbonate	146.19	3	-	3	1.16	(7.68)	Gen'd	CH3-CH(CH3)-O-CO-O-CH(CH3)-CH3	ALK5
DBE-5	Dimethyl Glutarate	160.17	2	1	2,3,4	0.52	(2.94)	Gen'd	CH3-O-CO-CH2-CH2-CH2-CO-O-CH3	ALK4
DBE-6	Dimethyl Adipate	174.20	3	-	3	2.02	(5.14)	Gen'd	CH3-O-CO-CH2-CH2-CH2-CH2-CO-O-CH3	ALK5
2BUETACT	2-Butoxyethyl Acetate	160.21	3	-	3	1.95	(9.59)	Gen'd	CH3-CH2-CH2-CH2-O-CH2-CH2-O-CO-CH3	ALK5
ETOX	Ethylene Oxide	44.05	3	-	3	0.051	(0.197)	Gen'd	*CH2-CH2-O-*	ALK1
PROX	Propylene Oxide	58.08	3	-	3	0.36	(1.06)	Gen'd	*CH(CH3)-CH2-O-*	ALK2
12BUOX	1,2-Epoxybutane	72.11	3	-	3	1.19	(2.88)	Gen'd	*CH(CH2-CH3)-CH2-O-*	ALK3
FORMACID	Formic Acid	46.03	3	-	3	0.087	(0.54)	Gen'd	HCO-OH	ALK2

Table C-1 (continued)

Name	Desctiption	MWt	Unc [a]	Exp [b]	Notes [c]	MIR [d]	UL MIR [e]		Representation [f]	Lump Gp. [g]
ACETACID	Acetic Acid	60.05	3	-	3	0.83	(1.42)	Gen'd	CH3-CO-OH	ALK2
PROPACID	Propionic Acid	74.08	3	-	3	1.35	(1.78)	Gen'd	CH3-CH2-CO-OH	ALK2
ME-ACRYL	Methyl Acrylate	86.09	4	-	3	3.43	13.38	Gen'd	CH2=CH-O-CO-CH3	OLE1
VIN-ACET	Vinyl Acetate	86.09	4	-	3	11.86	13.38	Gen'd	CH2=CH-CO-O-CH3	OLE1
ET-ACRYL	Ethyl Acrylate	100.11	4	-	3	8.28	14.38	Gen'd	CH2=CH-CO-O-CH2-CH3	OLE1
FURAN	Furan	68.08	4	3c	7	17.22	22.36	L.Mol	M-XYLENE	
FORMALD	Formaldehyde	30.03	2a	1	1,2,10	9.27	(17.42)	Expl		HCHO
ACETALD	Acetaldehyde	44.05	1	1	1,2,10	7.25	(23.54)	Expl		CCHO
PROPALD	Propionaldehyde	58.08	2	7	10	8.43	(27.27)	Expl		RCHO
2MEC3AL	2-Methylpropanal	72.11	3	-	3	6.30	(26.60)	Gen'd	CH3-CH(CHO)-CH3	RCHO
1C4RCHO	Butanal	72.11	3	-	3	7.15	(26.57)	Gen'd	CH3-CH2-CH2-CHO	RCHO
1C5RCHO	Pentanal	86.13	3	-	3	6.10	(22.26)	Gen'd	CH3-CH2-CH2-CH2-CHO	RCHO
22DMC3AL	2,2-Dimethylpropanal (pivaldehyde)	86.13	3	-	3	5.78	(22.26)	Gen'd	CH3-C(CH3)(CHO)-CH3	RCHO
3MC4RCHO	3-Methylbutanal	86.13	3	-	3	5.91	(22.26)	Gen'd	CH3-CH(CH3)-CH2-CHO	RCHO
GLTRALD	Glutaraldehyde	100.12	3	-	3	5.18	(19.18)	Gen'd	HCO-CH2-CH2-CH2-CHO	RCHO
1C6RCHO	Hexanal	100.16	3	-	3	5.17	(19.18)	Gen'd	CH3-CH2-CH2-CH2-CH2-CHO	RCHO
1C7RCHO	Heptanal	114.19	3	-	3	4.40	(16.80)	Gen'd	CH3-CH2-CH2-CH2-CH2-CH2-CHO	RCHO
1C8RCHO	Octanal	128.22	3	-	3	3.79	(14.97)	Gen'd	CH3-CH2-CH2-CH2-CH2-CH2-CH2-CHO	RCHO
C4-RCHO	C4 aldehydes	72.11	3			7.15	(26.57)	L.Mol	1C4RCHO	
C5-RCHO	C5 Aldehydes	86.14	3			6.10	(22.26)	L.Mol	1C5RCHO	
C6-RCHO	C6 Aldehydes	100.16	3			5.17	(19.18)	L.Mol	1C6RCHO	
C7-RCHO	C7 Aldehydes	114.19	3			4.40	(16.80)	L.Mol	1C7RCHO	
C8-RCHO	C8 Aldehydes	128.22	3			3.79	(14.97)	L.Mol	1C8RCHO	
GLYOXAL	Glyoxal	58.04	2	5	4,10	14.81	(18.19)	Expl		GLY
MEGLYOX	Methyl Glyoxal	72.07	3	-	10	16.99	(21.98)	Expl		MGLY
ACROLEIN	Acrolein	56.06	2	3	2,3,4	8.00	(28.26)	Gen'd	CH2=CH-CHO	MACR
CROTALD	Crotonaldehyde	70.09	3	-	3	10.34	(27.39)	Gen'd	CH3-CH=CH(CHO)	IPROD
METHACRO	Methacrolein	70.09	1	3	2,4,10	6.67	(27.39)	Gen'd	CH2=C(CHO)-CH3	MACR
HOMACR	Hydroxy Methacrolein	86.09	3	-	3	6.71	(22.30)	Gen'd	CH2=C(CHO)-CH2-OH	IPROD
BENZALD	Benzaldehyde	106.13	2			-0.58	(18.08)	Expl		BALD
TOLUALD	Tolualdehyde	120.15	3			-0.51	(15.98)	L.Mol	BENZALD	

Table C-1 (continued)

Name	Desctiption	MWt	Unc [a]	Exp [b]	Notes [c]	MIR [d]	UL MIR [e]		Representation [f]	Lump Gp. [g]
ACETONE	Acetone	58.08	1			0.45	(9.74)	Expl		ACET
CC4-KET	Cyclobutanone	70.09	4	-	3	0.77	12.14	Gen'd	*CH2-CH2-CH2-CO-*	MEK
MEK	Methyl Ethyl Ketone	72.11	1	1	2,3,4	1.59	(12.73)	Gen'd	CH3-CH2-CO-CH3	MEK
CC5-KET	Cyclopentanone	84.12	4	-	3	1.51	14.41	Gen'd	*CH2-CH2-CH2-CH2-CO-*	MEK
DEK	3-Pentanone	86.13	3	-	3	1.55	(12.37)	Gen'd	CH3-CH2-CO-CH2-CH3	MEK
MPK	2-Pentanone	86.13	3	3	2,3,4	3.34	(16.36)	Gen'd	CH3-CH2-CH2-CO-CH3	MEK
CC6-KET	Cyclohexanone	98.15	3	1a	2,3,4	1.76	(15.93)	Gen'd	*CH2-CH2-CH2-CH2-CH2-CO-*	PROD2
MTBK	Methyl t-Butyl Ketone	100.16	3	-	3	0.86	(9.17)	Gen'd	CH3-C(CH3)(CH3)-CO-CH3	MEK
MIBK	4-Methyl-2-Pentanone	100.16	2	1	2,3,4	4.62	(18.40)	Gen'd	CH3-CH(CH3)-CH2-CO-CH3	PROD2
MNBK	Methyl n-Butyl Ketone	100.16	3	-	3	3.82	(17.11)	Gen'd	CH3-CH2-CH2-CH2-CO-CH3	PROD2
DIPK	Di-Isopropyl Ketone	114.19	3	-	3	1.80	(13.01)	Gen'd	CH3-CH(CH3)-CO-CH(CH3)-CH3	PROD2
2M-3-HXO	2-Methyl-3-Hexanone	114.19	3	-	3	1.98	(16.18)	Gen'd	CH3-CH(CH3)-CO-CH2-CH2-CH3	PROD2
C7-KET-2	2-Heptanone	114.19	2	3	2,3,4	3.05	(15.74)	Gen'd	CH3-CH2-CH2-CH2-CH2-CO-CH3	PROD2
C8-KET-2	2-Octanone	128.22	3	-	3	1.81	(13.87)	Gen'd	CH3-CH2-CH2-CH2-CH2-CH2-CO-CH3	PROD2
C9-KET-2	2-Nonanone	142.24	3	-	3	1.42	(12.73)	Gen'd	CH3-CH2-CH2-CH2-CH2-CH2-CH2-CO-CH3	PROD2
DIBK	Di-isobutyl ketone (2,6-dimethyl-4-heptanone)	142.24	3	-	3	3.22	(13.45)	Gen'd	CH3-CH(CH3)-CH2-CO-CH2-CH(CH3)-CH3	PROD2
C10-K-2	2-Decanone	156.27	3	-	3	1.14	(11.70)	Gen'd	CH3-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CO-CH3	PROD2
KET5	C5 Ketones	86.13	3	-	7	3.34	(16.36)	L.Mol	MPK	
KET6	C6 Ketones	100.16	3	-	7	3.82	(17.11)	L.Mol	MNBK	
KET7	C7 Ketones	114.19	3	-	7	3.05	(15.74)	L.Mol	C7-KET-2	
KET8	C8 Ketones	128.22	4	-	7	1.81	13.87	L.Mol	C8-KET-2	
KET9	C9 Ketones	142.24	4	-	7	1.42	12.73	L.Mol	C9-KET-2	
KET10	C10 Ketones	156.27	4	-	7	1.14	11.70	L.Mol	C10-K-2	
KET6C	C6 Cyclic Ketones	98.15	4b	-	7	1.76	15.93	L.Mol	CC6-KET	
KET5C	C5 Cyclic Ketones	84.12	4b	-	7	1.51	14.41	L.Mol	CC5-KET	
KET7C	C7 Cyclic Ketones	112.17	4b	-	7	1.54	13.96	L.Mol	CC6-KET	
KET8C	C8 Cyclic Ketones	126.20	4b	-	7	1.37	12.38	L.Mol	CC6-KET	
KET9C	C9 Cyclic Ketones	140.23	4b	-	7	1.23	11.15	L.Mol	CC6-KET	
KET10C	C10 Cyclic Ketones	154.25	4b	-	7	1.12	10.14	L.Mol	CC6-KET	
BIACETYL	Biacetyl	86.09	2	7	10	21.75	(22.30)	Expl		BACL
MVK	Methylvinyl ketone	70.09	1	3	2,4,10	10.05	(27.39)	Gen'd	CH2=CH-CO-CH3	MVK

Table C-1 (continued)

Name	Desctiption	MWt	Unc [a]	Exp [b]	Notes [c]	MIR [d]	UL MIR [e]		Representation [f]	Lump Gp. [g]
HOACET	Hydroxy Acetone	74.08	3	-	3	3.22	(13.63)	Gen'd	CH3-CO-CH2-OH	MEK
MEOACET	Methoxy Acetone	88.11	3	-	3	2.33	(18.04)	Gen'd	CH3-O-CH2-CO-CH3	PROD2
DIACTALC	Diacetone Alcohol	116.16	3	9	3	0.76	(10.49)	Gen'd	CH3-C(CH3)(OH)-CH2-CO-CH3	MEK
PHENOL	Phenol	94.11	4	-	10	1.89	16.22	Expl		PHEN
O-CRESOL	o-Cresol	108.14	3c	4	2,4,10	2.41	(14.20)	Expl		CRES
M-CRESOL	m-Cresol	108.14	3c	4a	7	2.41	(14.20)	L.Mol	O-CRESOL	
P-CRESOL	p-Cresol	108.14	3c	4	7	2.41	(14.20)	L.Mol	O-CRESOL	
CRESOL	Alkyl Phenols	108.14	3c	6	7	2.41	(14.20)	L.Mol	O-CRESOL	
NO2-BENZ	Nitrobenzene	123.11	6c	-	7	0.075	0.37	Asn'd		ARO1
TDI	Toluene Diisocyanate	174.16	2c	1	2,8	-0.121	(6.80)	Asn'd		ARO1
P-TI	Para Toluene Isocyanate	134.15	2c	1	2,8	0.99	(7.94)	Asn'd		ARO1
MDI	Methylene Diphenylene Diisocyanate	250.26	3c	-	11	0.83	(5.55)	Asn'd		ARO1
ET-AMINE	Ethyl Amine	45.09	6d	8	13	8.37	12.71	Asn'd		ALK5
DM-AMINE	Dimethyl Amine	47.08	6d	-	13	9.64	12.23	Asn'd		ALK5
TM-AMINE	Trimethyl Amine	59.11	6d	8	13	7.58	14.62	Asn'd		ALK5
ME-NITRT	Methyl Nitrite	61.04	-	-	14			-		
ETOH-NH2	Ethanolamine	60.08	6d	-	13	6.51	9.57	Asn'd		ALK5
ETOH2-NH	Diethanol Amine	105.14	6d	-	13	4.36	10.96	Asn'd		ALK5
ETOH3-N	Triethanolamine	149.19	6d	-	13	2.98	10.29	Asn'd		ALK5
ACRYLNIT	Acrylonitrile	53.06	-					-		
NMP	N-Methyl-2-Pyrrolidone	99.13	2	1	15	2.83	(14.36)	Asn'd		OLE1
CH3-CL	Methyl Chloride	50.49	6d			0.039	0.051	Asn'd		ALK1
CL2-ME	Dichloromethane	84.94	6d			0.074	0.097	Asn'd		ALK1
ME-BR	Methyl Bromide	94.95	6d			0.0190	0.025	Asn'd		ALK1
CHCL3	Chloroform	119.39	6d			0.038	0.050	Asn'd		ALK1
CCL4	Carbon Tetrachloride	153.84	1					L.Mol	INERT	
ME-BR2	Methylene Bromide	173.85	-					-		
CL-ETHE	Vinyl Chloride	62.50	6d			3.19	6.90	Asn'd		ALK5
C2-CL	Ethyl Chloride	64.52	6d			0.28	0.72	Asn'd		ALK2
11CL2-C2	1,1-Dichloroethane	98.97	6d			0.113	0.29	Asn'd		ALK1
12CL2-C2	1,2-Dichloroethane	99.00	6d			0.110	0.29	Asn'd		ALK1

Table C-1 (continued)

Name	Desctiption	MWt	Unc [a]	Exp [b]	Notes [c]	MIR [d]	UL MIR [e]		Representation [f]	Lump Gp. [g]
C2-BR	Ethyl Bromide	108.97	6d			0.121	0.32	Asn’d		ALK1
112CL3C2	1,1,2-Trichloroethane	131.66	6d			0.066	0.171	Asn’d		ALK1
111-TCE	1,1,1-Trichloroethane	133.42	6d			0.0040	0.0107	Asn’d		ALK1
11BR2-C2	1,2-Dibromoethane	187.88	6d			0.052	0.136	Asn’d		ALK1
12CL2-C3	1,2-Dichloropropane	112.99	-					-		
C3-BR	n-Propyl Bromide	123.00	6d	1a,d	2,16	0.39	1.48	Asn’d		ALK2
C4-CL	1-Chlorobutane	92.57	-					-		
C4-BR	n-Butyl Bromide	137.03	6d	1a,d	2,16	0.67	3.27	Asn’d		ALK3
3CLME-C8	3-(Chloromethyl)-Heptane	148.68	-					-		
11CL2ETH	1,1-Dichloroethene	96.95	-					-		
T-12-DCE	Trans-1,2-Dichloroethene	96.95	6d	-	16	0.90	2.21	Asn’d		ALK3
CL3-ETHE	Trichloroethylene	131.40	6d	1d	2,16	0.67	1.64	Asn’d		ALK3
CL4-ETHE	Perchloroethylene	165.85	6d	-	16	0.045	0.117	Asn’d		ALK1
CL2IBUTE	2-(Cl-methyl)-3-Cl-Propene	125.00	6d	2a,d	16	1.28	9.20	Gen’d	CH2=C(CH2-Cl)-CH2-Cl	OLE1
CL-BEN	Monochlorobenzene	112.56	6d	-	8	0.41	1.95	Asn’d		ARO1
CL2-BEN	p-Dichlorobenzene	147.01	6d	-	8	0.23	1.10	Asn’d		ARO1
CF3-BEN	Benzotrifluoride	146.11	6d	-	8	0.29	0.92	Asn’d		ARO1
PCBTF	p-Trifluoromethyl-Cl-Benzene	180.56	6d	-	8	0.123	0.40	Asn’d		ARO1
CCL3NO2	Chloropicerin	164.38	-	-	17			-		
DMS	Dimethyl Sulfide	62.13	-					-		
DMSO	Dimethyl Sulfoxide	78.13	-	1d	18			-		
SI2OME6	Hexamethyldisiloxane	162.39	-e	1c	19			-		
SI2OMEOH	Hydroxymethyldisiloxane	164.36	-e	1c	19			-		
(SIOME)4	D4 Cyclosiloxane	296.64	-e	1c	19			-		
(SIOME)5	D5 Cyclosiloxane	370.80	-e	1c	19			-		
ARBROG	Base ROG Mixture	14.44		0	20	3.98		Mix		
RFA-TLEV	TLEV Exhaust -- RFA	14.04		0	21	4.37		Mix		
M85-TLEV	TLEV Exhaust -- M-85	27.45		0	21	1.67		Mix		
E85-TLEV	TLEV Exhaust -- E-85	20.74		0	21	2.93		Mix		
CNG-TLEV	TLEV Exhaust -- CNG	15.22		0	21	0.81		Mix		

Table C-1 (continued)

Name	Desctiption	MWt	Unc [a]	Exp [b]	Notes [c]	MIR [d]	UL MIR [e]	Representation [f]	Lump Gp. [g]
LPG-TLEV	TLEV Exhaust -- LPG	14.86		0	21	2.26		Mix	
PH2-TLEV	TLEV Exhaust -- Phase 2	14.12		0	21	4.33		Mix	
RFA-LEV	Final LEV -- RFA	14.03		0	22	3.91		Mix	
PH2-LEV	Final LEV -- Phase 2	14.22		0	22	3.81		Mix	
MS-A	Mineral Spirits "A" (Type I-B, 91% Alkanes)	14.10		0	23	1.49		Mix	
MS-B	Mineral Spirits "B" (Type II-C)	14.11		0	23	0.97		Mix	
MS-C	Mineral Spirits "C" (Type II-C)	14.12		0	23	0.97		Mix	
MS-D	Mineral Spirits "D" (Type II-C)	14.08		0	23	0.98		Mix	

[a] Uncertainty codes are given in Table C-2.

[b] Experimental data availability codes are given in Table C-3.

[c] Notes on representation of the detailed model species are given in Table C-4.

[d] Maximum incremental reactivity in units of grams O_3 per gram VOC.

[e] Upper limit maximum incremental reactivity in units of grams O_3 per gram VOC. Parentheses indicate that the MIR is not considered to be sufficiently uncertain that use of upper limit values are appropriate.

[f] Representation in the mechanism: "Expl" = explicit in the base mechanism; "Asn'd" = mechanistic parameters assigned; "Gen'd" = mechanistic parameters generated using the mechanism generation system, using the structure shown; "L.Mol" = represented on a mole for mole basis by the model species or mixture shown; "-" = not represented in current version of the mechanism; "Mix" = mixture.

[g] Lumped group used when represnting this compound in ambient simulations using the recommended condensed mechanism. Note that ETHE, ISOP, IPRD, MACR are short for ETHYLENE, ISOPRENE, ISOPROD, AND METHACRO, respectively.

Table C-2. Uncertainty codes used in the listing of the detailed model species.

Code	Description
-	No representation of this compound has been developed for this version of the mechanism.
0	Compound believed to be unreactive.
1	Considered to be relatively uncertain, or some uncertainties but reactivity is not expected to change significantly.
2	Uncertain mechanism may change somewhat if refined, but change is expected to be less than a factor of two. If the compound is predicted to inhibit O3, changes are not expected to affect predicted inhibition, but may affect magnitude of inhibition. This code is also used for (1) compounds whose reactivities are expected to be sensitive to the representation of the reactive products, whose accuracy is difficult to test experimentally and (2) compounds whose reactivities are expected to be highly sensitive to ambient conditions or to changes in the base mechanism.
3	Uncertain and may change if compound is studied (or studied further) or estimation methods are updated. Change in MIR could be as much as a factor of two. This code is also used for (1) compounds whose reactivities are expected to be sensitive to the representation of the reactive products, whose accuracy is difficult to test experimentally and (2) compounds whose reactivities are expected to be highly sensitive to ambient conditions or to changes in the base mechanism.
4	Uncertain and is expected to change if compound is studied or estimation methods are updated. It is recommended that uncertainty adjustments be employed in regulatory applications.
5	Non-negligible chance of the estimate being incorrect in significant respects. It is recommended that uncertainty adjustments be employed in regulatory applications.
6	Current mechanism is probably incorrect, but biases in atmospheric reactivity predictions are uncertain. It is recommended that uncertainty adjustments be employed in regulatory applications.
a	The reactivity of this compound is expected to be sensitive to ambient conditions and/or changes in the base mechanism.
b	Some uncertainty due to differences in reactivities of compounds represented by this class. Look at differences among compounds in this class for the magnitude of this uncertainty.
c	Parameterized mechanism used, with uncertain portions adjusted to fit chamber data for representative compounds.
d	Highly simplified “Placeholder” mechanism used to represent the approximate range of reactivity of this compound. Mechanism does not represent an estimate of the actual mechanism of the compound.
e	The current version of this mechanism does not represent these compounds, but based on previous studies they are expected to be O3 inhibitors under all conditions.

Table C-3. Notes on availability of experimental data for evaluating mechanisms for the detailed model species.

Code	Description
-	No data available to test ozone predictions for this compound.
1	Tested under MIR and other conditions; well tested.
2	Tested under MIR conditions. There may be limited data for other conditions in some cases.
3	Tested under some conditions, but not MIR reactivity.
4	Tested under some conditions, but data are limited, or are of low quality or precision.
5	This compound has not been studied by itself, but its mechanism has been evaluated using experiments where it is formed as the major reactive product, for which model simulations are highly sensitive to assumed mechanisms for this compound.
6	Experimental data are available for some members of this class or for complex mixtures containing significant amounts of compounds of this class.
7	Chamber data may be available to test mechanisms for this compound, but were not used in this evaluation. Data are believed to be limited, of low precision, not well characterized or difficult to characterize, or highly sensitive to chamber effects.
8	There may be chamber data available to test mechanisms for this compound, but their availability and utility for mechanism evaluation have not been assessed.
9	Attempts to conduct chamber experiments with this compound have been unsuccessful because of experimental difficulties. Probably not possible to study this compound using current
a	Model does not successfully simulate results of all chamber experiments. This may be due to experimental difficulties, though mechanism problems cannot be completely ruled out.
b	Reactivity of this compound may be sensitive to the nature of the light source, but data are available only from blacklight chambers. Effect of changing light source is uncertain and needs to be evaluated.
c.	The current version of the mechanism does not represent this compound or the available data were not used to evaluate how it is currently represented.
d	Although there are chamber data available for this compound and the model performance has been evaluated using them, the current mechanism does not represent halogen chemistry and the predictions of the mechanism may be inaccurate in ambient simulations.

Table C-4. Notes and comments for the listed detailed model species.

Note.	Notes or Comments
1	Mechanism believed to be fairly well established. See Atkinson (1990, 1994, 1997a) reviews.
2	Evaluation of the mechanism for this compound against chamber data is discussed in this report. See Section V and Appendix B.
3	Mechanism was derived using the mechanism generation system discussed in Section III.
4	Adjustments were made to mechanism to improve fits to chamber data.
5	It is uncertain whether the compound(s) used to represent this class is most appropriate for all complex mixtures containing this class.
6	The current mechanism gives reasonably good simulations of incremental reactivity experiments of mineral spirits samples believed to contain significant amounts of these compounds (Carter et al, 1996f). See Section V and Appendix B.
7	The appropriateness of the lumped molecule representation for this class is uncertain.
8	Parameterized mechanism used, with uncertain portions adjusted to fit chamber data for representative compounds. See Section IV.
9	An estimated mechanism was derived as discussed in Section IV.B.2.
10	The reactions of this compound is represented explicitly in the base mechanism. See Section II.C.
11	Mechanism for this compound estimated by analogy from para toluene isocyanate.
13	Mechanisms for amines have not been developed. A placeholder mechanism used to represent their approximate range of reactivity, given the OH rate constant. See Section IV.B.6
14	The reactions for this compound can be added to the mechanism if needed, but this has not been done for the current version of the mechanism.
15	An estimated mechanism was derived as discussed in Section IV.B.3.
16	The current version of the mechanism does not provide for representing reactions of ClOx or BrOx species. However, earlier versions of the mechanism that did represent these reactions did not perform well simulating chamber data for most of the halogenated compounds that were studied (Carter et al, 1996d, 1997d). A placeholder mechanism is used to estimate the approximate MIR given the compound’s OH rate constant. This mechanism probably overestimates the reactivity of these compounds under low NOx conditions.
17	The current version of the mechanism does not provide for representing reactions of ClOx species, and this compound is not currently represented. However, an earlier version of the mechanism that did represent these reactions gave reasonably good fits to the chamber data for this compound (1997h).
18	An experimental and modeling study of the reactivity of this compound is underway at our laboratories.
19	Volatile silicone compounds are not represented in the current version of the mechanism. They have previously been shown to be ozone inhibitors under all conditions likely to occur in the atmosphere (Carter et al, 1992).

Table C-4. Notes and comments for the listed detailed model species.

Note.	Notes or Comments
20	The Base ROG mixture is used to represent reactive VOCs from all sources in the atmospheric reactivity calculations, as discussed in Section ??. It is derived from the “all city average” mixture derived by Jeffries et al (1989) from analysis of air quality data, with minor modifications as discussed by Carter (1994a,b).
21	These are the "Transitional Low Emissions Vehicle" exhaust mixtures used by the California ARB to calculate reactivity adjustment factors for its Clean Fuels, Low-Emissions Vehicle regulations. Composition obtained from the CARB.
22	These are “Low Emissions Vehicle” exhaust mixtures provided by the California ARB.
23	These are the mineral spirits samples provided by Safety-Kleen Corporation for environmental chamber reactivity studies (Carter et al, 1997f). Contrary to the earlier version of the mechanism discussed by in that report, the current mechanism performs reasonably well in simulating the chamber results for these samples (see Section V and Appendix B). Sample "A" consists of ~6% aromatics and ~2.5% olefins with the remainder alkanes. The carbon number range is C8-C16, peaking at C11. The distribution of alkane types is similar to "C" and "D". Sample "B" is an all-alkane mixture in the C8-C16 range, peaking at C12-C13. GC-MS analysis indicates alkanes are ~5% normal, ~40% branched, and ~53% cyclic. Sample "C" is an all-alkane mixture in the C10-C14 range, peaking at C12. GC-MS analysis indicates alkanes are ~26% normal, ~23% branched, and ~52% cyclic. Sample "D" is an all-alkane mixture in the same weight range as Sample "C". GC-MS analysis indicates alkanes are ~24% normal, ~30% branched, and ~46% cyclic.

Table C-5. Summary of calculated incremental and relative reactivities in various scales. Calculated using the SAPRC-99 mechansim (8/30/99)

Compound or Mixture	MIR (gm O3 / gm VOC)					MOIR (gm/gm)			EBIR (gm/gm)			Base Case Relative Reactivities [a]									
	39 Scenarios			Avg. Conds		39 Scenarios			39 Scenarios			Ozone Yield (gm basis)					Max 8-Hour Avg (gm basis)				
	Avg.	Sdev			D%	Avg.	Sdev		Avg.	Sdev		Avg.	Max	Min	Sdev		Avg.	Max	Min	Sdev	
Base ROG Mixture	3.97	0.70	18%	4.12	4%	1.47	0.29	20%	0.87	0.26	30%	1.00	2.30	0.24	0.41	41%	1.00	1.62	0.38	0.31	31%
Carbon Monoxide	0.07	0.02	23%	0.07	3%	0.04	0.01	21%	0.03	0.01	25%	0.04	0.08	0.01	0.01	36%	0.03	0.05	0.01	0.01	29%
Methane	0.02	0.00	21%	0.02	2%	0.01	0.00	20%	0.01	0.00	26%	0.01	0.02	0.00	0.00	33%	0.01	0.01	0.00	0.00	25%
Ethane	0.35	0.09	27%	0.35	2%	0.22	0.07	30%	0.16	0.06	36%	0.19	0.34	0.05	0.05	26%	0.11	0.17	0.05	0.03	23%
Propane	0.64	0.16	25%	0.65	2%	0.40	0.11	27%	0.29	0.09	32%	0.33	0.60	0.10	0.08	25%	0.22	0.31	0.09	0.05	21%
n-Butane	1.48	0.39	26%	1.50	2%	0.89	0.26	29%	0.63	0.22	35%	0.71	1.20	0.23	0.16	22%	0.43	0.60	0.21	0.08	19%
n-Pentane	1.77	0.49	27%	1.80	2%	1.06	0.32	30%	0.73	0.27	37%	0.79	1.12	0.26	0.16	20%	0.49	0.65	0.23	0.08	17%
n-Hexane	1.71	0.50	29%	1.74	2%	1.05	0.33	31%	0.69	0.27	40%	0.71	0.96	0.23	0.16	23%	0.43	0.61	0.19	0.08	19%
n-Heptane	1.48	0.45	31%	1.51	2%	0.91	0.30	33%	0.58	0.25	43%	0.56	0.80	0.03	0.17	30%	0.32	0.50	0.05	0.09	29%
n-Octane	1.28	0.42	33%	1.30	2%	0.79	0.28	36%	0.49	0.23	48%	0.44	0.70	-0.17	0.19	43%	0.22	0.40	-0.12	0.11	50%
n-Nonane	1.10	0.38	35%	1.12	2%	0.69	0.26	38%	0.42	0.22	52%	0.36	0.61	-0.29	0.20	58%	0.15	0.33	-0.23	0.12	85%
n-Decane	0.97	0.36	37%	0.99	3%	0.62	0.25	40%	0.37	0.21	56%	0.30	0.55	-0.35	0.21	70%	0.10	0.27	-0.30	0.13	135%
n-Undecane	0.88	0.34	38%	0.91	3%	0.57	0.23	41%	0.34	0.20	58%	0.27	0.51	-0.37	0.21	77%	0.07	0.24	-0.33	0.13	195%
n-Dodecane	0.81	0.32	39%	0.83	3%	0.52	0.22	42%	0.31	0.19	59%	0.24	0.47	-0.39	0.20	83%	0.05	0.22	-0.34	0.13	267%
n-Tridecane	0.77	0.31	40%	0.79	3%	0.49	0.21	43%	0.30	0.18	59%	0.23	0.46	-0.38	0.19	82%	0.04	0.21	-0.33	0.13	340%
n-Tetradecane	0.73	0.30	41%	0.75	3%	0.47	0.20	43%	0.29	0.17	59%	0.23	0.44	-0.36	0.18	81%	0.03	0.20	-0.33	0.13	424%
n-Pentadecane	0.70	0.29	42%	0.73	4%	0.45	0.20	43%	0.28	0.17	59%	0.22	0.43	-0.34	0.17	77%	0.02	0.20	-0.32	0.13	520%
n-C16	0.67	0.28	42%	0.70	4%	0.43	0.19	43%	0.27	0.16	58%	0.22	0.42	-0.31	0.16	75%	0.02	0.19	-0.30	0.12	625%
n-C17	0.63	0.27	42%	0.65	4%	0.41	0.18	43%	0.26	0.15	58%	0.21	0.39	-0.29	0.15	75%	0.02	0.18	-0.28	0.12	626%
n-C18	0.59	0.25	42%	0.62	4%	0.38	0.17	43%	0.24	0.14	58%	0.19	0.37	-0.27	0.15	75%	0.02	0.17	-0.27	0.11	625%
n-C19	0.56	0.24	42%	0.58	4%	0.36	0.16	43%	0.23	0.13	58%	0.18	0.35	-0.26	0.14	75%	0.02	0.16	-0.25	0.10	624%
n-C20	0.53	0.23	42%	0.56	4%	0.35	0.15	43%	0.22	0.13	58%	0.17	0.33	-0.25	0.13	75%	0.02	0.15	-0.24	0.10	624%
n-C21	0.51	0.22	42%	0.53	4%	0.33	0.14	43%	0.21	0.12	58%	0.17	0.32	-0.24	0.12	75%	0.02	0.14	-0.23	0.09	623%
n-C22	0.49	0.21	42%	0.51	4%	0.31	0.14	43%	0.20	0.12	58%	0.16	0.30	-0.22	0.12	75%	0.01	0.14	-0.22	0.09	624%
3-Methyl Decane	0.91	0.35	38%	0.94	3%	0.58	0.24	41%	0.35	0.20	58%	0.27	0.52	-0.39	0.21	79%	0.07	0.25	-0.35	0.14	214%
Isobutane	1.48	0.32	21%	1.51	2%	0.83	0.16	20%	0.59	0.15	25%	0.72	1.42	0.27	0.20	27%	0.53	0.80	0.25	0.12	22%
Iso-Pentane	1.87	0.47	25%	1.91	2%	1.08	0.28	26%	0.77	0.24	31%	0.89	1.56	0.31	0.19	22%	0.57	0.79	0.28	0.11	19%
Neopentane	0.77	0.16	21%	0.78	2%	0.45	0.09	20%	0.32	0.08	26%	0.38	0.74	0.14	0.11	29%	0.27	0.43	0.13	0.06	22%
2-Methyl Pentane	2.02	0.53	26%	2.07	2%	1.12	0.33	30%	0.75	0.28	38%	0.82	1.09	0.33	0.16	19%	0.50	0.67	0.29	0.08	16%
3-Methylpentane	2.32	0.60	26%	2.38	2%	1.30	0.36	28%	0.90	0.31	34%	1.01	1.58	0.38	0.20	20%	0.63	0.83	0.33	0.11	17%
2,3-Dimethyl Butane	1.28	0.29	23%	1.32	3%	0.74	0.15	21%	0.51	0.14	27%	0.59	1.06	0.22	0.13	23%	0.44	0.64	0.20	0.09	19%
2,2-Dimethyl Butane	1.45	0.35	24%	1.48	2%	0.84	0.21	25%	0.58	0.18	31%	0.66	1.10	0.25	0.14	21%	0.43	0.56	0.22	0.07	17%
2,2-Dimethyl Pentane	1.45	0.38	26%	1.47	2%	0.83	0.24	29%	0.55	0.20	36%	0.60	0.81	0.23	0.11	19%	0.38	0.50	0.21	0.06	15%
3,3-Dimethyl Pentane	1.51	0.40	27%	1.54	2%	0.89	0.26	29%	0.61	0.22	35%	0.67	1.00	0.24	0.13	20%	0.40	0.54	0.21	0.07	17%
2,3-Dimethyl Pentane	1.75	0.44	25%	1.80	3%	0.97	0.26	26%	0.66	0.22	33%	0.72	1.03	0.29	0.13	18%	0.48	0.65	0.25	0.08	16%
3-Methyl Hexane	2.10	0.57	27%	2.15	2%	1.15	0.35	31%	0.76	0.30	39%	0.80	1.07	0.34	0.16	20%	0.47	0.66	0.28	0.09	19%
2,4-Dimethyl Pentane	1.90	0.47	25%	1.94	2%	1.03	0.28	27%	0.69	0.24	34%	0.76	1.05	0.33	0.13	17%	0.50	0.65	0.30	0.07	14%
2-Methyl Hexane	1.74	0.49	28%	1.77	2%	1.01	0.32	31%	0.66	0.26	40%	0.67	0.89	0.24	0.16	23%	0.40	0.58	0.18	0.08	21%
2,2,3-Trimethyl Butane	1.47	0.32	22%	1.51	3%	0.80	0.16	19%	0.54	0.14	26%	0.63	1.10	0.27	0.14	23%	0.48	0.69	0.24	0.09	18%
2,2,3,3-Tetrame. Butane	0.49	0.11	24%	0.49	1%	0.29	0.07	24%	0.19	0.06	31%	0.21	0.38	0.08	0.06	26%	0.15	0.22	0.07	0.03	17%

Table C-5. Summary of calculated incremental and relative reactivities in various scales. Calculated using the SAPRC-99 mechansim (8/30/99)

Compound or Mixture	MIR (gm O3 / gm VOC)					MOIR (gm/gm)			EBIR (gm/gm)			Base Case Relative Reactivities [a]									
	39 Scenarios			Avg. Conds		39 Scenarios			39 Scenarios			Ozone Yield (gm basis)					Max 8-Hour Avg (gm basis)				
	Avg.	Sdev			D%	Avg.	Sdev		Avg.	Sdev		Avg.	Max	Min	Sdev		Avg.	Max	Min	Sdev	
2,3-Dimethyl Hexane	1.62	0.45	28%	1.66	3%	0.92	0.27	30%	0.60	0.23	39%	0.61	0.84	0.23	0.14	23%	0.37	0.55	0.17	0.08	22%
2,2,4-Trimethyl Pentane	1.58	0.36	23%	1.62	2%	0.85	0.20	23%	0.57	0.17	30%	0.64	1.01	0.29	0.12	18%	0.46	0.59	0.26	0.07	14%
2,4-Dimethyl Hexane	2.13	0.57	27%	2.19	3%	1.14	0.34	30%	0.74	0.29	39%	0.76	1.00	0.31	0.17	22%	0.45	0.66	0.18	0.10	22%
2,3,4-Trimethyl Pentane	1.42	0.37	26%	1.47	3%	0.81	0.22	27%	0.53	0.19	35%	0.57	0.86	0.23	0.11	20%	0.37	0.52	0.19	0.06	18%
3-Methyl Heptane	1.65	0.49	30%	1.69	2%	0.96	0.32	33%	0.61	0.27	43%	0.60	0.85	0.07	0.18	30%	0.32	0.52	0.02	0.10	32%
2-Methyl Heptane	1.46	0.45	31%	1.49	2%	0.87	0.29	34%	0.55	0.25	45%	0.52	0.76	-0.04	0.18	34%	0.28	0.46	-0.03	0.10	37%
2,5-Dimethyl Hexane	1.90	0.50	27%	1.95	3%	1.03	0.30	29%	0.67	0.26	39%	0.68	0.90	0.24	0.15	23%	0.42	0.61	0.18	0.09	21%
4-Methyl Heptane	1.67	0.48	29%	1.71	2%	0.94	0.31	33%	0.60	0.26	44%	0.59	0.84	0.09	0.17	29%	0.32	0.50	0.02	0.10	32%
2,2-Dimethyl Hexane	1.34	0.37	28%	1.37	2%	0.76	0.24	31%	0.49	0.20	40%	0.49	0.66	0.16	0.11	23%	0.30	0.42	0.12	0.06	20%
2,3,5-Trimethyl Hexane	1.47	0.43	29%	1.51	2%	0.85	0.27	32%	0.54	0.23	42%	0.53	0.74	0.04	0.16	30%	0.30	0.47	0.04	0.09	30%
3,3-Diethyl Pentane	1.55	0.44	28%	1.59	2%	0.89	0.28	31%	0.59	0.23	40%	0.61	0.79	0.23	0.13	21%	0.33	0.49	0.16	0.07	22%
4-Ethyl Heptane	1.63	0.49	30%	1.67	3%	0.92	0.32	35%	0.58	0.27	46%	0.56	0.82	0.00	0.19	34%	0.27	0.47	-0.08	0.12	44%
2-Methyl Octane	1.15	0.39	34%	1.18	2%	0.71	0.27	38%	0.44	0.22	51%	0.37	0.63	-0.29	0.21	56%	0.16	0.34	-0.23	0.13	81%
2,2,5-Trimethyl Hexane	1.47	0.39	27%	1.51	3%	0.79	0.24	30%	0.51	0.20	39%	0.52	0.68	0.19	0.11	22%	0.31	0.45	0.13	0.07	21%
4-Methyl Octane	1.31	0.42	32%	1.34	2%	0.78	0.28	36%	0.49	0.24	49%	0.44	0.69	-0.18	0.20	45%	0.20	0.39	-0.17	0.12	60%
3,5-Dimethyl Heptane	2.03	0.59	29%	2.09	3%	1.12	0.37	33%	0.72	0.31	43%	0.71	0.99	0.12	0.21	29%	0.35	0.59	-0.04	0.14	39%
2,4-Dimethyl Heptane	1.75	0.50	29%	1.80	3%	0.96	0.32	33%	0.61	0.27	44%	0.58	0.85	0.01	0.19	33%	0.30	0.50	-0.06	0.12	40%
3-Methyl Nonane	1.05	0.37	36%	1.08	3%	0.65	0.26	39%	0.40	0.22	55%	0.32	0.58	-0.34	0.21	66%	0.11	0.30	-0.30	0.14	124%
2,6-Dimethyl Octane	1.44	0.44	31%	1.49	3%	0.80	0.28	35%	0.51	0.24	47%	0.47	0.72	-0.10	0.19	41%	0.21	0.41	-0.18	0.13	66%
4-Propyl Heptane	1.37	0.43	32%	1.41	3%	0.78	0.29	37%	0.49	0.24	49%	0.44	0.71	-0.14	0.20	44%	0.19	0.38	-0.19	0.13	69%
4-Methyl Nonane	1.18	0.40	34%	1.21	3%	0.71	0.27	38%	0.44	0.23	52%	0.38	0.63	-0.25	0.20	54%	0.15	0.33	-0.25	0.13	91%
2,4-Dimethyl Octane	1.35	0.43	32%	1.38	3%	0.78	0.29	36%	0.48	0.24	50%	0.43	0.69	-0.20	0.21	48%	0.18	0.38	-0.22	0.13	73%
2-Methyl Nonane	1.02	0.38	37%	1.05	3%	0.64	0.26	40%	0.39	0.22	56%	0.31	0.58	-0.36	0.22	70%	0.10	0.29	-0.33	0.14	149%
3,4-Diethyl Hexane	1.36	0.40	29%	1.39	2%	0.77	0.26	34%	0.49	0.22	44%	0.48	0.68	0.05	0.14	30%	0.24	0.39	-0.03	0.09	37%
4-Methyl Decane	0.95	0.36	37%	0.98	3%	0.60	0.24	41%	0.36	0.21	57%	0.29	0.54	-0.37	0.21	74%	0.08	0.26	-0.34	0.14	183%
2,6-Dimethyl Nonane	1.09	0.37	34%	1.12	3%	0.64	0.25	39%	0.40	0.21	53%	0.33	0.58	-0.28	0.20	61%	0.11	0.30	-0.29	0.14	123%
3,5-Diethyl Heptane	1.46	0.48	33%	1.51	3%	0.83	0.30	37%	0.52	0.26	50%	0.46	0.75	-0.19	0.23	48%	0.16	0.39	-0.31	0.17	104%
3-Methyl Undecane	0.83	0.33	39%	0.86	3%	0.53	0.22	42%	0.32	0.19	60%	0.25	0.48	-0.41	0.21	84%	0.04	0.22	-0.36	0.14	315%
5-Methyl Undecane	0.87	0.33	38%	0.90	3%	0.55	0.23	42%	0.33	0.19	58%	0.26	0.50	-0.38	0.20	78%	0.06	0.23	-0.35	0.14	251%
3,6-Dimethyl Decane	1.03	0.37	36%	1.06	4%	0.62	0.25	40%	0.38	0.21	55%	0.31	0.57	-0.33	0.21	67%	0.08	0.28	-0.34	0.15	179%
2,6-Diethyl Octane	1.27	0.42	33%	1.32	3%	0.74	0.27	37%	0.47	0.23	49%	0.42	0.67	-0.14	0.19	46%	0.16	0.36	-0.23	0.14	88%
3-Methyl Dodecane	0.77	0.31	40%	0.80	4%	0.50	0.21	43%	0.30	0.18	60%	0.23	0.46	-0.41	0.20	86%	0.03	0.21	-0.36	0.14	425%
5-Methyl Dodecane	0.79	0.32	40%	0.82	3%	0.51	0.22	43%	0.31	0.18	60%	0.24	0.47	-0.39	0.20	83%	0.04	0.21	-0.35	0.14	367%
3,6-Dimethyl Undecane	0.95	0.35	37%	0.98	4%	0.58	0.23	41%	0.35	0.20	56%	0.29	0.53	-0.34	0.20	69%	0.06	0.25	-0.34	0.14	227%
3,7-Diethyl Nonane	1.17	0.39	33%	1.22	4%	0.66	0.25	38%	0.42	0.21	51%	0.37	0.61	-0.18	0.19	51%	0.11	0.31	-0.28	0.14	124%
3-Methyl Tridecane	0.72	0.30	41%	0.75	3%	0.47	0.20	43%	0.29	0.17	60%	0.22	0.43	-0.40	0.19	86%	0.02	0.19	-0.35	0.13	556%
6-Methyl Tridecane	0.75	0.30	40%	0.78	3%	0.48	0.21	43%	0.29	0.17	59%	0.23	0.45	-0.37	0.19	82%	0.03	0.20	-0.34	0.13	422%
3,7-Dimethyl Dodecane	0.86	0.32	38%	0.89	4%	0.52	0.22	41%	0.32	0.18	57%	0.26	0.49	-0.33	0.19	71%	0.05	0.23	-0.33	0.14	274%
3,8-Diethyl Decane	0.77	0.32	41%	0.80	4%	0.49	0.21	43%	0.30	0.18	60%	0.23	0.46	-0.42	0.20	85%	0.02	0.20	-0.38	0.14	787%
3-Methyl Tetradecane	0.68	0.28	42%	0.71	4%	0.44	0.19	44%	0.27	0.16	60%	0.21	0.41	-0.37	0.18	85%	0.02	0.18	-0.33	0.13	691%
6-Methyl Tetradecane	0.71	0.29	41%	0.73	4%	0.45	0.20	43%	0.28	0.17	59%	0.22	0.43	-0.36	0.18	81%	0.02	0.19	-0.32	0.13	510%

Table C-5. Summary of calculated incremental and relative reactivities in various scales. Calculated using the SAPRC-99 mechansim (8/30/99)

Compound or Mixture	MIR (gm O3 / gm VOC)					MOIR (gm/gm)			EBIR (gm/gm)			Base Case Relative Reactivities [a]									
	39 Scenarios			Avg. Conds		39 Scenarios			39 Scenarios			Ozone Yield (gm basis)					Max 8-Hour Avg (gm basis)				
	Avg.	Sdev			D%	Avg.	Sdev		Avg.	Sdev		Avg.	Max	Min	Sdev		Avg.	Max	Min	Sdev	
3,7-Dimethyl Tridecane	0.77	0.30	39%	0.80	4%	0.48	0.20	42%	0.30	0.17	58%	0.24	0.45	-0.34	0.18	76%	0.03	0.21	-0.33	0.13	412%
3,9-Diethyl Undecane	0.72	0.30	42%	0.75	4%	0.46	0.20	43%	0.29	0.17	60%	0.22	0.44	-0.39	0.19	84%	0.01	0.19	-0.36	0.14	1039%
3-Methyl Pentadecane	0.64	0.27	42%	0.67	4%	0.42	0.18	44%	0.26	0.16	60%	0.20	0.40	-0.35	0.17	84%	0.01	0.18	-0.32	0.12	871%
7-Methyl Pentadecane	0.64	0.27	43%	0.67	4%	0.42	0.18	44%	0.26	0.16	60%	0.20	0.40	-0.36	0.17	85%	0.01	0.18	-0.32	0.12	940%
4,8-Dimethyl Tetradecane	0.69	0.29	42%	0.72	4%	0.44	0.19	44%	0.27	0.16	60%	0.21	0.42	-0.36	0.17	82%	0.01	0.18	-0.34	0.13	889%
Branched C5 Alkanes	1.87	0.47	25%	1.91	2%	1.08	0.28	26%	0.77	0.24	31%	0.89	1.56	0.31	0.19	22%	0.57	0.79	0.28	0.11	19%
Branched C6 Alkanes	1.72	0.43	25%	1.77	3%	0.97	0.25	26%	0.67	0.22	32%	0.75	1.15	0.29	0.14	19%	0.50	0.66	0.26	0.08	16%
Branched C7 Alkanes	1.91	0.50	26%	1.95	2%	1.05	0.30	29%	0.70	0.26	37%	0.75	0.96	0.31	0.14	19%	0.47	0.64	0.27	0.07	16%
Branched C8 Alkanes	1.85	0.52	28%	1.90	3%	1.02	0.32	32%	0.66	0.27	41%	0.66	0.90	0.17	0.17	26%	0.37	0.57	0.09	0.10	27%
Branched C9 Alkanes	1.49	0.46	31%	1.53	3%	0.85	0.30	35%	0.53	0.25	47%	0.49	0.75	-0.11	0.20	40%	0.24	0.43	-0.13	0.12	51%
Branched C10 Alkanes	1.27	0.42	33%	1.31	3%	0.74	0.27	37%	0.46	0.23	50%	0.41	0.66	-0.20	0.20	50%	0.16	0.36	-0.23	0.14	83%
Branched C11 alkanes	1.01	0.36	36%	1.04	3%	0.62	0.24	40%	0.37	0.21	55%	0.31	0.56	-0.32	0.21	68%	0.09	0.28	-0.32	0.14	152%
Branched C12 Alkanes	0.94	0.35	37%	0.97	3%	0.58	0.24	41%	0.35	0.20	57%	0.28	0.53	-0.36	0.21	73%	0.07	0.25	-0.35	0.14	217%
Branched C13 Alkanes	0.86	0.33	38%	0.89	3%	0.54	0.22	42%	0.33	0.19	58%	0.26	0.50	-0.37	0.20	76%	0.05	0.23	-0.35	0.14	285%
Branched C14 Alkanes	0.80	0.31	39%	0.82	3%	0.50	0.21	42%	0.31	0.18	58%	0.24	0.46	-0.36	0.19	77%	0.04	0.21	-0.33	0.13	348%
Branched C15 Alkanes	0.73	0.30	40%	0.76	4%	0.46	0.20	43%	0.29	0.17	59%	0.23	0.44	-0.35	0.18	79%	0.03	0.20	-0.33	0.13	482%
Branched C16 Alkanes	0.67	0.28	42%	0.69	4%	0.43	0.19	44%	0.27	0.16	60%	0.21	0.41	-0.36	0.17	83%	0.01	0.18	-0.33	0.13	894%
Branched C17 Alkanes	0.63	0.26	42%	0.65	4%	0.41	0.18	44%	0.25	0.15	60%	0.19	0.39	-0.34	0.16	83%	0.01	0.17	-0.31	0.12	895%
Branched C18 Alkanes	0.59	0.25	42%	0.62	4%	0.38	0.17	44%	0.24	0.14	60%	0.18	0.36	-0.32	0.15	83%	0.01	0.16	-0.29	0.11	895%
Cyclopropane	0.11	0.03	28%	0.11	1%	0.07	0.02	32%	0.05	0.02	39%	0.06	0.09	0.02	0.01	25%	0.03	0.05	0.02	0.01	21%
Cyclobutane	1.21	0.36	29%	1.23	2%	0.75	0.25	34%	0.54	0.22	40%	0.59	0.88	0.17	0.15	25%	0.32	0.46	0.15	0.08	25%
Cyclopentane	2.65	0.68	26%	2.71	2%	1.48	0.41	28%	1.01	0.35	35%	1.11	1.54	0.44	0.20	18%	0.71	0.95	0.40	0.11	16%
Isopropyl Cyclopropane	1.66	0.43	26%	1.69	2%	0.98	0.28	28%	0.69	0.24	35%	0.77	1.21	0.27	0.16	21%	0.48	0.64	0.24	0.08	18%
Methylcyclopentane	2.46	0.64	26%	2.53	3%	1.33	0.39	29%	0.88	0.33	37%	0.94	1.23	0.41	0.18	19%	0.57	0.79	0.35	0.10	18%
Cyclohexane	2.02	0.57	28%	2.06	2%	1.16	0.36	31%	0.77	0.31	40%	0.79	1.04	0.29	0.17	22%	0.48	0.67	0.25	0.09	19%
Cycloheptane	2.40	0.65	27%	2.49	4%	1.24	0.38	31%	0.81	0.33	40%	0.83	1.12	0.28	0.21	26%	0.46	0.74	0.07	0.16	34%
1,3-Dimeth. Cyclopentane	2.24	0.60	27%	2.30	3%	1.18	0.36	31%	0.77	0.31	40%	0.79	1.04	0.33	0.18	22%	0.45	0.67	0.12	0.12	27%
Methylcyclohexane	2.08	0.58	28%	2.15	3%	1.13	0.35	31%	0.73	0.30	41%	0.73	1.00	0.18	0.19	27%	0.42	0.65	0.08	0.12	29%
Ethyl Cyclopentane	2.36	0.65	28%	2.42	3%	1.27	0.40	32%	0.83	0.34	41%	0.85	1.14	0.35	0.20	24%	0.46	0.70	0.11	0.13	28%
Cyclooctane	1.83	0.55	30%	1.90	4%	0.98	0.34	34%	0.62	0.29	47%	0.57	0.89	-0.13	0.25	43%	0.25	0.52	-0.25	0.18	72%
Propyl Cyclopentane	2.00	0.58	29%	2.07	3%	1.08	0.36	34%	0.69	0.31	45%	0.66	0.97	0.04	0.22	33%	0.32	0.56	-0.11	0.15	47%
1,3-Dimethyl Cyclohexane	1.82	0.53	29%	1.89	4%	0.98	0.33	34%	0.62	0.28	45%	0.58	0.87	-0.08	0.23	39%	0.28	0.52	-0.17	0.16	56%
Ethylcyclohexane	1.95	0.56	29%	2.01	3%	1.06	0.35	33%	0.68	0.30	43%	0.67	0.95	0.09	0.20	31%	0.34	0.58	-0.04	0.14	40%
1,1,3-Trimethyl Cyclohex.	1.53	0.46	30%	1.57	3%	0.84	0.29	35%	0.51	0.25	48%	0.46	0.73	-0.24	0.22	48%	0.21	0.41	-0.23	0.15	70%
1-Eth.-4-Meth. Cyclohex.	1.74	0.52	30%	1.80	4%	0.94	0.33	35%	0.59	0.28	47%	0.54	0.85	-0.13	0.23	43%	0.23	0.48	-0.25	0.17	74%
Propyl Cyclohexane	1.71	0.52	30%	1.77	3%	0.94	0.33	35%	0.60	0.28	47%	0.57	0.85	-0.03	0.21	37%	0.26	0.48	-0.15	0.14	55%
Butyl Cyclohexane	1.33	0.44	33%	1.38	3%	0.77	0.29	37%	0.49	0.25	50%	0.43	0.71	-0.19	0.21	50%	0.16	0.37	-0.26	0.15	92%
1-Meth.-3-Isopr. Cyclohex.	1.38	0.44	32%	1.43	4%	0.78	0.28	36%	0.49	0.24	49%	0.44	0.71	-0.18	0.21	49%	0.17	0.40	-0.25	0.15	87%
1,4-Diethyl-Cyclohexane	1.62	0.50	31%	1.68	4%	0.88	0.31	36%	0.56	0.27	48%	0.51	0.80	-0.12	0.22	44%	0.19	0.44	-0.28	0.17	88%
1,3-Diethyl-Cyclohexane	1.45	0.47	33%	1.51	4%	0.81	0.30	37%	0.51	0.26	51%	0.45	0.74	-0.25	0.24	53%	0.14	0.39	-0.35	0.18	124%
Pentyl Cyclohexane	1.14	0.40	35%	1.17	3%	0.67	0.26	39%	0.42	0.22	53%	0.36	0.62	-0.26	0.21	58%	0.11	0.31	-0.30	0.15	135%

Table C-5. Summary of calculated incremental and relative reactivities in various scales. Calculated using the SAPRC-99 mechansim (8/30/99)

Compound or Mixture	MIR (gm O3 / gm VOC)					MOIR (gm/gm)			EBIR (gm/gm)			Base Case Relative Reactivities [a]									
	39 Scenarios			Avg. Conds		39 Scenarios			39 Scenarios			Ozone Yield (gm basis)					Max 8-Hour Avg (gm basis)				
	Avg.	Sdev			D%	Avg.	Sdev		Avg.	Sdev		Avg.	Max	Min	Sdev		Avg.	Max	Min	Sdev	
1-Ethyl-2-Propyl Cyclohex	1.11	0.42	38%	1.15	4%	0.67	0.28	41%	0.41	0.24	57%	0.33	0.62	-0.48	0.25	75%	0.06	0.29	-0.45	0.18	318%
13-Dieth-5-Me. Cyclohex.	1.28	0.44	34%	1.34	5%	0.72	0.28	39%	0.45	0.24	54%	0.38	0.68	-0.39	0.24	64%	0.08	0.32	-0.44	0.19	239%
1-Meth.-4-Pentyl Cyclohex.	1.00	0.38	38%	1.04	4%	0.60	0.25	41%	0.37	0.21	57%	0.30	0.57	-0.41	0.22	74%	0.05	0.26	-0.41	0.17	346%
1,3,5-Triethyl Cyclohex.	1.20	0.42	35%	1.26	5%	0.68	0.27	40%	0.42	0.23	54%	0.36	0.65	-0.38	0.23	65%	0.06	0.30	-0.44	0.19	317%
Hexyl Cyclohexane	0.94	0.36	38%	0.98	4%	0.59	0.24	41%	0.36	0.21	57%	0.29	0.55	-0.37	0.21	71%	0.06	0.26	-0.36	0.15	261%
1-Meth.-2-Hexyl-Cyclohex.	0.86	0.35	41%	0.89	4%	0.54	0.23	43%	0.33	0.20	60%	0.26	0.51	-0.47	0.22	85%	0.02	0.23	-0.42	0.16	963%
13-Dieth-5-Pent Cyclohx.	1.14	0.40	35%	1.19	5%	0.64	0.26	40%	0.41	0.22	54%	0.35	0.63	-0.33	0.21	62%	0.06	0.28	-0.41	0.18	304%
Heptyl Cyclohexane	0.84	0.34	40%	0.87	4%	0.53	0.23	43%	0.33	0.19	58%	0.26	0.50	-0.39	0.20	77%	0.03	0.23	-0.36	0.15	419%
1-Meth.-4-Heptyl Cyclohex.	0.75	0.33	43%	0.79	4%	0.48	0.22	45%	0.30	0.18	62%	0.22	0.47	-0.48	0.21	92%	0.00	0.19	-0.43	0.16	-3285%
13-Diprop-5-Eth Cyclohx.	1.09	0.39	35%	1.14	5%	0.61	0.24	40%	0.39	0.21	54%	0.34	0.60	-0.28	0.20	59%	0.06	0.27	-0.39	0.17	289%
Octyl Cyclohexane	0.78	0.32	41%	0.81	4%	0.49	0.21	43%	0.31	0.18	59%	0.25	0.47	-0.37	0.19	77%	0.03	0.21	-0.35	0.14	546%
1-Methyl-2-Octyl Cyclohex	0.73	0.31	43%	0.76	4%	0.47	0.21	44%	0.29	0.18	61%	0.23	0.46	-0.41	0.19	85%	0.00	0.19	-0.39	0.15	######
135-Tripropyl Cyclohex.	1.05	0.37	35%	1.10	5%	0.59	0.23	40%	0.38	0.20	54%	0.33	0.58	-0.24	0.19	57%	0.06	0.26	-0.37	0.16	272%
Nonyl Cyclohexane	0.73	0.30	42%	0.76	4%	0.47	0.20	43%	0.29	0.17	59%	0.23	0.45	-0.35	0.18	77%	0.02	0.20	-0.33	0.13	666%
1,3-Prop.-5-Butyl Cyclohex.	0.93	0.34	37%	0.98	5%	0.53	0.22	41%	0.34	0.19	54%	0.30	0.53	-0.24	0.18	59%	0.04	0.24	-0.36	0.15	344%
Decyl Cyclohexane	0.69	0.29	42%	0.72	4%	0.44	0.19	43%	0.28	0.16	59%	0.22	0.43	-0.33	0.17	76%	0.02	0.19	-0.33	0.13	847%
1-Methyl-4-Nonyl Cyclohex	0.66	0.29	45%	0.69	5%	0.43	0.19	45%	0.27	0.16	62%	0.20	0.43	-0.40	0.18	89%	-0.01	0.17	-0.40	0.14	-1240%
C6 Cycloalkanes	2.02	0.57	28%	2.06	2%	1.16	0.36	31%	0.77	0.31	40%	0.79	1.04	0.29	0.17	22%	0.48	0.67	0.25	0.09	19%
C7 Cycloalkanes	2.08	0.58	28%	2.15	3%	1.13	0.35	31%	0.73	0.30	41%	0.73	1.00	0.18	0.19	27%	0.42	0.65	0.08	0.12	29%
C8 Cycloalkanes	1.95	0.56	29%	2.01	3%	1.06	0.35	33%	0.68	0.30	43%	0.67	0.95	0.09	0.20	31%	0.34	0.58	-0.04	0.14	40%
C9 Bicycloalkanes	1.75	0.53	30%	1.81	3%	0.95	0.33	35%	0.60	0.28	47%	0.56	0.86	-0.08	0.23	40%	0.25	0.49	-0.20	0.16	64%
C9 Cycloalkanes	1.72	0.52	30%	1.78	3%	0.94	0.33	35%	0.59	0.28	47%	0.56	0.85	-0.08	0.22	40%	0.25	0.48	-0.20	0.16	64%
C10 Bicycloalkanes	1.46	0.47	32%	1.51	4%	0.82	0.30	36%	0.52	0.25	49%	0.47	0.75	-0.17	0.22	47%	0.18	0.41	-0.26	0.16	89%
C10 Cycloalkanes	1.44	0.46	32%	1.49	4%	0.81	0.30	36%	0.51	0.25	49%	0.46	0.74	-0.16	0.22	47%	0.18	0.40	-0.26	0.16	89%
C11 Bicycloalkanes	1.19	0.42	36%	1.24	4%	0.70	0.28	40%	0.43	0.24	55%	0.36	0.64	-0.38	0.24	65%	0.08	0.31	-0.40	0.18	210%
C11 Cycloalkanes	1.17	0.42	36%	1.22	4%	0.69	0.27	40%	0.43	0.23	55%	0.36	0.64	-0.38	0.23	65%	0.08	0.31	-0.40	0.17	210%
C12 Bicycloalkanes	1.06	0.39	37%	1.11	4%	0.63	0.26	41%	0.39	0.22	56%	0.32	0.59	-0.39	0.22	70%	0.06	0.28	-0.41	0.17	305%
C12 Cycloalkanes	1.05	0.39	37%	1.09	4%	0.62	0.25	41%	0.39	0.22	56%	0.32	0.58	-0.39	0.22	70%	0.05	0.27	-0.40	0.17	305%
C13 Bicycloalkanes	0.96	0.37	38%	1.00	4%	0.58	0.24	42%	0.36	0.21	57%	0.29	0.55	-0.40	0.21	73%	0.04	0.25	-0.40	0.16	442%
C13 Cycloalkanes	0.95	0.36	38%	0.99	4%	0.57	0.24	42%	0.36	0.20	57%	0.29	0.54	-0.39	0.21	73%	0.04	0.25	-0.40	0.16	442%
C14 Bicycloalkanes	0.88	0.35	39%	0.92	4%	0.54	0.23	42%	0.34	0.19	58%	0.27	0.52	-0.38	0.20	74%	0.03	0.23	-0.39	0.16	593%
C14 Cycloalkanes	0.87	0.34	39%	0.91	4%	0.53	0.22	42%	0.33	0.19	58%	0.27	0.51	-0.37	0.20	74%	0.03	0.23	-0.39	0.15	593%
C15 Bicycloalkanes	0.85	0.33	39%	0.88	4%	0.51	0.22	42%	0.32	0.18	57%	0.26	0.50	-0.34	0.19	71%	0.03	0.22	-0.37	0.15	558%
C15 Cycloalkanes	0.84	0.33	39%	0.87	4%	0.51	0.21	42%	0.32	0.18	57%	0.26	0.50	-0.33	0.19	71%	0.03	0.22	-0.37	0.15	558%
Ethene	9.53	1.53	16%	9.86	3%	3.59	0.49	14%	2.27	0.50	22%	2.87	5.30	2.35	0.59	21%	2.79	4.01	2.36	0.40	14%
Propene	12.19	1.92	16%	12.70	4%	4.29	0.64	15%	2.76	0.64	23%	3.50	6.42	2.88	0.64	18%	3.45	4.52	3.13	0.31	9%
1-Butene	10.91	1.92	18%	11.36	4%	3.94	0.73	19%	2.56	0.68	27%	3.18	5.43	2.61	0.50	16%	2.85	3.38	2.60	0.20	7%
3-Methyl-1-Butene	7.72	1.39	18%	8.04	4%	2.85	0.54	19%	1.87	0.51	27%	2.29	3.78	1.87	0.34	15%	2.00	2.34	1.83	0.13	7%
1-Pentene	8.00	1.45	18%	8.35	4%	2.95	0.57	19%	1.93	0.54	28%	2.36	3.83	1.93	0.34	15%	2.04	2.35	1.86	0.13	6%
1-Hexene	6.09	1.15	19%	6.37	4%	2.37	0.49	21%	1.56	0.45	29%	1.88	2.93	1.53	0.26	14%	1.60	1.95	1.45	0.12	8%
3-Methyl-1-Pentene	6.55	1.20	18%	6.84	4%	2.47	0.49	20%	1.62	0.46	28%	1.96	3.10	1.60	0.28	14%	1.62	1.90	1.43	0.11	7%

Table C-5. Summary of calculated incremental and relative reactivities in various scales. Calculated using the SAPRC-99 mechansim (8/30/99)

Compound or Mixture	MIR (gm O3 / gm VOC)					MOIR (gm/gm)			EBIR (gm/gm)			Base Case Relative Reactivities [a]									
	39 Scenarios			Avg. Conds		39 Scenarios			39 Scenarios			Ozone Yield (gm basis)					Max 8-Hour Avg (gm basis)				
	Avg.	Sdev			D%	Avg.	Sdev		Avg.	Sdev		Avg.	Max	Min	Sdev		Avg.	Max	Min	Sdev	
3,3-Dimethyl-1-Butene	6.46	1.16	18%	6.74	4%	2.47	0.44	18%	1.63	0.42	26%	2.00	3.28	1.63	0.30	15%	1.78	2.26	1.59	0.16	9%
4-Methyl-1-Pentene	6.21	1.15	19%	6.47	4%	2.34	0.48	20%	1.53	0.44	29%	1.84	2.85	1.51	0.25	13%	1.53	1.77	1.33	0.10	6%
1-Heptene	4.49	0.90	20%	4.69	4%	1.80	0.41	23%	1.19	0.37	32%	1.38	1.83	1.07	0.17	12%	1.06	1.27	0.71	0.11	10%
1-Octene	3.42	0.72	21%	3.56	4%	1.41	0.35	25%	0.92	0.31	34%	1.04	1.35	0.78	0.13	13%	0.73	0.91	0.37	0.11	15%
1-Nonene	2.82	0.62	22%	2.94	4%	1.20	0.32	27%	0.77	0.28	36%	0.85	1.13	0.62	0.13	16%	0.55	0.73	0.16	0.12	22%
1-Decene	2.39	0.54	23%	2.50	4%	1.03	0.29	28%	0.66	0.25	38%	0.71	0.97	0.47	0.13	18%	0.42	0.60	0.03	0.13	30%
1-Undecene	2.09	0.49	23%	2.19	5%	0.91	0.26	29%	0.58	0.23	39%	0.62	0.85	0.36	0.13	20%	0.35	0.52	-0.04	0.13	36%
1-Dodecene	1.87	0.44	24%	1.95	5%	0.81	0.24	29%	0.52	0.21	40%	0.55	0.76	0.29	0.12	22%	0.30	0.46	-0.07	0.12	41%
1-Tridecene	1.70	0.40	24%	1.78	5%	0.74	0.22	30%	0.48	0.19	40%	0.50	0.69	0.25	0.11	23%	0.26	0.41	-0.09	0.12	45%
1-Tetradecene	1.56	0.37	24%	1.63	4%	0.68	0.20	30%	0.44	0.18	41%	0.46	0.64	0.22	0.11	24%	0.23	0.38	-0.09	0.11	47%
1-Pentadecene	1.45	0.35	24%	1.51	5%	0.63	0.19	30%	0.41	0.17	41%	0.42	0.59	0.20	0.10	24%	0.21	0.35	-0.09	0.10	49%
C4 Terminal Alkenes	10.91	1.92	18%	11.36	4%	3.94	0.73	19%	2.56	0.68	27%	3.18	5.43	2.61	0.50	16%	2.85	3.38	2.60	0.20	7%
C5 Terminal Alkenes	8.00	1.45	18%	8.35	4%	2.95	0.57	19%	1.93	0.54	28%	2.36	3.83	1.93	0.34	15%	2.04	2.35	1.86	0.13	6%
C6 Terminal Alkenes	6.09	1.15	19%	6.37	4%	2.37	0.49	21%	1.56	0.45	29%	1.88	2.93	1.53	0.26	14%	1.60	1.95	1.45	0.12	8%
C7 Terminal Alkenes	4.49	0.90	20%	4.69	4%	1.80	0.41	23%	1.19	0.37	32%	1.38	1.83	1.07	0.17	12%	1.06	1.27	0.71	0.11	10%
C8 Terminal Alkenes	3.42	0.72	21%	3.56	4%	1.41	0.35	25%	0.92	0.31	34%	1.04	1.35	0.78	0.13	13%	0.73	0.91	0.37	0.11	15%
C9 Terminal Alkenes	2.82	0.62	22%	2.94	4%	1.20	0.32	27%	0.77	0.28	36%	0.85	1.13	0.62	0.13	16%	0.55	0.73	0.16	0.12	22%
C10 Terminal Alkenes	2.39	0.54	23%	2.50	4%	1.03	0.29	28%	0.66	0.25	38%	0.71	0.97	0.47	0.13	18%	0.42	0.60	0.03	0.13	30%
C11 Terminal Alkenes	2.09	0.49	23%	2.19	5%	0.91	0.26	29%	0.58	0.23	39%	0.62	0.85	0.36	0.13	20%	0.35	0.52	-0.04	0.13	36%
C12 Terminal Alkenes	1.87	0.44	24%	1.95	5%	0.81	0.24	29%	0.52	0.21	40%	0.55	0.76	0.29	0.12	22%	0.30	0.46	-0.07	0.12	41%
C13 Terminal Alkenes	1.70	0.40	24%	1.78	5%	0.74	0.22	30%	0.48	0.19	40%	0.50	0.69	0.25	0.11	23%	0.26	0.41	-0.09	0.12	45%
C14 Terminal Alkenes	1.56	0.37	24%	1.63	4%	0.68	0.20	30%	0.44	0.18	41%	0.46	0.64	0.22	0.11	24%	0.23	0.38	-0.09	0.11	47%
C15 Terminal Alkenes	1.45	0.35	24%	1.51	5%	0.63	0.19	30%	0.41	0.17	41%	0.42	0.59	0.20	0.10	24%	0.21	0.35	-0.09	0.10	49%
Isobutene	6.59	0.86	13%	6.91	5%	2.07	0.26	13%	1.19	0.27	23%	1.48	2.14	1.12	0.25	17%	2.00	2.52	1.64	0.21	10%
2-Methyl-1-Butene	6.78	0.96	14%	7.12	5%	2.24	0.33	15%	1.33	0.33	25%	1.63	2.46	1.34	0.21	13%	2.05	2.58	1.74	0.18	9%
23-Dimethyl-1-Butene	5.02	0.73	15%	5.27	5%	1.70	0.27	16%	1.01	0.26	26%	1.22	1.68	1.05	0.12	10%	1.47	1.78	1.25	0.12	8%
2-Ethyl-1-Butene	5.28	0.77	15%	5.54	5%	1.79	0.28	16%	1.07	0.27	26%	1.30	1.84	1.11	0.14	11%	1.53	1.84	1.30	0.12	8%
2-Methyl-1-Pentene	5.41	0.78	14%	5.68	5%	1.81	0.28	16%	1.08	0.28	26%	1.30	1.83	1.11	0.14	11%	1.57	1.88	1.32	0.13	8%
2,3,3-trimethyl-1-Butene	4.94	0.82	17%	5.17	5%	1.81	0.31	17%	1.14	0.30	27%	1.36	1.81	1.21	0.13	10%	1.53	1.97	1.25	0.16	10%
3-Methyl-2-Isopropyl-1-Butene	4.29	0.84	20%	4.45	4%	1.76	0.41	23%	1.12	0.36	32%	1.27	1.55	0.99	0.12	10%	1.05	1.21	0.76	0.09	9%
trans-2-Butene	14.51	2.14	15%	15.33	6%	4.62	0.63	14%	2.82	0.63	22%	3.63	6.84	2.81	0.70	19%	4.54	5.89	3.87	0.36	8%
cis-2-Butene	13.81	2.06	15%	14.58	6%	4.52	0.64	14%	2.82	0.64	23%	3.62	6.85	2.89	0.69	19%	4.21	5.38	3.69	0.32	7%
2-Methyl-2-Butene	14.97	2.15	14%	16.01	7%	4.27	0.57	13%	2.37	0.58	25%	3.05	5.29	1.95	0.73	24%	5.15	6.93	3.84	0.65	13%
trans-2-Pentene	10.86	1.86	17%	11.39	5%	3.79	0.66	17%	2.47	0.64	26%	3.11	5.72	2.55	0.56	18%	2.94	3.36	2.58	0.18	6%
cis-2-Pentene	10.86	1.86	17%	11.43	5%	3.79	0.66	17%	2.46	0.63	26%	3.10	5.69	2.54	0.55	18%	2.94	3.36	2.58	0.18	6%
2,3-Dimethyl-2-Butene	13.90	2.28	16%	14.85	7%	3.59	0.52	14%	1.77	0.54	31%	2.28	4.78	1.02	0.88	38%	5.12	7.34	3.22	0.95	19%
Cis-3-Methyl-2-Hexene	13.40	1.97	15%	14.30	7%	4.01	0.53	13%	2.30	0.55	24%	2.92	4.99	2.09	0.57	20%	4.44	5.83	3.43	0.50	11%
Trans 3-Methyl-2-Hexene	14.13	2.08	15%	15.09	7%	4.18	0.54	13%	2.38	0.57	24%	3.02	5.19	2.12	0.62	21%	4.73	6.31	3.60	0.56	12%
Trans 4-Methyl-2-Hexene	8.57	1.47	17%	9.00	5%	3.00	0.54	18%	1.94	0.51	26%	2.43	4.36	2.01	0.41	17%	2.27	2.54	1.94	0.14	6%
Trans-2-Hexene	8.68	1.50	17%	9.14	5%	3.04	0.54	18%	1.98	0.52	26%	2.48	4.46	2.04	0.42	17%	2.30	2.58	1.94	0.14	6%
Trans-3-Hexene	8.68	1.67	19%	9.07	4%	3.12	0.64	20%	2.07	0.60	29%	2.57	4.61	1.97	0.48	19%	2.07	2.51	1.64	0.20	10%

Table C-5. Summary of calculated incremental and relative reactivities in various scales. Calculated using the SAPRC-99 mechansim (8/30/99)

Compound or Mixture	MIR (gm O3 / gm VOC)					MOIR (gm/gm)			EBIR (gm/gm)			Base Case Relative Reactivities [a]									
	39 Scenarios			Avg. Conds		39 Scenarios			39 Scenarios			Ozone Yield (gm basis)					Max 8-Hour Avg (gm basis)				
	Avg.	Sdev			D%	Avg.	Sdev		Avg.	Sdev		Avg.	Max	Min	Sdev		Avg.	Max	Min	Sdev	
Cis-2-Hexene	8.68	1.50	17%	9.14	5%	3.04	0.54	18%	1.98	0.52	26%	2.48	4.46	2.04	0.42	17%	2.30	2.58	1.94	0.14	6%
2-Methyl-2-Pentene	12.40	1.81	15%	13.24	7%	3.71	0.52	14%	2.12	0.52	24%	2.67	4.32	2.05	0.45	17%	3.92	4.83	3.06	0.41	10%
Cis-3-Hexene	8.74	1.69	19%	9.14	5%	3.16	0.66	21%	2.10	0.61	29%	2.60	4.64	1.99	0.49	19%	2.08	2.52	1.63	0.21	10%
2,3-Dimethyl-2-Hexene	10.88	1.69	16%	11.63	7%	3.02	0.40	13%	1.58	0.42	27%	1.98	3.45	1.18	0.55	28%	3.79	5.10	2.60	0.58	15%
Trans 4,4-dimethyl-2-Hexene	7.16	1.22	17%	7.53	5%	2.49	0.43	18%	1.59	0.41	26%	1.97	3.35	1.67	0.29	15%	1.93	2.13	1.67	0.10	5%
Cis-3-Heptene	7.26	1.43	20%	7.60	5%	2.67	0.58	22%	1.78	0.53	30%	2.20	3.80	1.67	0.40	18%	1.66	2.02	1.14	0.19	11%
Trans-3-Heptene	7.26	1.43	20%	7.60	5%	2.67	0.58	22%	1.78	0.53	30%	2.20	3.80	1.67	0.40	18%	1.66	2.02	1.14	0.19	11%
Trans-2-Heptene	7.10	1.24	17%	7.46	5%	2.51	0.46	18%	1.63	0.44	27%	2.03	3.57	1.69	0.33	16%	1.82	2.06	1.41	0.13	7%
Trans-3-Octene	5.97	1.19	20%	6.26	5%	2.22	0.50	22%	1.48	0.46	31%	1.81	3.07	1.35	0.33	18%	1.31	1.61	0.77	0.18	13%
Cis-4-Octene	6.06	1.21	20%	6.37	5%	2.27	0.51	22%	1.52	0.47	31%	1.85	3.10	1.38	0.34	18%	1.32	1.63	0.77	0.18	14%
Trans-4-Octene	6.02	1.19	20%	6.30	5%	2.22	0.49	22%	1.48	0.45	30%	1.81	3.09	1.35	0.33	18%	1.32	1.62	0.79	0.17	13%
Trans 2,5-Dimethyl 3-Hexene	6.22	1.26	20%	6.50	5%	2.38	0.55	23%	1.61	0.50	31%	1.95	3.20	1.45	0.35	18%	1.35	1.68	0.76	0.19	14%
Trans 2,2-Dimethyl 3-Hexene	6.04	1.18	19%	6.33	5%	2.27	0.48	21%	1.51	0.45	30%	1.83	2.91	1.45	0.29	16%	1.44	1.74	0.99	0.14	10%
2,4,4-trimethyl-2-Pentene	5.98	0.96	16%	6.39	7%	1.94	0.34	18%	1.15	0.31	27%	1.40	1.97	1.18	0.15	10%	1.66	1.96	1.10	0.20	12%
Trans-4-Nonene	4.96	1.00	20%	5.19	5%	1.86	0.43	23%	1.25	0.39	32%	1.51	2.50	1.10	0.27	18%	1.04	1.30	0.50	0.16	16%
3,4-Diethyl-2-Hexene	3.86	0.83	22%	4.04	5%	1.62	0.42	26%	1.05	0.37	36%	1.17	1.52	0.81	0.15	13%	0.81	1.09	0.19	0.18	22%
Cis-5-Decene	4.30	0.89	21%	4.52	5%	1.63	0.38	24%	1.09	0.35	32%	1.31	2.13	0.94	0.24	18%	0.86	1.09	0.34	0.16	18%
Trans-4-Decene	4.27	0.89	21%	4.48	5%	1.62	0.39	24%	1.09	0.35	32%	1.31	2.12	0.93	0.24	18%	0.85	1.09	0.32	0.16	19%
Trans-5-Undecene	3.73	0.79	21%	3.90	5%	1.43	0.35	24%	0.96	0.32	33%	1.15	1.83	0.80	0.21	19%	0.72	0.93	0.21	0.15	21%
Trans-5-Dodecene	3.37	0.71	21%	3.53	5%	1.29	0.32	25%	0.87	0.29	33%	1.04	1.65	0.72	0.19	19%	0.64	0.83	0.16	0.14	22%
Trans-5-Tridecene	3.09	0.65	21%	3.23	5%	1.19	0.29	25%	0.80	0.27	33%	0.95	1.50	0.66	0.18	19%	0.58	0.76	0.13	0.13	23%
Trans-5-Tetradecene	2.85	0.60	21%	2.99	5%	1.10	0.27	25%	0.74	0.25	33%	0.88	1.38	0.61	0.16	19%	0.53	0.69	0.11	0.12	23%
Trans-5-Tetradecene	2.65	0.56	21%	2.78	5%	1.02	0.25	25%	0.69	0.23	34%	0.82	1.28	0.56	0.15	19%	0.49	0.64	0.09	0.12	24%
2-Pentenes	10.86	1.86	17%	11.39	5%	3.79	0.66	17%	2.46	0.63	26%	3.11	5.71	2.54	0.56	18%	2.94	3.36	2.58	0.18	6%
2-Hexenes	8.68	1.50	17%	9.14	5%	3.04	0.54	18%	1.98	0.52	26%	2.48	4.46	2.04	0.42	17%	2.30	2.58	1.94	0.14	6%
2-Heptenes	7.26	1.43	20%	7.60	5%	2.67	0.58	22%	1.78	0.53	30%	2.20	3.80	1.67	0.40	18%	1.66	2.02	1.14	0.19	11%
3-Octenes	5.97	1.19	20%	6.26	5%	2.22	0.50	22%	1.48	0.46	31%	1.81	3.07	1.35	0.33	18%	1.31	1.61	0.77	0.18	13%
3-Nonenes	5.04	1.02	20%	5.27	5%	1.89	0.44	23%	1.27	0.40	32%	1.54	2.54	1.12	0.28	18%	1.06	1.32	0.51	0.17	16%
C10 3-Alkenes	4.27	0.89	21%	4.48	5%	1.62	0.39	24%	1.09	0.35	32%	1.31	2.12	0.93	0.24	18%	0.85	1.09	0.32	0.16	19%
C11 3-Alkenes	3.73	0.79	21%	3.90	5%	1.43	0.35	24%	0.96	0.32	33%	1.15	1.83	0.80	0.21	19%	0.72	0.93	0.21	0.15	21%
C12 2-Alkenes	3.37	0.71	21%	3.53	5%	1.29	0.32	25%	0.87	0.29	33%	1.04	1.65	0.72	0.19	19%	0.64	0.83	0.16	0.14	22%
C12 3-Alkenes	3.37	0.71	21%	3.53	5%	1.29	0.32	25%	0.87	0.29	33%	1.04	1.65	0.72	0.19	19%	0.64	0.83	0.16	0.14	22%
C13 3-Alkenes	3.09	0.65	21%	3.23	5%	1.19	0.29	25%	0.80	0.27	33%	0.95	1.50	0.66	0.18	19%	0.58	0.76	0.13	0.13	23%
C14 3-Alkenes	2.85	0.60	21%	2.99	5%	1.10	0.27	25%	0.74	0.25	33%	0.88	1.38	0.61	0.16	19%	0.53	0.69	0.11	0.12	23%
C15 3-Alkenes	2.65	0.56	21%	2.78	5%	1.02	0.25	25%	0.69	0.23	34%	0.82	1.28	0.56	0.15	19%	0.49	0.64	0.09	0.12	24%
C4 Internal Alkenes	14.16	2.10	15%	14.95	6%	4.57	0.63	14%	2.82	0.63	22%	3.62	6.85	2.86	0.69	19%	4.38	5.63	3.80	0.34	8%
C5 Internal Alkenes	10.86	1.86	17%	11.39	5%	3.79	0.66	17%	2.46	0.63	26%	3.11	5.71	2.54	0.56	18%	2.94	3.36	2.58	0.18	6%
C6 Internal Alkenes	8.68	1.50	17%	9.14	5%	3.04	0.54	18%	1.98	0.52	26%	2.48	4.46	2.04	0.42	17%	2.30	2.58	1.94	0.14	6%
C7 Internal Alkenes	7.26	1.43	20%	7.60	5%	2.67	0.58	22%	1.78	0.53	30%	2.20	3.80	1.67	0.40	18%	1.66	2.02	1.14	0.19	11%
C8 Internal Alkenes	6.02	1.19	20%	6.30	5%	2.22	0.49	22%	1.48	0.45	30%	1.81	3.09	1.35	0.33	18%	1.32	1.62	0.79	0.17	13%
C9 Internal Alkenes	5.04	1.02	20%	5.27	5%	1.89	0.44	23%	1.27	0.40	32%	1.54	2.54	1.12	0.28	18%	1.06	1.32	0.51	0.17	16%

Table C-5. Summary of calculated incremental and relative reactivities in various scales. Calculated using the SAPRC-99 mechansim (8/30/99)

Compound or Mixture	MIR (gm O3 / gm VOC)					MOIR (gm/gm)			EBIR (gm/gm)			Base Case Relative Reactivities [a]									
	39 Scenarios			Avg. Conds		39 Scenarios			39 Scenarios			Ozone Yield (gm basis)					Max 8-Hour Avg (gm basis)				
	Avg.	Sdev			D%	Avg.	Sdev		Avg.	Sdev		Avg.	Max	Min	Sdev		Avg.	Max	Min	Sdev	
C10 Internal Alkenes	4.27	0.89	21%	4.48	5%	1.62	0.39	24%	1.09	0.35	32%	1.31	2.12	0.93	0.24	18%	0.85	1.09	0.32	0.16	19%
C11 Internal Alkenes	3.73	0.79	21%	3.90	5%	1.43	0.35	24%	0.96	0.32	33%	1.15	1.83	0.80	0.21	19%	0.72	0.93	0.21	0.15	21%
C12 Internal Alkenes	3.37	0.71	21%	3.53	5%	1.29	0.32	25%	0.87	0.29	33%	1.04	1.65	0.72	0.19	19%	0.64	0.83	0.16	0.14	22%
C13 Internal Alkenes	3.09	0.65	21%	3.23	5%	1.19	0.29	25%	0.80	0.27	33%	0.95	1.50	0.66	0.18	19%	0.58	0.76	0.13	0.13	23%
C14 Internal Alkenes	2.85	0.60	21%	2.99	5%	1.10	0.27	25%	0.74	0.25	33%	0.88	1.38	0.61	0.16	19%	0.53	0.69	0.11	0.12	23%
C15 Internal Alkenes	2.65	0.56	21%	2.78	5%	1.02	0.25	25%	0.69	0.23	34%	0.82	1.28	0.56	0.15	19%	0.49	0.64	0.09	0.12	24%
1,3-Butadiene	12.88	2.11	16%	13.45	4%	4.44	0.70	16%	2.85	0.70	24%	3.59	6.29	2.96	0.62	17%	3.61	4.53	3.21	0.29	8%
Isoprene	11.48	1.83	16%	12.01	5%	3.91	0.63	16%	2.47	0.62	25%	3.07	5.06	2.60	0.45	15%	3.10	3.64	2.83	0.19	6%
Cyclopentene	7.04	1.31	19%	7.40	5%	2.45	0.50	21%	1.58	0.46	29%	1.98	3.59	1.49	0.38	19%	1.63	2.01	1.30	0.18	11%
1-Methyl cyclohexene	12.33	1.86	15%	13.12	6%	3.62	0.46	13%	2.03	0.49	24%	2.56	4.15	1.86	0.50	19%	4.09	5.33	3.07	0.48	12%
Cyclohexene	5.47	1.09	20%	5.71	5%	2.07	0.46	22%	1.39	0.43	31%	1.71	2.85	1.28	0.32	19%	1.27	1.56	0.85	0.16	12%
1-Methyl Cyclohexene	7.35	1.17	16%	7.83	6%	2.39	0.40	17%	1.43	0.37	26%	1.76	2.69	1.54	0.20	11%	2.18	2.49	1.76	0.19	9%
4-Methyl Cyclohexene	4.39	0.90	21%	4.61	5%	1.69	0.40	24%	1.14	0.36	32%	1.38	2.21	0.99	0.25	18%	0.96	1.19	0.50	0.15	15%
1,2-Dimethyl Cyclohexene	6.58	1.12	17%	7.00	6%	2.22	0.41	18%	1.27	0.36	29%	1.48	1.72	1.21	0.13	9%	1.96	2.25	1.48	0.21	11%
Cyclopentadiene	7.25	1.36	19%	7.63	5%	2.52	0.52	21%	1.63	0.48	29%	2.04	3.70	1.53	0.39	19%	1.68	2.07	1.34	0.18	11%
C6 Cyclic or di-olefins	8.90	1.53	17%	9.36	5%	3.12	0.56	18%	2.03	0.53	26%	2.54	4.57	2.09	0.43	17%	2.35	2.64	1.99	0.15	6%
C7 Cyclic or di-olefins	7.25	1.27	17%	7.62	5%	2.57	0.47	18%	1.67	0.45	27%	2.08	3.65	1.72	0.34	16%	1.86	2.10	1.44	0.13	7%
C8 Cyclic or di-olefins	6.13	1.21	20%	6.41	5%	2.26	0.50	22%	1.50	0.46	30%	1.84	3.14	1.38	0.34	18%	1.35	1.65	0.80	0.18	13%
C9 Cyclic or di-olefins	5.12	1.04	20%	5.36	5%	1.92	0.44	23%	1.29	0.41	32%	1.56	2.58	1.14	0.28	18%	1.07	1.34	0.52	0.17	16%
C10 Cyclic or di-olefins	4.34	0.90	21%	4.55	5%	1.65	0.39	24%	1.10	0.36	32%	1.33	2.15	0.95	0.24	18%	0.86	1.10	0.32	0.16	19%
C11 Cyclic or di-olefins	3.78	0.80	21%	3.95	5%	1.45	0.35	24%	0.97	0.32	33%	1.17	1.85	0.81	0.22	19%	0.73	0.94	0.21	0.15	21%
C12 Cyclic or di-olefins	3.41	0.72	21%	3.57	4%	1.31	0.32	25%	0.88	0.29	33%	1.05	1.67	0.73	0.20	19%	0.65	0.84	0.16	0.14	22%
C13 Cyclic or di-olefins	3.12	0.66	21%	3.27	5%	1.20	0.30	25%	0.81	0.27	33%	0.96	1.51	0.67	0.18	19%	0.58	0.76	0.13	0.13	23%
C14 Cyclic or di-olefins	2.88	0.61	21%	3.02	5%	1.11	0.27	25%	0.74	0.25	33%	0.89	1.39	0.61	0.17	19%	0.54	0.70	0.11	0.13	23%
C15 Cyclic or di-olefins	2.68	0.57	21%	2.81	5%	1.03	0.26	25%	0.69	0.23	34%	0.83	1.29	0.57	0.15	19%	0.50	0.65	0.09	0.12	24%
a-Pinene	4.51	0.73	16%	4.79	6%	1.53	0.29	19%	0.91	0.26	29%	1.06	1.26	0.91	0.08	7%	1.19	1.39	0.73	0.15	13%
b-Pinene	3.58	0.70	20%	3.74	4%	1.43	0.34	24%	0.89	0.30	34%	0.99	1.20	0.79	0.10	10%	0.84	0.99	0.41	0.11	14%
3-Carene	3.47	0.69	20%	3.66	6%	1.29	0.30	23%	0.82	0.27	33%	0.96	1.20	0.72	0.11	11%	0.79	1.00	0.19	0.15	19%
Sabinene	3.96	0.73	19%	4.16	5%	1.49	0.34	23%	0.89	0.30	33%	0.99	1.15	0.74	0.09	10%	0.97	1.15	0.46	0.14	14%
d-Limonene	4.25	0.79	19%	4.51	6%	1.46	0.30	21%	0.90	0.27	30%	1.07	1.39	0.82	0.09	9%	1.13	1.40	0.44	0.19	17%
Benzene	0.91	0.22	25%	0.92	1%	0.37	0.15	40%	0.17	0.13	75%	0.16	0.30	-0.45	0.14	90%	0.17	0.23	0.03	0.04	24%
Toluene	4.24	0.79	19%	4.38	3%	1.16	0.33	29%	0.36	0.32	90%	0.24	0.94	-2.60	0.62	255%	0.69	0.96	-0.08	0.20	29%
Ethyl Benzene	3.03	0.63	21%	3.11	3%	1.04	0.32	31%	0.47	0.30	63%	0.42	0.80	-1.40	0.38	91%	0.56	0.72	0.02	0.12	22%
n-Propyl Benzene	2.40	0.51	21%	2.46	2%	0.83	0.27	32%	0.37	0.24	66%	0.32	0.65	-1.17	0.32	98%	0.43	0.57	-0.01	0.10	23%
Isopropyl Benzene (cumene)	2.53	0.53	21%	2.60	3%	0.87	0.27	32%	0.39	0.25	64%	0.35	0.67	-1.20	0.33	94%	0.46	0.60	0.01	0.10	22%
s-Butyl Benzene	2.15	0.45	21%	2.20	3%	0.74	0.24	32%	0.33	0.22	66%	0.29	0.58	-1.05	0.28	98%	0.39	0.51	-0.01	0.09	23%
n-Butyl Benzene	2.15	0.45	21%	2.20	3%	0.74	0.24	32%	0.33	0.22	66%	0.29	0.58	-1.05	0.28	98%	0.39	0.51	-0.01	0.09	23%
m-Xylene	11.04	1.67	15%	11.50	4%	3.01	0.44	15%	1.46	0.45	31%	1.70	3.29	-0.03	0.53	31%	2.73	3.38	2.07	0.29	11%
o-Xylene	7.87	1.30	17%	8.17	4%	2.37	0.45	19%	1.20	0.42	35%	1.34	2.03	-0.09	0.36	27%	1.76	1.99	1.40	0.14	8%
p-Xylene	4.56	0.84	18%	4.70	3%	1.38	0.35	26%	0.58	0.34	58%	0.51	1.06	-2.10	0.54	105%	0.83	1.04	0.04	0.18	22%
1,2,4-Trimethyl Benzene	7.57	1.21	16%	7.87	4%	2.25	0.39	17%	1.16	0.38	33%	1.32	2.13	-0.08	0.33	25%	1.76	2.15	1.28	0.16	9%

Table C-5. Summary of calculated incremental and relative reactivities in various scales. Calculated using the SAPRC-99 mechansim (8/30/99)

Compound or Mixture	MIR (gm O3 / gm VOC)					MOIR (gm/gm)			EBIR (gm/gm)			Base Case Relative Reactivities [a]									
	39 Scenarios			Avg. Conds		39 Scenarios			39 Scenarios			Ozone Yield (gm basis)					Max 8-Hour Avg (gm basis)				
	Avg.	Sdev			D%	Avg.	Sdev		Avg.	Sdev		Avg.	Max	Min	Sdev		Avg.	Max	Min	Sdev	
1,3,5-Trimethyl Benzene	11.76	1.80	15%	12.33	5%	3.25	0.42	13%	1.70	0.44	26%	2.07	3.70	1.47	0.43	21%	3.21	4.02	2.53	0.34	10%
1,2,3-Trimethyl Benzene	11.74	1.79	15%	12.26	4%	3.29	0.47	14%	1.71	0.47	28%	2.05	3.54	1.29	0.41	20%	2.98	3.70	2.33	0.29	10%
C9 Monosub. Benzenes	2.40	0.51	21%	2.46	2%	0.83	0.27	32%	0.37	0.24	66%	0.32	0.65	-1.17	0.32	98%	0.43	0.57	-0.01	0.10	23%
C10 Monosub. Benzenes	2.15	0.45	21%	2.20	3%	0.74	0.24	32%	0.33	0.22	66%	0.29	0.58	-1.05	0.28	98%	0.39	0.51	-0.01	0.09	23%
C11 Monosub. Benzenes	1.94	0.41	21%	1.99	2%	0.67	0.22	32%	0.30	0.20	66%	0.26	0.52	-0.95	0.26	98%	0.35	0.46	-0.01	0.08	23%
C12 Monosub. Benzenes	1.77	0.38	21%	1.82	2%	0.61	0.20	32%	0.27	0.18	66%	0.24	0.48	-0.87	0.23	98%	0.32	0.42	0.00	0.07	23%
C13 Monosub. Benzenes	1.63	0.35	21%	1.67	2%	0.57	0.18	32%	0.25	0.17	66%	0.22	0.44	-0.80	0.22	98%	0.29	0.39	0.00	0.07	23%
C8 Disub. Benzenes	7.86	1.26	16%	8.17	4%	2.26	0.41	18%	1.08	0.39	36%	1.19	2.14	-0.74	0.45	38%	1.78	2.14	1.31	0.18	10%
C9 Disub. Benzenes	6.94	1.11	16%	7.19	4%	2.00	0.36	18%	0.96	0.35	36%	1.05	1.89	-0.65	0.40	38%	1.58	1.89	1.15	0.16	10%
C10 Disub. Benzenes	6.22	0.99	16%	6.44	4%	1.79	0.32	18%	0.86	0.31	36%	0.94	1.69	-0.58	0.36	38%	1.41	1.69	1.03	0.15	10%
C11 Disub. Benzenes	5.63	0.90	16%	5.84	4%	1.62	0.29	18%	0.77	0.28	36%	0.85	1.53	-0.53	0.33	38%	1.28	1.53	0.94	0.13	10%
C12 Disub. Benzenes	5.14	0.82	16%	5.32	4%	1.48	0.27	18%	0.71	0.26	36%	0.78	1.40	-0.48	0.30	38%	1.17	1.40	0.86	0.12	10%
C13 Disub. Benzenes	4.73	0.75	16%	4.92	4%	1.36	0.24	18%	0.65	0.24	36%	0.72	1.29	-0.44	0.27	38%	1.07	1.28	0.79	0.11	10%
C9 Trisub. Benzenes	10.37	1.59	15%	10.82	4%	2.94	0.42	14%	1.52	0.43	28%	1.82	3.13	0.93	0.37	20%	2.65	3.30	2.12	0.25	9%
C10 Trisub. Benzenes	9.29	1.43	15%	9.69	4%	2.63	0.38	14%	1.37	0.38	28%	1.63	2.81	0.83	0.33	20%	2.38	2.95	1.90	0.23	9%
C11 Trisub. Benzenes	8.41	1.29	15%	8.80	5%	2.38	0.34	14%	1.24	0.35	28%	1.47	2.53	0.75	0.30	20%	2.15	2.67	1.72	0.20	9%
C12 Trisub. Benzenes	7.68	1.18	15%	8.02	4%	2.17	0.31	14%	1.13	0.32	28%	1.35	2.31	0.69	0.27	20%	1.96	2.44	1.57	0.19	9%
C13 Trisub. Benzenes	7.07	1.09	15%	7.40	5%	2.00	0.29	14%	1.04	0.29	28%	1.24	2.13	0.63	0.25	20%	1.81	2.25	1.44	0.17	9%
C10 Tetrasub. Benzenes	9.29	1.43	15%	9.69	4%	2.63	0.38	14%	1.37	0.38	28%	1.63	2.81	0.83	0.33	20%	2.38	2.95	1.90	0.23	9%
C11 Tetrasub. Benzenes	8.41	1.29	15%	8.80	5%	2.38	0.34	14%	1.24	0.35	28%	1.47	2.53	0.75	0.30	20%	2.15	2.67	1.72	0.20	9%
C12 Tetrasub. Benzenes	7.68	1.18	15%	8.02	4%	2.17	0.31	14%	1.13	0.32	28%	1.35	2.31	0.69	0.27	20%	1.96	2.44	1.57	0.19	9%
C11 Pentasub. Benzenes	8.41	1.29	15%	8.80	5%	2.38	0.34	14%	1.24	0.35	28%	1.47	2.53	0.75	0.30	20%	2.15	2.67	1.72	0.20	9%
C11 Pentasub. Benzenes	7.68	1.18	15%	8.02	4%	2.17	0.31	14%	1.13	0.32	28%	1.35	2.31	0.69	0.27	20%	1.96	2.44	1.57	0.19	9%
C12 Hexaasub. Benzenes	7.68	1.18	15%	8.02	4%	2.17	0.31	14%	1.13	0.32	28%	1.35	2.31	0.69	0.27	20%	1.96	2.44	1.57	0.19	9%
Naphthalene	3.49	0.63	18%	3.63	4%	1.03	0.27	26%	0.47	0.26	56%	0.47	0.85	-1.25	0.36	77%	0.64	0.83	-0.06	0.16	25%
Tetralin	3.01	0.48	16%	3.15	5%	0.40	0.25	61%	-0.27	0.36	-132%	-0.62	0.76	-6.23	1.15	-186%	0.14	0.76	-1.90	0.49	338%
Methyl Naphthalenes	4.89	0.78	16%	5.12	5%	1.28	0.22	17%	0.55	0.23	42%	0.59	1.38	-1.12	0.38	64%	1.06	1.47	0.33	0.22	20%
1-Methyl Naphthalene	4.89	0.78	16%	5.12	5%	1.28	0.22	17%	0.55	0.23	42%	0.59	1.38	-1.12	0.38	64%	1.06	1.47	0.33	0.22	20%
2-Methyl Naphthalene	4.89	0.78	16%	5.12	5%	1.28	0.22	17%	0.55	0.23	42%	0.59	1.38	-1.12	0.38	64%	1.06	1.47	0.33	0.22	20%
2,3-Dimethyl Naphth.	5.85	0.92	16%	6.16	5%	1.53	0.22	14%	0.70	0.24	34%	0.81	1.73	-0.43	0.33	40%	1.44	1.91	0.93	0.22	15%
Indan	3.36	0.54	16%	3.52	5%	0.45	0.27	61%	-0.30	0.40	-132%	-0.69	0.85	-6.96	1.29	-186%	0.16	0.85	-2.13	0.55	338%
Dimethyl Naphthalenes	5.85	0.92	16%	6.16	5%	1.53	0.22	14%	0.70	0.24	34%	0.81	1.73	-0.43	0.33	40%	1.44	1.91	0.93	0.22	15%
C12 Monosub. Naphth.	4.44	0.71	16%	4.65	5%	1.17	0.20	17%	0.50	0.21	42%	0.54	1.26	-1.02	0.34	64%	0.97	1.34	0.30	0.20	20%
C12 Disub. Naphthalenes	5.85	0.92	16%	6.16	5%	1.53	0.22	14%	0.70	0.24	34%	0.81	1.73	-0.43	0.33	40%	1.44	1.91	0.93	0.22	15%
C13 Monosub. Naphth.	4.08	0.65	16%	4.29	5%	1.07	0.18	17%	0.46	0.19	42%	0.49	1.16	-0.94	0.31	64%	0.89	1.23	0.28	0.18	20%
C13 Disub. Naphthalenes	5.37	0.84	16%	5.64	5%	1.41	0.20	14%	0.65	0.22	34%	0.74	1.59	-0.39	0.30	40%	1.32	1.75	0.85	0.20	15%
C13 Trisub. Naphthalenes	5.37	0.84	16%	5.64	5%	1.41	0.20	14%	0.65	0.22	34%	0.74	1.59	-0.39	0.30	40%	1.32	1.75	0.85	0.20	15%
C11 Tetralin or Indane	2.72	0.44	16%	2.85	5%	0.36	0.22	61%	-0.24	0.32	-132%	-0.56	0.69	-5.63	1.04	-186%	0.13	0.69	-1.72	0.44	339%
Styrene	2.17	0.46	21%	2.32	7%	-0.59	0.18	-30%	-1.53	0.56	-37%	-2.44	0.53	-11.49	2.06	-85%	-0.87	0.55	-3.75	0.99	-114%
a-Methyl Styrene	1.91	0.41	21%	2.05	7%	-0.52	0.15	-30%	-1.35	0.50	-37%	-2.15	0.47	-10.12	1.82	-85%	-0.77	0.48	-3.31	0.88	-114%
C9 Styrenes	1.91	0.41	21%	2.05	7%	-0.52	0.15	-30%	-1.35	0.50	-37%	-2.15	0.47	-10.12	1.82	-85%	-0.77	0.48	-3.31	0.88	-114%

Table C-5. Summary of calculated incremental and relative reactivities in various scales. Calculated using the SAPRC-99 mechansim (8/30/99)

Compound or Mixture	MIR (gm O3 / gm VOC)					MOIR (gm/gm)			EBIR (gm/gm)			Base Case Relative Reactivities [a]									
	39 Scenarios			Avg. Conds		39 Scenarios			39 Scenarios			Ozone Yield (gm basis)					Max 8-Hour Avg (gm basis)				
	Avg.	Sdev			D%	Avg.	Sdev		Avg.	Sdev		Avg.	Max	Min	Sdev		Avg.	Max	Min	Sdev	
C10 Styrenes	1.71	0.37	21%	1.83	7%	-0.46	0.14	-30%	-1.20	0.44	-37%	-1.92	0.42	-9.06	1.63	-85%	-0.69	0.43	-2.96	0.78	-114%
Acetylene	1.31	0.24	18%	1.33	2%	0.48	0.10	20%	0.28	0.08	29%	0.33	0.49	0.26	0.05	14%	0.30	0.37	0.25	0.03	9%
Methyl Acetylene	6.70	1.21	18%	6.90	3%	2.25	0.47	21%	1.34	0.41	31%	1.63	2.63	1.10	0.22	14%	1.36	1.61	0.99	0.12	9%
Ethyl Acetylene	6.23	1.14	18%	6.43	3%	2.11	0.46	22%	1.28	0.40	31%	1.55	2.45	1.03	0.22	14%	1.26	1.51	0.90	0.13	10%
2-Butyne	16.87	2.61	15%	17.54	4%	4.90	0.71	14%	2.83	0.66	23%	3.67	6.94	2.80	0.77	21%	4.14	5.20	3.35	0.44	11%
Methanol	0.77	0.15	20%	0.78	2%	0.35	0.06	18%	0.23	0.06	25%	0.28	0.51	0.16	0.07	25%	0.22	0.34	0.15	0.04	18%
Ethanol	1.88	0.48	26%	1.92	2%	1.00	0.29	30%	0.70	0.25	36%	0.81	1.37	0.32	0.19	23%	0.49	0.74	0.28	0.10	20%
Isopropyl Alcohol	0.80	0.16	21%	0.82	3%	0.41	0.07	18%	0.29	0.07	24%	0.36	0.72	0.15	0.10	27%	0.29	0.46	0.15	0.07	23%
n-Propyl Alcohol	3.00	0.74	25%	3.07	2%	1.44	0.44	30%	0.99	0.37	38%	1.14	1.73	0.57	0.25	22%	0.70	1.01	0.48	0.12	17%
t-Butyl Alcohol	0.50	0.10	21%	0.51	2%	0.26	0.05	20%	0.18	0.05	26%	0.21	0.40	0.10	0.06	27%	0.16	0.25	0.09	0.03	20%
n-Butyl Alcohol	3.57	0.82	23%	3.65	2%	1.64	0.45	27%	1.12	0.39	35%	1.29	2.01	0.72	0.25	19%	0.85	1.17	0.66	0.12	14%
Isobutyl Alcohol	2.49	0.57	23%	2.56	3%	1.15	0.30	27%	0.77	0.26	34%	0.89	1.33	0.50	0.15	17%	0.60	0.78	0.46	0.07	12%
s-Butyl Alcohol	1.77	0.40	23%	1.81	3%	0.89	0.22	25%	0.62	0.19	31%	0.73	1.28	0.34	0.15	21%	0.52	0.72	0.31	0.09	17%
Cyclopentanol	2.07	0.46	22%	2.13	3%	0.99	0.25	25%	0.68	0.22	32%	0.79	1.26	0.42	0.14	18%	0.57	0.75	0.39	0.08	14%
Pentyl Alcohol	3.48	0.78	22%	3.59	3%	1.56	0.41	27%	1.06	0.36	34%	1.23	1.89	0.73	0.23	19%	0.83	1.09	0.67	0.11	13%
2-Pentanol	1.94	0.44	23%	1.99	3%	0.95	0.24	26%	0.66	0.21	32%	0.76	1.25	0.37	0.14	19%	0.54	0.72	0.34	0.08	15%
3-Pentanol	1.92	0.44	23%	1.97	3%	0.92	0.24	26%	0.64	0.21	32%	0.75	1.25	0.38	0.15	20%	0.52	0.71	0.35	0.08	15%
Cyclohexanol	2.84	0.69	24%	2.93	3%	1.40	0.39	28%	0.95	0.33	35%	1.07	1.48	0.52	0.19	18%	0.72	0.91	0.47	0.10	14%
2-Hexanol	2.48	0.63	26%	2.53	2%	1.28	0.37	29%	0.87	0.32	36%	0.97	1.36	0.41	0.18	19%	0.62	0.80	0.37	0.10	15%
1-Hexanol	2.81	0.66	23%	2.90	3%	1.32	0.36	27%	0.90	0.31	35%	1.02	1.46	0.55	0.18	18%	0.68	0.85	0.50	0.09	14%
1-Heptanol	2.31	0.56	24%	2.38	3%	1.12	0.32	28%	0.75	0.28	37%	0.83	1.13	0.43	0.15	18%	0.53	0.68	0.36	0.08	15%
1-Octanol	2.13	0.54	25%	2.20	4%	1.04	0.30	29%	0.69	0.26	38%	0.74	1.00	0.38	0.14	19%	0.45	0.63	0.20	0.10	21%
2-Octanol	2.46	0.61	25%	2.54	3%	1.19	0.34	28%	0.81	0.29	36%	0.89	1.20	0.44	0.16	18%	0.55	0.75	0.33	0.10	17%
3-Octanol	2.87	0.68	24%	2.98	4%	1.33	0.36	27%	0.90	0.32	35%	1.02	1.38	0.55	0.18	17%	0.65	0.84	0.41	0.10	16%
4-Octanol	3.27	0.76	23%	3.39	4%	1.48	0.40	27%	1.00	0.36	36%	1.14	1.57	0.67	0.20	18%	0.71	0.91	0.42	0.11	16%
2-Ethyl-1-Hexanol	2.44	0.57	23%	2.51	3%	1.13	0.31	28%	0.74	0.27	36%	0.82	1.10	0.48	0.13	16%	0.53	0.67	0.37	0.07	14%
Ethylene Glycol	3.64	0.77	21%	3.77	4%	1.59	0.35	22%	1.11	0.32	29%	1.36	2.55	0.77	0.30	22%	0.95	1.31	0.70	0.14	15%
Propylene Glycol	2.77	0.58	21%	2.86	3%	1.20	0.29	24%	0.82	0.25	31%	0.99	1.68	0.62	0.19	19%	0.74	0.99	0.60	0.10	13%
Glycerol	3.20	0.75	23%	3.28	3%	1.49	0.41	27%	1.02	0.35	35%	1.18	1.80	0.63	0.22	19%	0.79	1.05	0.58	0.11	14%
1,2-Butandiol	2.19	0.48	22%	2.26	3%	0.99	0.25	25%	0.68	0.22	32%	0.81	1.37	0.46	0.16	19%	0.58	0.79	0.43	0.08	14%
1,2-Dihydroxy Hexane	2.56	0.61	24%	2.63	3%	1.22	0.33	27%	0.83	0.29	35%	0.95	1.42	0.49	0.18	19%	0.63	0.83	0.45	0.09	14%
Dimethyl Ether	1.05	0.21	20%	1.09	3%	0.62	0.10	16%	0.46	0.10	21%	0.59	1.29	0.19	0.20	34%	0.46	0.79	0.19	0.13	27%
Trimethylene Oxide	5.81	1.34	23%	6.03	4%	2.81	0.67	24%	2.05	0.61	30%	2.51	4.82	1.09	0.63	25%	1.71	2.62	1.02	0.35	20%
Dimethoxy methane	1.66	0.42	25%	1.68	1%	0.97	0.25	26%	0.68	0.22	32%	0.79	1.42	0.26	0.18	23%	0.55	0.82	0.24	0.11	21%
Tetrahydrofuran	5.39	1.15	21%	5.59	4%	2.44	0.56	23%	1.70	0.51	30%	2.02	3.33	1.14	0.38	19%	1.51	2.10	1.09	0.22	14%
Diethyl Ether	4.35	0.77	18%	4.51	4%	1.87	0.30	16%	1.26	0.30	23%	1.55	2.90	1.02	0.32	21%	1.40	2.11	0.99	0.23	17%
Alpha-Methyltetrahydrofuran	4.95	1.03	21%	5.16	4%	2.15	0.49	23%	1.49	0.45	30%	1.76	2.72	1.09	0.30	17%	1.35	1.85	1.05	0.17	13%
Tetrahydropyran	4.08	0.91	22%	4.24	4%	1.95	0.46	24%	1.35	0.42	31%	1.56	2.34	0.80	0.26	17%	1.15	1.57	0.75	0.16	14%
Methyl n-Butyl Ether	3.94	0.87	22%	4.08	4%	1.83	0.44	24%	1.27	0.39	31%	1.49	2.40	0.80	0.27	18%	1.09	1.50	0.76	0.16	14%
Methyl t-Butyl Ether	0.88	0.20	23%	0.90	2%	0.51	0.11	22%	0.35	0.10	28%	0.41	0.75	0.16	0.10	24%	0.30	0.44	0.15	0.06	20%
Ethyl Isopropyl Ether	4.17	0.71	17%	4.33	4%	1.66	0.27	16%	1.09	0.26	24%	1.34	2.32	1.05	0.23	17%	1.31	1.85	1.06	0.18	14%

Table C-5. Summary of calculated incremental and relative reactivities in various scales. Calculated using the SAPRC-99 mechansim (8/30/99)

Compound or Mixture	MIR (gm O3 / gm VOC)					MOIR (gm/gm)			EBIR (gm/gm)			Base Case Relative Reactivities [a]									
	39 Scenarios			Avg. Conds		39 Scenarios			39 Scenarios			Ozone Yield (gm basis)					Max 8-Hour Avg (gm basis)				
	Avg.	Sdev			D%	Avg.	Sdev		Avg.	Sdev		Avg.	Max	Min	Sdev		Avg.	Max	Min	Sdev	
Ethyl t-Butyl Ether	2.32	0.44	19%	2.39	3%	1.07	0.19	18%	0.72	0.18	25%	0.85	1.50	0.50	0.17	19%	0.72	1.04	0.47	0.11	15%
Di n-Propyl Ether	3.72	0.80	21%	3.86	4%	1.73	0.38	22%	1.20	0.35	29%	1.43	2.41	0.75	0.27	19%	1.06	1.50	0.70	0.16	15%
Ethyl n-Butyl Ether	4.14	0.85	20%	4.28	3%	1.81	0.40	22%	1.23	0.37	30%	1.45	2.24	0.92	0.22	16%	1.13	1.50	0.88	0.13	12%
Methyl t-Amyl Ether	2.38	0.50	21%	2.45	3%	1.16	0.24	20%	0.79	0.21	27%	0.93	1.58	0.47	0.17	18%	0.71	0.97	0.44	0.11	15%
2-Butyl Tetrahydrofuran	2.68	0.66	25%	2.80	5%	1.23	0.35	28%	0.83	0.31	37%	0.90	1.23	0.52	0.17	19%	0.52	0.78	0.05	0.15	29%
Di-n-butyl Ether	3.50	0.79	23%	3.63	4%	1.57	0.41	26%	1.07	0.36	34%	1.22	1.64	0.73	0.20	16%	0.82	1.08	0.51	0.12	15%
Di-Isobutyl Ether	1.51	0.38	25%	1.58	5%	0.76	0.20	26%	0.52	0.18	34%	0.55	0.82	0.26	0.10	18%	0.41	0.59	0.24	0.08	20%
Di-n-Pentyl Ether	3.17	0.78	25%	3.31	4%	1.50	0.42	28%	1.02	0.37	37%	1.12	1.53	0.59	0.20	18%	0.68	0.96	0.27	0.14	21%
2-Methoxyethanol	3.34	0.60	18%	3.46	4%	1.35	0.24	17%	0.90	0.22	25%	1.11	2.01	0.81	0.21	19%	0.98	1.38	0.78	0.13	13%
1-Methoxy-2-Propanol	3.22	0.70	22%	3.32	3%	1.49	0.34	23%	1.03	0.30	29%	1.23	2.12	0.64	0.24	19%	0.92	1.26	0.60	0.14	15%
2-Methoxy-1-Propanol	3.30	0.52	16%	3.43	4%	1.19	0.17	14%	0.76	0.17	23%	0.95	1.63	0.79	0.16	17%	1.00	1.38	0.88	0.11	11%
2-Ethoxyethanol	4.20	0.78	19%	4.35	3%	1.72	0.33	19%	1.14	0.31	27%	1.37	2.32	1.01	0.22	16%	1.18	1.57	0.98	0.13	11%
Diethylene Glycol	4.45	0.86	19%	4.60	3%	1.84	0.40	22%	1.21	0.36	30%	1.42	2.21	1.05	0.19	14%	1.18	1.45	1.02	0.10	8%
3-Ethoxy-1-Propanol	4.60	0.83	18%	4.77	4%	1.84	0.35	19%	1.21	0.32	27%	1.46	2.39	1.13	0.21	15%	1.29	1.69	1.11	0.13	10%
3-Methoxy-1-Butanol	1.05	0.22	21%	1.07	2%	0.54	0.11	21%	0.37	0.10	28%	0.43	0.79	0.21	0.09	22%	0.32	0.45	0.19	0.05	17%
2-Propoxyethanol	4.21	0.84	20%	4.36	3%	1.80	0.39	22%	1.21	0.35	29%	1.44	2.33	0.95	0.23	16%	1.16	1.49	0.91	0.13	11%
1-Ethoxy-2-Propanol	3.66	0.78	21%	3.78	3%	1.64	0.38	23%	1.12	0.34	31%	1.31	2.07	0.76	0.21	16%	1.00	1.31	0.72	0.12	12%
2-(2-Methoxyethoxy) Ethanol	3.79	0.77	20%	3.94	4%	1.64	0.37	22%	1.11	0.33	30%	1.30	1.97	0.83	0.19	15%	1.08	1.43	0.82	0.13	12%
2-Butoxyethanol	3.34	0.66	20%	3.46	4%	1.39	0.31	22%	0.91	0.28	30%	1.06	1.51	0.78	0.13	12%	0.85	1.03	0.75	0.07	8%
3 methoxy -3 methyl-Butanol	1.89	0.45	24%	1.94	2%	0.92	0.25	27%	0.63	0.22	35%	0.72	1.10	0.36	0.13	19%	0.47	0.62	0.33	0.07	14%
Dipropylene Glycol	3.26	0.74	23%	3.37	3%	1.50	0.38	25%	1.03	0.34	33%	1.19	1.79	0.64	0.20	17%	0.83	1.08	0.58	0.11	13%
2-(2-Ethoxyethoxy) EtOH	3.86	0.81	21%	4.01	4%	1.66	0.39	23%	1.11	0.35	31%	1.29	1.81	0.84	0.18	14%	1.03	1.34	0.82	0.11	11%
2-tert-Butoxy-1-Propanol	2.00	0.33	17%	2.08	4%	0.74	0.12	16%	0.46	0.12	25%	0.55	0.81	0.48	0.06	11%	0.54	0.64	0.48	0.04	7%
1-tert-Butoxy-2-Propanol	2.18	0.51	24%	2.25	3%	1.05	0.28	26%	0.72	0.24	34%	0.81	1.19	0.41	0.14	17%	0.54	0.70	0.36	0.07	14%
n-Butoxy-2-Propanol	3.29	0.75	23%	3.41	4%	1.51	0.39	26%	1.03	0.34	33%	1.18	1.72	0.66	0.20	17%	0.81	1.05	0.60	0.11	13%
Dipropylene Glycol Methyl Ether	2.96	0.66	22%	3.08	4%	1.34	0.33	25%	0.91	0.29	32%	1.04	1.42	0.58	0.16	15%	0.80	1.09	0.56	0.11	13%
2-(2-Butoxyethoxy)-EtOH	3.06	0.68	22%	3.20	4%	1.36	0.35	26%	0.92	0.31	34%	1.04	1.36	0.63	0.16	15%	0.74	0.95	0.49	0.10	13%
Tripropylene Glycol Monomethyl Ether	2.32	0.57	24%	2.42	4%	1.07	0.29	27%	0.72	0.25	35%	0.80	1.05	0.42	0.13	16%	0.54	0.78	0.20	0.11	20%
Methyl Formate	0.07	0.02	23%	0.07	2%	0.05	0.01	21%	0.04	0.01	25%	0.05	0.11	0.01	0.02	36%	0.03	0.06	0.01	0.01	30%
Ethyl Formate	0.58	0.15	26%	0.59	2%	0.33	0.10	30%	0.24	0.09	36%	0.29	0.51	0.10	0.07	26%	0.17	0.26	0.09	0.04	23%
Methyl Acetate	0.08	0.02	23%	0.09	2%	0.06	0.01	21%	0.05	0.01	26%	0.06	0.12	0.01	0.02	36%	0.04	0.07	0.01	0.01	29%
Methyl Propionate	0.76	0.18	23%	0.77	1%	0.36	0.10	28%	0.23	0.09	37%	0.26	0.41	0.14	0.05	17%	0.18	0.23	0.13	0.02	11%
n-Propyl Formate	1.05	0.30	29%	1.06	2%	0.59	0.20	34%	0.42	0.18	41%	0.47	0.72	0.16	0.13	27%	0.25	0.39	0.13	0.07	26%
Ethyl Acetate	0.72	0.18	25%	0.73	2%	0.39	0.11	29%	0.28	0.10	35%	0.32	0.57	0.13	0.07	23%	0.19	0.28	0.11	0.04	19%
Ethyl Propionate	0.94	0.24	26%	0.95	2%	0.52	0.16	31%	0.36	0.14	38%	0.40	0.65	0.16	0.09	22%	0.24	0.33	0.14	0.04	19%
n-Butyl Formate	1.10	0.31	28%	1.12	2%	0.63	0.20	32%	0.45	0.17	39%	0.50	0.77	0.17	0.12	24%	0.28	0.40	0.15	0.06	22%
Methyl Butyrate	1.25	0.28	22%	1.27	2%	0.60	0.15	25%	0.40	0.13	33%	0.45	0.73	0.24	0.07	16%	0.32	0.40	0.22	0.04	11%
Propyl Acetate	0.99	0.27	27%	1.01	2%	0.56	0.18	31%	0.40	0.15	38%	0.45	0.70	0.15	0.10	23%	0.25	0.36	0.14	0.05	21%
Isopropyl Acetate	1.33	0.26	19%	1.37	3%	0.66	0.11	17%	0.45	0.11	24%	0.55	1.06	0.27	0.13	24%	0.43	0.64	0.26	0.08	18%

Table C-5. Summary of calculated incremental and relative reactivities in various scales. Calculated using the SAPRC-99 mechansim (8/30/99)

Compound or Mixture	MIR (gm O3 / gm VOC)					MOIR (gm/gm)			EBIR (gm/gm)			Base Case Relative Reactivities [a]									
	39 Scenarios			Avg. Conds		39 Scenarios			39 Scenarios			Ozone Yield (gm basis)					Max 8-Hour Avg (gm basis)				
	Avg.	Sdev			D%	Avg.	Sdev		Avg.	Sdev		Avg.	Max	Min	Sdev		Avg.	Max	Min	Sdev	
Methyl Isobutyrate	0.78	0.21	27%	0.79	1%	0.42	0.14	32%	0.29	0.11	39%	0.32	0.48	0.13	0.07	22%	0.19	0.26	0.11	0.04	19%
t-Butyl Acetate	0.24	0.05	21%	0.24	2%	0.13	0.03	22%	0.09	0.03	29%	0.10	0.19	0.05	0.03	25%	0.07	0.11	0.04	0.01	17%
s-Butyl Acetate	1.61	0.39	24%	1.66	3%	0.87	0.21	25%	0.61	0.19	31%	0.71	1.23	0.28	0.15	21%	0.47	0.65	0.25	0.08	18%
n-Propyl Propionate	1.11	0.31	28%	1.13	2%	0.62	0.20	33%	0.43	0.17	40%	0.47	0.67	0.17	0.11	23%	0.26	0.35	0.15	0.06	21%
Ethyl Butyrate	1.40	0.34	24%	1.43	2%	0.71	0.19	27%	0.48	0.17	34%	0.55	0.85	0.26	0.10	18%	0.35	0.44	0.23	0.05	14%
Isobutyl Acetate	0.78	0.18	23%	0.80	3%	0.47	0.09	20%	0.33	0.09	26%	0.38	0.70	0.13	0.09	25%	0.28	0.42	0.12	0.06	21%
n-Butyl Acetate	1.08	0.30	28%	1.10	2%	0.63	0.19	31%	0.43	0.16	38%	0.47	0.67	0.16	0.10	21%	0.28	0.37	0.14	0.05	18%
2-Ethoxyethyl Acetate	2.10	0.41	20%	2.18	4%	0.94	0.19	20%	0.64	0.17	27%	0.76	1.19	0.45	0.12	16%	0.65	0.90	0.44	0.09	15%
n-Propyl Butyrate	1.36	0.36	27%	1.39	3%	0.71	0.22	30%	0.49	0.19	38%	0.53	0.74	0.22	0.11	20%	0.31	0.42	0.19	0.06	20%
Amyl Acetate	1.29	0.37	29%	1.31	2%	0.76	0.24	32%	0.50	0.20	40%	0.52	0.68	0.18	0.11	22%	0.31	0.44	0.15	0.06	19%
Butyl Propionate	1.11	0.31	28%	1.14	2%	0.63	0.20	32%	0.42	0.17	40%	0.45	0.61	0.17	0.09	21%	0.26	0.36	0.15	0.05	19%
Ethyl 3-Ethoxy Propionate	3.48	0.60	17%	3.61	4%	1.32	0.24	18%	0.84	0.22	27%	1.01	1.55	0.88	0.12	12%	0.91	1.08	0.85	0.05	5%
n-Butyl Butyrate	1.40	0.37	27%	1.44	3%	0.73	0.22	30%	0.49	0.19	39%	0.51	0.69	0.23	0.10	20%	0.30	0.43	0.15	0.07	22%
Isobutyl Isobutyrate	0.77	0.21	27%	0.79	2%	0.46	0.13	28%	0.30	0.11	36%	0.31	0.50	0.12	0.07	22%	0.20	0.29	0.10	0.04	18%
Isoamyl Isobutyrate	1.10	0.31	28%	1.12	2%	0.60	0.20	33%	0.39	0.17	43%	0.39	0.53	0.11	0.10	27%	0.21	0.31	0.03	0.06	31%
2-Ethyl-Hexyl Acetate	1.02	0.33	33%	1.05	3%	0.60	0.22	37%	0.38	0.18	49%	0.33	0.54	-0.15	0.16	47%	0.14	0.30	-0.16	0.10	70%
Propylene Carbonate	0.28	0.07	23%	0.29	2%	0.19	0.04	23%	0.14	0.04	28%	0.17	0.34	0.05	0.05	29%	0.11	0.17	0.05	0.03	25%
Methyl Lactate	2.84	0.58	20%	2.90	2%	1.01	0.25	25%	0.58	0.21	36%	0.67	0.96	0.26	0.11	16%	0.56	0.67	0.37	0.06	10%
Ethyl Lactate	2.73	0.57	21%	2.80	3%	1.06	0.27	25%	0.65	0.23	35%	0.74	1.10	0.46	0.11	14%	0.56	0.67	0.40	0.05	9%
1-Methoxy-2-Propyl Acetate	1.92	0.38	20%	2.01	4%	0.86	0.16	18%	0.60	0.15	25%	0.72	1.28	0.41	0.15	21%	0.58	0.84	0.39	0.09	15%
2-Methyoxy-1-propyl Acetate	1.29	0.25	19%	1.36	5%	0.59	0.09	15%	0.41	0.09	23%	0.49	0.92	0.27	0.11	22%	0.51	0.77	0.29	0.11	21%
Dimethyl Succinate	0.41	0.11	26%	0.41	1%	0.24	0.07	29%	0.16	0.06	36%	0.18	0.27	0.06	0.04	20%	0.11	0.15	0.06	0.02	16%
Diisopropyl Carbonate	1.16	0.24	21%	1.19	3%	0.57	0.12	20%	0.38	0.10	27%	0.44	0.71	0.23	0.08	18%	0.34	0.47	0.22	0.05	14%
Dimethyl Glutarate	0.52	0.15	29%	0.52	1%	0.32	0.10	32%	0.20	0.08	41%	0.21	0.30	0.07	0.05	24%	0.13	0.18	0.06	0.02	19%
Dimethyl Adipate	2.02	0.47	23%	2.07	3%	0.91	0.25	28%	0.59	0.22	37%	0.64	0.87	0.40	0.11	16%	0.42	0.51	0.27	0.06	14%
2-Butoxyethyl Acetate	1.95	0.46	23%	2.03	4%	0.92	0.24	26%	0.63	0.21	34%	0.71	0.92	0.38	0.11	16%	0.49	0.67	0.33	0.08	15%
Ethylene Oxide	0.05	0.01	23%	0.05	2%	0.04	0.01	21%	0.03	0.01	26%	0.04	0.08	0.01	0.01	36%	0.03	0.04	0.01	0.01	31%
Propylene Oxide	0.36	0.08	23%	0.36	2%	0.24	0.05	22%	0.19	0.05	27%	0.23	0.47	0.06	0.07	31%	0.15	0.24	0.06	0.04	27%
1,2-Epoxybutane	1.19	0.30	25%	1.21	2%	0.77	0.19	25%	0.57	0.17	30%	0.67	1.28	0.19	0.17	26%	0.43	0.63	0.17	0.10	24%
Formic Acid	0.09	0.02	23%	0.09	2%	0.06	0.01	20%	0.04	0.01	25%	0.05	0.11	0.01	0.02	35%	0.04	0.06	0.01	0.01	29%
Acetic Acid	0.83	0.16	20%	0.84	2%	0.37	0.08	21%	0.25	0.07	28%	0.30	0.55	0.17	0.06	20%	0.22	0.30	0.16	0.03	14%
Propionic Acid	1.35	0.31	23%	1.38	2%	0.59	0.16	28%	0.38	0.14	37%	0.43	0.67	0.26	0.08	18%	0.30	0.41	0.22	0.03	11%
Methyl Acrylate	3.43	0.53	15%	3.59	5%	1.15	0.15	13%	0.71	0.16	22%	0.89	1.49	0.73	0.15	17%	1.08	1.48	0.95	0.12	11%
Vinyl Acetate	11.86	1.80	15%	12.36	4%	3.46	0.44	13%	2.00	0.44	22%	2.58	4.59	1.93	0.54	21%	3.21	4.08	2.66	0.33	10%
Ethyl Acrylate	8.28	1.31	16%	8.63	4%	2.72	0.40	15%	1.67	0.39	24%	2.08	3.53	1.76	0.32	15%	2.22	2.71	1.96	0.14	6%
Furan	17.22	2.61	15%	17.94	4%	4.70	0.69	15%	2.29	0.71	31%	2.65	5.12	-0.05	0.83	31%	4.26	5.27	3.23	0.46	11%
Formaldehyde	9.27	1.54	17%	9.69	4%	2.31	0.31	13%	1.10	0.30	27%	1.46	3.47	0.68	0.57	39%	2.79	4.09	1.86	0.53	19%
Acetaldehyde	7.25	1.26	17%	7.61	5%	2.50	0.41	17%	1.66	0.40	24%	2.16	4.42	1.62	0.52	24%	1.80	2.25	1.40	0.19	11%
Propionaldehyde	8.43	1.56	19%	8.83	5%	2.93	0.56	19%	1.94	0.54	28%	2.46	4.60	1.86	0.51	21%	1.99	2.55	1.55	0.22	11%
2-Methylpropanal	6.30	1.16	18%	6.60	5%	2.22	0.41	19%	1.49	0.40	27%	1.91	3.72	1.42	0.43	23%	1.58	1.94	1.21	0.18	11%
Butanal	7.15	1.34	19%	7.51	5%	2.49	0.49	20%	1.65	0.46	28%	2.08	3.90	1.56	0.43	21%	1.68	2.16	1.30	0.19	11%

Table C-5. Summary of calculated incremental and relative reactivities in various scales. Calculated using the SAPRC-99 mechansim (8/30/99)

Compound or Mixture	MIR (gm O3 / gm VOC)					MOIR (gm/gm)			EBIR (gm/gm)			Base Case Relative Reactivities [a]									
	39 Scenarios			Avg. Conds		39 Scenarios			39 Scenarios			Ozone Yield (gm basis)					Max 8-Hour Avg (gm basis)				
	Avg.	Sdev			D%	Avg.	Sdev		Avg.	Sdev		Avg.	Max	Min	Sdev		Avg.	Max	Min	Sdev	
Pentanal	6.10	1.15	19%	6.41	5%	2.14	0.41	19%	1.43	0.39	27%	1.81	3.42	1.34	0.39	21%	1.46	1.81	1.11	0.17	11%
2,2-Dimethylpropanal (pivaldehyde)	5.78	1.06	18%	6.08	5%	2.00	0.37	18%	1.33	0.36	27%	1.70	3.30	1.26	0.38	22%	1.42	1.77	1.09	0.16	11%
3-Methylbutanal	5.91	1.08	18%	6.19	5%	2.04	0.37	18%	1.35	0.36	26%	1.72	3.26	1.29	0.37	21%	1.46	1.81	1.15	0.15	10%
Glutaraldehyde	5.18	0.99	19%	5.44	5%	1.82	0.34	19%	1.23	0.33	27%	1.59	3.17	1.14	0.39	25%	1.29	1.64	0.91	0.17	13%
Hexanal	5.17	0.97	19%	5.44	5%	1.82	0.36	20%	1.19	0.33	28%	1.50	2.69	1.13	0.29	19%	1.21	1.54	0.94	0.13	11%
Heptanal	4.40	0.83	19%	4.62	5%	1.55	0.31	20%	1.02	0.29	28%	1.27	2.21	0.97	0.23	18%	1.02	1.29	0.78	0.11	11%
Octanal	3.79	0.73	19%	3.98	5%	1.35	0.28	20%	0.89	0.26	29%	1.09	1.82	0.83	0.19	17%	0.86	1.10	0.62	0.10	12%
C4 aldehydes	7.15	1.34	19%	7.51	5%	2.49	0.49	20%	1.65	0.46	28%	2.08	3.90	1.56	0.43	21%	1.68	2.16	1.30	0.19	11%
C5 Aldehydes	6.10	1.15	19%	6.41	5%	2.14	0.41	19%	1.43	0.39	27%	1.81	3.42	1.34	0.39	21%	1.46	1.81	1.11	0.17	11%
C6 Aldehydes	5.17	0.97	19%	5.44	5%	1.82	0.36	20%	1.19	0.33	28%	1.50	2.69	1.13	0.29	19%	1.21	1.54	0.94	0.13	11%
C7 Aldehydes	4.40	0.83	19%	4.62	5%	1.55	0.31	20%	1.02	0.29	28%	1.27	2.21	0.97	0.23	18%	1.02	1.29	0.78	0.11	11%
C8 Aldehydes	3.79	0.73	19%	3.98	5%	1.35	0.28	20%	0.89	0.26	29%	1.09	1.82	0.83	0.19	17%	0.86	1.10	0.62	0.10	12%
Glyoxal	14.81	2.58	17%	15.55	5%	3.65	0.55	15%	1.73	0.50	29%	2.29	5.26	0.99	0.95	41%	4.94	7.66	2.87	1.01	20%
Methyl Glyoxal	16.99	2.86	17%	17.90	5%	4.26	0.55	13%	2.19	0.55	25%	2.93	5.91	1.58	0.98	34%	5.39	7.87	3.64	0.98	18%
Acrolein	8.00	1.54	19%	8.35	4%	2.69	0.56	21%	1.76	0.53	30%	2.24	4.13	1.58	0.49	22%	1.66	2.11	1.12	0.26	16%
Crotonaldehyde	10.34	1.67	16%	10.79	4%	3.25	0.49	15%	2.01	0.48	24%	2.59	4.81	2.03	0.50	19%	2.62	3.17	2.13	0.21	8%
Methacrolein	6.67	1.15	17%	6.99	5%	2.18	0.37	17%	1.40	0.36	26%	1.80	3.47	1.40	0.39	22%	1.66	1.95	1.28	0.16	10%
Hydroxy Methacrolein	6.71	1.16	17%	7.00	4%	2.33	0.41	18%	1.48	0.39	26%	1.85	3.24	1.52	0.32	17%	1.71	1.98	1.43	0.13	7%
Isoprene Product #1	7.33	1.20	16%	7.67	5%	2.43	0.38	16%	1.51	0.37	25%	1.90	3.31	1.59	0.31	16%	1.97	2.32	1.68	0.13	6%
Isoprene Product #2	7.28	1.19	16%	7.62	5%	2.42	0.39	16%	1.51	0.37	25%	1.90	3.31	1.59	0.31	16%	1.96	2.31	1.67	0.13	6%
Isoprene Product #3	7.97	1.19	15%	8.34	5%	2.35	0.30	13%	1.34	0.31	23%	1.71	2.85	1.31	0.32	18%	2.29	2.86	1.87	0.23	10%
Benzaldehyde	-0.58	0.26	-45%	-0.55	-5%	-1.57	0.24	-15%	-2.23	0.66	-29%	-3.40	-0.31	-14.25	2.40	-70%	-1.99	-0.43	-5.88	1.21	-61%
Tolualdehyde	-0.51	0.23	-45%	-0.49	-5%	-1.39	0.21	-15%	-1.97	0.58	-29%	-3.01	-0.28	-12.59	2.12	-70%	-1.76	-0.38	-5.20	1.07	-61%
Acetone	0.45	0.09	19%	0.46	3%	0.17	0.04	22%	0.11	0.03	30%	0.13	0.22	0.10	0.02	15%	0.10	0.13	0.08	0.01	9%
Cyclobutanone	0.77	0.21	27%	0.78	2%	0.44	0.14	31%	0.31	0.12	38%	0.35	0.55	0.13	0.08	23%	0.20	0.30	0.11	0.04	20%
Methyl Ethyl Ketone	1.59	0.34	21%	1.63	3%	0.67	0.18	27%	0.44	0.16	36%	0.50	0.78	0.35	0.08	17%	0.34	0.44	0.27	0.04	11%
Cyclopentanone	1.51	0.40	26%	1.54	2%	0.84	0.26	30%	0.59	0.22	37%	0.65	0.97	0.25	0.14	21%	0.39	0.53	0.22	0.07	18%
3-Pentanone	1.55	0.39	25%	1.59	2%	0.75	0.25	33%	0.51	0.21	41%	0.56	0.83	0.32	0.13	23%	0.32	0.45	0.18	0.06	20%
2-Pentanone	3.34	0.73	22%	3.43	3%	1.54	0.38	25%	1.05	0.33	32%	1.24	2.13	0.72	0.23	19%	0.82	1.11	0.66	0.11	13%
Cyclohexanone	1.76	0.49	28%	1.81	3%	0.94	0.30	32%	0.64	0.26	40%	0.68	0.96	0.27	0.15	22%	0.38	0.53	0.19	0.09	23%
Methyl t-Butyl Ketone	0.86	0.19	22%	0.88	2%	0.42	0.10	25%	0.27	0.09	32%	0.31	0.50	0.19	0.05	16%	0.21	0.26	0.18	0.02	10%
4-Methyl-2-Pentanone	4.62	0.83	18%	4.80	4%	1.80	0.31	17%	1.21	0.30	24%	1.50	2.77	1.14	0.29	20%	1.24	1.62	1.09	0.13	10%
Methyl n-Butyl Ketone	3.82	0.84	22%	3.94	3%	1.72	0.43	25%	1.17	0.38	33%	1.37	2.19	0.80	0.24	18%	0.92	1.17	0.74	0.12	13%
Di-Isopropyl Ketone	1.80	0.48	27%	1.85	3%	0.91	0.29	32%	0.62	0.25	40%	0.69	0.98	0.31	0.15	22%	0.37	0.51	0.17	0.09	24%
2-Methyl-3-Hexanone	1.98	0.51	26%	2.04	3%	0.99	0.29	30%	0.67	0.25	38%	0.75	1.04	0.35	0.15	20%	0.43	0.57	0.24	0.09	20%
2-Heptanone	3.05	0.73	24%	3.15	3%	1.45	0.40	27%	0.98	0.35	36%	1.09	1.46	0.59	0.18	17%	0.69	0.89	0.48	0.10	15%
2-Octanone	1.81	0.49	27%	1.87	3%	0.96	0.30	31%	0.63	0.25	41%	0.64	0.85	0.27	0.15	23%	0.36	0.55	0.11	0.10	26%
2-Nonanone	1.42	0.42	30%	1.46	3%	0.79	0.27	34%	0.50	0.23	45%	0.48	0.70	0.01	0.16	34%	0.24	0.42	-0.08	0.11	46%
Di-isobutyl ketone (2,6-dimethyl-4-heptanone)	3.22	0.69	21%	3.37	5%	1.33	0.31	24%	0.90	0.29	32%	1.04	1.45	0.71	0.16	16%	0.68	0.89	0.32	0.12	18%

Table C-5. Summary of calculated incremental and relative reactivities in various scales. Calculated using the SAPRC-99 mechansim (8/30/99)

Compound or Mixture	MIR (gm O3 / gm VOC)					MOIR (gm/gm)			EBIR (gm/gm)			Base Case Relative Reactivities [a]									
	39 Scenarios			Avg. Conds		39 Scenarios			39 Scenarios			Ozone Yield (gm basis)					Max 8-Hour Avg (gm basis)				
	Avg.	Sdev			D%	Avg.	Sdev		Avg.	Sdev		Avg.	Max	Min	Sdev		Avg.	Max	Min	Sdev	
2-Decanone	1.14	0.37	33%	1.17	3%	0.66	0.24	37%	0.41	0.20	49%	0.37	0.59	-0.15	0.17	47%	0.15	0.33	-0.19	0.12	77%
C5 Ketones	3.34	0.73	22%	3.43	3%	1.54	0.38	25%	1.05	0.33	32%	1.24	2.13	0.72	0.23	19%	0.82	1.11	0.66	0.11	13%
C6 Ketones	3.82	0.84	22%	3.94	3%	1.72	0.43	25%	1.17	0.38	33%	1.37	2.19	0.80	0.24	18%	0.92	1.17	0.74	0.12	13%
C7 Ketones	3.05	0.73	24%	3.15	3%	1.45	0.40	27%	0.98	0.35	36%	1.09	1.46	0.59	0.18	17%	0.69	0.89	0.48	0.10	15%
C8 Ketones	1.81	0.49	27%	1.87	3%	0.96	0.30	31%	0.63	0.25	41%	0.64	0.85	0.27	0.15	23%	0.36	0.55	0.11	0.10	26%
C9 Ketones	1.42	0.42	30%	1.46	3%	0.79	0.27	34%	0.50	0.23	45%	0.48	0.70	0.01	0.16	34%	0.24	0.42	-0.08	0.11	46%
C10 Ketones	1.14	0.37	33%	1.17	3%	0.66	0.24	37%	0.41	0.20	49%	0.37	0.59	-0.15	0.17	47%	0.15	0.33	-0.19	0.12	77%
C6 Cyclic Ketones	1.76	0.49	28%	1.81	3%	0.94	0.30	32%	0.64	0.26	40%	0.68	0.96	0.27	0.15	22%	0.38	0.53	0.19	0.09	23%
C5 Cyclic Ketones	1.51	0.40	26%	1.54	2%	0.84	0.26	30%	0.59	0.22	37%	0.65	0.97	0.25	0.14	21%	0.39	0.53	0.22	0.07	18%
C7 Cyclic Ketones	1.54	0.43	28%	1.58	3%	0.83	0.26	32%	0.56	0.22	40%	0.60	0.84	0.24	0.13	22%	0.33	0.47	0.17	0.08	23%
C8 Cyclic Ketones	1.37	0.38	28%	1.40	3%	0.73	0.23	32%	0.50	0.20	40%	0.53	0.75	0.21	0.11	22%	0.29	0.41	0.15	0.07	23%
C9 Cyclic Ketones	1.23	0.34	28%	1.26	3%	0.66	0.21	32%	0.45	0.18	40%	0.48	0.67	0.19	0.10	21%	0.26	0.37	0.13	0.06	23%
C10 Cyclic Ketones	1.12	0.31	28%	1.15	3%	0.60	0.19	32%	0.41	0.16	40%	0.44	0.61	0.17	0.09	21%	0.24	0.34	0.12	0.06	23%
Biacetyl	21.75	3.67	17%	22.97	6%	5.54	0.71	13%	2.97	0.72	24%	3.97	7.36	2.25	1.25	32%	7.18	10.65	5.01	1.27	18%
Methylvinyl ketone	10.05	1.67	17%	10.46	4%	3.54	0.63	18%	2.30	0.60	26%	2.89	5.21	2.39	0.51	18%	2.50	2.90	2.22	0.17	7%
Hydroxy Acetone	3.22	0.58	18%	3.32	3%	1.09	0.22	20%	0.64	0.19	30%	0.78	1.20	0.60	0.09	12%	0.67	0.81	0.57	0.05	7%
Methoxy Acetone	2.33	0.48	20%	2.42	4%	1.03	0.22	21%	0.72	0.20	28%	0.88	1.67	0.53	0.19	21%	0.63	0.87	0.50	0.09	14%
Diacetone Alcohol	0.76	0.19	25%	0.78	2%	0.38	0.12	32%	0.26	0.10	40%	0.29	0.41	0.15	0.06	20%	0.17	0.23	0.11	0.03	17%
Phenol	1.89	0.31	17%	1.99	5%	-0.67	0.26	-39%	-1.51	0.60	-40%	-2.44	0.40	-13.92	2.38	-97%	-0.97	0.35	-5.42	1.11	-114%
o-Cresol	2.41	0.38	16%	2.54	6%	-0.65	0.22	-34%	-1.64	0.61	-37%	-2.64	0.58	-14.45	2.50	-95%	-1.06	0.53	-5.86	1.30	-122%
m-Cresol	2.41	0.38	16%	2.54	6%	-0.65	0.22	-34%	-1.64	0.61	-37%	-2.64	0.58	-14.45	2.50	-95%	-1.06	0.53	-5.86	1.30	-122%
p-Cresol	2.41	0.38	16%	2.54	6%	-0.65	0.22	-34%	-1.64	0.61	-37%	-2.64	0.58	-14.45	2.50	-95%	-1.06	0.53	-5.86	1.30	-122%
Alkyl Phenols	2.41	0.38	16%	2.54	6%	-0.65	0.22	-34%	-1.64	0.61	-37%	-2.64	0.58	-14.45	2.50	-95%	-1.06	0.53	-5.86	1.30	-122%
Nitrobenzene	0.08	0.02	26%	0.08	1%	0.03	0.01	41%	0.01	0.01	78%	0.01	0.03	-0.04	0.01	94%	0.01	0.02	0.00	0.00	25%
Toluene Diisocyanate	-0.12	0.11	-87%	-0.10	-14%	-0.98	0.26	-26%	-1.33	0.51	-38%	-1.97	-0.10	-10.04	1.67	-85%	-0.93	-0.13	-3.56	0.62	-66%
Para Toluene Isocyanate	0.99	0.25	25%	1.04	5%	-0.85	0.33	-39%	-1.43	0.61	-43%	-2.15	0.17	-11.48	1.96	-91%	-0.78	0.14	-3.69	0.70	-89%
Methylene Diphenylene Diisocyanate	0.83	0.18	21%	0.88	5%	-0.45	0.21	-46%	-0.85	0.39	-46%	-1.33	0.16	-7.70	1.31	-98%	-0.50	0.13	-2.65	0.51	-100%
Ethyl Amine	8.37	1.44	17%	8.71	4%	3.16	0.53	17%	2.11	0.52	25%	2.65	4.80	2.10	0.50	19%	2.49	3.37	2.17	0.30	12%
Dimethyl Amine	9.64	1.60	17%	10.11	5%	3.36	0.52	15%	2.19	0.52	24%	2.80	5.03	2.29	0.53	19%	2.96	3.88	2.61	0.31	11%
Trimethyl Amine	7.58	1.26	17%	7.94	5%	2.66	0.41	15%	1.74	0.41	24%	2.21	3.99	1.81	0.42	19%	2.32	3.06	2.04	0.25	11%
Ethanolamine	6.51	1.11	17%	6.79	4%	2.42	0.40	17%	1.61	0.39	24%	2.03	3.68	1.62	0.38	19%	1.95	2.63	1.70	0.23	12%
Diethanol Amine	4.36	0.73	17%	4.58	5%	1.51	0.24	16%	0.98	0.24	24%	1.23	2.09	1.01	0.21	17%	1.28	1.60	1.15	0.11	9%
Triethanolamine	2.98	0.52	17%	3.13	5%	1.04	0.18	18%	0.67	0.17	26%	0.83	1.29	0.69	0.12	15%	0.81	1.02	0.65	0.07	8%
N-Methyl-2-Pyrrolidone	2.83	0.67	24%	2.91	3%	1.31	0.38	29%	0.87	0.34	38%	0.97	1.35	0.56	0.18	19%	0.59	0.75	0.36	0.10	17%
Methyl Chloride	0.04	0.01	25%	0.04	1%	0.02	0.01	29%	0.02	0.01	35%	0.02	0.03	0.01	0.00	24%	0.01	0.02	0.01	0.00	19%
Dichloromethane	0.07	0.02	25%	0.07	1%	0.04	0.01	28%	0.03	0.01	35%	0.04	0.06	0.01	0.01	24%	0.02	0.03	0.01	0.00	19%
Methyl Bromide	0.02	0.00	25%	0.02	1%	0.01	0.00	28%	0.01	0.00	35%	0.01	0.02	0.00	0.00	24%	0.01	0.01	0.00	0.00	19%
Chloroform	0.04	0.01	25%	0.04	1%	0.02	0.01	28%	0.02	0.01	35%	0.02	0.03	0.01	0.00	24%	0.01	0.02	0.01	0.00	19%
Vinyl Chloride	3.19	0.66	21%	3.29	3%	1.46	0.32	22%	1.01	0.29	28%	1.22	2.20	0.67	0.24	20%	0.92	1.27	0.63	0.14	15%
Ethyl Chloride	0.28	0.07	25%	0.28	2%	0.16	0.04	28%	0.11	0.04	34%	0.13	0.23	0.05	0.03	23%	0.08	0.12	0.04	0.02	19%

Table C-5. Summary of calculated incremental and relative reactivities in various scales. Calculated using the SAPRC-99 mechansim (8/30/99)

Compound or Mixture	MIR (gm O3 / gm VOC)					MOIR (gm/gm)			EBIR (gm/gm)			Base Case Relative Reactivities [a]									
	39 Scenarios			Avg. Conds		39 Scenarios			39 Scenarios			Ozone Yield (gm basis)					Max 8-Hour Avg (gm basis)				
	Avg.	Sdev			D%	Avg.	Sdev		Avg.	Sdev		Avg.	Max	Min	Sdev		Avg.	Max	Min	Sdev	
1,1-Dichloroethane	0.11	0.03	25%	0.11	2%	0.06	0.02	28%	0.05	0.02	34%	0.05	0.09	0.02	0.01	24%	0.03	0.05	0.02	0.01	19%
1,2-Dichloroethane	0.11	0.03	25%	0.11	1%	0.06	0.02	28%	0.04	0.02	34%	0.05	0.09	0.02	0.01	24%	0.03	0.05	0.02	0.01	19%
Ethyl Bromide	0.12	0.03	25%	0.12	1%	0.07	0.02	28%	0.05	0.02	34%	0.06	0.10	0.02	0.01	24%	0.04	0.05	0.02	0.01	19%
1,1,2-Trichloroethane	0.07	0.02	25%	0.07	1%	0.04	0.01	28%	0.03	0.01	35%	0.03	0.05	0.01	0.01	24%	0.02	0.03	0.01	0.00	19%
1,1,1-Trichloroethane	0.00	0.00	25%	0.00	1%	0.00	0.00	29%	0.00	0.00	35%	0.00	0.00	0.00	0.00	24%	0.00	0.00	0.00	0.00	20%
1,2-Dibromoethane	0.05	0.01	25%	0.05	1%	0.03	0.01	28%	0.02	0.01	35%	0.02	0.04	0.01	0.01	24%	0.02	0.02	0.01	0.00	19%
n-Propyl Bromide	0.39	0.09	24%	0.39	2%	0.21	0.06	27%	0.15	0.05	33%	0.18	0.31	0.07	0.04	23%	0.11	0.17	0.06	0.02	18%
n-Butyl Bromide	0.67	0.15	23%	0.68	2%	0.35	0.09	25%	0.24	0.08	32%	0.29	0.51	0.13	0.06	22%	0.20	0.28	0.12	0.03	17%
Trans-1,2-Dichloroethene	0.90	0.21	23%	0.91	2%	0.47	0.12	25%	0.33	0.11	32%	0.39	0.69	0.17	0.09	22%	0.26	0.38	0.15	0.05	17%
Trichloroethylene	0.67	0.15	23%	0.68	2%	0.35	0.09	25%	0.25	0.08	32%	0.29	0.51	0.12	0.06	22%	0.20	0.28	0.11	0.03	17%
Perchloroethylene	0.04	0.01	25%	0.05	1%	0.03	0.01	28%	0.02	0.01	35%	0.02	0.04	0.01	0.01	24%	0.01	0.02	0.01	0.00	19%
2-(Cl-methyl)-3-Cl-Propene	1.28	0.36	28%	1.36	6%	0.66	0.18	28%	0.51	0.16	32%	0.61	1.07	0.28	0.18	29%	0.27	0.79	-0.11	0.15	55%
Monochlorobenzene	0.40	0.10	25%	0.41	1%	0.17	0.07	40%	0.08	0.06	76%	0.07	0.14	-0.20	0.06	92%	0.08	0.10	0.01	0.02	24%
p-Dichlorobenzene	0.23	0.06	25%	0.23	1%	0.09	0.04	41%	0.04	0.03	77%	0.04	0.08	-0.12	0.04	92%	0.04	0.06	0.01	0.01	25%
Benzotrifluoride	0.29	0.06	22%	0.29	2%	0.08	0.03	38%	0.02	0.03	154%	0.01	0.07	-0.23	0.05	888%	0.04	0.06	-0.02	0.02	42%
p-Trifluoromethyl-Cl-Benzene	0.12	0.03	22%	0.13	2%	0.04	0.01	39%	0.01	0.01	159%	0.00	0.03	-0.10	0.02	989%	0.02	0.03	-0.01	0.01	42%
TLEV Exhaust -- RFA	4.37	0.76	17%	4.55	4%	1.58	0.30	19%	0.91	0.28	31%	1.04	1.11	0.88	0.04	4%	1.09	1.15	1.05	0.02	2%
TLEV Exhaust -- M-85	1.67	0.27	16%	1.72	3%	0.60	0.09	15%	0.35	0.09	25%	0.43	0.65	0.34	0.07	16%	0.47	0.63	0.40	0.05	10%
TLEV Exhaust -- E-85	2.93	0.59	20%	3.01	3%	1.28	0.29	23%	0.85	0.26	30%	1.02	1.74	0.67	0.18	17%	0.77	1.01	0.64	0.08	11%
TLEV Exhaust -- CNG	0.81	0.15	19%	0.84	3%	0.36	0.08	22%	0.24	0.07	29%	0.29	0.50	0.20	0.05	18%	0.24	0.32	0.21	0.03	11%
TLEV Exhaust -- LPG	2.26	0.39	17%	2.33	3%	0.92	0.16	17%	0.59	0.15	26%	0.72	1.24	0.58	0.12	16%	0.66	0.88	0.58	0.07	10%
TLEV Exhaust -- Phase 2	4.33	0.74	17%	4.49	4%	1.58	0.29	19%	0.92	0.27	30%	1.06	1.11	0.99	0.03	3%	1.11	1.17	1.08	0.03	2%
Final LEV -- RFA	3.91	0.70	18%	4.04	3%	1.45	0.29	20%	0.84	0.27	32%	0.95	1.00	0.71	0.05	5%	0.97	1.00	0.93	0.02	2%
Final LEV -- Phase 2	3.81	0.67	18%	3.95	4%	1.43	0.28	19%	0.84	0.25	30%	0.96	1.01	0.91	0.02	2%	0.97	1.03	0.93	0.03	3%
Mineral Spirits "A" (Type I-B, 91% Alkanes)	1.49	0.42	29%	1.54	4%	0.76	0.26	35%	0.46	0.23	49%	0.41	0.65	-0.27	0.20	50%	0.19	0.38	-0.21	0.14	74%
Mineral Spirits Sample "B" (Type II-C)	0.97	0.36	37%	1.00	4%	0.59	0.24	41%	0.36	0.20	56%	0.29	0.54	-0.37	0.21	71%	0.06	0.26	-0.37	0.15	266%
Mineral Spirits Sample "C" (Type II-C)	0.97	0.36	37%	1.01	4%	0.59	0.24	41%	0.36	0.21	57%	0.29	0.55	-0.38	0.21	72%	0.06	0.26	-0.37	0.15	255%
Mineral Spirits Sample "D" (Type II-C)	0.98	0.37	37%	1.02	4%	0.60	0.24	41%	0.37	0.21	57%	0.30	0.55	-0.38	0.21	72%	0.06	0.26	-0.37	0.15	242%

[a] Maximum, minimum, and standard deviations for base ROG mixture are incremental reactivities relative to the average.