

# **Chemical Mechanisms for Representation of Aromatic Hydrocarbons in Airshed Models: Effects of Structure on Ozone Reactivity**

William P. L. Carter

College of Engineering Center for Environmental Research and Technology

University of California

Riverside, California, USA 92521

Presented at the Workshop on

"Chemical Behavior of Aromatic Hydrocarbons in the Troposphere"

Valencia, Spain, February 27-29, 1999

## **Abstract**

The representation of aromatic hydrocarbons in the recently developed SAPRC-99 chemical mechanism for airshed models is discussed. Because of lack of available information, parameterized mechanisms adjusted to fit chamber data must still be used. The chamber data base employed consists of NO<sub>x</sub>-air irradiations of benzene, toluene, ethylbenzene, all three xylene and all three trimethylbenzene isomers in both blacklight and xenon-arc irradiated chambers, and of naphthalene, dimethylnaphthalene and tetralin in blacklight chambers alone. Significant differences in ozone formation potentials were observed that are not accounted for by differences in OH radical rate constants. These are accounted for in the model by using differing yields of model species used to represent the various photoreactive aromatic ring-opening products, with use of products with two different action spectra being necessary to fit data using differing light sources. Lower yields of photoreactive products are needed to fit the data for p-xylene or 1,2,4-trimethylbenzene compared to the other isomers, suggesting the formation of higher yields of less photoreactive unsaturated ketones compared to presumably more photoreactive unsaturated aldehydes. The parameterization that was found to successfully simulate the data for the alkylbenzenes was found to be less successful for benzene and the naphthalenes and tetralin, and a different parameterization performed better for the latter two. Implications of these results on predictions of O<sub>3</sub> impacts in the atmosphere are discussed.

## Introduction

Aromatic hydrocarbons are important constituents of anthropogenic emissions into the atmosphere, and they are known to be highly reactive towards forming ozone and manifestations of photochemical smog. Therefore, it is important that they be appropriately represented in the airshed models used to predict the effects of emissions on urban and regional air quality. The following are the minimum requirements for chemical mechanisms for aromatics in airshed models: They must be consistent (or at least not inconsistent) with current knowledge of the atmospheric reactions of aromatics and their major reactive products. They must be able to represent the differences in reactivities of the major types of aromatic hydrocarbons that are emitted, including differences among isomers. They must be able to give predictions that are consistent with results of environmental chamber experiments carried out under varying conditions. In addition, since representations of chemical transformations is usually the computationally intensive portion of airshed models, they preferably should not contain more species and reactions than necessary to satisfy the above requirements.

Despite continuing progress in recent years in improving our understanding of the reactions of aromatic compounds in the atmosphere, there is still insufficient information about these reactions and the products formed to provide a basis for developing predictive mechanisms to represent these reactions in airshed models. Therefore, such models must still use simplified or parameterized mechanisms that are adjusted to fit environmental chamber data. Most airshed models have used highly condensed mechanisms for aromatics that do not represent reactivity differences among aromatic isomers. This is the case for relatively detailed mechanisms such as the "SAPRC-90" mechanism of Carter (1990), as well as more condensed mechanisms such as RADM-2 (Stockwell et al, 1990), Carbon bond IV (Gery et al, 1988), and even the recently developed RACM mechanism of Stockwell et al (1997). These mechanisms have been developed and evaluated using available environmental chamber data for a relatively small number of aromatic compounds, primarily toluene and m-xylene (e.g., Gery et al, 1988, Carter and Lurmann, 1990, 1991, and references therein).

However, recently environmental chamber data have become available that can be used to separately evaluate mechanisms for the various aromatics isomers from benzene and toluene to ethylbenzene and all the xylene and trimethylbenzene isomers (Carter et al, 1995, 1997a). Significant reactivity differences among some of the aromatic isomers that are represented in the same way in the previous models have been observed. These data have been used in the development and evaluation of an updated version of the SAPRC mechanism referred to as

SAPRC-99 (Carter, 2000a), that represents the reactivity differences in the aromatics involved. The results of these experiments, and representation of the aromatics in this updated mechanism that takes these into account, are discussed in this paper.

### **Major Features of the SAPRC-99 Mechanism**

The SAPRC-99 mechanism is documented in detail by Carter (2000a). It represents a complete update of the earlier versions of the SAPRC mechanism (e.g., Carter, 1990, Carter et al, 1997a), and represents a much larger number of different types of compounds. It consists of a “base mechanism” that represents the reactions of the inorganics and common organic products, and separate representations for each of ~400 types of compounds. The latter can be used to derive condensed mechanisms for mixtures based on the specific compounds being represented, or for explicit representation of individual compounds for reactivity assessment. A computerized mechanism generation system is used to derive fully explicit mechanisms for compounds with no more than one double bond given their structure and assigned or estimated rate constants and branching ratios for competing reactions. However, parameterized mechanisms, adjusted to fit environmental chamber data, still need to be used for aromatics and a few other types of compounds, such as terpenes. This mechanism was comprehensively evaluated using the existing indoor environmental chamber data base from the University of California at Riverside, including experiments carried out very recently on a variety of individual compounds (Carter, 2000a, and references therein). This mechanism was then used to update the Maximum Incremental Reactivity (MIR) and other reactivity scales developed previously (Carter, 1994), which were expanded to include estimates for a much larger range of compounds. A condensed version of the mechanism was developed for use in airshed models (Carter, 2000b).

### **Environmental Chamber Data Base Used to Develop the SAPRC-99 Aromatics Mechanism**

The types of environmental chamber experiments used when developing the SAPRC-99 mechanism are summarized on Table 1. Note that the data base includes experiments for benzene and all C<sub>7</sub> and C<sub>8</sub> alkylbenzene isomers, all trimethylbenzene isomers, as well as a smaller number of experiments for naphthalene, dimethyl naphthalene, and tetralin. Except for the latter three, experiments were carried out with two differing light sources, with significant differences in spectral characteristics. The availability of data with differing light sources turned out to be important, as discussed in more detail below. However, only indoor chamber experiments were used in this evaluation, because of the greater uncertainty in characterizing conditions of outdoor

Table 1. Summary of environmental chamber experiments used when developing the SAPRC-99 mechanism.

Compound	Number of Experiments			
	Aromatic - NO <sub>x</sub>		Incremental Reactivity	
	Black Lights	Xenon Arc	Black Lights	Xenon Arc
Benzene	6	4	3	
Toluene [a]	9	6	4	2
Ethylbenzene	4	4	3	
o-Xylene [b]	6	6	2	
m-Xylene	11	7	7	2
p-Xylene	6	6	1	
1,2,3-Trimethylbenzene	6	3	2	
1,2,4-Trimethylbenzene	5	4	2	
1,3,5-Trimethylbenz. [b]	12	6	1	
Naphthalene	5			
2,3-Dimethylnaphalene	4			
Tetralin	5			
Styrene				6
Acetylene [c]				7

[a] Duplicate blacklight chamber experiments and experiments in the SAPRC EC not counted.

[b] Experiments in the SAPRC EC not counted.

[c] Used for adjusting the mechanism for glyoxal.

experiments. We have found in general that mechanisms adjusted to fit indoor experiments using differing light sources tend to be consistent with results of outdoor chamber experiments, at least to within their variability and characterization uncertainty (Carter and Lurmann, 1990, 1991; Carter and Atkinson, 1996).

The data obtained indicted significant differences in ozone reactivities of aromatic isomers, even after differences in their atmospheric reactions rates are taken into account. Examples of this are shown on Figure 1 through Figure 3, which give O<sub>3</sub>, NO, and aromatic concentration-time plots for experiments with similar initial reactant concentrations carried out under similar conditions. Figure 1 shows that even though toluene and ethylbenzene have very similar OH radical rate constants, the NO oxidation and O<sub>3</sub> formation rates are significantly

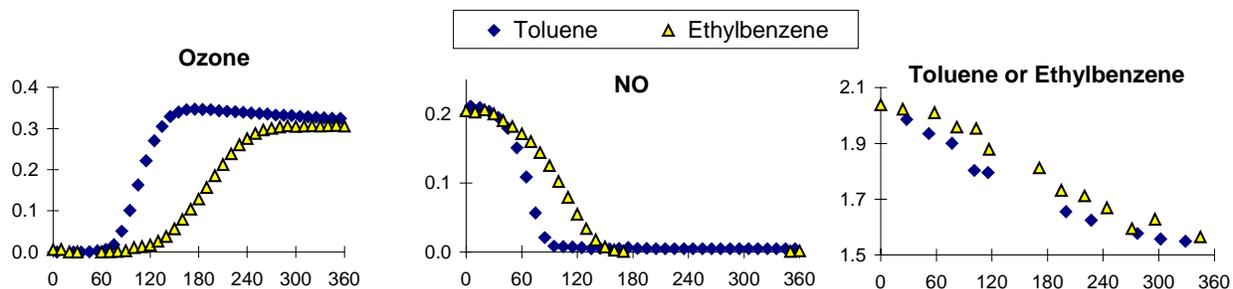


Figure 1. Differences in environmental chamber reactivities in between toluene and ethylbenzene in aromatic -  $\text{NO}_x$  - air environmental chamber experiments. Experiments were carried out in the xenon arc chamber with initial  $\text{NO}_x \approx 0.3$  ppm and initial aromatic  $\approx 2$  ppm. Concentrations are in ppm and time is in minutes.

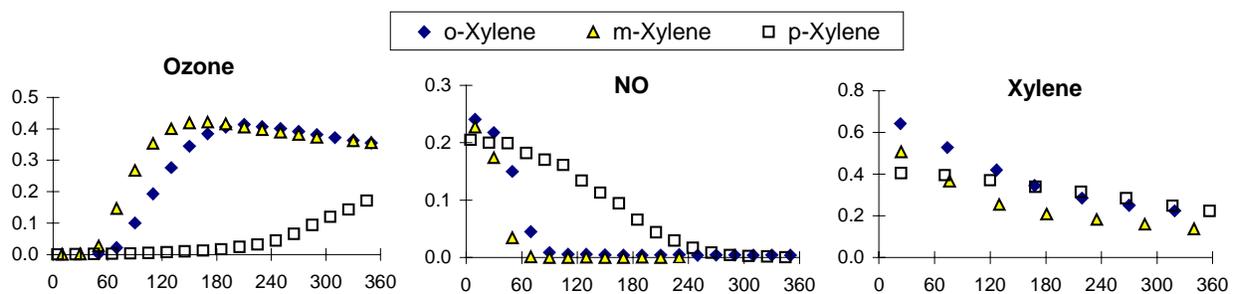


Figure 2. Differences in environmental chamber reactivities in among xylene isomers in aromatic -  $\text{NO}_x$  - air environmental chamber experiments. Experiments were carried out in the blacklight chamber with initial  $\text{NO}_x \approx 0.3$  ppm and initial aromatic  $\approx 0.5$  ppm. Concentrations are in ppm and time is in minutes.

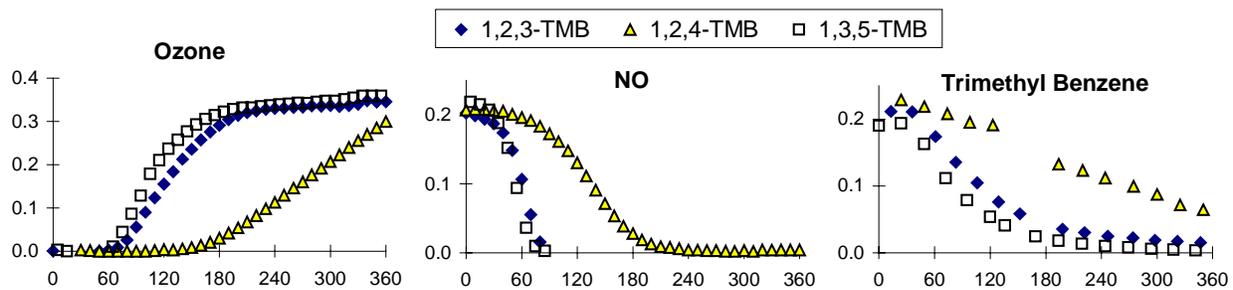
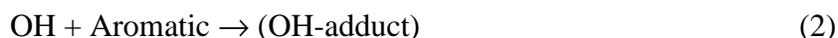
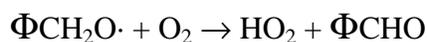
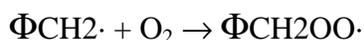


Figure 3. Differences in environmental chamber reactivities in among trimethylbenzene isomers in aromatic -  $\text{NO}_x$  - air environmental chamber experiments. Experiments were carried out in the xenon arc chamber with initial  $\text{NO}_x \approx 0.25$  ppm and initial aromatic  $\approx 0.2$  ppm. Concentrations are in ppm and time is in minutes.

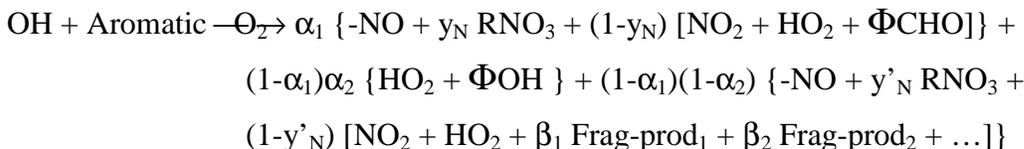
higher in the toluene experiment. Figure 2 shows that although o-xylene and m-xylene have very similar effects on O<sub>3</sub> formation and NO oxidation rates in comparable experiments, these measures of reactivity are much lower in the experiment with p-xylene. Likewise, Figure 3 shows that although 1,2,3- and 1,3,5-trimethylbenzene have similar reactivities when irradiated under comparable conditions, the O<sub>3</sub> formation and NO oxidation rates with comparable amounts of 1,2,4-trimethylbenzene are also much lower. These differences have no correlation with the OH radical rate constant differences among these isomers, which are relatively small compared to these reactivity differences.

### Representation of Aromatics in SAPRC-99

The major features of the representation of aromatics in the SAPRC-99 mechanism is similar to that used in previous versions of the SAPRC mechanisms, as well as the recent mechanisms developed by Stockwell et al (1990, 1997). It is based on the assumption that the overall process involves the following types of reactions, where “Φ” refers to an aromatic ring, and the probable structure of the OH-aromatic and OH-aromatic-O<sub>2</sub> adducts are as discussed elsewhere (e.g., Atkinson, 1990, 1994, 2000).



The overall process is then given by

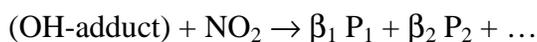
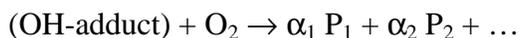


where the parameters in the mechanism, and their derivations, are as follows:

- $\alpha_1 = k_1/(k_1+k_2)$  = Fraction of OH that abstracts. These are derived based on measured product yields for the aromatic aldehyde predicted to be formed through reaction (1) or estimated based on reactions of analogous compounds.
- $\alpha_2 = k_3/(k_3+k_4)$  = Fraction of OH adduct that reacts with  $\text{O}_2$ , forming phenolic products. These are derived based on measured yields of the phenolic products predicted to be formed in Reaction (3) or estimated based on yields for analogous compounds.
- $y_N = k_{1n}/(k_{1n}+k_{1r})$ ;  $y'_N = k_{4n}/(k_{4n}+k_{4r})$ : Nitrate yields. These are derived based on benzyl nitrate yields from toluene as given by Atkinson (1994), and are used as the basis of estimating nitrate yields for the other aromatics.
- $\beta_1, \beta_2$ , etc = Fragmentation product yields. These include the  $\alpha$ -dicarbonyl products whose yields are determined based on measured yields or estimates based on measured yields from similar compounds, and other photoreactive products whose yields are adjusted to fit the chamber data as discussed below. To fit the chamber data it is necessary for the model to include the formation of significant yields of other photoreactive products besides the known yields of the  $\alpha$ -dicarbonyls.

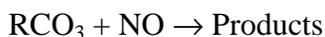
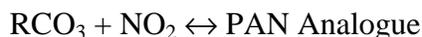
Although the mechanism for the reactions following Reaction (1) is considered to be reasonably well established, the details following OH addition to the aromatic ring are much more uncertain, and the overall process shown above following Reaction (2) does not represent all the possibilities that might reasonably be considered. Because of this, several alternative parameterizations were examined to determine if they could also give predictions that were consistent with the available chamber data. These included the following:

- Competition between the aromatic + OH adduct reacting with  $\text{O}_2$  and  $\text{NO}_2$ , where the rate constant ratio and the products for each route was separately optimized, i.e.,



This did not result in improved fits to the chamber data and did not predict a correct dependence of reactivity on  $\text{NO}_x$  levels.

- Formation of products that are not photoreactive but that react rapidly with OH to form the  $\alpha$ -dicarbonyls and other photoreactive products. Mechanisms using this assumption were not consistent with the chamber data.
- Adjusting the overall number of NO to NO<sub>2</sub> conversions in the reactions following OH addition to the aromatic ring. This did not give a sufficient improvement to the model performance to indicate that the assumed overall process shown above, which involves approximately one NO to NO<sub>2</sub> conversion, is necessarily incorrect.
- Treating the overall organic nitrate yields as an adjustable parameter. Assuming significantly different nitrate yields than initially estimated did not result in improvements in model performance in simulating the data. However, this had to be treated as an adjustable parameter in mechanisms for naphthalene and dimethyl naphthalene, where relatively high nitrate yields of 7-12% had to be assumed to give best fits to the data.
- Assuming non-negligible formation of radicals that react with NO<sub>2</sub> (as is assumed to be the case for phenoxy radicals). This did not result in improved fits to the data and gave incorrect predictions of how results of the experiments depended on NO<sub>x</sub> levels.
- Assuming non-negligible formation of radicals that react like PAN precursors, e.g.,



This did not result in improved fits in the simulations of the experiments for the alkylbenzenes. On the other hand, as discussed below it was necessary to include this mechanism in the representations of the reactions of the naphthalenes and tetralin in order to fit the chamber data for these compounds. Using the standard alkylbenzene parameterization alone, or the other alternative approaches as discussed above (except for adjusting the overall nitrate yields in the case of the naphthalenes) did not result in satisfactory fits to the data for these compounds.

The model species used to represent the various organic products formed from the reactions of the aromatics are summarized in Table 2. Other than the representation of the photoreactive products which is discussed below and the use of a different model species to represent aromatic ketones, the set of model species used in SAPRC-99 is similar to that used in previous versions of this mechanism (Carter, 1990; Carter et al, 1997a).

Table 2. Model species used to represent reactive aromatic products in the SAPRC-99 mechanism.

Model Species	Description
<u>Organic Nitrates</u>	
RNO3 .....	Any organic nitrate formed from RO <sub>2</sub> +NO
<u>Ring Retaining Products</u>	
PHEN .....	Phenol (from benzene only). Represented by analogy to the adjusted mechanism used for o-cresol.
CRES .....	Substituted Phenols. Represented by a mechanism adjusted to fit chamber data for o-cresol.
BALD .....	Aromatic aldehydes. Represented by the Benzaldehyde model species.
PROD2 .....	Aromatic ketones, e.g., Methyl Phenyl Ketone from ethylbenzene. Represented by the model species used to lumped higher aliphatic ketone products from alkanes, etc.
<u>α-Dicarbonyl Fragmentation Products</u>	
GLY .....	Glyoxal. Represented explicitly in the mechanism.
MGLY .....	Alkyl Glyoxals. Represented by the methyl glyoxal model species.
BACL .....	α-Dicarbonyl Ketones. Represented by the biacetyl model species, which was added to this version of the mechanism. (These were represented by MGLY in previous versions of the mechanism.)
<u>Unknown Fragmentation Products</u>	
DCB1 .....	Non-photoreactive products. The mechanisms for its reactions with OH radicals and O <sub>3</sub> is based on a simplification of estimated reactions for HCOCH=CHCHO.
DCB2 .....	Photoreactive products with action spectrum like Methyl Glyoxal. The mechanisms for its reactions with OH radicals, O <sub>3</sub> and by photolysis is based on a simplification of estimated reactions for CH <sub>3</sub> C(O)CH=CHCHO.
DCB3 .....	Photoreactive products with action spectrum like Acrolein. Otherwise same mechanism as used for DCB2

The main change in the representation of the aromatics in this version of the mechanism is the use of a larger number of model species to represent aromatic fragmentation products. In the SAPRC-90 mechanism of Carter (1990) MGLY was used to represent the  $\alpha$ -dicarbonyl ketones as well as the aldehydes besides glyoxal, and only a single additional model species, AFG2, was used to represent the uncharacterized reactive products formed from alkylbenzenes (with a separate model species, AFG1, used to represent these products formed from benzene.) In the SAPRC-97 mechanism of Carter et al (1997a), to fit chamber data with differing light sources (see discussion below) MGLY was also used to represent uncharacterized products with similar action spectra, and its yield, along with that of AFG2, was adjusted to fit chamber data. In SAPRC-99, all the three types of alpha-dicarbonyls are represented using separate model species, separate model species, DCB2 and DCB3, are used to represent uncharacterized fragmentation products with differing action spectra, and an unphotoreactive model species, DCB1 is added.

The main feature of both the SAPRC-97 and the SAPRC-99 mechanisms is the use of two different model species to represent uncharacterized photoreactive ring-fragmentation products with different action spectra. Figure 4 shows a comparison of the action spectrum (absorption coefficient x quantum yield) of methyl glyoxal with the absorption cross sections for acrolein as used in the SAPRC-99 mechanism. The action spectra for the other  $\alpha$ -dicarbonyls are similar to that shown for methyl glyoxal, while absorption spectrum for acrolein, which may be a better approximation to the action spectra of the other aromatic ring fragmentation products (which are expected to include various unsaturated carbonyls), is quite different. Thus, these types of products would be expected to have different ratios of photolysis rates depending on the spectrum of the light source.

Figure 4 also shows the spectra for sunlight and the blacklight and xenon arc light sources for the environmental chamber experiments used for aromatic mechanism development. These relative spectra are all normalized to give the same NO<sub>2</sub> photolysis rate. It can be seen that the blacklight and the xenon arc spectra are quite different in the wavelength region affecting  $\alpha$ -dicarbonyl and acrolein relative photolysis rates, with the  $\alpha$ -dicarbonyls being expected to photolyze significantly slower with blacklight irradiation than with sunlight or xenon arc lights. This means that if the mechanism used product species with inappropriate action spectra, it may not be correctly predicting how aromatic reactivity depends on the nature of the light source. The availability of chamber data with differing light sources is therefore very useful for evaluating the model's representation of aromatic photooxidation products.

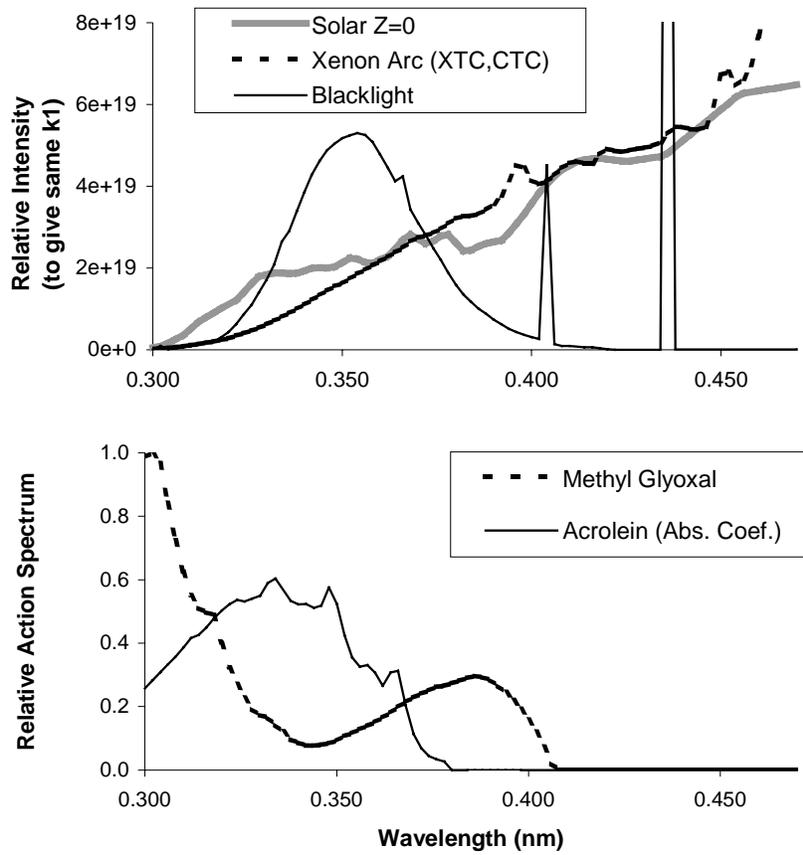


Figure 4. Comparison of spectra of natural and artificial light sources and action spectra of representative compounds representing aromatic ring fragmentation products.

The need to use model species with both types of action spectra for representing aromatic fragmentation products is shown on Figure 5, which compares results of model simulations using various adjusted mechanisms with results of toluene - NO<sub>x</sub> experiments carried out using various light sources. The data plotted are experimental and calculated changes in [O<sub>3</sub>]-[NO], or Δ([O<sub>3</sub>]-[NO]), which is used as a general measure of O<sub>3</sub> formation potential when evaluating mechanisms (e.g., see Carter and Lurmann, 1990). It can be seen that if the uncharacterized ring fragmentation products are assumed to have only one type of action spectrum then the same mechanism cannot simulate both blacklight and xenon arc environmental chamber data. If the data are adjusted to fit the xenon arc chamber runs, then models using acrolein-like action spectra cause overpredictions of reactivity in blacklight chamber runs, while models using species with α-dicarbonyl action spectra underpredict Δ([O<sub>3</sub>]-[NO]) reactivity in those runs. On the other hand, if uncharacterized product yields are represented by model species with both types of action spectra, and the yields of both are optimized, then good fits to results of

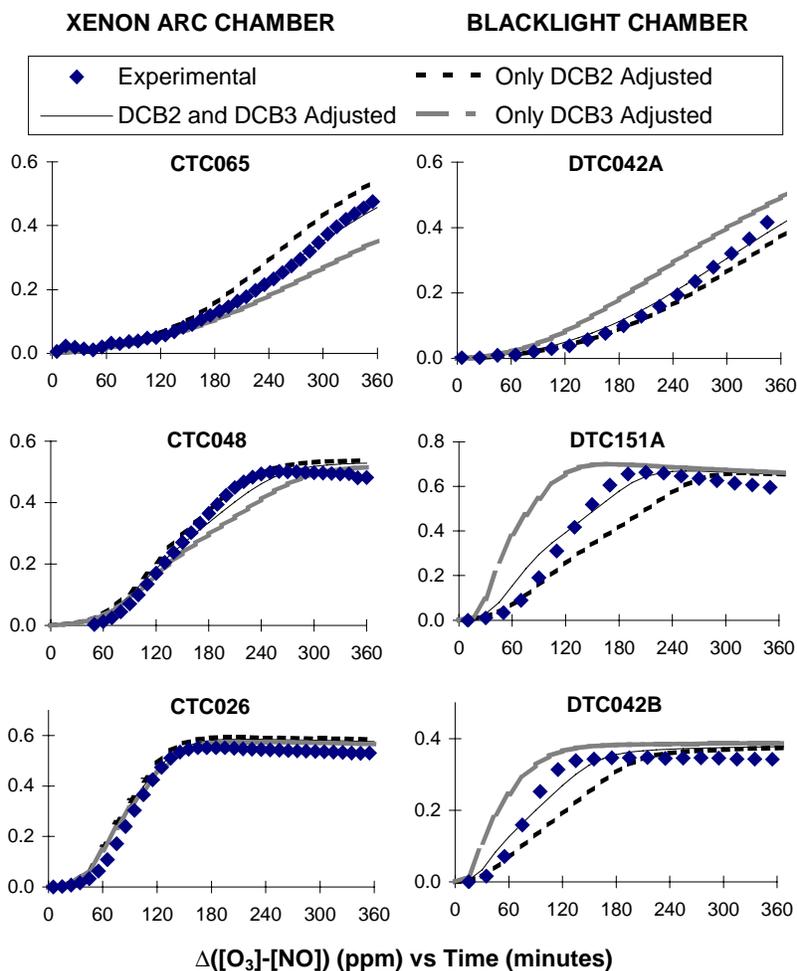


Figure 5. Model performance in simulating results of toluene - NO<sub>x</sub> experiments carried out in chambers with differing light sources. Comparison of results of adjusting yields of products with only one type of action spectrum with adjusting yields of products with both  $\alpha$ -dicarbonyl and acrolein type action spectra.

experiments with the different light sources can be obtained. Similar results are observed for the other aromatic hydrocarbons that were examined.

Although this parameterization and separate optimization of the DCB2 and DCB3 yields gave reasonably good model performance in simulating the available chamber data base for the alkylbenzenes, this was not the case for benzene itself nor for the naphthalenes and tetralin. In the case of benzene, as shown on Figure 6, his parameterization did not yield good fits to all of the data, and no reasonable alternative mechanisms gave any better fits to the data than those shown on Figure 6. It may be that there is an experimental problem with run ITC562, though problems with the mechanism also cannot be ruled out.

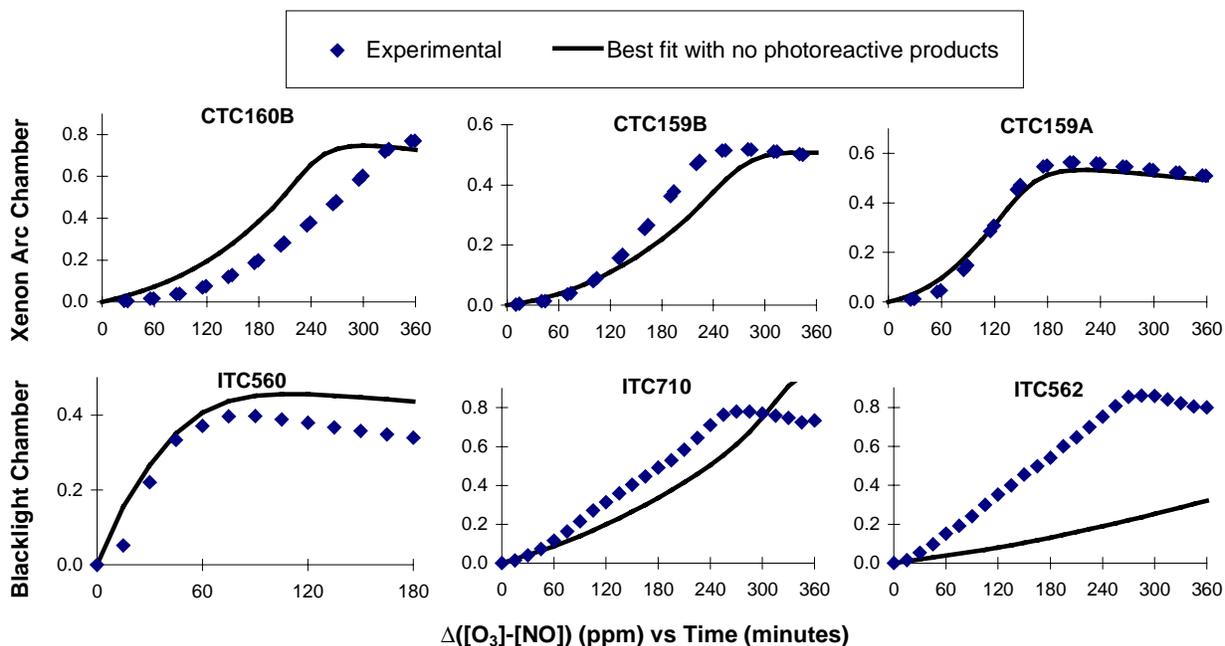


Figure 6. Model performance in simulating the results of selected benzene - NO<sub>x</sub> environmental chamber experiments.

In the case of the naphthalenes and tetralin, optimization of DCB yields alone also did not yield satisfactory to the data, as shown on Figure 7 for representative naphthalene and 2,3-dimethylnaphthalene runs. Note that only blacklight chamber data are available for these compounds, so strictly speaking separate optimization of DCB2 and DCB3 could not be carried out. In the case of these compounds, although DCB optimization alone could result in satisfactory predictions of effects of reactivity on initial reactant concentrations, satisfactory simulations to the data could be obtained if significant formation of radicals that react like PAN precursors, represented by the model species RCO3, is assumed. This was not the case for benzene or any of the alkylbenzenes. The mechanistic implications of this need to be investigated.

Table 3 gives a summary of the yields of photoreactive aromatic ring-opening product model species used in the SAPRC-99 mechanism. Note that because the current mechanism uses relatively high photolysis rates for glyoxal based on results of model simulations of acetylene chamber experiments (Carter et al, 1997b), best fits to the data were obtained if it was assumed that no other photoreactive products are formed in the NO<sub>x</sub> - air reactions of benzene. In the case of the alkylbenzenes, the photoreactive product yields were variable, depending on the isomer.

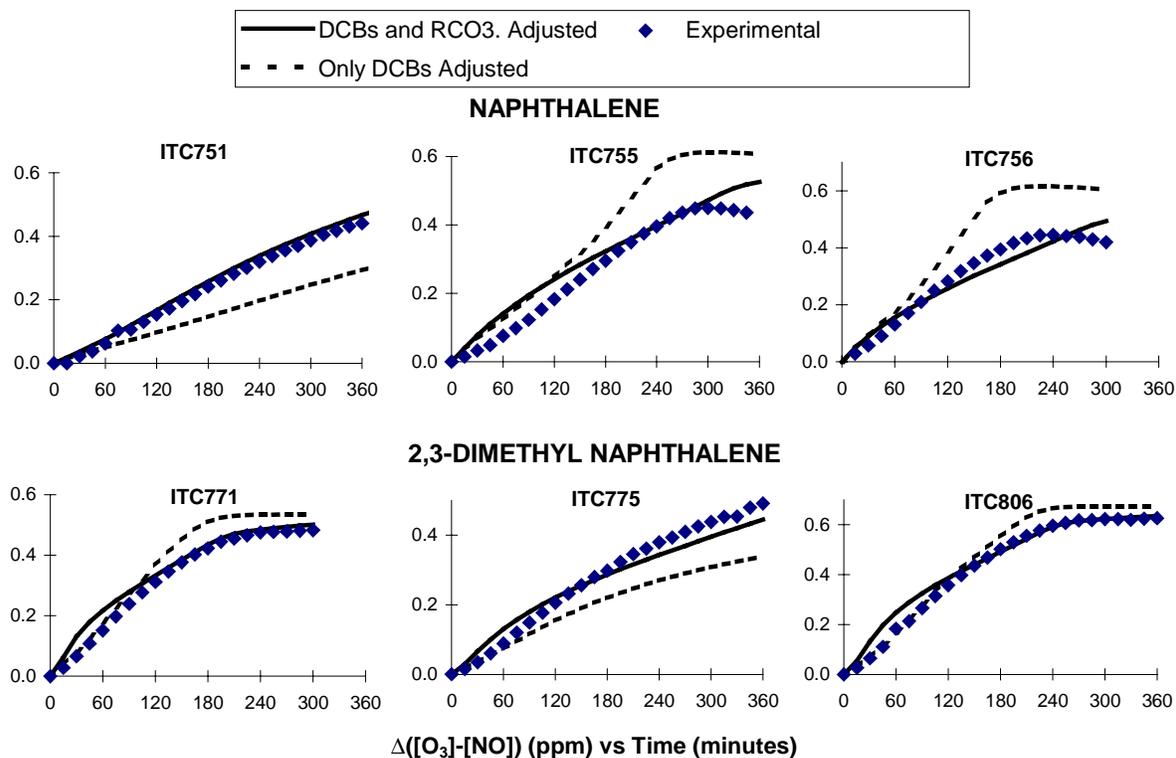


Figure 7. Effects of differing parameterizations on model simulations of naphthalene and 2,3-dimethylnaphthalene - NO<sub>x</sub> environmental chamber experiments. All experiments were carried out using a blacklight light source.

The variable adjusted yields of model species used to represent the uncharacterized photoreactive alkylbenzene ring fragmentation products indicate that either the reactivities of the products formed, or the distributions of reactive products, depend on the isomeric structure of the compound. The most notable result on Table 3 is the much lower total yields of photoreactive DCB products from ethylbenzene, *p*-xylene and 1,2,4-trimethylbenzene than is the case for the other alkylbenzenes. This is a result of the lower reactivities of these compounds in the chamber experiments, as indicated, for example, in Figure 1 through Figure 3. In the case of *p*-xylene and 1,2,4-trimethylbenzene, this result can be attributed to the formation of unsaturated diketone products, such as  $\text{CH}_3\text{C}(\text{O})\text{CH}=\text{CHC}(\text{O})\text{CH}_3$  from *p*-xylene or  $\text{CH}_3\text{C}(\text{O})\text{CH}=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{CH}_3$  from 1,2,4-trimethylbenzene, which would be expected to be formed from para-substituents. The data of Bierbach et al (1994) and Tuazon et al (1985) indicate that such diketones do not undergo significant radical-forming photo-decomposition, while photodecompositions of the unsaturated aldehydes appears to be quite rapid (Bierbach et al, 1994). Aromatic isomers without para

Table 3. Experimental and adjusted yields of model species used to represent photoreactive aromatic ring-opening products.

Compound	Yields Relative to Total Ring Fragmentation		
	Experimental	Adjusted to fit Chamber Data	
	Total $\alpha$ -Dicarbonyls	DCB2 ( $\alpha$ -Dicarbonyl Action Spectrum)	DCB3 (Acrolein Action Spectrum)
Benzene	0.14	~0	~0
Toluene	0.19	0.23	0.08
Ethyl Benzene	0.19 [a]	~0	0.09
o-Xylene	0.30	0.08	0.19
m-Xylene	0.30	0.39	0.15
p-Xylene	0.21	~0	0.02
1,2,3-Trimethylbenzene	0.40	0.10	0.20
1,2,4- Trimethylbenzene	0.33	~0	0.04
1,3,5- Trimethylbenzene	0.40	0.12	0.15

[a] No known data available. Estimated to be the same as for toluene.

substituents are not expected to form these diketones in significant yields, but to form the more photoreactive unsaturated aldehydes instead.

### Implications to Model Calculations of Atmospheric Ozone Impacts of Aromatic Isomers

The differences in mechanisms mean that they will have different effects on ozone formation when they are emitted into urban atmospheres. Effects of compounds on O<sub>3</sub> formation can be measured by the compounds *incremental reactivity*, which is defined as the change in O<sub>3</sub> caused by adding a small amount of the compound to the emissions, divided by the amount added (Carter and Atkinson, 1989; Carter, 1994). To examine the effects of different aspects of the mechanisms on reactivity, incremental reactivities can be considered to be the product of the *kinetic reactivity* and the *mechanistic reactivity*. The former is the fraction of the VOC emitted in the scenario that reacts and depends only on the reaction rate constants and the radical or light levels in the scenario. The mechanistic reactivity is the change in O<sub>3</sub> caused by adding the compound, divided by the amount that *reacts*, and, to a first approximation, depends on the other

Table 4. Calculated contributions of aspects of aromatic photooxidation mechanisms to atmospheric mechanistic reactivities.

Product Formed	Contribution to Moles O <sub>3</sub> Formed per mole Compound Reacted [a]		
	MIR (High NO <sub>x</sub> ) [b]	MOIR (Optimum NO <sub>x</sub> ) [c]	EBIR (Moderate NO <sub>x</sub> ) [d]
NO->NO <sub>2</sub> Conversion	1.3	0.6	0.5
Glyoxal	10.5	2.9	1.5
Methyl Glyoxal	14.9	4.4	2.5
Biacetyl	24.1	7.3	4.2
DCB1	7.1	3.3	2.3
DCB2	31.8	9.6	5.5
DCB3	34.8	10.4	5.9
Benzaldehyde	-1.0	-4.0	-5.7
Phenol	2.6	-2.4	-4.3
Cresols	3.7	-3.3	-5.9

[a] Calculated for OH radical rate constant of  $2 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  using the Averaged conditions scenario with NO<sub>x</sub> levels adjusted as indicated below (Carter, 1994).

[b] Scenarios where NO<sub>x</sub> levels are such that O<sub>3</sub> is most sensitive to reactive organic emissions.

[c] Scenarios where NO<sub>x</sub> levels are optimum for ozone formation.

[d] Scenarios where O<sub>3</sub> is equally sensitive to relative changes in reactive organic or NO<sub>x</sub> emissions.

aspects of the mechanism besides the rate constants, such as the reactivities of the products formed. Furthermore, for compounds such as aromatics that react only with OH, mechanistic reactivities can be apportioned to the different products that are formed by examining mechanistic reactivities of hypothetical species that react only to form the specific products being considered (Carter and Atkinson, 1989).

Table 4 shows the approximate contributions to reactivity of various aspects of the mechanism to the mechanistic reactivity of alkylbenzenes for that are calculated for representative urban scenarios developed by Carter (1994). As discussed by Carter and Atkinson (1989), the contributions of various aspects of the mechanism depend on scenario characteristics, particularly relative NO<sub>x</sub> levels, so these results are shown for three representative NO<sub>x</sub> levels

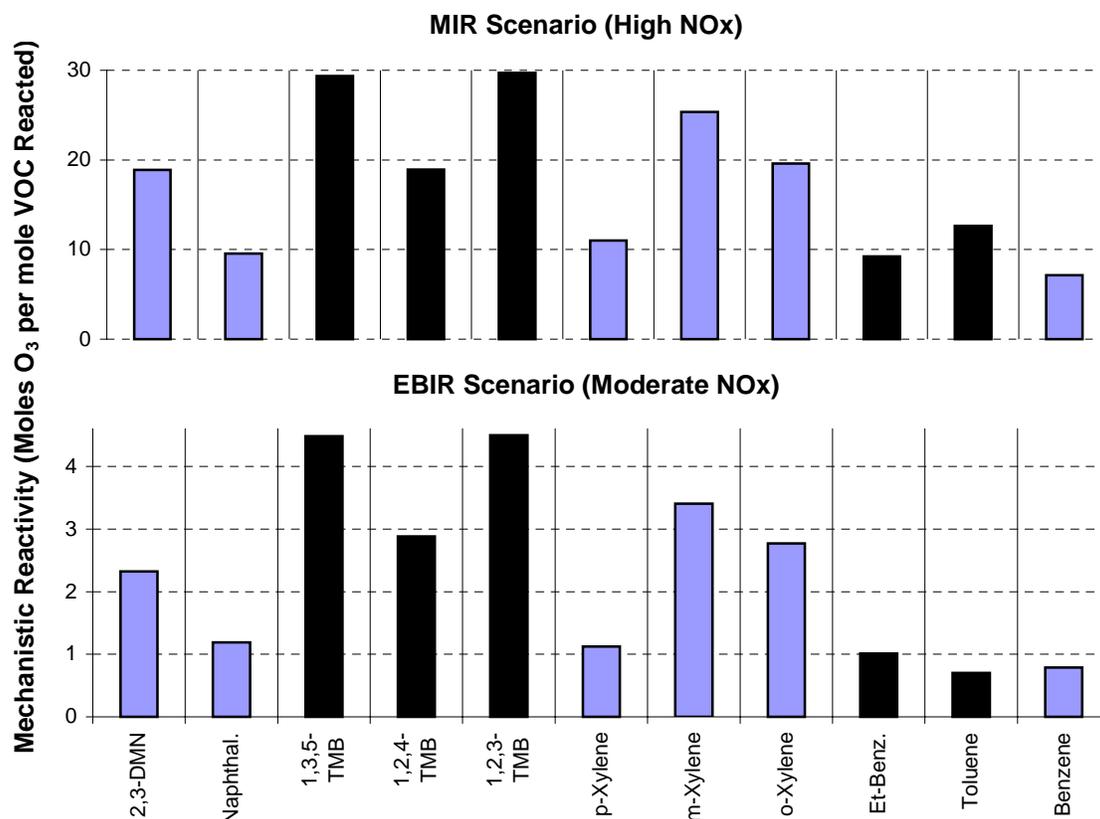


Figure 8. Mechanistic reactivities for representative atmospheric conditions calculated using the SAPRC-99 mechanisms and representative averaged conditions scenarios of Carter (1994).

used when deriving the reactivity scales of Carter (1994). Note that the ring fragmentation products, particularly DCB2 and DCB3 have significant effects on the O<sub>3</sub> impacts of these aromatics, particularly under the relatively high NO<sub>x</sub> MIR conditions. The inhibiting effects of benzaldehyde and (for low NO<sub>x</sub> conditions) phenols and cresols are not important under higher NO<sub>x</sub> conditions, but become relatively more important when NO<sub>x</sub> is limited. The latter is the main reason that incremental reactivities of aromatics become low or negative in scenarios where NO<sub>x</sub> is limited (Carter and Atkinson, 1989, Carter, 1994). By comparison, the NO to NO<sub>2</sub> conversions involved in the initial reactions of the aromatics have relatively small effects on overall O<sub>3</sub> formation.

The calculated overall mechanistic reactivities for the various aromatic compounds that are explicitly represented in the SAPRC-99 mechanism for representative scenarios are shown on Figure 8. As expected based on the data in Table 4, the compounds with the highest yields of

photoreactive fragmentation products have the highest mechanistic reactivities. However, the difference between toluene and ethylbenzene is not as great as one would expect given the differences in reactive fragmentation product yields. This may be due in part to the fact that toluene is predicted to form the inhibitor benzaldehyde while the product formed in the corresponding reaction in the ethylbenzene case is methyl phenyl ketone, which is represented by the positively reactive PROD2 model species. The para-substituted isomer is approximately half as reactive as the other isomers in the case of the xylenes, and approximately 1.5 times less reactive in the case of the trimethylbenzenes. This is less than the differences in reactivities seen in the chamber experiments, which tend to be more sensitive to some mechanistic differences than is the case for atmospheric conditions.

## Conclusions

Although there have been advances in recent years in our understanding of aromatic atmospheric photooxidation mechanisms and the types of products they form it is still not possible to derive predictive mechanisms for airshed models based on fundamental laboratory data and theory alone. Fortunately, existing chamber data are sufficient to derive parameterized mechanisms for the major alkylbenzenes, and the available data represent a sufficient range of reactant concentrations and lighting conditions to allow for a reasonably comprehensive evaluation. However, available data are insufficient for adequate mechanism evaluation for the naphthalenes and tetralin, and model performance in simulating the available experiments for benzenes is not totally satisfactory. The simulations of the experiments for the naphthalenes and tetralin suggest that the current parameterization used for representing the alkylbenzenes in the models may not be adequate for these compounds. Furthermore, chamber data are still not adequate for evaluating mechanisms for very low  $\text{NO}_x$  conditions, and work in improving the capabilities of environmental chambers to study low  $\text{NO}_x$  conditions is underway (Carter et al, 1999).

The current aromatics mechanism developed using the existing chamber data base predict that aromatic isomers differ by up to a factor of two in  $\text{O}_3$  reactivity in the atmosphere, even after differences in their OH radical rate constants are taken into account. Para-substituted isomers (p-xylene and 1,2,4-trimethylbenzene) are found to be the least reactive of the isomers. This “para effect” is attributed to the expectation that these compounds are more likely to form low photoreactivity unsaturated ketones as opposed to the much more photoreactive unsaturated aldehydes.

## References

- Atkinson, R. (1990): "Gas-Phase Tropospheric Chemistry of Organic Compounds: A Review," *Atmos. Environ.*, 24A, 1-24.
- Atkinson, R. (1994): "Gas-Phase Tropospheric Chemistry of Organic Compounds," *J. Phys. Chem. Ref. Data*, Monograph No. 2.
- Atkinson, R. (2000): "Atmospheric Chemistry of VOCs and NO<sub>x</sub>," *Atmospheric Environment*, 34, 2063-2101.
- Bierbach A., Barnes I., Becker K.H. and Wiesen E. (1994) Atmospheric chemistry of unsaturated carbonyls: Butenedial, 4-oxo-2-pentenal, 3-hexene-2,5-dione, maleic anhydride, 3H-furan-2-one, and 5-methyl-3H-furan-2-one. *Environ. Sci. Technol.*, 28, 715-729.
- Carter, W. P. L. (1990): "A Detailed Mechanism for the Gas-Phase Atmospheric Reactions of Organic Compounds," *Atmos. Environ.*, 24A, 481-518.
- Carter, W. P. L. (1994): "Development of Ozone Reactivity Scales for Volatile Organic Compounds," *J. Air & Waste Manage. Assoc.*, 44, 881-899.
- Carter, W. P. L. (2000a): "Documentation of the SAPRC-99 Chemical Mechanism for VOC Reactivity Assessment," Draft report to the California Air Resources Board, Contracts 92-329 and 95-308, April 11. Available at <http://cert.ucr.edu/~carter/absts.htm#saprc99>.
- Carter, W. P. L. (2000b): "Implementation of the SAPRC-99 Chemical Mechanism into the Models-3 Framework," Report to the U. S. Environmental Protection Agency, January 29. Available at <http://helium.ucr.edu/~carter/absts.htm#s99mod3>.
- Carter, W. P. L. and R. Atkinson (1989): "A Computer Modeling Study of Incremental Hydrocarbon Reactivity", *Environ. Sci. Technol.*, 23, 864.
- Carter, W. P. L., and F. W. Lurmann (1990): "Evaluation of the RADM Gas-Phase Chemical Mechanism," Final Report, EPA-600/3-90-001.
- Carter, W. P. L. and F. W. Lurmann (1991): "Evaluation of a Detailed Gas-Phase Atmospheric Reaction Mechanism using Environmental Chamber Data," *Atm. Environ.* 25A, 2771-2806.
- Carter, W. P. L. and R. Atkinson (1996): "Development and Evaluation of a Detailed Mechanism for the Atmospheric Reactions of Isoprene and NO<sub>x</sub>," *Int. J. Chem. Kinet.*, 28, 497-530.
- Carter, W. P. L., D. Luo, I. L. Malkina, and D. Fitz (1995): "The University of California, Riverside Environmental Chamber Data Base for Evaluating Oxidant Mechanism. Indoor Chamber Experiments through 1993," Report submitted to the U. S. Environmental Protection Agency, EPA/AREAL, Research Triangle Park, NC., March 20. Available at <http://cert.ucr.edu/~carter/absts.htm#databas>.

- Carter, W. P. L., D. Luo, and I. L. Malkina (1997a): "Environmental Chamber Studies for Development of an Updated Photochemical Mechanism for VOC Reactivity Assessment," Final report to the California Air Resources Board, the Coordinating Research Council, and the National Renewable Energy Laboratory, November 26. Available at <http://cert.ucr.edu/~carter/absts.htm#rct3rept>.
- Carter, W. P. L., D. Luo, and I. L. Malkina (1997b): "Investigation of the Atmospheric Ozone Formation Potential of Acetylene," Report to Carbind Graphite Corp., April 1.
- Carter, W. P. L., J. H. Seinfeld, D. R. Fitz and G. S. Tonnesen (1999): "Development of a Next-Generation Environmental Chamber Facility for Chemical Mechanism and VOC Reactivity Evaluation," Research Proposal to the United States Environmental Protection Agency, February 22. Available at <http://helium.ucr.edu/~carter/epacham/proposal.htm>.
- Gery, M. W., G. Z. Whitten, and J. P. Killus (1988): "Development and Testing of the CBM-IV For Urban and Regional Modeling," EPA-600/ 3-88-012, January.
- Stockwell, W. R., P. Middleton, J. S. Chang, and X. Tang (1990): "The Second Generation Regional Acid Deposition Model Chemical Mechanism for Regional Air Quality Modeling," *J. Geophys. Res.* 95, 16343- 16376.
- Stockwell, W.R., F. Kirchner, M. Kuhn, and S. Seefeld (1997): "A new mechanism for regional atmospheric chemistry modeling," *J. Geophys. Res.*, 102, 25847-25880.
- Tuazon, E.C., R. Atkinson R. and W. P. L. Carter W.P.L. (1985): "Atmospheric Chemistry of cis- and trans-3-Hexene-2,5-dione," *Environ. Sci. Technol.*, 19, 265-269.