DOCUMENTATION OF THE SAPRC-18 MECHANISM

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Summary

This document describes an updated the SAPRC gas-phase mechanism, designated SAPRC-18, that was developed for California Air Resources Board (CARB) project 11-761. The general features of the mechanism and the mechanism generation system it uses are described, how they differ from previous versions are discussed, the model species, reactions, and rate parameters used are listed, the results of the evaluation and adjustments using chamber data are summarized, and results of box model simulations of simplified ambient scenarios are compared with simulations using the earlier version of SAPRC. The updated mechanism incorporates more chemical detail than previous SAPRC mechanisms, uses a lumping approach that should be more compatible for SOA modeling, and incorporates new radical reactions, such as peroxy radical isomerizations, that were not used in previous mechanisms. The mechanism can simulate results of available chamber data about as well as SAPRC-11, though certain individual compounds are not simulated quite as well, as a result of use of fewer cases of compound-by-compound adjustments of uncertain parameters for this update. This indicates areas where additional work is needed. Additional information and the files needed to implement the mechanism are available at http://www.cert.ucr.edu/ ~carter /SAPRC/18.

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Introduction

The SAPRC gas-phase atmospheric chemical mechanisms are designed to represent the gas-phase reactions of volatile organic compounds (VOCs) and oxides of nitrogen (NO_x) in urban and regional model simulations of the lower troposphere. Previous versions that have been implemented in airshed models include SAPRC-90 (Carter, 1990), SAPRC-99 (Carter, 2000), SAPRC-07 (Carter, 2010a,b), SAPRC-07T (Hutzell et al, 2012), and SAPRC-11 (Carter and Heo, 2012, 2013). These previous mechanisms have two versions, the "detailed" versions where as many individual compounds are represented explicitly as necessary for calculation of ozone reactivity scales (e.g., Carter, 1994, 2010c), and various "condensed" versions for use in airshed models. Generally even the condensed versions implement more chemical detail and a lesser amount of condensation than most of the widely-used mechanisms for airshed modeling, with the main exception being the near-explicit "Master Chemical Mechanism" (MCM, see MCM, 2019). The most detailed of the previous SAPRC mechanisms, and the main version currently implemented in the CMAQ model, is SAPRC-07T (Hutzell et al, 2012), which is based on SAPRC-07 but represents several selected individual compounds explicitly rather than using lumped model species, either because of their importance in emissions or because of their importance for assessing impacts of toxic compounds. The latest version used in models is SAPRC-11, which is similar to SAPRC-07 in level of detail and reactions for most compounds, but has an updated representation of aromatic chemistry that performs better simulating environmental chamber data (Carter and Heo, 2013).

None of the current published versions of SAPRC are designed to predict formation of secondary organic aerosol (SOA), though they are used in airshed models in conjunction with separate models designed to predict SOA. A version of SAPRC-11 with additional reactions added to predict SOA from aromatics was developed (Carter et al, 2012), but extension of this approach to other classes of organics was not funded. Therefore, developing complete models for SOA predictions is beyond the scope of this project. However, eventually we will need to develop better approaches than the current practice of using parameterized SOA models that are independent of, and not informed by, the gas-phase mechanism and its predictions of low volatility SOA precursors. Therefore, modern gas-phase mechanisms need to be developed with the needs for proper predictions of SOA precursors in mind.

The SAPRC mechanisms as used in current models are becoming out of date and need to be updated if they are to continue to be used. In addition to incorporating new data in order to better represent the current state of the science, it needs to have a lumping approach that is more appropriate for SOA modeling. In view of this, the California Air Resources Board (CARB) funded the author to develop a complete update to the SAPRC gas-phase mechanism. This project is resulted in the development in a preliminary update to SAPRC, designated SAPRC-16, which is available and described online (Carter, 2016). The mechanism was not finalized for use regulatory modeling because the underlying mechanism generation system (discussed below) has been undergoing continuous updates, and unexpected results were obtained when it was implemented in 3D regional model and compared with SAPRC-11 (Venecek et al, 2018). In particular, although it gave similar predictions as SAPRC-11 (albeit with some differences), it gave significantly lower predictions of HO_2 than SAPRC-11 and measurements in a few, but not all, cases. This could not be duplicated in box model calculations and the reason for this behavior needs to be investigated. They concluded that further investigation is needed before SAPRC-16 is adopted for widespread use.

Although funding for further updates to SAPRC-16 has expired, the author is continuing this work on a voluntary basis. This has resulted in the development of the SAPRC-18 mechanism described in this report. Although updates to SAPRC are continuing, the current version of SAPRC-18 can be considered to be finalized, and further updates will be incorporated in the next version. SAPRC-18 is very similar to SAPRC-16 except for minor changes in estimated product yields for some reacting organics due to updates to the mechanism generation system. The lumping approach and (with a few exceptions) model species used are the same. The main difference concerns details of how certain reactions and rate constants are estimated if no data are available.

As with previous versions of SAPRC, the updated mechanism was evaluated by comparing its predictions of ozone formation, NO oxidation rates, and radical levels observed in the available database of environmental chamber experiments. These included the experiments used in the SAPRC-07 and SAPRC-11 evaluations, plus additional UCR chamber experiments, primarily with alkenes, carried out subsequently (Yarwood et al, 2012; Heo et al, 2014). The mechanism evaluation experiments included organic - NO_x, mixture - NO_x, and incremental reactivity experiments with a variety of compounds, as well as chamber characterization experiments. The mechanism evaluation approach for SAPRC-18 was similar to that used for previous versions, but involved fewer compound-by-compound adjustments of uncertain parameters to fit the chamber data than was the case for the previous versions. This was done primarily because a somewhat greater emphasis on developing and evaluating estimation methods that can be applied to a wide range of compounds, and because developing comprehensive reactivity scales for compounds that are relatively unimportant in emissions is beyond the scope of this project. However, chamber data for the full set of compounds studied for developing reactivity scales were used in this evaluation, providing a means to evaluate the performance of the estimation methods without compound-by-compound adjustments.

This document describes the current version of SAPRC-18 and supercedes previous documentation of SAPRC-16[1]. Although further work to update SAPRC mechanisms is underway, any future updates will be incorporated in a new version of the mechanism. This document gives an overview of the mechanism, discusses the lumping approach and model species employed, gives an overview of the mechanism generation system, discusses the evaluation against chamber data, compares selected predictions with SAPRC-11, and lists model species, reactions, and kinetic parameters. Although, more detailed documentation of the mechanism generation system (Carter, 2019, 2020a), and the scientific basis of its assignments is still in preparation, information about this can be obtained from the online system (Carter, 2020a) as discussed in Appendix B of this report.

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[1] The existing documentation of SAPRC-16 (Carter, 2016) is retained because it documents the version of SAPRC-16 used by Venecek et al (2018).

Mechanism Description

Characteristics of the SAPRC-18 Mechanism

The SAPRC-18 mechanism represents the results of the first complete update of the SAPRC series of mechanisms since the development of SAPRC-07 (Carter et al, 2010a,b) and its incremental update to SAPRC-11 (Carter and Heo, 2012). The previous mechanisms had two versions, a standard version for use in airshed model calculations with most VOCs represented using lumped model species, and an extended version that had the same base mechanism for the inorganics and organic product model species, but had many more emitted organic compounds represented explicitly. The latter is used for evaluating the mechanism against chamber data and also for calculating MIR and other reactivity scales (Carter, 1997, 2010a-c). The SAPRC-18 mechanism is similar in this respect, except that the explicitly represented compounds in the standard version is limited to the smaller number of compounds present in the experiments used to evaluate the mechanism. SAPRC-18, because updating the reactivity scales is beyond the scope of this project. However, it could be readily expanded to include the full set of compounds needed for a reactivity scale, using the same approach as used for the compounds already in the extended version.

SAPRC-18 is also similar to SAPRC-07 and SAPRC-11 in that it relies on an automated mechanism generation system, called MechGen, to derive explicit mechanisms for most organic compounds, which are used to derive lumped mechanisms for the models using various algorithms. The current version of this system is described later in report. Briefly, it uses assigned rate constants or branching ratios when data are available, and various structure-reactivity or other types of estimates to derive reactions for which there are inadequate data. This system was significantly updated as part of this update to SAPRC-18, with reactions of many more compounds, such as alkylbenzenes, now being able to be estimated, and new types of reactions, such as auto-oxidations of peroxy radicals being added, and all the assignments and estimation methods updated. It was also used to derive mechanisms for lumped model species based on generated mechanisms for the compounds they represent in current emissions, rather than selected individual compounds used for previous versions. This permits the mechanism of these lumped model species to be readily updated if the compositions of current emissions change significantly. However, the compositions used to derive mechanisms for lumped species in the current is considered to be sufficient for the current mechanism, and is considered to be a significant improvement over previous versions. Note that this approach requires generations of mechanisms for the many types of product compounds predicted to be formed, which are significantly more numerous than the representative product compounds used for previous SAPRC versions.

SAPRC-18 is a larger mechanism than previous versions in part because it uses more model species both for representing emitted organic compounds and for representing the many types of organic products that they form. This is to address the objectives of representing more explicitly the more important compounds in emissions, and more accurately representing the effects of the oxidized products they form on secondary products, NO_x recycling, and formation of low volatility products that can be SOA precursors. However, this is not the only reason that SAPRC-18 is much larger than previous versions.

A major difference in the structure of SAPRC-18 compared to SAPRC-11 and previous versions is the treatment the reactions of peroxy radical intermediates. Many of the intermediates formed in the atmospheric reactions of the VOCs are alkyl or alkoxy radicals that react primarily with O_2 or unimolecularly, and can be removed from the model by applying the steady state approximation and replacing them with the set of products they form. However, this cannot be done with peroxy and acyl peroxy radical intermediates because they primarily undergo bimolecular reactions with NO, NO_2, HO_2, or other peroxy radicals, so the products they form depend on the varying concentrations of NO_x and peroxy species. SAPRC-90 and 99 (Carter, 1990, 2000) eliminated them from the model by replacing them with the products formed when the peroxy radicals react with NO, because that was believed to be the major fate of such radicals under conditions where O_3 is formed. However, reactions with HO_2 and other peroxy radicals are non-negligible when NO_x is low, and different products are formed. To address this, SAPRC-07 and 11 used a somewhat more complex "operator" method to remove these radicals from the model, using separate model species to account for formation of different products under low NO_x conditions (Carter, 2010a,b). Both of these approaches require the assumption that peroxy radicals do not undergo unimolecular or "auto-oxidation" reactions, which is now known not to be the case for certain types of peroxy radicals that can be important in the atmosphere (e.g., Davis and Francisco, 2010; Crounse et al, 2012; Peeters et al, 2014). Therefore, these approaches cannot be used for SAPRC-18.

Instead, it is necessary to use an approach for representing peroxy radicals that is more like that used in the RADM and RACM mechanisms (e.g., Stockwell et al, 1990, 1997; Stockwell and Goliff, 2006; Goliff et al, 2013), where separate model species are used to represent the lumped peroxy radical intermediates formed in each of the types of organic compound reactions. Multiple intermediate peroxy radicals can be lumped and represented by a single model species if they all have the same or similar sources and do not have significant unimolecular reactions, but separate model species are needed for peroxy radical intermediates are formed in different reactions or that have non-negligible unimolecular reactions that compete with the bimolecular peroxy reactions such as with NO or HO_2. Because of this, appropriate representations of reactions of some compounds require multiple model species to represent the reactions of the different types of peroxy radicals involved. This results in far more model species being required to represent peroxy radical reactions in SAPRC-18 than SAPRC-11, even if the same number of lumped species are used to represent emitted or product compounds are the same.

The construction of SAPRC-18 involved two types of reactions: those that are constructed manually as done for most mechanisms, and those that are directly output by the mechanism generation system. The former consist of the reactions of the inorganics and the C_1 and some simple C_2 organic products that do not require a mechanism generation system to estimate, and also reactions of certain compounds, such as phenols and naphthalenes, that MechGen cannot process. The latter, which account for about ¾ of the reactions and about half of the model species in the mechanism, consist of the reactions and intermediates of the explicit and lumped organic compounds and products are derived by MechGen. Because of the large number of MechGen-derived reactions and intermediate peroxy model species, complete listings of this portion of the mechanism are only given in the electronic supplement to this report.

Although SAPRC-07 included a module for chlorine chemistry, including chlorine chemistry was beyond the scope of this project, so SAPRC-18 does not include chlorine chemistry.

Mechanism Listing Tables

The large tables listing and documenting this mechanism are given in supplementary tables that are given or discussed in Appendix A to this document. Some of the tables are too large to be usefully included in a report document, and are not included, or not included in their entirety, in Appendix A. Instead these are available in an Excel file that serves as an electronic supplement to this document, as discussed in Appendix A. Table A-1 lists and briefly describes all the model species in the mechanism for ambient simulations, and Table A-2 lists the species added for the extended mechanism for the chamber simulations. Additional information about the model species is given in footnotes to the table and in the following discussion. Table A-3 lists mixtures whose components were used as the basis of the mechanisms for the lumped species, based on their relative contributions to the mixtures and their detailed mechanisms. Table A-4 lists the reactions and rate parameters in the mechanism for atmospheric simulations and Table A-5 gives the reactions added for the extended mechanism used for chamber simulations. Footnotes to these describe the sources of the rate parameters and reaction mechanisms that were manually assigned. The complete tables in the electronic supplement table also includes reactions and intermediate peroxy radical model species that were output by the mechanism generation system (derived as discussed below), but to save space they are not included in the tables in Appendix A.

Model Species

Table 1 lists the emitted compounds that are represented explicitly in various versions of SAPRC, along with other compounds found to make significant contributions to current anthropogenic and biogenic emissions inventories. To assess their importance in anthropogenic emissions we used the total 2005 U.S. emissions profile provided by the EPA (Luecken, 2013) and to assess their importance in the biogenic emissions we used the total annual biogenic VOC emissions for the year 2000 calculated using the Megan 2.1 model (Guenther et al, 2012; Guenther 2014). These mixtures were also used to derive mechanisms of the lumped model species in the current version SAPRC-18 as discussed below. Note that, based on these mixtures, SAPRC-07T explicitly represented about a third of the mass and somewhat less than half of the reactivity of anthropogenic emissions explicitly, while standard SAPRC-18 explicitly represents about half of the mass and 60% of the reactivity of these emissions. Most of the biogenic emissions are represented explicitly by both mechanisms because of the importance of explicitly represented isoprene and α-pinene. It was decided that increasing the number of explicit compounds beyond those used in SAPRC-18 would result in only slight changes in the fractions of anthropogenic emissions represented while significantly increasing the size of the mechanism, so no additional explicit species were added to the standard mechanism. However, additional compounds could be made explicit for atmospheric simulations if desired, and would need to be explicit in extended versions of the mechanism to calculate their reactivities or evaluate their mechanisms using chamber data.

Table A-1 in Appendix A lists the model species in the standard SAPRC-18 mechanism and gives additional information and footnotes describing these species. These include inorganic and organic compounds whose mechanisms were derived manually; model species for emitted or oxidation product compounds represented explicitly, lumped model species, a summary of the explicit and lumped peroxy and acyl peroxy radical species (with a complete listing in the electronic supplement), model species for several other types of radical intermediates, and various counter species and chemical operators. The footnotes indicate which compounds can be held in steady state in order to minimize the number of model species that have to be stored and transported in 3-D model simulations. This includes essentially all of the many peroxy and acyl peroxy radical model species (over half of the species in the mechanism), so use of the steady state approximation is highly recommended.

The chemical operator species in the mechanism include the SumRO2 and SumRCO3 model species that compute the total of peroxy radical and acyl peroxy radical concentrations for the purpose of estimating rates of peroxy + peroxy or peroxy + acyl peroxy reactions. These are treated as active species and each reaction forming a peroxy or acyl peroxy radical also forms the same yield of one of these species, and their loss reactions are treated separately in reactions that affect only these species. This is different than the approach used in SAPRC-07 and SAPRC-11, where the rates of formation of products from peroxy + peroxy and other reactions are computed from relative rates of reactions of a representative peroxy radical model species, and has the advantage over SAPRC-07/11 in that it does not require special treatment when the mechanism is implemented into the model software. However, SAPRC-18 also has the chemical operators RO2C, RO2XC, and various zNitrate model species in order to represent effects of relatively effects of reactions of the relatively minor peroxy radical species predicted in the mechanisms without having to include them as separate model species. These are used for peroxy radicals that are predicted to be formed less than 10% of the time in the initial reactions of a compound and that cannot be lumped with any of the more important peroxy radicals involved. If this

Table 1. List of major emitted compounds in emissions mixtures that were considered for explicit representation when updating the SAPRC mechanism

Compound [a]	Model	Us Emissions [c]		Bio. [e]	Explicit [f]				Notes
	Species [b]	Wt%	MIR % [d]	Wt %	07	07T	Std	Ext	[g]
<u>Primarily Anthropogenic</u>									
toluene	TOLU	7.35	9.13	0.14		X	X		
n-butane	NC4	5.86	2.09				X		
isopentane	ALK4	3.34	1.50						1
acetone	ACET	3.14	0.35	4.35	X	X	X		
ethene	ETHEN	2.98	8.31	2.74	X	X	X		
benzene	BENZ	2.59	0.58		X	X	X		
ethane	ETHAN	2.47	0.21	0.03			X		
ethanol	ETOH	2.46	1.16	2.06		X	X		
propane	PROP	2.22	0.34	<0.01			X		
3-methyl-1-butene	OLE1	2.03	4.40						
m-xylene	MXYL	1.98	5.99			X	X		
p-xylene	PXYL	1.92	3.47			X	X		
n-pentane	ALK4	1.85	0.75	<0.01					1
propene	PROPE	1.70	6.13	1.53			X		
ethyl benzene	C2BEN	1.63	1.53				X		
o-xylene	OXYL	1.55	3.68			X	X		
formaldehyde	HCHO	1.50	4.41	0.50	X	X	X		
acetylene	ACETL	1.42	0.42				X		
acetaldehyde	MECHO	1.28	2.59	2.06	X	X	X		
isobutane	ALK3	1.23	0.47		X	X	X		
methanol	MEOH	0.98	0.21	9.91	X	X	X		
methyl ethyl ketone	MEK	0.91	0.42	0.03			X		2
1-butene	OLE1	0.89	2.67	0.77				X	
1,2,4-trimethyl benzene	BZ124	0.89	2.45			X			
m-ethyl toluene	ARO2	0.82	1.89				X	X	
isopropyl alcohol	OTH3	0.77	0.15					X	
2-methyl-1-butene	OLE3	0.72	1.42						3
2-methyl-2-butene	OLE4	0.54	2.37						3
trans-2-pentene	OLE2	0.43	1.41						
1,3-butadiene	BUT13	0.40	1.58			X	X		
1,3,5-trimethyl benzene	BZ135	0.39	1.43				X		
p-ethyl toluene	ARO2	0.38	0.52					X	
1-pentene	OLE1	0.37	0.84						
glyoxal	GLY	0.36	1.38		X	X	X		
methyl glyoxal	MGLY	0.30	1.53						4
o-ethyl toluene	ARO2	0.29	0.51					X	
styrene	STYRS	0.29	0.16						4
propionaldehyde	ETCHO	0.24	0.52				X		
2-pentenenes	OLE2	0.23	0.75						
n-propyl benzene	ARO1	0.22	0.14					X	
benzaldehyde	BALD	0.21	<0	<0.01					4

Table 1 (continued)

Compound [a]	Model	Us Emissions [c]		Bio. [e]	Explicit [f]				Notes
	Species [b]	Wt%	MIR % [d]	Wt %	07	07T	Std	Ext	[g]
1,2,3-trimethyl benzene	BZ123	0.20	0.73				X		
naphthalene	NAPS	0.16	0.17	<0.01					3,4
phenol	PHEN	0.16	0.14				X		5
trans-2-butene	OLE2	0.16	0.75					X	
isopropyl benzene	ARO1	0.13	0.10					X	
cis-2-butene	OLE2	0.13	0.56					X	
acrolein	ACRO	0.09	0.22			X	X		
methacrolein	MACR	0.06	0.12				X		2
isobutene	OLE3	0.05	0.10					X	3
biacetyl	BACL	0.04	0.28						4
Primarily Biogenic									
isoprene	ISOP	0.03	0.11	53.23		X	X		
a-pinene	APINE	0.10	0.14	6.58		X	X		
b-pinene	BPINE	0.07	0.07	1.88			X		
d-limonene	DLIMO	0.32	0.45	1.13			X		
sabinene	TERP	<0.01	<0.01	0.90				X	
beta-myrcene	TERP	<0.01	0.01	0.87					
3-carene	TERP	0.01	0.01	0.71				X	
acetic acid	AACID	0.03	0.01	0.37	X	X	X		
formic acid	HCOOH	0.02	<0.01	0.37	X	X	X		
2-methyl-3-butene-2-ol	OLEP	0	0	0.22					3
Fraction explicit									
All listed above		63	84	90					
SAPRC-07		14	18	20					
SAPRC-07T		31	46	82					
Standard SAPRC-18		48	60	87					
Extended SAPRC-18		52	68	89					

[a] Compounds are listed in decreasing order of total for mass fractions for total U.S. or biogenic mixtures.

[b] Name of model species used to represent the compound in the standard SAPRC-18 mechanism. Note that a different, unique model species is used if it is represented explicitly in the extended version.

[c] Total US Emissions based on the 2005ah_tox inventory using the criteria VOC emissions only from all sectors except biogenic & fires. Provided by Luecken (2013).

[d] Derived using the mass emissions fractions and the SAPRC-07 Maximum Incremental Reactivity scale of Carter (2010c).

[e] Global annual total biogenic VOC emissions for the year 2000 calculated using the using MEGAN 2.1 model algorithms in CLM4 (Guenther et al, 2012; Guenther 2014). "0.00% means emissions are nonzero but lower than 0.005%.

Table 1 (continued)

Compound [a]	Model Species [b]	Us Emissions [c] Wt%	MIR % [d]	Bio. [e] Wt %	Explicit [f] 07	07T	Std	Ext	Notes [g]

[f] Indicates whether this compound is represented explicitly. "Std": X = explicit in the standard mechanism; "Ext": X = explicit in the extended mechanism only.

07 Explicit in the standard SAPRC-07 and SAPRC-11 mechanisms
07T Explicit in SAPRC-07T
Std Explicit in the standard and extended versions of SAPRC-18
Ext Explicit in the current extended version of SAPRC-18 because it is important in some chamber experiments.

[g] Notes for individual compounds

1 Sensitivity calculations indicate that representing most alkanes explicitly has little effect on atmospheric simulation results.
2 This model species is also used to represent other species in SAPRC-07, so it does not represent this compound explicitly.
3 Although not represented explicitly, a new lumped model species is used in SAPRC-18 to better represent compounds of this type.
4 This is used to represent other compounds with a similar mechanism in SAPRC-07 and SAPRC-18, so this model species does not represent this compound explicitly.
5 Represented explicitly in SAPRC-11 but not SAPRC-07 or 07T.

approach were not used the mechanism would have a large number of peroxy radical model species representing only very minor pathways.

The model species added to the extended version of the mechanism used in the chamber simulations consist of those representing the 12 compounds indicated in Table 1 as being represented explicitly only in the extended mechanism, plus 62 additional compounds used in the mechanism evaluation chamber species, and a number of steady-state peroxy radical model species derived by the mechanism generation system to represent their reactions. These model species and their reactions are included in the tables in the electronic supplement, as discussed in Appendix A.

As indicated on Table A-1**,** the mechanisms for most of the lumped model species were derived from mechanisms for individual compounds that are represented by these model species, weighed by the mole fractions of the compounds present in representative mixtures. Several different mixtures were employed for this purpose, depending on the model species involved, as follows:

- The "UStot" mixture consists of the total U.S. anthropogenic VOC emissions profile provided by the EPA (Luecken, 2013). The anthropogenic VOC mixture used for previous SAPRC mechanisms for this purpose was not used because it is out of date and also because it is based only on ambient measurements, and does not include many types of compounds present in emissions inventories for which ambient measurements are limited or unavailable. Note that relatively unimportant compounds in the total profile can make non-negligible contributions to some lumped model species in the more detailed mechanisms, such as SAPRC-18, that represents most of the important compounds explicitly. If a compound is represented explicitly, in general it will not be included in mixtures used to derive lumped model species used for non-explicitly-represented compounds. This means that a fairly complete anthropogenic mixture us needed to for this purpose, not one that only has the most important compounds. This was used to derive model species used primarily to represent emitted hydrocarbons, such as the ALKx, OLEx, and

AROx species and a few others. It was not used to derive mechanisms for model species that primarily represent oxidized products.

- The "Megan2" mixture consists of total annual biogenic VOC emissions for the year 2000 calculated using the Megan 2.1 model (Guenther et al, 2012; Guenther 2014). This biogenic model was used because it appears to be the most up-to-date and best documented and it has modules that predict emissions of individual compounds rather than lumped model species. It was used to derive the mechanism of the TERP (terpene) model species and also was behind the choice of using the mechanism of β-caryophyllene to represent that of the SESQ species.
- The "UStot OHprods" mixture was derived from the distribution of products predicted to be formed from the reactions of of OH with the compounds in the UStot mixture in the presence of 0.5 ppb of NO, weighted by the mole fraction of the compounds in the mixture and the relative yields of the products. (The choice of 0.5 ppb to estimate branching ratios for unimolecular vs. NO reactions of peroxy radicals that have unimolecular reactions is somewhat arbitrary, but is considered to be reasonably representative. It may be revised in future versions of the mechanism if considered appropriate based on analyses of ambient simulations combined with sensitivity studies.) Only the compounds in the UStot mixture whose mechanisms could be processed using the mechanism generation system were used, but these are the major compounds affecting these products. This was used to derive the mechanisms for most of the model species used for organic products, except for hydroperoxy species formed primarily from reactions of peroxy radicals with HO_2, and for the carbonyl nitrates and dinitrates formed primarily from the reactions of NO_3 radicals with some alkenes. Examples include RCHO, KET2, the RNO3 species except for RCNO3 and RDNO3, and the AFGx species. The exceptions include model species used to represent products formed primarily in the isoprene system, discussed below.
- The "UStot NO3prods" mixture was derived as discussed above for UStot OHprods except that it is the predicted products of the reactions of NO_3 with the compounds in the UStot mixture. It was used to derive mechanisms for the carbonyl nitrate (RCNO3) and dinitrate (RDNO3) species that primarily represents these compounds.
- The "UStot HO2prods" mixture was derived from the mixture of hydroperoxide products formed in the reactions of HO_2 with the peroxy radicals predicted to be formed in the reactions of OH with the components of the UStot mixture. This included hydroperoxides formed from second-generation peroxy radicals formed in multi-step mechanisms, with relative yields based on the assumption that the HO_2 or peroxy + peroxy reactions are not important enough to significantly reduce yields of peroxy radical yields in multi-step mechanisms. This was used to derive mechanisms for most of the hydroperoxide model species. The one exception is RUOOH, which represents primarily hydroperoxide products formed from isoprene.

Some of these mixtures had many compounds represented by the various model species, but in order to keep the number of generated mechanisms to a manageable level we used only the compounds that contributed to 90% of the total moles, or the top 10 compounds, whichever was fewer. The specific compounds used to derive the mechanisms for each lumped model species, are listed in Table A-3. This table gives the contribution of each compound to the total number mole fractions of compounds represented by the model species in the mixture, and the structure of the compound as used in the mechanism generation system. Note that many of the compounds in the "prods" mixtures have not been given species names in the SAPRC detailed mechanisms, so they are not included in compound listings for SAPRC or in reactivity scales.

Reactions

Table A-4 lists the all the reactions in the standard SAPRC-18 mechanism, giving the rate constant parameters or files with photolysis information, the products formed, and footnotes giving additional information about the reactions. Table A-5 gives the additional reactions included in the extended mechanisms for the chamber simulations, and Table A-6 in the electronic supplement gives the absorption cross sections and (where applicable) quantum yields used for the photolysis reactions. Note that the tables given in Appendix A do not include all of the many reactions output by the mechanism generation system, but they are included in the corresponding tables in the electronic supplement. However, Table A-4 in Appendix a includes all the photolysis reactions output by the system, with footnotes indicating how the absorption cross sections and quantum yields (if used) were derived.

As discussed above, the mechanism consists of reactions that are manually assigned and reactions that were output by the mechanism generation system. The derivations of the rate parameters and products of the manually assigned reactions are indicated in the footnotes to Table A-4. These were updated where appropriate based on the latest evaluations and other published results, primarily the IUPAC (2019), NASA (2015), or Calvert et al, (2000, 2002, 2011, 2015). The footnotes in Table A-4 can be consulted for details.

Table 2 lists the reactions in the base mechanism whose rate constants at 300K or photolysis rates for direct overhead sunlight changed by more than 10% after this update, relative to SAPRC-11. It can be seen that the changes were relatively small for most reactions, except photolysis rates for new model species added to the mechanism (compared to those of the model species previously used for these compounds), rate constants for some organic + NO_3 reactions, rate constants for reactions involving peroxynitric acid, and the photolysis rate of glyoxal forming stable compounds (the photolysis forming radicals changed by only 2%). Not shown is the rate constant for the important OH + NO_2 reaction, which decreased by about 7%, which may make this a somewhat more reactive mechanism than SAPRC-11 if only this were considered. However, the effects of any of these changes are difficult to assess because of the other changes made to the mechanism. The largest changes concerned photolysis rates of new model species added to the mechanism to better represent photoreactive bifunctional compounds, and photolyses of photoreactive aromatic ring opening products, where the total yields in SAPRC-18 are determined by the mechanism generation system rather than being treated as adjustable products as they are in SAPRC-07 and SAPRC-11.

Approximately 75% of the reactions in the mechanism were derived from the output of the mechanism generation system (Carter, 2019, 2020a). As described elsewhere (Carter, 2000, 2010a, 2019) this system derives fully explicit mechanisms for the first-generation atmospheric reactions of many types of organics, and uses various "lumping rules" and condensation procedures to derive product yield parameters for compounds and mixtures for incorporation into the mechanism. The system processed the explicit reactions to generate merged or lumped reactions for a compound or mixture that can be inserted directly in the mechanism. These reactions either form product model species or chemical operators that are part of the base mechanism, or lumped or explicit peroxy species that are used only for the mechanism of the particular compound or mixture. The latter are designated by the VOC's model species name with a suffix _Px or _Ax, where "x" is an index number for this type of radical in the mechanism for this compound or mixture. Species with suffix _Px refer to peroxy radicals that do not isomerize or isomerize slowly enough for peroxy + peroxy reactions to occur so they are included in SumRO2, and species with _Ax refer to peroxy radicals that isomerize fast enough that only isomerization and NO reaction need to be included, and they are not part of SumRO2. These generated model species are included at the end of the species listing on Table A-1, which also indicates the compound or mixture each is associated with. Other radical intermediates that are not explicit or represented in the base mechanism are removed and replaced by model species representing the compounds or NO_x conversions that they form. The mechanism generation system is discussed in more detail in the following section.

Table 2. Reactions in the base mechanism whose rate constants changed by 10% or more.

Label	Reaction	Rate constant [a]		
		SAPRC-18	SAPRC-11	Change
13	N2O5 + H2O = #2 HNO3	[b]	2.50e-22	
14	N2O5 + H2O + H2O = #2 HNO3 + H2O	[b]	1.80e-39	
H338	AFG2A + HV = Products (compared to AFG1) [c]	3.87e-2	3.87e-1	-90%
H355	AFG2B + HV = Products (compared to AFG1) [c]	3.87e-2	3.87e-1	-90%
C042	MGLY + NO3 = Products	5.66e-16	2.53e-15	-78%
H333	AFG1 + HV = Products [c]	1.35e-1	3.87e-1	-65%
C042	MGLY + NO3 = Products	5.66e-16	2.53e-15	-78%
C037	GLY + NO3 = Products	4.00e-16	1.02e-15	-61%
C035	GLY + HV = HCHO + CO	1.66e-3	3.18e-3	-47%
33	HO2 + NO2 = HNO4	7.40e-13	1.12e-12	-34%
34	HNO4 = HO2 + NO2	7.89e-2	1.07e-1	-26%
24	OH + HONO = H2O + NO2	4.91e-12	5.95e-12	-18%
C041	MGLY + OH = Products	1.29e-11	1.50e-11	-14%
40	NO3 + HO2 =OH + NO2 + O2	3.50e-12	4.00e-12	-13%
C024	MECHO + NO3 = Products	2.49e-15	2.84e-15	-12%
38	HO2 + HO2 = HO2H + O2	2.49e-12	2.84e-12	-12%
39	HO2 + HO2 + H2O = HO2H + O2 + H2O	5.34e-30	6.09e-30	-12%
C010	HCOOH + OH = HO2 + CO2	4.00e-13	4.50e-13	-11%
S002	SumRO2 + HO2 = Products	6.82e-12	7.63e-12	-11%
26	OH + NO3 = HO2 + NO2	2.20e-11	2.00e-11	10%
C049	CRES + OH = Products	4.47e-11	4.06e-11	10%
C023	MECHO + HV = Radical products	4.65e-4	4.16e-4	12%
C006	HCHO + HV = H2 + CO	3.49e-3	3.12e-3	12%
21	O1D + M = O3P + M	3.68e-11	3.28e-11	12%
C048	PHEN + NO3 = Products	4.50e-12	3.80e-12	18%
C036	GLY + OH = Products	1.15e-11	9.63e-12	19%
C046	BALD + NO3 = Products	4.00e-15	2.73e-15	47%
H329	HPALD + HV = Products (was RCHO) [d]	3.95e-3	1.40e-3	182%
H290	RDNO3 + HV = Products (was RNO3) [d]	7.04e-4	2.35e-4	199%
H329	HPALD + HV = Products (was ROOH) [d]	3.95e-3	3.94e-4	903%
H312	CROOH + HV = Products (was ROOH) [d]	3.95e-3	3.94e-4	903%
32	HO2 + NO + H2O = HNO3 + H2O	2.20e-31	[e]	
31	HO2 + NO = HNO3	4.21e-14	[e]	

[a] Thermal rate constant at 300K in cm-molec-sec units or photolysis rate in sec^{-1} for overhead sunlight.

[b] Not included in SAPRC-18 since this is considered to be a heterogeneous reaction.

[c] These model species are used to represent unspecified photoreactive aromatic ring opening products. Their photolysis rates are fixed and yields adjusted in SAPRC-11, while their yields are derived using the mechanism generation system and their photolysis rates adjusted in SAPRC-18.

[d] This model species was added to the mechanism to better represent photoreactive bifunctional products. The model species used for them in the previous mechanism is shown in parentheses.

[e] This reaction route is not included in SAPRC-07 or SAPRC-11.

Mechanism Generation System

Overview

The SAPRC mechanism generation system (also called MechGen) is a computer program with various algorithms, tools, and assignments that can be used to derive fully explicit reaction schemes for organic compounds and intermediates in the atmosphere, and tools and assignments for incorporating the results in condensed SAPRC mechanisms. Previous versions were described in the documentation for the SAPRC-99 mechanism (Carter, 2000), with updates for SAPRC-07 described by Carter (2010a). Updated documentation of the capabilities, availability, and operations of the current system is available elsewhere (Carter, 2019). The documentation of the scientific basis for it kinetic and mechanistic estimates and assignments is in preparation, but can be obtained from within the system as discussed in Appendix B to this report. This section gives an overview of the current system as used for developing SAPRC-18, with emphasis on what has changed relative to the previous version that may affect the resulting mechanism and its predictions, and on specific procedures to generate reactions for SAPRC-18.

Table 3 gives a summary of the major types of reactions currently supported by the mechanism generation system. Footnotes to the table discuss updates and capability enhancements made for this version of the system. Although estimates for many types of reactions were added or modified, the following changes are notable.

The ability to generate mechanisms for the reactions of OH with alkylbenzenes, with the subsequent reactions of the OH-aromatic adducts, has been added. This includes (1) estimation of rate constants for OH addition to various positions on alkyl-substituted rings; (2) estimation of branching ratios for the various reactions of the OH-aromatic adducts with O_2; and (3) processing cycloaddition reactions of the OH-aromatic-O_2 adducts, whose subsequent reactions lead to formation of α-dicarbonyl and unsaturated 1,4-dicarbonyl ring opening products. The rate constants or relative branching ratios of the various reactions involved were estimated based on known rate constants and phenolic and α-dicarbonyl product yields for the various methylbenzenes. After adjusting the rate constants of the photoreactive unsaturated 1,4-dicarbonyl aldehydes, the estimated mechanisms perform fairly well simulating results of various methylbenzene - NO_x chamber experiments, though further adjustments and refinements may be needed to improve fits for experiments with ethyl and propyl benzenes. The system does not generate mechanisms for naphthalenes and the mechanisms it generates are not satisfactory for phenols or tetralins (significantly overpredicting reactivity), so parameterized mechanisms are still needed for these types of aromatic compounds.

The system was modified to associate more appropriate photolysis estimates for certain types of bifunctional compounds whose more rapid photolyses may impact simulations of radical levels and NO_x recycling in aged atmospheres. In particular, although the data of Barnes et al (1993) indicated that carbonyl nitrates and photolyze much faster than monofunctional nitrates, this was not incorporated in previous mechanisms. In addition, the data of Wolfe et al (2012) indicates that carbonyl hydroperoxides undergo much more rapid photolyses (forming OH) than monofunctional carbonyls or hydroperoxides, giving higher OH radical sources from low NO_x products of compounds like isoprene. Other bifunctional hydroperoxides may undergo more rapid photolyses for similar reasons The current mechanism lumps these more photoreactive bifunctional compounds into separate model species, and the mechanism generation system determines their appropriate absorption cross section and quantum yield assignments as well as generating the appropriate photolysis reaction.

Although H-shift isomerizations of peroxy radicals are known to be important in combustion systems, they have not been considered for atmospheric mechanisms until recently. Davis and Francisco (2010) carried out quantum chemical calculations of rate constants for H-shift reactions of various

Table 3. Summary of types of reactions supported by the current mechanism generation system and updates relative to SAPRC-07.

Reactant(s)		Type of reactions (* indicates a significant change for this version)	Notes
VOC + OH		H-atom abstraction	1
		Addition to double bonds	1
	*	Addition to aromatic rings.	2, 3
VOC + O_3		Addition to double bonds followed by Criegee biradical formation.	1
		Excited adduct addition to amines, followed by decomposition of adduct forming OH	2
VOC + NO_3		H-atom abstraction	1
		Addition to double bonds	1
VOC + O^3P		Addition to double bonds	1
VOC + $h\nu$		Breaking the weakest bond in saturated aldehydes, hydroperoxides, α-dicarbonyls, PAN compounds, and monofunctional organic nitrates	1, 4
		Breaking the weakest bonds in saturated ketones	1, 5
	*	Radical formation from α-unsaturated and β-carbonyl aldehydes	2, 6
		Radical formation or decompositions of other unsaturated carbonyls.	1, 4
	*	More rapid photolysis of carbonyl nitrates and dinitrates	2, 7
	*	Very rapid photolysis of carbonyl hydroperoxides	2, 8
Carbon-centered Radicals		Unimolecular decompositions of radicals with α-nitro, α-nitrato or α-peroxy groups	1
		Reaction with O_2 with H-abstraction from α-OH groups	1
		Addition of O_2 to radicals with allylic resonance	1
	*	Reactions of O_2 with aromatic - OH adducts	2, 9
		Addition of O_2 to other alkyl radicals	1
Peroxy or Acyl peroxy Radicals		Reactions with NO forming the corresponding alkoxy radical or organic nitrate	1
	*	Cyclization of aromatic OH-O2 adducts	2, 9
	*	Unimolecular H-shift reactions forming hydroperoxides	2, 10
	*	Reactions with NO_2 forming the corresponding peroxynitrate or PAN	11
	*	Reaction with HO_2 forming the corresponding hydroperoxide or other products	2, 12
	*	Reaction with NO_3 forming NO_2 and the corresponding alkoxy radical	2, 12
	*	Reaction with SumRO2 and SumRCO3 forming the corresponding alkoxy radical, carbonyl compound, or alcohol, depending on whether the radical has an alpha hydrogen.	2, 12

Table 3 (continued)

Reactant(s)		Type of reactions (* indicates a significant change for this version)	Notes
Alkoxy Radicals		α-H abstraction by O_2 forming the corresponding carbonyl compound	1, 13
		β-scission decompositions	1, 13
		H-shift isomerizations	14
		Ester rearrangement	1
Excited Crigiee biradicals		Decompositions, stabilization, or rearrangements of saturated biradicals	1
	*	Internal addition to the double bond of unsaturated biradicals, followed by O-O scission and epoxide formation.	2, 15

Notes:

1 Estimation methods, generated reactions, and estimated relative or absolute rate constants are generally the same as used in the previous versions.

2 This is new for SAPRC-18.

3 This is implemented for alkylbenzenes only. Naphthalenes, tetralins, and phenolic compounds are not supported

4 Some absorption cross sections and quantum yields were updated in the base mechanism.

5 Overall quantum yields were re-adjusted based on fits to chamber data. Higher quantum yields were used for the higher molecular weight ketones based on this re-evaluation.

6 The α-unsaturated and β-carbonyl aldehydes such as 2-butene 1,4-dial and compounds, lumped as AFG1, AFG2A, or AFG2B, are believed to be the main radical initiators in the reactions of the aromatic hydrocarbons. Their yields are determined by the mechanism generation system and their overall photolysis rates are adjusted to fit NO oxidation rates observed in aromatic - NO_x chamber experiments.

7 The data of Barnes et al (1993) indicate that carbonyl nitrates and dinitrates photolyze significantly faster than simple nitrates (about 12 and 3 times faster, relatively, for direct overhead sunlight) so they are lumped into different model species and separate sets of absorption cross sections and quantum yields are assigned to them.

8 The data of Wolfe et al (2012) suggest that alpha-unsaturated carbonyls with hydroperoxide groups photolyze at rates consistent with those calculated using absorption cross sections of alpha-unsaturated carbonyls but with unit quantum yields and with the reaction breaking the peroxy bond. This is assumed to be applicable to peroxides, PANs, and nitrates as well. However isoprene and 1,3-butadiene NOx experiments are not well simulated with this high a photolysis rate, so we arbitrarily cut the rate down by a factor of ~10 using an effective quantum yield of 0.1 This is highly uncertain.

9 The system generates three reactions for OH adducts to aromatic rings: (1) H-abstraction forming a phenolic product; (2) O_2 addition to form a peroxy radical that subsequently reacts to ultimately form the α-dicarbonyl and unsaturated dicarbonyl products assumed in previous versions of the mechanism, and (3) H abstraction forming OH and a 7-member ring cyclic ether triene. The latter is highly uncertain but it is necessary to assume that there are additional processes because known yields of phenolic products and α-dicarbonyls cannot account for all of the pathways following OH addition for benzene and alkylbenzenes. The OH-O_2 adduct formed in process (2) is assumed to primarily cyclize to form an allylic radical with a peroxy group in a second 6-member ring, which then adds O_2 and then reacts with NO to form carbonyl ring-opening products. The branching ratios were assigned based on the number of alkyl groups near the radical center and observed yields of phenolic and α-dicarbonyl products for benzene and the methylbenzenes.

Table 3 (continued)

10 H-shift isomerizations of peroxy radicals are estimated to be important or non-negligible for many peroxy and acyl peroxy radicals where hydrogen can be abstracted from aldehyde groups or to form allylic radicals via 6- or 7-member ring transition states (Davis and Francisco, 2010; Crounse et al, 2012; Peeters et al, 2014). Methods to estimate these rate constants were developed based on the quantum calculated rate constants of Davis and Francisco (2010) and the rate constants in the methacrolein system derived by Crounse et al (2012).

11 These reactions are not needed for mechanism generation for this and previous SAPRC versions because the peroxy nitrate formed from peroxy radicals rapidly decomposes back to the reactants, and acyl peroxy radicals are represented by explicit or lumped model species so their reactions do not need to be generated.

12 These reactions were not needed when generating mechanisms with previous SAPRC versions because the system was only used to determine products formed when peroxy + NO reactions dominate. Since the current mechanism can include these other peroxy radical reactions, these additional reactions are also generated to determine the products formed. In the case of reaction with HO_2, it is assumed that the corresponding hydroperoxide is a major product, and for reaction with NO_3 it is assumed that only NO_2 and the corresponding alkoxy radical is formed. The reactions with other peroxy or acyl peroxy radicals are represented as a single process with a generic radical, and depend on whether the radical has an abstractable alpha hydrogen.

13 Some estimation methods used for alkoxy radical reactions, and some thermochemical group assignments used for some of these estimates, were updated as part of this work. The most significant change is that new estimates for group contributions to heats of formation were added to allow estimation of more heats of reaction for alkoxy radical reactions where this is required for rate constant estimations, removing the need for manual assignments or estimates of which reactions dominate for many radicals whose heats of reactions could not previously be estimated because of missing thermochemical group additivity values.

14 The procedure used to estimate H-shift isomerizations was modified somewhat, though the estimates are generally similar for radicals formed in alkane oxidations. Rates of 1,4, and 1,6-H shifts were also estimated and their reactions generated if non-negligible, though in most cases they were negligible compared to 1,5-H shifts or competing processes.

15 This appears to be more chemically reasonable than assuming unsaturated biradicals react similarly to saturated radicals, with the overall process estimated to be highly exothermic and the level of excitation estimated to be sufficient to allow formation of a transition state with a four-member ring intermediate.

peroxy radicals and obtained parameters useful for estimating rate constants for such reactions. Crounse et al (2012) proposed that these reactions can be important in the reactions of methacrolein and derived rate constants that were also useful for estimating rates for other compounds. Such reactions are also an important feature of the LIM1 isoprene mechanism of Peeters et al (2014). Based on these data and other estimates, we derived procedures for estimating H-shift isomerizations of peroxy radicals, and found they are estimated to dominate over bimolecular reactions in many peroxy and peroxy acyl radicals with aldehyde groups (e.g., HC(O)CH=CHC(O)OO· from 2-butene 1,4-dial) and be non-negligible in radicals where the H-abstraction forms an allylic stabilized radical. These reactions were found to be non-negligible and affect product formation, especially but not only under low NO_x conditions. In many cases bifunctional hydroperoxides are formed that are predicted to be highly photoreactive as discussed above.

More detailed documentation of the estimation methods and assignments used in the current system about the various types of reaction is in preparation. However, information concerning the estimation methods and assignments can also be obtained by accessing the online version of the mechanism generation system (Carter, 2019, 2020a), as discussed in Appendix B.

Mechanism Generation Procedures

The mechanism generation system is capable of generating fully explicit mechanisms for the atmospheric reactions of many types of organic compounds and their oxidation products. Although in principle it could be used to generate all the reactions of a selected compound and its oxidation products leading either to nonvolatile compounds or CO or CO_2, in practice it is used to generate reactions leading to first generation products, with the subsequent reactions of the non-radical oxidation products not being generated. Reactions of these product compounds are treated by separately, either by generating reactions for selected product compounds, or by representing them using lumped model species derived from generated reactions of representative compounds.

The explicit mechanism generation procedure involves the following steps:

1. The structure of the organic compound whose mechanism is to be estimated is provided as an input to the system. The types of initial reactions that the compound can undergo are assigned based on the type of compound. For example, almost all compounds are assigned as reacting with OH radicals, compounds with double bonds are designated as reacting with OH, O_3, NO_3, and O^3P, aldehydes as reacting with OH, NO_3 or by photolysis, etc.
2. All possible modes of initial reactions believed to be potentially important under atmospheric conditions are generated and the rate constant for each route is estimated or assigned rate constants or branching ratios are used if data are available. Routes that occur less than 0.5% of the time are ignored. The explicit reactions are added to the list of reactions, along with its estimated or assigned relative or absolute rate constants. Each explicit reaction refers to an elementary process, with no lumping or combining consecutive processes. Attempts to react compounds with species whose reactions are not supported, such as photolysis or ozone reactions for alkanes, result in no reactions being generated.
3. The products of the reactions are examined to determine how they are to be processed. If the product is a stable compound or a type of radical that is to be represented by a model species when implemented into the model then they are treated as an end product in the system and their subsequent reactions are not generated. The latter include explicitly represented radicals such as OH, HO_2, methyl peroxy, t-butoxy, or acetyl peroxy radicals. The other radicals are added to the list of species whose subsequent reactions are to be generated.
4. All possible reactions of the next radical in the list are generated and their rate constants or branching ratios are estimated unless they have been already assigned. Routes that occur less than 0.5% of the time are ignored. In the case of peroxy or acyl peroxy radicals, the system first determines whether it undergoes unimolecular reactions, with the subsequent processing depending on the magnitude of the total estimated unimolecular rate constant as shown on Table 4. The reactions and their relative or absolute rate information and products are added to the list of explicit reactions, and products not previously generated are classified as discussed above in Step 3, with reacting intermediates then processed as discussed in this step.
5. This process is complete once the list of radials to be reacted has been completely processed. The result is a list of explicit reactions and their relative or absolute rate constants, and lists of final products and intermediate reactant radicals that were generated. This is referred to as the "explicit mechanism" for first generation reactions of the subject compound. Note that second and subsequent generation reactions can be derived by separately generating explicit mechanisms for subsequent generation products, and this was done for some of the major oxidation products

Table 4. Processing of reactions of peroxy and acyl peroxy radical intermediates in the SAPRC-18 mechanism generation system

Estimated unimolecular rate constant (sec^{-1}) [a]	Processing for Peroxy (RO_2) radicals	Processing for Acyl Peroxy ($RC(O)O_2$) radicals
< 3.4 x 10^{-3}	Unimolecular reactions are ignored. Reactions with NO, HO_2, NO_3, RO_2, and RCO_3 are generated. Radical may be lumped with other peroxy radicals from same reactions of the starting compound. All reactions forming this radical are also indicated as also forming SumRO2.	Reactions are not generated and the radical is treated as an end product in the generated mechanism, to be represented by the peroxy radical model species MECO3, HOCCO3, ETCO3, R2CO3, R2NCO3, BZCO3, ACO3, or MACO3, depending on the radical. All reactions forming these model species are also indicated as forming SumRCO3.
3.4 x 10^{-3} - 0.34	Unimolecular reactions are not ignored but reactions with NO, HO_2, NO_3, RO_2, and RCO_3 are also generated. Radical is not lumped with other peroxy intermediates from the starting compound. All reactions forming this radical are indicated as also forming SumRO2.	
0.34 - 1350.	Unimolecular reactions and reactions with NO are generated. Other bimolecular reactions are assumed not to be important, since the unimolecular reaction is estimated to be fast enough to dominate over these processes when NO is low. Not included in SumRO2 or SumRCO3 because peroxy + peroxy reactions are assumed not to be important.	Not applicable. It turns out that current estimates do not predict that any acyl peroxy radicals formed in the atmosphere decompose with rate constants in this range at room temperature (Carter, 2020a).
> 1350.	Only unimolecular reactions are generated, with bimolecular reactions assumed not to be important. Processed in the same way as reactions of alkyl and alkoxy radicals. Not included in SumRO2 or SumRCO3.	

[a] These rate constant limits are somewhat arbitrary but were determined by examining the distribution of estimated decomposition rate constants in atmospheric systems and relative importances of unimolecular vs. bimolecular reactions as a function of unimolecular rate constant for simplified representative conditions.

as discussed above. However, second and subsequent generation reactions of non-radical product compounds are not automatically generated by this system.

In previous versions of SAPRC, these explicit reactions were incorporated into the mechanism for airshed or box models by summing up the total yields of final products or NO consumptions or conversions under conditions where reactions of peroxy radicals with NO dominate, and using these for product yield parameters in generalized reactions with adjustable product yield parameters. This requires assuming that peroxy radicals that react with NO or HO_2 do not undergo significant unimolecular reactions, which not the case for many intermediates in the current mechanism. As discussed above, it is necessary to represent peroxy radicals involved in the reactions of organics as separate model species in the mechanisms so their competing reactions can be properly simulated. Therefore, the following approach was used for implementing explicitly generated mechanisms into SAPRC-18. Note that reactions with O_2 are treated as unimolecular for the purpose of this analysis, so the processed mechanisms cannot be used for situations where the O_2 concentration varies.

1. All reactions with the same reactants (with reactions with O_2 being treated as unimolecular for this purpose) were combined into a single reaction with variable product yields derived from the branching ratios of the competing reactions.
2. All radical intermediates that do not have generated bimolecular reactions (other than with O_2) are replaced by the set of products they form in the unimolecular or O_2 reactions. This is done recursively until there are no such reactants remaining. Therefore, these species do not need to be considered further. The remaining reactions include reactions of the starting compound and bimolecular and in some cases unimolecular reactions of various peroxy and acyl peroxy radical intermediates. (Note that acyl most acyl peroxy radicals are treated as final products and thus not included as new intermediates except for those represented as reacting unimolecularly or with NO only -- see Table 4). In some cases, this can yield relatively large numbers of model species representing peroxy radical intermediates, many with very low yields and contributions to the overall process.
3. Peroxy radical intermediates that do not have unimolecular reactions or whose unimolecular reactions are slow enough to ignore (see Table 4) and that are formed by the same (or nearly the same) set of reactions are lumped together for representation by a lumped peroxy model species. The yields of products of its bimolecular reactions determined by the relative contributions of the individual radicals that are lumped, multiplied by their product yields. This reduces the number of peroxy radical model species in mechanisms where multiple peroxy radicals that react similarly are formed from reactions of the same compound or set of intermediates. Other peroxy radical intermediates, and acyl peroxy radical intermediates that have generated unimolecular and NO reactions (see Table 4) are represented separately.
4. In order to further reduce the number of peroxy radical model species needed, and eliminate those with only minor contributions to the overall processes, the relative importance of each intermediate peroxy radical is determined from its yields and the yields of its precursors in the various reactions forming them. Those with overall yields of less than 10% relative to the initial reactions of the starting VOCs are eliminated by replacing them with the products they form considering only unimolecular or NO reactions, with the relative importance of unimolecular vs. NO reactions being estimated based on an atmospheric NO concentration of 0.5 ppb, and the peroxy + NO rate constant given for SumRO2 in Table A-4. The reactions of these minor peroxy radicals with NO_3, HO_2, and other peroxy radicals are ignored. Peroxy radicals formed in their reactions are treated in the same way, with their products being added to the products of the starting radical. The NO to NO_2 conversions in multi-step mechanisms are represented using the operator RO2C, the NO consumptions involved with nitrate formation in peroxy + NO reactions are represented by RO2XC, and the nitrates they form are represented by various zRNO3 species, depending on how the nitrate formed is lumped in the mechanism. The latter either react with NO to form the corresponding nitrate model species, or react with HO_2, NO_3, or other peroxy radicals to form model species representing other appropriate products. This is similar to the use of RO2C, RO2XC, and the zRNO3 species in the SAPRC-07 and -11 mechanisms (Carter, 2010a,b; Carter and Heo, 2012, 2013), except that for the earlier mechanisms they are used for essentially all peroxy radical reactions, not just those with relatively low contributions, as is the case for SAPRC-18.
5. The products in the remaining lumped reactions are replaced by the appropriate explicit or lumped model species, based on lumping rules that are specified for use with the mechanism. The peroxy radical model species that remain are given names such as (name)_P1, (name)_P2,

(name)_A1, etc, where (name) is the model species name used for the reactant (or an abbreviation thereof). The _P_n suffix is used for peroxy radicals that undergo all bimolecular reactions and that are included with SumRO2, and the _A_n suffix is used for those with only unimolecular and NO reactions and are not included with SumRO2.

6. The merged or lumped mechanisms derived as discussed above are given in the last section of Table A-4. They consist of lumped initial overall reactions of the organic with OH and other applicable species such as O_3, forming model species in the base mechanism and compound-specific peroxy radical model species, followed by the reactions compound-specific peroxy model species. These can include radical species formed in the initial reactions or in the reactions of some other radical species ultimately formed in the other reactions. The rate constants used for the initial reactions of the organic being processed are either those assigned for the individual compound as indicated in footnotes to Table A-4, or are derived from estimated rate constants of the individual reaction pathways if data are not available. The unimolecular rate constants of the peroxy intermediates are those estimated for the specific radicals, and their bimolecular rate constants are those given on Table A-4 for the corresponding reaction of SumRO2.

An analogous process is used when deriving mechanisms for lumped model species based on generated explicit mechanisms of its components (see Table A-3 for the compounds used to derive lumped mechanisms for each mixture). The only difference is that before step 1 all of the initial reactions of the components are merged together with relative yields determined by the fraction of the compound in the mixture multiplied by the relative yields of the initial reaction pathways for the compound, and treated as if they are reactions of the mixture as if it were a single reactant. The subsequent reactions generated for the compounds are then used to locate and process the reactions of the intermediate radicals formed in the initial reactions and the subsequent reactions as they are processed. The processing procedures for the subsequent reactions are exactly the same as used for processing mechanisms of single compounds. The result is a lumped mechanism for the mixture represented as a single model species, including the reactions of the major peroxy radicals formed in the reactions of its components. These reactions are included in Table A-4 for all the lumped model species whose mechanisms were derived this way.

Additional Information

Additional information concerning the operations and use of the mechanism generation system is available elsewhere (Carter, 2019). The mechanism generation system is incorporated into an online MOO system, which was originally developed as a programmable text-base virtual reality system (MOO, 1997, 2014, 2016). This type of text-based system is no longer widely used for online virtual reality experiences and the programming system is no longer being developed or supported. However, features of the object-oriented programming language made it much better suited for mechanism generation applications than Fortran or other programming languages that the author is familiar with, so that is why it was used for its initial development. In theory this system could be converted to another platform that is more widely used, but that is beyond the scope of the present project. The mechanism generation system can be accessed using a Telnet client to log in with administrative access to program the system, input its assignment data, generate reactions, process results for mechanism implementation, and download the results in text files for incorporation into the mechanism. Although the MOO system is capable of allowing non-administrative access via Telnet clients for others to work with the system, this capability is not currently implemented. However, the MOO system also allows users to access the system online (Carter, 2020a), and utilize it to generate mechanisms for selected compounds or obtain information about the system (see also Appendix B).

The online version of the current mechanism generation system can be accessed at http://mechgen.cert.ucr.edu, or through a link on the SAPRC mechanism web page (Carter, 2020b). Users need to log in so the system can keep proper track of operations of different users, but anyone can access the system. Once logged in, users can create radical or stable reactants (there is help on how to designate structures using the standard designation, or Smiles notation or detailed model species names can also be used), or one can select compounds to react from a menu listing compounds on the current SAPRC species list. The system can also be used to obtain information on the various types of estimation methods used, and give assigned rate constants and mechanisms where applicable, as discussed in Appendix B. This can be used to provide convenient documentation for how SAPRC-18 treats specific reactions of interest.

Evaluation Against Environmental Chamber Data

Use of Environmental Chamber Data in Mechanism Development

Environmental chamber experiments consist of irradiations of simplified ambient mixtures or single organic in the presence of NO_x in simulated sunlight, and measuring the resulting changes in reactant concentrations and formation of O_3 and other secondary pollutants under conditions characterized for modeling. If the conditions of the experiments are sufficiently well characterized for modeling, they provide the most direct means of testing mechanisms under atmospheric conditions without uncertainties regarding emissions, meteorology, mixing, and varying conditions. Over the years, we have developed a database of more than a thousand experiments of this type, focusing either on single organic compounds or simplified ambient mixtures, for the purpose of testing whether the mechanisms can predict the results of these experiments. If the mechanisms can simulate a comprehensive variety of experiments, then one can have increased confidence in its reliability for ambient simulations for regulatory or research applications. If the mechanism has significant biases in simulating chamber experiments with representative mixtures or important compounds, then results of ambient simulations will also be biased and indicate that it would be unsuitable for regulatory applications. This is why carrying out such experiments has been funded over the years, and evaluations against this large database has been a large part of SAPRC mechanism development throughout its history (Carter and Lurmann, 1991; Carter, 2000a, 2010a, Carter and Heo, 2012, 2013). These experiments were also used in the evaluation of the RADM mechanism (Carter and Lurmann, 1990). Most other widely used mechanisms have also been evaluated using some of these and other environmental chamber data, though none with such a large number and variety of experiments.

The ideal approach for mechanism development is to derive mechanisms based on our knowledge from laboratory studies, relevant theory, and informed estimates, and then use chamber experiments to independently evaluate their predictive capability. Unfortunately, this does not yet yield mechanisms with acceptable predictive capability There are a number of uncertain aspects of the mechanisms to which model simulations are highly sensitive, and mechanisms derived entirely independently of chamber data often give either gross underpredictions or overpredictions of measures of reactivity, or give concentration-time predictions that are quite different than observed. This may be useful to highlight our current state of knowledge and areas where research is needed, but in the meantime we need mechanisms with at least some predictive capability.

Therefore, the approach used in the development of SAPRC mechanisms when initially estimated mechanisms give unsatisfactory results is to do at least some adjustment of uncertain and sensitive parameters to improve simulations of experiments that are sensitive to the parameters being adjusted. The protocol is to base adjustments only on experiments that are sensitive to a single parameter for a single compound, and use experiments with mixtures or with more than one uncertain sensitive parameter for evaluation purposes. The types of uncertain and sensitive parameters that have been adjusted in developing SAPRC mechanisms include the following.

- Yields or photolysis rates of photoreactive aromatic products. When chamber data with aromatics were first modeled it was apparent that their reactivities are grossly underpredicted unless it is assumed they form a highly photoreactive product. Because the identities of these products were initially unknown (and are still uncertain) they were represented by lumped model species whose yields and/or photolysis rates were adjusted. For SAPRC-18, the mechanism generation system assumes that these products are unsaturated 1,4-dicarbonyl aldehydes, and uses various methods to estimate their yields. However, their photolysis rates still have to be adjusted to yield satisfactory fits to results of chamber experiments with aromatics.

- Nitrate yields in peroxy + NO reactions. Simulations of experiments with compounds that do not have strong internal radical sources are often so sensitive to this that even adjusting yields that have been actually measured to within the experimental uncertainty range has a noticeable effect on simulations of chamber experiments. These are particularly uncertain in the mechanisms for non-hydrocarbons, for which experimental data are limited, inconsistent, or nonexistent.

- Radical yields in O_3 + olefin reactions. It is necessary to assume lower radical yields than suggested by current available data (e.g., IUPAC, 2019, Calvert et al, 2000) in order to avoid significantly overpredicting measures of reactivity in experiments with higher 1-alkenes and other compounds.

- Quantum yields for unsaturated aldehydes or higher ketones. Simulations of experiments with photoreactive compounds such as aldehydes and ketones are highly sensitive to their photolysis rates in the mechanism. Some of these are uncertain and have to be adjusted for satisfactory results.

- Initial branching ratio in reactions with OH. Simulation results for certain compounds, such as esters, can be quite sensitive to initial branching ratios their atmospheric reactions, if the radicals they form have different effects on reactivity. In many cases there are no data concerning these rate constant ratios, and estimates can be uncertain.

- Parameterized mechanisms for phenols and bicyclic aromatics. We have not yet developed methods to estimate mechanisms for these compounds that satisfactorily simulate chamber experiments with these compounds. For that reason, it is necessary to continue to use parameterized mechanisms adjusted to fit chamber data if these compounds if they are to be represented in the model. Although this is not satisfactory for mechanisms intended to be more explicit or chemically detailed, it is better than the alternatives of ignoring them entirely or representing them in a way known to give poor predictions.

It should be pointed out that the mechanism adjustment protocols used in the development of SAPRC-18 were different in some respects than those used when developing previous versions of SAPRC. For all mechanisms, from the highly condensed Carbon Bond mechanisms through the highly detailed MCM, the first priority for predictive capability is accuracy an simulating experiments with the types of compounds that are the most important in ambient emissions. However, in the case of SAPRC-90 through SAPRC-07 and (for aromatics) SAPRC-11, an additional priority is accuracy in predicting ozone and other impacts of individual VOC compounds, as needed for the development of the MIR and other ozone reactivity scales (Carter, 1994, 2000, 2010a-c). This adds an additional priority of accurate predictions for compounds that may not be as important in current emissions, but may become more widely used in the future, or may be subject to reactivity-based emissions controls. Because of this, the development of SAPRC-07 and (for aromatics) SAPRC-11 included a number of compound-by-compound adjustments of uncertain parameters to remove biases in chamber simulations of the variety of individual compounds that have been studied, to minimize possible biases in calculated MIR or other reactivity metrics.

However, although this compound-by-compound adjustment significantly reduces biases in chamber simulations, it may not necessarily result in improved estimated mechanisms or reactivity values for the many compounds that have not been studied experimentally. What's worse, it may tend to mask cases where our general estimation methods are performing poorly. In addition, the amount of effort required to incorporate the adjustments into the mechanism generation system in a consistent and rational manner would significantly increase the time required for delivering an updated mechanism. This effort will be needed eventually when updated MIR or other reactivity scales are required, but updating the SAPRC reactivity scales is beyond the scope of the present project.

Therefore, for SAPRC-18, a modified protocol was used with respect to adjustments regarding photoreactive aromatic products, nitrate yields, and initial branching ratios. In the case of photoreactive aromatic products, the yields of model species used to represent them were based on estimation methods, and the only adjustments concerned the photolysis rates of the four model species used for this purpose. This differs from earlier versions where the yields of the photoreactive model species (with fixed photolysis rates) were adjusted for each compound for which there was chamber data. In the case of nitrate yields, the values found to fit the data without biases were used derive general estimation methods that were applied to all compounds without adjustments for individual compounds. In previous version, the adjustments were also made on a compound-by-compound basis. Thus in both of these cases, adjustments were made primarily for groups of compounds, with adjustments for individual compounds not being directly incorporated into the final mechanism, other than use to inform or evaluate general estimation methods. In addition the assigned branching ratios implemented in the mechanism generation system were restricted to those based on actual product data or rate constant measurements, and no adjustments to improve fits to O_3, NO_x, or overall radical data in chamber experiments were incorporated for SAPRC-18, while such adjustments were incorporated when needed to improve simulations of earlier versions. Although this results in more cases of biases in the evaluation metrics used (see below), it allows for a better evaluation of the general estimation methods that would not be possible otherwise.

Experiments Used

The performance of the SAPRC-18 mechanisms in simulating O_3 formation, rates of NO oxidation, and (for some experiments) integrated OH radical levels in 2256 environmental chamber experiments carried out in 10 different environmental chambers at 3 different laboratories. For comparison purposes, the SAPRC-11 mechanism was also evaluated using same experiments and metrics. Most of these experiments were used for the previous evaluations of the SAPRC-07 or SAPRC-11 mechanisms, though some more recent aromatic - NO_x experiments reported by Carter et al. (2012) and alkene - NO_x experiments reported by Heo et al (2014) have been added. Most of these experiments were carried out in the various environmental chambers at the University of California at Riverside, as described by Carter et al (1993, 1995, 2005), though 28 experiments carried out using the TVA chamber (Simonaitis and Bailey, 1995; Bailey et al, 1996, Carter, 2004) and 25 recent CSIRO chamber experiments (White, 2010) are also included. This dataset only included indoor chamber experiments because of the greater difficulties in characterizing light conditions well enough for evaluating mechanisms with the metrics used.

The experiments are summarized in Table A-7 and Table A-9 in the electronic supplement to this report. Four types of experiments were used for mechanism evaluation, each being used for different purposes. These are briefly discussed below.

Characterization Experiments

The characterization experiments consisted of two types of experiments that are very sensitive to the most important chamber effects that affect mechanism evaluation: the chamber-dependent radical source and NO_x offgasing. The "radical source" characterization experiments consist of CO - NO_x and alkane - NO_x irradiations, both of which have relatively well established mechanisms but whose results in terms of NO oxidation rates are extremely sensitive to chamber-dependent radical sources (Carter et al, 1982; Carter and Lurmann, 1990, 1991) The second consist of CO - air or alkane - air irradiations, where the amount of O_3 formed is extremely dependent on chamber-dependent NO_x sources. In most cases, the magnitudes of the radical source and NO_x offgasing rates that fit the data are of comparable magnitude, and both can be attributed to offgasing of HONO, whose rapid photolysis produces both OH radicals and NO. For this and previous evaluations, experiments were split up into sets where chamber effect parameters are assumed to be the same, and the averages of the HONO offgasing parameter used was the average that fit the data for all the characterization runs in each set. Therefore, the ability of the model to fit results of the 256 characterization runs indicate the run-to-run variability of the values of the HONO offgasing parameter that best fits data for the individual experiments.

Single VOC - NO_x Experiments

The Single VOC - NO_x experiments consisted of irradiations of single compounds in the presence of NO_x, and were the primary mechanism evaluation experiments for most compounds. The exceptions are experiments with alkanes and other compounds that tend to be radical inhibitors or have no internal radical sources. This is because the magnitude of chamber radical sources used in the calculations are much more important in affecting the model results than the actual mechanisms of the compounds. However, alkenes, aromatics, aldehydes, and photoreactive ketones have sufficient radical sources in their mechanisms (i.e., their reactions, or the reactions of their products, include more radical initiation than radical termination reactions) that their modeling results are not as sensitive to uncertain or variable chamber effects, so VOC - NO_x irradiations for those compounds are useful for mechanism evaluation. Therefore, when appropriate adjustments can be made to uncertain parameters in the mechanism of a compound to improve model simulations of experiments with that compound. Cases where this was done in the mechanism development process for the compound are indicated in footnotes when the model evaluation results are presented. A total of 835 such experiments were used to evaluate mechanisms for 38 compounds.

Surrogate Mixture Experiments

The Surrogate mixture experiments consisted of irradiations of various hydrocarbon or hydrocarbon + formaldehyde mixtures designed to approximately represent ambient reactive VOC mixtures in the presence of NO_x. Such experiments are not useful for evaluating mechanisms of single compounds but provide a test of the mechanism as a whole for ambient simulations. They are also useful for serving as the base case for incremental reactivity experiments, as discussed below. A number of mixtures were used in evaluations of previous versions of SAPRC, but for this work we restrict ourselves to standard surrogate experiments used in UCR chamber experiments, including the incremental reactivity experiments discussed below. This is because some mixture experiments are not as well characterized, and results of modeling some of the nonstandard mixture experiments did not appear to clear information about model biases (e.g., Carter, 2000, 2010a). The mixtures used in this evaluation were as follows:

- The Mini-Surrogate consists of a highly simplified 3-component atmospheric surrogate, consisting of n-hexane (to represent all alkanes), ethene (to represent alkenes) and m-xylene (to represent aromatics). This was used primarily as a base case for many of the incremental reactivity experiments, but a number of additional experiments with varying reactant concentrations were also carried out.
- The Standard Surrogate consists of a 7- or 8-component mixture of n-butane, n-octane, ethene, propene, *trans*-2-butene, toluene, m-xylene and (for a some experiments) formaldehyde, representing the major types of compounds in anthropogenic emissions. This was used as the base case for many incremental reactivity experiments, and also to evaluate effects of initial reactant concentrations on model biases.
- The Non-Aromatic Surrogate consists of the standard surrogate mixture with aromatics removed, and no formaldehyde. This was used to evaluate the extent to which model biases observed for the standard surrogate experiments can be attributed to uncertainties in the aromatics mechanisms.

Incremental Reactivity Experiments

The Incremental reactivity experiments consist of experiments to determine the effect of adding a test compound to a surrogate - NO_x irradiation. Most of these were carried out using dual reactors, with the surrogate and NO_x injected into both reactors and mixed and the test compound injected into only one, and both being irradiated under the same conditions. However, some of the earlier "Mini-Surrogate" reactivity runs were carried out in a single reactor with base case experiments alternating with added test compound experiments, with the base case results associated with each added compound experiment being derived by a statistical analysis (Carter et al, 1993). Although such experiments were carried out with a number of surrogate mixtures and surrogate and NO_x concentrations, for this evaluation we report results only for the three major types of reactivity experiments, as follows:

- Base Case Set 1: "MS-MIR". The base case consists of mini-surrogate (MS) - NO_x irradiations at relatively low ROG/NO_x conditions corresponding roughly to "maximum incremental reactivity (MIR)" conditions, where O_3 formation is most sensitive to VOC additions. Most of these experiments did not achieve "true" ozone maximum concentrations because ozone was still increasing at the end of the six-hour irradiations. A total of 84 such experiments were used to evaluate mechanisms for 66 compounds.
- Base Case Set 2: "SS-MIR". The base case is similar to Set 1 except that the standard surrogate (SS) is used instead of the mini-surrogate. Most had ROG/NO_x ratios that corresponded roughly to MIR conditions. A total of 134 such experiments were used to evaluate mechanisms for 59 compounds.
- Base Case Set 3: "SS-MOIR". The base case is similar to Set 2 in that it uses the standard surrogate (SS), but in this case the NO_x levels are sufficiently low that a true O_3 maximum is achieved, or almost achieved within 6 hours of the base case irradiation. Most had ROG/NO_x ratios corresponding to approximately half the NO_x levels that are most efficient for O_3 formation, and all can be considered to approximately represent conditions of the MOIR or EBIR reactivity scales (Carter, 1994). A total of 103 such experiments were used to evaluate mechanisms for 57 compounds.

A few of the reactivity experiments we used in previous evaluations did not fall into the above categories, but in general the results were comparable to those for the three types of experiments used.

Evaluation Metrics

The primary evaluation metric used in this work was the ability of the model to simulate both maximum O_3 yields and rates of of NO oxidized and ozone formed in the experiments, as measured by the quantity Δ(O3-NO), and the maximum rate of NO oxidation and O_3 formation. These are defined as follows:

$$\Delta(O_3\text{-}NO)_t = \{[O_3]_t - [NO]_t\} - \{[O_3]_0 - [NO]_0\} = [O_3]_t + [NO]_0 - [NO]_t$$

$$\text{Max } \Delta(O_3\text{-}NO) \text{ rate} = \frac{\Delta(O_3\text{-}NO) \text{ at the time of ½ the maximum or final } \Delta(O_3\text{-}NO)}{\text{Time of ½ the maximum or final } \Delta(O_3\text{-}NO)}$$

$\Delta(O_3\text{-}NO)$ gives a measure of reactivity that is useful regardless of whether NO or O_3 is in excess, and has been used in previous evaluations. The maximum $\Delta(O_3\text{-}NO)$ formation rate as defined above gives a measure of the rate of NO oxidation and O_3 formation, and is a good complement to the maximum O_3 yield, which is also used as an evaluation metric. However, the maximum O_3 is only an independent metric if the experiment actually achieved a true O_3 maximum, rather than having O_3 still increasing when the experiment ends, and thus be a measure primarily of the O_3 formation rate. For this reason, fits to the maximum O_3 are not shown in experiments where O_3 is still increasing at the end, since the experiment gives no information on maximum O_3 formation potential.

In the case of the incremental reactivity experiments, model performance was evaluated by its ability to predict the effects of adding the test compound on both $\Delta(O_3\text{-NO})$ and integrated OH levels. In the case of $\Delta(O_3\text{-NO})$, the metric used for the reactivity runs was $\Delta\Delta(O_3\text{-NO})$, which is defined as

$$\Delta\Delta(O_3\text{-NO}) = \text{Average}_{\text{hour=1 to final}} \left(\text{Test } \Delta(O_3\text{-NO})_{\text{hour}} - \text{Base } \Delta(O_3\text{-NO})_{\text{hour}}\right)$$

If dilution is small, the integrated OH can be derived from

$$\text{Integrated OH} = \text{IntOH} = k(\text{OH} + \text{m-Xylene}) \times \ln\left(\frac{\text{Initial [m-Xylene]}}{\text{Final [m-Xylene]}}\right)$$

$$\text{IntOH/kOH} = \ln\left(\frac{\text{Initial [m-Xylene]}}{\text{Final [m-Xylene]}}\right),$$

where m-xylene is used as the OH tracer because it is present in all the reactivity experiments, reacts primarily with OH, and reacts rapidly enough to give a reasonably sensitive measure of OH levels. In order to make the evaluation results independent of the OH + m-xylene rate constant, the ability of the model to predict integrated OH is measured by fits to the unitless quantity $\ln([\text{m-xylene}]_0/[\text{m-xylene}]_{\text{final}})$., which is designated IntOH/kOH. Note that even though the final xylene concentration is also affected by dilution, dilution is taken into account in the model calculations, so any corrections for dilution would cancel out when evaluating model performance for IntOH/kOH.

The IntOH/kOH metric was not used for single compound-NO_x experiments because most did not contain a suitable tracer other than perhaps the compound added, which is often unsuitable for this purpose because it either reacts too slowly for its consumption to be precisely measured, or it consumed by other reactions in addition to with OH. In addition, it could not be used for the earlier Set 1 experiments where the base case experiment alternated with the added compound experiment because the statistical analysis of the base case IntOH conditions was not updated.

Regardless of which metric used, the model performance for simulating a set of experiments with a given compound are reported using the quantity "average model bias" or "average relative model bias". The average bias is defined as the average of the difference between model prediction and experimental measurement, which would be positive if the model overpredicts and negative if it underpredicts. The average relative bias is the average of the relative biases of the experiments, defined as the difference between model prediction and experimental measurement, divided by the average of the experimental measurement and model prediction. (The average is used in the denominator so the distribution of biases would be symmetrical.) The standard deviations of these averages, which indicate run-to-run variability of the biases, are shown for SAPRC-18 but not for SAPRC-11, because they are generally similar.

Results and Discussion

The performance of the SAPRC-18 and SAPRC-11 mechanisms in simulating the various metrics are given for each experiment in Table A-8 and Table A-9 of the electronic supplement to this report, with summary results shown in various figures in this section. Figure 1 shows the average relative model biases for predictions of the maximum $\Delta(O_3\text{-NO})$ formation rate and maximum ozone for the characterization, single VOC-NO_x and mixture-NO_x experiments. Footnotes to the table indicate compounds for which adjustments to improve fits to the chamber experiments when developing the SAPRC-18 mechanism, and provide relevant comments. Figure 2 shows the average biases for $\Delta\Delta(O_3\text{-NO})$ and ΔIntOH/kOH for the incremental reactivity experiments. These results are discussed below for the different types of experiments.

Figure 1. Performance of the SAPRC-18 and SAPRC-11 mechanisms in simulating rates of formation of the $\Delta[O_3\text{-}NO]$ and maximum ozone concentrations in the characterization, single VOC-NO_x , and mixture-NO_x experiments.

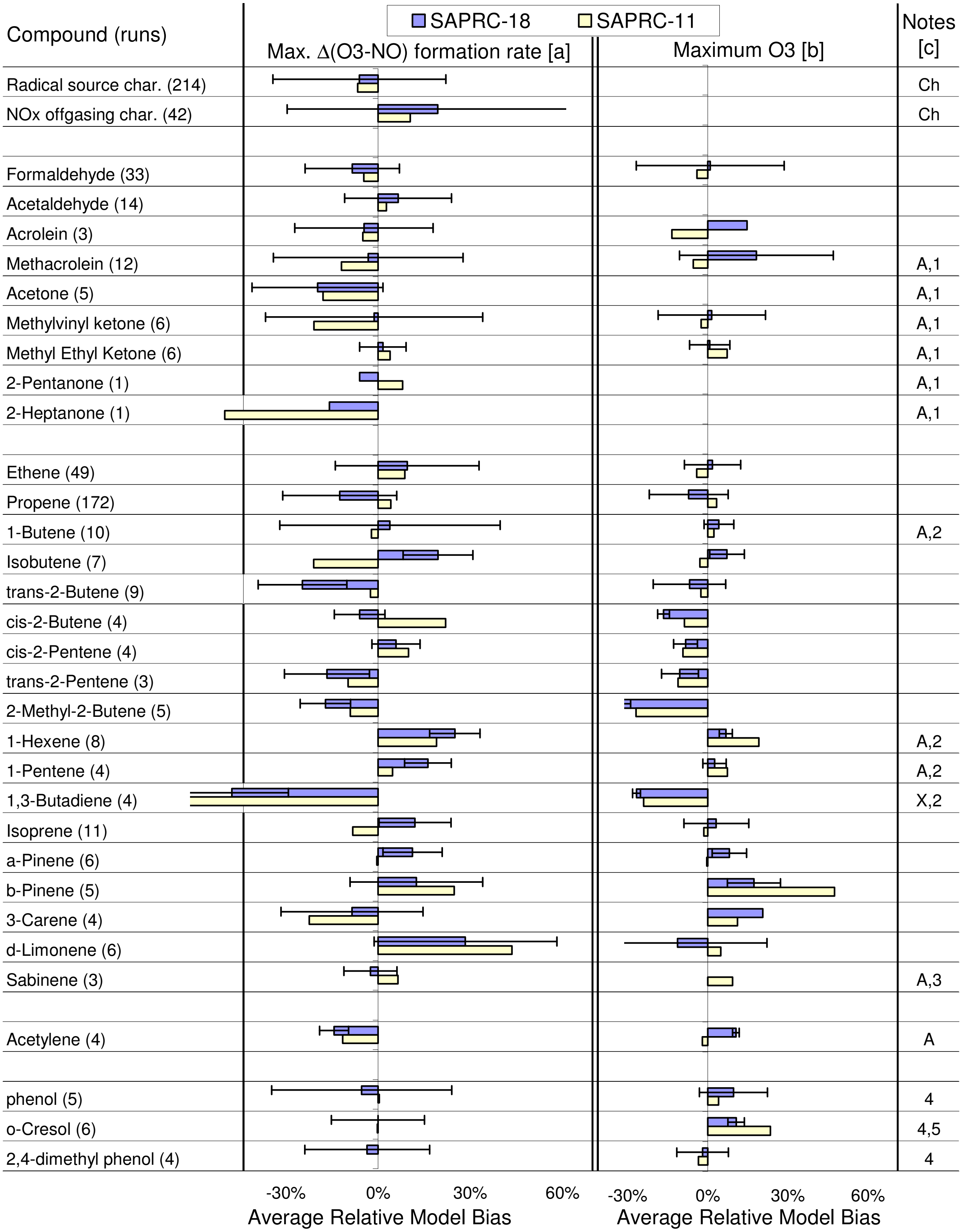


Figure 1 (continued)

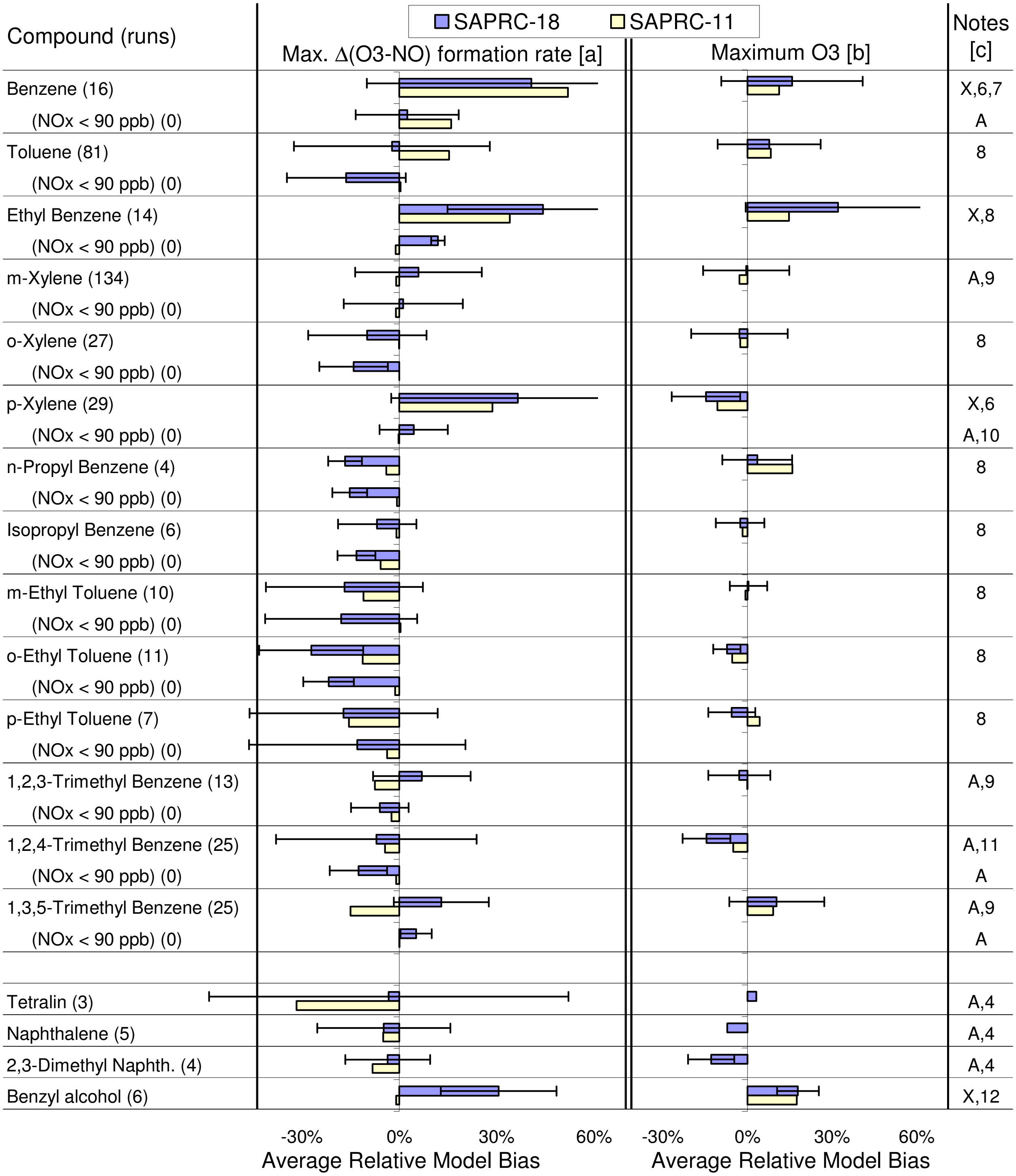
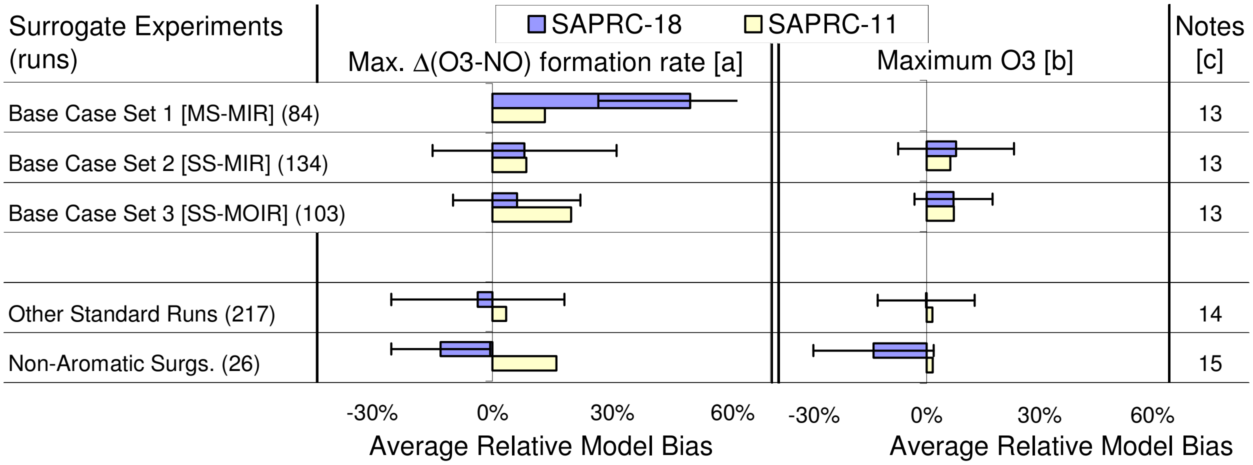


Figure 1 (continued)



Notes

[a] The NO oxidation rate is the average rate of change of Δ(O3-NO) up to the time of one half the ozone maximum. The average bias is the average of (model - experimental) / experimental for all experiments of this type, and the average error is the average of the absolute values of this quantity.

[b] Averages of fits to maximum ozone in experiments where a true ozone maximum is attained. Experiments where O_3 is not still increasing during the last hour of the experiment excluded.

[c] Notes are as follows:

Ch These were used to derive chamber model parameters, which were adjusted to minimize biases. Errors indicate run-to-run variability and not necessarily mechanism performance issues.

A Adjustments made to improve fits for this individual compound.

X The ability of the mechanism to predict rates of NO oxidation and final ozone yields needs to be improved. This should be investigated for future updates to the mechanism. See text.

1 Photolysis rates adjusted to improve fits to results of single VOC - NO_x experiments.

2 Radical formation from the reactions of the ethyl- and higher alkyl-substituted excited Criegee intermediates were lowered in order to fit results of higher 1-alkene - NO_x chamber experiments.

3 The nitrate yields from the reactions of NO with the first-generation peroxy radicals were increased to 25% from an estimated ~12% in order to have acceptable fits to the initial NO oxidation rate.

4 A parameterized mechanism, similar to that used for SAPRC-11, was used. Parameter values were adjusted to fit chamber data, though in some cases they were not optimized for this version.

5 An older high NO_x o-cresol - NOx experiment, where the model gave significantly different results than the other runs that were carried out more recently, was not included in the average. There were also m- and p-cresol - NOx runs carried out around the same time and conditions but the results were similar and also not consistent with the lower concentration o-cresol runs and the model adjusted to fit them. Because of this, these are also excluded from this evaluation, so only o-cresol data are available to evaluate the model used for cresols.

6 Average bias is positive because experiments indicate that the reactivity increases as NOx levels are decreased, which is not predicted by the mechanism. The mechanism was adjusted to optimize fits for low NOx conditions that are more representative of most current atmospheres, resulting in overpredictions at higher NO_x. This problem existed in previous versions of SAPRC and was not corrected with this update.

7 The photolysis rate of the BUDAL (1,2-butenedial) model species was adjusted to fit NO

Figure 1 (continued)

oxidation rates in benzene experiments with NOx < 100 ppb.

8 No adjustments made to optimize fits for this compound because fits to data for other compounds (benzene, m- and p-xylenes, and the trimethylbenzenes) were used to determine the photolysis rates of the photoreactive model species, chosen based on their predicted yields of these species.

9 The photolysis rate of the AFG2A model species was adjusted to fit the data for m-xylene, 1,2,3-trimethylbenzene and 1,3,5-trimethylbenzene, which are the methylbenzenes where this is the major model species used for the photoreactive products.

10 The photolysis rate of the AFG1 model species was adjusted to fit the data for p-xylene, the only methylbenzene where this is the major model species used for the photoreactive products.

11 The photolysis rate of the AFG2B model species was adjusted to fit the data for 1,2,4-trimethylbenzene, the only methylbenzene where is the major model species used for the photoreactive products.

12 The mechanism for this compound was not optimized.

13 These are base case results for the incremental reactivity experiments for the indicated set.

14 These are other standard surrogate experiments that were not carried out in conjunction with incremental reactivity experiments.

15 These consisted of standard surrogate experiments with the aromatic components removed.

Characterization Experiments

The performance of the mechanisms in simulating the characterization experiments are shown under the of Max Δ(O_3-NO) rate column on the first plot in Figure 1. Note that this is the same as simply the O_3 formation rate for the NO_x offgasing experiments because there is no initial NO. The results are similar for both models because the same chamber effects model was used for both, though the parameters that fit the data for SAPRC-18 were reoptimized with the new mechanism, so they are not exactly the same. The relatively low biases are due to the fact that the parameters were adjusted to minimize biases, so the standard deviations give the best indication of run-to-run variability in these chamber effects chamber effects parameters that best fit the data for individual experiments. The results are much more variable for the NO_x offgasing experiments, as indicated by the larger standard deviation. However, given the nature and variability of chamber effects in these chambers, this is probably the best performance that can be obtained, at least for this chamber model. It is important to note that variability of these chamber effects are much less important in simulations of the other types of experiments that are used in this mechanism evaluation, because except for the characterization runs we did not use any experiments found to be highly sensitive to chamber effects.

Single Compound Evaluation Experiments

Both the single VOC-NO_x and the incremental reactivity experiments are useful for evaluating mechanisms for single compounds, but each have different advantages and disadvantages. Single VOC-NO_x experiments, whose mechanism evaluation results are shown on Figure 1, have the advantage that uncertainties in mechanisms of other VOCs do not affect the results, making it less likely that there will be compensating errors if adjustments are made to fit the data. However, a single VOC-NO_x experiment is not a good representation of ambient conditions, especially if the VOC has no internal radical sources (making the results dominated by chamber effects), but also if the VOC is unusually reactive, resulting in transformations occurring in short timescales relative to the sampling frequency, making measurements of NO oxidation and O_3 formation rates less precise. These issues are addressed in incremental reactivity experiments, where the effects of the VOC's reactions are assessed under conditions more representative of actual polluted atmospheres. The evaluation results for those experiments are shown on Figure 2.

Figure 2. Summary of average model errors for $\Delta\Delta$(O3-NO) and ΔIntOH in the SAPRC-18 and SAPRC-11 simulations of the incremental reactivity experiments.

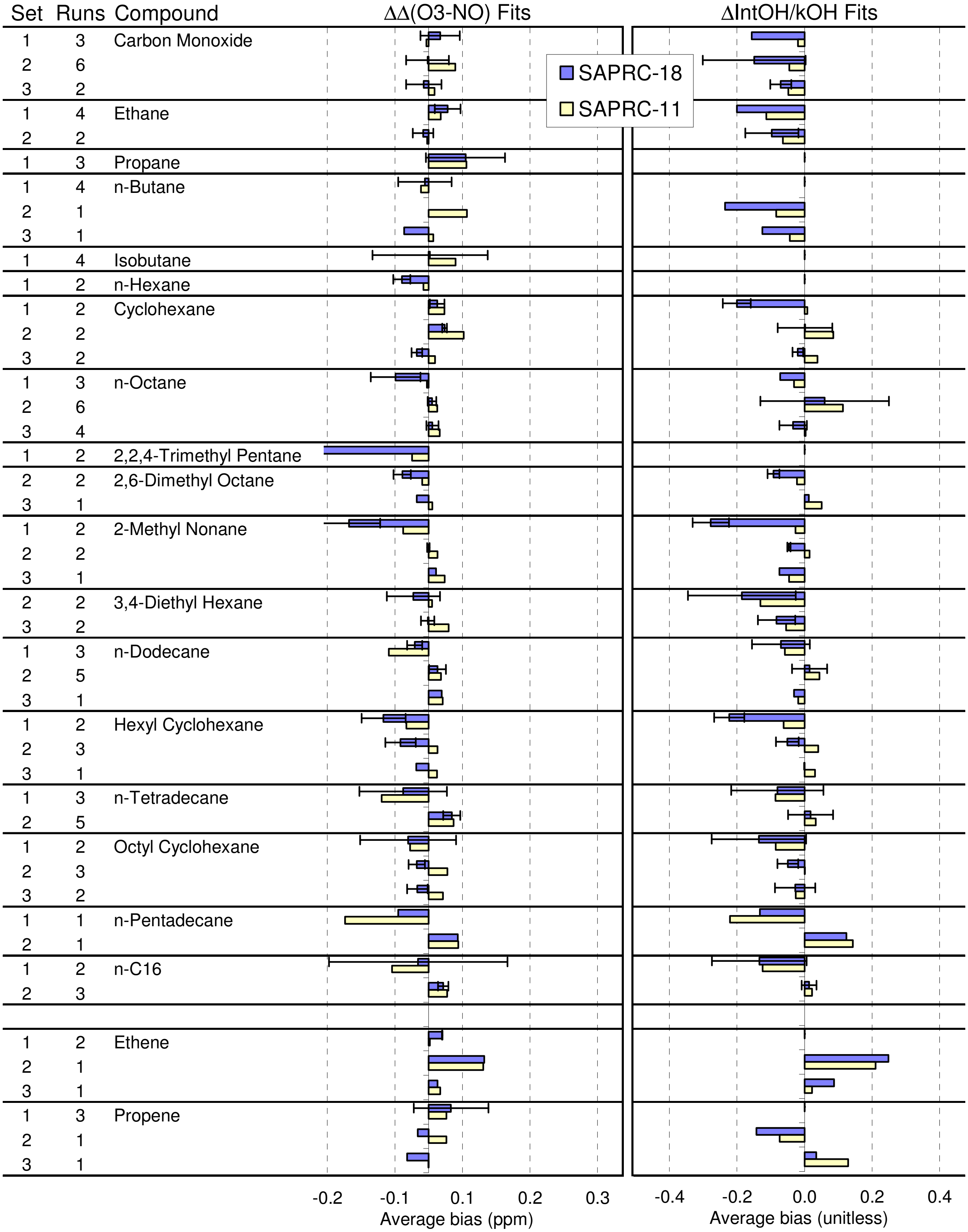
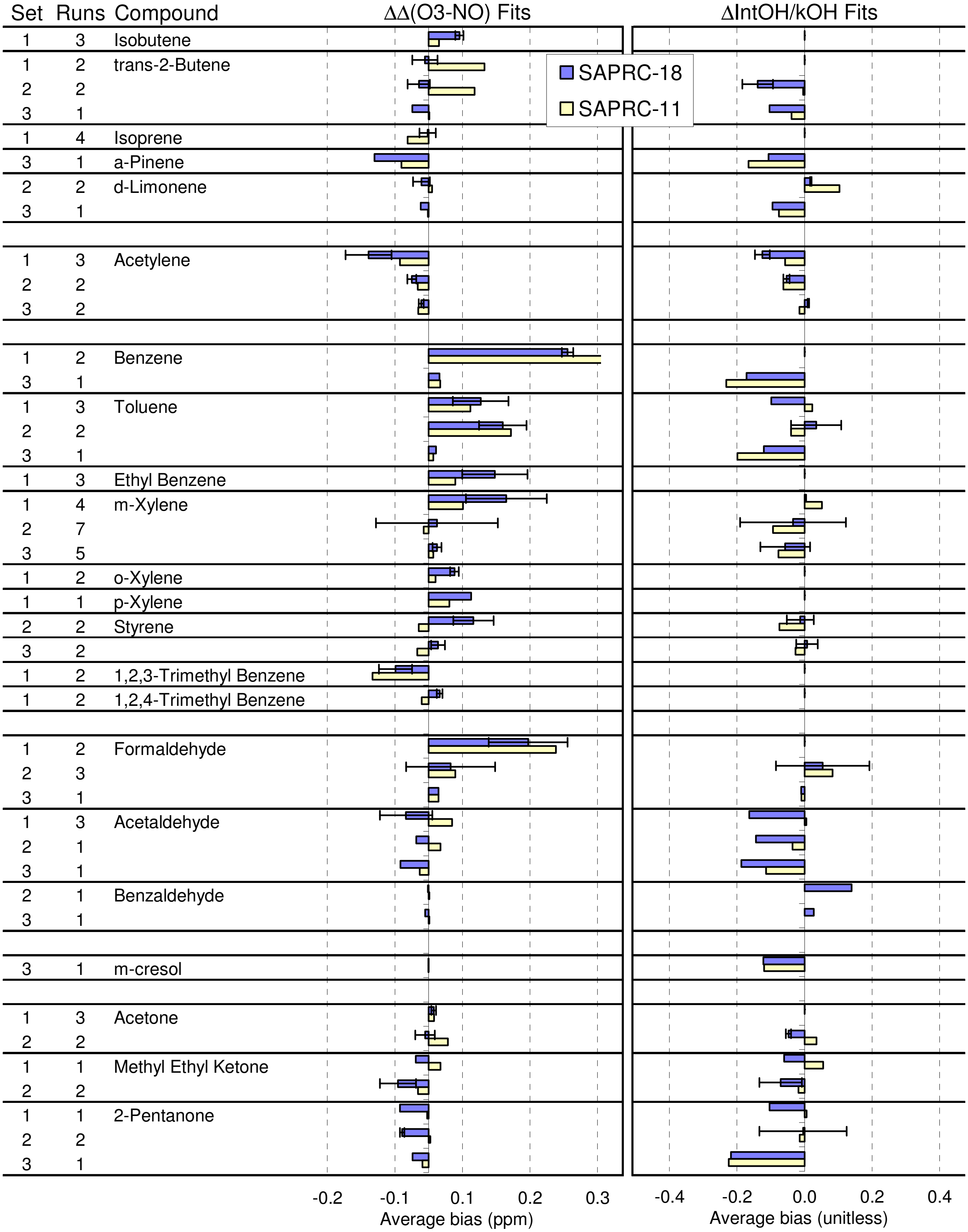


Figure 2 (continued)



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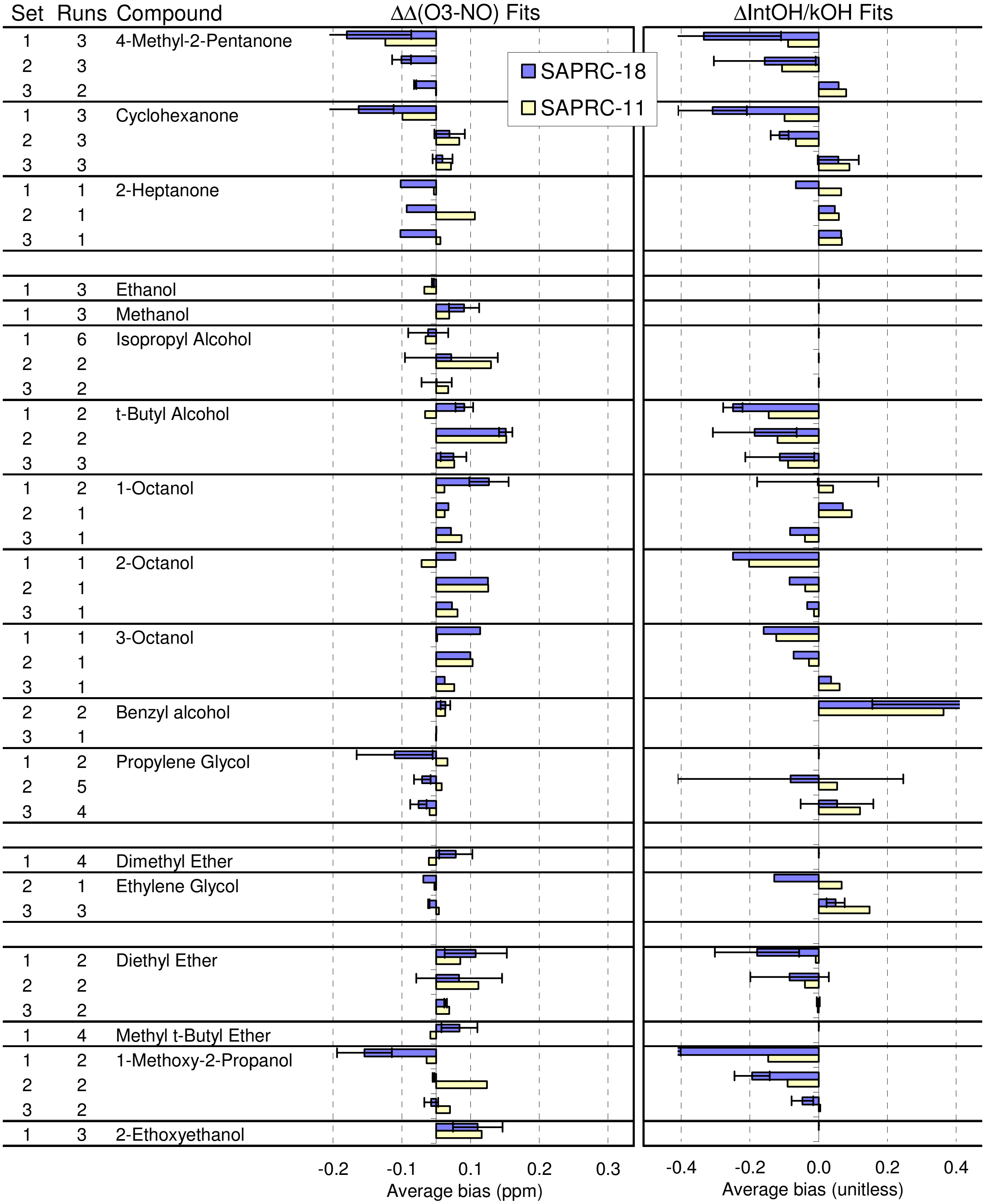

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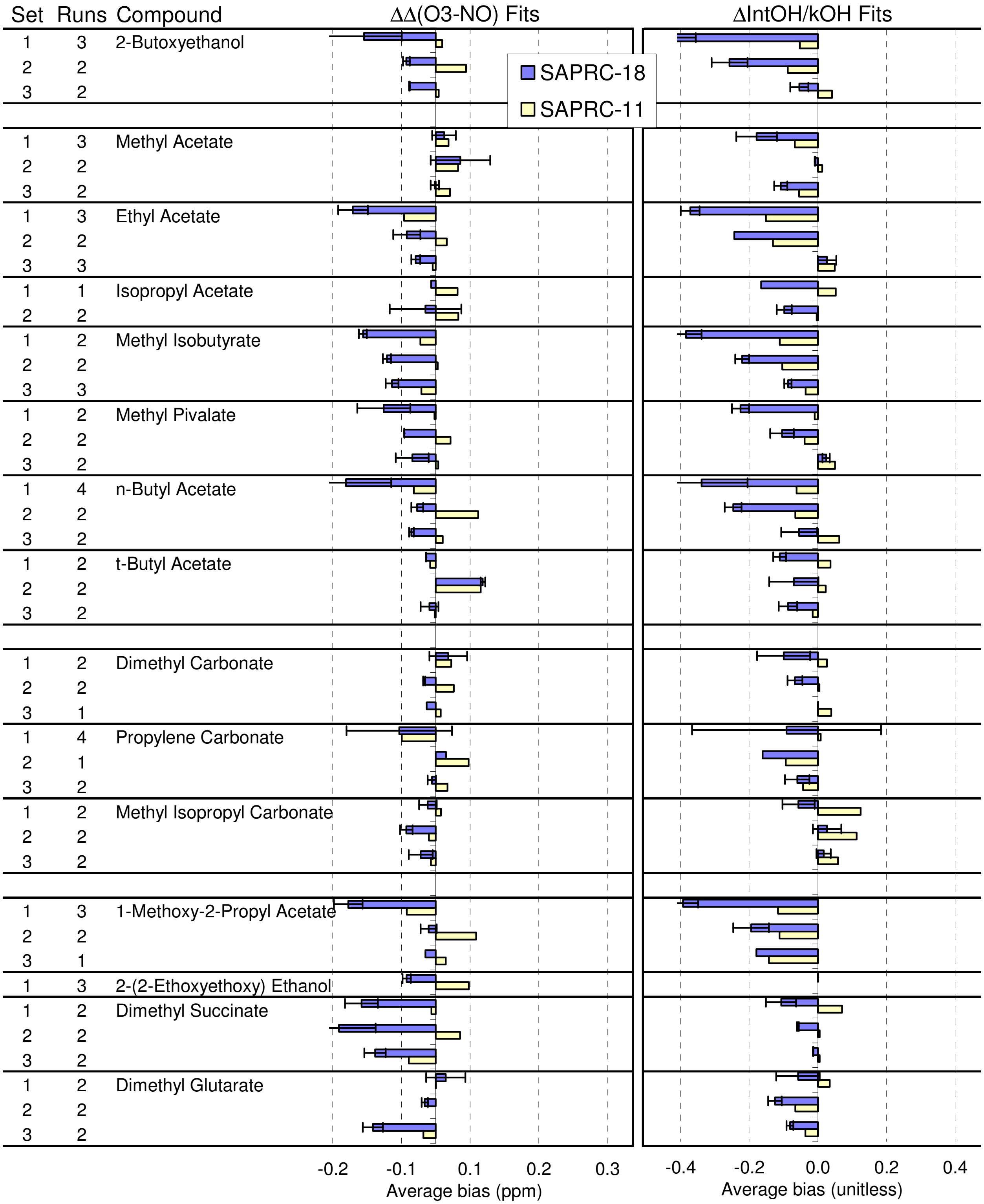

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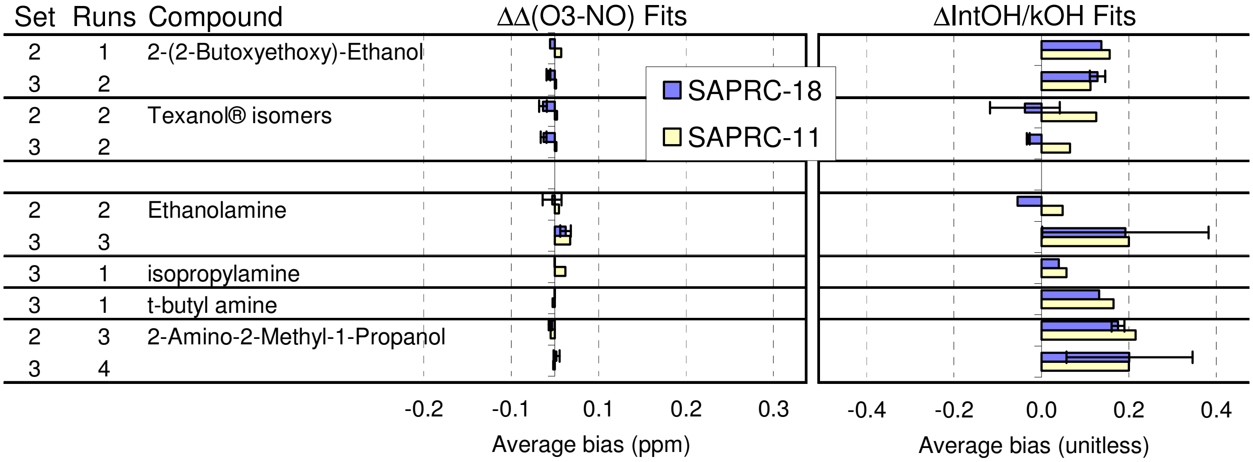


On the other hand, the mechanism evaluation results for incremental reactivity experiments are influenced at least to some extent by uncertainties in the mechanisms of the atmospheric surrogate mixtures used in the base mixture in the reactivity experiments. To some extent, biases or errors in the base case mechanisms cancel out when predictions of the effects of adding a test compound, but not if the model predicted environment in the experiment is significantly different from what is observed. For example, if reactions involving O_3 are important in affecting the impact of an added VOC, the model predicts sufficiently different O_3 formation in the base case experiment than actually observed, then different incremental reactivity results would be predicted even if the mechanism for the added VOC is entirely correct. Therefore, one needs to examine the performance of the mechanisms in simulating the base case experiments before assessing the performance in simulating incremental reactivities of these experiments.

The last set of plots on Figure 1 show the average performances of the mechanisms in simulating the NO oxidation and O_3 formation rates and maximum O_3 for the three sets of base case experiments used in this evaluation. Note no maximum O_3 metric is shown for the "MIR"-type base experiments because they do not achieve an O_3 maximum before the end of the experiments. The results indicate that SAPRC-18 has a significant bias for overpredicting NO oxidation and O_3 formation rates in the Set 1 experiments, but is reasonably unbiased simulations O_3 formation rates and maximum yields in the other types of experiments. On the other hand, SAPRC-11 simulates the Set 1 experiments reasonably well, but has somewhat greater bias in simulating the Set 3 runs, though probably not to a significant extent. Possible causes for the relatively poor performance in the SAPRC-18 simulations of the mini-surrogate, MIR experiments are discussed below. But regardless of the causes, these results mean that, all else being equal, poorer performance for SAPRC-18 in predicting incremental reactivities in these experiments may not necessarily indicate a less predictive mechanism for the test compound.

The results show that in general the performance of SAPRC-18 in simulating these both the single VOC - NO_x (Figure 1) and the incremental reactivity results (Figure 2) was generally similar to that for SAPRC-11, though there are more cases where SAPRC-18 did not perform quite as well as SAPRC-11 than the other way around. This is primarily because fewer cases of adjustments applied to individual compound mechanisms in the development of SAPRC-18 than was the case for SAPRC-11. This is particularly the case for aromatics, where total yields of photoreactive model species were adjusted for each compound for SAPRC-11, while for SAPRC-18 the yields of these species were determined by the mechanism generation system, with the photolysis rates of the four model species being adjusted using data for selected compounds with high predicted yields of these species. In addition, SAPRC-11 incorporates many more cases than SAPRC-18 where aspects of the mechanisms such as nitrate yields in reactions of peroxy radicals with NO and uncertain branching ratios for initial reactions were adjusted to optimize model performance. This is because the evaluation of SAPRC-18 was focused more on evaluating the performance of the estimates of the mechanism generation system, while the evaluations of the previous SAPRC versions were focused more on evaluating the ability of the mechanisms to predict reactivity scales (Carter, 2010a,b). The adjustments that were made in the development of SAPRC-18 were focused more on compounds or classes of compounds that are important in current emissions, rather than many individual compounds that are relatively less important in emissions, but must be considered when developing reactivity scales.

The evaluation results for the various types of compounds are discussed below.

CO and Alkanes. As indicated above, only incremental reactivity results can be used to evaluate mechanisms for CO and alkanes because of their lack of internal radical sources. The performance of SAPRC-18 in simulating effects on $\Delta(O_3\text{-}NO)$ is reasonably satisfactory, except for 2,2,4-trimethylpentane and 2-methyl nonane in the Set 1 experiments. Poorer performance in the Set 1 experiments can be explained by the poor performance in simulating the base case, as discussed below, and indeed the results for 2-methyl nonane in the other sets of reactivity runs are reasonably well simulated. (There are only Set 1 experiments for 2,2,4-trimethyl pentane). On the other hand, SAPRC-18 performs better than SAPRC-11 in simulating Set 1 results for n-pentadecane and hexadecane, but reasonably well for the other types of runs.

SAPRC-18 appears to have a bias towards underpredicting effects of CO and alkanes on OH levels, though again the performance for the Set 1 runs is not as good as the other types. SAPRC-11 appears to be much less biased in this regard, with the possible exception of n-C_{15+}. Note that CO is not considered to have uncertainties in its mechanism (with only a single reaction with a well-studied rate constant, forming an inert product), so if biases are observed in incremental reactivities of this compound reflect issues with the base mechanism rather than the mechanism of CO. The similar results for many of the alkanes suggest that this may be a factor for these compounds as well.

Alkenes and Acetylene. Single VOC-NO_x runs are considered most useful for evaluating alkene mechanisms because they tend to be less sensitive to uncertainties in chamber effects and they are not affected by mechanisms for the base case mixtures in reactivity experiments. The results on Figure 1 indicate good to fair model performance for most compounds, with similar magnitudes (though not always signs) of biases for SAPRC-18 and SAPRC-11. Both mechanisms performed poorly for 1,3-butadiene and not very well for 2-methyl-2-butene and d-limonene, and SAPRC-11 performed poorly for β-pinene. However, it was necessary to make adjustments to the SAPRC-18 sabinene mechanism to satisfactorily simulate the results of the sabinene-NO_x experiments (see footnote in Table 1); otherwise the SAPRC-18 significantly overpredicted the reactivity of this compound.

Not as many alkenes were studied using incremental reactivity experiments, but the model performance for the compounds that were studied were generally satisfactory or comparable to results discussed above for the alkanes. They did not clearly indicate any mechanism problems for the compounds studied.

Benzene and Alkylbenzenes. As with alkenes, single VOC-NO_x experiments are also considered to be most useful for evaluating aromatic mechanisms, with the results being very sensitive to the yields and photolysis rates assumed in the model for the highly photoreactive unsaturated dicarbonyl products these compounds are believed to form. In the case of benzene, none of the SAPRC mechanisms correctly predict the effect of total NO_x on the rates of NO oxidation and O_3 formation in benzene - NO_x experiments, so further work on the mechanism for this compound is needed. This problem was discussed in conjunction with the documentation of the previous mechanisms (Carter, 2010a,b, Carter and Heo, 2013), and wasn't solved with this update. Therefore, any adjustments made to improve model performance (for either SAPRC-18 or SAPRC-11) for benzene, ethyl benzene, and p-xylene were made using data for experiments where the initial NO_x concentrations were less than 90 ppb, which are more representative of the atmospheric conditions where the mechanism may be used. There did not appear to be large dependence on initial NO_x in evaluation results for the other alkylbenzenes, as indicated on Figure 1.

In general, SAPRC-11 performed quite well in simulating the lower NO_x experiments for benzene, ethyl benzene, and p-xylene and the experiments for the other compounds at all NO_x levels because the total yields of photoreactive model species were adjusted for each aromatic to optimize the fits. SAPRC-18 did not perform quite as well because these yields were held fixed at the values predicted by the mechanism generation system, and only the photolysis rates of the four model species used to represent photoreactive products being adjusted. Figure 1 shows that SAPRC-18 tends to overpredict rates of NO oxidation and O_3 formation for ethylbenzene and p-xylene, but underpredict these rates for the ethyl- and propyl-substituted benzenes, for which no adjustments were made. However, the SAPRC-18 predicted maximum O_3 reasonably well for all compounds except for ethyl benzene, and that may be because there were no lower NO_x experiments for that compound where a true O_3 maximum was attained.

Not as many aromatics were studied using incremental reactivity experiments, but the results on Figure 2 are generally consistent with those for the single aromatic-NO_x experiments shown on Figure 1. The MIR reactivity experiments (Sets 1 and 2) had relatively high NO_x levels, which may explain the overprediction observed for $\Delta\Delta(O_3\text{-}NO)$ observed for those types of runs. This overprediction was also observed for the MIR m-xylene experiments, despite the fact that unbiased fits were observed on the m-xylene - NO_x runs (Figure 1). This may have a role in the tendency of SAPRC-18 to overpredict reactivity in the base case MS-MIR (Set 1) experiments, since m-xylene is the most important component of that surrogate in terms of affecting the results. The negative bias in fitting ΔIntOH for benzene and toluene is consistent with the CO and alkane results, and the lower bias for the xylenes may be have something to do with the fact that the aromatics tend to enhance radical levels, while they are depressed by CO and alkanes.

Aldehydes and Ketones. Single VOC-NO_x experiments are also useful for evaluating mechanisms for aldehydes and most ketones studied because of radical sources caused by their photolyses. The exception is benzaldehyde, which is a radical inhibiter and therefore its mechanism can only be evaluated using incremental reactivity experiments. In addition, photolysis rates appear to be lower in the higher ketones such as 2-pentanone and 2-hexanone, so the incremental reactivity experiments may be a more reliable test of their mechanisms. Reasonably good model performance was observed for both mechanisms for these compounds, though fits are not as good for the Set 1 reactivity experiments for 4-methyl-2-pentanone and cyclohexanone. Note that photolysis rates of the ketones were adjusted in to fit results of the ketone experiments, as indicated by footnotes to Figure 1

Phenols. Currently we have no estimated mechanisms for phenols, and highly parameterized mechanisms adjusted to fit chamber data have to be used. Attempts to utilize the methods used to estimate or derive mechanisms for alkylbenzenes result in gross overpredictions of reactivities of these compounds, and this situation continues with SAPRC-18. Although much less reactive than alkylbenzenes, these compounds are sufficiently reactive that single VOC-NO_x experiments can be used to adjust or evaluate mechanisms for these compounds, and sufficient data are available to derive adjusted mechanisms for phenol, o-cresol, 2,6-dimethyl phenol. For that reason the mechanisms show relatively low bias for simulating NO oxidation and O_3 formation rates and yields for these compounds (Figure 1), though there is relatively large run-to-run variability in the fits. These data were used to derive the parameterized mechanisms for the PHEN, CRES, and XYNL model species used to represent phenol, all cresols, and all xylenols and multi-substituted phenols, respectively. However, the CRES model derived to fit the data for the six o-cresol experiments did not perform well simulating the single VOC-NO_x experiments with m- and p-cresol (not shown), though it did perform well in simulating the single incremental reactivity experiment with m-cresol (Plot 2 on Figure 2). However, the predictive capabilities of these parameterized mechanisms are uncertain, and work is needed to improve our understanding of how these compounds actually react in the atmosphere.

Tetralin and Naphthalenes. This situation with tetralin and naphthalenes is very similar to that with the phenols -- use of an alkylbenzene-type mechanism grossly overpredicts the reactivities of these compounds and the details of their mechanisms cannot currently be estimated. Therefore, parameterized mechanisms adjusted to fit available data also have to be used. These are also sufficiently reactive that VOC-NO_x experiments can be used to derive or evaluate these mechanisms, which is fortunate since no incremental reactivity data are available for these compounds. Because of this adjustment, relatively little bias is seen in the SAPRC-18 simulations, though the run-to-run scatter is relatively high for tetralin, which is one compound where SAPRC-11 was not optimized. As with phenols, the predictive capabilities of these parameterized mechanisms are uncertain, and more work is needed.

Alcohols, Glycols, Ethers, Esters, Carbonates, etc. Incremental reactivity experiments for a wide variety of compounds with alcohol, ether, and carbonyl groups have been carried out for the purpose of improving estimates of O_3 impacts of these compounds in the MIR or other reactivity scales (Carter, 1994, 2000, 2010a-c). Most of these compounds that we studied to not have sufficient internal radical sources for VOC-NO_x experiments to be useful for mechanism evaluation, so incremental reactivity experiments have to be used. The one exception is benzyl alcohol, where the unadjusted mechanism did not perform particularly well in simulating the results of the VOC-NO_x experiments (Figure 1, bottom of plot 2) or the effect on integrated OH in the incremental reactivity experiments (Figure 2, plot 3). The reactivity results for the other alcohols, as well as glycols, ethers, and alcohol ethers were simulated reasonably well (Figure 2, plots 3 and 4), with the performance comparable to SAPRC-11 (for which few adjustments were made) and the results for the alkanes. There were cases of poorer performance for the MS-MIR (Set 1) reactivity experiments for some compounds, as also observed for alkanes.

On the other hand, SAPRC-18 did not perform nearly as well in simulating reactivity results for the esters as did SAPRC-11. This is because, as discussed above, there are many cases of compound-by-compound adjustment used in the development of their mechanisms in SAPRC-07 and SAPRC-11, while there was essentially none for SAPRC-18. Although this results in somewhat worse model performance in some cases, it means that the evaluation results for these compounds provides a means to assess the performance of our current estimates in the mechanism generation system to predict atmospheric impacts of compounds that have not been studied. Although there are cases where SAPRC-18 performs reasonably well (methyl, isopropyl and t-butyl acetates, and the three carbonates), there appears to be a general bias for SAPRC-11 to underpredict $\Delta\Delta(O_3\text{-}NO)$, and also to underpredict ΔIntOH to a greater extent than most other compounds. Although these biases are not so large that they indicate that the mechanisms are grossly in error, they clearly should be improved.

Amines. Incremental reactivity experiments have also been carried out using several amines. Note that the mechanisms of ethanolamine and isopropylamine are different from those of t-butyl amine and 2-amino-2-methyl-1-propanol (AMP) in that the former two are quite reactive in promoting ozone formation, while the latter two are strong ozone and radical inhibitors. (This is because the former two have α hydrogens that allow intermediates to react further forming radicals, where the latter two do not. [Carter, 2008].) Despite their differences, both mechanisms give good simulations of $\Delta\Delta(O_3\text{-}NO)$, though they tend to overpredict ΔIntOH, especially for the inhibiting compounds. Since most compounds tend to underpredict ΔIntOH, this suggests that there may be issues with amine mechanisms in this regard. Note that no adjustments were made to improve the fits for either mechanism.

Mixture Experiments

Although they are generally of limited utility for evaluating mechanisms for individual compounds, mixture experiments provide a means to evaluate the performance of the mechanism as a whole under under atmospheric conditions. The last plot on Figure 1 summarizes the performances of the mechanisms in simulating Δ(O$_3$-NO) and maximum O$_3$ in the various atmospheric surrogate mixture - NO$_x$ experiments. Those that were used as the base case for the incremental reactivity experiments are shown separately, as discussed above. The group designated "Other standard runs" all employed the same standard surrogate at the SS-MIR and SS-MOIR base cases (sets 2 and 3), but at varying total VOC and NO$_x$ levels for various purposes not associated with any reactivity experiments. The "Non-Aromatic Surgs." experiments employed the same surrogate as those in the standard runs, but with the aromatics removed, and were also carried out with varying total VOC and NO$_x$ levels. Although as discussed above SAPRC-18 tended to overpredict NO oxidation and O$_3$ formation rates of the mini-surrogate, MIR (Set 1) base case experiments as discussed above, it simulated the standard surrogate runs with relatively little overall bias when all results are averaged, though it has a tendency to underpredict O$_3$ formation rates and yields in the non-aromatic surrogate experiments.

It was noted previously that the SAPRC-07 and SAPRC-11 mechanisms tended to underpredict Δ(O$_3$-NO) in the standard surrogate experiments at low surrogate/NO$_x$ ratios, with the underprediction becoming less and eventually not occurring if the ratio becomes sufficiently large (Carter et al, 2005, Carter and Heo, 2013). This is associated with the model for the aromatics since this is not observed in simulations when the aromatics are removed from the surrogate. This is shown on Figure 3, which gives a plot of the model biases in simulating final Δ(O$_3$-NO) against the initial surrogate / NO$_x$ ratios for the various types of surrogate experiments. The update to SAPRC-18 did not significantly change this situation with the standard surrogate experiments, with the bias tending to be less negative or more positive as the surrogate / NO$_x$ ratio is increased. Such a dependence is probably also the case with the mini-surrogate experiments, though it is less definitive because of the more limited range of surrogate / NO$_x$ ratios. As with previous versions, there is no such dependence of for the surrogate experiments with the aromatics removed, suggesting this is likely due to some issue with the aromatics mechanism.

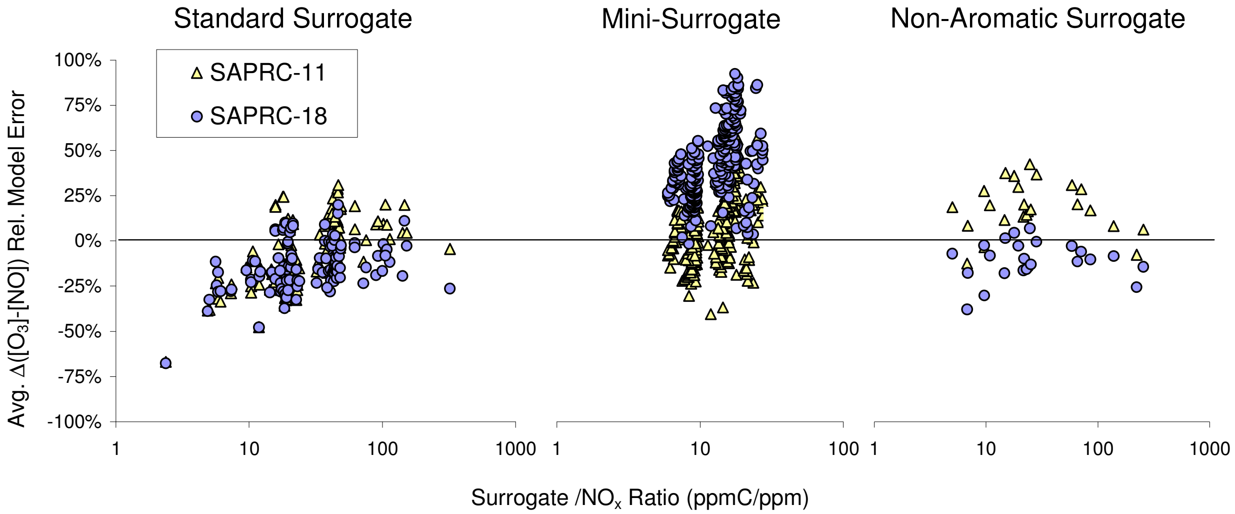


Figure 3. Plots of errors in predictions of final Δ(O3-NO)calculated using the SAPRC-18 and SAPRC-11 mechanisms against the initial surrogate/NO$_x$ ratios for the various atmospheric surrogates and non-aromatic surrogate - NO$_x$ experiments..

The relatively large positive biases in the simulations of $\Delta(O_3\text{-}NO)$ for the mini-surrogate experiments in SAPRC-18 despite the low biases for SAPRC-11 is likely due to the large sensitivity of model simulations of these experiments due to changes in the mechanism for m-xylene, the major compound affecting the reactivity of this mixture. During the development of SAPRC-07 and SAPRC-11, it was observed that small changes made to the yield of the photoreactive model species that was adjusted to fit the m-xylene - NO_x experiments had large effects on predicted model biases for simulations of these mini-surrogate experiments. As discussed above, fewer such adjustments were made in the case of the SAPRC-18 mechanism, though photolysis rates of the AFG2A model species was adjusted in part to optimize fits to m-xylene experiments. Fits to the results of the 1,2,3- and 1,3,5-trimethyl benzene were also considered, AFG2A photolysis rate that fit the m-xylene experiments also fit the data for these trimethylbenzenes. It is possible that further adjustments of the "AFG" photolysis, or different methods of representing or lumping photoreactive aromatic products, may improve the fits to the full set of data including the mini-surrogate runs, but this was not investigated because the protocol was to limit adjustments to fits to single compound or reactivity experiments.

Examples of Atmospheric Box Model Simulations

The electronic supplement to this document contains inputs and outputs of a test simulation for the purpose of verifying model implementation. These simulations employ 0.1 ppm NO_x, 1ppmC of an anthropogenic mixture from emissions inventories, and 0.25 ppmC of a biogenic mixture, with nonzero inputs for all emitted model species in the mechanism. The photolysis rate constants are held constant at specified values appropriate for direct overhead sunlight, but they were all set to zero after 480 minutes to simulate dark chemistry. Representative results are shown in Figure 4. The simulation gave nonzero values for all reactive model species in the mechanism.

The effects of the mechanism updates were examined by conducting multi-day box model simulations of simplified ambient scenarios where both VOCs and NO_x were emitted continuously during the daylight hours. These were similar to the simulations used to test effects of mechanism condensations when developing the condensed versions of SAPRC-07 as discussed by Carter (2010d), and that reference can be consulted for details. These simulations all had the same inputs except for the total amounts of NO_x that was emitted, which were varied such that the ROG/NO_x ratio of emitted reactants (C/N) ranged from approximately 5 to approximately 70 moles carbon per mole nitrogen. In order to place the treatment of heterogeneous reactions on an equal basis, the nonzero N_2O_5+H_2O rate constants in SAPRC-11 were set to zero so they would be the same as used in SAPRC-18, since these reactions are now assumed to be entirely heterogeneous and has zero rate constants in SAPRC-18. Figure 5 shows a comparison of the results of these simulations using SAPRC-18 and SAPRC-11 for representative compounds and C/N ratios. Note that ratios of 5 and 7 correspond to maximum incremental reactivity (MIR) and maximum ozone (MOIR) conditions, respectively, while the ratio of 70 represents very low NO_x conditions. Results with intermediate ratios between 7 and 70 were similar.

It can be seen that the updated mechanism gives about the same results as SAPRC-11 for ozone, OH, HO_2 and NO_2, though it has different predictions of HNO_3 under both low and high NO_x conditions and consistently predicts lower H_2O_2 levels. The lower H_2O_2 prediction is consistent with the decrease in the rate constant for its formation from HO_2, as indicated on Table 2. Note that the fact that SAPRC-18 gives about the same HO_2 predictions as SAPRC-11 is not consistent with the results of Venecek et al (2018), who observed that SAPRC-16, an earlier version of SAPRC-18, gave much lower HO_2 predictions under some conditions in regional model. It is not clear how the changes made to SAPRC-16 could affect this issue, but this needs to be investigated once SAPRC-18 is implemented in 3D models.

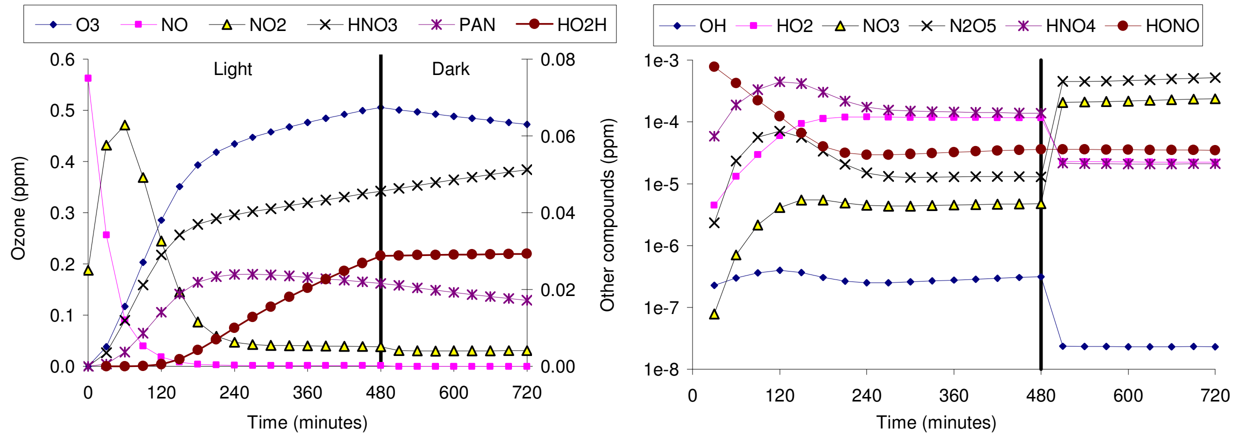


Figure 4. Concentration-time plots of selected species in the test simulation provided to verify correct implementation of SAPRC-18 in airshed model software.

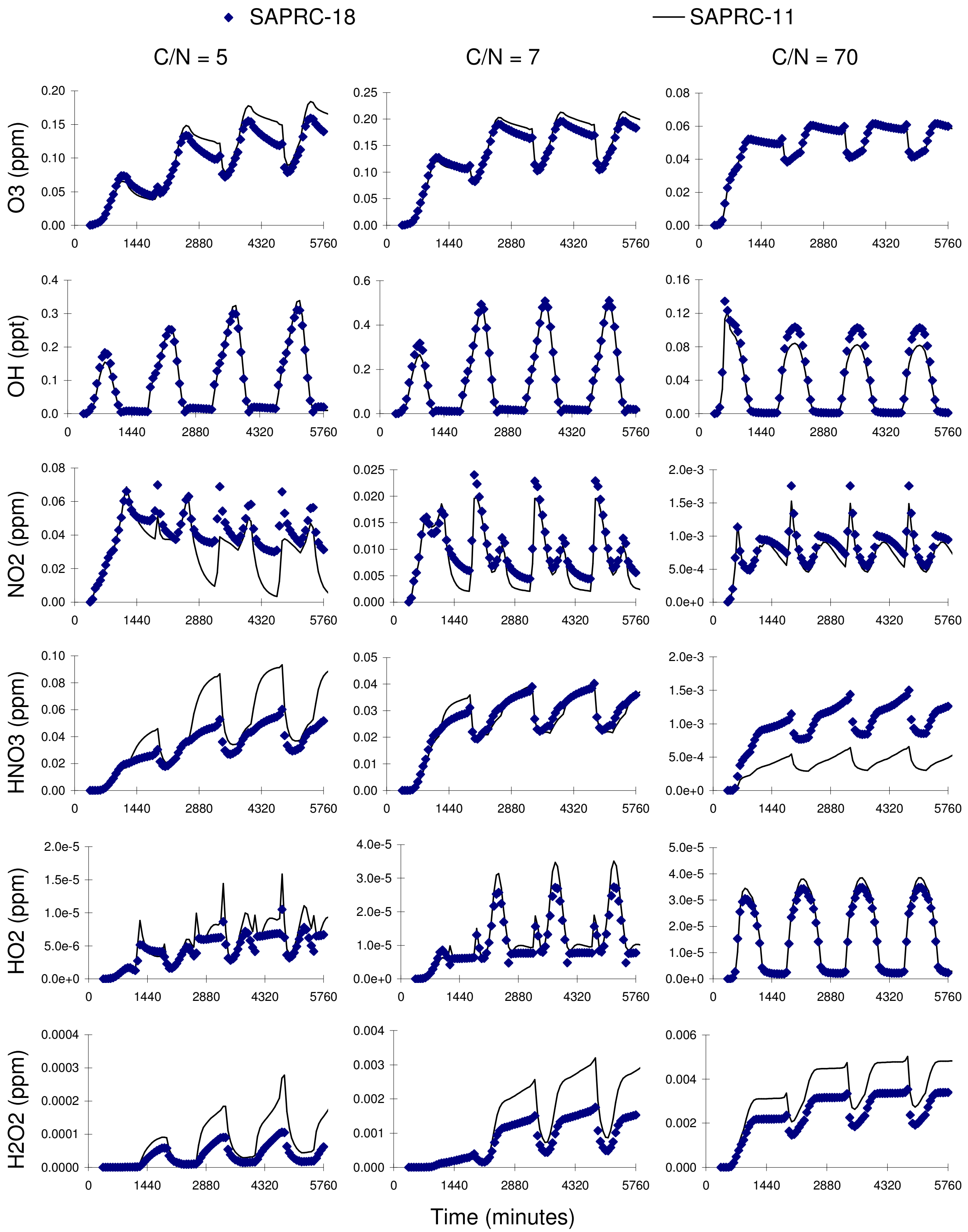


Figure 5. Results of model simulations of O_3, H_2O_2, and OH radicals in the four-day box model ambient simulations using the SAPRC-18 and SAPRC-11 mechanisms.

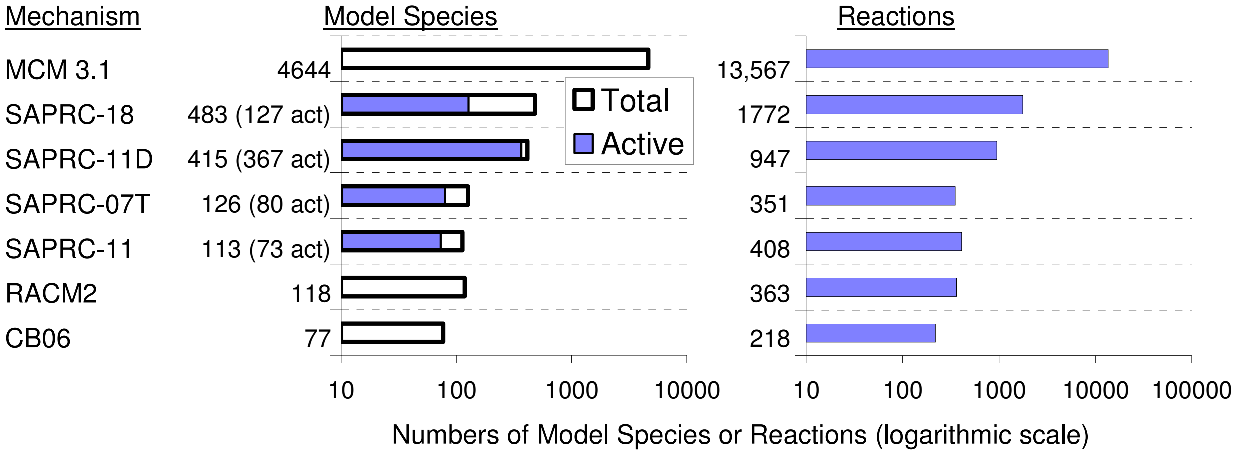
Discussion

The SAPRC-18 mechanism represents the results of the first complete update of all aspects of the SAPRC series of mechanisms since the development of SAPRC-07 (Carter, 2010a,b). The objective was to provide airshed modelers with an up-to-date mechanism with more of the chemical detail needed for more reliable toxics and SOA modeling, but not too large that it is impractical for use in 3D airshed models. An additional objective is to use the mechanism generation system to assure a direct and documented relationship between the mechanism and the underlying kinetic and mechanistic data, theories, and estimates. This is consistent with the systematic mechanism development approach outlined by Kaduwela et al (2015), involving first developing detailed mechanisms based on available data, mechanism generation tools, and structure-reactivity and other estimation methods, evaluating the detailed mechanisms using chamber and ambient data, then utilizing various methods to reduce or condense the detailed mechanism for specific airshed model applications.

For this work, the objective was to derive a mechanism that contains as much chemical detail as might be needed for model applications that benefit from chemical detail, but not more than necessary for this purpose. Such applications include modeling formation and destruction of toxic organic process, explicitly representing individual compounds that are important in emissions or of particular environmental concern, and predicting the formation of secondary organic aerosol (SOA) precursors based on the actual gas-phase chemistry. Because of this, a number of model species were added to the mechanism to explicitly represent selected important compounds and to take into account potential differences in SOA formation potential as well as gas-phase reactivity characteristics when representing reactions of oxidized products. This makes the mechanism well suited to be adapted to existing parameterized SOA models, and potentially to improved SOA treatments that take into account greater information it provides concerning the chemical compositions of the low organic products that are predicted to be formed. However, development of SOA models was beyond the scope of this project.

Comparisons of model sizes for SAPRC and other mechanisms are shown on Figure 6 and Figure 7. The earlier SAPRC mechanisms shown include SAPRC-07 (Carter, 2010a,b), SAPRC-11 (Carter and Heo, 2013), and SAPRC-11D, a version of SAPRC-11 where essentially all of the emitted species that have mechanisms developed are represented explicitly (Heo et al, 2014). The other mechanisms shown include MCM version 3.1 (Jenkin et al, 2003; Bloss et al, 2005; MCM, 2019), a version of the most widely-used semi-explicit mechanism, RACM2 (Goliff et al, 2013), the most recent of the RADM/RACM series of mechanisms by Stockwell and co-workers (e.g., Stockwell et al, 1990, 1997; Stockwell and Goliff, 2006, Goliff et al, 2013), and CB06 (Yarwood et al, 2010) is a representative of the widely-used Carbon bond series of mechanisms (e.g., Gery et al, 1998; Yarwood et al, 2005, Sarwar et al, 2008).

Figure 6 shows that the current mechanism is larger than any previous version of SAPRC mechanisms in terms of both numbers of reactions and model species, though still smaller, by more than an order of magnitude, than the MCM mechanisms. It is also larger than any known existing versions of the RADM/RACM or Carbon Bond mechanisms, as expected because of the greater level of chemical detail. Because of its more explicit treatment of peroxy reactions, discussed above, SAPRC-18 has even more reactions and species than SAPRC-11D, despite the fact that the latter mechanisms has many more model species to represent primary VOC emissions (see below). However, the steady-state approximation can be applied to almost all of the intermediate model species that are needed to implement this peroxy radical representation, reducing the number of model species that have to be transported during model simulations by almost a factor of 4, making it more consistent with the other SAPRC versions. This means that significant efficiencies could be achieved by implementing the



(Active" refers to the numbers of active species in SAPRC mechanisms, i.e., species where use of the steady-state approximation is not appropriate. This has not been specified in the documentation for the other mechanisms.)

Figure 6. Comparisons of numbers of explicitly represented emitted VOC species, all model species and reactions in various recent mechanisms.

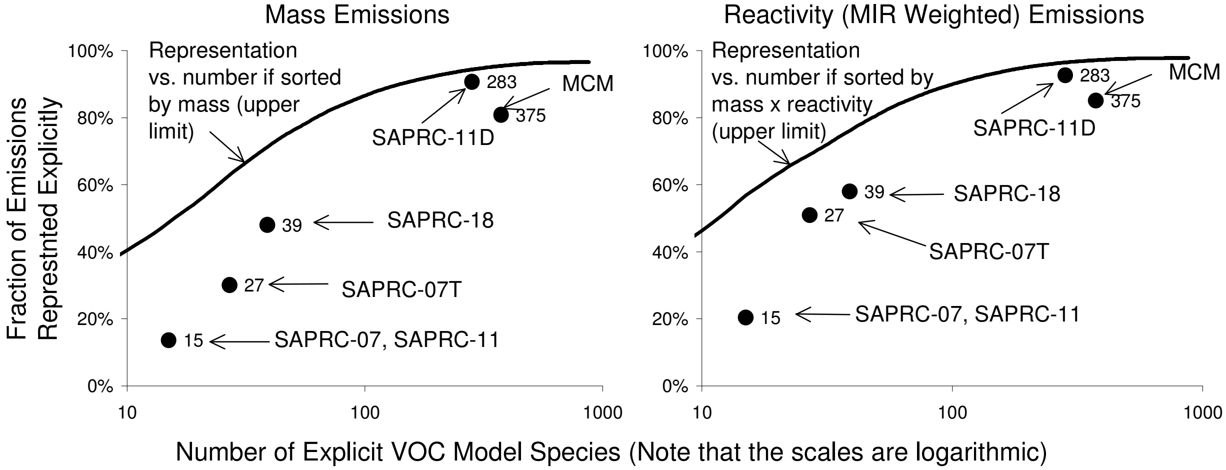


Figure 7. Contributions of explicitly represented emitted VOC compounds to the total mass and total MIR reactivity of anthropogenic emissions for various SAPRC mechanisms and MCM 3.3. The fractions do not include the ≤~5% of the emitted mass that cannot be speciated.

mechanism using software that can take advantage of the steady-state approximation[2]. However, the number of reactions will still be over 4 times greater than previous versions.

One goal of explicit and detailed mechanism development is to represent all emitted VOC compounds with explicit model species. Although this is not attainable in practice (because of many compounds are emitted in very small amounts and because some types of emissions are difficult to speciate) and not necessarily important in most model applications, it reduces lumping approximations for species emitted in larger quantities, and makes the mechanism potentially more useful for applications such as toxics modeling or source attribution. Figure 7 shows the extent to which these mechanisms represent individual compounds in anthropogenic VOC emissions explicitly, as opposed to being lumped with other compounds in simulations using the mechanisms. This figure shows plots of fractions of total anthropogenic mass (left plot) or reactivity as measured by MIR (Carter, 2010c) (right plot) against numbers of explicitly represented VOCs in a mixture representing total anthropogenic emissions (Carter, 2015)[3]. It can be seen that none of the mechanisms have enough model species to represent all anthropogenic emissions explicitly, though SAPRC-11D comes pretty close. Although MCM has more VOC model species, some of them are not currently contained in U.S. speciation profiles, and many compounds with nonnegligible contributions these profiles are not represented in MCM. The "upper limit" lines on Figure 7 indicates that increasing the fractions represented beyond those for SAPRC-11D and MCM would require hundreds of additional model species.

The target number of explicitly represented emitted compounds in SAPRC-18 was determined subjectively, by looking at the points of diminishing improvements in terms of chemical detail vs. numbers of species. SAPRC-18 represents about half of the emitted mass and reactivity explicitly, which is considered to represent an appropriate balance. It was built by extending SAPRC-07T by adding more explicit species, including some low reactivity compounds making large contributions to the mass. Although lumping the other half of the emissions introduces lumping approximations, this half represents many compounds with small contributions (though not in the aggregate), so errors in secondary pollutant predictions for individual compounds would be small and tend to cancel out. Of course, more model species are needed if the objective is to represent everything as explicitly as possible (as is the case for the MCM), or if we want to follow predictions of very large numbers of compounds.

However, SAPRC-18 is probably larger and has more detail than needed for many practical model applications, such as looking at the effects of emissions on ozone formation or overall radical levels, or supporting parameterized SOA models that only need input concerning how much certain model species react. A much more compact version of the mechanism would be expected to give very similar results, as was observed when CSAPRC-07, the condensed version of SAPRC-07, was developed from SAPRC-07 (Carter, 2010d). However, development of condensation techniques is beyond the scope of the present study. Instead, although efficiency is an overall longer-term objective, the objective for the current effort is to err on the side of being too detailed rather than too condensed in cases where the most appropriate level of detail is unclear. This way, the current version of SAPRC-18 can serve as a basis for subsequent work to develop condensed versions for specific applications. This is would not be possible if the application required chemical detail that the mechanism does not have.

The capability of the SAPRC-18 mechanism to predict effects of individual compounds on O_3 formation and (in many cases) OH radical levels was evaluated against the essentially the same large

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[2] Even greater efficiencies are expected by using the steady-state approximation on most of the many radical intermediates in the MCM.

[3] The mixture was derived by averaging relative emissions of various speciation categories for the profiles designed "US Emit", "CA Emit" and "Tx Emit" in Table 4 of Carter (2015). Each category was assigned a distribution of actual compounds, and these were used to derive the total average emissions in terms of relative amounts of individual compounds + unspeciated mass, which was 2-5%.

database of environmental chamber experiments as used for SAPRC-07 or SAPRC-11 (Carter, 2010a,b, Carter and Heo, 2012, 2013). The model performance of SAPRC-18 in simulating these data was comparable to that for SAPRC-11, and was about the same for ambient mixtures or compounds important in emissions. However, for certain types of compounds, such as some esters and individual alkylbenzenes, SAPRC-18 did not perform quite as well as SAPRC-11. This is because there was less compound-by-compound adjustment of uncertain aspects of the mechanisms when developing SAPRC-18 than was the case for SAPRC-07 and 11. A greater priority was given in SAPRC-18 to developing and evaluating general estimation methods applicable to wide ranges of compounds that may have been studied previously, as opposed to minimizing biases for each one of the many individual compounds studied. Consequently, the environmental chamber data were used less for mechanism adjustment, and more for evaluating the performance of our overall estimation methods, than is the case with previous versions.

Although the evaluation using the chamber data indicated problems with certain compounds that will need to be investigated further, the current mechanism performs reasonably well for the major compounds that are important in ambient simulations. However, additional work is needed for certain classes of compounds before the mechanism is used to update the MIR and other reactivity scales.

Additional work is also needed before this update to SAPRC-18 is ready for routine use in research and regulatory models. It needs to be implemented into 3D models and compared with previous mechanisms and ambient data, as done by Venecek et al (2018) with a previous version of this mechanism, SAPRC-16. Although it gave very similar predictions as SAPRC-11 in most cases, there were differences in HO_2 predictions that could not be explained. Any unexpected differences in model predictions due to mechanism updates should be investigated to assure that the changed predictions are not due to problems with the updates or the implementation.

Although SAPRC-07 included a module for chlorine chemistry, including chlorine chemistry was beyond the scope of this project, so chlorine chemistry is not part of this version of SAPRC-18. It would be relatively straightforward to update and add the inorganic portion of the SAPRC-07 chlorine module to this mechanism, and also the reactions of Cl· with many of the VOCs. MechGen can already predict reactions of alkanes and other saturated VOCs where the major reaction is Cl atoms abstracting a hydrogen and forming the same types of radicals that are formed in their OH reactions, albeit with somewhat different branching ratios, which MechGen can estimate. However, adding chlorine to double bonds forms Cl-substituted radicals that require additional thermochemical estimates to MechGen to process. This is another area that could be addressed in future versions of MechGen and the mechanism, should there be sufficient interest.

Work is continuing on documenting and improving the mechanism generation system that forms the basis for much of this mechanism in terms of reactions of organics. In addition, we plan to investigate possible condensation or reduction schemes that will make the mechanism more efficient to use in routine calculations. However, unless errors are found during the implementation and testing of the mechanism or completion of the documentation of the mechanism generation system, the mechanism documented in this report is the final version of SAPRC-18. Other than error corrections, any updates, condensations, or changes to levels of chemical detail will be incorporated into the next version of SAPRC.

Finally it should be pointed that the author, who has been the sole developer of the SAPRC mechanisms, is nearing full retirement. This may well be the last major update of the SAPRC mechanisms made by the current developer. Someone else will need to take over this effort if this series of mechanisms is to continue to be supported into the future.

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Appendix A. Supplementary Information Available

Because of their size, the following large tables are not included in the main body of this report, and are given only in part in this Appendix. Instead, these tables are given in their entirety in an Excel file, Saprc18.xls, which serves as an electronic supplement to this report. This is available, along with the text of this report and related documents and links, at the SAPRC-18 web site at http://www.cert.ucr.edu/~carter/SAPRC/18 (Carter, 2020c).

Table	Contents	Availability
Table A-1	List of model species in the mechanism for atmospheric and environmental chamber simulations	Appendix A (partial) and Saprc18.xls
Table A-2	List of model species added to the mechanism for evaluations against environmental chamber data	Appendix A (partial) and Saprc18.xls
Table A-3	Mixtures used to derive mechanisms of the mixture-dependent lumped organic model species	Appendix A (complete) and Saprc18.xls
Table A-4	List of reactions and documentation notes in the version of SAPRC-18 for atmospheric simulations	Appendix A (partial) and Saprc18.xls
Table A-5	List of reactions of VOC compounds added to the mechanism for evaluations against environmental chamber data	Appendix A (small parts) and Saprc18.xls
Table A-7	List of organic compounds that can be represented in airshed calculations using SAPRC-18 the model species used for them	Saprc18.xls only
Table A-6	Absorption cross sections and quantum yields for all the photolysis sets in the SAPRC-18 mechanism	Saprc18.xls only
Table A-7. Table A-8	List of environmental chamber experiments used for mechanism evaluation, and biases in the simulations of selected metrics using SAPRC-18 and SAPRC-11	Saprc18.xls only
Table A-9	List of incremental reactivity environmental chamber experiments used in the mechanism evaluation, and biases in the simulations of selected metrics using SAPRC-18 and SAPRC-11	Saprc18.xls only
Additional content	Model simulation inputs and outputs for testing mechanism implementation into model software (selected output is shown on Figure 4)	Saprc18.xls only

In addition to the latest version of this report, including this document and its electronic supplement Saprc18.xls, the SAPRC-18 web site also contains available documentation for the SAPRC-18 mechanism generation system (e.g., Carter, 2019), files needed to implement the mechanism, a link to the online mechanism generation system (Carter, 2020a), and a link to the emissions speciation database (Carter, 2020d) that now includes SAPRC-18 among the mechanisms it supports. These will be updated as new or revised documentation become available, or if corrections are needed to the mechanism.

If corrections to SAPRC-18 are found to be needed, new versions of this report, and the updated files implementing the mechanism, will be uploaded to the SAPRC-18 web site. The revised report(s) will include an appendix describing the changes that were made. Archives of previous versions will remain online if they implemented in models or used in publications.

Table A-1. List of model species in the mechanism for atmospheric and environmental chamber simulations.

Type Name	Based on [a]	Note [b]	Atoms C	Atoms N	Molec Wt [c]	Description
Constant Species.						
O2			-	-	32.00	Oxygen
M			-	-	28.85	Air
H2O			-	-	18.02	Water
H2			-	-	2.02	Hydrogen Molecules
HV		1	-	-	0.00	Light
Active Inorganic Species.						
O3			-	-	48.00	Ozone
NO			-	1	30.01	Nitric Oxide
NO2			-	1	46.01	Nitrogen Dioxide
NO3			-	1	62.01	Nitrate Radical
N2O5			-	2	108.02	Nitrogen Pentoxide
HONO			-	1	47.02	Nitrous Acid
HNO3			-	1	63.02	Nitric Acid
HNO4			-	1	79.02	Peroxynitric Acid
HO2H			-	-	34.01	Hydrogen Peroxide
CO			1	-	28.01	Carbon Monoxide
SO2			-	-	64.06	Sulfur Dioxide
Active Radical Species and Operators						
OH		2	-	-	17.01	Hydroxyl Radicals
HO2			-	-	33.01	Hydroperoxide Radicals
SumRO2		3	-	-		Total peroxy radical concentration
SumRCO3		3	-	-		Total acyl peroxy radical concentration
Steady State Inorganic Radical Species						
O3P			-	-		Ground State Oxygen Atoms
O1D			-	-		Excited Oxygen Atoms
Explicitly represented organics						
CH4	METHANE		1	-	16.04	Methane
ETHAN	ETHANE		2	-	30.07	Ethane
ETHEN	ETHENE		2	-	28.05	Ethylene
ACETL	ACETYLEN		2	-	26.04	Acetylene
PROP	PROPANE	4	3	-	44.10	Propane
NC4	N-C4	4	4	-	58.12	n-Butane
PROPE	PROPENE	4	3	-	42.08	Propene
BUT13	13-BUTDE	4	4	-	54.09	1,3-Butadiene
ISOP	ISOPRENE	4	5	-	68.12	Isoprene
APINE	A-PINENE	4	10	-	136.23	a-Pinene
BPINE	B-PINENE	4	10	-	136.23	b-Pinene
DLIMO	D-LIMONE	4	10	-	136.23	d-Limonene
BENZ	BENZENE	4	6	-	78.11	Benzene

Table A-1 (continued)

Type Name	Based on [a]	Note [b]	Atoms C	Atoms N	Molec Wt [c]	Description
TOLU	TOLUENE	4	7	-	92.14	Toluene
C2BEN	C2-BENZ	4	8	-	106.17	Ethyl Benzene
MXYL	M-XYLENE	4	8	-	106.17	m-Xylene
OXYL	O-XYLENE	4	8	-	106.17	o-Xylene
PXYL	P-XYLENE	4	8	-	106.17	p-Xylene
BZ123	123-TMB	4	9	-	120.19	1,2,3-Trimethyl Benzene
BZ124	124-TMB	4	9	-	120.19	1,2,4-Trimethyl Benzene
BZ135	135-TMB	4	9	-	120.19	1,3,5-Trimethyl Benzene
HCHO	FORMALD		1	-	30.03	Formaldehyde
MEOH	MEOH		1	-	32.04	Methanol
HCOOH	FORMACID		1	-	46.03	Formic Acid
MEOOH			1	-	48.04	Methyl Hydroperoxide
MECHO	ACETALD		2	-	44.05	Acetaldehyde
GLCHO	GLCLALD		2	-	60.05	Glycolaldehyde
ETOH	ETOH		2	-	46.07	Ethanol
AACID	ACETACID		2	-	60.05	Acetic Acid.
PAA	PAA		2	-	76.05	Peroxyacetic acid
ETOOH			2	-	62.07	Ethyl hydroperoxide
GLY	GLYOXAL		2	-	58.04	Glyoxal
ETCHO	PROPALD		3	-	58.08	Propionaldehyde
ACET	ACETONE		3	-	58.08	Acetone
MGLY	MEGLYOX		3	-	72.07	Methyl Glyoxal
ACRO	ACROLEIN	4	3	-	56.06	Acrolein
MEK	MEK	4	4	-	72.11	Methyl ethyl ketone
BACL	BIACETYL		4	-	86.09	Biacetyl
MACR	METHACRO	4	4	-	70.09	Methacrolein
MVK	MVK	4	4	-	70.09	Methyl Vinyl Ketone
PHEN	PHENOL	5	6	-	94.11	Phenol
BUDAL	BUTEDIAL	4	4		84.07	2-Butene-1,4-dial
Lumped Organic Compounds						
Mechanism for representative compounds or estimated parameterized mechanisms used.						
SESQ	B-CARYOP	4,6	15	-	204.35	Sesquiterpenes
BENX	BENZENE	4,7	6	-	78.11	Aromatics other than benzene that have kOH between 3.4 x 10^{-13} and 1.7 x 10^{-12} cm^3 $molec^{-1}$ s^{-1}
NAPS	NAPHTHAL	5,6	11	-	142.20	Naphthalenes, tetralins, and indans
STYRS	STYRENE	4,6	8	-	104.15	Aromatics other than styrene with double bonds outside of the aromatic ring.
ACYLS	ET-ACTYL	4,6	4	-	54.09	Acetylenes other than acetylene
FURNS	FURAN	4,6	5	-	68.07	Furans (mechanism based on furan)
RCOOH	PROPACID	4,6	3	-	74.08	C3+ organic acids (mechanism based on propionic acid).
BALD	BENZALD	6	7	-	106.13	Aromatic aldehydes (e.g., benzaldehyde)
CRES	O-CRESOL	5,6	7	-	108.14	Cresols

Table A-1 (continued)

Type Name	Based on [a]	Note [b]	Atoms C	Atoms N	Molec Wt [c]	Description
XYNL	24M-PHEN	5,6	8	-	122.16	Xylenols and higher alkylphenols
NPHE		8	6	1	139.11	Nitrophenols
SVPHE		9	7	-	124.14	Semi-volatile products of reactions of phenols
NAPPRD		8	12		172.22	Phenolic and other products formed from naphthalenes.
IMINE		11	2	1	34.07	Any compound with C=N bond. Assumed to rapidly hydrolize.
INHIB	AMP	12	4	-	89.14	Inhibiting compound such as siloxanes, aromatic isocyanates, alkyl iodides
PHOT		13	4	-	86.09	Unspecified photoreactive compounds such as nitrites or chloropicrin
Lumped Organic Compounds						
Mechanism for representative mixture used, derived using the mechanism generation system.						
ALK3	mix=ALK3	14,15	5	-	72.05	Alkanes that have kOH between 1.7 and 3.4 x 10^{-12} cm^3 $molec^{-1}$ s^{-1}
ALK4	mix=ALK4	14,15	6	-	86.12	Alkanes that have kOH between 3.4 and 6.8 x 10^{-12} cm^3 $molec^{-1}$ s^{-1}
ALK5	mix=ALK5	14,15	8	-	113.64	Alkanes that have kOH greater than 6.8 x 10^{-12} cm^3 $molec^{-1}$ s^{-1}
OLE1	mix=OLE1	14,15	5	-	70.13	Monoalkenes with only CH_2=CH- groups or allenes with kOH less than 5 x 10^{-12} cm^3 $molec^{-1}$ s^{-1}
OLE2	mix=OLE2	14,15	5	-	70.13	Monoalkenes with only -CH=CH- groups or allenes with kOH between than 5 x 10^{-12} and 4.8 x 10^{-11} cm^3 $molec^{-1}$ s^{-1}, and no double bonds in rings
OLE3	mix=OLE3	14,15	5	-	70.13	Alkenes other than terpenes or sesquiterpenes with only -CR=CH2 groups.
OLE4	mix=OLE4	14,15	5	-	70.13	Alkenes other than terpenes with non-conjugated -CH=CR- or -CR=CR- groups and possibly other double bonds and no double bonds in rings
OLEC	mix=OLEC	14,15	5	-	68.27	Cycloalkenes other than terpenes and sesquiterpenes with at least one double bond in the ring
OLED	mix=OLED	14,15	10	-	136.23	Conjugated dialkenes other than terpenes.
TERP	mix=TERP	14,16	10	-	136.23	Terpenes not represented explicitly
AMINS	mix=AMINS	14,15	2	1	43.45	Amines
ARO1	mix=ARO1	14,15	9	-	121.62	Aromatics that have kOH between 1.7 x 10^{-12} and 1.4 x 10^{-11} cm^3 $molec^{-1}$ s^{-1}
ARO2	mix=ARO2	14,15	9	-	120.33	Aromatics other than naphthalenes, tetralins, or indans that have kOH greater than 1.4 x 10^{-11} cm^3 $molec^{-1}$ s^{-1}
OTH1	mix=OTH1	14,17	3	-	77.75	Volatile saturated compounds that react only with OH, and have kOH between 1.4 x 10^{-13} and 1.7 x 10^{-12} cm^3 $molec^{-1}$ s^{-1}

Table A-1 (continued)

Type Name	Based on [a]	Note [b]	Atoms		Molec Wt [c]	Description
			C	N		
OTH2	mix=OTH2	14,15	3	-	62.09	Volatile saturated compounds that react only with OH, and have kOH between 1.7 and 3.4 x 10^{-12} cm^{3} molec^{-1} s^{-1}
OTH3	mix=OTH3	14,15	4	-	79.78	Volatile saturated compounds that react only with OH, and have kOH between 3.4 x 10^{-12} and 1.0 x 10^{-11} cm^{3} molec^{-1} s^{-1}
OTH4	mix=OTH4	14,15	4	-	92.61	Volatile saturated compounds that react only with OH, and have kOH greater than 1.0 x 10^{-11} cm^{3} molec^{-1} s^{-1}
RCHO	mix=RCHO	14,17	4	-	79.03	C4+ saturated aldehydes
RTCHO	mix=RTCHO	14,17	10	-	168.23	C10+ saturated aldeydes (mostly from terpenes)
KET2	mix=KET2	14,17	6	-	114.15	Photoreactive saturated ketones
LVKS	mix=LVKS	14,17	8	-	142.76	Ketones with at least 1 C=C double bond.
OLEP	mix=OLEP	14,17	10	-	188.86	Non-photoreactive, non-hydrocarbon compounds with C=C double bonds
OLEA1	mix=OLEA1	14,18	6	-	109.60	Unsaturated aldehydes with C=C next to -CHO
OLEA2	mix=OLEA2	14,17	10	-	168.84	Unsaturated aldehydes with C=C not next to the -CHO
		14,17				
RANO3	mix=RANO3	14,19	8	1	164.56	Aromatic organic nitrates
RCNO3	mix=RCNO3	14,17	5	1	156.13	Volatile organic carbonly nitrates
RHNO3	mix=RHNO3	14,17	8	1	190.23	Volatile organic hydroxy nitrates
RPNO3	mix=RPNO3	14,19	8	1	211.42	Organic nitrates with peroxy groups (formed primarily from aromatics)
RDNO3	mix=RDNO3	14,17	8	2	234.76	Volatile organic dinitrates
R1NO3	mix=R1NO3	14,17	5	1	130.46	Other volatile organic nitrates that react with OH radicals slower than 5 x 10^{-12} cm^{3} molec^{-2} sec^{-1}
R2NO3	mix=R2NO3	14,20	8	1	177.64	Other volatile organic nitrates that react with OH radicals faster than 5 x 10^{-12} cm^{3} molec^{-2} sec^{-1}
RUOOH	mix=RUOOH	14,21	6	-	132.41	Hydroperoxides with C=C double bonds
RAOOH	mix=RAOOH	14,18	7	-	179.26	Hydroperoxides with other peroxy groups and C=C bonds -- formed primarily from aromatics
HPALD	mix=HPALD	14,21	6	-	136.59	Unsaturated hydroperoxy carbonyls with CO-C=C-OOH structures
CROOH	mix=CROOH	14,21	7	-	169.88	Hydroperoxy carbonyls (other than HPALDs)
ROOH	mix=ROOH	14,17	5	-	106.24	Other hydroperoxides with 3+ carbons and vapor pressure greater than 1 ppb
AFG1	mix=AFG1	14,17	5	-	99.59	Monounsaturated 1,4-dialdehydes formed from aromatics
AFG2A	mix=AFG2A	14,17	5	-	106.88	Monounsaturated 1,4 aldehyde-ketones formed from aromatics, with at no substituents other than the aldehyde on the double bonds
AFG2B	mix=AFG2B	14,17	6	-	121.39	Monounsaturated 1,4 aldehyde-ketones formed from aromatics, with at least one substituent other than the aldehyde on a double bond

Table A-1 (continued)

Type Name	Based on [a]	Note [b]	Atoms		Molec Wt [c]	Description
			C	N		
AFG3	mix=AFG3	14,15	6	-	118.99	Monounsaturated 1,4-diketone aromatic products
PAN and PAN Analogues						
PAN			2	1	121.05	Peroxyacetyl nitrate
HOPAN		22	2	1	137.05	PAN analogue from glycolaldehyde, $HOCH_2C(O)OONO_2$
PPN			3	1	135.08	Peroxy propionyl nitrate
PAN2			3	1	135.08	Higher alkyl PAN analogues that react with OH radicals with a rate constant of 1 x 10^{-11} cm^3 molec^{-1} s^{-1} or less
PAN2N		23	2	2	182.05	Pan analogues with nitrate groups -- assumed to be primarily $O_2NOCH_2C(O)OONO_2$
PBZN			7	1	183.13	PAN analogues formed from Aromatic Aldehydes
APAN		22	3	1	133.06	PAN analogue formed from Acrolein
MAPAN			4	1	147.09	PAN analogues formed from Methacrolein and other unsaturated PAN analogues.
Non-Reacting Species (Active for testing -- can be removed if not needed)						
CO2			1	-	44.01	Carbon Dioxide
SULF					98.08	Sulfates (SO_3 or H_2SO_4)
NROG		24	-		1.00	Unreactive mass
NVOL		25	-		1.00	Nonvolatile mass
RNNO3		26	10	1	216.23	Organic nitrates with vapor pressure less than 1 ppb
OTHN		26	12	-	240.28	Other organic products with vapor pressures less than 1 ppb
NAMIN		27	4	2	89.14	Nitramines
MALAH		29	4	-	98.06	Maleic anhydride
IEPOX		24	5		118.13	Any 3-member ring cyclic ether with at least 2 OH groups.
Non-reacting counter species (Set to "dummy" as distributed to avoid numerical problems. Set to "Active" for testing.)						
XC		30	1	-	14.03	Lost Carbon or carbon in unreactive products
XN		31	-	1	46.01	Lost Nitrogen or nitrogen in unreactive products
Peroxy Radical Species in Base Mechanism						
MEO2		32	1	-		Methyl peroxy radicals
ETO2		32	2	-		Ethyl peroxy radicals
ETHEO2		32	2	-		Peroxy radical formed from ethene + OH
ETHEO2N		32	2	1		Peroxy radical formed from ethene + NO3
HCOMEO2		32	2	-		HCO-CH2OO. radicals, formed from acetaldehyde and other compounds.
C3RO2		32	3	-		C3 peroxy radicals formed from OH + ethane. Used to represent RO2 formed from PAN2.
ACETO2		32	3	-		CH_3-CO-CH_2OO. (formed from acetone)

Table A-1 (continued)

Type Name	Based on [a]	Note [b]	Atoms		Molec Wt [c]	Description
			C	N		
BZO2		32	6	-		Benzyl peroxy and substituted benzyl peroxy radicals
Acyl peroxy radical species						
MECO3		33	2	-		Acetyl Peroxy Radicals (forms PAN)
HOCCO3		22,33	2	-		Acyl peroxy radicals from glycolaldehyde, HOCH2C(O)OO. (forms HOPAN)
ETCO3		33	3	-		Peroxy propionyl radicals (forms PPN)
R2CO3		33	3	-		Higher saturated peroxy acyl radicals (forms PAN2)
R2NCO3		23,33	2	1		Peroxy acyl radicals with nitrate groups -- assumed to be primarily .OOC(O)CH_2ONO2
BZCO3		33	7	-		Peroxyacyl radical formed from Aromatic Aldehydes (forms PBZN)
ACO3		22,33	3	-		Peroxyacyl radicals formed from acrolein. (forms APAN)
MACO3		33	4	-		Peroxyacyl radicals formed from methacrolein and other unsaturated aldehydes (forms MAPAN)
Other organic radical or reactive intermediate species						
TBUO		34	4	-		t-Butoxy Radicals
BZO		34	6	-		Phenoxy or substituted phenoxy radicals
HCHO2		35	1	-	46.03	Unsubstituted stabilized Criegee biradical
MECHO2		35	2	-	60.05	Methyl substituted stabilized Criegee biradical
RCHO2		35	3	-	74.08	Other stabilized Criegee biradicals
Radical operator species						
RO2C		36	-	-		Peroxy Radical Operator representing NO to NO2 and NO3 to NO2 conversions, and the effects of peroxy radical reactions on acyl peroxy and other peroxy radicals (used in some multi-step mechanisms).
RO2XC		36	-	-		Peroxy Radical Operator representing NO consumption (used in conjunction with organic nitrate formation), and the effects of peroxy radical reactions on NO3, acyl peroxy radicals, and other peroxy radicals. (used in some multi-step mechanisms)
zR1NO3		36	5	-		Formation of R1NO3 after reaction with NO for lumped low yield peroxy reactions
zR2NO3		36	8	-		As above, but for R2NO3
zRANO3		36	8	-		As above, but for RANO3
zRCNO3		36	5	-		As above, but for RCNO3
zRHNO3		36	8	-		As above, but for RHNO3
zRDNO3		36	8	1		As above, but for RDNO3
zRPNO3		36	8	-		As above, but for RPNO3

Table A-1 (continued)

Type Name	Based on [a]	Note [b]	Atoms C	Atoms N	Molec Wt [c]	Description
zRNNO3		36	10	-		As above, but for RNNO3
xNAMIN		27,37	4	1		Nitramine precursor frormed from amines with no alpha hydrogens
NPRAD		8	12	-		Simplified representative of unknown naphthalene intermediates that react with NO2 forming products
Peroxy radical Intermediates in generated mechanisms (several such species for each reacting compound) See the electronic version for a complete listing [d]						
<spec>_Pn		38				Peroxy radical intermediates with slow or no unimolecular reactions. This is the n'th such intermediate formed in the reactions of the model species <spec>.
<spec>_An		39				Peroxy radical intermediates with relatively fast unimolecular reactions. This is the n'th such intermediate formed in the reactions of the model species <spec>.

[a] Detailed model species or mixture name used to derive the mechanism (organic compounds). See mechanism listing and notes if blank. See Table A-3 for compounds used to derive mixtures. See "DMS Asst's" sheet for listing of detailed model species.

[b] Notes for individual species

1 Fraction of light intensity relative to maximum or clear sunlight. May not be needed depending on photolyses are handled by the model. It is not included in MEC files prepared for the CMAQ model.

2 It may be appropriate to use the steady state approximation for this species but this is not possible using the way the SAPRC modeling software implements the steady state approximation.

3 These are the sums of total concentrations of peroxy (SumRO2) or acyl peroxy (SumRCO3) radicals that react with other peroxy radicals, and are used to compute the rates of these peroxy + peroxy reactions. Every reaction that forms a peroxy or acyl peroxy radical of this type also forms the corresponding "Sum" species at the same yield, and their loss reactions with NO, NO2 (for SumRCO3), HO2, and each other are included as separate reactions. Note that this gives only an approximation of the rates of these peroxy + peroxy reactions because it ignores loss by unimolecular reactions that are non-negligible for some peroxy radicals and also it neglects the fact that self-reactions involve loss of two rather than one radical. However, tests against a more exact solution give essentially the same results in atmospheric simulations, so the complexity of using a more exact solution is not necessary. Note that peroxy or acyl peroxy radicals that have unimolecular reaction rate constants greater than around 0.33 sec^{-1} are assumed not to have significant bimolecular reactions other than with NO and those that have unimolecular rate constants greater than about 133 sec^{-1} are assumed to have no bimolecular reactions. These are not included in these "Sum" species since they do not react with other peroxy radicals.

4 Mechanism derived using the current SAPRC mechanism generation system.

5 The detailed mechanism for this type of compound cannot yet be estimated. A simplified parameterized mechanism that is adjusted to fit chamber data is used.

Table A-1 (continued)

6 The compound used to derive the mechanism is the most important compound of this type according to the representative anthropogenic and biogenic mixtures.

7 The benzene mechanism may overestimate the reactivity of some compounds of this type, but their contributions to total reactivity is generally negligible.

8 The detailed mechanism for this type of compound cannot yet be estimated. A simplified parameterized mechanism is used.

9 A highly parameterized mechanism based on those used for the phenols is used. This is highly uncertain because there are no data to evaluate it.

10 The identities and mechanisms of these products are unknown. A highly simplified mechanism is used.

11 The main compound of this type is $CH_3CH=NH$, which is assumed to rapidly hydrolyze to form acetaldehyde and ammonia. Therefore it is treated as in steady state and replaced by the formation of MECHO and XN. "Lost nitrogen" is used for ammonia because it is not included in the gas-phase mechanism, but should be replaced with NH3 if it is added to the mechanism.

12 Compounds that efficiently inhibit radicals can have very different mechanisms, but amines such as AMP appear to be the most important in emissions so AMP is used to represent their mechanisms. Although this can be highly approximate, it is better than ignoring inhibiting compounds by treating them as unreactive, which is the usual practice for most mechanisms.

13 A highly simplified mechanism is used for photoreactive compounds that are relatively unimportant in emissions and not well represented by other model species.

14 The mechanism for this model species are derived from mechanisms of the individual components of the mixture of representative compounds represented by this model species, which in turn are derived using the mechanism generation system. The mixture used is indicated in the other footnote. The compositions and derivations of these mixtures are given in Table A-3.

15 The mixture used is the "U.S total" emissions mixture, which is the same as the "US Emit" mixture given by Carter (2015).

16 The mixture used is the "Megan G" biogenic mixture of Guenther (2014), as given by Carter (2015). See also Guenther et al (2012).

17 The mixture used is the mixture of products predicted from the reactions of OH with the components of the "U.S total" emissions mixture.

18 The mixture used is the mixture of products predicted from the reactions of OH with isoprene. This is the main source for compounds represented by this model species in ambient simulations.

19 The mixture used is the mixture of products predicted from the reactions of NO_3 radicals with the components of the "U.S total" emissions mixture. This is the only significant source for compounds represented by this model species in ambient simulations.

20 The mixture used is the mixture of products predicted from the reactions of HO_2 with peroxy radicals formed in the reactions of OH with isoprene. This is the main source for compounds represented by this model species in ambient simulations.

21 The mixture used is the mixture of products predicted from the reactions of HO_2 with peroxy radicals formed in the reactions of OH with the components of the "U.S total" emissions mixture.

22 It may not be a bad approximation for atmospheric simulations to lump HOPAN with PAN or APAN with MAPAN, but they are kept separate for now. The same is applicable for the acyl peroxy radical model species they form.

23 This is represented separately from other higher saturated PAN analogues in order to account better for the fate of nitrogen. The same is applicable for the acyl peroxy radical model species this forms. This is a non-negligible product in the reactions of carbonyl nitrates.

Table A-1 (continued)

24 This represents unreactive compounds on a mass rather than molar basis, both in emissions and when formed as a product of organic reactions. Note that the yields given for the reactions forming unreactive compounds are given by moles unreactive compound(s) formed x their molecular weights, to give mass yields.

25 The "NVOL" model species is used to represent nonvolatile mass in "gas" emissions profiles and is not used in the gas-phase mechanism. Note that it is not used to represent nonvolatile compounds formed in the gas-phase reactions. These are represented by "RNNO3" on a molar basis if the compound is an organic nitrate and by "OTHN" on a molar basis if not.

26 Compounds represented by these model species are estimated to be non-volatile and their gas-phase reactions are not included in the mechanism. Their molecular weights can be used to estimate their mass contributions to the total SOA formed.

27 These are predicted to be important products in reactions of amines without alpha hydrogens, which are predicted to form radicals that react primarily with NO_2 to form nitramines. Nitramines are not expected to be highly reactive in the gas phase so the mechanism has gas-phase reactions for them.

28 This is a relatively slow reacting product predicted to be formed in high yields from photolyses of photoreactive aromatic products that is assumed to be unreactive in the mechanism. It is retained as a product because it is potentially useful to indicate the extent of these reactions.

29 These are believed to be important SOA precursors formed in isoprene reactions under low NOx conditions. They are not expected to be very reactive in the gas phase but are expected to add water in the condensed phase to form highly nonvolatile compounds.

30 This is a counter species used to track carbon imbalance in lumped reactions, and can be formed in non-negligible (positive or negative) yields in some lumped reactions. It is recommended not to use this as an active species in ambient simulations because sometimes it can go negative and cause numerical instability for some solvers. It is not included in MEC files prepared for the CMAQ model.

31 This is a counter species used to track nitrogen imbalance in lumped reactions. Reactions forming or losing it are generally minor but sometimes nonnegligible in ambient simulations, and it is used primarily track nitrate formation in low yield peroxy reactions. It should be minor in ambient simulations but can be used to check this. It should not go negative but if it does it may cause numerical instability for some solvers. If numerical problems are observed, try removing this as an active species.

32 The steady state approximation can be used for all of these peroxy radical model species. Their concentrations are included in SumRO2, so any reaction forming them also forms SumRO2.

33 The steady state approximation can be used for all of these acyl peroxy radical model species. Their concentrations are included in SumRCO3, so any reaction forming them also forms SumRCO3.

34 These react primarily with NO_2, but low NO_x reactions are also included.

35 The mechanism includes reactions of the stabilized Crigiee biradicals is reaction with water, SO_2 and NO_2, with the reaction with water generally dominating. However, the rate constants for the reaction with water are uncertain, and its relative importance may vary with structure in a way that is not represented in the current mechanism.

36 If a peroxy radical is estimated to be formed in less than 10% overall yield in a generated mechanism, it is not represented explicitly but by the mixture of products predicted to be formed from its reactions, and reactions of radicals it form, with NO and unimolecular reactions (if applicable). This reaction lumping approach is similar to the approach used in earlier versions of SAPRC, but is used in this version only for the more minor pathways, to avoid the need for

multiple model species only to represent relatively unimportant pathways. The ratio of NO to unimolecular reactions is estimated for this purpose using a representative NO concentration of 0.5 ppb. (Both the fraction reaction where this approximation is used and the representative NO concentration is a mechanism generation option that can be changed.) The model species "RO2C" is used to represent the effects of NO to NO_2 conversions from multi-generational peroxy reactions, and "RO2XC" is used to reflect the consumption of NO to form nitrates. The formation of nitrates in these minor NO reactions are represented by the zRNO3 model species, which primarily react with NO to form the corresponding nitrate but can also react under low NO_x conditions to form non-nitrate products.

37 This represents the formation of the NAMIN model species after an NO to NO_2 conversion, similar to the treatment of such products in SAPRC-07, but in this case only used when this is formed in low yields.

38 These are peroxy radical model species derived by the mechanism generation system to represent reactions of peroxy radicals formed in yields of greater than 10%. Some of these can undergo unimolecular reactions but in all cases the unimolecular rate constant is estimated to be less than 0.33 sec^{-1}, which is sufficiently low that reactions with peroxy radicals are expected to be non-negligible. Peroxy radicals that are formed by the same reactions and that are estimated to have negligible unimolecular reactions (estimated rate constant less than 3.3×10^{-3} sec^{-1}) are lumped together, but those with non-negligible unimolecular reactions are represented separately. The compounds whose mechanism uses these radicals are indicated in the "Description" column of this table in the electronic supplement, and also by the name of the radical. The steady state approximation can be used for all of these model species so they do not have to be transported. SumRO2 includes the concentrations of all these species, and any reaction forming them also forms SumRO2 in equal yields.

39 These are peroxy radical model species derived by the mechanism generation system to represent reactions of peroxy radicals formed in yields of greater than 10%, and that have unimolecular reactions with rate constants between 0.33 and 133 sec^{-1}. Peroxy radicals with lower unimolecular rate constants are assumed to react with other peroxy radicals and are included with "_Pn" model species discussed in the previous footnote, while those with higher unimolecular rate constants are assumed to react only unimolecularly and are replaced by their products. Peroxy radicals with this unimolecular rate constant rang are assumed to react either unimolecularly or with NO but not by other bimolecular reactions, so they are not included in SumRO2. The steady state approximation should be used for all of these model species so they do not have to be transported.

[c] Molecular weights are not assigned for steady state or counter species. They should not be needed.

[d] The electronic version of this table is available at http://www.cert.ucr.edu/~carter/SAPRC/18/Saprc18.xls.

Table A-2. List of model species added to the mechanism for evaluating mechanisms against environmental chamber data..

Type and Name	Atoms		Molecular Weight	Description (and SAPRC standard model species name)
	C	N		
Chamber VOCs				
NC6	6	-	86.18	n-Hexane (N-C6)
NC8	8	-	114.23	n-Octane (N-C8)
CYCC6	6	-	84.16	Cyclohexane
C2BUT	4	-	56.11	Cis-2-Butene (C-2-BUTE)
T2BUT	4	-	56.11	Trans-2-Butene (T-2-BUTE)
N-C6F14	6	-	338.04	Perfluoro-n-hexane
CL2IBUTE	4	-	125.00	2-(Chloromethyl)-3-chloropropene
BUTE1	4	-	56.11	1-Butene (1-BUTENE)
PNTE1	5	-	70.13	1-Pentene (1-PENTEN)
HEXE1	6	-	84.16	1-Hexene (1-HEXENE)
IBUTE	4	-	56.11	Isobutene (ISOBUTEN)
M2BU2	5	-	70.13	2-Methyl-2-Butene (2M-2-BUT)
C2C5E	5	-	70.13	cis-2-Pentene (C-2-PENT)
T2C5E	5	-	70.13	trans-2-Pentene (T-2-PENT)
NC3BZ	9	-	120.19	n-Propyl Benzene (N-C3-BEN)
IC3BZ	9	-	120.19	Isopropyl Benzene (cumene) (I-C3-BEN)
METTL	9	-	120.19	m-Ethyl Toluene (M-ET-TOL)
OETTL	9	-	120.19	o-Ethyl Toluene (O-ET-TOL)
PETTL	9	-	120.19	p-Ethyl Toluene (P-ET-TOL)
TETRL	10	-	132.20	Tetralin (TETRALIN)
NAPH	10	-	128.17	Naphthalene (NAPHTHAL)
NAP23	12	-	156.22	2,3-Dimethyl Naphthalene (23-DMN)
MPK	5	-	86.13	2-Pentanone
CC6K	6	-	98.14	Cyclohexanone (CC6-KET)
MIBK	6	-	100.16	4-Methyl-2-Pentanone
C7KT2	7	-	114.19	2-Heptanone (C7-KET-2)
BZCOH	7	-	108.14	Benzyl alcohol (BZ-CH2OH)
NC12	12	-	170.33	n-Dodecane (N-C12)
NC14	14	-	198.39	n-Tetradecane (N-C14)
NC15	15	-	212.41	n-Pentadecane (N-C15)
NC16	16	-	226.44	n-C16 (N-C16)
IC4	4	-	58.12	Isobutane (2-ME-C3)
ISOC8	8	-	114.23	2,2,4-Trimethyl Pentane (224TM-C5)
I3C10	10	-	142.28	2,6-Dimethyl Octane (26DM-C8)
IC10	10	-	142.28	2-Methyl Nonane (2-ME-C9)
I2C10	10	-	142.28	3,4-Diethyl Hexane (34-DE-C6)
C6CY6	12	-	168.32	Hexyl Cyclohexane (C6-CYCC6)
C8CY6	14	-	196.37	Octyl Cyclohexane (C8-CYCC6)
CC6E	6	-	82.14	Cyclohexene (CYC-HEXE)
CARE3	10	-	136.23	3-Carene (3-CARENE)
SABIN	10	-	136.23	Sabinene (SABINENE)

Table A-2 (continued)

Type and Name	Atoms		Molecular Weight	Description (and SAPRC standard model species name)
	C	N		
STYR	8	-	104.15	Styrene (STYRENE)
IC3OH	3	-	60.10	Isopropyl Alcohol (I-C3-OH)
TC4OH	4	-	74.12	t-Butyl Alcohol (T-C4-OH)
C81OH	8	-	130.23	1-Octanol (1-C8-OH)
C8OH2	8	-	130.23	2-Octanol (2-C8-OH)
C8OH3	8	-	130.23	3-Octanol (3-C8-OH)
ETGLC	2	-	62.07	Ethylene Glycol (ET-GLYCL)
PGLCL	3	-	76.09	Propylene Glycol (PR-GLYCL)
MEOME	2	-	46.07	Dimethyl Ether (ME-O-ME)
ETOET	4	-	74.12	Diethyl Ether (ET-O-ET)
MTBE	5	-	88.15	Methyl t-Butyl Ether
MEPOL	4	-	90.12	1-Methoxy-2-Propanol (MEOC3OH)
ETOXL	4	-	90.12	2-Ethoxyethanol (ETO-ETOH)
BUOET	6	-	118.17	2-Butoxyethanol (BUO-ETOH)
DGEE	6	-	134.17	2-(2-Ethoxyethoxy) Ethanol
DGBE	8	-	162.23	2-(2-Butoxyethoxy)-Ethanol
MEACT	3	-	74.08	Methyl Acetate (ME-ACET)
ETACT	4	-	88.11	Ethyl Acetate (ET-ACET)
IPRAC	5	-	102.13	Isopropyl Acetate (IPR-ACET)
MIBUT	5	-	102.13	Methyl Isobutyrate (ME-IBUAT)
MPVAT	6	-	116.16	Methyl Pivalate (ME-PVAT)
BUACT	6	-	116.16	n-Butyl Acetate (BU-ACET)
TBACT	6	-	116.16	t-Butyl Acetate (TBU-ACET)
DMC	3	-	90.08	Dimethyl Carbonate
PC	4	-	102.09	Propylene Carbonate
MIPRC	5	-	118.13	Methyl Isopropyl Carbonate (MIPR-CB)
PGMEA	6	-	132.16	1-Methoxy-2-Propyl Acetate (PGME-ACT)
DBE4	6	-	146.14	Dimethyl Succinate (DBE-4)
DBE5	7	-	160.17	Dimethyl Glutarate (DBE-5)
IPRAM	3	1	59.11	isopropylamine (IPR-AMIN)
TBUAM	4	1	73.14	t-butyl amine (TBU-AMIN)
ETOAM	2	1	61.08	Ethanolamine (ETOH-NH2)
AMP	4	1	89.14	2-Amino-2-Methyl-1-Propanol
FURAN	4	-	68.07	Furan
TEXOL	12	-	216.32	Texanol® isomers
<u>Peroxy radical Intermediates in generated mechanisms (slow or no unimolecular reactions)</u>				
See the electronic version for a complete listing [a]				
<spec>_Pn	Same as <spec>		Not used	Peroxy radical intermediates with slow or no unimolecular reactions (Pn) or with relatively fast unimolecular reactions. This is the n'th such intermediate formed in the reactions of the model species <spec>.
<spec>_An	Same as <spec>		Not used	

[a] See Table A-2 in Saprc18.xls, the electronic version of this report. This Excel file is available online at http://www.cert.ucr.edu/~carter/SAPRC/18.

Table A-3. Mixtures used to derive mechanisms of the mixture-dependent lumped organic model species.

Species	Fac [a]	DMS [b]	Mixture derivation or compound structure [c]
ALK3	99.8%	Total	Derived from UStot Mixture
	62.9%	2-ME-C3	CH3-CH(CH3)-CH3
	25.8%	224TM-C5	CH3-CH(CH3)-CH2-C(CH3)(CH3)-CH3
	11.1%	22-DM-C4	CH3-CH2-C(CH3)(CH3)-CH3
ALK4	90.9%	Total	Derived from UStot Mixture
	31.8%	2-ME-C4	CH3-CH2-CH(CH3)-CH3
	15.4%	N-C5	CH3-CH2-CH2-CH2-CH3
	9.8%	2-ME-C5	CH3-CH2-CH2-CH(CH3)-CH3
	7.9%	N-C6	CH3-CH2-CH2-CH2-CH2-CH3
	6.0%	3-ME-C5	CH3-CH2-CH(CH3)-CH2-CH3
	4.7%	ME-CYCC5	CH3-CH*-CH2-CH2-CH2-CH2*
	3.9%	N-C7	CH3-CH2-CH2-CH2-CH2-CH2-CH3
	3.3%	23-DM-C4	CH3-CH(CH3)-CH(CH3)-CH3
	2.9%	23-DM-C5	CH3-CH2-CH(CH3)-CH(CH3)-CH3
	2.8%	2-ME-C6	CH3-CH2-CH2-CH2-CH(CH3)-CH3
	2.4%	3-ME-C6	CH3-CH2-CH2-CH(CH3)-CH2-CH3
ALK5	90.3%	Total	Derived from UStot Mixture
	17.6%	ME-CYCC6	CH3-CH*-CH2-CH2-CH2-CH2-CH2*
	12.1%	CYCC6	CH2*-CH2-CH2-CH2-CH2-CH2*
	11.7%	N-C8	CH3-CH2-CH2-CH2-CH2-CH2-CH2-CH3
	7.4%	3-ME-C7	CH3-CH2-CH2-CH2-CH(CH3)-CH2-CH3
	5.4%	N-C12	CH3-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH3
	5.4%	N-C9	CH3-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH3
	5.0%	N-C10	CH3-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH3
	4.8%	25-DM-C6	CH3-CH(CH3)-CH2-CH2-CH(CH3)-CH3
	4.0%	23-DM-C6	CH3-CH2-CH2-CH(CH3)-CH(CH3)-CH3
	3.8%	N-C11	CH3-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH3
	3.2%	ET-CYCC6	CH3-CH2-CH*-CH2-CH2-CH2-CH2-CH2*
	2.8%	13DMCYC6	CH3-CH*-CH2-CH2-CH2-CH(CH3)-CH2*
	2.7%	3ME-C8	CH3-CH2-CH2-CH2-CH2-CH(CH3)-CH2-CH3
	2.7%	3ET-C5	CH3-CH2-CH(CH2-CH3)-CH2-CH3
	1.7%	ET-CYCC5	CH3-CH2-CH*-CH2-CH2-CH2-CH2*
OLE1	90.6%	Total	Derived from UStot Mixture
	50.0%	3M-1-BUT	CH2=CH-CH(CH3)-CH3
	29.6%	1-BUTENE	CH2=CH-CH2-CH3
	11.1%	1-PENTEN	CH2=CH-CH2-CH2-CH3
OLE2	92.2%	Total	Derived from UStot Mixture
	35.3%	T-2-PENT	CH3-^CH=CH-^CH2-CH3
	19.1%	T-2-BUTE	CH3-^CH=CH-^CH3
	17.3%	C-2-PENT	CH3-^CH=CH-vCH2-CH3
	15.6%	C-2-BUTE	CH3-^CH=CH-vCH3
	2.7%	T4M2-C5E	CH3-^CH=CH-^CH(CH3)-CH3
	2.2%	T-3-C6E	CH3-CH2-^CH=CH-^CH2-CH3
OLE3	93.4%	Total	Derived from UStot Mixture

Table A-3. (continued).

Species	Fac [a]	DMS [b]	Mixture derivation or compound structure [c]
	52.8%	2M-1-BUT	CH2=C(CH3)-CH2-CH3
	40.6%	ISOBUTEN	CH2=C(CH3)-CH3
OLE4	91.4%	Total	Derived from UStot Mixture
	82.3%	2M-2-BUT	CH3-CH=C(CH3)-CH3
	9.1%	2M-2-C5E	CH3-CH2-CH=C(CH3)-CH3
OLEC	95.1%	Total	Derived from UStot Mixture
	57.6%	CYC-PNTE	CH*=CH-CH2-CH2-CH2*
	29.1%	3MECC5E	CH3-CH*-CH=CH-CH2-CH2*
	8.4%	CYC-HEXE	CH*=CH-CH2-CH2-CH2-CH2*
OLED	99.9%	Total	Derived from UStot Mixture
	69.0%	B-OCIMEN	CH2=CH-C(CH3)=CH-CH2-CH=C(CH3)-CH3
	30.9%	MYRCENE	CH2=CH-C(=CH2)-CH2-CH2-CH=C(CH3)-CH3
TERP	90.8%	Total	Derived from Megan2 Mixture
	40.6%	SABINENE	CH2=C*1-CH2-CH2-C*2(CH2-CH*12)-CH(CH3)-CH3
	32.0%	3-CARENE	CH3-C*1=CH-CH2-CH*2-CH(CH2*1)-C*2(CH3)-CH3
	18.2%	CAMPHENE	CH2=C*1-CH*2-CH2-CH2-CH(CH2*2)-C*1(CH3)-CH3
AMINS	90.9%	Total	Derived from UStot Mixture
	51.6%	ET-AMINE	CH3-CH2-NH2
	39.3%	TM-AMINE	CH3-N(CH3)-CH3
ARO1	92.0%	Total	Derived from UStot Mixture
	44.3%	N-C3-BEN	CH3-CH2-CH2-aC*-aCH-aCH-aCH-aCH-aCH*
	27.0%	2MPR-BEN	CH3-CH(CH3)-CH2-aC*-aCH-aCH-aCH-aCH-aCH*
	20.6%	I-C3-BEN	CH3-CH(CH3)-aC*-aCH-aCH-aCH-aCH-aCH*
ARO2	90.9%	Total	Derived from UStot Mixture
	31.9%	M-ET-TOL	CH3-CH2-aC*-aCH-aCH-aCH-aC(CH3)-aCH*
	14.9%	P-CYMENE	CH3-CH(CH3)-aC*-aCH-aCH-aC(CH3)-aCH-aCH*
	13.6%	P-ET-TOL	CH3-CH2-aC*-aCH-aCH-aC(CH3)-aCH-aCH*
	10.7%	O-ET-TOL	CH3-CH2-aC*-aCH-aCH-aCH-aCH-aC*-CH3
	10.3%	O-CYMENE	CH3-CH(CH3)-aC*-aCH-aCH-aCH-aCH-aC*-CH3
	6.3%	M-CYMENE	CH3-CH(CH3)-aC*-aCH-aCH-aCH-aC(CH3)-aCH*
	3.1%	12M4ETBN	CH3-CH2-aC*-aCH-aCH-aC(CH3)-aC(CH3)-aCH*
OTH1	95.6%	Total	Derived from UStot OHprods Mixture
	78.1%	ME-FORM	CH3-O-CHO
	17.5%		CH3-C(CH3)(CH3)-O-CHO
OTH2	99.2%	Total	Derived from UStot Mixture
	76.0%	ME-O-ME	CH3-O-CH3
	23.2%	MTBE	CH3-O-C(CH3)(CH3)-CH3
OTH3	91.8%	Total	Derived from UStot Mixture
	61.2%	I-C3-OH	CH3-CH(CH3)-OH
	19.4%	PR-ACET	CH3-CH2-CH2-O-CO-CH3
	4.9%	BU-ACET	CH3-CH2-CH2-CH2-O-CO-CH3
	3.4%	IPR-ACET	CH3-CO-O-CH(CH3)-CH3
	2.8%	S-C4-OH	CH3-CH2-CH(CH3)-OH

Table A-3. (continued).

Species	Fac [a]	DMS [b]	Mixture derivation or compound structure [c]
OTH4	90.8%	Total	Derived from UStot Mixture
	29.0%	ET-GLYCL	HO-CH2-CH2-OH
	28.0%	PR-GLYCL	CH3-CH(OH)-CH2-OH
	17.8%	BUO-ETOH	CH3-CH2-CH2-CH2-O-CH2-CH2-OH
	4.1%	THF	CH2*-CH2-CH2-O-CH2*
	3.0%	1-C6OH	CH3-CH2-CH2-CH2-CH2-CH2-OH
	1.8%	MOEOETOH	CH3-O-CH2-CH2-O-CH2-CH2-OH
	1.7%	DET-GLCL	HO-CH2-CH2-O-CH2-CH2-OH
	1.3%	MEOC3OH	CH3-O-CH2-CH(CH3)-OH
	1.2%	PGME-ACT	CH3-CO-O-CH(CH3)-CH2-O-CH3
	1.0%	DPR-GLCL	CH3-CH(OH)-CH2-O-CH2-CH(CH3)-OH
	1.0%	PROXC3OH	CH3-CH2-CH2-O-CH2-CH(CH3)-OH
	1.0%	GLYCERL	HO-CH2-CH(OH)-CH2-OH
RCHO	83.2%	Total	Derived from UStot OHprods Mixture
	24.1%	2MEC3AL	CH3-CH(CH3)-CHO
	15.2%		HCO-CH2-CH2-CH2-OH
	8.3%	1C4RCHO	CH3-CH2-CH2-CHO
	7.1%		HCO-CH2-CHO
	4.9%		CH3-CH(OH)-CH2-CH2-CHO
	4.8%		CH3-CH(CHO)-CH2-CH2-OH
	4.4%		CH3-CH(CH2-CHO)-CH2-OH
	3.7%	RCHO-2	CH3-C(CH3)(OH)-CH2-CH2-CHO
	2.9%		CH3-CH(CHO)-OH
	1.6%	GLTRALD	HCO-CH2-CH2-CH2-CHO
	1.4%		HCO-CH(CH2-CH2-OH)-CO-CH2-OH
	1.3%		CH3-CO-CH2-CH(OH)-CH2-CH2-CHO
	1.2%		HCO-CH2-CH2-O-CHO
	1.2%		CH3-C(CH3)(CHO)-CH2-C(CH3)(CH3)-OH
	1.1%		CH3-CH(CHO)-CH2-CH(CH3)-OH
RTCHO	99.9%	Total	Derived from UStot OHprods Mixture
	81.8%		CH3-CO-CH*-CH2-CH(CH2-CHO)-C*(CH3)-CH3
	18.1%		CH3-CO-CH2-CH*-CH(CH2-CHO)-C*(CH3)-CH3
KET2	78.8%	Total	Derived from UStot OHprods Mixture
	19.7%	PROD2-1	CH3-CO-CH2-CH2-CH2-OH
	7.6%	HOACET	CH3-CO-CH2-OH
	7.4%	PROD2-6	CH3-CO-CH2-CH2-CH(CH3)-OH
	7.4%	DEK	CH3-CH2-CO-CH2-CH3
	7.2%	PROD2-7	CH3-CH2-CO-CH2-CH2-CH2-OH
	6.7%		CH3-C*(CH3)-O-CO-CH2-CH*-CH2-CH2-CO-CH2-OH
	5.0%		CH3-C*1(CH3)-CH*2-CH2-CH2-CO-CH*1-CH2*2
	4.1%	PROD2-2	CH3-CO-CH2-CH(CH3)-CH2-OH
	3.1%	MPK	CH3-CH2-CH2-CO-CH3
	3.0%	PROD2-3	CH3-CH2-CO-CH2-CH2-CH(CH3)-OH
	1.8%	PROD2-10	CH3-CH2-CH(OH)-CH2-CH2-CO-CH3
	1.7%	CC6-KET	CH2*-CH2-CH2-CO-CH2-CH2*
	1.6%	PROD2-9	CH3-CO-CH2-CH2-C(CH3)(CH3)-OH

Table A-3. (continued).

Species	Fac [a]	DMS [b]	Mixture derivation or compound structure [c]
	1.4%		CH3-CH2-CH2-CO-CH2-CH2-CH2-OH
	1.2%	DIACTALC	CH3-CO-CH2-C(CH3)(CH3)-OH
LVKS	90.5%		Derived from UStot OHprods Mixture
	40.7%	UEDKET	CH2=CH-CO-CH2-CH2-CO-CH(CH3)-CH3
	12.1%		CH3-CO-CH=CH-CH*-O-CH*-CO-CH3
	9.6%		CH3-CH(CH3)-C*=CH-CO-CH2-CH2*
	6.9%		CH2=CH-CO-CH2-OH
	5.0%		CH3-C*=CH-CH2-CH2-C(=CH-CO-CH2-CH2*)-CH2-OH
	4.8%		HO-CH2-C*=CH-CO-CH2-CH2*
	3.9%		CH3-CO-CH=CH-CH*-CH2-CO-O-C*(CH3)-CH3
	1.9%		CH3-C(CH3)=CH-CH2-CO-C(CH3)=CH-CH2-OH
	1.5%		CH3-CO-CH=CH-CH*-O-C*(CH3)-CO-CH3
	1.4%		CH2=C*-CH2-CH2-CH(CH2-CO*)-CO-CH3
	1.3%		CH3-CO-CH=C(CH3)-CH*-O-CH*-CO-CH3
	1.3%		CH3-CO-CH=CH-C*(CH3)-O-CH*-CO-CH3
OLEP	95.7%	Total	Derived from UStot OHprods Mixture
	57.1%		CH3-C(CH3)=CH-C*(CH3)-O-CO-CH2-CH*-OH
	20.6%		CH3-C(CH3)=CH-C*(CH2-OH)-CH2-CH2-CO-O*
	18.0%		CH3-C(=CH-CH2-CH2-CO-CH2-OH)-CH2-CH2-CH*-O-CO-CH2-C*(CH3)-CH3
OLEA1	89.7%	Total	Derived from UStot OHprods Mixture
	20.4%	HOMACR	CH2=C(CHO)-CH2-OH
	17.1%		CH3-C*(CHO)-O-CH*-CH=CH-CHO
	15.5%	IP-MHY1	CH3-C(CHO)=CH-CH2-OH
	12.6%	IP-HMY	CH3-C(=CH-CHO)-CH2-OH
	7.8%		HCO-CH=CH-CH*-O-CH*-CHO
	2.5%	UEAKET1	CH3-CO-CH*-O-CH*-CH=CH-CHO
	2.4%		CH3-C(CHO)=CH-CH*-O-C*(CH3)-CHO
	1.9%		CH3-CO-C*(CH3)-O-CH*-CH=CH-CHO
	1.7%		CH2=C(CHO)-CHO
	1.5%		HCO-C*=CH-CH2-O-O-CH2*
	1.4%		HCO-CH=C(CH2-OH)-CH2-OH
	1.4%		CH3-C(CH3)=CH-CHO
	1.3%		CH3-C(=CH-CHO)-CH*-CH2-CO-O-C*(CH3)-CH3
	1.1%		CH2=C(CHO)-CH*-CH2-CH(OH)-C(CH3)(CH3)-O-O*
	1.1%		CH3-C*(CHO)-O-C*(CH3)-CH=CH-CHO
OLEA2	90.5%	Total	Derived from UStot OHprods Mixture
	20.3%		CH3-C*=CH-C(CH3)(CH3)-CH(CHO)-CH2-CH*-OH
	18.1%		CH2=C(CH3)-CH(CH2-CHO)-CH2-CH2-CO-CH3
	17.2%		CH2=C(CH2-CH2-CHO)-CH*-CH2-C(CH3)(CH3)-CH*-CH2-CH2-CO-CH3
	15.0%		CH2=C(CH2-OH)-CH(CHO)-OH
	10.6%	UEAKET2	CH3-CO-CH=CH-CH*-O-CH*-CHO
	7.3%		CH3-C*(CH3)-CH=C(CH2-OH)-CH2-CH2-CH*-CHO
	2.0%		CH3-CO-CH=CH-CH*-O-C*(CH3)-CHO
RANO3	91.1%	Total	Derived from UStot OHprods Mixture

Table A-3. (continued).

Species	Fac [a]	DMS [b]	Mixture derivation or compound structure [c]
	35.3%		O2NO-CH2-aC*-aCH-aCH-aCH-aCH-aCH*
	25.7%		CH3-CH(ONO2)-aC*-aCH-aCH-aCH-aCH-aCH*
	5.3%		CH3-aC*-aCH-aCH-aC(CH2-ONO2)-aCH-aCH*
	5.0%		CH3-aC*-aCH-aCH-aCH-aCH-aC*-CH2-ONO2
	4.7%		O2NO-CH2-CH2-aC*-aCH-aCH-aCH-aCH-aCH*
	3.4%		CH3-aC*-aCH-aCH-aCH-aC(CH2-ONO2)-aCH*
	3.4%		CH3-C(CH3)(ONO2)-aC*-aCH-aCH-aC(CH3)-aCH-aCH*
	2.1%		CH3-C(CH3)(ONO2)-aC*-aCH-aCH-aCH-aCH-aC*-CH3
	1.7%		CH3-CH(ONO2)-aC*-aCH-aCH-aC(CH3)-aCH-aCH*
	1.6%		CH3-CH(ONO2)-CH2-aC*-aCH-aCH-aCH-aCH-aCH*
	1.6%		CH3-CH2-CH(ONO2)-aC*-aCH-aCH-aCH-aCH-aCH*
	1.3%		CH3-CH(ONO2)-aC*-aCH-aCH-aCH-aC(CH3)-aCH*
RCNO3	90.6%	Total	Derived from UStot NO3prods Mixture
	26.6%		CH3-CO-CH2-ONO2
	15.9%		CH2=C(CHO)-CH2-ONO2
	13.7%		CH3-C*(CH3)-O-CO-CH2-CH*-CH2-CH2-CO-CH2-ONO2
	12.5%		HCO-CH2-ONO2
	5.0%		CH3-C*(CH3)-CH(ONO2)-CH2-CH*-CH2-CH2-CO-CH2-ONO2
	3.6%		CH3-CH2-CO-CH2-ONO2
	3.0%		CH2=CH-CO-CH2-CH2-CO-CH2-ONO2
	2.7%		CH2=CH-C(CH3)(CHO)-ONO2
	1.9%		HO-CH2-CH2-CH2-CO-CH2-ONO2
	1.5%		CH3-CO-CH(ONO2)-CH2-OH
	1.4%		CH2=CH-CO-CH2-ONO2
	1.1%		CH2=CH-C(ONO2)(CH2-CH2-CO-CH2-ONO2)-CH(CH3)-CH3
	1.1%		CH3-C(CH3)(ONO2)-CH*-CH2-CH2-CH(CH2*)-CO-CH2-ONO2
	0.7%		CH3-C(=CH-CHO)-CH2-ONO2
RHNO3	68.7%	Total	Derived from UStot OHprods Mixture
	16.0%	RNO3-I01	CH2=CH-C(CH3)(ONO2)-CH2-OH
	11.1%	RNO3-I02	CH2=C(CH3)-CH(ONO2)-CH2-OH
	7.2%		CH3-C*1(CH3)-CH*2-CH2-CH(ONO2)-C(CH3)(OH)-CH*1-CH2*2
	6.5%		CH3-C*=CH-C(CH3)(CH3)-CH(CH2-ONO2)-CH2-CH*-OH
	5.5%		CH3-C*1(CH3)-CH*2-CH2-CH(OH)-C(CH3)(ONO2)-CH*1-CH2*2
	3.3%		CH3-CH(CH3)-C*(CH=C(CH2-OH)-CH2-CH2*)-CH2-ONO2
	3.3%		CH3-CH(CH3)-C*(ONO2)-CH2-CH=C(CH2-OH)-CH2-CH2*
	2.7%		CH3-C*=CH-C(CH3)(CH3)-CH(ONO2)-CH2-CH*-OH
	2.3%		CH3-C*(CH3)-CH=C(CH2-OH)-CH2-CH2-CH*-CH2-ONO2
	2.1%		CH2=C*1-CH2-CH2-CH(OH)-C(CH3)(ONO2)-CH2-CH2-CH*2-CH*1-CH2-C*2(CH3)-CH3
	2.0%		CH3-C*1(CH3)-CH*2-CH2-CH(OH)-C(CH3)(ONO2)-CH2-CH*21
	2.0%		CH2=C(CH3)-CH*-CH2-CH2-C(CH3)(ONO2)-CH(OH)-CH2*
	2.0%		CH3-C*1(CH3)-CH*2-CH2-CH2-C(ONO2)(CH2-OH)-CH*1-CH2*2
	1.4%		CH3-C*1(CH3)-CH*2-CH2-CH2-CH(CH2*2)-C*1(ONO2)-CH2-OH
	1.3%	RNO3-I10	CH2=CH-C(CH3)(OH)-CH2-ONO2
RPNO3	71.6%	Total	Derived from UStot OHprods Mixture
	12.9%		CH3-C*12-O-O-CH(CH=CH-CH*1-ONO2)-CH*2-OH

Table A-3. (continued).

Species	Fac [a]	DMS [b]	Mixture derivation or compound structure [c]
	12.9%		CH3-C*12-CH=CH-CH(ONO2)-CH(O-O*1)-CH*2-OH
	10.2%		CH3-C*12-CH=CH-CH(ONO2)-C(CH3)(O-O*1)-CH*2-OH
	7.9%		CH2=CH-C(CH3)(ONO2)-CH*-CH2-CH(OH)-C(CH3)(CH3)-O-O*
	4.6%		HO-CH*1-CH*2-CH=CH-CH(ONO2)-CH*1-O-O*2
	3.1%		CH2=CH-C(CH3)(ONO2)-CH*-CH2-CH(O-O*)-C(CH3)(CH3)-OH
	2.5%		CH3-C*1=CH-C*2(CH3)-O-O-C(CH3)(CH*2-OH)-CH*1-ONO2
	2.4%		CH3-C*1(OH)-CH*2-CH=CH-CH(ONO2)-CH*1-O-O*2
	2.3%		CH3-C*1=CH-CH(ONO2)-C*2(CH3)-O-O-CH*1-CH*2-OH
	2.3%		CH3-C*1(ONO2)-CH=CH-C*2(CH3)-O-O-CH*1-CH*2-OH
	2.2%		CH3-CH2-C*12-CH=CH-CH(ONO2)-C(CH3)(O-O*1)-CH*2-OH
	2.2%		CH3-CH2-C*12-O-O-C(CH3)(CH=CH-CH*1-ONO2)-CH*2-OH
	2.0%		CH3-C*1(ONO2)-CH=CH-C*2(CH3)-O-O-C*1(CH3)-CH*2-OH
	2.0%		CH3-C*1=CH-CH(ONO2)-C*2(CH3)-O-O-C*1(CH3)-CH*2-OH
	2.0%		CH3-CH2-C*12-CH=CH-CH(ONO2)-CH(O-O*1)-CH*2-OH
RDNO3	91.0%	Total	Derived from UStot NO3prods Mixture
	31.6%		CH3-C*1(CH3)-CH*2-CH2-CH(ONO2)-C(CH3)(ONO2)-CH*1-CH2*2
	27.0%		CH2=CH-C(CH3)(ONO2)-CH2-ONO2
	9.1%		CH3-C*1(CH3)-CH*2-CH2-CH2-C(ONO2)(CH2-ONO2)-CH*1-CH2*2
	5.5%		CH2=C(CH3)-CH*-CH2-CH2-C(CH3)(ONO2)-CH(ONO2)-CH2*
	4.3%		CH3-CH(CH3)-C*12-CH2-CH2-C(ONO2)(CH2-ONO2)-CH*1-CH2*2
	3.4%		CH3-C*1(CH3)-CH*2-CH2-CH(ONO2)-C(CH3)(ONO2)-CH2-CH*21
	2.8%		CH2=CH-C(CH3)(ONO2)-CH*-CH2-CH(ONO2)-C(CH3)(CH3)-O-O*
	1.9%		CH3-C*1(CH3)-CH*2-CH2-CH2-CH(CH2*2)-C*1(ONO2)-CH2-ONO2
	1.9%		CH3-CH(ONO2)-CH2-ONO2
	1.8%		CH3-CH(CH3)-CH(ONO2)-CH2-ONO2
	1.6%		CH3-C(=CH-CH2-ONO2)-CH2-ONO2
R1NO3	69.6%	Total	Derived from UStot OHprods Mixture
	13.3%	2C4-ONO2	CH3-CH2-CH(CH3)-ONO2
	12.0%		CH3-CH2-C(CH3)(CH3)-ONO2
	6.4%	IC3-ONO2	CH3-CH(CH3)-ONO2
	4.9%		CH3-CH2-CH2-CH(CH3)-ONO2
	4.5%		CH3-C(CH3)(CH3)-ONO2
	4.2%		CH3-CH(CH3)-CH(CH3)-ONO2
	3.7%		CH3-CH2-CH2-C(CH3)(CH3)-ONO2
	3.2%		CH3-CH2-CH2-CH(ONO2)-CH2-CH3
	3.1%		CH3-CH2-CH(ONO2)-CH2-CH3
	3.0%		CH3-C(CH3)(CH3)-CH2-C(CH3)(CH3)-ONO2
	2.7%		CH3-CH2-C(CH3)(ONO2)-CH2-CH3
	2.5%		CH3-CH2-CH2-CH2-CH(CH3)-ONO2
	2.2%		CH3-CH(CH3)-C(CH3)(CH3)-ONO2
	2.0%		CH3-CH2-CH2-ONO2
	1.9%		CH3-CH2-CH2-CH2-ONO2
R2NO3	54.9%	Total	Derived from UStot OHprods Mixture
	8.9%		CH3-C*1=CH-CH2-C*2(ONO2)-CH2-CH*1-C*2(CH3)-CH3
	6.8%		O2NO-CH*-CH2-CH2-CH2-CH2-CH2*
	4.0%		CH3-C*1=CH-CH(ONO2)-CH*2-CH2-CH*1-C*2(CH3)-CH3

Table A-3. (continued).

Species	Fac [a]	DMS [b]	Mixture derivation or compound structure [c]
	4.0%		CH3-C*(ONO2)-CH2-CH2-CH2-CH2-CH2*
	3.5%		CH3-CH*-CH2-CH2-CH2-CH(ONO2)-CH2*
	3.4%		CH2=C*1-CH2-CH2-C*2(ONO2)-CH2-CH*1-C*2(CH3)-CH3
	3.4%		CH3-C*1=CH-CH2-CH*2-CH2-C*1(ONO2)-C*2(CH3)-CH3
	3.4%		CH3-C*1=C*2-CH2-CH(CH2-CH*1-ONO2)-C*2(CH3)-CH3
	3.3%		CH3-CH2-CH2-CH2-CH2-CH(ONO2)-CH2-CH3
	3.3%		CH3-CH2-CH2-CH2-CH(ONO2)-CH2-CH2-CH3
	2.7%		CH3-CH*-CH2-CH2-CH2-CH2-CH*-ONO2
	2.5%		CH3-CH2-CH2-CH2-CH2-CH2-CH(CH3)-ONO2
	2.0%		CH2=C*1-CH2-CH(ONO2)-CH*2-CH2-CH*1-C*2(CH3)-CH3
	1.9%		CH3-CH2-CH(CH3)-CH2-CH(CH3)-ONO2
	1.8%		CH3-CH*-CH2-CH2-CH(ONO2)-CH2-CH2*
RUOOH	90.8%	Total	Derived from UStot HO2prods Mixture
	37.3%		CH2=CH-C(CH3)(CH2-OH)-O-OH
	25.8%		CH2=C(CH3)-CH(CH2-OH)-O-OH
	6.4%		CH3-C*=CH-C(CH3)(CH3)-CH(CH2-O-OH)-CH2-CH*-OH
	3.0%		CH2=CH-C(CH3)(OH)-CH2-O-OH
	3.0%		CH2=C(CH3)-CH(OH)-CH2-O-OH
	3.0%		CH2=C(CH2-O-OH)-CH(OH)-CH2-O-OH
	2.9%		CH3-C*=CH-C(CH3)(CH3)-CH(CH2-CH*-OH)-O-OH
	2.3%		CH3-C*(CH3)-CH=C(CH2-OH)-CH2-CH2-CH*-CH2-O-OH
	2.0%		CH2=C(CH3)-CH*-CH2-CH2-C(CH3)(O-OH)-CH(OH)-CH2*
	1.9%		CH2=C(CH2-OH)-CH(CH2-O-OH)-O-OH
	1.6%		CH3-CH(CH3)-C*(CH=C(CH2-OH)-CH2-CH2*)-CH2-O-OH
	1.6%		CH3-CH(CH3)-C*(CH2-CH=C(CH2-OH)-CH2-CH2*)-O-OH
RAOOH	77.1%	Total	Derived from UStot HO2prods Mixture
	16.0%		CH3-C*12-O-O-CH(CH=CH-CH*1-O-OH)-CH*2-OH
	16.0%		CH3-C*12-CH=CH-CH(O-OH)-CH(O-O*1)-CH*2-OH
	9.7%		CH3-C*12-CH=CH-CH(O-OH)-C(CH3)(O-O*1)-CH*2-OH
	9.1%		HO-O-CH*1-CH=CH-CH*2-O-O-CH*1-CH*2-OH
	5.6%		CH2=CH-C(CH3)(O-OH)-CH*-CH2-CH(OH)-C(CH3)(CH3)-O-O*
	3.0%		CH3-C*1(OH)-CH*2-CH=CH-CH(O-OH)-CH*1-O-O*2
	2.2%		CH3-C*1=CH-CH(O-OH)-C*2(CH3)-O-O-CH*1-CH*2-OH
	2.2%		CH3-C*1(CH=CH-C*2(CH3)-O-O-CH*1-CH*2-OH)-O-OH
	2.2%		CH2=CH-C(CH3)(O-OH)-CH*-CH2-CH(O-O*)-C(CH3)(CH3)-OH
	2.0%		CH3-C*1=CH-C*2(CH3)-O-O-C(CH3)(CH*2-OH)-CH*1-O-OH
	1.9%		CH3-CH2-C*12-CH=CH-CH(O-OH)-CH(O-O*1)-CH*2-OH
	1.9%		CH3-CH2-C*12-O-O-CH(CH=CH-CH*1-O-OH)-CH*2-OH
	1.7%		CH3-C*1(OH)-CH*2-O-O-C*1(CH3)-CH=CH-CH*2-O-OH
	1.7%		CH3-C*1(OH)-CH*2-CH=CH-CH(O-OH)-C*1(CH3)-O-O*2
	1.7%		CH3-CH2-C*12-CH=CH-CH(O-OH)-C(CH3)(O-O*1)-CH*2-OH
HPALD	90.2%	Total	Derived from UStot OHprods Mixture
	37.8%		CH3-C(CHO)=CH-CH2-O-OH
	31.3%		CH3-C(=CH-CHO)-CH2-O-OH
	4.5%		CH3-CO-CH=CH-CH(CH2-CHO)-C(CH3)(CH3)-O-OH
	4.5%		CH3-C*=CH-CO-O-C*(OH)-CH2-CH(O-OH)-C(CH3)(CH3)-O-OH

Table A-3. (continued).

Species	Fac [a]	DMS [b]	Mixture derivation or compound structure [c]
	3.6%		HCO-CH=C(CH2-OH)-CH2-O-OH
	2.1%		CH3-C(=CH-CH2-O-OH)-CO-CH2-CHO
	1.8%		CH3-C(=CH-C(CH3)(CH3)-O-OH)-CO-CH2-CO-O-OH
	1.6%		CH3-C(CH3)(O-OH)-CH(CH2-CH*-O-CO-CH=C*-CH2-OH)-O-OH
	1.6%		CH2=CH-C(CH3)(CO-CH=CH-C(CH3)(CH3)-O-OH)-O-OH
	1.5%		CH3-C(CH3)(O-OH)-CH*-CH=CH-CO-CH2-CH2*
CROOH	90.2%	Total	Derived from UStot HO2prods Mixture
	15.0%		CH3-C*(CH3)-CH(CH2-CH2-CO-CH2-OH)-CH2-CH*-O-OH
	14.4%		CH3-C(CH3)(O-OH)-CH*-CH2-CH2-CH(CH2*)-CO-CH2-OH
	12.6%		HO-CH2-CO-CH*-CH2-CH2-CH(CH2*)-O-OH
	7.7%		CH3-CO-CH2-CH2-CH2-CH2-O-OH
	5.8%		CH3-CO-CH(CH2-CH2-CH2-OH)-O-OH
	5.2%		CH3-CH(CH2-CH2-CH2-CO-O-OH)-O-OH
	4.4%		HO-O-CH2-CH2-CH2-CH2-CH2-CO-O-OH
	4.2%		CH3-CO-CH2-C(CH3)(CH3)-O-OH
	3.7%		CH3-CH(OH)-CH2-CH2-CH(CO-O-OH)-O-OH
	3.5%		CH3-CO-CH2-CH2-CH2-CH2-CH2-O-OH
	3.3%		CH3-CH(CH2-CH2-CO-O-OH)-CH2-O-OH
	3.3%		CH3-CH(CH2-CH2-O-OH)-CH2-CO-O-OH
	2.6%		CH3-CO-CH2-CH(CH2-CH2-CH2-OH)-O-OH
	2.4%		HO-O-CH2-CO-O-OH
	2.3%		CH3-CH(CH2-CH2-CH2-CH2-CO-O-OH)-O-OH
ROOH	52.8%	Total	Derived from UStot HO2prods Mixture
	9.4%		CH3-CH2-CH(CH3)-O-OH
	8.0%		CH3-CH(CH3)-O-OH
	5.4%		CH3-CH2-C(CH3)(CH3)-O-OH
	4.4%		CH3-C*1(CH3)-CH*2-CH2-CH(O-OH)-C(CH3)(OH)-CH*1-CH2*2
	4.1%		CH3-CH(CH2-OH)-O-OH
	3.4%		CH3-C*1(CH3)-CH*2-CH2-CH(OH)-C(CH3)(O-OH)-CH*1-CH2*2
	3.2%	TBU-OOH	CH3-C(CH3)(CH3)-O-OH
	2.6%		CH3-CH2-CH2-O-OH
	2.4%		CH3-CH(OH)-CH2-O-OH
	2.2%		CH3-CH2-CH2-CH(CH3)-O-OH
	1.9%		CH3-CH(CH3)-CH(CH3)-O-OH
	1.7%		CH3-CH(OH)-CH2-CH2-CH2-O-OH
	1.4%		CH3-CH2-CH(CH2-CH3)-O-OH
	1.4%		CH3-CH2-CH2-CH2-O-OH
	1.3%		CH3-CH(CH3)-CH(CH2-OH)-O-OH
AFG1	91.3%	Total	Derived from UStot OHprods Mixture
	66.0%	2MBUTDAL	CH3-C(CHO)=CH-CHO
	13.7%		CH3-C(CHO)=C(CHO)-OH
	7.8%		CH3-CH2-C(CHO)=CH-CHO
	3.9%		HCO-CH=C(CHO)-CH2-OH
AFG2A	95.3%	Total	Derived from UStot OHprods Mixture
	74.6%	4OX2PEAL	CH3-CO-CH=CH-CHO
	8.4%		CH3-CH2-CO-CH=CH-CHO

Table A-3. (continued).

Species	Fac [a]	DMS [b]	Mixture derivation or compound structure [c]
	6.3%		CH3-CH(CH3)-CO-CH=C(CHO)-CH2-CH2-O-OH
	6.0%	2M4OX2PA	CH3-CO-CH=C(CH3)-CHO
AFG2B	90.5%	Total	Derived from UStot OHprods Mixture
	55.7%	3M4OX2PA	CH3-CO-C(CH3)=CH-CHO
	29.3%		CH3-CO-C(OH)=CH-CHO
	5.4%		CH3-C(CHO)=C*-CO-O-CH(CH2-O-OH)-C*(CH3)-CH3
AFG3	96.0%	Total	Derived from UStot OHprods Mixture
	71.5%	3HXE25DO	CH3-CO-CH=CH-CO-CH3
	9.1%		CH3-CH2-CO-CH=CH-CO-CH3
	8.4%		CH3-CO-CH=CH-CO-CH(CH3)-CH3
	6.9%		CH3-CH(CH3)-CO-CH=CH-CO-CH2-OH

[a] Contribution of the compound used when deriving the mechanism of the mixture (molar). Does not include all compounds in the mixture because some compounds had very low yields, the mechanism of the compounds are not typical of most in the mixture, or because the mechanism generation system is not expected to process them properly. "Total" is total of fractions for the compounds used.

[b] See Table A-7 in the electronic supplement a description of the detailed model species (DMS). If blank, this is a generated product that is not a regular detailed model species. The "Structure" column indicates the compound that was used.

[c] For compounds, this column gives the structure used in the mechanism generation system. Note that the symbol "*" is used to designate ring closure (with two **'s showing a 2nd ring), and lower case "c" indicates an aromatic carbon. For mixtures, this gives the mixture used to obtain the compounds used to derive the mechanisms and the mole fractions. In all cases these are compounds represented by the model species in the first column, listed in descending order of relative importance. Abbreviations used for the mixtures are as follows:

UStot	Total US Emissions based on the 2005ah_tox inventory using the criteria VOC emissions only from all sectors except biogenic and fires (Luecken, 2013).
UStot OHprods	First generation products of the reactions of OH radicals with the compounds in the UStot mixture.
UStot NO3prods	First generation products of the reactions of NO_3 radicals with the compounds in the UStot mixture.
USTOT HO2prods	First generation products of the reactions of HO_2 with the peroxy radicals formed in the reactions of OH radicals with the compounds in the UStot mixture.
Megan2	Global annual total biogenic VOC emissions for the year 2000 calculated using the using MEGAN 2.1 model algorithms in CLM4 (Guenther, 2012, 2014).
Isoprene OHprods	First generation products of the reactions of OH radicals with isoprene.
Isoprene HO2prods	First generation products of the reactions of HO_2 with the peroxy radicals formed in the reactions of OH radicals with isoprene.

Table A-4. List of reactions and documentation notes in the version of SAPRC-18 for atmospheric simulations.

Label	Reaction and Products [a]	Rate Parameters [b]				Notes
		k(300)	A	Ea	B	[c]
	Inorganic Reactions					
1	NO2 + HV = NO + O3P	Phot Set= NO2-06				1
2	O3P + O2 + M = O3 + M	5.90e-34	6.00e-34	-	2.40	1
3	O3P + O3 = #2 O2	7.96e-15	8.00e-12	4.09	-	1
4	O3P + NO = NO2	1.66e-12	Falloff, F=0.60, N=1.00			1
		0:	9.00e-32	-	-1.50	
		Inf:	3.00e-11	-	-	
5	O3P + NO2 = NO + O2	1.03e-11	5.10e-12	-0.42	-	1
6	O3P + NO2 = NO3	3.28e-12	Falloff, F=0.60, N=1.00			1
		0:	2.50e-31	-	-1.80	
		Inf:	2.20e-11	-	-0.70	
7	O3 + NO = NO2 + O2	1.95e-14	3.00e-12	2.98	-	1
8	O3 + NO2 = O2 + NO3	3.23e-17	1.20e-13	4.87	-	1
9	NO + NO3 = #2 NO2	2.65e-11	1.50e-11	-0.34	-	1
10	NO + NO + O2 = #2 NO2	1.95e-38	3.30e-39	-1.05	-	2
11	NO2 + NO3 = N2O5	1.24e-12	Falloff, F=0.35, N=1.33			2
		0:	3.60e-30	-	-4.10	
		Inf:	1.90e-12	-	0.20	
12	N2O5 = NO2 + NO3	4.46e-2	Falloff, F=0.35, N=1.33			2
		0:	1.30e-3	-	-3.50	
		Inf:	9.70e+14	22.02	0.10	
13	N2O5 + H2O = #2 HNO3	0				3
14	N2O5 + H2O + H2O = #2 HNO3 + H2O	0				3
15	NO2 + NO3 = NO + NO2 + O2	6.56e-16	4.50e-14	2.50	-	1
16	NO3 + HV = NO + O2	Phot Set= NO3NO-06				1
17	NO3 + HV = NO2 + O3P	Phot Set= NO3NO2-6				1
18	O3 + HV = O1D + O2	Phot Set= O3O1D-06				1
19	O3 + HV = O3P + O2	Phot Set= O3O3P-06				1
20	O1D + H2O = #2 OH	1.99e-10	1.63e-10	-0.12	-	1
21	O1D + M = O3P + M	3.69e-11	2.65e-11	-0.20	-	4
22	OH + NO = HONO	7.41e-12	Falloff, F=0.60, N=1.00			1
		0:	7.00e-31	-	-2.60	
		Inf:	3.60e-11	-	-0.10	
23	HONO + HV = OH + NO	Phot Set= HONO-06				1
24	OH + HONO = H2O + NO2	4.86e-12	1.80e-11	0.78	-	1
25	OH + NO2 = HNO3	9.89e-12	Falloff, F=0.41, N=1.24			2
		0:	3.20e-30	-	-4.50	
		Inf:	3.00e-11	-	-	
26	OH + NO3 = HO2 + NO2	2.20e-11				1
27	OH + HNO3 = H2O + NO3	1.54e-13	k = k0+k3M/(1+k3M/k2)			1
		k0:	2.40e-14	-0.91	-	
		k2:	2.70e-17	-4.37	-	
		k3:	6.50e-34	-2.65	-	
28	HNO3 + HV = OH + NO2	Phot Set= HNO3				1
29	OH + O3 = HO2 + O2	7.25e-14	1.70e-12	1.87	-	1
30	HO2 + NO = OH + NO2	8.17e-12	3.30e-12	-0.54	-	1
31	HO2 + NO = HNO3	4.33e-14	k = k1 + k2 [M]			5
		k1:	2.39e-12	3.40	-13.77	

Table A-4 (continued)

Label	Reaction and Products [a]	Rate Parameters [b] k(300)	A	Ea	B	Notes [c]
		k2:	1.83e-32	1.53	-4.85	
32	HO2 + NO + H2O = HNO3 + H2O	2.35e-31	1.20e-35	-5.85	-	6
33	HO2 + NO2 = HNO4	7.50e-13	Falloff, F=0.40, N=1.26			2
		0:	1.40e-31	-	-3.10	
		Inf:	4.00e-12	-	-	
34	HNO4 = HO2 + NO2	6.20e-2	Falloff, F=0.40, N=1.26			2
		0:	4.10e-5	-	-	
		Inf:	6.00e+15	22.20	-	
35	HNO4 + HV = #.8 {HO2 + NO2} + #.2 {OH + NO3}		Phot Set= HNO4-06			1
36	HNO4 + OH = H2O + NO2 + O2	4.65e-12	1.30e-12	-0.76	-	1
37	HO2 + O3 = OH + #2 O2	1.93e-15	1.00e-14	0.97	-	1
38	HO2 + HO2 = HO2H + O2	2.54e-12	k = k1 + k2 [M]			1
		k1:	3.00e-13	-0.91	-	
		k2:	2.10e-33	-1.83	-	
39	HO2 + HO2 + H2O = HO2H + O2 + H2O	5.71e-30	k = k1 + k2 [M]			1
		k1:	4.20e-34	-5.29	-	
		k2:	2.94e-54	-6.20	-	
40	NO3 + HO2 =OH + NO2 + O2	3.50e-12				1
41	NO3 + NO3 = #2 NO2 + O2	2.28e-16	8.50e-13	4.87	-	1
42	HO2H + HV = #2 OH		Phot Set= H2O2			1
43	HO2H + OH = HO2 + H2O	1.80e-12				1
44	OH + HO2 = H2O + O2	1.11e-10	4.80e-11	-0.50	-	1
45	SO2 + OH = HO2 + SULF	9.59e-13	Falloff, F=0.60, N=1.00			1
		0:	3.30e-31	-	-4.30	
		Inf:	1.60e-12	-	-	
46	H2 + OH = HO2 + H2O	6.67e-15	2.80e-12	3.58	-	1
	Reactions of explicit and lumped organic compounds used in all simulations (excluding reactions output by the mechanism generation system, which are given in the electronic supplement)					
C001	CH4 + OH = MEO2 + SumRO2	6.34e-15	2.45e-12	3.53	-	1,7
C002	MEOH + OH = HCHO + HO2	9.11e-13	2.90e-12	0.69	-	1
C003	MEOOH + OH = H2O + #.4 {HCHO + OH} + #.6 {MEO2 + SumRO2}	7.43e-12	3.80e-12	-0.40	-	1,7
C004	MEOOH + HV = HCHO + HO2 + OH		Phot Set= COOH			2
C005	HCHO + HV = #2 HO2 + CO		Phot Set= HCHOR-13			8
C006	HCHO + HV = H2 + CO		Phot Set= HCHOM-13			8
C007	HCHO + OH = HO2 + CO + H2O	8.37e-12	5.50e-12	-0.25	-	1
C008	HCHO + NO3 = HNO3 + HO2 + CO	5.80e-16				1
C009	CO + OH = HO2 + CO2	2.28e-13	k = k1 + k2 [M]			2
		k1:	1.44e-13	-	-	
		k2:	3.43e-33	-	-	
C010	HCOOH + OH = HO2 + CO2	4.00e-13				1
C011	ETHAN + OH = ETO2 + SumRO2	2.50e-13	7.66e-12	2.03	-	1,7
Cx11	PROP + OH = C3RO2 + SumRO2	1.11e-12	1.00e-11	1.30	-	1,7
C012	ETHEN + OH = ETHEO2 + SumRO2	7.90e-12	Falloff, F=0.60, N=1.00			1,7
		0:	1.10e-28	-	-3.50	
		Inf:	8.40e-12	-	-1.75	
C013	ETHEN + O3 = #.16 HO2 + #.16 OH + #.51 CO + #.12 CO2 + HCHO + #.37 HCHO2	1.76e-18	1.20e-14	5.23	-	1
C014	ETHEN + NO3 = ETHEO2N + SumRO2	2.10e-16	3.30e-12	5.72	-	2,7

Table A-4 (continued)

Label	Reaction and Products [a]	Rate Parameters [b]				Notes [c]
		k(300)	A	Ea	B	
C015	ETHEN + O3P = #4.405 NROG + #.8 HO2 + #.51 CO + #.51 MEO2 + #.29 HCOMEO2 + #.1 MECHO + #.8 SumRO2 + #.2 XC	7.30e-13	1.07e-11	1.59	-	9,7
C016	ACETL + OH = #.3 HO2 + #.7 OH + #.3 CO + #.3 HCOOH + #.7 GLY	7.47e-13	Falloff, F=0.60, N=1.00			1
		0:	5.50e-30	-	-	
		Inf:	8.30e-13	-	2.00	
C017	ACETL + O3 = #1.5 HO2 + #.5 OH + #1.5 CO + #.5 CO2	1.06e-20	1.00e-14	8.15	-	1
C018	ETOH + OH = #.95 {HO2 + MECHO} + #.05 ETHEO2 + #0.05 SumRO2	3.32e-12	3.32e-12	-	-	1,7
C019	AACID + OH = H2O + MEO2 + CO2 + SumRO2	6.90e-13	3.15e-14	-1.83	-	1,7
C020	ETOOH + OH = #1.233 NROG + #.594 OH + #.567 MECHO + #.406 ETO2 + #.054 XC + #0.406 SumRO2	6.04e-12				10,7
C021	ETOOH + HV = OH + HO2 + MECHO		Phot Set= COOH			16
C022	MECHO + OH = H2O + #.95 {MECO3 + SumRCO3} + #.05 {HCOMEO2 + SumRO2}	1.50e-11	4.63e-12	-0.70	-	1,7
C023	MECHO + HV = HO2 + #.9 {CO + MEO2 + SumRO2} + #.1 {MECO3 + SumRCO3}		Phot Set= CCHOR-13			11,7
C024	MECHO + NO3 = HNO3 + MECO3 + SumRCO3	2.38e-15	1.40e-12	3.78	-	1,7
C025	ETCHO + OH = H2O + ETCO3 + SumRCO3	1.91e-11	4.90e-12	-0.80	-	2,12,7
C026	ETCHO + NO3 = HNO3 + ETCO3 + SumRCO3	6.30e-15	1.40e-12	3.20	-	2,7
C027	ETCHO + HV = HO2 + #.9 ETO2 + #.9 CO + #.1 ETCO3 + #.9 SumRO2 + #.1 SumRCO3		Phot Set= C2CHO			2,7
C028	GLCHO + OH = #.2 HO2 + #.8 {HOCCO3 + SumRCO3} + #.2 GLY	8.00e-12				2,7
C029	GLCHO + NO3 = HNO3 + #.991 {HOCCO3 + SumRCO3} + #.009 {CO + HCHO + HO2}	6.30e-15	1.40e-12	3.20	-	13,7
C030	GLCHO + HV = #.93 CO + #.1 MEOH + #.07 OH + #1.66 HO2 + #.83 HCHO + #.07 {HCOMEO2 + SumRO2}		Phot Set= GLALD-14			14,7
C031	PAA + OH = H2O + MECO3 + SumRCO3	2.55e-12				10,7
C032	PAA + HV = MEO2 + CO2 + OH + SumRO2		Phot Set= PAA			15,7
C033	GLY + HV = #2 {CO + HO2}		Phot Set= GLY-I13R			2
C035	GLY + HV = HCHO + CO		Phot Set= GLY-I13M			2
C036	GLY + OH = #1.7 CO + #.7 HO2 + #.3 {OH + CO2}	1.15e-11	1.15e-11	-	-	1
C037	GLY + NO3 = HNO3 + #1.7 CO + #.7 HO2 + #.3 {OH + CO2}	4.00e-16				2
C038	ACET + OH = H2O + ACETO2 + SumRO2	1.78e-13	1.46e-12	1.25	-	17,7
C039	ACET + HV = MECO3 + MEO2 + SumRO2		Phot Set= ACET-06, qy= 5.0e-1			18,7
C040	MGLY + HV = HO2 + CO + MECO3 + SumRCO3		Phot Set= MGLY-13			19,7
C041	MGLY + OH = CO + MECO3 + SumRCO3	1.31e-11	1.90e-12	-1.14	-	2,7
C042	MGLY + NO3 = HNO3 + CO + MECO3 + SumRCO3	5.37e-16	1.40e-12	4.66	-	20,7
C043	BACL + HV = #2 MECO3 + #2 SumRCO3		Phot Set= BACL-11			21,7
C044	BALD + OH = BZCO3 + SumRCO3	1.20e-11				2,7
C045	BALD + HV = #7 XC		Phot Set= BALD-11, qy= 9.0e-2			22
C046	BALD + NO3 = HNO3 + BZCO3 + SumRCO3	4.00e-15				23,7
C047	PHEN + OH = #.730 HO2 + #.100 BZO + #.170 OH + #.200 RO2C + #.700 SVPHE + #.030 AFG1 + #.170 OLEA1 + #.030 GLY + #.200 SumRO2 + #-0.730 XC	2.78e-11	4.50e-13	-2.44	-	23,7,24

Table A-4 (continued)

Label	Reaction and Products [a]	Rate Parameters [b]				Notes [c]
		k(300)	A	Ea	B	
C048	PHEN + NO3 = #.130 HNO3 + #.730 HO2 + #.100 BZO + #.170 OH + #.200 RO2C + #.870 NPHE + #.030 AFG1 + #.170 OLEA1 + #.030 GLY + #.200 SumRO2 + #-1.050 XC	4.50e-12				23,7,24
C049	CRES + OH = #.785 HO2 + #.100 BZO + #.115 OH + #.200 RO2C + #.700 SVPHE + #.043 AFG2A + #.043 AFG2B + #.115 OLEA1 + #.043 GLY + #.043 MGLY + #.200 SumRO2 + #.122 XC	4.57e-11	1.60e-12	-1.99	-	23,7,24
C050	CRES + NO3 = #.185 HNO3 + #.785 HO2 + #.100 BZO + #.115 OH + #.200 RO2C + #.815 NPHE + #.043 AFG2A + #.043 AFG2B + #.115 OLEA1 + #.043 GLY + #.043 MGLY + #.200 SumRO2 + #.132 XC	1.40e-11				23,7,24
C051	XYNL + OH = #.726 HO2 + #.100 BZO + #.174 OH + #.330 RO2C + #.570 SVPHE + #.078 AFG2A + #.078 AFG2B + #.174 OLEA1 + #.078 GLY + #.078 MGLY + #.330 SumRO2 + #1.118 XC	7.30e-11				23,7,24
C052	XYNL + NO3 = #.256 HNO3 + #.726 HO2 + #.100 BZO + #.174 OH + #.330 RO2C + #.744 NPHE + #.078 AFG2A + #.078 AFG2B + #.174 OLEA1 + #.078 GLY + #.078 MGLY + #.330 SumRO2 + #.644 XC	3.12e-11				25,7,24
C053	SVPHE + OH = #.600 HO2 + #.200 BZO + #.200 OH + #.400 RO2C + #.400 OTHN + #.100 AFG2A + #.100 AFG2B + #.600 OLEA1 + #.100 GLY + #.100 MGLY + #.400 SumRO2 + #-4.200 XC	2.00e-10				24,7,26
C054	SVPHE + NO3 = #.400 HNO3 + #.600 HO2 + #.200 BZO + #.200 OH + #.400 RO2C + #.200 NPHE + #.400 RNNO3 + #.100 AFG2A + #.100 AFG2B + #.600 OLEA1 + #.100 GLY + #.100 MGLY + #.400 SumRO2 + #-4.600 XC	1.70e-10				24,7,26
C055	NPHE + OH = BZO + NO2	3.50e-12				27
C056	NPHE + HV = HONO + PHEN	Phot Set= NO2-06, qy= 1.5e-3				28
C057	NAPS + OH = #.740 HO2 + #.700 NAPPRD + #.040 RO2C + #.020 AFG2A + #.020 AFG2B + #.040 GLY + #.330 NPRAD + #.250 MACO3 + #.050 SumRO2 + #.250 SumRCO3 + #-2.660 XC	2.30e-11	1.55e-11	-0.23	-	29,7,23
C058	NAPPRD + OH = HO2 + OTHN	Same k as rxn C053				30
C059	NAPPRD + NO3 = HNO3 + OTHN	Same k as rxn C054				30
C060	PHOT + HV = #2 {HO2 + RO2C + SumRO2} + OTH2 + #1 XC	Phot Set= BACL-11				31,7
C061	IMINE = MECHO + XN	1.00e+0				32
	Reactions used to compute loss processes for operators used to represent total RO2 and RCO3 radicals					
S001	SumRO2 + NO = NO	9.13e-12	2.55e-12	-0.76	-	34,33
S002	SumRO2 + HO2 = HO2	1.49e-11				34,33a
S003	SumRO2 + NO3 = NO3	2.30e-12				34,33
S004	SumRO2 + SumRO2 =	1.60e-14				34,41
S005	SumRCO3 + NO2 = NO2	7.71e-12	7.70e-12	-	-0.20	42,35
S006	SumRCO3 + NO = NO	2.10e-11	6.70e-12	-0.68	-	42,36
S007	SumRCO3 + HO2 = HO2	2.20e-11	3.14e-12	-1.15	-	42,37
S008	SumRCO3 + NO3 = NO3	4.00e-12				42,38
S009	SumRCO3 + SumRO2 =	1.60e-11	4.40e-13	-2.13	-	34,42,39

Table A-4 (continued)

Label	Reaction and Products [a]	Rate Parameters [b]				Notes [c]
		k(300)	A	Ea	B	
S010	SumRCO3 + SumRCO3 =	1.70e-11				42,40
	Reactions of peroxy radicals (excluding operator and reactions output by the mechanism generation system)					
P001	MEO2 + NO = NO2 + HCHO + HO2	7.66e-12	2.80e-12	-0.60	-	1
P002	MEO2 + HO2 = #.9 MEOOH + #.1 {HCHO + H2O} + O2	5.21e-12	3.80e-13	-1.55	-	2
P003	MEO2 + NO3 = HCHO + HO2 + NO2	1.20e-12				2
P004	MEO2 + SumRO2 = SumRO2 + #.5 HO2 + #.75 HCHO + #.25 MEOH	2.16e-13				34,43
P005	MEO2 + SumRCO3 = SumRCO3 + #.9 {HCHO + HO2} + #.1 {HCHO + O2}	1.07e-11	2.00e-12	-0.99	-	42,44
P006	ETO2 + NO = NO2 + MECHO + HO2		Same k as rxn S001			33
P007	ETO2 + HO2 = ETOOH + O2		Same k as rxn S002			33
P008	ETO2 + NO3 = MECHO + HO2 + NO2		Same k as rxn S003			33
P009	ETO2 + SumRO2 = SumRO2 + #.6 HO2 + #.8 MECHO + #.2 ETOH	7.60e-14				34,45
P010	ETO2 + SumRCO3 = SumRCO3 + MECHO + HO2	1.60e-11	4.40e-13	-2.13	-	43,7
P011	C3RO2 + NO = #.959 HO2 + #.959 NO2 + #.697 ACET + #.262 ETCHO + #.041 R1NO3 + #-0.082 XC		Same k as rxn S001			45a
P012	C3RO2 + NO3 = HO2 + NO2 + #.726 ACET + #.274 ETCHO		Same k as rxn S003			45a
P013	C3RO2 + HO2 = ROOH + #-2 XC		Same k as rxn S002			45a
P014	C3RO2 + SumRO2 = SumRO2 + #.545 ACET + #.5 HO2 + #.25 OTH3 + #.205 ETCHO + #-0.25 XC		Same k as rxn S004			45a
P015	C3RO2 + SumRCO3 = SumRCO3 + #.726 ACET + #.5 HO2 + #.274 ETCHO		Same k as rxn S009			45a
P016	ETHEO2 + NO = NO2 + #1.602 HCHO + #.199 GLCHO + HO2		Same k as rxn S001			33,46
P017	ETHEO2 + NO3 = NO2 + #1.602 HCHO + #.199 GLCHO + HO2		Same k as rxn S002			33,46
P018	ETHEO2 + HO2 = ROOH + #-3 XC		Same k as rxn S003			33
P019	ETHEO2 + SumRO2 = SumRO2 + #.801 HCHO + #.5 HO2 + #.349 GLCHO + #.25 OTH4 + #-.499 XC		Same k as rxn S004			34,41
P020	ETHEO2 + SumRCO3 = SumRCO3 + #.801 HCHO + #.599 GLCHO + #.5 HO2 + #.001 XC		Same k as rxn S009			42,39
P021	HCOMEO2 = RO2C + HOCCO3	5.90e-1	1.64e+11	15.61	-	47
P022	HCOMEO2 + NO = NO2 + #.923 CO + #.923 HCHO + #.077 GLY + HO2		Same k as rxn S001			33,46
P023	HCOMEO2 + NO3 = NO2 + #.923 CO + #.923 HCHO + #.077 GLY + HO2		Same k as rxn S002			33,46
P024	HCOMEO2 + HO2 = ROOH + #-3 XC		Same k as rxn S003			33
P025	HCOMEO2 + SumRO2 = SumRO2 + #.25 GLCHO + #.288 GLY + #.462 CO + #.462 HCHO + #.5 HO2		Same k as rxn S004			34,41
P026	HCOMEO2 + SumRCO3 = SumRCO3 + #.538 GLY + #.462 CO + #.462 HCHO + #.5 HO2		Same k as rxn S009			42,39
P027	ETHEO2N + NO = #1.013 NO2 + #.026 HCHO + #.987 RCNO3 + #.987 HO2 + #-2.961 XC		Same k as rxn S001			33,46
P028	ETHEO2N + NO3 = #1.013 NO2 + #.026 HCHO + #.987 RCNO3 + #.987 HO2 + #-2.961 XC		Same k as rxn S002			33,46
P029	ETHEO2N + HO2 = RHNO3 + #-6 XC		Same k as rxn S003			33

Table A-4 (continued)

Label	Reaction and Products [a]	Rate Parameters [b]				Notes [c]
		k(300)	A	Ea	B	
P030	ETHEO2N + SumRO2 = SumRO2 + #.25 RHNO3 + #.743 RCNO3 + #.007 NO2 + #.013 HCHO + #.493 HO2 + #-3.728 XC		Same k as rxn S004			34,41
P031	ETHEO2N + SumRCO3 = SumRCO3 + #.993 RCNO3 + #.007 NO2 + #.013 HCHO + #.493 HO2 + #-2.978 XC		Same k as rxn S009			42,39
P032	ACETO2 + NO = NO2 + MECO3 + HCHO + SumRCO3		Same k as rxn S001			33,46
P033	ACETO2 + NO3 = NO2 + MECO3 + HCHO + SumRCO3		Same k as rxn S002			33,46
P034	ACETO2 + HO2 = ROOH + #-2 XC		Same k as rxn S003			33
P035	ACETO2 + SumRO2 = SumRO2 + #.5 MECO3 + #.5 HCHO + #.25 KET2 + #.25 MGLY + #0.5 SumRCO3 + #-.75 XC		Same k as rxn S004			34,41
P036	ACETO2 + SumRCO3 = SumRCO3 + #.5 MECO3 + #.5 HCHO + #.5 MGLY + #0.5 SumRCO3		Same k as rxn S009			42,39
P037	BZO2 + NO = NO2 + BZO		Same k as rxn S001			33,46
P038	BZO2 + HO2 = ROOH + O2 + XC		Same k as rxn S002			33,46
P039	BZO2 + NO3 = BZO + NO2		Same k as rxn S003			33
P040	BZO2 + SumRO2 = SumRO2 + BZO		Same k as rxn S004			34,41
P041	BZO2 + SumRCO3 = SumRCO3 + BZO		Same k as rxn S009			42,39
	Reactions of other peroxy radical operator species used to represent relatively minor processes using a SAPRC-11-like peroxy lumping approach.					
P042	RO2C + NO = NO2		Same k as rxn S001			48
P043	RO2C + HO2 =		Same k as rxn S002			48
P044	RO2C + NO3 = NO2		Same k as rxn S003			48
P045	RO2C + SumRO2 = SumRO2		Same k as rxn S004			48
P046	RO2C + SumRCO3 = SumRCO3		Same k as rxn S009			48
P047	RO2XC + NO = XN		Same k as rxn S001			49
P048	RO2XC + HO2 =		Same k as rxn S002			49
P049	RO2XC + NO3 = NO2		Same k as rxn S003			49
P050	RO2XC + SumRO2 = SumRO2		Same k as rxn S004			49
P051	RO2XC + SumRCO3 = SumRCO3		Same k as rxn S009			49
P052	zR1NO3 + NO = NO + R1NO3 + #-1 XN		Same k as rxn S001			49
P053	zR1NO3 + HO2 = HO2 + ROOH		Same k as rxn S002			49
P054	zR1NO3 + NO3 = NO3 + KET2 + #-1 XC		Same k as rxn S003			49
P055	zR1NO3 + SumRO2 = SumRO2 + OTH3 + #1 XC		Same k as rxn S004			49
P056	zR1NO3 + SumRCO3 = SumRCO3 + OTH3 + #1 XC		Same k as rxn S009			49
P057	zR2NO3 + NO = NO + R2NO3 + #-1 XN		Same k as rxn S001			49
P058	zR2NO3 + HO2 = HO2 + ROOH + #3 XC		Same k as rxn S002			49
P059	zR2NO3 + NO3 = NO3 + OTH3 + #4 XC		Same k as rxn S003			49
P060	zR2NO3 + SumRO2 = SumRO2 + OTH4 + #4 XC		Same k as rxn S004			49
P061	zR2NO3 + SumRCO3 = SumRCO3 + OTH4 + #4 XC		Same k as rxn S009			49
P062	zRANO3 + NO = NO + RANO3 + #-1 XN		Same k as rxn S001			49
P063	zRANO3 + HO2 = HO2 + ROOH + #3 XC		Same k as rxn S002			49
P064	zRANO3 + NO3 = NO3 + BALD + #1 XC		Same k as rxn S003			49
P065	zRANO3 + SumRO2 = SumRO2 + ARO2 + #-1 XC		Same k as rxn S004			49
P066	zRANO3 + SumRCO3 = SumRCO3 + ARO2 + #-1 XC		Same k as rxn S009			49
P067	zRCNO3 + NO = NO + RCNO3 + #-1 XN		Same k as rxn S001			49
P068	zRCNO3 + HO2 = HO2 + CROOH + #-2 XC		Same k as rxn S002			49

Table A-4 (continued)

Label	Reaction and Products [a]	Rate Parameters [b]				Notes
		k(300)	A	Ea	B	[c]
P069	zRCNO3 + NO3 = NO3 + RCHO + XC	Same k as rxn S003				49
P070	zRCNO3 + SumRO2 = SumRO2 + KET2 + #-1 XC	Same k as rxn S004				49
P071	zRCNO3 + SumRCO3 = SumRCO3 + KET2 + #-1 XC	Same k as rxn S009				49
P072	zRHNO3 + NO = NO + RHNO3 + #-1 XN	Same k as rxn S001				49
P073	zRHNO3 + HO2 = HO2 + ROOH + #3 XC	Same k as rxn S002				49
P074	zRHNO3 + NO3 = NO3 + KET2 + #2 XC	Same k as rxn S003				49
P075	zRHNO3 + SumRO2 = SumRO2 + OTH4 + #4 XC	Same k as rxn S004				49
P076	zRHNO3 + SumRCO3 = SumRCO3 + OTH4 + #4 XC	Same k as rxn S009				49
P077	zRDNO3 + NO = NO + RDNO3 + #-1 XN	Same k as rxn S001				49
P078	zRDNO3 + HO2 = HO2 + RHNO3	Same k as rxn S002				49
P079	zRDNO3 + NO3 = NO3 + RCHO + XN + #4 XC	Same k as rxn S003				49
P080	zRDNO3 + SumRO2 = SumRO2 + RHNO3	Same k as rxn S004				49
P081	zRDNO3 + SumRCO3 = SumRCO3 + RHNO3	Same k as rxn S009				49
P082	zRPNO3 + NO = NO + RPNO3 + #-1 XN	Same k as rxn S001				49
P083	zRPNO3 + HO2 = HO2 + RAOOH + #1 XC	Same k as rxn S002				49
P084	zRPNO3 + NO3 = NO3 + OLEA1 + #2 XC	Same k as rxn S003				49
P085	zRPNO3 + SumRO2 = SumRO2 + OLEP + #-2 XC	Same k as rxn S004				49
P086	zRPNO3 + SumRCO3 = SumRCO3 + OLEP + #-2 XC	Same k as rxn S009				49
P087	zRNNO3 + NO = NO + RNNO3 + #-1 XN	Same k as rxn S001				49
P088	zRNNO3 + HO2 = HO2 + OTHN + #-2 XC	Same k as rxn S002				49
P089	zRNNO3 + NO3 = NO3 + OTHN + #-2 XC	Same k as rxn S003				49
P090	zRNNO3 + SumRO2 = SumRO2 + OTHN + #-2 XC	Same k as rxn S004				49
P091	zRNNO3 + SumRCO3 = SumRCO3 + OTHN + #-2 XC	Same k as rxn S009				49
	Reactions of acyl peroxy radicals and PANs (excluding operator and reactions output by the mechanism generation system)					
Q001	MECO3 + NO2 = PAN	8.69e-12	Falloff, F=0.60, N=1.00			1
		0:	9.70e-29	-	-5.60	
		Inf:	9.30e-12	-	-1.50	
Q002	MECO3 + NO = MEO2 + CO2 + NO2 + SumRO2	2.00e-11	8.10e-12	-0.54	-	1,7
Q003	MECO3 + HO2 = #.37 PAA + #.13 {O3 + AACID} + #.5 {OH + MEO2 + CO2} + #0.5 SumRO2	Same k as rxn S008				7,37
Q004	MECO3 + NO3 = MEO2 + CO2 + NO2 + O2 + SumRO2	4.00e-12				2,7
Q005	MECO3 + SumRO2 = SumRO2 + #.9 {MEO2 + CO2} + #.1 AACID + #0.9 SumRO2	Same k as rxn S009				34,39
Q006	MECO3 + SumRCO3 = SumRCO3 + CO2 + MEO2 + SumRO2	1.55e-11	2.90e-12	-0.99	-	42,50
Q007	PAN = MECO3 + NO2 + SumRCO3	3.82e-4	Falloff, F=0.60, N=1.00			1,7
		0:	1.08e+0	-	-5.60	
		Inf:	1.03e+17	27.82	-1.50	
Q008	PAN + HV = #.7 {MECO3 + NO2 + SumRCO3} + #.3 {MEO2 + CO2 + NO3 + SumRO2}	Phot Set= PAN-11				1,7
Q009	HOCCO3 + NO2 = HOPAN	Same k as rxn S005				35
Q010	HOCCO3 + NO = NO2 + HCHO + HO2 + CO2	Same k as rxn S006				36
Q011	HOCCO3 + HO2 = #.37 PAA + #.13 {O3 + AACID} + #.5 {OH + HCHO + HO2 + CO2}	Same k as rxn S007				37
Q012	HOCCO3 + NO3 = NO2 + HCHO + HO2 + CO2 + O2	Same k as rxn S008				38
Q013	HOCCO3 + SumRO2 = SumRO2 + HCHO + HO2 + CO2	Same k as rxn S009				34,39

Table A-4 (continued)

Label	Reaction and Products [a]	Rate Parameters [b] k(300)	 A	 Ea	 B	Notes [c]
Q014	HOCCO3 + SumRCO3 = SumRCO3 + HCHO + HO2 + CO2	Same k as rxn S010				42,40
Q015	HOPAN = HOCCO3 + NO2 + SumRCO3	Same k as rxn Q007				51,7
Q016	HOPAN + HV = #.6 {HOCCO3 + NO2 + SumRCO3} + #.4 {HCHO + HO2 + CO2 + NO3}	Phot Set= PPN-11				52,7
Q017	ETCO3 + NO2 = PPN	7.41e-12	Falloff, F=0.60, N=1.00			1
		0:	9.00e-28	-	-8.90	
		Inf:	7.70e-12	-	-0.20	
Q018	ETCO3 + NO = NO2 + ETO2 + CO2 + SumRO2	2.10e-11	6.70e-12	-0.68	-	2,7
Q019	ETCO3 + HO2 = #.37 RCOOH + #.13 {O3 + RCOOH} + #.5 {OH + ETO2 + CO2} + #0.5 SumRO2	Same k as rxn S007				7,37
Q020	ETCO3 + NO3 = NO2 + ETO2 + CO2 + O2 + SumRO2	Same k as rxn S008				38
Q021	ETCO3 + SumRO2 = SumRO2 + ETO2 + CO2 + SumRO2	Same k as rxn S009				34,39
Q022	ETCO3 + SumRCO3 = SumRCO3 + ETO2 + CO2 + SumRO2	Same k as rxn S010				42,40
Q023	PPN = ETCO3 + NO2 + SumRCO3	3.26e-4	Falloff, F=0.60, N=1.00			53,7
		0:	1.00e+1	-	-8.90	
		Inf:	8.56e+16	27.82	-0.20	
Q024	PPN + HV = #.6 {ETCO3 + NO2} + #.4 {ETO2 + CO2 + NO3} + #0.4 SumRO2	Phot Set= PPN-11				54,7
Q025	ACO3 + NO2 = APAN	Same k as rxn S005				35
Q026	ACO3 + NO = NO2 + HO2 + CO + CO2 + HCHO	Same k as rxn S006				36
Q027	ACO3 + HO2 = #.37 RCOOH + #.13 {O3 + RCOOH} + #.5 {OH + HO2 + CO + CO2 + HCHO}	Same k as rxn S007				7,37
Q028	ACO3 + NO3 = NO2 + HO2 + CO + CO2 + HCHO + O2	Same k as rxn S008				38
Q029	ACO3 + SumRO2 = SumRO2 + HO2 + CO + CO2 + HCHO	Same k as rxn S009				34,39
Q030	ACO3 + SumRCO3 = SumRCO3 + CO2 + HO2 + CO + HCHO + O2	Same k as rxn S010				42,40
Q031	MACO3 + NO2 = MAPAN	Same k as rxn S005				35
Q032	MACO3 + NO = NO2 + CO2 + HCHO + MECO3 + SumRCO3	Same k as rxn S006				36
Q033	MACO3 + HO2 = #.37 RCOOH + #.13 {O3 + RCOOH} + #.5 {OH + HCHO + MECO3 + CO2} + #.5 XC + #.5 SumRCO3	Same k as rxn S007				7,37
Q034	MACO3 + NO3 = NO2 + CO2 + HCHO + MECO3 + O2 + SumRCO3	Same k as rxn S008				38
Q035	MACO3 + SumRO2 = SumRO2 + CO2 + HCHO + MECO3 + SumRCO3	Same k as rxn S009				34,39
Q036	MACO3 + SumRCO3 = SumRCO3 + CO2 + HCHO + MECO3 + O2 + SumRCO3	Same k as rxn S010				42,40
Q037	R2CO3 + NO2 = PAN2	Same k as rxn S005				35
Q038	R2CO3 + NO = NO2 + C3RO2 + CO2 + #-1 XC	Same k as rxn S006				36

Table A-4 (continued)

Label	Reaction and Products [a]	Rate Parameters [b]				Notes
		k(300)	A	Ea	B	[c]
Q039	R2CO3 + HO2 = #.37 RCOOH + #.13 {O3 + RCOOH} + #.5 {OH + C3RO2 + CO2} + #-.5 XC + #.5 SumRCO3	Same k as rxn S007				7,37
Q040	R2CO3 + NO3 = NO2 + C3RO2 + CO2 + O2 + #-1 XC	Same k as rxn S008				38
Q041	R2CO3 + SumRO2 = SumRO2 + C3RO2 + CO2 + #-1 XC	Same k as rxn S009				34,39
Q042	R2CO3 + SumRCO3 = SumRCO3 + ETO2 + CO2 + SumRO2	Same k as rxn S010				42,40
Q043	PAN2 = R2CO3 + NO2 + SumRCO3	3.39e-4	8.56e+16	27.82	-0.20	55,7
Q044	PAN2 + HV = #.6 {R2CO3 + NO2} + #.4 {C3RO2 + CO2 + NO3} + #-.4 XC + #0.6 SumRCO3	Phot Set= PPN-11				56,7
Q045	R2NCO3 + NO2 = PAN2N	Same k as rxn S005				35
Q046	R2NCO3 + NO = #2 NO2 + HCHO + CO2	Same k as rxn S006				36
Q047	R2NCO3 + HO2 = #.37 RCOOH + #.13 {O3 + RCOOH} + #.5 {OH + NO2 + HCHO + CO2} + #-.5 XC + #.5 XN + #.5 SumRCO3	Same k as rxn S007				7,37
Q048	R2NCO3 + NO3 = #2 NO2 + HCHO + CO2 + O2	Same k as rxn S008				38
Q049	R2NCO3 + SumRO2 = SumRO2 + NO2 + HCHO + CO2	Same k as rxn S009				34,39
Q050	R2NCO3 + SumRCO3 = SumRCO3 + CO2 + HCHO + NO2	Same k as rxn S010				42,40
Q051	PAN2N = R2NCO3 + NO2 + SumRCO3	Same k as rxn Q023				55,7
Q052	PAN2N + HV = #.6 {R2NCO3 + NO2} + #.4 {NO2 + HCHO + CO2 + NO3} + #0.6 SumRCO3	Phot Set= PPN-11				57,7
Q053	BZCO3 + NO2 = PBZN	1.11e-11				58
Q054	BZCO3 + NO = NO2 + CO2 + BZO2 + SumRO2	1.60e-11				58,7
Q055	BZCO3 + HO2 = #.37 RCOOH + #.13 {O3 + RCOOH} + #.5 {OH + BZO2 + CO2} + #2 XC + #5 SumRO2	Same k as rxn S007				37
Q056	BZCO3 + NO3 = NO2 + CO2 + BZO2 + O2 + SumRO2	Same k as rxn S008				38
Q057	BZCO3 + SumRO2 = SumRO2 + BZO2 + CO2 + SumRO2	Same k as rxn S009				34,39
Q058	BZCO3 + SumRCO3 = SumRCO3 + CO2 + BZO2 + SumRO2	Same k as rxn S010				42,40
Q059	PBZN = BZCO3 + NO2 + SumRCO3	3.18e-4	2.10e+16	27.03	-	58,7
Q060	PBZN + HV = #.6 {BZCO3 + NO2} + #.4 {CO2 + BZO2 + NO3} + #0.3 SumRO2	Phot Set= PPN-11				59,7
	Reactions of non-acylperoxy radicals that react with NO2					
X001	TBUO + NO2 = R1NO3 + #-1 XC	2.24e-11	3.50e-12	-1.10	-	60
X002	TBUO = ACET + MEO2 + SumRO2	1.43e+3	1.40e+13	13.62	-	61,7
X003	BZO + NO2 = NPHE	2.08e-12				62
X004	BZO + HO2 = CRES + #-1 XC	Same k as rxn S002				63
X005	BZO = CRES + #-1 XC + HO2	1.00e-3				64
X006	NPRAD + NO2 = NPHE + #6 XC	Same k as rxn S005				65
X007	NPRAD + HO2 = NAPPRD	Same k as rxn S007				65
X008	NPRAD = NAPPRD	1.00e-3				64
X009	xNAMIN + NO2 = NAMIN	Same k as rxn S005				66
X010	xNAMIN + HO2 = AMINS + #2 XC	Same k as rxn S007				66
X011	xNAMIN = AMINS + #2 XC	1.00e-3				64

Table A-4 (continued)

Label	Reaction and Products [a]	Rate Parameters [b] k(300)	A	Ea	B	Notes [c]
	Reactions of stabilized Criegee biradicals					
CB01	HCHO2 + SO2 = SULF + HCHO	3.80e-11				1,67
CB02	HCHO2 + NO2 = HCHO + NO3	7.00e-12				68,67
CB03	HCHO2 + H2O = HCOOH	2.40e-15				69,67
CB04	MECHO2 + SO2 = SULF + MECHO	Same k as rxn CB01				67
CB05	MECHO2 + NO2 = MECHO + NO3	Same k as rxn CB02				67
CB06	MECHO2 + H2O = AACID	Same k as rxn CB03				67
CB07	RCHO2 + SO2 = SULF + RCHO + #-1 XC	Same k as rxn CB01				67
CB08	RCHO2 + NO2 = RCHO + NO3 + #-1 XC	Same k as rxn CB02				67
CB09	RCHO2 + H2O = RCOOH	Same k as rxn CB03				67
	From this point on, all reactions are output by the mechanism generation system. The number of generated reactions is too large to be useful in a printed document. Documentation of the generated photolysis reactions is shown below. Derivation methods for the other types of reactions can be obtained from the online system [d]					
	Photolysis reactions.					
	ACRO + hv = (radical products)	Phot. Set = ACROL-16				70
	MEK + HV = (radical products)	Phot Set= MEK, qy= 0.175				71
	MACR + HV = (products)	Phot Set= MACR-06				72
	MVK + HV = (products)	Phot Set= MVK-16				73
	BUDAL + HV = MALAH + OH + HO2	Phot Set= AFGS, qy= 0.2				74,75
	RCHO + HV = (radical products)	Phot Set= C2CHO				76
	RTCHO + HV = (radical products)	Phot Set= C2CHO				76
	KET2 + HV = (radical products)	Phot Set= MEK, qy= 0.1				71
	LVKS + HV = (products)	Phot Set= MVK-16				73
	OLEA1 + HV = (products)	Phot Set= MACR-06				72
	RANO3 + HV = NO2 + (radical products)	Phot Set= IC3ONO2				77
	RANO3 + HV = NO2 + (radical products)	Phot Set= CRBNIT				78
	RHNO3 + HV = NO2 + (radical products)	Phot Set= IC3ONO2				77
	RPNO3 + HV = (radical products)	Phot Set= COOH				16,79
	RDNO3 + HV = NO2 + (radical products)	Phot Set= DIONO2				80
	R1NO3 + HV = NO2 + (radical products)	Phot Set= IC3ONO2				77
	R2NO3 + HV = NO2 + (radical products)	Phot Set= IC3ONO2				77
	RUOOH + HV = (radical products)	Phot Set= COOH				16
	RAOOH + HV = (radical products)	Phot Set= COOH				16
	HPALD + HV = (radical products)	Phot Set= HPALDS, qy=0.1				81
	ROOH + HV = (radical products)	Phot Set= COOH				16
	AFG1 + HV = (radical products)	Phot Set= AFGS, qy= 0.45				74,82
	AFG2A + HV = (radical products)	Phot Set= AFGS, qy= 0.45				74,83
	AFG2B + HV = (radical products)	Phot Set= AFGS, qy= 0.45				74,84
	APAN + HV = (radical products)	Phot Set= PPN-11				52
	MAPAN + HV = (radical products)	Phot Set= PPN-11				52

Notes

[a] 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.

[b] 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

Table A-4 (continued)

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:

Phot Set = *name*: The absorption cross sections and (if applicable) wavelength-dependent quantum yields for the photolysis reaction, where "*name*" indicates the photolysis set used. The absorption cross sections and (where applicable) quantum yields for each photolysis set are given in Table A-6 in the electronic supplement of this report. If a "qy=*number*" notation is given, the number given is the overall quantum yield, which is assumed to be wavelength independent.

Falloff: The rate constant as a function of temperature and pressure is calculated using k(T,M) = {k0(T)·[M]/[1 + k0(T)·[M]/kinf(T)]}· F^Z, where Z = {1 + [log10{k0(T)·[M])/kinf(T)}/N]^2 }$^{-1}$, [M] is the total pressure in molecules cm^{-3}, F and N are as indicated on the table, and the temperature dependences of k and kinf are as indicated on the table.

k = k0+k3M(1+k3M/k2): The rate constant as a function of temperature and pressure is calculated using k(T,M) = k0(T) + k3(T)·[M] ·(1 + k3(T)·[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.

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 for (reaction): Uses the same rate constant as the reaction indicated.

[c] Documentation notes are as follows:

1 Based on the NASA (2015) evaluation.

2 Based on the IUPAC (2019) evaluation.

3 IUPAC (2019) does not recommend incorporation of this reaction in models of the atmosphere but sets an upper limit of 1×10^{-22} cm^3 molec^{-1} s^{-1} for the bimolecular process only. NASA (2011) gave an upper limit of 2.0×10^{-21} cm^3 molec^{-1} s^{-1}. It is recommended that this reaction not be included in gas-phase mechanisms, but that models include this as a heterogeneous process if appropriate.

4 Derived from the recommendations of the NASA (2015) evaluation for O_2 and N_2 and their mole fractions in air.

5 The temperature and pressure-dependence parameters were adjusted to fit the rate constants for the HNO_3 forming reaction calculated using the temperature-dependent rate expression of NASA (2015) for the total HO_2 + NO reaction and the temperature- and pressure-dependent expression for the ratio of the rate constant for the HNO_3-forming reaction relative to the total rate constant as given by Butkovska et al (2007), which is recommended by IUPAC (2019). The data were fit for a standard atmosphere for 0 - 5 KM altitude, and atmospheres for 0 - 5 KM with the temperature increased or decreased by 10K.

6 Temperature-dependence parameters adjusted to fit the rate constant for a water concentration corresponding to 50% RH at 300K as a function of temperature at 1 atmosphere, using the parameters given by Stavrakou et al (2013). The reaction is assumed not to be pressure-dependent. This formula somewhat overpredicts the reaction at 100%RH, but probably not by more than the likely uncertainty.

7 SumRO2 or SumRCO3 is added as a product to all reactions that form peroxy or acyl peroxy radicals that react with other peroxy radicals. See discussion of SumRO2 and SumRCO3 in footnotes to Table A-1.

8 Absorption cross-sections and quantum yields at 298K and 1 atmosphere are from the IUPAC (2019) recommendation. IUPAC gives recommendation for effect of temperature on the absorption cross-sections, but the effect is negligible (<1% change in action spectrum) for tropospheric modeling applications. The recommendation indicates no significant temperature or pressure effects on quantum yields for radical formation, but that the quantum yield for H_2 + CO formation increases with decreasing pressure. The pressure effect is expected to increase the overall rate constant by about 15% at 15 KM, which is probably a small effect compared to the other uncertainties in modeling reaction rates at such altitudes.

9 Rate constant expression from Calvert et al (2000).

10 Rate constant and mechanism derived using the estimation methods in the current version of the SAPRC mechanism generation system.

11 Absorption cross sections and quantum yields based on current IUPAC (2019) recommendation. Relative

Table A-4 (continued)

product yields based on calculation using IUPAC (2019) wavelength-dependent quantum yields for both processes and solar Z=0 relative spectral distribution.

12 Abstraction from methyl or ethyl groups, estimated to occur ~4% of the time, is ignored.

13 Assume this reacts with same rate constant as analogous reaction of acetaldehyde.

14 The NASA (2015) recommendation is used for absorption cross sections and overall quantum yields for the three initial reactions, which were HCO + $HOCH_2$(.) (83%); CO + CH_3OH (10%); and OH + $HCOCH_2$(.) (7%).

15 Absorption cross sections of Orlando and Tyndall (2003) for peroxyacetic acid used with unit quantum yields assumed.

16 Assumed to have the same photolysis rate as methyl hydroperoxide

17 ACETO2 is $CH_3C(O)CH_2OO$. The Arrhenius parameters were derived to get same rate constants in the 270-330K temperature range as those derived using the current IUPAC (2019) recommended temperature-dependence parameters.

18 Absorption cross sections and quantum yields based on IUPAC (2019) recommendations. The absorption cross sections are for T=298K. Total quantum yields are calculated for 1 atm and T=298K using the complex expression recommended by IUPAC. For atmospheric conditions the recommendation is to assume most of the reaction occurs via formation of CH_3CO. and CH_3. However, it is necessary to reduce the acetone photolysis rate by a factor of 0.5 in order for the mechanism to correctly simulate effects of acetone on NO oxidation and ozone formation in incremental reactivity environmental chamber experiments.

19 Absorption cross-sections from IUPAC (2019). Pressure-dependent quantum yields derived using the pressure-dependence recommendation given by IUPAC, but for 425 torr N_2. This "pressure" adjustment was made so the calculated photolysis rates, relative to NO_2, are consistent with the data of Plum et al (1983) and Klotz et al (2000).

20 Rate constant at 296 from Talukdar et al (2011). Temperature dependence estimated by assuming that the A factor per -CHO group is the same as used for acetaldehyde.

21 Absorption cross sections of IUPAC (2019) used. IUPAC gives no recommendation of quantum yields, and no new data seem to be available since SAPRC-07 was developed. Quantum yields derived in the same way as for SAPRC-07, based on recommendation of pressure-dependence of quantum yields for methyl glyoxal from IUPAC, with pressure dependence adjusted to get same photolysis rates relative to NO2 as measured by Plum et al (1983) and Klotz et al (2000).

22 Absorption cross sections recommended by Calvert et al (2011). Based on the discussion there, photolysis under atmospheric conditions forms primarily non-radical products, with benzene + CO formation being important at wavelengths that are too low to be important at ground-level conditions. However, using their recommended quantum yields for the higher wavelengths significantly overpredicts rates of consumption of benzaldehyde measured in chamber experiments, which were used as the basis for the photolysis rate used in previous version of this mechanism. Therefore, for this mechanism the overall quantum yield was derived to give the same atmospheric photolysis rate as used in SAPRC-07. The overall quantum yield derived (0.09) is higher than used in SAPRC-07 because the updated absorption cross sections give lower photolysis rates for the same quantum yields at higher wavelengths. Calvert et al (2011) gives no recommendation as to the major products formed at higher wavelengths, but indicates that they are "unidentified products leading to polymer". Currently they are represented as lost carbon, but it may be more appropriate to represent them using a non-volatile model species such as OTHN.

23 Rate constant expression from review of Calvert et al (2015).

24 The current mechanism generation system does not reliably predict mechanisms for phenolic compounds, predicting much higher rates of ozone formation and NO oxidation in chamber experiments than observed experimentally. Therefore, for this version of the mechanism we retain the simplified and parameterized representation of the reactions of these compounds used in SAPRC-07 and SAPRC-11, with phenolic product model species changed to be consistent with those used in the current mechanism and parameters adjusted to give best fits to the chamber data. Note that the rate constants and mechanisms for CRES and XYNL are based on measured rate constants and chamber data for o-cresol and 2,4-dimethyl phenol, respectively, which are taken as representative. These mechanisms are highly uncertain.

Table A-4 (continued)

25 Rate constant expression from the review of Calvert et al (2011).

26 The SVPHE model species is used to represent unspecified semi-volatile, non-nitrogen-containing products of the reactions of OH and NO_3 with phenolic compounds. A highly simplified parameterized mechanism is used based roughly on the simplified representations used for the phenolic compounds themselves. This is highly uncertain.

27 NPHE is used to represent various nitrogen-containing aromatic products formed primarily in the reactions of phenolic compounds or naphthalenes, and its mechanism is based that estimated for nitrophenols. The rate constant used is from SAPRC-07, and is in the range cited by Barnes (2006) for various nitrocresols. The reaction is assumed to occur via abstraction of H from OH, analogous to pathway in the phenol and cresol + OH reactions that occur with similar rates.

28 Rates of photolysis of nitrophenols forming HONO, relative to the photolysis rate of NO_2, based on the data of Bejan et al (2006) for 2-nitrophenol and various methyl substituted 2-nitrophenols. The co-products are unknown, and are assumed to go mainly into the particle phase and its gas-phase reactivity is assumed not to be significant. Loss by other photolysis processes might be significant, but are ignored. Nitrophenols were found to have lifetimes relative to photolysis in the Euphore chamber of 1-2 hours (Barnes, private communication, 2007). A photolysis rate relative to NO_2 of 0.015 corresponds approximately to this range. The products formed are unknown, but based on the data of Bejan et al (2006) it is apparent that NO_2 formation is not important and that HONO formation represents only about 10% of this process. We assume that the co-product forming HONO has similar reactivity of phenol and that the product for the other routes can be represented by the NPHE model species, so this reaction has no effect on the model and is ignored.

29 The "NAPS" model species is used to represent all naphthalenes but its mechanism is based on that derived for naphthalene. The current mechanism generation system is not yet capable of predicting mechanisms for naphthalene, so the highly simplified and parameterized representation used in SAPRC-07 is retained, with the product model species changed to be consistent with the model species used in this version of the mechanism, and the parameters adjusted to fit results of naphthalene - NO_x chamber experiments.

30 The NAPPRD model species is used to represent unspecified non-nitrogen-containing products of the reactions of OH with phenolic naphthalenes. A highly simplified mechanism is used, with the same rate constants as used in the simplified mechanism for NVPHE, used for unspecified products in the reactions of the phenols.

31 The model species "PHOT" is used to represent highly photoreactive model species such as nitrites, which are not important enough in emissions to be represented by separate model species, but is not well represented by other model species. A highly simplified mechanism is used for such compounds, using photolysis rates calculated for biacetyl. This model species should not be used for assessing impacts of specific compounds, only for representing compounds in as minor components in mixtures.

32 The main compound represented by IMINE is $CH_3CH{=}NH$, which is assumed to rapidly hydrolyze to form acetaldehyde and ammonia. Therefore it is treated as in steady state and replaced by the formation of MECHO and XN. "Lost nitrogen" is used for ammonia because it is not included in the gas-phase mechanism. The rate constant is arbitrarily set at 1 sec^{-1}, but is irrelevant if the steady state approximation is used.

33 The rate constants used for the reactions of peroxy radicals other than methyl peroxy with NO, HO2, and NO3 are the IUPAC (2019) recommendations for the corresponding reactions of ethyl peroxy.

33a The rate constant used by model to estimate consumption rate for all peroxy radicals by reaction with HO_2 is from the general estimate above for non-oxygenated peroxy radicals with 5 carbons (see Appendix B), which is the approximate average carbon number of the mixture of anthropogenic emissions used for developing the general mechanism.

34 The SumRO2 counter species is the sum of concentrations of all explicitly represented peroxy radical (RO_2) species and of the operators RO2C and RO2XC that are used for peroxy radicals not represented explicitly. The products formed would depend on the peroxy radical that this peroxy radical is reacting with, but it is assumed that most have alpha hydrogens and can form disproportionation products. For the current mechanism and mechanism generation system, it is assumed that half react to form O_2 + the corresponding alkoxy radicals and half disproportionate, with the two disproportionation reactions assumed to be equally

probable if the peroxy radical has an alpha hydrogen. If the radical does not have an alpha hydrogen, the H is assumed to be abstracted from the other radical. Note that the current peroxy lumping approach requires that the same rate constant be used for the reaction of a given peroxy radical with any other peroxy radical if the latter is represented by SumRO2. SumRO2 is shown as a product in its reactions with individual peroxy or acyl peroxy species since its loss by these reactions are represented separately by its reactions with SumRO2 or SumRCO3.

35 The rate constant expression is based on the NASA (2015) recommendation for the high pressure limit for $CH_3CH_2C(O)OO + NO_2$.

36 The rate constant based on the IUPAC (2019) recommendation for $CH_3CH_2C(O)OO + NO$.

37 The rate constant expression and product branching ratios used for all acyl peroxy + HO_2 reactions is based on the IUPAC (2019) recommendation for acetyl peroxy + HO_2. (The data sheet for this specific recommendation is at http://iupac.pole-ether.fr/htdocs/datasheets/pdf/HOx_VOC54_HO2_CH3CO3.pdf.)

38 The rate constant expression for all acyl peroxy + NO_3 reactions is based on the IUPAC (2019) recommendation for acetyl peroxy + NO_3.

39 The rate constant and product yields used are the IUPAC (2019) recommendation for ethyl peroxy + acetyl peroxy. No information could be found about reactions of other peroxy or acyl peroxy combinations.

40 The rate constant used is the IUPAC (2019) recommendation for self-reactions of $CH_3CH_2C(O)OO$ radicals. Because of lack of information, this is assumed to apply to all acyl peroxy + acyl peroxy reactions except for acetyl peroxy.

41 The peroxy + peroxy rate constants are highly variable depending on the radical, but the peroxy lumping approach does not allow use of separate rate constants for each pair of rate constants. The rate constant used for estimating total rates of consumption of peroxy radicals by peroxy+perpoxy reactions are approximated by those appropriate for secondary peroxy + secondary peroxy reactions, based on averages of such rate constants.

42 The SumRCO3 counter species is the sum of concentrations of all lumped or explicitly represented acyl peroxy radical (RCO_3) species that react with other peroxy radicals. Except when reacting with methyl peroxy radicals, the major reaction of these species with RO_2 or other RCO_3 radials is formation of the corresponding alkoxy radical, which rapidly decomposes to CO_2 and the corresponding alkyl radical. SumRCO3 is shown as a product in its reactions with individual peroxy or acyl peroxy species since its loss by these reactions are represented separately by its reactions with SumRO2 or SumRCO3.

43 The rate constant used for all methyl peroxy + other peroxy reactions is the average of IUPAC (2019) recommendations for methyl peroxy + methyl peroxy and methyl peroxy + ethyl peroxy rate reactions (3.5 and 2 x 10^{-13} cm^3 $molec^{-1}$ s^{-1}, respectively). This may overpredict rates of these reactions for other radicals, though other primary + primary peroxy reactions have higher rate constants than this (IUPAC, 2019).

44 The rate constant and product yields used are the IUPAC (2019) recommendation for methyl peroxy + acetyl peroxy.

45 The rate constant used for all ethyl peroxy + other peroxy reactions is the IUPAC (2019) recommendation for the ethyl peroxy self reaction. This is higher than its rate constant for reaction with methyl peroxy, but lower than other primary + primary peroxy reactions (IUPAC, 2019).

45a Reactions based on estimates for 2-propyl peroxy radicals.

46 The branching ratios and overall product yields are estimated using the procedures in the mechanism generation system.

47 This represents the isomerization of $HC(O)CH_2OO$ to form $HOOCH_2C(O)$ radicals, which undergoes O_2 addition and additional isomerization to form $HOOC(O)CH_2OO$., which reacts primarily with NO and isomerizes to form $HOCH_2C(O)OO$, represented by HOCO3. The conversion of NO to NO_2 in these reactions is represented by RO2C and the reactions of the intermediate peroxy radicals with NO_3 or other peroxy radicals are ignored because of the relatively low yield of this radical. This is based on the procedure used processing reactions in the mechanism generation system for inclusion in the mechanism.

48 The chemical operator RO2C is used to represent NO to NO_2 conversions in reactions of peroxy radicals that are formed in relatively low yields (less than 10% yields in the photooxidations of organics processed

using the mechanism generation system). This is similar to the approach used in SAPRC-99 for all peroxy radicals, and is based on the approximation that the products can be approximated by those that are formed when reactions with NO dominate. The rate constants used are the same as used for the corresponding reactions of SumRO2, which are based primarily on rate constants used for ethyl peroxy radicals.

49 The chemical operator RO2XC is used to represent NO consumption in the nitrate formation reactions of peroxy radicals that are formed in relatively low yields (less than 10% yields in the photooxidations of organics processed using the mechanism generation system). The zNitrate chemical operators are used to determine which nitrate is formed in these reactions, with a zNitrate species being used for each nitrate model species in the mechanism. The zNitrate species are used rather than the nitrate itself to properly account for nitrogen balance when the peroxy radicals react. These are also used to represent the formation of hydroperoxides when these radicals react with HO2 and the formation of other products when they react with NO_3, RO_2 or RCO_3 radicals. This is similar to the approach used in SAPRC-07 for all peroxy radicals. The rate constants used are the same as used for the corresponding reactions of SumRO2, which are based primarily on rate constants used for ethyl peroxy radicals.

50 The rate constant used is the IUPAC (2019) recommendation for acetyl peroxy self-reactions.

51 Assumed to have the same rate constant as the decomposition of PAN.

52 Same photolysis rate and analogous mechanism as used for PPN.

53 Computed using the NASA (2015) recommended rate constant for the reverse reaction and the NASA(2015) recommended equilibrium constant for the zero or infinite pressure limits, assuming the same type of pressure dependence for both forward and reverse.

54 The absorption cross-sections used are those recommended by NASA (2015). They also recommend NO_3 quantum yield of 0.39 at 308 nm. This is assumed for all wavelengths of relevance, with total quantum yield of 1.

55 Unless indicated otherwise, the rate constant expression used for the decomposition of PAN analogue model species is that for the high pressure limit assigned for PPN. This is also used for PAN analogues whose reactions are derived using the mechanism generation system.

56 Absorption cross sections, quantum yields, and reactions based on those used for PPN. PAN2 is the lumped higher saturated PAN excluding PAN and PPN. ETO2 is replaced by NC3OO, the set of peroxy radicals formed from OH + propane.

57 Absorption cross sections, quantum yields, and reactions based on those used for PPN. PAN2N is assumed to be primarily $O_2NOCH_2C(O)OONO_2$, so the products are derived based on this.

58 Rate constants expressions based on the data of Caralp et al (1999).

59 Absorption cross sections, quantum yields, and reactions based on those used for PPN.

60 Rate constant from Lotz and Zellner (2000). The reaction with NO is ignored because nitrite formation expected to be rapidly reversed by photolysis.

61 Rate constant expression from Blitz et al (1999).

62 Rate constant from Platz et al (1998).

63 Assumed to have the same rate constant as used for ethyl peroxy + HO2.

64 This is added to avoid problems in the (generally unlikely) conditions where these radicals are formed when concentrations of both NO_2 and HO_2 are low. The rate constant used is that used in the SAPRC-99 mechanism (Carter, 2000), which is arbitrary and is such that this process becomes significant only if $[NO_2] < \sim 3 \times 10^{-6}$ ppm and $[HO_2] < 1\times10^{-5}$ ppm. The likely process is reaction with some VOC forming compounds similar to those formed when the radicals react with HO2.

65 The NPRAD model species represents unknown naphthalene intermediates that react with NO2 forming nitrogen-containing products. In the absence of NO_2 the reaction with HO_2 is assumed to be the major fate, with the reaction with NO_2 forming a compound represented by NPHE and the reaction with HO_2 forming compounds represented by NAPPRD, the unspecified non-nitrogen-containing product of reactions of naphthalenes. The rate constants are unknown but are estimated to be similar to those for the reactions of acyl peroxy radicals.

Table A-4 (continued)

66 The xNAMIN model species represents nitrogen-centered radicals that do not have alpha hydrogens and can only react with NO_2 or other radicals. In the absence of NO_2 the reaction with HO_2 is assumed to be the major fate, with the reaction with NO_2 forming a nitramine and the reaction with HO_2 forming an amine. The rate constants are unknown but are estimated to be similar to those for the reactions of acyl peroxy radicals.

67 Previous versions of SAPRC assumed that reaction with H_2O, forming the acid, was the major fate of stabilized Criegee biradicals, and represented their formation by the formation of the acid. These are now represented separately in order to account for effects of their reactions with SO_2 and NO_2 as well as H_2O. The rate constants probably depend on the radical, but for now the same rate constants are used for all reactions. See Sarwar et al (2013) for a discussion of stabilized Criegee biradical reactions and rate constants.

68 Rate constant from Welz et al (2012).

69 This reaction is predicted to be the major fate of Criegee biradicals under most atmospheric conditions, even if it has a rate constant lower than the upper limit of Welz et al (2012). The rate constant estimate used here is based on the estimate used by Sarwar et al (2013), which in turn is based on the rate constant ratio relative to reaction with SO_2 given by Calvert et al (1978). This is highly uncertain.

70 Absorption cross-sections are the NASA (2011) recommendation for acrolein. The quantum yields were derived using the pressure and wavelength-dependent expression given by IUPAC (2019) for methyl vinyl ketone, with the parameter representing total pressure adjusted to yield the NASA-recommended quantum yield of 0.0065 at 313 nm and 1 atm. pressure. Product distribution based on the data of Gardner et al (1987) for acrolein, as shown on Figure IX-C-7 of Calvert et al (2011) for 1 atm air.

71 Absorption cross sections of methyl ethyl ketone, based on IUPAC (2019) recommendations, are used for all simple saturated ketones. The wavelength-dependent quantum yields are uncertain, so an effective quantum yields assumed to be the same for all wavelengths, are used. These are assumed to depend on the number of carbons or groups in the molecule, and are adjusted to fit results of ketone - NO_x irradiations for methyl ethyl ketone, 2-pentanone, methyl isobutyl ketone, and 2-heptanone. The data suggest that the overall quantum yields may decrease with the size of the molecule, but the quantum yields that fit the data for 2-heptanone are assumed to apply to larger ketones as well. The mechanism generation system assigns overall quantum yields of 0.1 for MEK through C_6 ketones, and 0.02 for C_7+ ketones. The overall quantum yield for KET2 represents the distribution of ketones represented by this model species (see Table A-3).

72 Absorption cross sections used were IUPAC (2019) recommendations for methacrolein. The quantum yields were derived using the pressure and wavelength-dependent expression given by IUPAC (2019) for methyl vinyl ketone, with the total pressure adjusted so that the radical forming photolysis rates for the chamber experiments are the same as those that fit the chamber data for experiments with methacrolein. IUPAC (2019) gave no recommendations concerning branching ratios product formation, so we assume the product distribution is the same as for the analogous reactions of acrolein.

73 The absorption cross sections and quantum yields used are approximated by those of methyl vinyl ketone, which are based on IUPAC (2019) recommendations. The decline in absorption cross sections with wavelength above 395 nm estimated by linear interpolation. However, the quantum yields calculated for 1 atm overpredicts photolysis rates for chamber experiments that give best fits to data. The effective pressure was increased to 5 atm to give quantum yields that are consistent with modeling chamber data. Note that photolyses of all lumped vinyl ketones (LVKS) are assumed to be the same as used for MEK.

74 Absorption cross sections used for model species used to represent unsaturated 1,4-dicarbonyl aldehydes are based on absorption cross sections of trans-2-butene 1,4-dial and cis and trans 4-oxo-2-pentenal from Liu et al (1999) as reported by Calvert et al (2002). Cross sections used for lumped species based on a previous estimate of the distribution of these products from aromatics, giving 31.6% butenedial and 68.4% 4-oxo-2-pentenal. These have not been updated, but are reasonably representative. Note that these are multiplied by overall wavelength-independent quantum yields that are adjusted to fit chamber data, which would tend to compensate for minor errors in the cross sections when the photolysis rates are calculated.

75 Overall quantum yield adjusted to minimize biases in simulations of rates of formation of $\Delta(O_3\text{-}NO)$ in he simulations of benzene - NO_x chamber experiments where initial NO_x is less than 90 ppb. BUDAL is the only photoreactive dicarbonyl product predicted to be formed from benzene. Note this results in biases in

simulations of experiments at higher NO_x levels, and no adjustment can fit all the data. The lower NO_x experiments are used because these are more representative of atmospheric conditions.

76 Absorption cross-sections and total quantum yields based on IUPAC (2019) recommendation for propionaldehyde. No recommendations are given concerning quantum yields for individual processes, so we assume the same relative quantum yields as used for the analogous reactions of acetaldehyde.

77 The IUPAC (2019) recommendations for absorption cross sections of isopropyl nitrate are used for all organic nitrates. This has somewhat stronger absorptions than n-propyl or lower nitrates, but is taken as representative of the higher nitrates that tend to be formed in higher yields in the reactions of interest. IUPAC (2019) recommends assuming unit quantum yields.

78 The absorption cross sections used for carbonyl nitrates are based on those given by Barnes et al, (1993) for various alpha carbonyl nitrates. Unit quantum yields are assumed based on the discussion given by Barnes et al (1993). Formation of NO_2 from the nitrate groups is assumed to dominate. Although this is derived on data for α-carbonyl nitrates, it is also used for all carbonyl nitrates based on the assumption that excitation of the carbonyl group ultimately results in decomposition at the nitrate group, as is the case for alpha carbonyl nitrates. This is uncertain and may result in overestimation of photolysis rates of β- and other carbonyl nitrates.

79 The absorption cross sections for methyl hydroperoxide is used for hydroperoxy-substituted nitrates because it is assumed that most of the photolysis reaction is at the hydroperoxy group. This is uncertain, and may give an underestimate of the photolysis rate.

80 The absorption cross sections used for dinitrates are based on those given by Barnes et al (1993) for various dinitrates. Unit quantum yields are assumed based on the discussion given by Barnes et al (1993). Formation of NO_2 from the nitrate group is assumed to dominate. Although this is derived on data for α-dinitrates and 1,4-dinitrooxy-2-butene, it is also used for all dinitrates. This is uncertain and may result in overestimation of photolysis rates of other dinitrates.

81 The data of Wolfe et al (2012) suggest that α-unsaturated carbonyls with hydroperoxide groups photolyze at rates consistent with those calculated using absorption cross sections of α-unsaturated carbonyls but with unit quantum yields and with the reaction breaking the peroxy bond, forming OH. This gives a photolysis rate that is about 100 times faster than simple hydroperoxides. However isoprene-NO_x experiments are not well simulated with this high a photolysis rate, so we arbitrarily cut the rate down by a factor of ~10 using an effective quantum yield of 0.1. This is uncertain.

82 Overall quantum yield adjusted to fit rates of formation of $\Delta(O_3\text{-}NO)$ in the model simulations of the p-xylene - NO_x chamber experiments. P-xylene is the only methylbenzene where a photoreactive products lumped with AFG1 is predicted to be formed.

83 Overall quantum yield adjusted to fit rates of formation of $\Delta(O_3\text{-}NO)$ in the model simulations of the m-xylene and 1,2,3- and 1,3,5-trimethylbenzene chamber experiments. These are the trimethylbenzenes that are predicted to form photoreactive products lumped as AFG2A to a significant extent.

84 Overall quantum yield adjusted to fit rates of formation of $\Delta(O_3\text{-}NO)$ in the model simulations of the 1,2,4-trimethylbenzene - NO_x experiments. This is the only aromatic that is predicted to form species lumped with AFG2B to any significant extent.

[d] Complete documentation of assignments used in mechanism generation system is still in preparation. However, information about estimation methods and assignments for specific reactions can be obtained as discussed in Appendix B.

Table A-5. List of reactions of individual VOC compounds that were added to the SAPRC-18 mechanism to for evaluating their mechanisms against chamber data.

Label	Reaction and Products [a]	Rate Parameters [b]			Notes [c]
		k298	A	Ea	
Manually Assigned reactions of VOC tracer species					
CH01	CL2IBUTE + OH = HO2 + RO2C + #4 XC + SumRO2	3.16E-11	3.16E-11		1
CH02	N-C6F14 = #6 XC	0			
Manually Adjusted mechanisms					
CH03	NAPH + OH = #.741 HO2 + #.707 NAPPRD + #.034 RO2C + #.017 AFG2A + #.017 AFG2B + #.034 GLY + #.330 NPRAD + #.250 MACO3 + #.043 SumRO2 + #.250 SumRCO3 + #-3.699 XC	2.30E-11	1.55E-11	-117	2
CH04	NAP23 + OH = #.728 HO2 + #.640 NAPPRD + #.088 RO2C + #.044 AFG2A + #.044 AFG2B + #.088 MGLY + #.200 NPRAD + #.250 MACO3 + #.110 SumRO2 + #.250 SumRCO3 + #.172 XC	7.68E-11	7.68E-11		2
CH05	TETRL + OH = #.919 HO2 + #.595 NAPPRD + #.324 RO2C + #.022 AFG2A + #.022 AFG2B + #.044 MGLY + #.180 NPRAD + #.280 ARO2 + #.070 RO2XC + #.070 zRANO3 + #.405 SumRO2 + #-2.754 XC	3.40E-11	3.40E-11		2
Reactions of Chamber VOCs generated by the Mechanism Generation System					
	From this point on, all reactions are output by the mechanism generation system. (Derivation methods can be obtained from the online system . See Footnote [d] in Table A-4)				
	The number of generated reactions is too large to be useful in a printed document. A complete listing is available in Table A-5 in the electronic supplement to this report.				

[a] 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.

[b] The rate constants are given by $k(T) = A \cdot \exp(Ea/T)$, where the units of k and A are cm3 molec-1 s-1, and Ea is in deg K..

[c] Documentation footnotes are as follows.

1 This is assumed to be unreactive and is used as an inert tracer compound in some experiments.

2 The current mechanism generation system does not reliably predict mechanisms for bicyclic aromatic compounds, predicting much higher rates of ozone formation and NO oxidation in chamber experiments than observed experimentally. Therefore, for this version of the mechanism we retain the simplified and parameterized representation of the reactions of these compounds used in SAPRC-07 and SAPRC-11, with parameters adjusted to give best fits to the chamber data for naphthalene, 2,3-dimethyl naphthalene, and tetralin - NOx chamber experiments.

The following tables are either too large or are not particularly useful in a printed or PDF document and are instead given only in the electronic supplement to this report, Saprc18.xls. This Excel file can be obtained online at http://www.cert.ucr.edu/~carter/SAPRC/18.

Table A-6.	Absorption cross sections and quantum yields for all the photolysis sets in the SAPRC-18 mechanism.
Table A-7.	List of all detailed model species currently represented in the SAPRC-18 mechanism and the model species used to represent them in ambient simulations.
Table A-8.	List of characterization, VOC-NO_x, and mixture-NO_x environmental chamber experiments used for mechanism evaluation, and biases in the simulations of rates of formation of the $\Delta[O_3\text{-NO}]$ and maximum ozone concentrations using the SAPRC-18 and SAPRC-11 mechanisms.
Table A-9.	List of incremental reactivity environmental chamber experiments used in the mechanism evaluation, and biases in the simulations of $\Delta\Delta$(O3-NO) and ΔIntOH/kOH using the SAPRC-18 and SAPRC-11 mechanisms.

The following are included in Saprc18.xls for the purpose of testing implementation of the mechanism. Selected results of this calculation are shown on Figure 4.

Table A-10.	Input conditions for implementation test calculation using SAPRC box modeling software (Carter, 2020b)
Table A-11.	Output concentrations for implementation test calculation, using inputs in Table A-10.

Appendix B. Use of the Mechanism Generation System to Obtain Information on Assignments and Estimation Methods

Documentation of the mechanism generation system is still in preparation as of the date of this report, but the online system at http://mechgen.cert.ucr.edu (Carter, 2010a) can be used to obtain the estimation methods and kinetic and mechanistic assignments used. Information on how to use the online system is given by Carter (2019), and also through various "help" links within the system. The system will require a username and password for logging in, but accounts can be created immediately and this is only to provide users a means to access the system without affecting other users. The online system can be used to obtain information about the estimation methods or assignments used in one of three ways:

- The user can run individual reactions on a step-by-step basis (Carter, 2019), and the system will output information on how the reactions and rate constants were derived -- either the estimation method used or the source of the assignment employed -- along with the reactions and rate constants it generates. The user first creates a VOC or radical as described online or select it from the list of products of a previously-generated reaction. Its reactions will either be generated automatically if it is a radical, or the user will be presented with a menu of available initial reactions (e.g., with OH, O_3, NO_3, or photolysis if applicable) that the user can select to generate a type of reaction.
- The user can select "Show Estimation Methods" from the main menu, and then select the type of reaction. The system will then output information on how these types of reactions are estimated.
- Information on assigned rate constants or branching ratios can be obtained using the "Show SAPRC-18 Mechanism Assignments" link at the main menu (2nd bullet below "Other Actions"), then selecting the type of assignments for which information is desired. However, if the menu item is "Show [some other type of mechanism assignments]", then you first need to change to the model that uses the standard SAPRC-18 assignments, which may be different for some reactants. The assignment option used is shown on the 3rd line from the top of the main page, with a link to change it. Click on the "(change)" link, and then select "SAPRC-18 Mechanism Assignments" from the list. The resulting menu after you select "Show … mechanism assignments" will allow four choices:
    - "All Rate Constants". Select the type of rate constant and all the assignments for this type will be shown on the resulting page.
    - "For Individual SAPRC VOC species (by type)". This will give a menu of available types of compounds for which there are assignments, such as "normal alkanes", etc. Selecting one of these will give a list of compounds. Selecting one of those will give all the assignments that were used when generating mechanisms for that compound. Note that only compounds whose mechanisms were previously generated (in most cases in the process of updating SAPRC-18) and for which assignments have been made will have an active link ont hose lists.
    - "For Individual SAPRC VOC species (by list)". Same as the above except for compounds are sorted by name.

- "Other assignments (not associated with a particular SAPRC VOC species)". This will output assignments for radical reactions that are not necessarily associated with a particular reacting compound.

All the assignment data can also be downloaded in computer readable form using links on the Mechanism Assignments page. The bottom of the page has two links to download the data, one in csv format and one as a text file primarily useful for debugging.