

# DOCUMENTATION OF THE SAPRC-22 MECHANISM

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## Summary

This document describes an updated version of the SAPRC gas-phase mechanisms, designated SAPRC-22. This employs a similar base mechanism and lumping approach for organic compounds as used in SAPRC-16 and 18, but uses the more computationally efficient method to represent reactions of peroxy radicals that requires many fewer species and reactions, resulting in a mechanism closer in size to the widely-used SAPRC-07 mechanism. As with previous SAPRC mechanisms, the reactions of almost all of the organics were derived using the SAPRC mechanism generation system (MechGen), which has been recently updated and documented. SAPRC-22 incorporates some potentially significant updates to the organic chemistry, which the underlying chemistry incorporated in MechGen now being documented in a separate paper that is being submitted for publication. As with previous SAPRC versions, SAPRC-22 was evaluated by comparing its predictions of O<sub>3</sub> formation and NO oxidation rates against a large body of chamber experiments, and its performance was comparable to that of previous versions, despite less compound-by-compound adjustment of uncertain mechanism parameters. It is concluded that SAPRC-22 is an appropriate replacement to SAPRC-07, with more updated chemistry, more tracking of toxic species, and comparable size and computer demands.

This report describes the general features of SAPRC-22 and how it was developed using the mechanism generation system. All the reactions and species in the base mechanism are documented and the generated mechanisms are summarized in the body of this report, and an electronic supplement contains complete mechanism listings and other large tables, and also files useful for mechanism implementation and duplicating the calculations discussed in this report. Additional information and the files needed to implement the mechanism are available at <https://intra.cert.ucr.edu/~carter/SAPRC/22>.

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# 1. Introduction

The SAPRC series of mechanism are designed for use in airshed models to predict the effects of reactions of emitted volatile organic compounds (VOCs) in the presence of  $\text{NO}_x$  to form  $\text{O}_3$  and other secondary pollutants, including toxic organic products and precursors to particle formation. The most widely used of these has been the SAPRC-07 (Carter et al, 2010a,b; Hutzell et al, 2010), which was implemented in a number of airshed models, though it has been subsequently updated as discussed above. The versions for airshed models are similar in objective and approach (though somewhat larger in size in some cases) to the RADM/RACM (Stockwell et al, 1990, 1997, 2006, Goliff et al, 2013) or Carbon Bond (Gery et al, 1988, Yarwood et al, 2005, 2010, Sarwar et al, 2008) series of mechanisms that are also widely used in airshed models, which use a limited number of model species to represent the reactions of the many emitted organic compounds and their reaction products, and uses the steady state assumptions and other approximations to reduce the number of model species needed to represent reactions of intermediate radicals. More detailed versions of SAPRC mechanisms represent the major emitted organics explicitly, but use the same lumped model species to represent reactions of their oxidized products. These detailed versions are used for calculation of MIR and other ozone reactivity scales for organic compounds (Carter, 1994, 2010a-c), and for evaluating the mechanisms using environmental chamber data, but are generally not used in other modeling applications.

The widely-used SAPRC-07 mechanism was updated in 2011 to SAPRC-11 to improve its ability to simulate results of environmental chamber experiments with aromatics (Carter and Heo, 2012, 2013), and then it underwent a complete update in 2016-2020 to the SAPRC-16 through SAPRC-18 mechanisms (Carter, 2015, Venecek et al, 2018, Carter, 2020a). The update of SAPRC-07 to SAPRC-11 was an incremental update that focused mainly on aromatics, while the update to SAPRC-16 was a major update to all portions of the mechanism, using a larger number of model species to better represent precursors to secondary organic aerosol (SOA) formation, and to using a more accurate method to represent peroxy radical reactions, which required use of a much larger number of model species to represent reactions of peroxy radicals than the previous mechanisms. This more accurate peroxy radical representation was considered necessary in order for the model to represent effects of unimolecular, "auto-oxidation" reactions of peroxy radicals, which were not previously recognized to be important, and which was not readily compatible with the way previous versions of SAPRC represented effects of peroxy radical reactions, which relied on the assumption that reactions with  $\text{NO}$  and (to a lesser extent) other bimolecular reactions were their major fate.

Unfortunately, the modeling community has been hesitant to incorporate SAPRC-16 or 18 because of their large size, which may not be necessary for most regulatory models. Although the more accurate peroxy radical representation method is better suited to mechanisms where there are competitions between unimolecular and bimolecular peroxy reactions, the use of the large number of model species and reactions it requires may not be necessary for the purposes of many if not most modeling applications. This may not be necessary for models used primarily for ozone predictions, or predictions of most of the known toxic gas-phase species of current interest. This complexity and increased accuracy in representing auto-oxidation reaction may be necessary for accurate SOA modeling, but only if the SOA module in the model incorporates the complete gas-phase chemistry. Current regulatory models use separate SOA modules that take only limited input from the gas-phase mechanism, so they do not benefit with the greater complexity and accuracy of SAPRC-16 and later versions.

Another problem with the latest versions of the SAPRC mechanisms is that the SAPRC mechanism generation system, MechGen (Carter, 2023a,b), which is used to derive mechanisms for almost all organic compounds the recent SAPRC mechanisms, has been continuously evolving as it is being developed. Because of this, both SAPRC-16 and 18 became out-of-date shortly after they

were developed. In addition, MechGen have not been comprehensively documented or discussed in the peer-reviewed literature, which means that the mechanisms that depend on it are also inadequately documented. The reliance of SAPRC mechanisms on MechGen follows the approach outlined by Kaduwela et al (2015) for mechanism development, involving use of detailed mechanisms and mechanism generation system to serve as the bridge between fundamental science and mechanisms for airshed models. However, MechGen needs to be more stable and better documented if it is to serve as the scientific basis for chemical mechanisms used in modeling.

Because of these considerations, it was decided in early 2022 to pause the continued development of updates for of MechGen until all its existing components can be documented for publication and peer review, and therefore provide a stable basis and citable reference for updated versions of the SAPRC mechanism and other scientific applications. This documentation effort took place during second half of 2022 and a draft manuscript and supplementary section containing details has been prepared and is now under internal review prior to submission to publication in early 2023 (Carter, 2023c). This documentation process required re-examining all the many components, and some revisions to MechGen were found to be necessary, which rendered portions of SAPRC-18 out of date. Most recently, in mid-2023 it was found necessary to completely update the methods to estimate rate constant for peroxy radical isomerization reactions, with the results indicating that such isomerizations are even more widespread than estimated when SAPRC-18 was developed. This required further updates to MechGen and its documentation. However, now this documentation effort is now sufficiently complete to serve as the basis for more stable and documented updated SAPRC mechanisms.

This report presents and describes the newly-developed SAPRC-22 mechanism, which is an update to SAPRC-18, and which was derived from the newly updated and documented version of MechGen (Carter, 2023a-c). This can be thought of as an incremental update to SAPRC-18, with several additional explicit species added. Several versions were examined, all being based on the same detailed mechanisms and having similar levels of chemical detail in terms of lumping organic compounds as SAPRC-18, but differing in the method used to represent peroxy radical reactions. The most detailed "full" version employs a more detailed and accurate method for representing peroxy radical reactions similar to that incorporated in SAPRC-18, now requires far too many intermediate species to be practical for regulatory modeling. The most condensed version examined used the "chemical operator" approach to represent peroxy radical reactions, which is comparable to that used in SAPRC-07 and 11. This requires far fewer species and reactions to represent the reactions of peroxy radicals in the models, and should satisfy the need for an updated version of SAPRC without excessive requirements for computer resources. Unfortunately, because of the peroxy isomerization reactions, it is strictly only valid for an assumed "effective NO" concentration, what must be specified when the mechanism is derived. The version that was adopted for SAPRC-22 was a modification of the most condensed version where a single intermediate was added to the representation of VOC reactions to account for the effects of absolute NO levels on predictions of product yields. This was found to give predictions that are sufficiently close to the full version, to be suitable for regulatory modeling, while not requiring significantly more computer resources than SAPRC-07.

This report gives a description of the new mechanism and how it was derived using the mechanism generation system, describes box model simulations used to develop and evaluate the mechanism, and other information needed to implement the mechanism in airshed models. It includes an electronic supplement consisting of an Excel file containing the large tables, complete mechanism listings, and input and output data to implementation test simulations, and also text files for use in implementing the mechanism using SAPRC and other modeling software systems.

It should be emphasized that, as with previous versions, SAPRC-22 is designed primarily for predictions of gas-phase species. Halogen chemistry was included in SAPRC-07 but has not yet been incorporated into SAPRC-16 through 22 because this was beyond the scope the more recent SAPRC

updates. SOA prediction is also beyond the scope of this project, even though SAPRC-22 includes most of the lumped model species added to SAPRC-16 and 18 to improve representation of SOA precursors. Additional work is needed before gas-phase mechanisms such as SAPRC can be directly used to reliably predict formation of condensable species based on detailed chemistry, which may require far more chemical detail than is practical for regulatory models. In the meantime, continued use of separate SOA modules linked to the output of the gas-phase mechanism is still required for SOA predictions.

## 2. Mechanism Description

### 2.1. Mechanism Size and Comparison with Recent SAPRC Mechanisms

Table 1 gives a summary of the numbers of species and reactions recent SAPRC mechanisms, including the two versions of SAPRC-22 developed in this work. The number of model species used for emitted and product species, and the compounds represented explicitly, varies with the version of the mechanism, tending to increase as the mechanism is updated through SAPRC-18 to take into account increased chemical knowledge and the desire to track more toxic species in airshed model calculations. Another factor in affecting the sizes of these mechanisms in models is the method used to represent the effects of peroxy radical reactions, which are also indicated on the table and discussed further below. Note that the two versions of SAPRC-22 shown on the table differ only how peroxy radical reactions are represented, with both versions using the same model species for stable compounds. The different methods used to represent peroxy radical reactions are discussed later in Section 2.4.2.

The numbers of model species used to represent emitted and oxidized product organic compounds also affects the size of the mechanism, and increased from SAPRC-99 through SAPRC-18 and then declined somewhat for SAPRC-22. The individual emitted and product compounds represented explicitly in the recent and current versions of SAPRC are listed in Table 2, and the model species used for the other compounds are listed in Table 3. The numbers of explicit and lumped model species has increased with each version through SAPRC-18 in order to more accurately represent the mechanisms of the wide range of organic compounds that react in the atmosphere. The numbers of explicitly represented emitted compounds increased for the "toxics" version of SAPRC-07 at the request of the EPA so more compounds of regulatory interest can be tracked, and it was increased further for SAPRC-22 for the same reason at the request of the CARB modelers. SAPRC-18 also uses the approach of representing individual emitted compounds that are particularly important in emissions explicitly. In addition to allowing these important compounds to be tracked and be more accurately represented in model simulations, it also allows the (usually) higher molecular weight compounds that would otherwise be lumped with them to be represented with model species that better represents their mechanisms. Another factor in affecting the sizes of these mechanisms in models is the method used to represent the effects of peroxy radical reactions, which are also indicated on the table and discussed further below. These characteristics are discussed further below.

The numbers of model species used to represent emitted and oxidized product organic compounds also affects the size of the mechanism, and increased from SAPRC-99 through SAPRC-18 and then stayed about the same for SAPRC-22. The individual emitted and product compounds represented explicitly in the recent and current versions of SAPRC are listed in Table 2, and the model species used for the other compounds are listed in Table 3. The numbers of explicit and lumped model species has increased with each version through SAPRC-18, in order to more accurately represent the mechanisms of the wide range of organic compounds that react in the atmosphere. The numbers of explicitly represented emitted compounds increased for the "toxics" version of SAPRC-07 at the request of the EPA so more compounds of regulatory interest can be tracked, and it was increased further for

Table 1. Summary of mechanism sizes and related information for various versions of lumped SAPRC mechanisms for airshed models

Mechanism Version [a]	SAPRC-99	SAPRC-07 (in CMAQ)	SAPRC-18	SAPRC-22 (full)	SAPRC-22 (reduced)	SAPRC-22 (standard)
Model Species	82	126	516	1143	210	260
Inorganics	22	23	22	19	19	19
Explicit organics						
Primarily emitted	3	13	21	30	30	30
Primarily products	9	10	24	16	16	16
Lumped organics						
Primarily emitted	10	13	32	23	23	23
Primarily products	26	26	42	40	40	40
Intermediates [b]	12	41	375	1015	82	132
Reactions	211	569 [b]	1772	5750	647	747
Peroxy method [c]	SAPRC-99	SAPRC-07	SAPRC-16	SAPRC-16	SAPRC-07 (revised)	Hybrid

[a] Information for versions prior to SAPRC-22 are applicable to versions available online at the SAPRC mechanism web site (Carter, 2019b).

[b] Includes inorganic intermediates such as O<sup>3</sup>P and O<sup>1</sup>D, peroxy radical operators, explicit peroxy radicals, and other intermediates where use of the steady state approximation is recommended.

[c] Method used to represent peroxy reactions. See text.

SAPRC-22 for the same reason at the request of the CARB modelers. SAPRC-18 also uses the approach of representing individual emitted compounds that are particularly important in emissions explicitly. In addition to allowing these important compounds to be tracked and be more accurately represented in model simulations, it also allows the (usually) higher molecular weight compounds that would otherwise be lumped with them to be represented with model species that better represents their mechanisms.

## 2.2. Mechanism Listings

Table A-1 and Table A-2 give listings of the model species and reactions in the SAPRC-22 mechanism. These are given at the end of this report because of their size. Footnotes to Table A-1 describe the model species and what they represent, and footnotes to Table A-2 document the rate constants used the base mechanism and other aspects of the reaction as applicable. The derivations of rate constants and mechanisms for the MechGen-derived reactions are described elsewhere (Carter, 2023c), so are not discussed here. Because of their size, these tables are also abbreviated in some respects, with not all of the peroxy operators shown on Table A-1 and not all of the products are shown on Table A-2 for the MechGen-derived reactions. Complete listings of the model species and products of all reactions are given in Table B-1 and Table B-2 in the electronic supplement (see Section 5). Complete mechanism listings can also be obtained from files implementing the mechanism, which are available at <https://intra.engr.ucr.edu/~carter/SAPRC/22/>.

Table 2. List of reactive organic compounds that are represented explicitly in various versions of lumped SAPRC mechanisms for airshed models.

Compound (primarily emitted)	Explicit in [a]				Compound (primarily product)	Explicit in [a]			
	99	07T	18	22		99	07T	18	22
Explicit in all versions					Explicit in all versions				
Methane	X	X	X	X	Formaldehyde	X	X	X	X
Ethylene	X	X	X	X	Methanol	X	X	X	X
Isoprene	X	X	X	X	Formic Acid	X	X	X	X
Added for "Toxics" version of SAPRC-07					Explicit in most versions				
Propene		X	X	X	Glyoxal	X	X	X	X
1,3-Butadiene		X	X	X	Acetaldehyde	X	X	X	X
$\alpha$ -Pinene		X	X	X	Peroxyacetyl nitrate	X	X	X	X
Acetylene		X	X	X	Acetone	X	X	X	X
Benzene		X	X	X	Added for SAPRC-07T				
Toluene		X	X	X	Ethanol		X	X	X
m-Xylene		X	X	X	Glycolaldehyde		X	X	X
o-Xylene		X	X	X	Added for SAPRC-16/18 but not kept for 22				
p-Xylene		X	X	X	Glycolaldehyde's PAN			X	
1,2,4-Trimethyl Benzene		X	X	X	Peroxy acetic acid			X	
Added for SAPRC-16/18					Ethyl hydroperoxide			X	
Ethyl Benzene			X	X	Peroxy propionyl nitrate			X	
Ethane			X	X	Added for SAPRC-16/18 and kept for 22				
Propane			X	X	Propionaldehyde			X	X
n-Butane			X	X	Acrolein			X	X
$\beta$ -Pinene			X	X	Methyl ethyl ketone	[b]	[b]	X	X
d-Limonene			X		Methacrolein	[b]	[b]	X	X
1,2,3-Trimethyl Benzene			X	X	Methyl Vinyl Ketone	[b]	[b]	X	X
1,2,4-Trimethyl Benzene		X	X	X	2-Butene-1,4-dial			X	X
1,3,5-Trimethyl Benzene			X	X	Maleic anhydride			X	X
Added for SAPRC-22					Phenol			X	X
Methyl t-Butyl Ether				X					
Vinyl chloride				X					
Acrylonitrile				X					
Perchloroethylene				X					
p-dichlorobenzene				X					
Methylene chloride				X					
Ethylene dibromide				X					
Ethylene dichloride				X					
Ethylene oxide				X					

[a] "X" indicates that the compound is explicit in the SAPRC-99, SAPRC-07T, SAPRC-18 or SAPRC-22 mechanisms. Blank indicates it is represented using a lumped model species that is also used for other similar compounds.

[b] Methyl ethyl ketone (MEK), methacrolein (METHACRO or MACR) or methyl vinyl ketone (MVK) model species are used to represent chemically similar compounds that are lumped with them.

Table 3. List of lumped model species used in various representative SAPRC mechanisms.

Lumped Model Species				Description
SAPRC-99	SAPRC-07T	SAPRC-18	SAPRC-22	
Alkanes and other saturated compounds that react only with OH				
ALK1	ALK1	ALK3	ALK1	Used for saturated compounds that react only OH radicals.
ALK2	ALK2	ALK4	ALK2	Assigned based on the OH rate constant, alkane status (for SAPRC-18) and molecule size (for SAPRC-22). Primarily used for alkanes, alcohols, and ethers. (The approach used for SAPRC-22 is based on that for SAPRC-07, except ALK6 is used for those with 12 or more carbons + oxygens.
ALK3	ALK3	ALK5	ALK3	
ALK4	ALK4	OTH1	ALK4	
ALK5	ALK5	OTH2	ALK5	
		OTH3 OTH4	ALK6	
Alkenes and other non-photoreactive, non-aromatic compounds with C=C bonds				
OLE1	OLE1	OLE1	OLE1	Alkenes
OLE2	OLE2	OLE2	OLE2	(kOH and/or number of substituents around the double bond used to determine model species)
		OLE3	OLE3	
		OLE4	OLE4	
		OLEC	[a]	
		OLED	[a]	Dialkenes
TERP	TERP	TERP	TERP	Terpenes
	SESQ	SESQ	SESQ	Sesquiterpenes
		OLEP	OLEP	Non-photoreactive oxygenated alkenes
Acetylenes				
		ACYLS	[b]	C <sub>3+</sub> Acetylenes
Aromatics and furans				
		BENX	BENX	Aromatic hydrocarbons
ARO1	ARO1	ARO1	ARO1	(kOH used to determine model species)
ARO2	ARO2	ARO2	ARO2	
		NAPS	NAPS	Naphthalenes
		STYRS	STYRS	Styrenes
		FURNS	FURNS	Furans
Reduced nitrogen compounds				
		AMINS	AMINS	Amines
			TAMNS	Amines bonded to a tertiary carbon (inhibiting)
		IMINE	IMINE	Imines
		NAMIN	NAMIN	Nitramines
Aldehydes				
RCHO	RCHO	RCHO	RCHO	Saturated aldehydes
		RTCHO	[c]	Unsaturated aldehydes
ISO-PROD	IPRD	OLEA1	OLEA1	
		OLEA2	OLEA2	
MGLY	MGLY	MGLY	MGLY	alpha-carbonyl aldehydes
BALD	BALD	BALD	BALD	Aromatic aldehydes
DCB1	AFG1	AFG1	AFG1	Photoreactive aromatic ring opening products
DCB2	AFG2	AFG2A	AFG2A	
		AFG2B	AFG2B	
Ketones				
MEK	MEK	KET2	KET2	Saturated ketones
PROD2	PROD2	LVKS	LVKS	Unsaturated ketones
BACL	BACL	BACL	BACL	alpha-diketones
DCB3	AFG3	AFG3	AFG3	Various non-photoreactive aromatic ring opening products

Table 3 (continued)

Lumped Model Species				Description
SAPRC-99	SAPRC-07T	SAPRC-18	SAPRC-22	
Organic acids				
RCO-OH	RCOOH	RCOOH	OACID	Organic acids
RCO-OOH	RCO3H		PACID	Organic peroxy acids
Aromatic oxygenates and nitrates				
CRES	CRES	CRES XYNL CATL	CRES XYNL CATL	Phenols and catechols
NPHE	NPHE	NPHE NAPPRD	NPHE NAPPRD	Nitrophenols Unspecified products from naphthalenes
Organic nitrates				
RNO3	RNO3	R1NO3 R2NO3 RCNO3 RHNO3 RANO3 RPNO3 RDNO3	R1NO3 R2NO3 RCNO3 RHNO3 RANO3 RPNO3 RDNO3	Saturated organic nitrates (KOH used to determine model species) Carbonyl nitrates Hydroxy nitrates Organic nitrates formed primarily from aromatics Organic nitrates with hydroperoxy groups Organic dinitrates
PAN Analogues				
	PAN2	PAN2	PAN2	Saturated PAN analogues
	MA-PAN	MAPAN	APANS	Unsaturated PAN analogues
	PBZN	PBZN PAN2N	PBZN [d]	Aromatic PAN analogues PAN analogues with additional nitrate groups
Organic hydroperoxides				
ROOH	ROOH R6OOH	ROOH	ROOH	Hydroperoxides
	RAOOH	RUOOH RAOOH HPALD CROOH	RUOOH RAOOH HPCRB	Unsaturated organic hydroperoxides Cyclic hydroperoxide with peroxy groups from aromatics Organic hydroperoxides with carbonyl groups
Unreactive model species				
NROG	NROG	NROG RNNO3 OTHN	NROG RNNO3 OTHN	Volatile unreactive Non-volatile organic nitrates Other non-volatile products

[a] It was determined that there are insufficient amounts of emitted alkenes of this type to justify using separate model species for them. They are lumped with OLE2 or OLE4 depending on the number of substituents about the double bond(s).

[b] There are insufficient amounts of higher acetylenes emitted to justify using separate model species for them. Because they react primarily with OH, they are represented by ALKx, depending on their OH rate constants.

[c] RTCHO was used for C<sub>10+</sub> aldehydes formed from primarily from terpenes primarily to aid SOA predictions. Lumping these with RCHO is sufficient for gas-phase predictions

[d] The amount of such compounds predicted to be formed (primarily from NO<sub>3</sub> + alkene reactions) was determined to be insufficient to justify having separate PAN and RCO3 model species for them.

### 2.3. Base Mechanism and Rate Constant Changes

The base mechanism consists of the reactions of the inorganic species and the  $C_1$  organics that were derived manually based on a review of the literature and available evaluations. This portion of the mechanism as used in SAPRC-11 was essentially the same in SAPRC-07 but underwent a major update for SAPRC-16, with very little further changes for SAPRC-18 or SAPRC-22. Table 4 summarizes the reactions in the base mechanism where the rate constant changed by more than 10% relative to SAPRC-07 or where reactions were added or removed. Also shown are the reactions with larger changes in rate constants for explicitly represented organics and in photolysis rates for lumped photoreactive model species. Not shown are changes in rate constants or mechanisms for lumped species that were derived using MechGen, which reflect changes in estimation methods between the times that SAPRC-07 (Carter, 2000) and SAPRC-22 (Carter, 2023c) were developed. The portions of the mechanism derived using the mechanism generation system are discussed in the following section.

Although a majority of rate constants in the base or explicit mechanisms were not changed significantly, Table 4 shows that there were a number with relative changes greater than 10%, and several where the change was greater than a factor of 2. The largest changes were generally for photolysis reactions, particularly for some types of bifunctional species that are represented separately in SAPRC-22, but lumped with monofunctional compounds in SAPRC-07, are now assumed to photolyze much more rapidly (Carter, 2023c) and are represented by separate model species. There was also a large increase in the generic peroxy +  $HO_2$  rate constant that will affect  $NO_x$  levels where these reactions become important. On the other hand, the large decreases in dicarbonyl +  $NO_3$  rate constants will have small effects on model predictions because these reactions are generally unimportant (except perhaps at nighttime), and the changes regarding phenoxy and phenyl peroxy radicals do not significantly impact predictions of the effects and products of reactions forming these radicals.

In general, the effects of the changes in rate constants and mechanism would depend significantly on the environmental conditions being simulated. The effects of these changes on several box model simulations are presented in Section **Error! Reference source not found.**, but a comprehensive study of the effects of the changes under a variety of conditions will require 3D regional model calculations, which is beyond the scope of this report.

### 2.4. Use of the SAPRC Mechanism Generation System

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 using the explicit reactions to derive condensed SAPRC mechanisms. Previous versions were described in the documentation for the SAPRC-99 mechanism (Carter, 2000), with updates for SAPRC-07 (Carter, 2010a,b), SAPRC-16 (Carter, 2016), SAPRC-18 (Carter, 2020a) and this work. Complete documentation of the current capabilities of the software and the current basis of the chemical mechanistic assignments and estimates of the system is in preparation and will be available elsewhere (Carter, 2023b,c). In addition, information about the various estimates and assignments used when generating mechanisms can be obtained using the web based interface offered by MechGen (Carter, 2023a,b). The major types of reactions currently supported by the mechanism generation system are summarized on Table 5.

Although MechGen could be used to generate all the reactions of a selected compound and its oxidation products leading either to unreactive or nonvolatile compounds or CO or  $CO_2$ , for SAPRC mechanism development it is used primarily to generate reactions leading to first generation products, with the subsequent reactions of the non-radical organic oxidation products not automatically being generated. Reactions of these product compounds are treated by separately, either by generating reactions

Table 4. Reactions in the base mechanism whose rate constants changed by 10% or more.

Reaction	Rate constant [a]		
	SAPRC-07	SAPRC-22	Change [b]
<u>Base inorganic and C1 mechanism</u>			
HO2 + NO	[c]	4.33e-14	
HO2 + NO + H2O	[c]	2.35e-31	
N2O5 + H2O	2.50e-22	[d]	
N2O5 + H2O + H2O	1.80e-39	[d]	
MEO2 + HO2 = MEOOH + O2	4.72e-12	5.21e-12	10%
MEO2 + HO2 = HCHO + O2 + H2O	4.69e-13	0	
HO2 + NO2 = HNO4	1.14e-12	7.50e-13	-41%
HNO4 = HO2 + NO2	8.55e-2	6.20e-2	-32%
OH + NO3	5.98e-12	4.86e-12	-21%
HO2 + HO2	2.90e-12	2.54e-12	-13%
HO2 + HO2 + H2O	6.53e-30	5.71e-30	-13%
HO2 + NO3	4.00e-12	3.50e-12	-13%
O1D + M = O3P + M	3.29e-11	3.69e-11	11%
HCHO + HV = H2 + CO	5.20e-5	5.81e-5	11%
<u>Organic radicals in base mechanism</u>			
BZO + NO2 = NPHE	3.80e-11	2.08e-12	fac 18.3 lower
BZO = other products (unimolecular)	1.00e-3	[e]	
BZO + O3 = BZO2	[c]	2.86e-13	
BZO2 + NO, HO2, NO3, RO2, RCO3	[f]	[g]	
Generic RO2 + HO2	7.79e-12	1.49e-11	fac 1.9 higher
Generic RCO3 + HO2	1.39e-11	2.20e-11	45%
TBUO = ACET + MEO2	9.87e+2	1.43e+3	36%
<u>PAN analogues in base mechanism</u>			
MECO3 + NO2 = PAN	9.46e-12	8.69e-12	-8%
PAN = NO2 + MECO3	4.64e-4	3.82e-4	-19%
R2CO3 + NO2 = PAN2	1.22e-11	7.70e-12	-45%
PAN2 = NO2 + R2CO3	4.01e-4	3.39e-4	-17%
BZCO3 + NO2 = PBZN	1.37e-11	1.11e-11	-21%
PBZN = BZCO3 + NO2	3.12e-4	3.18e-4	2%
<u>Photolysis changes for explicitly represented organics</u>			
Methyl vinyl ketone + hv	1.25e-6	5.32e-6	fac 4.3 higher
Glyoxal + hv = HCHO + CO	5.30e-5	2.76e-5	fac 1.9 lower
PBZN + hv	1.02e-6	1.91e-6	fac 1.9 higher
Acrolein + hv	2.95e-6	3.89e-6	28%
Acetaldehyde + hv	6.93e-6	7.74e-6	11%
<u>Photolysis changes for lumped organics</u>			
Nitrophenols + hv = HONO	1.81e-5	1.81e-5	0%
Nitrophenols + hv = Other products	1.81e-4		
Aromatic fragmentation product #1 + hv	6.45e-3	1.42e-3	fac 4.5 lower
Dinitrates + hv	3.92e-6	1.17e-5	fac 3.0 higher
Hydroperoxy carbonyls + hv	2.34e-5	6.59e-5	fac 2.8 higher

Table 4 (continued)

Reaction	Rate constant [a]		
	SAPRC-07	SAPRC-22	Change [b]
Carbonyl nitrates + hv	2.34e-5	5.05e-5	fac 2.2 higher
Lumped higher PANs + hv	1.02e-6	1.91e-6	fac 1.9 higher
<u>Rate constant changes for explicitly represented VOCs</u>			
Methyl glyoxal + NO <sub>3</sub>	2.43e-15	5.00e-16	fac 4.9 lower
Glyoxal + NO <sub>3</sub>	9.63e-16	4.00e-16	fac 2.4 lower
p-Xylene + OH	1.43e-11	1.21e-11	-17%
a-Pinene + O <sub>3</sub>	8.44e-17	9.59e-17	13%
Methyl ethyl ketone + OH	1.18e-12	1.05e-12	-12%

- [a] Rate constant units are in cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1</sup> or sec<sup>-1</sup> units. Thermal rate constants are for 298K. Photolysis rate constants are for direct overhead sunlight (see Table 8 for the calculation method, and Table B-2 for a listing of all photolysis rate constants in SAPRC-22).
- [b] Factor increase or decrease if change is more than a factor of 2, or (SAPRC-22 - SAPRC-07) / Average, if the change is less than that.
- [c] These reactions were not considered when SAPRC-07 was developed.
- [d] Not included in the SAPRC-22 gas-phase mechanism since this is now considered to be a heterogeneous reaction.
- [e] The pseudo-unimolecular loss of phenoxy radicals was added to SAPRC-07 to avoid problems when both NO<sub>2</sub> and HO<sub>2</sub> are low. It is not needed for SAPRC-22 because of the addition of the phenoxy + O<sub>3</sub> reaction, which was omitted from previous versions.
- [f] The phenyl peroxy radical is represented using chemical operators in SAPRC-07. This method could not be used in SAPRC-22 because of the inclusion of phenyl peroxy + O<sub>3</sub> reaction means it cannot be treated like other peroxy radicals.
- [g] The same rate constants are used as used for other C<sub>2+</sub> peroxy radicals.

for selected product compounds, or by representing them using lumped model species derived from generated reactions of representative compound, as discussed below.

#### 2.4.1. Mechanism Generation Process

The operations of the SAPRC mechanism generation system are described in more detail elsewhere (Carter, 2023b), but relevant features will be summarized here. For each initial reaction of the subject VOC or intermediate radical formed, the system first determines whether there any existing rate constant or mechanism assignments for the reactions, and uses them if available to generate the reaction. If no such assignments have been made (as is usually the case), the system generates the various possible reactions and uses various SARs or estimation methods to estimate the rate constants or branching ratios involved. In some cases there are many possible pathways, some of which may be negligible. The system does not generate reactions it determines to be negligible based on criteria discussed in the following paragraph. 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 (kUni). Unimolecular reactions are treated as the only fate of the peroxy radical if kUni greater ~450 sec<sup>-1</sup>, are not generated if kUni is less than 2.25 x 10<sup>-3</sup> sec<sup>-1</sup>, while both unimolecular and bimolecular of peroxy radicals are generated if kUni is between these levels

Table 5. Summary of types of reactions supported by the SAPRC mechanism generation system.

Reactant(s)	Type of reactions [a]
VOC + OH	H-atom abstraction Addition to double bonds Addition to aromatic rings.
VOC + O <sub>3</sub>	Addition to double bonds followed by Criegee biradical formation. <u>Excited adduct addition to amines, followed by decomposition of adduct forming OH</u>
VOC + NO <sub>3</sub>	H-atom abstraction Addition to double bonds
VOC + O <sup>3</sup> P	Addition to double bonds
VOC + hv	Breaking the weakest bond in saturated aldehydes, hydroperoxides, $\alpha$ -dicarbonyls, PAN compounds, and monofunctional organic nitrates Breaking the weakest bonds in saturated ketones Radical formation from $\alpha$ -unsaturated and $\beta$ -carbonyl aldehydes Radical formation or decompositions of other unsaturated carbonyls. More rapid photolysis of carbonyl nitrates and dinitrates Very rapid photolysis of carbonyl hydroperoxides
VOC Uni.	<u>Thermal decompositions of peroxy nitrates</u>
Carbon-centered Radicals	Unimolecular decompositions of radicals with $\alpha$ -nitro, $\alpha$ -nitrate or $\alpha$ -peroxy groups Reaction with O <sub>2</sub> with H-abstraction from $\alpha$ -OH groups Addition of O <sub>2</sub> to radicals with allylic resonance Reactions of O <sub>2</sub> with aromatic - OH adducts Addition of O <sub>2</sub> to other alkyl radicals
Peroxy of Acyl peroxy Radicals	Reactions with NO forming the corresponding alkoxy radical or organic nitrate Cyclization of aromatic OH-O <sub>2</sub> adducts Unimolecular H-shift reactions forming hydroperoxides Reactions with NO <sub>2</sub> forming the corresponding peroxy nitrate or PAN Reaction with HO <sub>2</sub> forming the corresponding hydroperoxide or other products Reaction with NO <sub>3</sub> forming NO <sub>2</sub> and the corresponding alkoxy radical Reaction with other peroxy radicals forming the corresponding alkoxy radical, carbonyl compound, or alcohol, depending on whether the radical has an alpha hydrogen.
Alkoxy Radicals	$\alpha$ -H abstraction by O <sub>2</sub> forming the corresponding carbonyl compound $\beta$ -scission decompositions H-shift isomerizations Ester rearrangement
Criegee intermediates	Decompositions, stabilization, or rearrangements of excited intermediates Decompositions of stabilized intermediates or reactions with H <sub>2</sub> O

[a] See Carter (2023c) for a complete description of the types of reactions that may be generated and assignments and estimates made for them.

These peroxy kUnl limits were assigned after examining various unimolecular vs bimolecular branching ratios that may occur with atmospheric NO and HO<sub>2</sub> levels.

Each generated reaction forms one or several species. If the species is a stable organic compound (i.e., is not a radical or a rapidly reacting species such as an excited intermediate), or is a radical that is directly represented by a lumped model species in the base mechanism (as is the case for all acyl peroxy radicals in the current SAPRC lumped mechanisms), then it is categorized as a product of the reaction of the starting VOC and it is not reacted further. Otherwise, it is added to the list of intermediates to be reacted<sup>1</sup>, with the process ending when all those formed have been reacted. The result of this process yields a series of explicit reactions of the VOC and the intermediates with the reactions of the type listed on Table 5. Thousands of such reactions can be generated for larger VOCs, forming hundreds of stable products; and this does not count the reactions of the many reactive stable products.

The system uses a "de minimis yield" parameter, which is set at 0.5% for SAPRC mechanisms, to determine which minor reactions can be ignored when mechanisms are generated. In the version used for SAPRC-18 and previous mechanisms, this yield test was applied independently at each reaction step, even if the reactant at the step is an intermediate formed in relatively low (but over 0.5%) yield from another intermediate also formed in a relatively low yield. This can result in many products being formed in extremely low yields that would be negligible by any reasonable criterion. To address this, for SAPRC-22 the yield test is modified so the system will ignore reaction pathways if the relative yield of the pathway multiplied by an estimated upper limit yield of the reactant is less than the de minimis yield parameter. Because the relative importance of intermediates in mechanisms depend on the relative levels of NO<sub>x</sub>, O<sub>3</sub>, OH, HO<sub>2</sub>, and other radicals that are present in the reaction system, it is necessary to define a set of environmental conditions where the concentrations of these species are specified, and thus the relative yields of all the reaction pathways, relative to the amount of starting compound reacting, can be determined. MechGen has algorithms that can derive these yields given a set of environmental conditions, provided that no reactive intermediate in the generated mechanism have reactions that ultimately re-forms itself<sup>2</sup>. Because the mechanism may be used in simulations representing a variety of conditions, mechanism are generated based on estimated yields derived for three different representative environmental conditions, with the de minimis yield test being applied to the reactant yield in the environment where its yield is the highest for the particular series of competitive reactions being generated. The three environmental conditions used for mechanism generation are described in Section 3.2, and represent high NO<sub>x</sub> and low NO<sub>x</sub> daytime conditions and moderate NO<sub>x</sub> nighttime conditions. Note that when reaction pathways are neglected due to low yields, the yields of competing pathways are increased accordingly, to maintain mass balance during the mechanism generation process.

This modified yield test procedure resulted in a more efficient mechanism generation process, with far fewer very minor pathways and very low yield intermediates and products, while having no significant effect on the major pathways and products that are predicted.

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<sup>1</sup> The intermediates in the queue are reacted according to the following priority: (1) most carbons; (2) most hydrogens; (3) highest estimated yield (see used to judge if reactions are non-negligible – see following paragraph); and (4) first formed. This is to minimize cases where reactions that form an intermediate are processed after the reactions of the intermediate, which can result in incorrect yield estimates.

<sup>2</sup> This requirement can be satisfied for mechanisms generated for SAPRC-22 as long as phenoxy radicals are represented by lumped species (so their interconversions involving phenoxy + O<sub>3</sub> and phenyl peroxy + NO to not have to be generated), reversible radical addition to bonds followed by decomposition are represented by a single net addition process, and formation of reactive peroxy nitrates are either ignored or their reactions are generated separately. It is also necessary to ignore the fast H-shift "scrambling" reactions that interconvert isomers of hydroperoxy-substituted peroxy radicals (Carter, 2023c).

Despite the improved procedure used to eliminate negligible processes, the generated mechanisms are still much larger than necessary or appropriate for use in airshed model calculations, and need to be reduced further before MechGen output are integrated into SAPRC. In view of this, MechGen applies the following "post processing" procedures to prepare the generated mechanism for implementation into SAPRC:

1. Reactive intermediates that only undergo rapid unimolecular reactions ( $k_{\text{Uni}} > 1 \text{ min}^{-1}$ ) or that only react with  $\text{O}_2$  are replaced by the products that they ultimately form. This is equivalent to assuming they are in steady state, which should be a good approximation for these intermediates. Branching ratios are based on ratios of rate constants at 298 K and (where applicable) atmospheric  $\text{O}_2$  levels. Effects of temperatures or varying  $\text{O}_2$  levels on these branching ratios are not considered. This eliminates essentially all types of carbon-centered and alkoxy radicals (other than phenoxy), and all types of reactive excited intermediates from the mechanism, as well as peroxy radicals that undergo isomerizations at  $k_{\text{Uni}} > 450 \text{ sec}^{-1}$ . The only remaining intermediates in the mechanisms in the mechanisms generated for SAPRC-22 are peroxy radicals that undergo bimolecular and in some cases also unimolecular reactions at competitive rates<sup>3</sup>.

2. Reactions that occur in parallel (have the same reactants but different products) are combined into single reactions with non-integer product yield coefficients that reflect ratios of rate constants of the competing processes. Temperature dependence in the rate constant ratios (if any) are not considered, though the temperature dependence of the total rate constant is retained. This greatly reduces the number of reactions in the mechanism. It can also reduce the number of species formed in the mechanism because products formed in reactions occurring less than 0.5% of the time are removed.

3. Each individual organic product compound predicted to be formed in the generated mechanism is assigned a lumped model species to represent it in the processed mechanism. The SAPRC-22 lumped model species are assigned as indicated in Table A-1 and its footnotes. MechGen uses various "lumping rules", which assign compounds to model species based primarily on groups<sup>4</sup> or combinations of groups in the molecule, and in some cases the OH rate constant or estimated vapor pressure, to control this process. Acyl peroxy radicals ( $\text{RC}(\text{O})\text{OO}\cdot$  or  $\text{RCO}_3$ ) are also lumped as shown on Table A-1, and for that reason MechGen does not need to generate reactions for such radicals when mechanisms are generated. This greatly reduces the number of product species in the mechanism, but only slightly reduces the numbers of remaining intermediates, which all represent various peroxy radicals.

4. Finally, the numbers of model species used to represent the peroxy radicals are reduced using various approaches. As indicated above and discussed in more detail below, different SAPRC mechanism use different approaches in this regard, and this is a major factor affecting differences in mechanism sizes (e.g., see Table 1). Because different peroxy representation methods were investigated and used when developing SAPRC-22, MechGen provides several options in this regard, as discussed in more detail in the following section.

MechGen will also derive mechanisms for lumped model species based on mechanisms generated for individual compounds they represent. This process is discussed below in Section 0.

Once MechGen has completed processing the reactions of all organic compounds and mixtures, the reactions of the organics in the mechanism is output to a file that is imported into a master spreadsheet that also has the base mechanism and other information needed to compile the mechanism.

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<sup>3</sup> This would also include alkoxy radicals that only have bimolecular reactions, such as phenoxy radicals, which are lumped in SAPRC mechanisms, or  $\text{CF}_3\text{O}\cdot$ , which is currently not handled by MechGen.

<sup>4</sup> MechGen represents molecules as sets of "groups" that consist of one major atom (such as carbon and nitrogen) and variable numbers of hydrogen or oxygens bonded to them (Carter, 2023b). Examples include  $-\text{CH}_3$ ,  $=\text{CH}-$ ,  $-\text{C}(\text{O})-$ ,  $-\text{OH}$ ,  $-\text{O}-$ ,  $-\text{ONO}_2$ , etc.

Macros in this spreadsheet then produce text files used by various modeling systems to implement the mechanism in models.

## 2.4.2. Peroxy Radical Representation Methods

Many types of intermediate radicals, such as carbon-centered or alkoxy radicals, react primarily with  $O_2$  or via unimolecular reactions such that the products ultimately formed do not depend on the presence of reactants whose concentrations vary, and thus can be replaced by the product(s) they form to a good chemical approximation. However, this is not the case for peroxy radicals, which are critical intermediates that are (in most cases) primarily consumed by bimolecular reactions with  $NO$ ,  $HO_2$ , and to a lesser extent  $NO_3$  and other peroxy radicals, so the products they ultimately formed depend on the variable concentrations of these species. It is now realized that many peroxy radicals also undergo unimolecular "auto oxidation" isomerization reactions, but the ultimate products they form still depend on  $NO$  and other reactants unless the isomerizations are sufficiently fast that the bimolecular reactions can be neglected, which is sometimes but not always the case. This is why a more accurate peroxy representation was adopted for SAPRC-16, and utilized in SAPRC-18, resulting in much larger mechanism compared to other versions of SAPRC. Explicitly representing each of these intermediates requires large numbers of model species and reactions, so mechanisms for airshed models have to use various approaches to reduce the numbers of reactions and intermediates required.

Mechanisms designed primarily for ozone predictions can take advantage of the fact that reactions with  $NO$  is the major bimolecular loss process for peroxy radicals under conditions where  $O_3$  formation occurs, so ignoring or only approximately representing the competing reactions have only small effects on ozone predictions. SAPRC-99 (Carter, 2000) and earlier versions of SAPRC, and also versions of Carbon Bond, made the assumption that the major loss process for peroxy radicals was reaction with  $NO$ , so peroxy radicals generated in the mechanisms can be replaced by the products they ultimately form, plus the chemical "operators" that represent the amounts of  $NO$  converted to  $NO_2$  (designated "RO2-R," in SAPRC-99) or are consumed in conjunction with nitrate formation (designated "RO2-N," in SAPRC-99). This resulted in no additional model species being added to represent any radical intermediates, other than those (such as methyl peroxy and lumped acyl peroxy radicals) represented explicitly, and thus represents the maximum degree of condensation in this respect.

While this "SAPRC-99" approach is sufficient for modeling ozone formation, much of the atmosphere represented by regional models have relatively low  $NO_x$  levels, and reactions with  $HO_2$  and (to a much lesser extent) other peroxy radicals become important or dominate. In addition, reactions with  $NO_3$  radicals become important fates for peroxy radicals at nighttime. The hydroperoxides formed from peroxy +  $HO_2$  reactions have generally lower vapor pressures than the products from the alkoxy radicals formed in the  $NO$  reactions, and thus can make greater contributions to SOA formation, whose predictions are increasingly important in models. In order to take the changes in product yields, and particularly the increased hydroperoxide yields, that occur under lower  $NO_x$  conditions, the SAPRC-07 mechanism extended this chemical operator approach to include "x" operators to represent the formation of products from alkoxy radicals formed peroxy +  $NO$  and  $NO_3$  reactions, "z" operators to represent the formations of organic nitrates in the  $NO$  reactions, and "y" operators to represent the formation of hydroperoxides (Carter, 2010a,b), and other products formed in peroxy +  $HO_2$  reactions. This has the significant advantage of not require separate model species for the peroxy radicals themselves, though it does require including a series model species and reactions for the operators used for each product (lumped or explicit) that might be formed. This approach is also used in SAPRC-11 (Carter and Heo, 2012, 2013) and a modified version of it is extended to SAPRC-22 as discussed below. The operators used for representing peroxy reactions in standard SAPRC-22, which are analogous to those used in SAPRC-07 and 11, are included in the model species listings in Table B-1 and summarized in footnotes to Table A-1.

The SAPRC-07 operator method required incorporating the assumptions that all peroxy radicals are consumed by bimolecular reactions and making the additional approximations that (1) the rate constants for these bimolecular reactions are approximately the same for all peroxy radicals, and (2) that relative yields of products formed in NO vs. other reactions for peroxy radicals formed from other peroxy radicals in multi-step mechanisms can be estimated in the same way as from those formed directly. The first approximation ignores the fact that rate constants reactions between organic peroxy radicals can vary by orders of magnitude, but these are very minor processes compared to other peroxy radical reactions (e.g., see Table 10 in Section 3.2 below), so the net effect of this approximation is relatively minor under most conditions. The second approximation neglects the fact that reactions the formation of peroxy radicals from the reactions of other peroxy radicals is reduced when the parent peroxy radical reacts to form other products. In addition, it is now realized that many peroxy radicals are also consumed by "auto oxidation" isomerization reactions, so the assumption that all are peroxy radicals are consumed by bimolecular reactions is incorrect. This would not be a problem if the major isomerization reactions are either so fast that the peroxy radical can be replaced by the products they form (as with carbon centered and alkoxy radicals), or are so slow they can be neglected, as is the case for most peroxy radicals formed from saturated hydrocarbons. However, the SAPRC-07 methods cannot handle cases where the reactions are competitive, at least not without modifications or additional approximations.

For these reasons, a more explicit approach to representing peroxy radicals was adopted for the SAPRC-16 and retained for SAPRC-18. This approach represents explicitly all the peroxy radicals predicted in the generated mechanisms at relative yields greater than 5%, though peroxy radicals formed in the same reactions and that do not undergo isomerizations are lumped together, since they generally react in parallel with the approximately the same rate constants for the major processes. The lower yield peroxy radicals are then represented using a modification of the more approximate SAPRC-07 operator approach, with an "effective NO" concentration assigned to estimate fractions of peroxy radicals that react via unimolecular vs. bimolecular reactions for the purpose of deriving product yields in the overall reactions. This is referred to as the "revised SAPRC-07 method" in the subsequent discussion, with "EffNO" being used as abbreviation for the effective NO parameter.

Assuming a constant NO concentration when deriving product yields for the revised SAPRC-07 representation is an approximation because the actual NO concentration can vary, so it is important that the choice in EffNO be appropriate for the environment being modeled. However, using this approach for low yield radicals in the SAPRC-16 representation is necessary to avoid having very large numbers of very low yield model species mechanisms for compounds with very large generated mechanisms. Although an EffNO parameters still has to be specified, its exact values is not as important for mechanisms derived using the SAPRC-16 peroxy lumping method, since its choice affects only low yield products.

Table 6 provides an example of the application of the peroxy lumping methods used in the simple case of the reaction of OH radicals with n-butane. The table shows only reactions of peroxy radicals with NO and HO<sub>2</sub>, but the reactions with NO<sub>3</sub> and other peroxy radicals are treated similarly (and not directly used to derive the SAPRC-07 representations). The names and structures of the species used are given at the top, columns on the right give the explicit reactions (in terms of the species names) and their relative yields where applicable, and the column on the left give the merged and combined reactions as processed for the condensed mechanism. The top portion shows how the reactions are combined using the SAPRC-16 or 18 method, with those incorporated into the mechanism shown in the cells with double lines. Note that in this case the SAPRC-16 method uses two peroxy radical model species, one ("RO2-12") representing the two radicals formed in the initial reactions of OH with n-butane which can be combined because they do not isomerize), and the other ("RO2-3") representing the peroxy radical formed following the isomerization of RO2-2 (1-butyl peroxy). The bottom box shows how these are all combined to form a single reaction for the SAPRC-07 representation. Note that the "SumRO2"

Table 6. Illustration of reaction lumping using the reaction of n-butane with OH as an example

Name	Structure	Name	Structure	Name	Structure
NC4	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	R3.	HOCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> ·	R1NO3-2	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> ONO <sub>2</sub>
R1.	CH <sub>3</sub> CH <sub>2</sub> CH(·)CH <sub>3</sub>	RO2-3	HOCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OO·	MEK	CH <sub>3</sub> CH <sub>2</sub> C(O)CH <sub>3</sub>
RO2-1	CH <sub>3</sub> CH <sub>2</sub> CH(OO·)CH <sub>3</sub>	RO-3	·OCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	RCHO-1	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CHO
RO-1	CH <sub>3</sub> CH <sub>2</sub> CH(O·)CH <sub>3</sub>	R4.	HOCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH(·)OH	RCHO-2	HC(O)CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH
R2.	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> ·	C2.	CH <sub>3</sub> CH <sub>2</sub> ·	ROOH-1	CH <sub>3</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )OOH
RO2-2	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OO·	ETO2	CH <sub>3</sub> CH <sub>2</sub> OO·	ROOH-2	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OOH
RO-2	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> O·	R1NO3-1	CH <sub>3</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )ONO <sub>2</sub>	MECHO	CH <sub>3</sub> CHO

Ratio	Explicit reactions *	Processed for lumping (* Not shown: RO <sub>2</sub> + NO <sub>3</sub> , RO <sub>2</sub> and RCO <sub>3</sub> )
87%	NC4 + OH -> H2O + R1.	NC4 + OH -> 0.87 RO2-1 + 0.13 RO2-2 + SumRO2
	R1. + O2 -> RO2-1	
13%	NC4 + OH -> H2O + R2.	RO2-1 + NO -> 0.93 {RO-1 + NO2} + 0.07 R1NO3-1 RO-1 -> 0.59 {MEK + HO2} + 0.41 {MECHO + ETO2}
	R2. + O2 -> RO2-2	
93%	RO2-1 + NO -> RO-1 + NO2	RO2-1 + NO -> 0.93*0.59 {MEK + HO2} + 0.93*0.41 {MECHO + ETO2} + 0.93 NO2 + 0.07 R1NO3-1
7%	RO2-1 + NO -> R1NO3-1	
59%	RO-1 + O2 -> MEK + HO2	RO2-1 + HO2 -> ROOH-1
41%	RO-1 -> MECHO + C2.	
	C2. + O2 -> ETO2	RO2-2 + NO -> 0.93 {RO-2 + NO2} + 0.07 R1NO3-2 RO-2 -> 0.83 {RO2-3 + SumRO2} + 0.17 {RCHO-1 + HO2}
93%	RO2-1 + HO2 -> ROOH-1 + O2	
93%	RO2-2 + NO -> RO-2 + NO2	RO2-2 + NO -> 0.93*0.83 {RO2-3 + SumRO2} + 0.93*0.17 {RCHO-1 + HO2} + 0.93 NO2 + 0.07 R1NO3-2
7%	RO2-2 + NO -> R1NO3-2	
83%	RO-2 -> R3.	RO2-2 + HO2 -> ROOH-2
17%	RO-2 + O2 -> RCHO-1 + HO2	
	R3. + O2 -> RO2-3	Reactions used for the SAPRC-16 peroxy method are highlighted below
	RO2-2 + HO2 -> ROOH-2 + O2	
	Merge the two peroxy radicals formed in the same reaction: RO2-12 = 0.87 RO2-1 + 0.13 RO2-2	NC4 + OH -> RO2-12 + SumRO2
		RO2-12 + NO -> 0.87*0.93*0.59 {MEK + HO2} + 0.87*0.93*0.41 {MECHO + ETO2} + 0.87*0.93 NO2 + 0.87*0.07 R1NO3-1 + 0.13*0.93*0.83 {RO2-3 + SumRO2} + 0.13*0.93*0.17 {RCHO-1 + HO2} + 0.13*0.93 NO2 + 0.13*0.07 R1NO3-2
		RO2-12 + HO2 -> 0.87 ROOH-1 + 0.13 ROOH-2
93%	RO2-3 + NO -> RO-3 + NO2	RO2-3 + NO -> 0.93 RO-3 + 0.07 RHNO3
7%	RO2-3 + NO -> RHNO3	RO-3 -> RCHO-2 + HO2
	RO-3 -> R4.	RO2-3 + NO -> 0.93 {RCHO-2 + HO2} + 0.07 RHNO3
	R4 + O2 -> RCHO-2 + HO2	RO2-3 + HO2 -> ROOH-3
	RO2-3 + HO2 -> ROOH-3 + O2	
	Reactions used for the SAPRC-07 peroxy method are shown to the right. (RO2C and RO2XC represent effects on NO and NO <sub>2</sub> . See Table A-1 for the operator list for SAPRC-22)	NC4 + OH -> 0.87*0.93*0.59 {xMEK + xHO2} + 0.87*0.93*0.41 {xMECHO + xETO2} + 0.87*0.93 RO2C + 0.87*0.07 {zR1NO3-1 + RO2XC} + 0.13*0.93*0.83*0.93 {xRCHO-2 + xHO2 + RO2C} + 0.13*0.93*0.83*0.07 {zRHNO3 + RO2XC} + 0.13*0.93*0.17 {xRCHO-1 + xHO2} + 0.13*0.93 RO2C + 0.13*0.07 {zR1NO3-2 + RO2XC} + 0.87 yROOH-1 + 0.13 yROOH-2 + {1 + 0.13*0.93*0.83} SumRO2

Table 7. Illustration of reaction lumping using portions of the reactions of 1,3-butadiene with OH radicals as an example.

Name	Structure	Name	Structure	Name	Structure
BUT13	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	RO2-1	$\text{HOCH}_2\text{CH}=\text{CH}-\text{CH}_2\text{OO}\cdot$	R3.	$\text{HOCH}_2\text{CH}=\text{CH}-\text{CH}(\cdot)\text{OH}$
R1.	$\cdot\text{CH}_2\text{CH}=\text{CH}-\text{CH}_2\text{OH} \leftrightarrow \text{CH}_2=\text{CH}-\text{CH}_2(\cdot)\text{OH}$	R2.	$\text{HOCH}(\cdot)\text{CH}=\text{CH}-\text{CH}_2\text{OOH}$	HPCRB	$\text{HC}(\text{O})\text{CH}=\text{CH}-\text{CH}_2\text{OOH}$
		RO-1	$\text{HOCH}_2\text{CH}=\text{CH}-\text{CH}_2\text{O}\cdot$	OLEA1	$\text{HOCH}_2\text{CH}=\text{CH}-\text{CHO}$

Ratio	Example explicit reactions	Example reactions processed for lumping
95%	BUT13 + OH -> R1.	BUT13 + OH = 0.95*0.33 RO2-1 + other products
5%	BUT13 + OH -> other products	
62%	R1. + O2 -> other products	
33%	R1. + O2 -> RO2-1	
	RO2-1 -> R2. (k = kUni <sub>1</sub> )	RO2-1 -> 0.92 {HPCRB + HO2} + other products
92%	R2. + O2 -> HPCRB + HO2	
8%	R2. + O2 -> other products	
95%	RO2-1 + NO -> RO-1 + NO2	RO2-1 + NO -> 0.95 {RO-1b + NO2} + 0.05 RHNO3 (k = kNO)
5%	RO2-1 + NO -> RHNO3-2	
	RO-1 -> R3.	
	R3. + O2 -> OLEA1 + HO2	
Combine RO2-1 reactions, assuming fraction unimolecular = $f_{\text{UNI}_1} = k_{\text{Uni}_1} / (k_{\text{Uni}_1} + k_{\text{NO}}[\text{NO}^{\text{eff}}])$ (This is an example of the "revised SAPRC-07" method used in this work.)		
$\text{BUT13} + \text{OH} \rightarrow 0.95*0.33*f_{\text{Uni}_1}*0.92 \{ \text{HPCRB} + \text{HO}_2 \} + 0.95*0.33*(1-f_{\text{Uni}_1})*0.95 \{ x\text{OLEA1} + x\text{HO}_2 + \text{RO2C} \} + \text{other products}$		

species is added as a product to any reaction forming a peroxy radical in both representations, so that rates of peroxy + total peroxy reactions can be calculated in the model. Table 6 shows how all the product yield coefficients in the lumped representations are calculated from the relative rates of the various competing reactions in the explicit mechanism.

An illustration of how an assigned "effective NO" concentration is used to derive the SAPRC-07-type representation of peroxy radical reactions in a case where both unimolecular and bimolecular peroxy reactions need to be represented, as is the case for portions of the isoprene + OH mechanism, is shown on Table 7. 1,3-Butadiene is used as the example because it has a somewhat simpler mechanism. This peroxy lumping method is referred to as the "revised SAPRC-07" approach in the subsequent discussion.

The "Full" version of SAPRC-22 employs essentially the same peroxy lumping approach as SAPRC-16 and 18, except that it does not lump together peroxy radicals that react in parallel, since that did not result in a significant reduction of numbers of model species. These mechanisms explicitly represent all peroxy radicals that are formed in yields of 5% or higher under standard conditions (see Section 0 for a discussion of how generated mechanisms are processed and yields are derived, and Section 3.1 for a discussion of standard conditions). Peroxy radicals formed in yields lower than 5% are represented using revised SAPRC-07 operator method discussed above. Note that this gives a mechanism that is much larger than SAPRC-18 (see Table 1), because of the revised estimation methods for unimolecular reactions of peroxy radicals results in a much larger number of non-negligible that need to be represented explicitly than was the case when SAPRC-18 was developed. This gives too large a

mechanism to be appropriate for airshed modeling, but can serve as a standard in box model calculations when assessing predictions using more reduced approaches.

An important parameter in the SAPRC-16/18 peroxy lumping method used to derive the full version of SAPRC-22 is the 5% cutoff, indicating the maximum yield of peroxy radicals to be represented explicitly, as opposed to using the revised SAPRC-07 method with an assigned EffNO. Using a higher value for this cutoff would decrease the number of peroxy radicals that have to be represented explicitly, with the limit being a 100% cutoff, which is equivalent to using the revised SAPRC-07 method for all reactions, requiring no peroxy intermediates other than the SAPRC-07 operators.

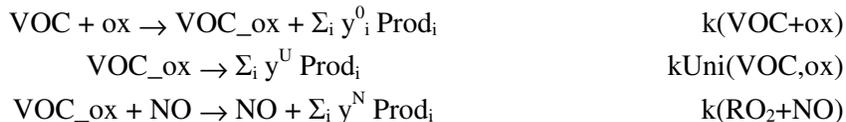
The "Reduced" version of SAPRC-22 employs the revised SAPRC-07 approach for all reactions, which is equivalent to using the SAPRC-16 method with a 100% cutoff. This mechanism is comparable in size to the widely-used SAPRC-07 mechanism (see Table 1), making it suitable for use in 3D models, at least in terms of its size. However, the size advantage relative to the full version is offset by the mechanism being much more sensitive to the choice of the EffNO parameter, at least for predictions of product yields that are affected by competitions between unimolecular and bimolecular reactions of peroxy radicals. A high effective NO value would represent the higher NO<sub>x</sub> urban conditions where O<sub>3</sub> formation is most sensitive to VOCs, such as those used to derive the MIR scale (Carter, 1994), whereas a low value represents regional or remote conditions where O<sub>3</sub> is affected primarily by NO<sub>x</sub> availability and reactions of organics are less important in affecting O<sub>3</sub> predictions. In view of this, and the fact that the SAPRC-22 mechanism is expected to be used primarily for modeling regions affected by urban emissions, it was decided to use an EffNO value of 0.5 ppb when deriving the reduced version of SAPRC-22. This is approximately representative of "equal benefit incremental reactivity" (EBIR) scenarios used in reactivity scale calculations (e.g., Carter, 1994), with the total pollutant levels reduced to be more representative of current pollution levels. EBIR scenarios represent intermediate NO<sub>x</sub> conditions where O<sub>3</sub> is equally sensitive to relative changes in VOC and NO<sub>x</sub> emissions, and is one of the scenarios used in this work to compare different mechanisms and is described in Section 3.1, below. However, this may not be appropriate for all applications where SAPRC-22 may be employed, such as modeling reactions in plumes or near other NO<sub>x</sub> sources.

Test calculations discussed later in this report indicate that the full and reduced versions of SAPRC-22 give very close predictions of O<sub>3</sub> and most other species in ambient simulations, except for certain organic products predicted from isoprene whose yields are highly dependent on NO<sub>x</sub> levels. Products from other compounds, are also affected, but differences in predictions in simulations of complex ambient mixtures are not as noticeable because of their relatively lower contributions to total emissions. The full and reduced versions also give very similar results when evaluating results of chamber experiments, except for experiments with 1,3-butadiene, isoprene and terpenes. Therefore, use of the condensed version may be satisfactory if the main interest is predictions of ozone and atmospheric lifetimes, but is not as satisfactory if predictions of oxidized products and SOA precursors is a priority.

In order to obtain better balance between mechanism size and accuracy in product predictions, we developed a new "hybrid" peroxy lumping approach that provides a means to derive yields that depend on NO levels with a minimum number of additional reactions and model species, without having to use an assumed EffNO parameter. Rather than having a single, lumped overall reaction for each VOC reaction that represents the distribution of products formed ultimately with an assumed effective NO level, a single intermediate model species is added for each initial VOC reaction that has both a unimolecular and NO reaction, so together they can predict how yields vary with absolute NO levels without having to represent all the intermediate peroxy radicals explicitly. If reactions of any VOC model species with an atmospheric oxidant, ox (e.g., OH, O<sub>3</sub>, etc) is given by



but if the product or operator yields,  $y_i$  depend on an as assumed EffNO, this dependence can be removed by using the following representation:



Here, "VOC\_ox" is a new intermediate species added to the mechanism, and the  $y_i^0$ 's,  $y_i^U$ 's,  $y_i^N$ 's, and  $k\text{Uni}$  values are derived using the revised SAPRC-07 approach as follows:

$y_i^{\text{lowNO}}$  = Yield of  $\text{Prod}_i$  derived using an EffNO low enough so yields are insensitive to EffNO

$y_i^{\text{highNO}}$  = Yield of  $\text{Prod}_i$  derived using an EffNO high enough so yields are insensitive to EffNO

$y_i^{\text{midNO}}$  = Yield of  $\text{Prod}_i$  using an EffNO in the range where product yields are sensitive NO

$$y_i^0 = \min(y_i^{\text{highNO}}, y_i^{\text{lowNO}})$$

$$y_i^U = y_i^{\text{lowNO}} - y_i^0$$

$$y_i^N = y_i^{\text{highNO}} - y_i^0$$

$$k\text{Uni}_i = k(\text{RO}_2+\text{NO}) \times (y_i^{\text{highNO}} - y_i^{\text{midNO}}) / (y_i^{\text{midNO}} - y_i^{\text{lowNO}})$$

$$k\text{Uni}(\text{VOC},\text{ox}) = \text{Avg}(\text{for 3 highest } |y_i^{\text{highNO}} - y_i^{\text{lowNO}}|) k\text{Uni}_i$$

and the  $y_i^{\text{lowNO}}$ ,  $y_i^{\text{highNO}}$ , and  $y_i^{\text{midNO}}$  values are derived using the revised SAPRC-07 method used for the reduced versions, but for high, low, and middle EffNO levels. The low and high values were chosen so that the product yields predicted are applicable for either low or high  $\text{NO}_x$  conditions, but are not sensitive to the specific values used, which were arbitrarily chosen to be 0.1 ppt and 1 ppm, respectively. The  $y_i^{\text{midNO}}$ 's were derived using an EffNO of 5 ppb, which was chosen to represent the range of NO levels where the yields are the most dependent on the EffNO values chosen. If  $y_i^{\text{highNO}} = y_i^{\text{lowNO}}$  for all products, then the additional species and reactions are not added, and the reaction is represented using the same modified SAPRC-07 approach as in the condensed version. If there is no product where  $|y_i^{\text{highNO}} - y_i^{\text{lowNO}}| > 0.015$ , then the intermediate and the additional reactions are not added, and the modified SAPRC-07 approach is used, employing the  $y_i^{\text{midNO}}$  values as the yields. This is to avoid adding the additional model species and reactions where there is only minor a difference between high and low NO yields.

Isoprene is an example of a compound where yields of several major products in its reaction with OH are affected by absolute NO levels because of peroxy intermediates that have non-negligible unimolecular reactions. Figure 1 shows the NO dependences of the yields of two representative types of isoprene products, unsaturated aldehydes other than methacrolein formed following peroxy + NO reactions and unsaturated hydroperoxy carbonyls formed after competing unimolecular reactions of the same radicals, calculated using the revised SAPRC-07 approach as a function of the EffNO parameter. The lines on the figure show the yields derived using the hybrid approach discussed above, which fit the yields derived from varying EffNO reasonably well. The fit is not perfect because in general there are several unimolecular reactions with different rate constants that may affect overall yields, while the hybrid approach uses only one "best fit" rate constant. However, the fit is reasonably good, and this isoprene + OH case is probably reasonably representative.

The "Standard" version of SAPRC-22 employs this hybrid peroxy lumping approach, and is included in the summary of versions of SAPRC-22 given on Table 1. It was derived with  $y_i^{\text{lowNO}}$  and  $y_i^{\text{highNO}}$  values of 0.1 ppt and 1 ppm, respectively, where yields are insensitive to the EffNO value used, and the  $y_i^{\text{midNO}}$  values using 5 ppb, where the yields are highly sensitive to EffNO, as shown on Figure 1. It is considered a good compromise between the somewhat more accurate but very large "full" version

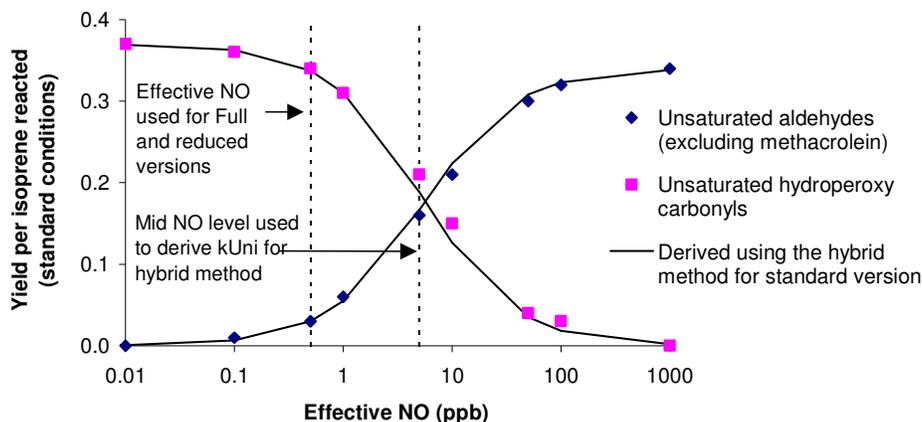


Figure 1. Comparison of yields of isoprene products whose predicted yields are highly dependent on absolute NO levels derived revised SAPRC-07 approach with varying EffNO levels against those calculated using the hybrid approach used for the standard mechanism with varying NO levels.

and the less accurate "reduced" version, and is thus recommended for use in most general airshed model applications because it does not require using a constant EffNO parameter. As discussed below, it does not give exactly the same predictions as the full version in all cases because of the approximate treatments in the revised SAPRC-07 approach of bimolecular reactions of peroxy radicals with  $\text{NO}_3$  and other peroxy radicals. However, the differences are relatively small in most cases.

### 2.4.3. Generated Mechanisms for Lumped Model Species

Mechanisms used for most lumped model species are derived from mechanisms of the representative individual compounds the model species are designed to represent. MechGen does this by averaging or combining mechanisms of the compounds in the representative mixtures, as discussed below. The exact procedure depended on the peroxy lumping approach employed.

In the case of the reduced mechanism, where each initial reaction of individual VOCs is a single reaction given a list of product species and yields, the mechanisms of the corresponding reaction of the mixture is derived by weighted averages of the products of each initial reaction that the compounds undergo, with the rate constants for the initial reactions of the lumped species being the weighted average of the rate constants for corresponding reactions of the constituents. Note that all lumped model species must have the same types of reactions as the compounds they represent, so there are no cases where some species lumped together have a certain type of initial reaction (e.g., with  $\text{O}_3$  or  $\text{NO}_3$ ), while others do not. There are also no cases where species lumped together have significantly different atmospheric photolysis rates, since this is one of the criteria used to determine how to lump photoreactive species.

In the case of the full or standard mechanisms, the initial reactions of the VOCs in the initially derived explicit mechanisms are also merged using weighted averages of the product yields and rate constants, but since the explicit mechanisms are used as the starting point the products also include intermediate species. The representations of the subsequent reactions of the intermediate species formed from the components of the mixture are then derived using the same procedure as used when deriving the lumped mechanisms for individual compounds.

Four mixtures representing ambient conditions were used to determine which compounds to take as representative of the various lumped model species, depending on the primary sources of the compounds in the model simulation in terms of emissions or formation. The mixtures used when developing lumped mechanisms for SAPRC-22 are indicated in the model species listing on Table A-1 and the specific compound used for each lumped species are given in Table B-5 in the electronic supplement. These were as follows:

The "EmitMix" mixture was used to represent anthropogenic VOC emissions and consisted of annual statewide 2018 California VOC emissions from all sources, excluding wildfires and biogenics. This was provided by CARB staff (Chenxia Cai, private communication, November 2022) in terms of speciation categories used by the CARB, and was used to derive speciation in terms of individual compounds using the assignments in the Carter (2015, 2023d) speciation database. Approximately 90% of the mass of this mixture could be identified as chemical compounds where MechGen could assign lumped model species. This was used to derive mixtures to use to derive mechanisms for model species representing primarily anthropogenic emissions, such as ALKn, OLEn, AROn, AMINS, etc. Note that compounds that are represented explicitly, such as, for example, propene, toluene, and the di- and trimethyl benzene isomers (see Table 2 for a complete list), are excluded from these mixtures. The composition of this mixture as used in this work is given in Table B-6 in the electronic supplement.

The "BioMix" mixture was used to represent biogenic emissions, and consisted of the statewide 2018 biogenic emissions in California, and was also provided by the CARB staff (Chenxia Cai, private communication, November 2022). It was used to derive the mixture of terpenes to derive the mechanism of the TERP model species that represents terpenes that are not represented explicitly. Note that  $\alpha$  and  $\beta$  pinenes are excluded from this TERP mixture because they are represented explicitly (Table 2). The composition of this mixture as used in this work is given in Table B-7 in the electronic supplement.

The "Products" mixture consisted of the mixture of organic oxidation products that resulted from reacting a mixture consisting of reacting equal parts (by mass) of the anthropogenic (EmitMix) and biogenic (BioMix) mixtures under standard reaction conditions. Standard reaction conditions represented approximately EBIR conditions where  $O_3$  is equally sensitive to relative changes in VOC and  $O_3$ , which is one of the four environmental conditions derived in this work as discussed in Section 3.2 for the purpose of mechanism processing and sensitivity analysis. If these background reactant concentrations and photolysis frequencies are assumed to be constant, and if a reaction time is specified (6 hours is used in this work), then the distribution of products formed when the VOC reacts under these conditions can be determined. (This is an approximation because the subsequent reactions of the non-radical products are not taken into account.) The relative concentrations in this "Products" mixture is derived by multiplying the compositions of the 50:50 anthropogenic + biogenic mixtures times the yields of all of the products formed when they react under standard conditions, with products formed from different compounds being summed up. This was used to derive mixtures for model species that primarily represent oxidation products, such as RCHO, KET2, CRES, etc. This calculation is done within MechGen. Note that oxidation products represented explicitly, such as acetaldehyde, glyoxal, 2-butene-1,4-dial (see Table 2 for a complete list) are excluded from these mixtures.

The "Products2" mixture consists of oxidation products that result from reacting the "Products" mixture under the standard set of conditions as discussed above. It is used to derive the mixture of catechols that result from the reactions of the phenolic compounds in the atmosphere. Although some phenolic compounds are emitted directly, most are formed as products in the reactions of aromatic hydrocarbons, so their relative levels in the "Products" mixture would be more representative to their relative atmospheric levels, and thus to relative amounts of different catechols formed in their reactions.

In some cases, there were large numbers of individual compounds represented by a given model species in the mixture representing their emissions or formation, but with only a few compounds making

significant contributions. In those cases, only the compounds whose total mole fractions summed up to 90% of the total, or only the top 15 compounds (which ever was less), were used in to derive mechanisms for any lumped species. Table B-5 in the Supplementary Materials give the mixtures used to derive mechanisms of all the mixture-dependent model species used for SAPRC-22. Note that these mixtures are the same for both the standard and full version of SAPRC-22.

Although it was necessary to assume anthropogenic and biogenic mixture compositions in order to derive mechanisms for lumped model species, it should be recognized that the resulting mechanisms are not very sensitive to the exact composition of these mixtures. This is in part because the most important compound in emissions are represented explicitly, and the relatively large numbers of model species used for product compounds means that the compounds being lumped together are very chemically similar, giving similar mechanisms being derived even if the mixture of compounds used to derive their mechanisms change. Therefore, even though the anthropogenic and biogenic mixtures used to derive lumped mechanisms are based on California data, use of different mixtures will probably not result in mechanisms that give significantly different predictions, so this mechanism should be equally usable for non-California scenarios.

## **2.5. Emissions Assignments**

An important but often overlooked part of developing new atmospheric mechanisms is providing assignments of model species to the many hundreds of categories of compounds and mixtures used in emissions speciation profiles. Assignments of SAPRC-22 model species to all the individual compounds in the SAPRC detailed model species database are given in Table B-4 in the electronic supplement. This includes the major compounds identified in emissions, including those for which ozone reactivity scales have been calculated (Carter, 1994, 2010c).

Previously, we developed a speciation assignment database for assigning model species used in various mechanisms to speciation categories used in various emissions databases, including the Speciate database maintained by the EPA, and emissions categories used by the CARB (Carter, 2015). In addition to various SAPRC mechanisms, it includes model species assignments for Carbon Bond IV, RADM2, RACM2, and other mechanisms. This database has two parts: the assignments of actual compounds to categories used in the various databases (which includes mixtures as well as individual compounds), which is mechanism independent, then the assignments of model species to the individual compounds for the different mechanisms. The second part was updated as part of this work to include assignments of SAPRC-22. This revised speciation database is now available online at the Speciation Database website (Carter, 2023d).

When providing the anthropogenic and biogenic emissions data used to derive lumped mechanisms as discussed in Section 0 or for box model simulations described in Section 3.1, the CARB staff also provided a list of new speciation categories added to the California emissions database. Although there was insufficient time and resources available in this project to update the assignments of the new categories to chemical compounds, or to add new compounds to the speciation database, the new categories and compounds were found not to be important in the anthropogenic or biogenic emissions data that were used in this work, so the lack of assignments for them should not be important in affecting the mixture assignments discussed in Section 0 or for box model simulations described in Section 3.1. Assignments for these new categories can be made later if required.

### 3. Test Calculations

Several atmospheric box model scenarios were simulated in order to compare predictions of the three versions of SAPRC-22 with different peroxy lumping approaches with each other and also with SAPRC07. These simulations were also used to derive oxidant concentrations to define standard conditions for determining which routes can be neglected when generating mechanisms and for estimating relative product yields (see Section 3.2). The derivations of the test scenarios and the results of the test and evaluation calculations are discussed in this section.

#### 3.1. Ambient Model Scenarios and Calculations

##### 3.1.1. Scenario Inputs

The conditions and inputs of the box model scenarios used to compare different mechanisms under simulated but simplified ambient conditions, and to derive sets of standard conditions for mechanism derivation and analysis, are summarized on Table 8. These were based on averages of inputs to the 39 simplified urban scenarios used to derive the MIR and other reactivity scales (Carter, 1994), except they involved four simulated days rather than one, and had lower pollutant levels in order to better represent current ozone pollution levels in the United States. (The reactivity scenarios were based on ambient data and emissions in the '80's, and reflect higher pollutant levels than currently is the case.) No pollutants were present initially except for background CO and methane, both VOC and NO<sub>x</sub> emissions occurred at constant fluxes during the day and none at nighttime. The mixing height started at 100 meters in the morning and increased to 540 meters each day, during which the air mass was being diluted with clean air from aloft. The mixing height declined back to 100 meters at night, but this did not affect the simulation because there was no mixing or dilution during the period. The photolysis rates were calculated as a function of solar zenith angle using the same actinic fluxes used for the reactivity scale calculations (Carter, 1994, 2010a), with the zenith angles calculated from the time of day using the latitude and declination of Los Angeles and daylight savings time. The simulated results for days 2-3 were used for the mechanism comparisons, and those for days 2 and 4 were used to derive the standard conditions. The first simulated day was used to establish background levels, since the initial and background conditions were essentially clean air.

Four different scenarios were employed, each with the same inputs except for the amounts of NO<sub>x</sub> emissions. The daily VOC emissions fluxes were set at ¼ the average used in the reactivity calculations (Carter, 1994), which gave maximum ozone levels more representative of current O<sub>3</sub> pollution conditions than the average of the Carter (1994) reactivity scenarios, where the maximum O<sub>3</sub> was 180-230 ppb, depending on NO<sub>x</sub> inputs. The reduced VOC inputs gave maximum ozone levels of ~140 ppb in the maximum O<sub>3</sub> scenario, so they still represent highly polluted conditions. NO<sub>x</sub> inputs were adjusted to derive approximate MIR, MOIR, EBIR, and lower NO<sub>x</sub> conditions, representing high NO<sub>x</sub> conditions where O<sub>3</sub> is most sensitive to VOC emissions (MIR), lower NO<sub>x</sub> conditions that achieve peak O<sub>3</sub> levels, still lower NO<sub>x</sub> where O<sub>3</sub> is equally sensitive to relative changes in VOC and NO<sub>x</sub> conditions (EBIR), and even lower NO<sub>x</sub> conditions where NO<sub>x</sub> is about 10% that yielding maximum O<sub>3</sub>. These conditions were determined by varying O<sub>3</sub> to determine the highest day 2-4 O<sub>3</sub> levels (to establish the MOIR scenario), with the NO<sub>x</sub> for the MIR and EBIR scenarios being based on ratios of MIR/MOIR and EBIR/MOIR NO<sub>x</sub> inputs (1.53 and 0.65, respectively) derived for the Carter (1994) reactivity scenarios. The low NO<sub>x</sub> scenario had NO<sub>x</sub> inputs at 10% of the MOIR level, which is arbitrary but reasonably representative of low NO<sub>x</sub> conditions.

Table 8. Summary of inputs for the box model simulations of multi-day, urban pollution scenarios used in this work.

Input types	Input values and description										
Simulation times	Total of 4 days and 15 hours, data for the 2nd-4th day used.										
Start time	6:00 AM solar daylight (8:00 AM solar)										
End Time	9:00 PM solar daylight (8:00 PM solar)										
Photolysis rate calculation	Calculated using the same actinic fluxes as a function of solar zenith angle as used for the incremental reactivity calculations of Carter (1994). These were calculated by Jeffries (unpublished results, ~1992). The zenith angle as a function of solar time was calculated for a latitude of 31.1 degrees north and 23.5 degrees west, appropriate for Los Angeles, CA.										
Mixing heights	Reacting air mass is diluted by clean air as height raises, total volume reduced as it declines. Same schedule each day. Constant at 100 meters at the start of the simulation until 6:00 AM, then raises linearly to 250 meters at 9 PM, and declines back to 100 meters by 6AM the next day. (No emissions input while the height is declining.)										
Initial concentrations	2 ppm CO and 2 ppm methane. No other pollutants										
Water concentration	$2 \times 10^4$ ppm, or ~50% RH.										
Temperature	Constant at 300 K.										
Aloft pollutants	None. Reactants diluted by clean air when the mixing height goes up.										
VOC and NO <sub>x</sub> emissions schedule	VOC and NO <sub>x</sub> are emitted at constant fluxes beginning at 8:00 AM and ending at 6:15 PM local time. No emissions at other times.										
VOC emissions flux	VOC emissions flux for all scenarios is 3.85 micromoles C/meter <sup>2</sup> /day. This is ¼ the average daily VOC emissions flux used in the reactivity scenarios of Carter (1994). Adjusted downward to better represent current U.S. pollution levels.										
NO <sub>x</sub> emissions fluxes	NO <sub>x</sub> emissions varied by scenario, as follows: <table border="1" data-bbox="479 1291 1234 1459"> <thead> <tr> <th>Scenario</th> <th>NO<sub>x</sub> emissions flux (micromoles/meter<sup>2</sup>/day)</th> </tr> </thead> <tbody> <tr> <td>MIR</td> <td>0.87 (1.53 x MOIR value)</td> </tr> <tr> <td>MOIR</td> <td>0.67 (adjusted to yield maximum ozone)</td> </tr> <tr> <td>EBIR</td> <td>0.37 (0.65 x MOIR value)</td> </tr> <tr> <td>Low NO<sub>x</sub></td> <td>0.06 (approximately 1/10 MOIR value)</td> </tr> </tbody> </table>	Scenario	NO <sub>x</sub> emissions flux (micromoles/meter <sup>2</sup> /day)	MIR	0.87 (1.53 x MOIR value)	MOIR	0.67 (adjusted to yield maximum ozone)	EBIR	0.37 (0.65 x MOIR value)	Low NO <sub>x</sub>	0.06 (approximately 1/10 MOIR value)
Scenario	NO <sub>x</sub> emissions flux (micromoles/meter <sup>2</sup> /day)										
MIR	0.87 (1.53 x MOIR value)										
MOIR	0.67 (adjusted to yield maximum ozone)										
EBIR	0.37 (0.65 x MOIR value)										
Low NO <sub>x</sub>	0.06 (approximately 1/10 MOIR value)										
VOC Speciation	Equal mass fractions of the 2018 California anthropogenic and the 2018 biogenic mixtures, as given in Table B-6 and Table B-7 in the electronic supplement. These tables also give the model species assignments for these compounds.										
NO <sub>x</sub> Speciation	75% NO and 25% NO <sub>2</sub> by moles. No HONO co-emissions.										

### 3.1.2. Mechanism Comparison Results

Figure 2 and Figure 3 show results of model simulations of representative species for the 2nd and 3rd say of these four scenarios using the three versions of SAPRC-22 developed in this work. The results for O<sub>3</sub>, NO<sub>x</sub>, OH, and other inorganics were essentially indistinguishable among the versions, and were also similar for most of the major organic species, with the data on Figure 2 being representative. However, there are larger differences between versions for some types of organic species, with Figure 3 showing the species where the largest differences are seen. As shown on Figure 1, above, the lumped unsaturated aldehydes (other than acrolein and methacrolein, which are represented explicitly and where predictions are essentially the same for the two versions) (OLEA1) and the lumped hydroperoxy carbonyls (HPCRB), formed primarily from isoprene, show the greatest differences between the full and reduced versions among the higher yield products. These differences are significantly reduced when the standard version, which accounts for effects of absolute NO on product yields, is used. Use of the standard version also reduces differences in predictions of the lumped very low volatility products (OTHN). However, for some other species, particularly lumped unsaturated hydroperoxides (RUOOH), and to a lesser extent peroxy acids (PACID) and unsaturated PAN analogues (APANS), the difference between the full and other versions are greater, and additional reactions added to the standard version do not reduce these differences. In these cases, the differences can be attributed to effects of approximations incorporated in the SAPRC-07 peroxy lumping method regarding treatments of peroxy + NO<sub>x</sub> and peroxy + peroxy reactions. The full version of the mechanism would be required for more accurate predictions for these relatively minor species, but for most model applications this is not sufficient to justify use of the much larger mechanism that gives very close predictions for most species of interest.

Figure 4 compares predictions of the standard SAPRC-22 mechanism of representative species in these same scenarios with predictions of previous versions of the SAPRC mechanism, starting with SAPRC-07. It can be seen that the different versions give very similar O<sub>3</sub> predictions, with the greatest differences being in the higher NO<sub>x</sub>, approximate MIR scenario, where O<sub>3</sub> tends to be most sensitive to mechanisms used for reactions of VOCs. Predictions for OH are also very similar, with the greatest difference in this case being the very low NO<sub>x</sub> scenario, where SAPRC-22 and -18 gave higher OH predictions than the earlier mechanisms. The differences are greater for other species, where in most cases, where predictions of SAPRC-22 are generally closer to those for SAPRC-18, which is to be expected since SAPRC-22 was developed from SAPRC-18. Some of the differences between SAPRC-22 and SAPRC-18 can be attributed to recent updates in the mechanism generation system used during their development.

## 3.2. Standard Conditions used for Mechanism Preparation and Analysis

The results of SAPRC-22 simulations of selected times in selected scenarios were used to define the standard conditions used to determine which reactions can be neglected during mechanism generation (Section 2.4.1), and to derive compositions of mixtures representing lumped organic products (Section 2.4.3). Since the derivation of SAPRC-22 depends on some these standard conditions, the initial calculations used a previous version of the mechanism, whose predictions of species concentrations defining the standard conditions were essentially the same as the final version delivered for this project. The standard conditions and their derivations are discussed in the following section.

The four sets of standard conditions used in this work are summarized on Table 9. The concentrations of the reactive species defining the conditions were derived by averaging the data for selected scenarios for selected time periods. These periods are shown Figure 5, which shows plots of fractions that peroxy radical reactions with various species as a function of time for the EBIR and low NO<sub>x</sub> scenarios. (The results for the MIR and MOIR scenarios are similar to those for EBIR, except that

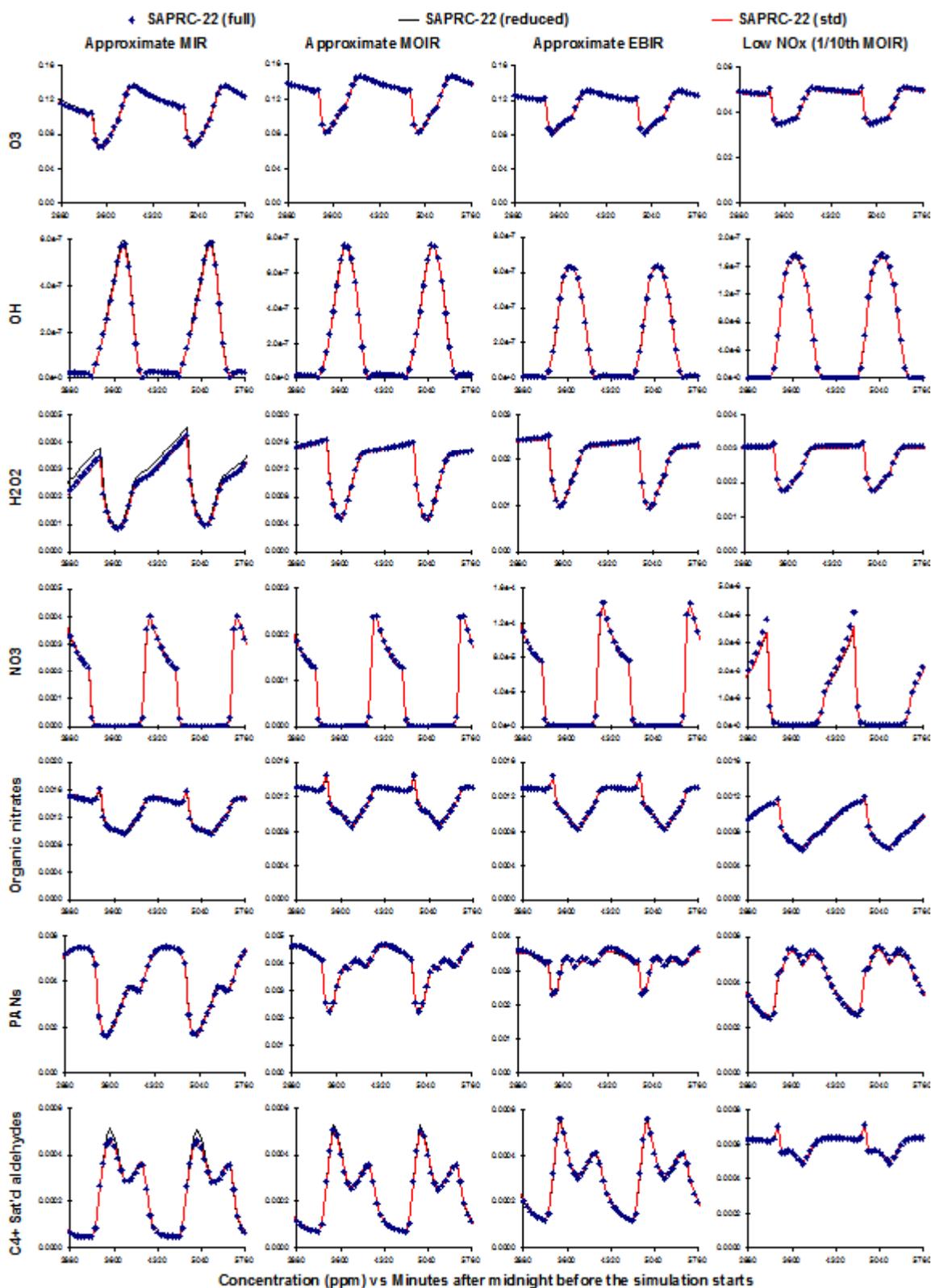


Figure 2. Plots of model simulations of selected species in the 2nd and 3rd day of the multi-day ambient simulations using various versions of SAPRC-22 developed in this work.

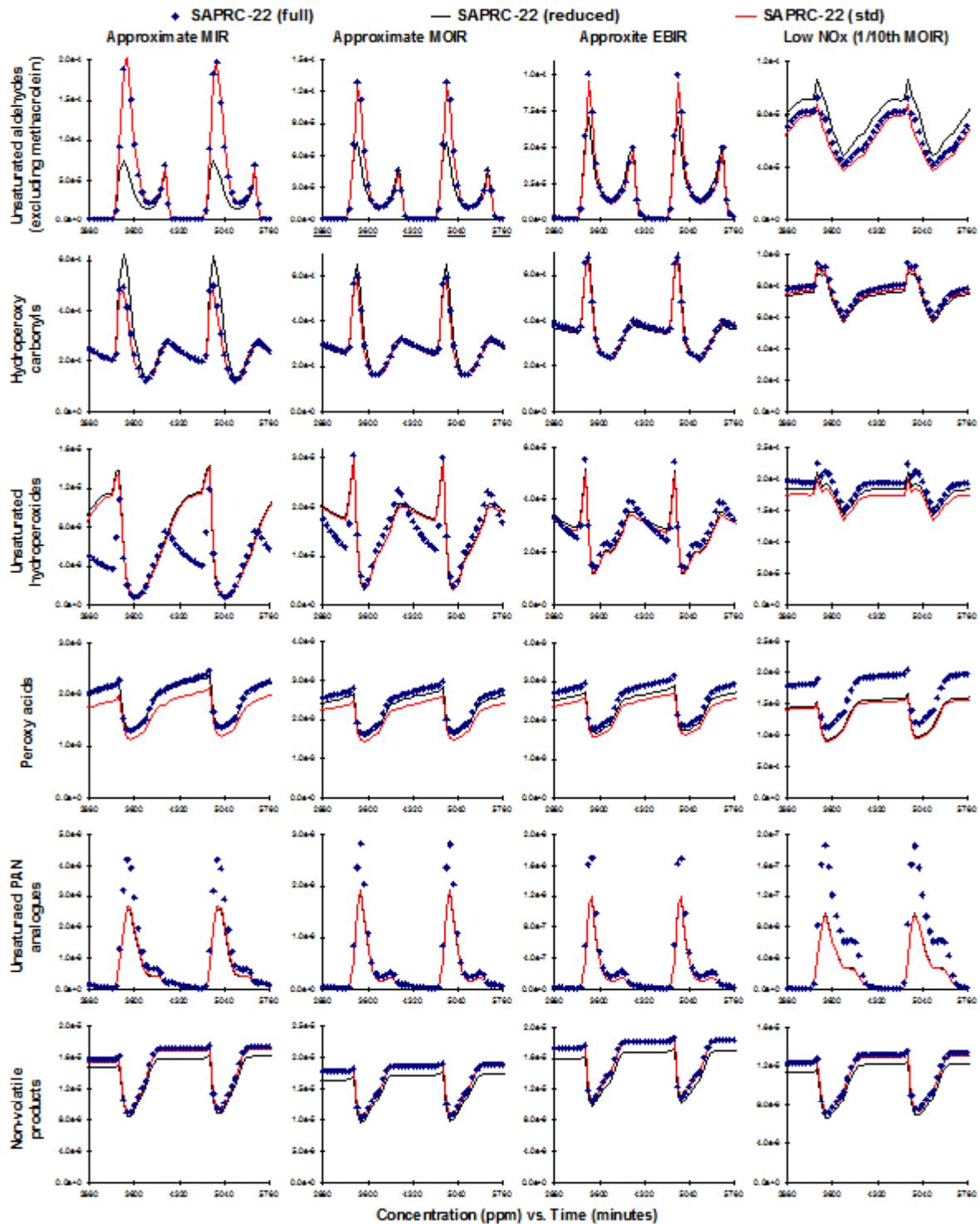


Figure 3. Plots of model simulations of organic product species that appeared to be most sensitive to differences in SAPRC-22 lumping approaches on the 2nd and 3rd day of the multi-day ambient simulations using various versions of SAPRC-22..

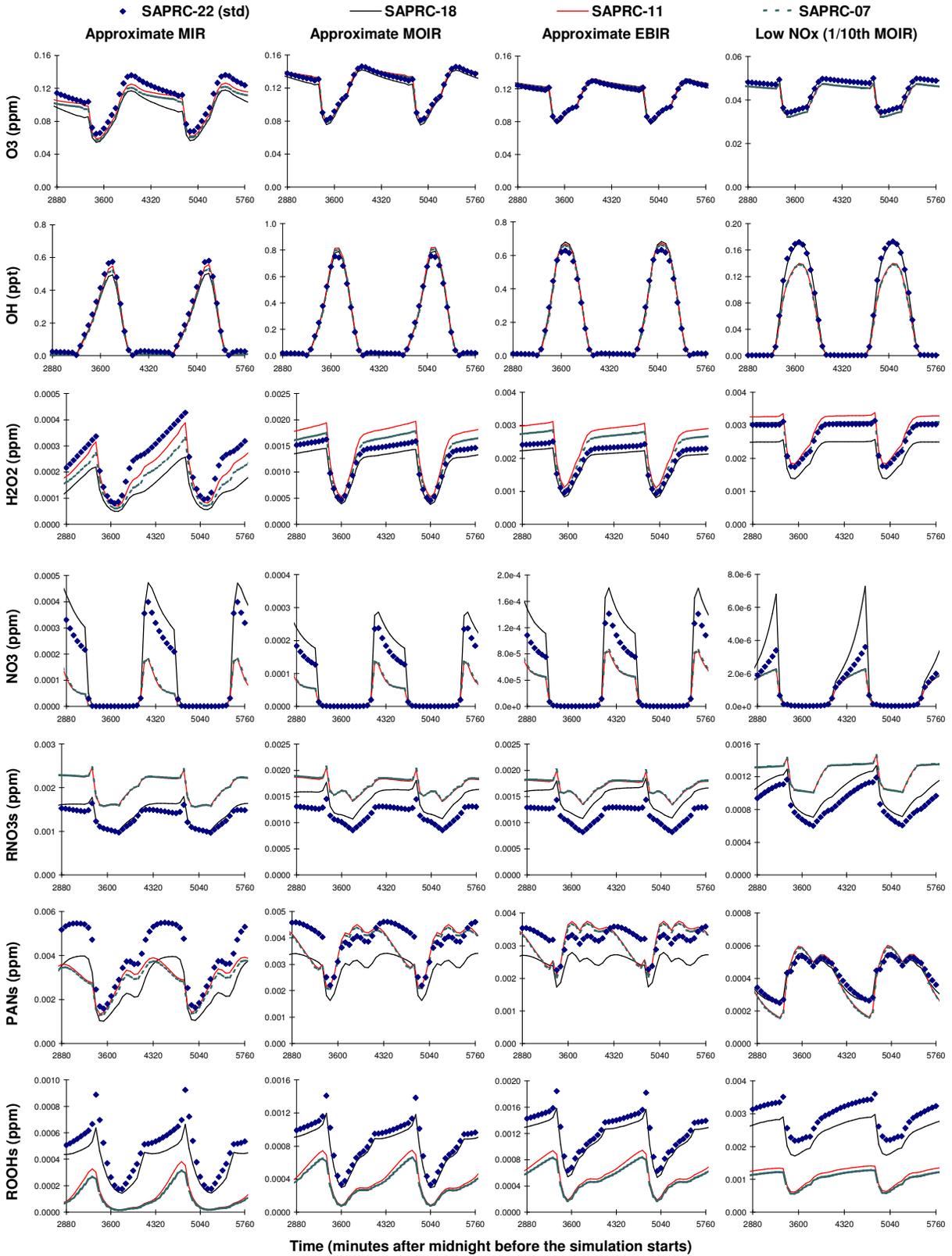


Figure 4. Comparisons of predictions of using SAPRC-07 through SAPRC-22 for selected species in the 2nd and 3rd day of the multi-day ambient simulations.

Table 9. Concentrations of species and parameters used to define the standard sets of environmental conditions used in this work .

Species or parameter	Input or species concentration ( $\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$ )			
	High NO <sub>x</sub> (MIR)	Standard (EBIR)	Low NO <sub>x</sub>	Nighttime (EBIR)
Use [a]	MG	PY, S	MG	MG
OH	7.51e+6	1.11e+7	3.69e+6	2.86e+5
O <sub>3</sub>	1.78e+12	2.26e+12	9.20e+11	2.90e+12
O <sub>3</sub> P	5.50e+4	2.84e+4	8.85e+3	~0
NO	9.58e+10	1.59e+10	4.12e+9	7.43e+5
NO <sub>2</sub>	3.15e+11	8.63e+10	1.32e+10	4.88e+10
NO <sub>3</sub>	8.54e+6	9.92e+6	1.25e+6	2.25e+9
HO <sub>2</sub>	~0	6.00e+8	7.17e+8	1.27e+8
Total RO <sub>2</sub> 's	~0	4.59e+8	6.69e+8	2.35e+8
Total RCO <sub>3</sub> 's	~0	7.30e+7	7.27e+7	1.04e+8
Reaction time [b]	6 hours			
T, RH	300K and 50% RH			
Photolysis rates	Calculated for direct overhead sunlight [c]			

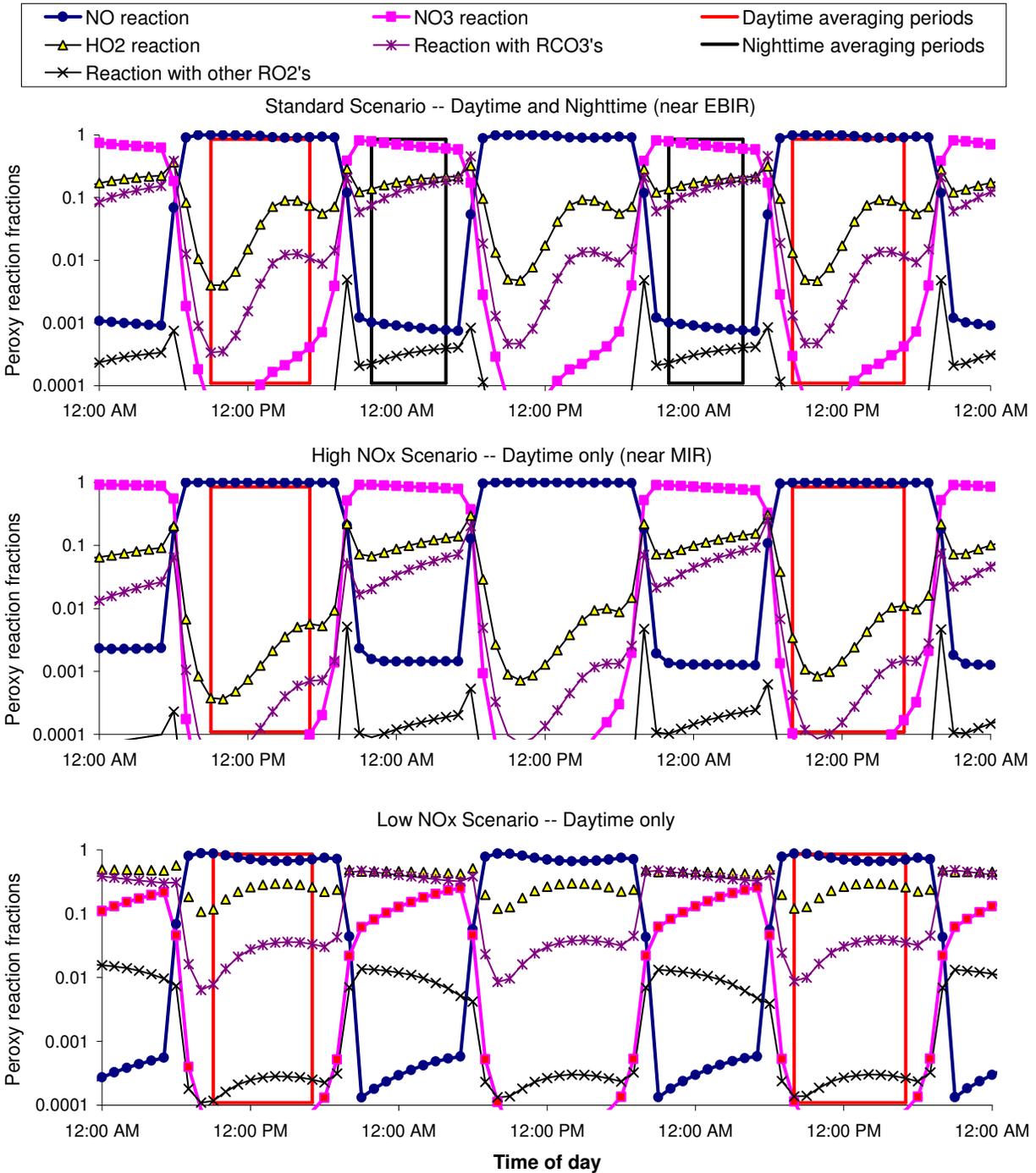
[a] Usage codes: MG: used for mechanism generation to determine reactions that can be neglected; PY: used to derive product yields for deriving mechanisms of lumped model species; S: used for comparisons of product yields with different lumping methods.

[b] This is only used when deriving product yields for lumped model species mechanisms to determine how much product can be formed when the starting compounds have insufficient time to react completely.

[c] Actinic fluxes are the same as those used for the box model calculations except they are assumed to be constant at a solar zenith angle of zero.

the fractions reacting with NO are close to unity during more of the daytime periods, and the fractions for the other reaction pathways are lower. Note that a set of standard conditions representing maximum O<sub>3</sub> (MOIR) conditions was not needed for mechanism generation because MOIR conditions are intermediate between the MIR and EBIR conditions that are already used for this purpose, and because the EBIR conditions was judged to be more appropriate for applications using a single set of conditions, since it represents intermediate NO<sub>x</sub> levels.

The standard conditions are used to determine relative amounts of the starting compounds are consumed by OH, O<sub>3</sub>, other oxidants, or photolysis, and to determine relative rates of competing reactions of the peroxy radicals, including unimolecular reactions when applicable. The former are determined by assigned concentrations of OH, O<sub>3</sub>, NO<sub>3</sub>, O<sup>3</sup>P and the actinic fluxes, while the latter are determined by concentrations of NO, HO<sub>2</sub>, NO<sub>3</sub>, and total peroxy and acyl peroxy radical levels. The relative amounts of peroxy radical reactions for the various conditions are shown on Table 10. It can be seen that essentially all peroxy radicals react with NO under high NO<sub>x</sub> or MIR conditions, while all but 7% react this way under the standard (EBIR or medium NO<sub>x</sub>) conditions, and over ¾'s react this way under low NO<sub>x</sub> conditions. However, as expected since NO is rapidly titrated by O<sub>3</sub> at nighttime, reaction with NO is a minor loss process for nighttime conditions, where more than half of the consumption is due



Note: The mechanism used for this figure was derived using a slightly earlier version of MechGen, but the results should be essentially the same.

Figure 5. Plots of fractions of the various types of bimolecular reactions of peroxy radicals against time for the scenarios used to derive standard conditions, showing the time periods where concentrations were averaged to yield the standard concentrations given on Table 9.

Table 10. Relative amounts that peroxy radicals undergo their various possible bimolecular reactions in the four sets of environmental conditions used in this work.

Reaction	Fraction peroxy radical reacts with the indicated reactant			
	High NO <sub>x</sub> (MIR)	Standard (EBIR)	Low NO <sub>x</sub>	Nighttime (EBIR)
NO	100%	93%	76%	0.08%
HO <sub>2</sub>	~0	6%	22%	22%
NO <sub>3</sub>	0.002%	0.01%	0.01%	59%
Total RCO <sub>3</sub> 's	~0	0.8%	2%	19%
Total RO <sub>2</sub> 's	~0	0.005%	0.02%	0.04%

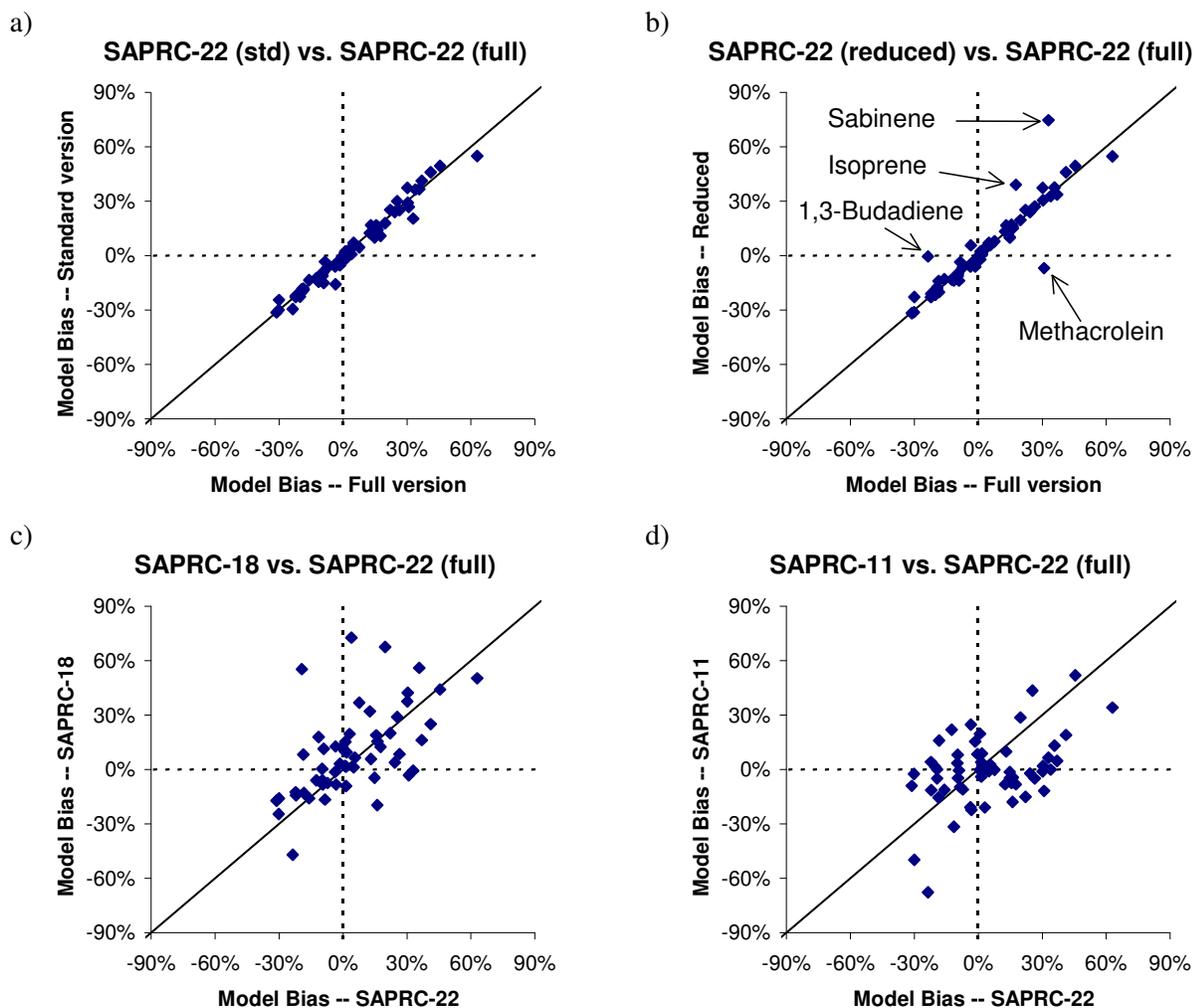
to reaction with NO<sub>3</sub>. These ratios are shown as a function of time Figure 5, which shows the time periods over which the data were averaged to obtain the values in Table 9 and Table 10.

### 3.3. Evaluation Against Chamber Data

The capability of the SAPRC-22 mechanism to predict effects of individual compounds on O<sub>3</sub> formation, NO oxidation, and (in many cases) OH radical levels was evaluated against the essentially the same large database of environmental chamber experiments and using the same modeling procedures as used for previous versions of SAPRC, including SAPRC-07 (Carter, 2010a,b), SAPRC-11 (Carter and Heo, 2012, 2013) and SAPRC-18 (Carter, 2020a). A complete discussion of these results is beyond the scope of this report, so only a brief summary will be given here. Except as indicated below, the model performance of SAPRC-22 in simulating these data was very similar to that for SAPRC-18, was comparable to that for SAPRC-11, and was about the same for ambient mixtures or compounds important in emissions. This is probably as good as can be reasonably be expected considering uncertainties in chamber data and characterization, as well as uncertainties in the chemistry. However, for certain types of compounds, such as some esters and individual alkylbenzenes, SAPRC-18 and 22 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 and 22 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.

Figure 6 compares model biases for various of SAPRC-22 and also SAPRC-18 and SAPRC-11 for the various types of experiments used for mechanism evaluation. Most of the points are experiments with single compounds, but several are for various surrogates representing ambient mixtures. Figure 6a shows that the both the full and standard versions give essentially the same results in simulating the chamber data, and Figure 6b shows that the reduced version gives very close results for most compounds, except for 1,3-butadiene, isoprene, sabinene, and methacrolein, where competitions between peroxy isomerizations and bimolecular reactions are apparently more important. Figure 6c and d show that the distribution of biases for SAPRC-18 and 11 are similar to those for SAPRC-22, there are much greater differences among different types of experiments. Some experiments are simulated better using the earlier mechanisms, while some are simulated better using SAPRC-18 or 22. For example, about 60% of the types of experiments are simulated somewhat better using SAPRC-11 than SAPRC-22.

Note that, unlike the case for SAPRC-07 and 11, there was no adjustment of uncertain mechanism parameters to fit the experimental chamber data during the process of updating the mechanism to SAPRC-18 or 22. However, some of the estimation methods used by MechGen when generating mechanisms, such estimations of nitrate yields in reactions of peroxy radicals with NO and of radical forming processes in reactions of Criegee intermediates were derived based on fits to chamber data as discussed by Carter (2023c). No adjustments were made for individual compounds, however, which is why the chamber run fit statistics are not quite as good for SAPRC-18 and 22 as for previous versions, such as SAPRC-11, where much more compound-by-compound adjustment were carried out. However, compound-by-compound adjustment of sensitive uncertain parameters may be appropriate for mechanisms used to calculate ozone reactivity scales, but updating the mechanism for this purpose is beyond the scope of the present project.



$$\text{Average bias is } ([\text{model}] - [\text{experimental}]) / \text{average} ([\text{model}], [\text{experimental}])$$

Figure 6. Comparisons of average biases in the simulations of rates of NO oxidation and maximum O<sub>3</sub> concentrations in the evaluations of versions of SAPRC-22 and earlier SAPRC mechanisms against NO<sub>x</sub> - air chamber experiments with all the compounds and mixtures used for SAPRC mechanism evaluations..

### 3.4. Mechanism Implementation Test Calculation

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<sub>x</sub>, 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. The input conditions used for the SAPRC box modeling software (Carter, 2020b) are given in Table B-8 in the electronic supplement. The simulation gave nonzero values for all reactive model species in the mechanism. The simulations were carried out for both the standard and full version of SAPRC-22, and the results in the Table B-8 and Table 11, respectively in the electronic supplement, where they can be compared with results calculated using other solvers with the same inputs. Representative results are shown in Figure 7.

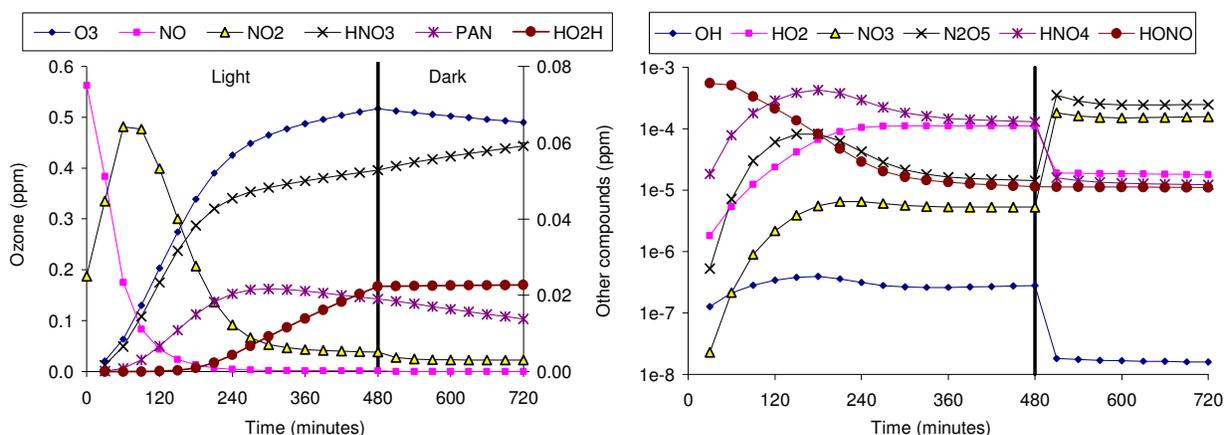


Figure 7. Concentration-time plots of selected species in the test simulation provided to verify correct implementation of SAPRC-18 in airshed model software.

## 4. Discussion

The SAPRC-22 mechanism is the latest version of the SAPRC series of gas-phase atmospheric mechanisms for airshed models, and incorporates our current understanding of atmospheric reactions of organic compounds. The objective is to provide airshed modelers with an up-to-date mechanism with more of the chemical detail needed for more reliable ozone, toxics and eventually SOA modeling, but not so large that it is impractical for use in 3D airshed models. A unique feature of the current SAPRC mechanisms is their close link to the automated mechanism generation system, MechGen, that predicts detailed atmospheric reactions of emitted and oxidized organic compounds, using known kinetic and mechanistic data where available, and up-to-date estimates and structure-activity (SAR) estimation methods when not. 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 mechanism for consistency with available data, then utilizing various methods to reduce or condense the detailed mechanism for specific airshed model applications.

The SAPRC-16 mechanism (Carter, 2016, Venecek et al, 2017) represented the first complete update of the SAPRC mechanisms since the widely-used SAPRC-07 mechanism was developed (Carter,

2010a,b). Unfortunately, the scientific basis of the MechGen system used to derive most of its organic reactions was not completely documented at the time, and the system was continually changing as it was being updated to incorporate new data and estimation methods. This resulted in SAPRC-16, and its successor SAPRC-18, becoming out of date shortly after they were released. Because the scientific and regulatory community requires a stable as well as a documented mechanism, it was decided to freeze the continued development of MechGen while it is being documented for peer-reviewed publication, and update the SAPRC mechanism only after it is completed. This documentation has now been prepared and will be soon submitted for publication, and this now-documented version of MechGen has been used to develop the SAPRC-22 mechanisms discussed in this report. Although this is not the first version of SAPRC to use a mechanism generation system, it is the first where the system is comprehensively documented. Although MechGen or its successors may continue to be developed into the future and serve as the basis for new SAPRC or SAPRC-like mechanisms, the version used to derive SAPRC-22 will continue to be available to provide information and background for this mechanism, and to duplicate predictions used in its development.

However, inadequate documentation and stability was not the only problem with the SAPRC-16 and 18. In order to better account for auto-oxidation reactions of peroxy radicals and better support predictions of SOA precursors that may be influenced by such reactions, these mechanisms utilize a more accurate and detailed representation of peroxy radical reactions than employed in previous versions, requiring the use of many more model species and reactions to represent reactive intermediates. This has increased the computer resource and time requirements to use these mechanisms in 3D airshed models, which has inhibited the use of these updated mechanisms for regulatory modeling. Because the CARB has been relying on SAPRC-07 mechanisms for their regulatory modeling but needs to have a more up-to-date version, they contracted the author to develop an updated version of SAPRC that is more comparable in size to SAPRC-07, though with additional model species to better track selected toxics.

To address this need, the newly developed SAPRC-22 utilizes a somewhat modified version of the more approximate method that earlier versions used to represent peroxy reactions, though modified to account for auto-oxidation reactions by adding an extra intermediate when representing reactions where auto-oxidation is a factor. To assess the effects of this approximation on model predictions, a "full" version of SAPRC-22 was developed that was the same as the standard version except that it employed more accurate peroxy representation methods similar to that employed in SAPRC-16 and 18, and its predictions were compared with those of the standard mechanisms. The results indicated that the approximations did affect predicted yields of some types of organic products, but O<sub>3</sub>, OH radicals and other oxidants were not significantly affected, and the products whose predictions were most affected were formed in relatively low yields, and expected to be sensitive to uncertain details in the complex mechanisms.

Therefore, the standard version of SAPRC-22 should be a good replacement to SAPRC-07 because of the updated chemistry that now includes auto-oxidation reactions, greater chemical detail for some toxic species and SOA precursors, and its comparable size and computer resource demands. It may not have as accurate a representation of peroxy chemistry as does SAPRC-16 or 18, but it is better than that used in SAPRC-07 because it can at least approximately incorporate their unimolecular reactions, and gives very close predictions of O<sub>3</sub> and the major toxic species of current interest as the version of SAPRC-22 with the more accurate peroxy representation.

One reason for the added size and complexity of the SAPRC-16 and 18 mechanisms is the desire to have the gas-phase mechanism provide better support for SOA predictions, where chemical detail is much more important. However, it now appears likely that accurately predicting precursors to SOA formation based on actual chemistry will require far larger mechanisms that is currently used in most modeling applications. Previous work with the GeckoA mechanism generation system has indicated that multi-generation reactions, which are poorly represented in current lumped mechanisms, are important

sources of SOA precursors (Aumont et al, 2005, 2012, 2013). This means that even the full version of SAPRC-22 would probably not give any more reliable predictions of SOA precursors than other lumped mechanisms, even if the uncertainty in our ability to estimate the underlying chemistry of formation of SOA precursors were not significant (which it is). Because no lumped mechanisms are considered sufficient for SOA predictions, current models use separate SOA modules to predict SOA formation using empirically derived parameters with relatively little input from the gas-phase mechanism. Although less accurate, it has the advantage of requiring less chemical detail in the gas-phase mechanism. This will have to continue to be the case until either computers become more powerful or until we develop other methods to make SOA predictions based on considerations of detailed chemistry.

Although SAPRC-07 included a module for chlorine chemistry, including halogen chemistry was beyond the scope of this project, so it is not part of SAPRC-22. It would be relatively straightforward to add and update 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.

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-22. Other than error corrections, any updates, condensations, or changes to levels of chemical detail will be incorporated into the next version of MechGen and SAPRC.

Finally it should be pointed that the author, who has been the sole developer of the SAPRC mechanisms, is getting closer to 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.

## 5. Supplementary Information Available

This report includes an electronic supplement giving large tables needed to completely document the mechanism and files and data needed to implement the versions of SAPRC-22 mechanism discussed in this report using the SAPRC (Carter, 2020b), CMAQ (2022), and KPP (Sandu et al, 2022) modeling systems. An Excel file containing the large tables, files for implementing the mechanism, and the text of this report, is available at the SAPRC-22 web site at <https://intra.cert.ucr.edu/~carter/SAPRC/22/>. The supplementary tables and the files available online are listed on Table 11.

The SAPRC-22 web site also contains links to the SAPRC software and files that can be used to test the mechanism and evaluate against chamber data, available documentation of MechGen and access to its online version, and the speciation database website that now includes assignments of SAPRC-22 model species to various speciation categories used in emissions databases (Carter, 2015, 2023d).

Table 11. Supplementary information needed for mechanism documentation and implementation, and links to other relevant data and software that is available online.

<u>File or link</u>	<u>Contents or Target</u>
S22doc.pdf	Text of this report
S22supp.xls	Supplementary tables, as follows:
Table B-1.	List of model species in the standard SAPRC-22 mechanism
Table B-2.	List of reactions and kinetic parameters in the standard SAPRC-22 mechanism
Table B-3.	Absorption cross sections and quantum yields for the photolysis reactions
Table B-4.	List of SAPRC detailed model species and assignments to SAPRC-22 model species
Table B-5.	Mixtures or compounds used to derive mechanisms of the lumped organic model species.
Table B-6.	Composition of the California 2018 anthropogenic emissions mixture used to derive mixtures to derive mechanisms of lumped model species representing emitted organics
Table B-7.	Composition of the California 2018 biogenic emissions mixture used to derive mixtures to derive mechanisms of lumped model species representing emitted organics
Table B-8.	Input conditions for implementation test calculation using SAPRC box model software. These were used as inputs for the test calculations shown on Table B-9.
Table B-9.	Output concentrations of test calculations using the standard SAPRC-22 mechanism
SAPRC22.rxn SAPRC22.mec S22-KPP.zip	Input files for the standard SAPRC-22 mechanism in SAPRC (.rxn), Models-3 (.mec), and KPP (S22-KPP.zip) formats. Note that the format of the KPP files have not been verified.
SAPRC22std.xls SAPRC22full.xls SAPRC22red.xls	Spreadsheet containing all information needed to implement the standard, full, and reduced version of SAPRC-22, including macros to output .rxn, .mec, and KPPfiles such as those listed above..
PHF.zip	Absorption cross sections and quantum yields used by SAPRC-22, in format used by SAPRC box modeling software
Link to SAPRC software	Link to the SAPRC box modeling software and files at <a href="https://intra.engr.ucr.edu/~carter/SAPRC/SAPRCfiles.htm">https://intra.engr.ucr.edu/~carter/SAPRC/SAPRCfiles.htm</a> . These can be used for implementing and running versions of the SAPRC mechanisms, including SAPRC-22. Includes files for evaluating mechanisms against SAPRC chamber data.
Link to MechGen documentation	Available documentation of the SAPRC Mechanism Generation System (MechGen) that was used to derive the mechanisms for organics used in SAPRC-22. Currently only preliminary and incomplete documentation is available while the more comprehensive draft documentation is being reviewed and finalized.
Link to MechGen	Link to the online version of MechGen, at <a href="http://mechgen.cert.ucr.edu">http://mechgen.cert.ucr.edu</a>
Speciation database link	Link to the emissions speciation database at <a href="https://intra.engr.ucr.edu/~carter/emitdb">https://intra.engr.ucr.edu/~carter/emitdb</a> . This now includes speciation assignments for SAPRC-22.

## 6. Acknowledgements

This work was supported in part by the California Air Resources Board primarily through contract no 21AQP011, in part by the University of California Retirement system, and in part by EPA cooperative agreement no. 84000701, Kelley Barsanti, PI. Helpful discussions with Ajith Kwduwela, Chenxia Cai, and Majiong Jiang regarding CARB modeling needs, and with Kelley Barsanti and John Orlando regarding MechGen documentation and updates relevant to this project, are acknowledged. However, conclusions and statements in this document are entirely those of the author.

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## 8. Mechanism Listing tables

Table A-1 and Table A-2 give lists of all the model species and reactions in the standard version of the SAPRC-22 mechanism. Footnotes to Table A-1 describe the model species used and footnotes to Table A-2 document the sources of the rate constants and reactions. Note that the footnotes do not discuss the derivation of the mechanisms derived using MechGen; this information can be obtained from MechGen output and documentation (Carter, 2023a-c). The listing on Table A-1 and reactions on Table A-2 do not include all the x(product), y(product) and z(product) chemical operators used, only representative examples and listings of all operators used in the footnotes. Complete listings of species and reactions, including all the species and reactions in the full mechanism, are given in the SAPRC22std.xls and SAPRC22full.xls files included in supplementary materials available online (see Table 11, above).

Table A-1. List of model species in the SAPRC-22 mechanisms.

Type and Name	Mechanism derivation [a]	Note [b]	Atoms		Molec. wt [c]	Description
			C	N		
<u>Constant Species.</u>						
O2	Base		-	-	32.00	Oxygen
M	Base		-	-	28.85	Air
H2O	Base		-	-	18.02	Water
HV	Base	1	-	-	0.00	Light
<u>Active Inorganic Species.</u>						
O3	Base		-	-	48.00	Ozone
NO	Base		-	1	30.01	Nitric Oxide
NO2	Base		-	1	46.01	Nitrogen Dioxide
NO3	Base		-	1	62.01	Nitrate Radical
N2O5	Base		-	2	108.02	Nitrogen Pentoxide
HONO	Base		-	1	47.02	Nitrous Acid
HNO3	Base		-	1	63.02	Nitric Acid
HNO4	Base		-	1	79.02	Peroxynitric Acid
HO2H	Base		-	-	34.01	Hydrogen Peroxide
CO	Base		1	-	28.01	Carbon Monoxide
H2	Base		-	-	2.02	Hydrogen Molecules
SO2	Base		-	-	64.06	Sulfur Dioxide
<u>Active Radical Species and Operators</u>						
OH	Base	2	-	-	17.01	Hydroxyl Radicals
HO2	Base		-	-	33.01	Hydroperoxide Radicals
<u>Steady State Inorganic Radical Species</u>						
O3P	Base		-	-		Ground State Oxygen Atoms
O1D	Base		-	-		Excited Oxygen Atoms
<u>Peroxy Radical Species in Base Mechanism</u>						
MEO2	Base	3	1	-		Methyl peroxy radicals
ETO2	Base	3	2	-		Ethyl peroxy radicals
BZO2	Base	3	6	-		Benzyl peroxy and substituted benzyl peroxy radicals
SumRO2	Base	4	-	-		Total peroxy radical concentration
SumRCO3	Base	4	-	-		Total acyl peroxy radical concentration
<u>Acyl peroxy radical species</u>						
MECO3	Base	3	2	-		Acetyl Peroxy Radicals (forms PAN)
R2CO3	Base	3	3	-		Higher saturated peroxy acyl radicals (forms PAN2)
BZCO3	Base	3	7	-		Peroxyacyl radical formed from Aromatic Aldehydes (forms PBZN)
MACO3	Base	3	4	-		Peroxyacyl radicals formed from methacrolein and other unsaturated aldehydes (forms MAPAN)
<u>Other organic radical or reactive intermediate species</u>						
TBUO	Base	3	4	-	73.11	t-Butoxy Radicals
BZO	Base	3	6	-	93.10	Phenoxy or substituted phenoxy radicals
HCHO2	Base	3	1	-	46.03	Unsubstituted stabilized Criegee biradical
MECHO2	Base	3	2	-	60.05	Methyl substituted stabilized Criegee biradical

Table A-1 (continued)

Type and Name	Mechanism derivation [a]	Note [b]	Atoms		Molec. wt [c]	Description
			C	N		
RCHO2	Base	3	3	-	74.08	Other stabilized Criegee biradicals
<u>Radical operator species</u>						
RO2C	Base	5	-	-		Peroxy Radical Operator representing NO to NO <sub>2</sub> and NO <sub>3</sub> to NO <sub>2</sub> conversions, and the effects of peroxy radical reactions on acyl peroxy and other peroxy radicals.
RO2XC	Base	6	-	-1		Peroxy Radical Operator representing NO consumption (used in conjunction with organic nitrate formation), and the effects of peroxy radical reactions on NO <sub>3</sub> , acyl peroxy radicals, and other peroxy radicals. (used in some multi-step mechanisms)
x(product) (46 total)	Base	3, 7	varies			Formation of a product or radical after reactions of peroxy radicals with NO.
y(product) (5 total)	Base	3, 8	varies			Formation of a hydroperoxide product after reactions of peroxy radicals with HO <sub>2</sub> .
z(product) (9 total)	Base	3, 9	varies			Formation of an organic nitrate product after the reactions of peroxy radicals with NO.
spec_OH (16 total)	MechGen	3, 10	-	-		Peroxy radical operator used to represent the effects of absolute NO levels on product yields in reactions of VOC model species with OH.
spec_N3 (4 total)	MechGen	3, 10	-	-		As above, but for reactions with NO <sub>3</sub> .
spec_O3 (7 total)	MechGen	3, 10	-	-		As above, but for reactions with O <sub>3</sub> .
spec_HV (9 total)	MechGen	3, 10	-	-		As above, but for photolysis reactions.
NPRAD	Base	3, 11	12	-		Simplified representative of unknown naphthalene intermediates that react with NO <sub>2</sub> forming products
PNAMIN	Base	3, 12	4	1		N-centered radicals with no alpha hydrogens that primarily react with NO <sub>2</sub> to form Nitramines.
<u>Explicitly represented organics</u>						
CH4	Base	13	1	-	16.04	Methane
ETHAN	MechGen	14	2	-	30.07	Ethane
PROP	MechGen	14	3	-	44.10	Propane
NC4	MechGen	14	4	-	58.12	n-Butane
ETHEN	MechGen	14	2	-	28.05	Ethylene
PROPE	MechGen	14	3	-	42.08	Propene
ISOP	MechGen	13	5	-	68.12	Isoprene
BUT13	MechGen	14	4	-	54.09	1,3-Butadiene
APINE	MechGen	14	10	-	136.23	a-Pinene
BPINE	MechGen	14	10	-	136.23	b-Pinene
ACETL	MechGen	14	2	-	26.04	Acetylene
BENZ	MechGen	13	6	-	78.11	Benzene
TOLU	MechGen	14	7	-	92.14	Toluene
OXYL	MechGen	14	8	-	106.17	o-Xylene
MXYL	MechGen	14	8	-	106.17	m-Xylene
PXYL	MechGen	14	8	-	106.17	p-Xylene

Table A-1 (continued)

Type and Name	Mechanism derivation [a]	Note [b]	Atoms		Molec. wt [c]	Description
			C	N		
BZ123	MechGen	14	9	-	120.19	1,2,3-Trimethyl Benzene
BZ124	MechGen	14	9	-	120.19	1,2,4-Trimethyl Benzene
BZ135	MechGen	14	9	-	120.19	1,3,5-Trimethyl Benzene
C2BEN	MechGen	14	8	-	106.17	Ethyl Benzene
MTBE	MechGen	15	5	-	88.14	Methyl t-Butyl Ether
HCHO	MechGen	13	1	-	30.03	Formaldehyde
MEOH	MechGen	13	1	-	32.04	Methanol
HCOOH	MechGen	13	1	-	46.03	Formic Acid
MEOOH	MechGen	16	1	-	48.04	Methyl Hydroperoxide
MECHO	MechGen	14	2	-	44.05	Acetaldehyde
ETOH	MechGen	14	2	-	46.07	Ethanol
GLY	MechGen	13	2	-	58.04	Glyoxal
GLCHO	MechGen	13	2	-	60.05	Glycolaldehyde
ETCHO	MechGen	16	3	-	58.08	Propionaldehyde
ACRO	MechGen	13	3	-	56.06	Acrolein
ACET	MechGen	13	3	-	58.08	Acetone
MEK	MechGen	13	4	-	72.11	Methyl ethyl ketone
MACR	MechGen	13	4	-	70.09	Methacrolein
MVK	MechGen	13	4	-	70.09	Methyl Vinyl Ketone
BUDAL	MechGen	16	4	-	84.07	2-Butene-1,4-dial
PHEN	MechGen	13	6	-	94.11	Phenol

Explicitly represented toxic species or other compounds of interest

CLETHE	Simplified	17	2	-	62.50	Vinyl chloride
ACRLNT	Simplified	17	3	1	53.06	Acrylonitrile
PCE	Simplified	17	2	-	165.83	Perchloroethylene
PCLBEN	Simplified	17	6	-	147.00	p-dichlorobenzene
MECL2	Simplified	17	1	-	84.93	Methylene chloride
ETBR2	Simplified	17	2	-	187.86	Ethylene dibromide
ETCL2	Simplified	17	2	-	98.96	Ethylene dichloride
ETOX	Simplified	17	2	-	44.05	Ethylene oxide
CHCL3	Simplified	17	1	-	119.38	Chloroform
CCL4	Unreactive	17	1	-	153.82	Carbon tetrachloride (unreactive)

Lumped Organic Compounds - Primarily emitted

ALK1	mix=ALK1	18	3	-	74.08	Saturated compounds that react only with OH, and have kOH between $1.4 \times 10^{-13}$ and $3.5 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
ALK2	mix=ALK2	18	4	-	88.11	Saturated compounds that have kOH between $3.5 \times 10^{-13}$ and $1.7 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
ALK3	mix=ALK3	18	5	-	80.54	Saturated compounds that and have kOH between $1.7 \times 10^{-12}$ and $3.5 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
ALK4	mix=ALK4	18	5	-	71.04	Saturated compounds that and have kOH between $3.5 \times 10^{-12}$ and $6.0 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
ALK5	mix=ALK5	18	6	-	96.98	Saturated compounds that and have kOH greater than $6.0 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ and have fewer than 12 carbons + oxygens.
ALK6	mix=ALK6	18	13	-	200.16	Saturated compounds that and have kOH greater than $6.0 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ and have 12 or more carbons + oxygens.

Table A-1 (continued)

Type and Name	Mechanism derivation [a]	Note [b]	Atoms		Molec. wt [c]	Description
			C	N		
OLE1	Mix=EmitMix	18	5	-	68.66	Alkenes other than ethene with kOH between $8 \times 10^{-12}$ and $6 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
OLE2	Mix=EmitMix	18	5	-	64.92	Alkenes other than terpenes or 1,3-butadiene that have OH rate constants greater than $6 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ .
OLE3	Mix=EmitMix	18	4	-	58.05	Alkenes other than terpenes or sesquiterpenes with only -CR=CH <sub>2</sub> groups.
OLE4	Mix=EmitMix	18	5	-	71.51	Alkenes other than terpenes with non-conjugated -CH=CR- or -CR=CR- groups and possibly other double bonds and no double bonds in rings
TERP	Mix=BioMix	19	10	-	136.23	Lumped terpenes (C <sub>10</sub> H <sub>16</sub> and at least one ring and alkene group)
SESQ	B-CARYOP	20	15	-	204.35	Sesquiterpenes
BENX	BENZENE	20	6	-	78.11	Benzene and substituted benzenes that react with kOH between $5 \times 10^{-13}$ and $5 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
ARO1	Mix=EmitMix	18	10	-	128.78	Alkylbenzenes that react with kOH between $5 \times 10^{-12}$ and $1 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ . Mostly alkylbenzenes with only one substituent
ARO2	Mix=EmitMix	18	9	-	126.42	Alkylbenzenes that react with kOH higher than $1 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ . Mostly alkylbenzenes with more than one substituent
NAPS	NAPHTHAL	11, 20	11	-	142.20	Naphthalenes, tetralins, and indans
FURNS	FURAN	20	4	-	68.07	Furans (mechanism based on furan)
STYRS	STYRENE	20	8	-	104.15	Styrenes
AMINS	Mix=EmitMix	18	3	1	52.06	Amines
TAMNS	TBU-AMIN	20	4	1	73.14	Amines bonded to a tertiary carbon (inhibiting)
PHOT	Base simplified	21	4	-	86.09	Unspecified photoreactive compounds such as nitrites or chloropicrin
<b>Lumped Organic Compounds - Primarily formed as products</b>						
RCHO	Mix=Products	22	5	-	100.45	C <sub>4</sub> + saturated aldehydes with 9 or fewer carbons
OLEA1	Mix=Products	22	7	-	143.12	Unsaturated aldehydes with C=C next to -CHO (mostly from aromatics)
OLEA2	Mix=Products	22	8	-	151.84	Unsaturated aldehydes with C=C not next to the -CHO (mostly from aromatics)
KET2	Mix=Products	22	5	-	99.82	Photoreactive saturated ketones
LVKS	Mix=Products	22	8	-	154.23	Ketones with at least 1 C=C double bond.
OLEP	Mix=Products	22	8	-	160.86	Non-photoreactive, non-hydrocarbon compounds with C=C double bonds
OACID	Mix=Products	22	2	-	60.05	Organic acids
PACID	PAA	20	2	-	76.05	Organic peroxyacids
MGLY	MEGLYOX	20	3	-	72.06	Methyl Glyoxal and other alpha-keto aldehydes
BACL	BIACETYL	20	4	-	86.09	Biacetyl and other alpha-diketones
CRES	Mix=Products	22	7	-	108.14	Cresols
XYNL	Mix=Products	22	8	-	124.84	Xylenols and higher alkylphenols
CATL	Mix=Products2	23	7	-	124.14	Dihydroxy phenols
CATL3	Base simplified	23a	7	-	140.14	Tri- and multi-hydroxy phenols
BALD	Base simplified	24	7	-	72.06	Aromatic aldehydes (e.g., benzaldehyde)
NPHE	Base simplified	24	6	1	86.09	Nitrophenols
RCNO3	Mix=Products	22	6	1	180.91	Volatile organic carbonyl nitrates

Table A-1 (continued)

Type and Name	Mechanism derivation [a]	Note [b]	Atoms		Molec. wt [c]	Description
			C	N		
RHNO3	Mix=Products	22	8	1	176.59	Volatile organic hydroxy nitrates
RANO3	Mix=Products	22	9	1	230.33	Organic nitrates with peroxy groups (formed primarily from aromatics)
RPNO3	Mix=Products	22	9	1	230.33	Organic nitrates with hydroperoxy groups
RDNO3	Mix=Products	22	9	2	249.44	Volatile organic dinitrates
R1NO3	Mix=Products	22	6	1	146.57	Other volatile organic nitrates that react with OH radicals slower than $5 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
R2NO3	Mix=Products	22	9	1	190.37	Other volatile organic nitrates that react with OH radicals faster than $5 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
ROOH	Mix=Products	22	4	-	97.00	Other hydroperoxides with 3+ carbons and vapor pressure greater than 1 ppb
RAOOH	Mix=Products	22	8	-	188.67	Hydroperoxides with peroxy groups and with C=C double bonds (mainly hydroperoxides formed from reaction with NO with OH-aromatic-O2 adducts after peroxy cyclization)
RUOOH	Mix=Products	22	7	-	145.11	Hydroperoxides with C=C double bonds
HPCRB	Mix=Products	22	5	-	128.44	Unsaturated hydroperoxy carbonyls
AFG1	Mix=Products	22	5	-	99.49	Monounsaturated 1,4-dialdehydes formed from aromatics
AFG2A	Mix=Products	22	5	-	101.70	Monounsaturated 1,4 aldehyde-ketones formed from aromatics, with at no substituents other than the aldehyde on the double bonds
AFG2B	Mix=Products	22	6	-	112.13	Monounsaturated 1,4 aldehyde-ketones formed from aromatics, with at least one substituent other than the aldehyde on a double bond
AFG3	Mix=Products	22	6	-	112.13	Monounsaturated 1,4-diketone aromatic products
NAPPRD	Base simplified	24	12	-	172.22	Phenolic and other products formed from naphthalenes.
IMINE	Base simplified	25	2	1	34.07	Any compound with C=N bond. Assumed to rapidly hydrolyze.
<u>PAN and PAN Analogues</u>						
PAN	MechGen	13	2	1	121.05	Peroxyacetyl nitrate
PAN2	PBN	20	4	1	149.10	Higher saturated PAN analogues
APANS	MAPAN	20	4	1	147.09	PAN analogues formed from Methacrolein and other unsaturated PAN analogues.
PBZN	Base simplified	24	7	1	183.13	PAN analogues formed from Aromatic Aldehydes
<u>Non-Reacting Species (Active for testing -- can be removed if not needed)</u>						
CO2	Inert		1	-	44.01	Carbon Dioxide
SULF	Inert		-	-	98.08	Sulfates (SO <sub>3</sub> or H <sub>2</sub> SO <sub>4</sub> )
RNNO3	Inert	26	10	1	216.23	Organic nitrates with vapor pressure less than 1e-13 atmospheres (0.1 ppt)
OTHN	Inert	26	12	-	240.28	Other organic products with vapor pressures less than $1 \times 10^{-13}$ atmospheres (0.1 ppt)
NAMIN	Inert		4	2	89.14	Nitramines
MALAH	Inert		4	-	98.06	Maleic anhydride
INHIB	Inert	27	4	-	90.00	Radical inhibiting compounds (treated as unreactive)
NROG	Inert	28	-	-	1.00	Unreactive mass
NVOL	Inert	29	-	-	1.00	Nonvolatile mass

Table A-1 (continued)

[a] Mechanism derivation notes:

Base: Part of the base mechanism, with reactions derived manually from results of data evaluations and other information. See mechanism listing on Table A-2, and footnotes to the reactions.

Base simplified: Part of the extended base mechanism, with represented by a simplified or parameterized mechanism either adjusted to fit chamber data or to give a simplified representation of the overall effects of the reactions.

Simplified: This compound, which is included in the mechanism for tracking purposes only and is not expected to significantly affect formation of secondary pollutants, is represented using a simplified mechanism primarily to track its rate of consumption.

MechGen: Mechanism for this compound derived using MechGen.

Mix=(mixture): Derived by MechGen from the compositions of mixtures that are represented using this model species, as discussed in the text. Mixtures used as follows. EmitMix: compounds identified in anthropogenic emissions; BioMix: compounds in biogenic emissions; Products: compounds formed from reactions of compounds in EmitMix and BioMix; Products2: compounds from reactions of compounds in the "Products" mixture.

Compound name (all caps): Mechanism approximated by the MechGen-derived mechanism of the indicated compound. Compounds used are: benzene, naphthalene, furan, styrene, peroxy acetic acid (PAA), methyl glyoxal, biacetyl, b-caryophyllene,  $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OONO}_2$  (MAPAN), and  $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OONO}_2$  (PBN).

Inert: Compound treated as unreactive. It could be removed from the model if its simulated concentrations are not of interest.

[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.
- 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 Use of the steady state approximation for this species is recommended to reduce computer time and memory if the simulation software provides for this.
- 4 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, NO<sub>2</sub> (for SumRCO3), HO<sub>2</sub>, and each other are included as separate reactions. Peroxy radicals undergo rapid isomerizations are not included because they are replaced by the products they form.
- 5 Represents the conversions of NO to NO<sub>2</sub> by reactions of peroxy radicals for all the peroxy radicals generated by MechGen in the standard mechanism that are represented using the SAPRC-07 peroxy lumping approach.
- 6 Represents the consumption of NO by reactions of peroxy radicals forming organic nitrates for all the peroxy radicals generated by MechGen that are represented using the SAPRC-07 peroxy lumping approach.
- 7 Represents the formation of various products or radicals following the reactions of alkoxy radicals formed from the reactions of peroxy radicals (primarily the reaction with NO but to a lesser extent for reactions with NO<sub>3</sub>, SumRO2 or SumRCO3). The carbon and nitrogen numbers are the same as those assigned to the model species formed. Used for NO<sub>2</sub>, NO<sub>3</sub>, OH, HO<sub>2</sub>, HCHO, GLY, HCOOH, MECHO, ETCHO, GLCHO, MEK, ACRO, ACET, MACR, MVK, BACL, MGLY, BUDAL, FURNS, BALD, BENX, RCHO, KET2, LVKS, OLEA1, OLEA2, OLEP, OACID, PACID, AMINS, RPNO3, RCNO3, RHNO3, RDNO3, HPCRB, AFG1, AFG2A, AFG2B, AFG3, PAN2, MEO2, ETO2, MECO3, R2CO3, MACO3 and TBUO in the standard mechanism.
- 8 Represents the formation of hydroperoxide products following the reactions of peroxy radicals with HO<sub>2</sub>. Used for RUOOH, RAOOH, HPCRB, ROOH and RPNO3.

Table A-1 (continued)

- 9 Represents the formation of organic nitrate products following the reactions of peroxy radicals with NO. Used for RCNO<sub>3</sub>, RHNO<sub>3</sub>, RANO<sub>3</sub>, RPNO<sub>3</sub>, RDNO<sub>3</sub>, R1NO<sub>3</sub>, R2NO<sub>3</sub>, RNNO<sub>3</sub> and PAN<sub>2</sub>.
- 10 As discussed in Section 2.4.2, these intermediates were used in the standard version of SAPRC-22 to account for dependences of overall product yields on absolute NO levels in reaction sequences that involve competitions between peroxy unimolecular and bimolecular reactions. These are used only when absolute NO concentrations changed overall product yields by more than 0.015. "Spec" refers to the reacting model species. Examples include ISOP\_OH, OLE2\_O3, MACR\_N3, and RCHO\_HV. See Table A-2 for a complete list.
- 11 MechGen is currently not capable of handling mechanisms for naphthalenes, PAHs, and tetralins, so a simplified parameterized representation adjusted to fit chamber data where available, has to be used. "NPRAD" is one of the model species needed to implement these parameterized mechanisms.
- 12 Amines with no  $\alpha$  hydrogens cannot react with O<sub>2</sub>, so their main atmospheric sinks would be reactions with NO<sub>x</sub> or HO<sub>2</sub>. This is the intermediate used to represent these radicals.
- 13 These are represented explicitly in SAPRC-11 and later versions of SAPRC.
- 14 These are represented explicitly in the "toxics" version of SAPRC-07 as implemented in CMAQ.
- 15 MTBE is included as an explicit compound at the request of the CARB staff.
- 16 These are represented explicitly in SAPRC-18.
- 17 These compounds are of regulatory interest and are represented explicitly so their concentrations can be tracked in atmospheric models, even though they are not emitted in sufficient quantities or are sufficiently reactive to affect predictions of secondary pollutants. Except for carbon tetrachloride, which is unreactive, they are represented by highly simplified mechanisms designed primarily to track their consumption due to reaction with OH radicals. Note that these are not included in the extended mechanism.
- 18 The mechanisms for these model species were derived from mechanisms of the major components of the mixture representing anthropogenic emissions. See text.
- 19 The mechanism for TERP was derived from mechanisms of the major terpenes in the mixture representing anthropogenic emissions. Note that MechGen lumps all compounds with formula C<sub>10</sub>H<sub>16</sub> that contains at least one ring and one more double bond as a terpene. Otherwise it is lumped as OLE<sub>x</sub> or ALK<sub>x</sub>, depending on the presence and types of double bond(s).
- 20 Mechanism derived from that of a representative compound that is either the major compound represented by this model species or that is assumed to have a similar mechanism in cases where MechGen cannot derive a mechanism for compounds of this type.
- 21 A highly simplified mechanism is used for emitted photoreactive species that are not well represented by other model species but which are too reactive for their reactions to be ignored.
- 22 The mechanisms for these model species were derived from mechanisms of compounds major compounds represented by these model species that are formed from the reactions of the compounds in the anthropogenic or biogenic emissions mixture (with each mixture weighted equally). The product compounds are weighted both by contribution of the reactants in the emissions mixture and the yields of the products when they react under standard atmospheric conditions, as discussed in the text.
- 23 The mechanisms for the lumped catechol are derived from the mechanisms of the catechols in the mixture of phenol, cresol, and xylenol product compounds (see above footnote).
- 23a The CATL3 model species is used to represent phenols with three or more -OH's. The mechanism is assigned based on CATL reactions but simplified and assuming that all products are non-volatile.
- 24 MechGen is currently not capable of generating mechanisms for these types of aromatics, so an estimated simplified mechanism is used to represent them.
- 25 These compounds are formed in reactions of amines with  $\alpha$  hydrogens. MechGen is not capable of deriving mechanisms for such compounds, but it is expected that they would be rapidly hydrolyzed in the atmosphere, forming a carbonyl compound, which is the reaction assigned to this model species.

Table A-1 (continued)

- 26 These are only used for non-volatile products; NVOL is used for non-volatile emissions. Molecular weights based on weighed averages of major product compounds formed from the reactions of the anthropogenic and biogenic emissions that are lumped using these species.
- 27 The current mechanism does not have a good way to represent inhibiting compounds (other than those lumped as TAMINS), so treating them as unreactive is less bad than representing them using a reactive species. New species would have to be added to the mechanism if such compounds become important in emissions.
- 28 The "NROG" model species is used to represent unreactive compounds either in emissions or which are formed as products and are not otherwise represented. Because such compounds can have a large range of carbon numbers and molecular weights, the amounts of this model species are meaningful only on a mass basis, so this model species is not assigned any carbon or nitrogen number and is given a molecular weight of unity. Simulated concentrations would be in units proportional to mass.
- 29 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. Because emitted non-volatile compounds can have a large range of carbon numbers and molecular weights, the amounts of this model species are meaningful only on a mass basis, so this model species is not assigned any carbon or nitrogen number and is given a molecular weight of unity. Simulated concentrations would be in units proportional to mass.

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

Table A-2. List of reactions and documentation notes in the standard SAPRC-22 mechanisms.

Label.	Rate Parameters [a]				Notes [b]	Reaction and Products [a]
	k298	A	Ea	B		
<u>Inorganic reactions</u>						
1	Phot Set= NO2-06				1	NO2 + HV = NO + O3P
2	5.90e-34	6.00e-34	-	2.40	1	O3P + O2 + M = O3 + M
3	7.96e-15	8.00e-12	4.094	-	1	O3P + O3 = #2 O2
4	1.66e-12	Falloff, F=0.60, N=1.00			1	O3P + NO = NO2
	0:	9.00e-32	-	-1.50		
	Inf:	3.00e-11	-	-		
5	1.03e-11	5.10e-12	-0.417	-	1	O3P + NO2 = NO + O2
6	3.28e-12	Falloff, F=0.60, N=1.00			1	O3P + NO2 = NO3
	0:	2.50e-31	-	-1.80		
	Inf:	2.20e-11	-	-0.70		
7	1.95e-14	3.00e-12	2.981	-	1	O3 + NO = NO2 + O2
8	3.23e-17	1.20e-13	4.869	-	1	O3 + NO2 = O2 + NO3
9	2.65e-11	1.50e-11	-0.338	-	1	NO + NO3 = #2 NO2
10	1.95e-38	3.30e-39	-1.053	-	2	NO + NO + O2 = #2 NO2
11	1.24e-12	Falloff, F=0.35, N=1.33			2	NO2 + NO3 = N2O5
	0:	3.60e-30	-	-4.10		
	Inf:	1.90e-12	-	0.20		
12	4.46e-2	Falloff, F=0.35, N=1.33			2	N2O5 = NO2 + NO3
	0:	1.30e-3	-	-3.50		
	Inf:	9.70e+14	22.018	0.10		
13	-				3	N2O5 + H2O = #2 HNO3
14	-				3	N2O5 + H2O + H2O = #2 HNO3 + H2O
15	6.56e-16	4.50e-14	2.504	-	1	NO2 + NO3 = NO + NO2 + O2
16	Phot Set= NO3NO-06				1	NO3 + HV = NO + O2
17	Phot Set= NO3NO2-6				1	NO3 + HV = NO2 + O3P
18	Phot Set= O3O1D-06				1	O3 + HV = O1D + O2
19	Phot Set= O3O3P-06				1	O3 + HV = O3P + O2
20	1.99e-10	1.63e-10	-0.119	-	1	O1D + H2O = #2 OH
21	3.69e-11	2.65e-11	-0.196	-	4	O1D + M = O3P + M
22	7.41e-12	Falloff, F=0.60, N=1.00			1	OH + NO = HONO
	0:	7.00e-31	-	-2.60		
	Inf:	3.60e-11	-	-0.10		
23	Phot Set= HONO-06				1	HONO + HV = OH + NO

Table A-2 (continued)

Label.	Rate Parameters [a]				Notes [b]	Reaction and Products [a]
	k298	A	Ea	B		
24	4.86e-12	1.80e-11	0.775	-	1	OH + HONO = H2O + NO2
25	9.89e-12	Falloff, F=0.41, N=1.24			2	OH + NO2 = HNO3
	0:	3.20e-30	-	-4.50		
	Inf:	3.00e-11	-	-		
26	2.20e-11				1	OH + NO3 = HO2 + NO2
27	1.54e-13	k = k0+k3M/(1+k3M/k2)			1	OH + HNO3 = H2O + NO3
	k0:	2.40e-14	-0.914	-		
	k2:	2.70e-17	-4.370	-		
	k3:	6.50e-34	-2.653	-		
28		Phot Set= HNO3			1	HNO3 + HV = OH + NO2
29	7.25e-14	1.70e-12	1.868	-	1	OH + O3 = HO2 + O2
30	8.17e-12	3.30e-12	-0.537	-	1	HO2 + NO = OH + NO2
31	4.33e-14	k = k1 + k2 [M]			5	HO2 + NO = HNO3
	k1:	2.39e-12	3.400	-13.77		
	k2:	1.83e-32	1.534	-4.85		
32	2.35e-31	1.20e-35	-5.850	-	6	HO2 + NO + H2O = HNO3 + H2O
33	7.50e-13	Falloff, F=0.40, N=1.26			2	HO2 + NO2 = HNO4
	0:	1.40e-31	-	-3.10		
	Inf:	4.00e-12	-	-		
34	6.20e-2	Falloff, F=0.40, N=1.26			2	HNO4 = HO2 + NO2
	0:	4.10e-5	-	-		
	Inf:	6.00e+15	22.197	-		
35		Phot Set= HNO4-06			1	HNO4 + HV = #.8 {HO2 + NO2} + #.2 {OH + NO3}
36	4.65e-12	1.30e-12	-0.755	-	1	HNO4 + OH = H2O + NO2 + O2
37	1.93e-15	1.00e-14	0.974	-	1	HO2 + O3 = OH + #2 O2
38	2.54e-12	k = k1 + k2 [M]			1	HO2 + HO2 = HO2H + O2
	k1:	3.00e-13	-0.914	-		
	k2:	2.10e-33	-1.828	-		
39	5.71e-30	k = k1 + k2 [M]			1	HO2 + HO2 + H2O = HO2H + O2 + H2O
	k1:	4.20e-34	-5.286	-		
	k2:	2.94e-54	-6.200	-		
40	3.50e-12				1	NO3 + HO2 = OH + NO2 + O2
41	2.28e-16	8.50e-13	4.869	-	1	NO3 + NO3 = #2 NO2 + O2
42		Phot Set= H2O2			1	HO2H + HV = #2 OH
43	1.80e-12				1	HO2H + OH = HO2 + H2O

Table A-2 (continued)

Label.	Rate Parameters [a]				Notes [b]	Reaction and Products [a]
	k298	A	Ea	B		
44	1.11e-10	4.80e-11	-0.497	-	1	OH + HO2 = H2O + O2
45	2.28e-13	k = k1 + k2 [M]			2	CO + OH = HO2 + CO2
	k1:	1.44e-13	-	-		
	k2:	3.43e-33	-	-		
46	6.67e-15	2.80e-12	3.577	-	1	H2 + OH = HO2 + H2O
<u>Reactions used to compute loss processes for operators used to represent total RO2 and RCO3 radicals</u>						
R2NO	9.13e-12	2.55e-12	-0.755	-	7,8	SumRO2 + NO = NO
R2H2	1.49e-11				8,9	SumRO2 + HO2 = HO2
R2N3	2.30e-12				7,8	SumRO2 + NO3 = NO3
R2R2	1.60e-14				8,10	SumRO2 + SumRO2 =
R3N2	7.71e-12	7.70e-12	-	-0.20	11,12	SumRCO3 + NO2 = NO2
R3NO	2.10e-11	6.70e-12	-0.676	-	11,13	SumRCO3 + NO = NO
R3H2	2.20e-11	3.14e-12	-1.153	-	11,14	SumRCO3 + HO2 = HO2
R3N3	4.00e-12				11,15	SumRCO3 + NO3 = NO3
R3R2	1.60e-11	4.40e-13	-2.126	-	8,11,16	SumRCO3 + SumRO2 =
R3R3	1.70e-11				11,17	SumRCO3 + SumRCO3 =
<u>Reactions of operator species designed to represent the net effects of reactions of peroxy radicals that are not represented explicitly.</u>						
57	Same k as rxn R2NO				7,18	RO2C + NO = NO2
58	Same k as rxn R2H2				7,18	RO2C + HO2 =
59	Same k as rxn R2N3				7,18	RO2C + NO3 = NO2
60	Same k as rxn R2R2				8,18	RO2C + SumRO2 = SumRO2
61	Same k as rxn R3R2				11,18	RO2C + SumRCO3 = SumRCO3
62	Same k as rxn R2NO				7,19	RO2XC + NO =
63	Same k as rxn R2H2				7,19	RO2XC + HO2 =
64	Same k as rxn R2N3				7,19	RO2XC + NO3 = NO2
65	Same k as rxn R2R2				8,19	RO2XC + SumRO2 = SumRO2
66	Same k as rxn R3R2				11,19	RO2XC + SumRCO3 = SumRCO3
<u>Manually assigned reactions of peroxy and acyl peroxy radicals</u>						
67	7.66e-12	2.80e-12	-0.596	-	1	MEO2 + NO = NO2 + HCHO + HO2
68	5.21e-12	3.80e-13	-1.550	-	2	MEO2 + HO2 = #.9 MEOOH + #.1 {HCHO + H2O} + O2
69	1.20e-12				2	MEO2 + NO3 = HCHO + HO2 + NO2
70	2.16e-13				8,20	MEO2 + SumRO2 = #.3 HO2 + #.65 HCHO + #.35 MEOH
71	1.07e-11	2.00e-12	-0.994	-	11,21	MEO2 + SumRCO3 = #.9 HO2 + HCHO
72	9.13e-12	2.55e-12	-0.755	-	7	ETO2 + NO = NO2 + HO2 + MECHO

Table A-2 (continued)

Label.	Rate Parameters [a]				Notes [b]	Reaction and Products [a]
	k298	A	Ea	B		
73	7.44e-12				7	ETO2 + HO2 = ROOH
74	2.30e-12				7	ETO2 + NO3 = NO2 + HO2 + MECHO
75	2.90e-14				8,22	ETO2 + SumRO2 = #.5 HO2 + #.25 ETOH + #.75 MECHO
76	1.60e-11				20	ETO2 + SumRCO3 = #.8 HO2 + MECHO
77	Same k as rxn R2NO				7	BZO2 + NO = NO2 + BZO
78	Same k as rxn R2H2				7	BZO2 + HO2 = ROOH + O2
79	Same k as rxn R2N3				7	BZO2 + NO3 = BZO + NO2
80	Same k as rxn R2R2				8,10	BZO2 + SumRO2 = SumRO2 + BZO
81	Same k as rxn R3R2				11,16	BZO2 + SumRCO3 = SumRCO3 + BZO
Q1NO	2.00e-11	8.10e-12	-0.537	-	1,23	MECO3 + NO = NO2 + MEO2 + CO2 + SumRO2
Q1N2	8.69e-12	Falloff, F=0.60, N=1.00			1	MECO3 + NO2 = PAN
	0:	9.70e-29	-	-5.60		
	Inf:	9.30e-12	-	-1.50		
Q1N3	4.00e-12				14	MECO3 + NO3 = NO2 + MEO2 + CO2 + SumRO2
Q1H2	2.20e-11				15	MECO3 + HO2 = #.13 O3 + #.5 OH + #.5 MEO2 + #.13 OACID + #.37 PACID + #.5 CO2 + #.5 SumRO2
Q1R2	1.60e-11				16	MECO3 + SumRO2 = #.9 MEO2 + #.1 OACID + #.9 CO2 + #.9 SumRO2
Q1R3	1.40e-11				17	MECO3 + SumRCO3 = MEO2 + CO2 + SumRO2
Q4N2	1.11e-11				24	BZCO3 + NO2 = PBZN
Q4NO	1.60e-11				24,23	BZCO3 + NO = NO2 + CO2 + BZO2 + SumRO2
Q4H2	Same k as rxn 53				14	BZCO3 + HO2 = #.37 ALK5 + #.13 {O3 + ALK5} + #.5 {OH + BZO2 + CO2} + #.5 SumRO2
Q4N3	Same k as rxn R3H2				15	BZCO3 + NO3 = NO2 + CO2 + BZO2 + O2 + SumRO2
Q4R2	Same k as rxn R3N3				8,16	BZCO3 + SumRO2 = SumRO2 + BZO2 + CO2 + SumRO2
Q4R3	Same k as rxn R3R2				11,17	BZCO3 + SumRCO3 = SumRCO3 + CO2 + BZO2 + SumRO2
<u>Manually assigned reactions of other types of radical intermediates</u>						
94	2.24e-11	3.50e-12	-1.100	-	25	TBUO + NO2 = R1NO3
95	1.43e+3	1.40e+13	13.624	-	26,23	TBUO = ACET + MEO2 + SumRO2
96	2.08e-12				27	BZO + NO2 = NPHE
97	Same k as rxn R2H2				28	BZO + HO2 = CRES
98	2.86e-13				29	BZO + O3 = BZO2 + O2 + SumRO2
99	1.49e-11				29	BZO + BZO =
100	Same k as rxn R3N2				30	NPRAD + NO2 = NPHE
101	Same k as rxn R3H2				30	NPRAD + HO2 = NAPPRD
102	1.00e-3				31	NPRAD = NAPPRD
103	Same k as rxn R3N2				32	PNAMIN + NO2 = NAMIN

Table A-2 (continued)

Label.	Rate Parameters [a]				Notes [b]	Reaction and Products [a]
	k298	A	Ea	B		
104	Same k as rxn R3H2				32	PNAMIN + HO2 = AMINS
105	1.00e-3				31	PNAMIN = AMINS
<u>Reactions of stabilized Criegee intermediates</u>						
G1N2	7.00e-12				33	HCHO2 + NO2 = HCHO + NO3
G1WA	2.40e-15				34	HCHO2 + H2O = HCOOH
G2N2	Same k as rxn G1N2				35	MECHO2 + NO2 = MECHO + NO3
G2WA	Same k as rxn G1WA				35	MECHO2 + H2O = OACID
G3N2	Same k as rxn G1N2				35	RCHO2 + NO2 = RCHO + NO3
G3WA	Same k as rxn G1WA				35	RCHO2 + H2O = OACID
<u>Reactions of SO2</u>						
S2OH	9.59e-13	Falloff, F=0.60, N=1.00			1	SO2 + OH = HO2 + SULF
G1S2	3.80e-11				1,36	HCHO2 + SO2 = SULF + HCHO
G2S2	Same k as rxn G1S2				36	MECHO2 + SO2 = SULF + MECHO
G3S2	Same k as rxn G1S2				36	RCHO2 + SO2 = SULF + RCHO
<u>Reactions of explicit and lumped organic compounds assigned manually</u>						
C1OH	6.34e-15	2.45e-12	3.527	-	1,23	CH4 + OH = MEO2 + SumRO2
117	Phot Set= HCHOR-13				37	HCHO + HV = #2 HO2 + CO
118	Phot Set= HCHOM-13				37	HCHO + HV = H2 + CO
119	8.37e-12	5.50e-12	-0.248	-	1	HCHO + OH = HO2 + CO + H2O
120	5.80e-16				1	HCHO + NO3 = HNO3 + HO2 + CO
P1UI	3.82e-4	Falloff, F=0.60, N=1.00			1,23	PAN = NO2 + MECO3 + SumRCO3
	0:	1.08e+0	-	-5.60		
	Inf:	1.03e+17	27.821	-1.50		
P1HV	Phot Set= PAN-11				1,23,G	PAN + HV = #.6 NO2 + #.4 NO3 + #.4 MEO2 + #.6 MECO3 + #.4 CO2 + #.4 SumRO2 + #.6 SumRCO3
123	Phot Set= GLY-I13R				2	GLY + HV = #2 {CO + HO2}
124	Phot Set= GLY-I13M				2	GLY + HV = HCHO + CO
125	1.15e-11	1.15e-11	-	-	1	GLY + OH = #1.7 CO + #.7 HO2 + #.3 {OH + CO2}
126	4.00e-16				2	GLY + NO3 = HNO3 + #1.7 CO + #.7 HO2 + #.3 {OH + CO2}
BLOH	1.20e-11				2,23	BALD + OH = BZCO3 + SumRCO3
BLHV	Phot Set= BALD-11, qy= 9.0e-2				38	BALD + HV =
BLN3	4.00e-15				39,23	BALD + NO3 = HNO3 + BZCO3 + SumRCO3
PBUI	3.18e-4	2.10e+16	27.026	-	24,23	PBZN = BZCO3 + NO2 + SumRCO3
PBHV	Phot Set= PPN-11				40,23	PBZN + HV = #.6 {BZCO3 + NO2} + #.4 {CO2 + BZO2 + NO3} + #.4 SumRO2 + #.6 SumRCO3
NPOH	3.50e-12				41	NPHE + OH = BZO + NO2

Table A-2 (continued)

Label.	Rate Parameters [a]				Notes [b]	Reaction and Products [a]
	k298	A	Ea	B		
NPHV	Phot Set= NO2-06, qy= 1.5e-3				42	NPHE + HV = HONO + PHEN
NAOH	2.30e-11	1.55e-11	-0.233	-	43,23	NAPS + OH = #.741 HO2 + #.707 CATL + #.034 RO2C + #.017 AFG2A + #.017 AFG2B + #.034 GLY + #.330 NPRAD + #.250 MACO3 + #.034 SumRO2 + #.250 SumRCO3
CTOH	5.97e-10				44	CATL3 + OH = HO2 + OTHN
CTN3	4.86e-10				44	CATL3 + NO3 = HNO3 + OTHN
PNOH	2.00e-10				45	NAPPRD + OH = HO2 + OTHN
PNN3	1.70e-10				45	NAPPRD + NO3 = HNO3 + OTHN
137	Phot Set= BACL-11				23,46	PHOT + HV = #2 {HO2 + RO2C + SumRO2} + ALK3
138	2.78e-4				47	IMINE = MECHO
<u>Reactions of reactive toxic species included for tracking purposes</u>						
147	7.56e-12	2.54e-12	-0.646	-	48	CLETHE + OH = xHO2 + RO2C + xHCHO + yROOH + SumRO2
148	4.13e-12				48	ACRLNT + OH = xHO2 + RO2C + xHCHO + yROOH + SumRO2
149	1.60e-13	3.50e-12	1.828	-	48	PCE + OH = xHO2 + RO2C + yROOH + SumRO2
150	4.03e-13				48	PCLBEN + OH = xHO2 + RO2C + yROOH + SumRO2
151	1.00e-13	1.80e-12	1.709	-	48	MECL2 + OH = xHO2 + RO2C + yROOH + SumRO2
152	2.22e-13	7.69e-12	2.098	-	48	ETBR2 + OH = xHO2 + RO2C + yROOH + SumRO2
153	2.40e-13	8.69e-12	2.126	-	48	ETCL2 + OH = xHO2 + RO2C + yROOH + SumRO2
154	9.21e-14	1.63e-12	1.701	-	48	ETOX + OH = xHO2 + RO2C + yROOH + SumRO2
155	1.04e-13	1.80e-12	1.689	-	48	CHCL3 + OH = xHO2 + RO2C + yROOH + SumRO2
<u>Operator reactions representing the formation of individual products formed in peroxy radical reactions [c]</u>						
	Same k as rxn R2NO				7,49	x(Spec) + NO = NO + (Spec)
	Same k as rxn R2H2				7,49	x(Spec) + HO2 = HO2
	Same k as rxn R2N3				7,49	x(Spec) + NO3 = NO3 + (Spec)
	Same k as rxn R2R2				8,49	x(Spec) + SumRO2 = SumRO2 + #.5 (Spec)
	Same k as rxn R3R2				11,49	x(Spec) + SumRCO3 = SumRCO3 + (Spec)
	Same k as rxn R2NO				7,50	y(Spec) + NO = NO
	Same k as rxn R2H2				7,50	y(Spec) + HO2 = HO2 + (Spec)
	Same k as rxn R2N3				7,50	y(Spec) + NO3 = NO3
	Same k as rxn R2R2				8,50	y(Spec) + SumRO2 = SumRO2 + #.5 (Spec-2)
	Same k as rxn R3R2				11,50	y(Spec) + SumRCO3 = SumRCO3
	Same k as rxn R2NO				7,51	z(Spec) + NO = NO + (Spec)

Table A-2 (continued)

Label	Rate Parameters [a]				Notes [b]	Reaction and Products [a]
	k298	A	Ea	B		
					7,51	z(Spec) + HO2 = HO2
					7,51	z(Spec) + NO3 = NO3 + (Spec-2) + HO2
					8,51	z(Spec) + SumRO2 = SumRO2 + #.5 (Spec-2) + #.5 HO2
					11,51	z(Spec) + SumRCO3 = SumRCO3 + (Spec-2) + HO2
<u>Reactions of lumped radicals imported directly from MechGen [d]</u>						
Q2NO	2.10e-11	6.70e-12	-0.676	-	52	R2CO3 + NO = NO2 + #.95 xHO2 + #.96 RO2C + #.04 RO2XC + #.95 xETCHO + #.04 zR1NO3 + CO2 + yROOH + SumRO2
Q2N2	7.70e-12				52	R2CO3 + NO2 = PAN2
Q2N3	4.00e-12				52	R2CO3 + NO3 = NO2 + #.95 xHO2 + #.96 RO2C + #.04 RO2XC + #.95 xETCHO + #.04 zR1NO3 + CO2 + yROOH + SumRO2
Q2H2	2.20e-11				52	R2CO3 + HO2 = #.13 O3 + #.5 OH + #.48 xHO2 + #.48 RO2C + #.02 RO2XC + #.48 xETCHO + #.13 OACID + #.37 PACID + #.02 zR1NO3 + #.5 CO2 + #.5 yROOH + #.5 SumRO2
Q2R2	1.44e-11				52	R2CO3 + SumRO2 = #.95 xHO2 + #.96 RO2C + #.04 RO2XC + #.95 xETCHO + #.04 zR1NO3 + CO2 + yROOH + SumRO2
Q5UI	3.98e+1	7.79e+8	9.942	-	52	MACO3 = #.93 xHO2 + #.93 RO2C + #.07 RO2XC + #.93 xPACID + #.07 zRCNO3 + SumRO2
Q5NO	2.10e-11	6.70e-12	-0.676	-	52	MACO3 + NO = NO2 + MEO2 + HCHO + CO + CO2 + SumRO2
Q5N2	7.70e-12				52	MACO3 + NO2 = APANS
<u>Reactions of explicitly represented VOCs or intermediates imported directly from MechGen [d]</u>						
C2OH	2.49e-13	1.51e-12	1.059	1.92	48	ETHAN + OH = ETO2 + SumRO2
C3OH	1.11e-12	2.00e-12	0.342	1.76	48	PROP + OH = #.95 xHO2 + #.01 xMEO2 + #.96 RO2C + #.04 RO2XC + #.01 xMECHO + #.27 xETCHO + #.68 xACET + #.04 zR1NO3 + yROOH + SumRO2
C4OH	2.38e-12	2.09e-12	-0.083	1.82	48	NC4 + OH = #.59 xHO2 + #.33 xETO2 + #1.02 RO2C + #.08 RO2XC + #.33 xMECHO + #.12 xRCHO + #.48 xMEK + #.07 zR1NO3 + #.01 zRHNO3 + #1.1 yROOH + #1.1 SumRO2
E1OH	7.90e-12	Falloff, F=0.60, N=1.00			48	ETHEN + OH = xHO2 + RO2C + #1.48 xHCHO + #.26 xGLCHO + yROOH + SumRO2
	0:	1.10E-28	-	-3.5	53	
	Inf:	8.40E-12	-	-1.75	53	
E1O3	1.55e-18	6.82e-15	4.968	-	48	ETHEN + O3 = #.17 OH + #.27 HO2 + #.42 HCHO2 + HCHO + #.18 H2 + #.35 CO + #.23 CO2
E1N3	2.10e-16	3.30e-12	5.723	-	48	ETHEN + NO3 = #.01 xNO2 + #.99 xHO2 + RO2C + #.01 xHCHO + #.99 xRCNO3 + yRPNO3 + SumRO2
E1OP	7.30e-13	1.07e-11	1.590	-	54	ETHEN + O3P = #1.09 HO2 + #.51 MEO2 + #.1 MECHO + #.51 CO + #4.41 NROG + #.51 SumRO2
E2OH	2.44e-11	1.20e-11	-0.417	-0.62	48	PROPE + OH = #.97 xHO2 + #.97 RO2C + #.03 RO2XC + #.97 xHCHO + #.97 xMECHO + #.03 zRHNO3 + yROOH + SumRO2

Table A-2 (continued)

Label.	Rate Parameters [a]				Notes [b]	Reaction and Products [a]
	k298	A	Ea	B		
E2O3	1.05e-17	5.77e-15	3.736	-	48	PROPE + O3 = PROPE_O3 + #.3 OH + #.17 HO2 + #.16 xHO2 + #.03 MEO2 + #.21 HCHO2 + #.12 MECHO2 + #.22 RO2C + #.5 HCHO + #.05 xHCHO + #.05 MEOH + #.5 MECHO + #.09 H2 + #.22 CO + #.24 CO2 + #.09 CH4 + #.25 SumRO2
492	2.45e+0				53	PROPE_O3 = #.05 xOH + #.16 xPACID + #.05 CO2
493	9.13e-12	2.55e-12	-0.755	-	53	PROPE_O3 + NO = NO + #.06 xHO2 + #.15 xHCHO + #.2 CO + #.18 yHPCRB
E2N3	9.54e-15	4.60e-13	2.295	-	48	PROPE + NO3 = #.29 xNO2 + #.68 xHO2 + #.97 RO2C + #.03 RO2XC + #.29 xHCHO + #.29 xMECHO + #.68 xRCNO3 + #.03 zRDNO3 + yRPNO3 + SumRO2
E2OP	3.99e-12	1.02e-11	0.556	-	54	PROPE + O3P = #.25 ETCHO + #.25 ACET + #.5 ALK2
IPOH	9.99e-11	2.70e-11	-0.775	-	48	ISOP + OH = ISOP_OH + #.57 xHO2 + #.55 RO2C + #.05 RO2XC + #.5 xHCHO + #.23 xMACR + #.27 xMVK + #.05 zRHNO3 + #.05 xFURNS + #.6 yRUOOH + #.6 SumRO2
497	1.31e+0				53	ISOP_OH = #.06 xOH + #.32 HO2 + #.31 HPCRB + #.06 xHPCRB
498	9.13e-12	2.55e-12	-0.755	-	53	ISOP_OH + NO = NO + #.33 xHO2 + #.38 RO2C + #.05 RO2XC + #.03 xHCHO + #.34 xOLEA1 + #.05 zRHNO3 + #.42 yRUOOH + #.43 SumRO2
IPO3	1.28e-17	1.05e-14	3.974	-	48	ISOP + O3 = #.13 OH + #.62 HO2 + #.16 MECO3 + #.23 HCHO2 + #.06 RCHO2 + #.4 HCHO + #.39 MACR + #.16 MVK + #.05 OLEP + #.1 H2 + #.33 CO + #.13 CO2 + #.16 SumRCO3
IPN3	6.52e-13	2.95e-12	0.894	-	48	ISOP + NO3 = ISOP_N3 + #.71 xNO2 + #.07 xHO2 + #.91 RO2C + #.1 RO2XC + #.49 xHCHO + #.22 xOLEA1 + #.48 xMVK + #.04 xRCNO3 + #.1 zRDNO3 + yRPNO3 + #1.01 SumRO2
501	1.07e+0				53	ISOP_N3 = #.11 xNO2 + #.04 xRPNO3 + #.12 xHPCRB
502	9.13e-12	2.55e-12	-0.755	-	53	ISOP_N3 + NO = NO + #.11 xHO2 + #.14 RO2C + #.01 RO2XC + #.09 xHCHO + #.05 xRHNO3 + #.09 xRCNO3 + #.01 zRDNO3 + #.11 yRPNO3 + #.15 SumRO2
IPOP	3.50e-11				54	ISOP + O3P = #.25 HO2 + #.25 MEO2 + #.75 OLEP + #.25 SumRO2
E3OH	6.63e-11	1.12e-11	-1.053	-	48	BUT13 + OH = BUT13_OH + #.63 xHO2 + #.66 RO2C + #.04 RO2XC + #.61 xHCHO + #.58 xACRO + #.02 xOLEA1 + #.04 zRHNO3 + #.05 xFURNS + #.69 yRUOOH + #.7 SumRO2
505	1.17e+0				53	BUT13_OH = #.02 xOH + #.31 HO2 + #.31 HPCRB
506	9.13e-12	2.55e-12	-0.755	-	53	BUT13_OH + NO = NO + #.31 xHO2 + #.3 RO2C + #.02 RO2XC + #.29 xOLEA1 + #.02 zRHNO3 + #.33 yRUOOH + #.32 SumRO2
E3O3	6.31e-18	1.34e-14	4.537	-	48	BUT13 + O3 = BUT13_O3 + #.08 OH + #.5 HO2 + #.27 xHO2 + #.21 HCHO2 + #.14 RCHO2 + #.36 RO2C + #.5 HCHO + #.09 xHCHO + #.5 ACRO + #.09 H2 + #.54 CO + #.12 CO2 + #.36 SumRO2
508	2.63e+0				53	BUT13_O3 = #.09 xOH + #.27 xPACID + #.09 CO2
509	9.13e-12	2.55e-12	-0.755	-	53	BUT13_O3 + NO = NO + #.09 xHO2 + #.25 xHCHO + #.02 xGLY + #.33 CO + #.3 yHPCRB
E3N3	1.10e-13				48	BUT13 + NO3 = #.89 xNO2 + #.06 xHO2 + #.94 RO2C + #.06 RO2XC + #.74 xHCHO + #.74 xACRO + #.14 xOLEA1 + #.06 xRCNO3 + #.06 zRDNO3 + yRPNO3 + SumRO2
E3OP	1.98e-11	2.26e-11	0.079	-	54	BUT13 + O3P = #.25 OLEA2 + #.25 MVK + #.5 OLEP

Table A-2 (continued)

Label.	Rate Parameters [a]				Notes [b]	Reaction and Products [a]
	k298	A	Ea	B		
APOH	5.31e-11	1.34e-11	-0.815	-	48	APINE + OH = APINE_OH + #.01 HO2 + #.67 xHO2 + #1.05 RO2C + #.29 RO2XC + #.08 xHCHO + #.51 xRCHO + #.08 xOLEA2 + #.17 xACET + #.06 xMVK + #.03 xLVKS + #.01 zR2NO3 + #.28 zRHNO3 + #.02 xHPCRB + #.53 yROOH + #.7 yRUOOH + #.12 yHPCRB + #1.34 SumRO2
513	3.93e+0				53	APINE_OH = #.01 xOH + #.07 xHPCRB
514	9.13e-12	2.55e-12	-0.755	-	53	APINE_OH + NO = NO + #.07 RO2C + #.02 RO2XC + #.01 xHCHO + #.06 xOLEA2 + #.02 zRHNO3 + #.09 yHPCRB + #.09 SumRO2
APO3	9.59e-17	8.22e-16	1.272	-	48	APINE + O3 = #.68 OH + #.03 xOH + #.01 HO2 + #.16 xHO2 + #.03 xMECO3 + #.2 xR2CO3 + #.29 RCHO2 + #.79 RO2C + #.26 RO2XC + #.2 xHCHO + #.15 xRCHO + #.09 xACET + #.03 KET2 + #.03 xBACL + #.07 xPACID + #.26 zRCNO3 + #.17 CO + #.03 CO2 + #.81 yHPCRB + #1.05 SumRO2
APN3	6.22e-12	1.20e-12	-0.974	-	48	APINE + NO3 = #.81 xNO2 + #.81 RO2C + #.19 RO2XC + #.81 xRCHO + #.19 zRDNO3 + yRPNO3 + SumRO2
APOP	3.20e-11				54	APINE + O3P = #.5 KET2 + #.5 ALK4
BPOH	7.58e-11	1.62e-11	-0.914	-	48	BPINE + OH = BPINE_OH + #.01 xOH + #.49 xHO2 + #.03 xR2CO3 + #1.45 RO2C + #.43 RO2XC + #.35 xHCHO + #.03 xRCHO + #.23 xOLEA2 + #.29 xACET + #.11 xKET2 + #.02 xPACID + #.02 zR2NO3 + #.31 zRHNO3 + #.09 zRCNO3 + #.02 xHPCRB + #.32 yROOH + yRUOOH + #.47 yHPCRB + #1.88 SumRO2
519	3.45e+0				53	BPINE_OH = #.04 xOH + #.01 HO2 + #.04 xPACID + #.1 xHPCRB + #.01 CO2
520	9.13e-12	2.55e-12	-0.755	-	53	BPINE_OH + NO = NO + #.13 RO2C + #.03 RO2XC + #.02 xHCHO + #.01 xRCHO + #.08 xOLEA2 + #.03 zRHNO3 + #.01 zRCNO3 + #.01 yRUOOH + #.19 yHPCRB + #.16 SumRO2
BPO3	1.89e-17	1.39e-15	2.544	-	48	BPINE + O3 = #.39 OH + #.19 HO2 + #.19 xR2CO3 + #.21 HCHO2 + #.2 RCHO2 + #.19 RO2C + #.06 RO2XC + #.5 HCHO + #.5 KET2 + #.06 zRCNO3 + #.09 H2 + #.17 CO + #.12 CO2 + #.21 yHPCRB + #.25 SumRO2
BPN3	2.50e-12				48	BPINE + NO3 = #.06 xOH + #.18 xHO2 + #.14 xR2CO3 + #2.25 RO2C + #.63 RO2XC + #.04 xHCHO + #.02 xRCHO + #.27 xACET + #.14 xPACID + #.23 xRCNO3 + #.43 zRCNO3 + #.19 zRDNO3 + #.04 CO2 + yRPNO3 + #2.88 SumRO2
BPOP	2.70e-11				54	BPINE + O3P = #.5 RCHO + #.5 ALK5
ACOH	7.47e-13	Falloff, F=0.60, N=1.00			1	ACETL + OH = #.67 OH + #.33 HO2 + #.33 HCOOH + #.67 GLY + #.33 CO
	0:	5.50E-30	-	-		
	Inf:	8.30E-13	-	2		
ACO3	1.00e-20				48	ACETL + O3 = #.26 HO2 + #.34 RCHO2 + #.34 HCHO + #.18 HCOOH + #.31 CO + #.47 CO2
BZOH	1.21e-12	2.30e-12	0.378	-	48	BENZ + OH = #.69 HO2 + #.28 xHO2 + #.28 RO2C + #.04 RO2XC + #.28 xGLY + #.12 OLEA2 + #.57 PHEN + #.28 xBUDAL + #.04 zRANO3 + #.31 yRAOOH + #.32 SumRO2
TLOH	5.64e-12	1.80e-12	-0.676	-	48	TOLU + OH = #.41 HO2 + #.5 xHO2 + #.5 RO2C + #.08 RO2XC + #.22 xGLY + #.22 xMGLY + #.01 OLEA1 + #.2 OLEA2 + #.19 CRES + #.06 xBALD + #.22 xBUDAL + #.02 xAFG1 + #.19 xAFG2A + #.01 zR1NO3 + #.07 zRANO3 + #.08 yROOH + #.51 yRAOOH + #.58 SumRO2

Table A-2 (continued)

Label	Rate Parameters [a]				Notes [b]	Reaction and Products [a]
	k298	A	Ea	B		
OXOH	1.36e-11				48	OXYL + OH = #.35 HO2 + #.54 xHO2 + #.54 RO2C + #.11 RO2XC + #.12 xGLY + #.22 xMGLY + #.1 OLEA1 + #.1 OLEA2 + #.06 LVKS + #.15 xBACL + #.08 XYNL + #.06 xBALD + #.15 xBUDAL + #.01 xAFG1 + #.22 xAFG2A + #.11 xAFG2B + #.02 zR2NO3 + #.09 zRANO3 + #.08 yROOH + #.57 yRAOOH + #.65 SumRO2
MXOH	2.31e-11				48	MXYL + OH = #.21 HO2 + #.66 xHO2 + #.66 RO2C + #.13 RO2XC + #.04 xGLY + #.59 xMGLY + #.13 OLEA2 + #.07 XYNL + #.03 xBALD + #.05 xAFG1 + #.58 xAFG2A + #.01 zR2NO3 + #.12 zRANO3 + #.03 yROOH + #.75 yRAOOH + #.79 SumRO2
PXOH	1.21e-11	4.14e-12	-0.634	-	48	PXYL + OH = #.38 HO2 + #.52 xHO2 + #.52 RO2C + #.11 RO2XC + #.16 xGLY + #.29 xMGLY + #.02 OLEA1 + #.23 OLEA2 + #.14 XYNL + #.07 xBALD + #.29 xAFG1 + #.16 xAFG3 + #.02 zR2NO3 + #.09 zRANO3 + #.09 yROOH + #.53 yRAOOH + #.63 SumRO2
X1OH	3.27e-11				48	BZ123 + OH = #.18 HO2 + #.67 xHO2 + #.67 RO2C + #.15 RO2XC + #.03 xGLY + #.07 xMGLY + #.03 OLEA1 + #.03 OLEA2 + #.1 LVKS + #.54 xBACL + #.02 XYNL + #.02 xBALD + #.54 xAFG2A + #.1 xAFG2B + #.01 zR2NO3 + #.14 zRANO3 + #.03 yROOH + #.78 yRAOOH + #.82 SumRO2
X2OH	3.25e-11				48	BZ124 + OH = #.23 HO2 + #.63 xHO2 + #.63 RO2C + #.14 RO2XC + #.03 xGLY + #.51 xMGLY + #.04 OLEA1 + #.11 OLEA2 + #.02 LVKS + #.06 xBACL + #.05 XYNL + #.03 xBALD + #.08 xAFG1 + #.04 xAFG2A + #.27 xAFG2B + #.21 xAFG3 + #.01 zR2NO3 + #.13 zRANO3 + #.04 yROOH + #.73 yRAOOH + #.77 SumRO2
X3OH	5.86e-11				48	BZ135 + OH = #.17 HO2 + #.68 xHO2 + #.68 RO2C + #.15 RO2XC + #.67 xMGLY + #.11 OLEA2 + #.05 XYNL + #.02 xBALD + #.67 xAFG2A + #.01 zR2NO3 + #.15 zRANO3 + #.02 yROOH + #.81 yRAOOH + #.83 SumRO2
EBOH	7.00e-12				48	C2BEN + OH = #.36 HO2 + #.51 xHO2 + #.01 xMEO2 + #.54 RO2C + #.12 RO2XC + #.02 xHCHO + #.18 xGLY + #.18 xMGLY + #.01 OLEA1 + #.17 OLEA2 + #.16 XYNL + #.03 xBALD + #.18 xBUDAL + #.02 xAFG1 + #.16 xAFG2A + #.05 zR2NO3 + #.07 zRANO3 + #.13 xBENX + #.23 yROOH + #.44 yRAOOH + #.66 SumRO2
MTOH	3.09e-12	1.87e-13	-1.675	3.34	48	MTBE + OH = #.72 xHO2 + #.19 xMEO2 + #.12 RO2C + #.09 RO2XC + #.2 xHCHO + #.09 zR1NO3 + #.17 ALK1 + #.72 ALK2 + #.01 ALK3 + #.89 yROOH + #.121 SumRO2
MLOH	8.78e-13	2.32e-13	-0.799	2.72	48	MEOH + OH = HO2 + HCHO
FAOH	4.50e-13				48	HCOOH + OH = HO2 + CO2
H1OH	1.00e-11	5.30e-12	-0.378	-	48	MEOOH + OH = #.03 OH + #.97 MEO2 + #.03 HCHO + #.97 SumRO2
H1HV		Phot Set=	COOH		55	MEOOH + HV = OH + HO2 + HCHO
A2OH	1.49e-11	2.40e-12	-1.085	0.77	48	MECHO + OH = #.01 xOH + #.04 xHO2 + #.95 MECO3 + #.05 RO2C + #.02 xHCHO + #.03 xPACID + #.01 CO + #.01 CO2 + #.01 yHPCRB + #.05 SumRO2 + #.95 SumRCO3
A2N3	2.73e-15	1.40e-12	3.696	-	48	MECHO + NO3 = HNO3 + MECO3 + SumRCO3
A2HV		Phot Set=	CCHOR-13		56	MECHO + HV = HO2 + #.9 MEO2 + #.1 MECO3 + #.9 CO + #.9 SumRO2 + #.1 SumRCO3

Table A-2 (continued)

Label	Rate Parameters [a]				Notes [b]	Reaction and Products [a]
	k298	A	Ea	B		
EAOH	3.32e-12	4.42e-13	-1.204	2.29	48	ETOH + OH = #.95 HO2 + #.05 xHO2 + #.05 RO2C + #.07 xHCHO + #.95 MECHO + #.01 xGLCHO + #.05 yROOH + #.05 SumRO2
GAOH	1.10e-11				48	GLCHO + OH = #.2 HO2 + #.8 R2CO3 + #.2 GLY + #.8 SumRCO3
GAN3	1.84e-14				48	GLCHO + NO3 = HNO3 + #.1 HO2 + #.9 R2CO3 + #.1 GLY + #.9 SumRCO3
GAHV		Phot Set= GLALD-14			57	GLCHO + HV = #.07 OH + #.01 xOH + #1.66 HO2 + #.06 xHO2 + #.07 RO2C + #.83 HCHO + #.03 xHCHO + #.1 MEOH + #.04 xPACID + #.95 CO + #.01 CO2 + #.02 yHPCRB + #.07 SumRO2
A3OH	1.99e-11	6.63e-13	-2.023	1.99	48	ETCHO + OH = #.04 xHO2 + #.96 R2CO3 + #.04 RO2C + #.04 xMECHO + #.01 xPACID + #.04 CO + #.03 yHPCRB + #.04 SumRO2 + #.96 SumRCO3
A3N3	6.30e-15				48	ETCHO + NO3 = HNO3 + R2CO3 + SumRCO3
A3HV		Phot Set= C2CHOabs			58	ETCHO + HV = HO2 + ETO2 + CO + SumRO2
AROH	2.17e-11	7.10e-12	-0.662	-	48	ACRO + OH = ACRO_OH + #.31 xHO2 + #.68 MACO3 + #.31 RO2C + #.01 RO2XC + #.07 xHCHO + #.24 xGLCHO + #.01 xGLY + #.01 zRHNO3 + #.24 CO + #.22 yHPCRB + #.32 SumRO2 + #.68 SumRCO3
551	1.12e+0				53	ACRO_OH = #.06 xPACID
552	9.13e-12	2.55e-12	-0.755	-	53	ACRO_OH + NO = NO + #.06 xGLY + #.06 yHPCRB
ARO3	2.80e-19				48	ACRO + O3 = #.15 OH + #.27 HO2 + #.38 HCHO2 + #.03 RCHO2 + #.13 HCHO + #.02 HCOOH + #.9 GLY + #.16 H2 + #.34 CO + #.26 CO2
ARN3	1.10e-15				48	ACRO + NO3 = #.94 HNO3 + #.06 xHO2 + #.94 MACO3 + #.06 RO2C + #.06 xRCNO3 + #.06 CO + #.05 yRPNO3 + #.06 SumRO2 + #.94 SumRCO3
ARHV		Phot Set= ACROL-16			59	ACRO + HV = ACRO_HV + #.22 OH + #.49 HO2 + #.17 xHO2 + #.05 MEO2 + #.15 MACO3 + #.22 RO2C + #.15 HCHO + #.06 xHCHO + #.06 MEOH + #1.06 CO + #.16 CO2 + #.12 CH4 + #.25 ETHEN + #.27 SumRO2 + #.15 SumRCO3
556	2.46e+0				53	ACRO_HV = #.06 xOH + #.17 xPACID + #.06 CO2
557	9.13e-12	2.55e-12	-0.755	-	53	ACRO_HV + NO = NO + #.05 xHO2 + #.15 xHCHO + #.21 CO + #.19 yHPCRB
K3OH	1.87e-13	1.97e-14	-1.347	3.88	48	ACET + OH = #.96 xMECO3 + #.96 RO2C + #.04 RO2XC + #.96 xHCHO + #.04 zRCNO3 + #.85 yHPCRB + SumRO2
K3HV		Phot Set= ACET-06			56	ACET + HV = MEO2 + MECO3 + SumRO2 + SumRCO3
K4OH	1.05e-12	5.42e-14	-1.767	3.57	48	MEK + OH = #.29 xHO2 + #.55 xMECO3 + #.08 xR2CO3 + #.94 RO2C + #.07 RO2XC + #.11 xHCHO + #.54 xMECHO + #.29 xRCHO + #.07 zRCNO3 + #.91 yHPCRB + #1.01 SumRO2
K4HV		Phot Set= MEK-06, qy= 1.75e-1			60	MEK + HV = #.15 MEO2 + #.85 ETO2 + #.85 MECO3 + #.15 R2CO3 + SumRO2 + SumRCO3
MAOH	2.86e-11	8.00e-12	-0.755	-	48	MACR + OH = MACR_OH + #.05 xHO2 + #.21 MACO3 + #.75 RO2C + #.04 RO2XC + #.05 xHCHO + #.61 xKET2 + #.79 SumRO2 + #.21 SumRCO3
563	5.55e-1				53	MACR_OH = #.69 xOH + #.08 xKET2 + #.05 xPACID + #.04 zRCNO3 + #.69 CO2
564	9.13e-12	2.55e-12	-0.755	-	53	MACR_OH + NO = NO + #.69 xHO2 + #.09 xHCHO + #.14 xMGLY + #.04 zRHNO3 + #.61 CO + #.68 yHPCRB

Table A-2 (continued)

Label.	Rate Parameters [a]				Notes [b]	Reaction and Products [a]
	k298	A	Ea	B		
MAO3	1.22e-18	1.40e-15	4.173	-	48	MACR + O3 = #.19 OH + #.01 xOH + #.25 HO2 + #.03 xHO2 + #.01 MECO3 + #.38 HCHO2 + #.03 RCHO2 + #.04 RO2C + #.1 HCHO + #.02 xHCHO + #.02 MECHO + #.9 MGLY + #.01 OACID + #.02 xPACID + #.16 H2 + #.38 CO + #.24 CO2 + #.01 yHPCRB + #.04 SumRO2 + #.01 SumRCO3
MAN3	3.40e-15				48	MACR + NO3 = MACR_N3 + #.3 HNO3 + #.3 MACO3 + #.66 RO2C + #.04 RO2XC + #.66 xRCNO3 + #.7 SumRO2 + #.3 SumRCO3
567	5.24e-1				53	MACR_N3 = #.66 xOH + #.04 zRCNO3 + #.66 CO2
568	9.13e-12	2.55e-12	-0.755	-	53	MACR_N3 + NO = NO + #.66 xHO2 + #.04 zRDNO3 + #.66 CO + #.59 yRPNO3
MAHV		Phot Set= MACR-06			61	MACR + HV = #.45 OH + #.3 HO2 + #.15 MEO2 + #.43 xMECO3 + #.15 MACO3 + #.43 RO2C + #.02 RO2XC + #.15 HCHO + #.43 xHCHO + #.02 zRCNO3 + CO + #.25 PROPE + #.38 yHPCRB + #.6 SumRO2 + #.15 SumRCO3
MVOH	2.01e-11	2.60e-12	-1.212	-	48	MVK + OH = #.28 xHO2 + #.66 xMECO3 + #.95 RO2C + #.05 RO2XC + #.28 xHCHO + #.66 xGLCHO + #.28 xMGLY + #.05 zRCNO3 + #.9 yHPCRB + SumRO2
MVO3	5.17e-18	8.50e-16	3.021	-	48	MVK + O3 = #.18 OH + #.26 HO2 + #.02 xHO2 + #.4 HCHO2 + #.01 RCHO2 + #.02 RO2C + #.05 HCHO + #.01 xHCHO + #.01 MECHO + #.95 MGLY + #.01 xPACID + #.17 H2 + #.36 CO + #.23 CO2 + #.01 yHPCRB + #.02 SumRO2
MVHV		Phot Set= MVK-16			56	MVK + HV = #.4 MEO2 + #.4 MACO3 + #.6 CO + #.6 PROPE + #.4 SumRO2 + #.4 SumRCO3
F1OH	5.29e-11				48	BUDAL + OH = BUDAL_OH + #.29 OH + #.44 xHO2 + #.44 RO2C + #.02 RO2XC + #.41 xGLY + #.05 xPACID + #.02 CO + #.29 MALAH + #.46 SumRO2
574	2.08e+1				53	BUDAL_OH = #.25 OH + #.39 xPACID + #.02 zRCNO3 + #.25 MALAH
575	9.13e-12	2.55e-12	-0.755	-	53	BUDAL_OH + NO = NO + #.25 xHO2 + #.25 RO2C + #.62 xGLY + #.25 CO + #.35 yHPCRB + #.25 SumRO2
F1HV		Phot Set= AFGS, qy= 2.50e-1			62	BUDAL + HV = OH + HO2 + MALAH
PHOH	2.82e-11	4.70e-13	-2.424	-	48	PHEN + OH = #.85 HO2 + #.07 xHO2 + #.07 BZO + #.07 RO2C + #.01 RO2XC + #.03 xGLY + #.04 xMGLY + #.01 OLEA1 + #.04 OLEA2 + #.03 OLEP + #.77 CATL + #.04 xBUDAL + #.01 xAFG1 + #.02 xAFG2A + #.01 zRANO3 + #.08 yRAOOH + #.08 SumRO2
PHN3	4.50e-12				48	PHEN + NO3 = HNO3 + BZO
<u>Reactions of lumped emitted and product VOCs imported directly from MechGen [d, e]</u>						
L1OH	3.35e-13				G	ALK1 + OH = #.96 xHO2 + #.01 xMECO3 + #.97 RO2C + #.03 RO2XC + #.01 xHCHO + #.09 xMGLY + #.43 xOACID + #.03 zRCNO3 + #.43 CO + #.39.33 NROG + #.62 yHPCRB + SumRO2
L2OH	1.67e-12				G	ALK2 + OH = #.1 xHO2 + #.01 xMEO2 + #.84 xMECO3 + #.95 RO2C + #.05 RO2XC + #.01 xHCHO + #.08 xRCHO + #.01 xMGLY + #.84 xOACID + #.05 zRCNO3 + #.1.38 NROG + #.64 yHPCRB + SumRO2

Table A-2 (continued)

Label	Rate Parameters [a]				Notes [b]	Reaction and Products [a]
	k298	A	Ea	B		
L3OH	2.85e-12				G	ALK3 + OH = #.34 xHO2 + #.14 xETO2 + #.07 xR2CO3 + #.33 xTBUO + #1.2 RO2C + #.12 RO2XC + #.1 xHCHO + #.1 xMECHO + #.09 xRCHO + #.07 xACET + #.01 xKET2 + #.12 xOACID + #.06 zR1NO3 + #.02 zRHNO3 + #.03 zRCNO3 + #.05 CO + #.12 ALK1 + #16.91 NROG + #.81 yROOH + #.33 yHPCRB + #1.32 SumRO2
L4OH	4.54e-12				G	ALK4 + OH = #.01 xOH + #.26 HO2 + #.37 xHO2 + #.23 xETO2 + #.96 RO2C + #.12 RO2XC + #.05 xHCHO + #.12 xMECHO + #.05 xETCHO + #.07 xRCHO + #.26 ACET + #.3 xACET + #.03 xMEK + #.15 xKET2 + #.09 zR1NO3 + #.03 zRHNO3 + #.01 CO2 + #1.05 yROOH + #.01 yHPCRB + #1.08 SumRO2
L5OH	1.14e-11				G	ALK5 + OH = ALK5_OH + #.3 HO2 + #.39 xHO2 + #.02 xETO2 + #.01 xR2CO3 + RO2C + #.22 RO2XC + #.01 HCHO + #.03 xHCHO + #.04 xMECHO + #.02 xETCHO + #.06 GLCHO + #.01 xGLCHO + #.1 RCHO + #.04 xRCHO + #.05 xACET + #.05 xMEK + #.13 KET2 + #.23 xKET2 + #.01 xPACID + #.08 zR1NO3 + #.05 zR2NO3 + #.06 zRHNO3 + #.02 zRCNO3 + #.01 ALK4 + #.01 ALK5 + #1.05 yROOH + #.12 yHPCRB + #1.22 SumRO2
584	6.87e-1				53	ALK5_OH = #.02 HO2 + #.03 xHO2 + #.03 xPACID + #.06 xHPCRB
585	9.13e-12	2.55e-12	-0.755	-	53	ALK5_OH + NO = NO + #.02 xMECO3 + #.02 xR2CO3 + #.1 RO2C + #.02 RO2XC + #.01 xETCHO + #.06 xRCHO + #.01 xACET + #.01 zRHNO3 + #.01 zRCNO3 + #.01 CO + #.01 ALK5 + #.05 yROOH + #.09 yHPCRB + #.12 SumRO2
L6OH	1.69e-11				G	ALK6 + OH = #.16 HO2 + #.46 xHO2 + #.01 xMEO2 + #.02 xR2CO3 + #1.09 RO2C + #.35 RO2XC + #.09 xHCHO + #.01 xMECHO + #.01 xETCHO + #.07 RCHO + #.09 xRCHO + #.2 xACET + #.09 KET2 + #.27 xKET2 + #.01 xPACID + #.15 zR2NO3 + #.12 zRHNO3 + #.08 zRCNO3 + #.01 xHPCRB + #.03 ALK2 + #.06 ALK3 + #.01 ALK4 + #.02 ALK5 + #1.05 yROOH + #.34 yHPCRB + #1.44 SumRO2
O1OH	3.18e-11				G	OLE1 + OH = #.78 xHO2 + #.01 xMEO2 + #.11 xTBUO + #1.12 RO2C + #.1 RO2XC + #.69 xHCHO + #.01 xMECHO + #.35 xETCHO + #.15 xGLCHO + #.35 xRCHO + #.02 xACRO + #.03 xACET + #.02 xKET2 + #.01 xMVK + #.01 zR1NO3 + #.01 zR2NO3 + #.08 zRHNO3 + #1.15 yROOH + #.07 yRUOOH + #1.22 SumRO2
O1O3	8.70e-18				G	OLE1 + O3 = #.26 OH + #.01 xOH + #.17 HO2 + #.16 xHO2 + #.01 ETO2 + #.01 xTBUO + #.21 HCHO2 + #.17 RCHO2 + #.18 RO2C + #.01 RO2XC + #.5 HCHO + #.02 ETOH + #.08 xMECHO + #.19 ETCHO + #.04 xETCHO + #.31 RCHO + #.02 xRCHO + #.04 xACET + #.01 zRCNO3 + #.09 H2 + #.37 CO + #.24 CO2 + #.03 ETHAN + #.02 PROP + #.01 NC4 + #.01 ALK2 + #.02 ALK3 + #.01 ALK4 + #.02 yROOH + #.14 yHPCRB + #.2 SumRO2
O1N3	1.44e-14				G	OLE1 + NO3 = #.09 xNO2 + #.55 xHO2 + #.09 xETO2 + #.15 xTBUO + #1.41 RO2C + #.13 RO2XC + #.09 xHCHO + #.09 xETCHO + #.01 xRCHO + #.14 xACET + #.02 zR1NO3 + #.81 xRCNO3 + #.11 zRDNO3 + #1.22 yRPNO3 + #.31 yROOH + #1.54 SumRO2
O1OP	4.43e-12				G	OLE1 + O3P = #.25 RCHO + #.1 MEK + #.15 KET2 + #.09 ALK2 + #.36 ALK3 + #.05 ALK4

Table A-2 (continued)

Label	Rate Parameters [a]				Notes [b]	Reaction and Products [a]
	k298	A	Ea	B		
O2OH	6.29e-11				G	OLE2 + OH = #.93 xHO2 + #.94 RO2C + #.07 RO2XC + #1.25 xMECHO + #.4 xETCHO + #.12 xRCHO + #.07 zRHNO3 + #.99 yROOH + #.02 yRUOOH + #1.01 SumRO2
O2O3	1.90e-16				G	OLE2 + O3 = OLE2_O3 + #.46 OH + #.06 HO2 + #.32 xHO2 + #.04 MEO2 + #.01 ETO2 + #.15 MECHO2 + #.1 RCHO2 + #.4 RO2C + #.07 xHCHO + #.06 MEOH + #.02 ETOH + #.67 MECHO + #.09 xMECHO + #.22 ETCHO + #.01 xETCHO + #.07 RCHO + #.01 xACET + #.19 CO + #.23 CO2 + #.12 CH4 + #.03 ETHAN + #.09 yHPCRB + #.45 SumRO2
593	2.54e+0				53	OLE2_O3 = #.01 OH + #.08 xOH + #.01 RCHO + #.22 xPACID + #.07 CO2
594	9.13e-12	2.55e-12	-0.755	-	53	OLE2_O3 + NO = NO + #.08 xHO2 + #.01 RO2C + #.2 xHCHO + #.02 xGLY + #.27 CO + #.26 yHPCRB + #.02 SumRO2
O2N3	4.34e-13				G	OLE2 + NO3 = #.8 xNO2 + #.11 xHO2 + #1.01 RO2C + #.08 RO2XC + #1.11 xMECHO + #.33 xETCHO + #.09 xRCHO + #.01 xACET + #.12 xRCNO3 + #.08 zRDNO3 + #1.08 yRPNO3 + #.01 yROOH + #1.09 SumRO2
O2OP	1.95e-11				G	OLE2 + O3P = #.21 MEK + #.29 KET2 + #.21 ALK1 + #.22 ALK2 + #.07 ALK3
O3OH	5.26e-11				G	OLE3 + OH = #.94 xHO2 + #.94 RO2C + #.06 RO2XC + #.94 xHCHO + #.82 xACET + #.13 xMEK + #.06 zRHNO3 + yROOH + SumRO2
O3O3	1.18e-17				G	OLE3 + O3 = #.58 OH + #.14 HO2 + #.45 xMECO3 + #.03 xR2CO3 + #.21 HCHO2 + #.48 RO2C + #.02 RO2XC + #.5 HCHO + #.45 xHCHO + #.03 xMECHO + #.43 ACET + #.07 MEK + #.02 zRCNO3 + #.09 H2 + #.17 CO + #.12 CO2 + #.42 yHPCRB + #.5 SumRO2
O3N3	3.62e-13				G	OLE3 + NO3 = #.86 xNO2 + #.01 xMEO2 + #.07 xETO2 + #.94 RO2C + #.06 RO2XC + #.86 xHCHO + #.8 xACET + #.06 xMEK + #.08 xRCNO3 + #.06 zRDNO3 + yRPNO3 + SumRO2
O3OP	1.70e-11				G	OLE3 + O3P = #.5 RCHO + #.5 ALK2
O4OH	8.71e-11				G	OLE4 + OH = #.91 xHO2 + #.91 RO2C + #.08 RO2XC + #.83 xMECHO + #.09 xETCHO + #.91 xACET + #.08 zRHNO3 + yROOH + #.99 SumRO2
O4O3	4.05e-16				G	OLE4 + O3 = OLE4_O3 + #.72 OH + #.03 HO2 + #.17 xHO2 + #.03 MEO2 + #.48 xMECO3 + #.1 MECHO2 + #.01 RCHO2 + #.7 RO2C + #.02 RO2XC + #.53 xHCHO + #.04 MEOH + #.45 MECHO + #.02 xMECHO + #.05 ETCHO + #.5 ACET + #.02 zRCNO3 + #.07 CO + #.12 CO2 + #.08 CH4 + #.01 ETHAN + #.44 yHPCRB + #.75 SumRO2
603	2.62e+0				53	OLE4_O3 = #.05 xOH + #.15 xPACID + #.05 CO2
604	9.13e-12	2.55e-12	-0.755	-	53	OLE4_O3 + NO = NO + #.05 xHO2 + #.13 xHCHO + #.18 CO + #.17 yHPCRB
O4N3	9.31e-12				G	OLE4 + NO3 = #.91 xNO2 + #.92 RO2C + #.09 RO2XC + #.83 xMECHO + #.08 xETCHO + #.91 xACET + #.09 zRDNO3 + yRPNO3 + #1.01 SumRO2
O4OP	5.11e-11				G	OLE4 + O3P = #.5 KET2 + #.5 ALK2

Table A-2 (continued)

Label	Rate Parameters [a]				Notes [b]	Reaction and Products [a]
	k298	A	Ea	B		
TPOH	1.10e-10				G	TERP + OH = TERP_OH + #.01 xOH + #.01 HO2 + #.6 xHO2 + #.02 xR2CO3 + #.01 xMACO3 + #1.1 RO2C + #.29 RO2XC + #.16 xHCHO + #.29 xRCHO + #.13 xOLEA2 + #.09 xACET + #.05 xKET2 + #.01 xMVK + #.04 xLVKS + #.05 xOLEP + #.01 xAFG2A + #.01 zR2NO3 + #.2 zRHNO3 + #.07 zRCNO3 + #.01 xHPCRB + #.51 yROOH + #.55 yRUOOH + #.27 yHPCRB + #1.39 SumRO2
608	2.70e+0				53	TERP_OH = #.05 xOH + #.03 xPACID + #.02 xAFG2A + #.06 xHPCRB
609	9.13e-12	2.55e-12	-0.755	-	53	TERP_OH + NO = NO + #.02 xHO2 + #.01 xR2CO3 + #.13 RO2C + #.04 RO2XC + #.01 xHCHO + #.03 xRCHO + #.03 xOLEA1 + #.01 xOLEA2 + #.01 zR2NO3 + #.01 zRHNO3 + #.03 zRCNO3 + #.01 yROOH + #.01 yRUOOH + #.2 yHPCRB + #.17 SumRO2
TPO3	1.17e-16				G	TERP + O3 = TERP_O3 + #.57 OH + #.02 xOH + #.13 HO2 + #.09 xHO2 + #.08 xMECO3 + #.07 xR2CO3 + #.08 HCHO2 + #.25 RCHO2 + #.36 RO2C + #.11 RO2XC + #.18 HCHO + #.06 xHCHO + #.12 xRCHO + #.03 xGLY + #.01 xMACR + #.01 ACET + #.01 xACET + #.17 KET2 + #.01 LVKS + #.02 OLEP + #.01 xPACID + #.01 xAFG3 + #.11 zRCNO3 + #.01 xHPCRB + #.03 H2 + #.12 CO + #.06 CO2 + #.01 yROOH + #.39 yHPCRB + #.47 SumRO2
611	1.22e+0				53	TERP_O3 = #.01 OH + #.03 xOH + #.08 xHO2 + #.01 xPACID + #.04 xHPCRB
612	9.13e-12	2.55e-12	-0.755	-	53	TERP_O3 + NO = NO + #.04 xMECO3 + #.01 xR2CO3 + #.04 xMACO3 + #.06 RO2C + #.03 RO2XC + #.04 xHCHO + #.01 xRCHO + #.04 xOLEA2 + #.03 zRCNO3 + #.01 CO + #.08 yHPCRB + #.09 SumRO2
TPN3	1.10e-11				G	TERP + NO3 = TERP_N3 + #.51 xNO2 + #.02 xOH + #.07 xHO2 + #.03 xR2CO3 + #1.17 RO2C + #.29 RO2XC + #.02 xHCHO + #.29 xRCHO + #.21 xOLEA2 + #.15 xACET + #.01 xMVK + #.01 xOLEP + #.13 xRCNO3 + #.09 zRCNO3 + #.19 zRDNO3 + yRPNO3 + #.05 yROOH + #.01 yRUOOH + #.01 yHPCRB + #1.46 SumRO2
614	2.47e+0				53	TERP_N3 = #.01 xNO2 + #.07 xOH + #.02 xPACID + #.03 xRCNO3 + #.02 xHPCRB
615	9.13e-12	2.55e-12	-0.755	-	53	TERP_N3 + NO = NO + #.04 xHO2 + #.12 RO2C + #.04 RO2XC + #.01 xACET + #.04 zRCNO3 + #.01 zRDNO3 + #.01 yRPNO3 + #.16 SumRO2
TPOP	4.24e-11				G	TERP + O3P = #.16 RCHO + #.04 OLEA2 + #.18 KET2 + #.01 LVKS + #.27 OLEP + #.18 ALK3 + #.08 ALK4 + #.08 ALK5
SQOH	2.00e-10				G	SESQ + OH = SESQ_OH + #.05 xOH + #.03 HO2 + #.57 xHO2 + #.83 RO2C + #.25 RO2XC + #.04 xHCHO + #.45 xOLEA2 + #.01 xACET + #.07 xOLEP + #.18 zRHNO3 + #.03 zRCNO3 + #.02 xHPCRB + #.01 yROOH + #.97 yRUOOH + #.09 yHPCRB + #1.08 SumRO2
618	3.19e+0				53	SESQ_OH = #.03 xOH + #.08 xHO2 + #.02 xLVKS + #.01 xOLEP + #.03 zRPNO3 + #.06 xHPCRB + #.01 yROOH
619	9.13e-12	2.55e-12	-0.755	-	53	SESQ_OH + NO = NO + #.25 RO2C + #.09 RO2XC + #.08 xHCHO + #.07 xOLEA2 + #.09 xACET + #.12 zRHNO3 + #.01 zRCNO3 + #.11 yRUOOH + #.23 yHPCRB + #.34 SumRO2
SQO3	3.14e-16				G	SESQ + O3 = SESQ_O3 + #.66 OH + #.02 xOH + #.01 HO2 + #.07 xHO2 + #.15 xMACO3 + #.33 RCHO2 + #.25 RO2C + #.1 RO2XC + #.01 HCHO + #.15 xHCHO + #.01 OLEP + #.07 zRCNO3 + #.01 xHPCRB + #.22 yHPCRB + #.35 SumRO2

Table A-2 (continued)

Label	Rate Parameters [a]				Notes [b]	Reaction and Products [a]
	k298	A	Ea	B		
621	4.27e+0				53	SESQ_O3 = #.03 xOH + #.29 xHO2 + #.05 OTHN + #.03 zRNNO3
622	9.13e-12	2.55e-12	-0.755	-	53	SESQ_O3 + NO = NO + #.17 xMECO3 + #.35 RO2C + #.14 RO2XC + #.02 xHCHO + #.02 xRCHO + #.22 xOLEA2 + #.02 xACET + #.16 zRCNO3 + #.51 yHPCRB + #.49 SumRO2
SQN3	1.90e-11				G	SESQ + NO3 = #.74 xNO2 + #.03 xOH + #.01 xHO2 + #.84 RO2C + #.23 RO2XC + #.74 xOLEA2 + #.03 xRCNO3 + #.01 zRCNO3 + #.21 zRDNO3 + #.01 RNNO3 + yRPNO3 + #1.07 SumRO2
SQOP	6.85e-11				G	SESQ + O3P = #.13 OLEA2 + #.87 OLEP
BXOH	1.21e-12				G	BENX + OH = #.69 HO2 + #.28 xHO2 + #.28 RO2C + #.04 RO2XC + #.28 xGLY + #.12 OLEA2 + #.57 PHEN + #.28 xBUDAL + #.04 zRANO3 + #.31 yRAOOH + #.32 SumRO2
B1OH	7.69e-12				G	ARO1 + OH = #.26 HO2 + #.48 xHO2 + #.05 xETO2 + #.75 RO2C + #.21 RO2XC + #.01 xHCHO + #.06 xMECHO + #.11 xETCHO + #.01 xRCHO + #.13 xGLY + #.13 xMGLY + #.01 OLEA1 + #.13 OLEA2 + #.12 XYNL + #.2 xBALD + #.13 xBUDAL + #.01 xAFG1 + #.11 xAFG2A + #.03 zR1NO3 + #.11 zR2NO3 + #.01 zRHNO3 + #.06 zRANO3 + #.04 ARO1 + #3.11 NROG + #.64 yROOH + #.32 yRAOOH + #.96 SumRO2
B2OH	2.20e-11				G	ARO2 + OH = #.28 HO2 + #.56 xHO2 + #.61 RO2C + #.15 RO2XC + #.01 xHCHO + #.07 xGLY + #.39 xMGLY + #.02 OLEA1 + #.13 OLEA2 + #.01 xKET2 + #.01 LVKS + #.03 xBACL + #.01 xOACID + #.08 XYNL + #.04 BALD + #.03 xBALD + #.03 xBUDAL + #.07 xAFG1 + #.29 xAFG2A + #.04 xAFG2B + #.05 xAFG3 + #.02 zR2NO3 + #.01 zRCNO3 + #.11 zRANO3 + #.03 xBENX + #1.67 NROG + #.11 yROOH + #.59 yRAOOH + #.04 yHPCRB + #.76 SumRO2
FUOH	3.84e-11				G	FURNS + OH = #.75 HO2 + #.24 xHO2 + #.24 RO2C + #.01 RO2XC + #.07 xRCHO + #.03 xOLEA1 + #.14 xOLEP + #.75 BUDAL + #.01 zRHNO3 + #.08 CO + #.15 yRUOOH + #.01 yHPCRB + #.25 SumRO2
FUO3	2.40e-18				G	FURNS + O3 = #.44 HO2 + #.33 xHO2 + #.4 RCHO2 + #.33 RO2C + #.01 RO2XC + #.14 OLEA1 + #.01 zRCNO3 + #.07 HPCRB + #.74 CO + #.19 CO2 + #.33 ALK1 + #.2 yHPCRB + #.34 SumRO2
FUN3	1.20e-12				G	FURNS + NO3 = #.08 xNO2 + #.87 xHO2 + #.95 RO2C + #.05 RO2XC + #.07 xOLEA1 + #.01 xOLEP + #.87 xRCNO3 + #.05 zRDNO3 + #.28 CO + #.63 yRPNO3 + SumRO2
STOH	5.80e-11				G	STYRS + OH = #.06 HO2 + #.79 xHO2 + #.79 RO2C + #.15 RO2XC + #.74 xHCHO + #.02 xGLY + #.02 xMGLY + #.03 OLEA2 + #.02 XYNL + #.74 xBALD + #.02 xBUDAL + #.02 xAFG2A + #.14 zRHNO3 + #.01 zRANO3 + #.88 yROOH + #.06 yRAOOH + #.94 SumRO2
STO3	1.60e-17				G	STYRS + O3 = #.03 xBZO + #.08 OH + #.17 HO2 + #.21 HCHO2 + #.34 RCHO2 + #.03 RO2C + #.5 HCHO + #.05 PHEN + #.5 BALD + #.09 H2 + #.22 CO + #.23 CO2 + #.09 BENZ + #.03 yROOH + #.03 SumRO2
AMOH	4.35e-11				G	AMINS + OH = #.02 HO2 + #.96 xHO2 + #.01 xMEO2 + #.97 RO2C + #.02 RO2XC + #.08 xHCHO + #.02 RCHO + #.02 zR2NO3 + #.97 xAMINS + #.99 yROOH + #.99 SumRO2
AMO3	3.09e-18				G	AMINS + O3 = #.61 AMINS + #29.54 NROG
TAOH	1.01e-11				G	TAMNS + OH = #.03 xMEO2 + #.06 RO2C + #.03 xHCHO + #.03 xAMINS + #.97 PNAMIN + #.06 yROOH + #.06 SumRO2

Table A-2 (continued)

Label	Rate Parameters [a]				Notes [b]	Reaction and Products [a]
	k298	A	Ea	B		
A4OH	3.12e-11				G	RCHO + OH = #.02 xOH + #.05 HO2 + #.05 xHO2 + #.01 xMECO3 + #.81 R2CO3 + #.16 RO2C + #.04 RO2XC + #.03 xHCHO + #.04 RCHO + #.04 xRCHO + #.02 MGLY + #.03 xACET + #.01 xBACL + #.02 xPACID + #.04 zRCNO3 + #.03 CO + #.01 ALK4 + #.07 NROG + #.15 yHPCRB + #.2 SumRO2 + #.81 SumRCO3
A4N3	2.09e-14				G	RCHO + NO3 = HNO3 + #.04 HO2 + #.95 R2CO3 + #.02 RO2C + #.01 RO2XC + #.02 RCHO + #.02 MGLY + #.01 zRCNO3 + #.02 yHPCRB + #.03 SumRO2 + #.95 SumRCO3
A4HV		Phot Set= C2CHOabs			G,63	RCHO + HV = RCHO_HV + #1.21 HO2 + #.6 xHO2 + #.04 xMECO3 + #.76 RO2C + #.14 RO2XC + #.09 xHCHO + #.09 MECHO + #.02 xMECHO + #.03 xETCHO + #.12 GLCHO + #.42 xRCHO + #.06 xACET + #.03 xKET2 + #.01 xPACID + #.01 zRHNO3 + #.12 zRCNO3 + CO + #.01 ALK4 + #.04 NROG + #.31 yROOH + #.51 yHPCRB + #.9 SumRO2
639	2.25e+0				53	RCHO_HV = #.01 xOH + #.06 xPACID + #.01 CO2
640	9.13e-12	2.55e-12	-0.755	-	53	RCHO_HV + NO = NO + #.01 xHO2 + #.01 RO2C + #.04 xHCHO + #.01 xRCHO + #.05 CO + #.06 yHPCRB + #.01 SumRO2
A5OH	5.06e-11				G	OLEA1 + OH = OLEA1_OH + #.17 HO2 + #.27 xHO2 + #.03 MACO3 + #.6 RO2C + #.05 RO2XC + #.2 xGLCHO + #.06 RCHO + #.05 xGLY + #.19 xKET2 + #.02 xPACID + #.05 AFG1 + #.01 AFG2A + #.04 AFG2B + #.01 HPCRB + #.06 CO2 + #.05 yHPCRB + #.65 SumRO2 + #.03 SumRCO3
642	9.69e-1				53	OLEA1_OH = #.33 xOH + #.15 HO2 + #.01 xHCHO + #.19 xKET2 + #.19 xPACID + #.02 AFG2A + #.04 AFG2B + #.05 zRCNO3 + #.09 HPCRB + #.27 CO2
643	9.13e-12	2.55e-12	-0.755	-	53	OLEA1_OH + NO = NO + #.43 xHO2 + #.14 RO2C + #.01 RO2XC + #.09 xHCOOH + #.25 xGLCHO + #.08 xGLY + #.48 xMGLY + #.06 zRHNO3 + #.1 CO + #.59 yHPCRB + #.15 SumRO2
A5O3	3.50e-18				G	OLEA1 + O3 = #.62 OH + #.71 HO2 + #.16 RCHO2 + #.04 HCHO + #.1 MEOH + #.02 HCOOH + #.01 MECHO + #.06 GLCHO + #.42 GLY + #.81 MGLY + #.02 KET2 + #.01 OACID + #.06 CO + #.33 CO2 + #.05 ALK4
A5N3	9.62e-14				G	OLEA1 + NO3 = #.56 xNO2 + #.04 HNO3 + #.22 HO2 + #.16 xHO2 + #.71 RO2C + #.06 RO2XC + #.01 xHCHO + #.52 xGLCHO + #.03 xGLY + #.03 xKET2 + #.52 xPACID + #.02 AFG1 + #.01 AFG2B + #.15 xRHNO3 + #.19 RCNO3 + #.01 xRCNO3 + #.05 zRCNO3 + #.02 zRDNO3 + #.15 CO + #.17 yRPNO3 + #.77 SumRO2
A5HV		Phot Set= MACR-06			G,63	OLEA1 + HV = #.43 OH + #.86 HO2 + #.01 xHO2 + #.1 MEO2 + #.03 MACO3 + #.01 RO2C + #.01 xHCHO + #.01 HCOOH + #.09 GLCHO + #.06 MGLY + #.03 KET2 + #.25 OLEP + #.01 xPACID + #.03 AFG2A + #.08 AFG2B + #.99 CO + #.03 CO2 + #.02 ALK4 + #.01 ALK5 + #.11 SumRO2 + #.03 SumRCO3

Table A-2 (continued)

Label.	Rate Parameters [a]				Notes [b]	Reaction and Products [a]
	k298	A	Ea	B		
A6OH	9.04e-11				G	OLEA2 + OH = OLEA2_OH + #.08 OH + #.16 xOH + #.11 HO2 + #.24 xHO2 + #.01 xMECO3 + #.03 xR2CO3 + #.12 MACO3 + #.03 xMACO3 + #.51 RO2C + #.1 RO2XC + #.01 xHCHO + #.03 xGLCHO + #.23 xRCHO + #.03 xGLY + #.01 xMGLY + #.04 OLEA1 + #.05 OLEA2 + #.01 xOLEA2 + #.02 LVKS + #.1 xPACID + #.01 xAFG3 + #.05 zRHNO3 + #.05 zRCNO3 + #.08 HPCRB + #.01 xHPCRB + #.18 CO + #.09 CO2 + #.07 MALAH + #.3 yHPCRB + #.61 SumRO2 + #.12 SumRCO3
648	3.25e+0				53	OLEA2_OH = #.01 OH + #.07 xOH + #.02 HO2 + #.03 xMACO3 + #.13 xPACID + #.04 HPCRB + #.04 xHPCRB + #.02 MALAH
649	9.13e-12	2.55e-12	-0.755	-	53	OLEA2_OH + NO = NO + #.08 xHO2 + #.04 xMECO3 + #.15 RO2C + #.01 RO2XC + #.04 xRCHO + #.06 xMGLY + #.01 zRCNO3 + #.01 CO + #.06 CO2 + #.15 yHPCRB + #.16 SumRO2
A6O3	2.99e-17				G	OLEA2 + O3 = OLEA2_O3 + #.44 OH + #.16 HO2 + #.17 xHO2 + #.03 xMECO3 + #.03 HCHO2 + #.34 RCHO2 + #.24 RO2C + #.01 RO2XC + #.02 HCHO + #.03 xHCHO + #.01 HCOOH + #.21 RCHO + #.32 GLY + #.01 xGLY + #.36 MGLY + #.05 BA CL + #.01 xPACID + #.01 zRCNO3 + #.01 H2 + #.38 CO + #.15 CO2 + #.03 yHPCRB + #.25 SumRO2
651	1.44e+0				53	OLEA2_O3 = #.01 OH + #.08 xOH + #.01 HO2 + #.01 RCHO + #.06 xBA CL + #.13 xPACID + #.03 xHPCRB + #.06 CO2
652	9.13e-12	2.55e-12	-0.755	-	53	OLEA2_O3 + NO = NO + #.05 xHO2 + #.03 xR2CO3 + #.04 RO2C + #.02 RO2XC + #.03 xHCHO + #.06 xGLY + #.12 xMGLY + #.02 zRCNO3 + #.12 CO + #.22 yHPCRB + #.06 SumRO2
A6N3	3.30e-12				G	OLEA2 + NO3 = OLEA2_N3 + #.32 xNO2 + #.49 HNO3 + #.2 xOH + #.06 xHO2 + #.01 xMECO3 + #.03 xR2CO3 + #.1 MACO3 + #.06 xMACO3 + #.67 RO2C + #.16 RO2XC + #.02 xHCHO + #.26 xRCHO + #.01 xMGLY + #.19 xPACID + #.01 xAFG3 + #.07 xRCNO3 + #.1 zRCNO3 + #.06 zRDNO3 + #.09 CO + #.1 CO2 + #.05 MALAH + #.29 yRPNO3 + #.83 SumRO2 + #.1 SumRCO3
654	3.07e+0				53	OLEA2_N3 = #.05 xOH + #.07 xMACO3 + #.21 xPACID + #.01 xAFG3 + #.04 xRCNO3 + #.04 xHPCRB + #.05 MALAH
655	9.13e-12	2.55e-12	-0.755	-	53	OLEA2_N3 + NO = NO + #.07 xHO2 + #.03 xMECO3 + #.21 RO2C + #.01 RO2XC + #.04 xRCHO + #.04 xMGLY + #.02 xACET + #.01 xRHNO3 + #.01 zRDNO3 + #.02 CO + #.14 CO2 + #.1 yRPNO3 + #.22 SumRO2
A6HV		Phot Set= C2CHOabs			G,63	OLEA2 + HV = OLEA2_HV + #.28 OH + HO2 + #.45 xHO2 + #.05 xMECO3 + #.64 RO2C + #.15 RO2XC + #.04 xHCHO + #.04 xRCHO + #.06 OLEA2 + #.07 xOLEA2 + #.01 xACET + #.04 xLVKS + #.26 OLEP + #.26 xAFG2A + #.02 xAFG2B + #.01 xAFG3 + #.08 zRHNO3 + #.06 zRCNO3 + #.03 xHPCRB + #.1.21 CO + #.26 yRUOOH + #.46 yHPCRB + #.79 SumRO2
657	1.71e+0				53	OLEA2_HV = #.02 OH + #.04 xOH + #.01 OLEP + #.06 xHPCRB
658	9.13e-12	2.55e-12	-0.755	-	53	OLEA2_HV + NO = NO + #.02 xHO2 + #.01 xMECO3 + #.08 RO2C + #.02 RO2XC + #.01 xHCHO + #.07 xOLEA2 + #.02 zRHNO3 + #.01 zRCNO3 + #.02 CO + #.12 yHPCRB + #.1 SumRO2

Table A-2 (continued)

Label.	Rate Parameters [a]				Notes [b]	Reaction and Products [a]
	k298	A	Ea	B		
K5OH	9.96e-12				G	KET2 + OH = #.01 xOH + #.53 HO2 + #.18 xHO2 + #.01 MECO3 + #.05 xMECO3 + #.01 R2CO3 + #.13 xR2CO3 + #.49 RO2C + #.08 RO2XC + #.02 HCHO + #.16 xHCHO + #.1 xMECHO + #.01 xETCHO + #.14 RCHO + #.19 xRCHO + #.31 MGLY + #.01 xACET + #.08 KET2 + #.03 xKET2 + #.08 zRCNO3 + #.54 yHPCRB + #.57 SumRO2 + #.02 SumRCO3
K5HV	Phot Set= MEK-06, qy= 7.53e-2				G,60	KET2 + HV = #.46 HO2 + #.2 xHO2 + #.08 MEO2 + #.14 ETO2 + #.48 MECO3 + #.42 R2CO3 + #.21 RO2C + #.01 RO2XC + #.31 HCHO + #.02 xHCHO + #.01 xMECHO + #.03 xETCHO + #.16 xRCHO + #.01 zRHNO3 + #.1 CO + #.09 ALK4 + #.01 ALK5 + #.22 yROOH + #.44 SumRO2 + #.9 SumRCO3
K6OH	6.81e-11				G	LVKS + OH = LVKS_OH + #.03 HO2 + #.13 xHO2 + #.1 MECO3 + #.15 xMECO3 + #.22 xR2CO3 + #.49 RO2C + #.06 RO2XC + #.04 xHCHO + #.06 xRCHO + #.01 MGLY + #.02 xMGLY + #.1 OLEA1 + #.02 xACET + #.22 xKET2 + #.04 xBACL + #.01 xPACID + #.01 xAFG2B + #.06 zRCNO3 + #.02 HPCRB + #.07 xHPCRB + #.01 CO + #.51 yHPCRB + #.55 SumRO2 + #.1 SumRCO3
662	6.74e+0				53	LVKS_OH = #.31 HO2 + #.31 HPCRB + #.08 xHPCRB + #.07 CO
663	9.13e-12	2.55e-12	-0.755	-	53	LVKS_OH + NO = NO + #.27 xHO2 + #.28 RO2C + #.04 RO2XC + #.08 xRCHO + #.27 xMGLY + #.27 xACET + #.04 zRCNO3 + #.3 yHPCRB + #.32 SumRO2
K6O3	1.94e-17				G	LVKS + O3 = LVKS_O3 + #.58 OH + #.1 HO2 + #.02 xHO2 + #.42 xMECO3 + #.01 xR2CO3 + #.11 HCHO2 + #.12 RCHO2 + #.5 RO2C + #.02 RO2XC + #.03 HCHO + #.37 xHCHO + #.01 MECHO + #.03 RCHO + #.01 xGLY + #.64 MGLY + #.04 ACET + #.05 KET2 + #.27 BACL + #.01 OACID + #.01 xPACID + #.02 zRCNO3 + #.05 H2 + #.26 CO + #.12 CO2 + #.34 yHPCRB + #.53 SumRO2
665	5.62e+0				53	LVKS_O3 = #.05 xMECO3 + #.01 RO2C + #.12 xPACID + #.01 CO2
666	9.13e-12	2.55e-12	-0.755	-	53	LVKS_O3 + NO = NO + #.05 xHO2 + #.01 RO2XC + #.03 xHCHO + #.01 zRCNO3 + #.02 CO + #.1 yHPCRB
K6HV	Phot Set= MVK-16				G,63	LVKS + HV = #.05 xOH + #.12 HO2 + #.28 MEO2 + #.05 xMECO3 + #.28 MACO3 + #.1 RO2C + #.02 RO2XC + #.12 HCHO + #.05 xMGLY + #.35 OLEP + #.05 xPACID + #.02 zRCNO3 + #.6 CO + #.25 OLE4 + #.05 MALAH + #.4 SumRO2 + #.28 SumRCO3
O5OH	7.93e-11				G	OLEP + OH = #.12 HO2 + #.28 xHO2 + #.36 R2CO3 + #.16 xR2CO3 + #.45 RO2C + #.08 RO2XC + #.27 xRCHO + #.01 MGLY + #.01 xMGLY + #.01 LVKS + #.04 BACL + #.04 OLEP + #.01 AFG3 + #.08 zRCNO3 + #.5 yHPCRB + #.53 SumRO2 + #.36 SumRCO3
O5O3	7.86e-17				G	OLEP + O3 = #.3 OH + #.26 HO2 + #.01 xHO2 + #.09 xR2CO3 + #.51 RCHO2 + #.1 RO2C + #.02 RO2XC + #.04 xHCHO + #.02 RCHO + #.02 xRCHO + #.02 xGLY + #.25 MGLY + #.03 KET2 + #.12 BACL + #.01 xPACID + #.02 zRCNO3 + #.02 HPCRB + #.14 CO + #.14 CO2 + #.1 yHPCRB + #.12 SumRO2
O5N3	3.52e-12				G	OLEP + NO3 = #.27 xNO2 + #.12 HNO3 + #.11 HO2 + #.15 xHO2 + #.32 xR2CO3 + #.01 MACO3 + #.79 RO2C + #.14 RO2XC + #.36 xRCHO + #.05 xGLY + #.09 xMGLY + #.03 xACET + #.04 xKET2 + #.07 OLEP + #.03 AFG3 + #.15 xRCNO3 + #.14 zRCNO3 + #.93 SumRO2 + #.01 SumRCO3

Table A-2 (continued)

Label	Rate Parameters [a]				Notes [b]	Reaction and Products [a]
	k298	A	Ea	B		
OA OH	7.47e-13				G	OACID + OH = #.3 xHO2 + #.7 MEO2 + #.3 RO2C + #.02 xHCHO + #.28 xMGLY + #.72 CO2 + #.26 yHPCRB + SumRO2
PA OH	3.00e-14				G	PACID + OH = #.19 xOH + #.56 xHO2 + #.26 MECO3 + #.74 RO2C + #.19 xHCHO + #.56 xPACID + #.19 CO2 + #.74 SumRO2 + #.26 SumRCO3
PA HV		Phot Set= PAA			G,64	PACID + HV = OH + MEO2 + CO2 + SumRO2
MG OH	1.19e-11				G	MGLY + OH = #.01 xHO2 + #.99 MECO3 + #.01 RO2C + #.01 xHCHO + #.01 xPACID + CO + #.01 SumRO2 + #.99 SumRCO3
MG N3	5.00e-16				G	MGLY + NO3 = HNO3 + MECO3 + CO + SumRCO3
MG HV		Phot Set= MGLY-13			G,65	MGLY + HV = HO2 + MECO3 + CO + SumRCO3
BA HV		Phot Set= BACL-11			G,66	BACL + HV = #2 MECO3 + #2 SumRCO3
CR OH	4.65e-11				G	CRES + OH = #.84 HO2 + #.11 xHO2 + #.03 BZO + #.11 RO2C + #.02 RO2XC + #.02 xGLY + #.05 xMGLY + #.02 OLEA1 + #.08 OLEA2 + #.17 LVKS + #.03 xBACL + #.14 OLEP + #.42 CATL + #.01 xBALD + #.03 xBUDAL + #.01 xAFG1 + #.04 xAFG2A + #.02 xAFG2B + #.02 zRANO3 + #.01 yROOH + #.11 yRAOOH + #.13 SumRO2
CR N3	1.27e-11				G	CRES + NO3 = HNO3 + BZO
XL OH	6.73e-11				G	XYNL + OH = #.79 HO2 + #.16 xHO2 + #.02 BZO + #.16 RO2C + #.03 RO2XC + #.01 xGLY + #.04 xMGLY + #.02 OLEA1 + #.06 OLEA2 + #.26 LVKS + #.1 xBACL + #.16 OLEP + #.01 XYNL + #.27 CATL + #.01 xBUDAL + #.01 xAFG1 + #.09 xAFG2A + #.03 xAFG2B + #.01 xAFG3 + #.03 zRANO3 + #.02 yROOH + #.18 yRAOOH + #.19 SumRO2
XL N3	3.09e-11				G	XYNL + NO3 = HNO3 + BZO
CA OH	1.56e-10				G	CATL + OH = #.96 HO2 + #.03 xHO2 + #.01 BZO + #.03 RO2C + #.01 OLEA1 + #.02 OLEA2 + #.72 LVKS + #.02 xBACL + #.06 OLEP + #.13 CATL3 + #.02 xAFG2A + #.03 yRAOOH + #.03 SumRO2
CAN3	4.04e-11				G	CATL + NO3 = HNO3 + BZO
N4 OH	1.78e-11				G	RCNO3 + OH = RCNO3_OH + #.09 xNO2 + #.27 NO2 + #.01 OH + #.01 xOH + #.03 HO2 + #.09 xHO2 + #.04 xMECO3 + #.32 R2CO3 + #.04 xR2CO3 + #.38 RO2C + #.06 RO2XC + #.06 xHCHO + #.04 xMECHO + #.02 RCHO + #.04 xRCHO + #.01 xGLY + #.02 MGLY + #.04 xACET + #.07 KET2 + #.07 BACL + #.02 xBACL + #.01 OLEP + #.03 PACID + #.03 xPACID + #.04 RCNO3 + #.15 xRCNO3 + #.06 zRCNO3 + #.01 CO + #.01 CO2 + #.05 ALK2 + #3.73 NROG + #.02 yRPNO3 + #.02 yHPCRB + #.44 SumRO2 + #.32 SumRCO3
685	2.06e+0				53	RCNO3_OH = #.01 xOH + #.04 HO2 + #.04 RCNO3
686	9.13e-12	2.55e-12	-0.755	-	53	RCNO3_OH + NO = NO + #.02 xR2CO3 + #.06 RO2C + #.02 RO2XC + #.02 xHCHO + #.03 xRCNO3 + #.02 zRCNO3 + #.02 yHPCRB + #.08 SumRO2

Table A-2 (continued)

Label.	Rate Parameters [a]				Notes [b]	Reaction and Products [a]
	k298	A	Ea	B		
N4HV	Phot Set= CRBNIT				G,67	RCNO3 + HV = RCNO3_HV + #.62 NO2 + #.01 xOH + #.46 HO2 + #.31 xHO2 + #.06 ETO2 + #.15 MECO3 + #.06 R2CO3 + #.03 xR2CO3 + #.51 RO2C + #.1 RO2XC + #.04 HCHO + #.01 xHCHO + #.04 MECHO + #.17 RCHO + #.03 xRCHO + #.05 xACET + #.03 xKET2 + #.03 OACID + #.02 xOACID + #.02 xPACID + #.02 AFG2A + #.03 RCNO3 + #.19 xRCNO3 + #.1 zRCNO3 + #.46 CO + #.01 CO2 + #.6.89 NROG + #.04 yRPNO3 + #.15 yHPCRB + #.67 SumRO2 + #.21 SumRCO3
688	4.46e-1				53	RCNO3_HV = #.15 HO2 + #.01 xACET + #.05 PACID + #.02 xPACID + #.01 AFG2A + #.05 xRCNO3 + #.08 HPCRB
689	9.13e-12	2.55e-12	-0.755	-	53	RCNO3_HV + NO = NO + #.03 xOH + #.04 xMECO3 + #.03 xR2CO3 + #.16 RO2C + #.03 RO2XC + #.01 xHCHO + #.12 xRCHO + #.02 xKET2 + #.04 xRHNO3 + #.02 zRCNO3 + #.03 CO + #.05 CO2 + #.11 yHPCRB + #.19 SumRO2
N3OH	3.66e-11				G	RHNO3 + OH = #.01 xNO2 + #.6 NO2 + #.08 HO2 + #.26 xHO2 + #.29 RO2C + #.05 RO2XC + #.05 xHCHO + #.03 xGLCHO + #.01 xACET + #.01 KET2 + #.06 xKET2 + #.01 LVKS + #.05 xRHNO3 + #.08 RCNO3 + #.21 xRCNO3 + #.04 zRDNO3 + #.02 ALK4 + #.57 ALK5 + #.32 yRPNO3 + #.34 SumRO2
N3HV	Phot Set= IC3ONO2				G,63	RHNO3 + HV = #.01 xNO2 + NO2 + #.93 HO2 + #.05 xHO2 + #.11 RO2C + #.02 RO2XC + #.73 HCHO + #.01 xHCHO + #.02 MECHO + #.04 RCHO + #.02 xRCHO + #.32 MACR + #.06 OLEA1 + #.02 OLEA2 + #.01 xOLEA2 + #.04 ACET + #.37 MVK + #.01 xMVK + #.02 zRHNO3 + #.01 HPCRB + #.01 xHPCRB + #.07 FURNS + #.07 yRUOOH + #.05 yHPCRB + #.13 SumRO2
N5OH	4.49e-11				G	RANO3 + OH = #.42 NO2 + #.58 HO2 + #.01 OLEP + #.02 AFG2A + #.11 RHNO3 + #.47 RCNO3 + #.01 ALK5 + #.37 ALK6
N5HV	Phot Set= COOH				G,68	RANO3 + HV = #.34 RHNO3 + #.66 RCNO3
N6OH	4.11e-11				G	RPNO3 + OH = #.18 xNO2 + #.35 NO2 + #.19 OH + #.03 xOH + #.15 HO2 + #.03 xHO2 + #.35 RO2C + #.08 RO2XC + #.09 xHCHO + #.09 xRCHO + #.05 xOLEA1 + #.03 xACET + #.02 xMVK + #.16 RHNO3 + #.02 RCNO3 + #.03 xRCNO3 + #.02 zRCNO3 + #.15 RPNO3 + #.02 xRPNO3 + #.06 zRDNO3 + #.35 ROOH + #.01 HPCRB + #.02 xHPCRB + #.33 yRPNO3 + #.43 SumRO2
N6HV	Phot Set= COOH				G,68	RPNO3 + HV = RPNO3_HV + #.9 NO2 + OH + #.01 HO2 + #.01 xHO2 + #.01 xR2CO3 + #.06 RO2C + #.02 RO2XC + #.63 HCHO + #.2 RCHO + #.54 OLEA1 + #.01 xACET + #.16 MVK + #.01 RCNO3 + #.01 xRCNO3 + #.02 zRCNO3 + #.08 SumRO2
696	8.74e-1				53	RPNO3_HV = #.04 NO2 + #.02 HO2 + #.01 xPACID + #.01 RPNO3 + #.04 HPCRB
697	9.13e-12	2.55e-12	-0.755	-	53	RPNO3_HV + NO = NO + #.05 xHO2 + #.05 RO2C + #.04 xHCHO + #.02 xRHNO3 + #.03 xRCNO3 + #.06 yRPNO3 + #.05 SumRO2
NDOH	1.27e-11				G	RDNO3 + OH = #.23 xNO2 + #.49 NO2 + #.05 xHO2 + #.77 RO2C + #.23 RO2XC + #.08 xHCHO + #.15 xACET + #.47 RHNO3 + #.02 RCNO3 + #.24 xRCNO3 + #.08 zRCNO3 + #.15 zRDNO3 + #.04 xRDNO3 + #.01 CO + SumRO2

Table A-2 (continued)

Label.	Rate Parameters [a]				Notes [b]	Reaction and Products [a]
	k298	A	Ea	B		
NDHV	Phot Set= DIONO2				G,69	RDNO3 + HV = RDNO3_HV + #1.83 NO2 + #.03 HO2 + #.02 xHO2 + #.01 xR2CO3 + #.17 RO2C + #.05 RO2XC + #.23 HCHO + #.01 xHCHO + #.4 RCHO + #.2 OLEA1 + #.03 xACET + #.23 MVK + #.01 xPACID + #.03 RCNO3 + #.03 xRCNO3 + #.05 zRCNO3 + #.22 SumRO2
700	8.74e-1				53	RDNO3_HV = #.04 NO2 + #.01 xOH + #.01 HO2 + #.01 xPACID + #.01 RPNO3 + #.04 HPCRB + #.01 CO2
701	9.13e-12	2.55e-12	-0.755	-	53	RDNO3_HV + NO = NO + #.05 xHO2 + #.05 RO2C + #.04 xHCHO + #.02 xRHNO3 + #.03 xRCNO3 + #.05 yRPNO3 + #.05 SumRO2
N1OH	1.47e-12				G	R1NO3 + OH = #.41 xNO2 + #.17 NO2 + #.29 xHO2 + #.99 RO2C + #.12 RO2XC + #.1 xHCHO + #.29 xMECHO + #.05 xETCHO + #.02 xRCHO + #.05 ACET + #.26 xACET + #.05 MEK + #.04 xMEK + #.07 KET2 + #.05 xKET2 + #.1 xRHNO3 + #.19 xRCNO3 + #.01 xRPNO3 + #.12 zRDNO3 + #1.12 yRPNO3 + #1.11 SumRO2
N1HV	Phot Set= IC3ONO2				G,63	R1NO3 + HV = #.04 TBUO + #-0.01 xNO2 + NO2 + #.19 HO2 + #.38 xHO2 + #.32 ETO2 + #.01 xTBUO + #.46 RO2C + #.05 RO2XC + #.05 xHCHO + #.12 MECHO + #.03 ETCHO + #.03 xETCHO + #.02 xRCHO + #.34 ACET + #.12 xACET + #.11 MEK + #.05 KET2 + #.22 xKET2 + #.05 zRHNO3 + #.01 xRHNO3 + #.51 yROOH + #.83 SumRO2
N2OH	1.16e-11				G	R2NO3 + OH = #.18 xNO2 + #.05 NO2 + #.43 xHO2 + #1.17 RO2C + #.33 RO2XC + #.01 xHCHO + #.07 xRCHO + #.01 xACET + #.05 KET2 + #.08 xKET2 + #.02 xOLEP + #.04 xRHNO3 + #.4 xRCNO3 + #.01 zRCNO3 + #.32 zRDNO3 + #.01 xHPCRB + #.02 CO + #1.44 yRPNO3 + #1.5 SumRO2
N2HV	Phot Set= IC3ONO2				G,63	R2NO3 + HV = R2NO3_HV + #-0.04 xNO2 + NO2 + #.1 HO2 + #.61 xHO2 + #.01 xMECO3 + #.01 xR2CO3 + #.82 RO2C + #.19 RO2XC + #.04 xRCHO + #.01 xACET + #.09 KET2 + #.44 xKET2 + #.02 xMVK + #.03 xPACID + #.13 zRHNO3 + #.04 xRHNO3 + #.06 zRCNO3 + #.02 CO + #.61 yROOH + #.36 yHPCRB + #1.01 SumRO2
706	1.28e+0				53	R2NO3_HV = #.02 HO2 + #.02 xHO2 + #.05 xPACID + #.06 xHPCRB
707	9.13e-12	2.55e-12	-0.755	-	53	R2NO3_HV + NO = NO + #.13 RO2C + #.03 RO2XC + #.1 xRCHO + #.01 xACET + #.01 zRHNO3 + #.03 zRCNO3 + #.16 yHPCRB + #.16 SumRO2
H4OH	8.27e-11				G	RAOOH + OH = #.76 OH + #.17 HO2 + #.06 xHO2 + #.06 RO2C + #.01 RO2XC + #.31 RCHO + #.02 xGLY + #.04 xMGLY + #.01 KET2 + #.04 OLEP + #.02 xBUDAL + #.02 AFG2A + #.03 xAFG2A + #.01 zRANO3 + #.17 HPCRB + #.01 ALK5 + #.37 ALK6 + #.07 yRAOOH + #.07 SumRO2
H4HV	Phot Set= COOH				G,63	RAOOH + HV = HPCRB
H3OH	5.87e-11				G	RUOOH + OH = #.64 OH + #.08 HO2 + #.25 xHO2 + #.25 RO2C + #.02 RO2XC + #.12 xHCHO + #.03 xGLCHO + #.03 xMACR + #.06 xKET2 + #.06 xMVK + #.02 LVKS + #.01 zRHNO3 + #.01 zRPNO3 + #.08 HPCRB + #.16 xHPCRB + #.02 ALK4 + #.6 ALK5 + #.01 xFURNS + #.17 yROOH + #.1 yRUOOH + #.27 SumRO2
H3HV	Phot Set= COOH				G,63	RUOOH + HV = OH + HO2 + #.86 HCHO + #.4 MACR + #.04 OLEA1 + #.47 MVK + #.09 FURNS

Table A-2 (continued)

Label	Rate Parameters [a]				Notes [b]	Reaction and Products [a]
	k298	A	Ea	B		
H5OH	5.38e-11				G	HPCRB + OH = #.58 OH + #.01 HO2 + #.38 xHO2 + #.38 RO2C + #.03 RO2XC + #.03 xHCHO + #.34 RCHO + #.05 xGLY + #.26 xMGLY + #.01 OLEA1 + #.21 OLEP + #.03 xPACID + #.02 AFG1 + #.03 zRPNO3 + #.01 HPCRB + #.35 xHPCRB + #.04 CO + #.39 yHPCRB + #.41 SumRO2
H5HV	Phot Set= HPALDS, qy= 1.00e-1				G,70	HPCRB + HV = HPCRB_HV + OH + #.54 HO2 + #.09 xHO2 + #.06 RO2C + #.11 HCHO + #.03 xHCHO + #.11 OLEA1 + #.03 xPACID + #.11 AFG2A + #.29 AFG2B + #.02 xAFG2B + #.07 SumRO2
714	2.11e+1				53	HPCRB_HV = #.36 HO2 + #.01 RO2XC + #.03 xHCHO + #.03 xPACID + #.11 AFG2A + #.25 AFG2B + #.01 xAFG2B + #.01 zRCNO3
715	9.13e-12	2.55e-12	-0.755	-	53	HPCRB_HV + NO = NO + #.07 xHO2 + #.4 RO2C + #.39 SumRO2
H2OH	1.24e-11				G	ROOH + OH = #.2 OH + #.06 xOH + #.22 HO2 + #.38 xHO2 + #.07 xETO2 + #.02 xTBUO + #.59 RO2C + #.05 RO2XC + #.01 HCHO + #.34 xHCHO + #.14 xMECHO + #.01 xETCHO + #.06 GLCHO + #.04 xGLCHO + #.01 RCHO + #.03 xRCHO + #.02 ACET + #.14 xACET + #.02 MEK + #.02 xMEK + #.09 KET2 + #.03 xKET2 + #.02 zR1NO3 + #.01 zRHNO3 + #.01 zRCNO3 + #.02 zRPNO3 + #.22 HPCRB + #.03 xHPCRB + #.61 yROOH + #.03 yHPCRB + #.64 SumRO2
H2HV	Phot Set= COOH				G,63	ROOH + HV = #.02 TBUO + OH + #.79 HO2 + #.06 xHO2 + #.11 ETO2 + #.09 RO2C + #.01 RO2XC + #.74 HCHO + #.23 MECHO + #.01 ETCHO + #.09 GLCHO + #.08 RCHO + #.16 ACET + #.03 xACET + #.04 MEK + #.05 KET2 + #.03 xKET2 + #.01 zRCNO3 + #.06 yROOH + #.03 yHPCRB + #.21 SumRO2
F2OH	3.39e-11				G	AFG1 + OH = AFG1_OH + #.24 OH + #.01 xOH + #.02 HO2 + #.2 xHO2 + #.18 RO2C + #.02 RO2XC + #.18 xGLY + #.02 xPACID + #.02 HPCRB + #.01 CO + #.24 MALAH + #.2 SumRO2
719	1.77e+1				53	AFG1_OH = #.19 OH + #.01 xOH + #.32 HO2 + #.19 xPACID + #.02 zRCNO3 + #.32 HPCRB + #.01 xHPCRB + #.18 MALAH
720	9.13e-12	2.55e-12	-0.755	-	53	AFG1_OH + NO = NO + #.39 xHO2 + #.52 RO2C + #.03 RO2XC + #.39 xGLY + #.56 xMGLY + #.2 CO + #.43 yHPCRB + #.55 SumRO2
F2HV	Phot Set= AFGS, qy= 2.20e-1				G,62	AFG1 + HV = AFG1_HV + #.26 OH + #.54 xOH + #.94 HO2 + #.03 xHO2 + #.06 MEO2 + #.03 RO2C + #.23 PACID + #.05 xPACID + #.01 AFG1 + #.02 AFG2A + #.02 xHPCRB + #.03 CO + #.09 SumRO2
722	1.80e+1				53	AFG1_HV = #.01 OH + #.17 xOH + #.33 xPACID + #.33 xHPCRB
723	9.13e-12	2.55e-12	-0.755	-	53	AFG1_HV + NO = NO + #.1 xHO2 + #.64 RO2C + #.08 RO2XC + #.08 zRCNO3 + #.05 CO + #.49 MALAH + #.72 SumRO2
F3OH	5.99e-11				G	AFG2A + OH = #.57 xHO2 + #.15 xMECO3 + #.01 xR2CO3 + #.2 MACO3 + #.73 RO2C + #.07 RO2XC + #.03 xRCHO + #.47 xGLY + #.54 xMGLY + #.23 xPACID + #.07 zRCNO3 + #.03 CO + #.47 yHPCRB + #.8 SumRO2 + #.2 SumRCO3
F3HV	Phot Set= AFGS, qy= 2.50e-1				G,62	AFG2A + HV = OH + #.91 MEO2 + #.09 ETO2 + MALAH + SumRO2
F4OH	4.58e-11				G	AFG2B + OH = AFG2B_OH + #.02 HO2 + #.4 xHO2 + #.17 MACO3 + #.4 RO2C + #.05 RO2XC + #.39 xGLY + #.39 xBACL + #.05 zRCNO3 + #.02 HPCRB + #.38 yHPCRB + #.45 SumRO2 + #.17 SumRCO3
727	1.46e+1				53	AFG2B_OH = #.36 HO2 + #.36 HPCRB

Table A-2 (continued)

Label	Rate Parameters [a]				Notes [b]	Reaction and Products [a]
	k298	A	Ea	B		
728	9.13e-12	2.55e-12	-0.755	-	53	AFG2B_OH + NO = NO + #.2 xHO2 + #.12 xMECO3 + #.32 RO2C + #.04 RO2XC + #.13 xRCHO + #.2 xGLY + #.2 xBACL + #.04 zRCNO3 + #.31 yHPCRB + #.36 SumRO2
F4HV	Phot Set= AFGS, qy= 2.20e-1				G,62	AFG2B + HV = #.86 OH + #.1 xOH + #.03 xHO2 + MEO2 + #.04 RO2C + #.08 xPACID + #.05 xHPCRB + #.03 CO + #.87 MALAH + #1.04 SumRO2
F5OH	7.20e-11				G	AFG3 + OH = #.27 xHO2 + #.62 xMECO3 + #.88 RO2C + #.11 RO2XC + #.62 xRCHO + #.54 xMGLY + #.11 zRCNO3 + #.85 yHPCRB + #.99 SumRO2
P2UI	3.39e-4				G	PAN2 = NO2 + R2CO3 + SumRCO3
P2OH	3.42e-12				G	PAN2 + OH = #.05 NO3 + #.73 xNO3 + #1.15 xHO2 + #1.55 RO2C + #.07 RO2XC + #.17 xHCHO + #.66 xMECHO + #.07 xETCHO + #.15 xPAN2 + #.07 zPAN2 + #.5 CO + #.73 CO2 + #.05 ALK3 + #1.62 SumRO2
P2HV	Phot Set= PPN-11				G,71	PAN2 + HV = NO2 + R2CO3 + SumRCO3
P4UI	3.39e-4				G	APANS = NO2 + MACO3 + SumRCO3
P4OH	2.90e-11				G	APANS + OH = #.74 NO3 + #.18 xNO3 + #.07 xHO2 + #.25 RO2C + #.01 RO2XC + #.07 xHCHO + #.18 xKET2 + #.19 OACID + #.07 xPAN2 + #.01 zPAN2 + #.18 CO2 + #.56 ALK4 + #.26 SumRO2
P4O3	8.20e-18				G	APANS + O3 = #.05 NO2 + #.19 OH + #.34 HO2 + #.38 HCHO2 + #.01 RCHO2 + #.1 HCHO + #.9 PAN2 + #.16 H2 + #.31 CO + #.21 CO2
P4N3	1.60e-16				G	APANS + NO3 = HO2
P4HV	Phot Set= PPN-11				G	APANS + HV = #.6 NO2 + #.4 NO3 + #.4 MEO2 + #.6 MACO3 + #.4 HCHO + #.4 CO + #.4 CO2 + #.4 SumRO2 + #.6 SumRCO3

## Notes

[a] Except as indicated, the rate constants are given by  $k(T) = A \cdot (T/300)^B \cdot e^{-E_a/RT}$ , where the units of k and A are  $\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$ ,  $E_a$  are  $\text{kcal mol}^{-1}$ , T is  $^\circ\text{K}$ , and  $R=0.0019872 \text{ kcal mol}^{-1} \text{ deg}^{-1}$ . 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 B-3 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  $k(T,M) = \{k_0(T) \cdot [M] / [1 + k_0(T) \cdot [M] / k_{inf}(T)]\} \cdot F^Z$ , where  $Z = \{1 + [\log_{10}\{k_0(T) \cdot [M] / k_{inf}(T)\} / N]^2\}^{-1}$ , [M] is the total pressure in  $\text{molecules cm}^{-3}$ , 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  $k(T,M) = k_0(T) + k_3(T) \cdot [M] \cdot (1 + k_3(T) \cdot [M] / k_2(T))$ , where [M] is the total bath gas (air) concentration in  $\text{molecules cm}^{-3}$ , 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  $k(T,M) = k_1(T) + k_2(T) \cdot [M]$ , where [M] is the total bath gas

Table A-2 (continued)

(air) concentration in molecules cm<sup>-3</sup>, and the temperature dependences for k<sub>1</sub>, and k<sub>2</sub> are as indicated on the table.

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

[b] Documentation notes are as follows:

- G The rate constant and product distribution derived using the MechGen mechanism generation system as documented by Carter (2023c). Overall reactions are derived using the lumping procedures described in the text. See Carter (2023c) for a discussion of how the rate constant parameters or photolysis rate constants are derived, and for documentation of the detailed mechanisms that were used to derive these lumped reactions.
- 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  $1 \times 10^{-22}$  cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1</sup> for the bimolecular process only. NASA (2011) gives an upper limit of  $2.0 \times 10^{-21}$  cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1</sup>. 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<sub>2</sub> and N<sub>2</sub> and their mole fractions in air.
  - 5 The temperature and pressure-dependence parameters were adjusted to fit the rate constants for the HNO<sub>3</sub> forming reaction calculated using the temperature-dependent rate expression of NASA (2015) for the total HO<sub>2</sub> + NO reaction and the temperature- and pressure-dependent expression for the ratio of the rate constant for the HNO<sub>3</sub>-forming reaction relative to the total rate constant as given by Butkowska 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 The rate constants used for the reactions of peroxy radicals other than methyl peroxy with NO, HO<sub>2</sub>, and NO<sub>3</sub> are the IUPAC (2019) recommendations for the corresponding reactions of ethyl peroxy.
  - 8 The SumRO<sub>2</sub> counter species is the sum of concentrations of all explicitly represented peroxy radical (RO<sub>2</sub>) species and of the operators RO<sub>2</sub>C and RO<sub>2</sub>XC 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<sub>2</sub> + 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 SumRO<sub>2</sub>. SumRO<sub>2</sub> 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 SumRO<sub>2</sub> or SumRCO<sub>3</sub>. See Carter (2023c) for a discussion of the derivation or rate constants and mechanisms used for peroxy radicals in MechGen, which are used for these reactions as well.
  - 9 The rate constant used by model to estimate consumption rate for all peroxy radicals by reaction with HO<sub>2</sub> is from the general estimate above for non-oxygenated peroxy radicals with 5 carbons (Carter, 2023c), which is the approximate average carbon number of the mixture of anthropogenic emissions used for developing the general mechanism.

Table A-2 (continued)

- 10 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 + peroxy reactions are approximated by those appropriate for secondary peroxy + secondary peroxy reactions, based on averages of such rate constants tabulated by Carter (2023c).
- 11 The SumRCO3 counter species is the sum of concentrations of all lumped or explicitly represented acyl peroxy radical (RCO3) species that react with other peroxy radicals. Except when reacting with methyl peroxy radicals, the major reaction of these species with RO2 or other RCO3 radicals is formation of the corresponding alkoxy radical, which rapidly decomposes to CO2 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. See Carter (2023c) for a discussion of the derivation of rate constants and mechanisms used for acyl peroxy radicals in MechGen, which are used for these reactions as well.
- 12 The rate constant expression is based on the NASA (2015) recommendation for the high pressure limit for  $\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{OO} + \text{NO}_2$ .
- 13 The rate constant based on the IUPAC (2019) recommendation for  $\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{OO} + \text{NO}$ .
- 14 The rate constant expression and product branching ratios used for all acyl peroxy +  $\text{HO}_2$  reactions is based on the IUPAC (2019) recommendation for acetyl peroxy +  $\text{HO}_2$ .
- 15 The rate constant expression for all acyl peroxy +  $\text{NO}_3$  reactions is based on the IUPAC (2019) recommendation for acetyl peroxy +  $\text{NO}_3$ .
- 16 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.
- 17 The rate constant used is the IUPAC (2019) recommendation for self-reactions of  $\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{OO}$  radicals. Because of lack of information, this is assumed to apply to all acyl peroxy + acyl peroxy reactions except for acetyl peroxy.
- 18 The chemical operator RO2C is used to represent NO to  $\text{NO}_2$  conversions in reactions of peroxy radicals that are not represented explicitly. This is the approach used in SAPRC-07 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.
- 19 The chemical operator RO2XC is used to represent NO consumption in the nitrate formation reactions of peroxy radicals that are not represented explicitly. This is also part of the approach used in SAPRC-07.
- 20 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  $2 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ , 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).
- 21 The rate constant and product yields used are the IUPAC (2019) recommendation for methyl peroxy + acetyl peroxy.
- 22 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).
- 23 SumRO2 or SumRCO3 is added as a product to all reactions that form peroxy or acyl peroxy radicals that react with other peroxy radicals.
- 24 Rate constants expressions based on the data of Caralp et al (1999).
- 25 Rate constant from Lotz and Zellner (2000). The reaction with NO is ignored because nitrite formation expected to be rapidly reversed by photolysis.

Table A-2 (continued)

- 26 Rate constant expression from Blitz et al (1999).
- 27 Rate constant from Platz et al (1998).
- 28 Assumed to have the same rate constant as used for ethyl peroxy + HO<sub>2</sub>.
- 29 Rate constant from Tao and Li (1999).
- 30 The NPRAD model species represents unknown naphthalene intermediates that react with NO<sub>2</sub> forming nitrogen-containing products. In the absence of NO<sub>2</sub> the reaction with HO<sub>2</sub> is assumed to be the major fate, with the reaction with NO<sub>2</sub> forming a compound represented by NPHE and the reaction with HO<sub>2</sub> 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.
- 31 This is added to avoid problems in the (generally unlikely) conditions where these radicals are formed when concentrations of both NO<sub>2</sub> and HO<sub>2</sub> are low. The rate constant used is arbitrary and is such that this process becomes significant only if [NO<sub>2</sub>] < ~3 x 10<sup>-6</sup> ppm and [HO<sub>2</sub>] < 1x10<sup>-5</sup> ppm. The likely process is reaction with some VOC forming compounds similar to those formed when the radicals react with HO<sub>2</sub>.
- 32 The PNAMIN model species represents nitrogen-centered radicals that do not have alpha hydrogens and can only react with NO<sub>2</sub> or other radicals. The reaction with NO<sub>2</sub> is usually the major fate, since reaction with NO forms highly photoreactive nitrosoamines, which rapidly re-forms the radicals. In the absence of NO<sub>2</sub> the reaction with HO<sub>2</sub> is assumed to be the major fate, with the reaction with NO<sub>2</sub> forming a nitramine and the reaction with HO<sub>2</sub> forming an amine. The rate constants are unknown but are estimated to be similar to those for the reactions of acyl peroxy radicals.
- 33 Rate constant from Welz et al (2012).
- 34 This reaction is predicted to be the major fate of most types of Criegee intermediates 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<sub>2</sub> given by Calvert et al (1978). This is highly uncertain, and varies with the intermediate.
- 35 Assumed to have the same rate constants as assigned for HCHO<sub>2</sub>. Note that these reactions are only applicable to stabilized biradicals that do not have rapid unimolecular reactions. Reactions of excited or reactive stabilized Criegee intermediates are handled by MechGen and are discussed by Carter (2023c).
- 36 Previous versions of SAPRC assumed that reaction with H<sub>2</sub>O, forming the acid, was the major fate of stabilized Criegee biradicals that did not have rapid unimolecular reactions, 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<sub>2</sub> and NO<sub>2</sub> as well as H<sub>2</sub>O. 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) and Vereecken et al (2017) for a discussion of stabilized Criegee reactions and rate constants, and Carter (2023c) for a discussion of how MechGen treats unimolecular reactions of excited and stabilized Criegee intermediates.
- 37 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<sub>2</sub> + 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.
- 38 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

Table A-2 (continued)

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.

- 39 Rate constant expression from review of Calvert et al (2015).
- 40 Absorption cross sections, quantum yields, and reactions based on those used for PPN.
- 41 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.
- 42 Rates of photolysis of nitrophenols forming HONO, relative to the photolysis rate of NO<sub>2</sub>, 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<sub>2</sub> 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<sub>2</sub> 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.
- 43 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 based on that 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<sub>x</sub> chamber experiments. The rate constant used is that recommended by Calvert et al (2015) for naphthalene.
- 33 Rate constant from Welz et al (2012).
- 34 This reaction is predicted to be the major fate of most types of Criegee intermediates 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<sub>2</sub> given by Calvert et al (1978). This is highly uncertain, and varies with the intermediate.
- 35 Assumed to have the same rate constants as assigned for HCHO<sub>2</sub>. Note that these reactions are only applicable to stabilized biradicals that do not have rapid unimolecular reactions. Reactions of excited or reactive stabilized Criegee intermediates are handled by MechGen and are discussed by Carter (2023c).
- 36 Previous versions of SAPRC assumed that reaction with H<sub>2</sub>O, forming the acid, was the major fate of stabilized Criegee biradicals that did not have rapid unimolecular reactions, 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<sub>2</sub> and NO<sub>2</sub> as well as H<sub>2</sub>O. The rate constants probably depend on the radical, but for now the same rate constants are

Table A-2 (continued)

- used for all reactions. See Sarwar et al (2013) and Vereecken et al (2017) for a discussion of stabilized Criegee reactions and rate constants, and Carter (2023c) for a discussion of how MechGen treats unimolecular reactions of excited and stabilized Criegee intermediates.
- 37 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<sub>2</sub> + 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.
  - 38 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.
  - 39 Rate constant expression from review of Calvert et al (2015).
  - 40 Absorption cross sections, quantum yields, and reactions based on those used for PPN.
  - 41 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.
  - 42 Rates of photolysis of nitrophenols forming HONO, relative to the photolysis rate of NO<sub>2</sub>, 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<sub>2</sub> 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<sub>2</sub> 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.
  - 43 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 based on that 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<sub>x</sub> chamber experiments. The rate constant used is that recommended by Calvert et al (2015) for naphthalene.
  - 44 The CATL3 model species is used to represent phenols with three or more -OH's. The mechanism is assigned based on CATL reactions but simplified

Table A-2 (continued)

and assuming that all products are non-volatile. The rate constants are based on those estimated for 2,3,4-trihydroxy toluene, which is the highest yield product for reaction of OH with lumped CATL.

- 45 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.
- 46 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.
- 47 The main compound represented by IMINE is  $\text{CH}_3\text{CH}=\text{NH}$ , 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. The ammonia that is also formed is not represented because it is expected to be relatively unreactive and is not included in the gas-phase mechanism. The rate constant is arbitrarily set at 1 hour<sup>-1</sup>. The major gas-phase reaction would be expected to react with OH radicals, probably forming the same products with a similar lifetime.
- 48 Rate constants from the compilation of McGillen et al (2020, 2021).
- 49 The x(Spec) operators represent the formation of various products or radicals following the reactions of alkoxy radicals formed from the reactions of peroxy radicals (primarily the reaction with NO but to a lesser extent for reactions with NO<sub>3</sub>, SumRO<sub>2</sub> or SumRCO<sub>3</sub>). They are represented as reacting with the same species and rate constants used for SumRO<sub>2</sub>, the model species representing the sum of all peroxy radicals. Alkoxy radicals and their subsequent products are assumed to be formed in 100% yields in reactions of these operators with NO, NO<sub>3</sub>, and RCO<sub>3</sub>, and in 50% yields in their reactions with RO<sub>2</sub>. Note that the reactions of peroxy radicals with NO forming nitrates are represented separately using the z(product) model species, and the formation of non-alkoxy products in their reactions HO<sub>2</sub> and RO<sub>2</sub> are represented using the y(product) model species.
- There are five reactions such as those shown for each of the 46 species that is assigned an x(Spec) operator, making a total of 230 such reactions (numbers 154-398). The 46 species of this type are as follows: OH, HO<sub>2</sub>, NO<sub>2</sub>, NO<sub>3</sub>, HCHO, GLY, HCOOH, MECHO, ETCHO, GLCHO, MEK, ACRO, ACET, MACR, MVK, BACL, MGLY, BUDAL, FURNS, BALD, BENX, RCHO, KET2, LVKS, OLEA1, OLEA2, OLEP, OACID, PACID, AMINS, R2NO<sub>3</sub>, RPNO<sub>3</sub>, RCNO<sub>3</sub>, RHNO<sub>3</sub>, RDNO<sub>3</sub>, RUOOH, HPCRB, AFG1, AFG2A, AFG2B, AFG3, PAN2, MEO2, ETO2, MECO3, R2CO3, MACO3, and TBUO.
- 50 The y(product) operator is used primarily to represent the formation of hydroperoxide species from the reactions of peroxy radicals with HO<sub>2</sub>. These are only used in the standard version of SAPRC-22. They also approximately represent the formation of disproportion products (with assumed 50% yields -- see Carter, 2023), with a single VOC model species chosen to represent the distribution of carbonyl and alcohol products predicted to be formed in these relatively minor reactions. The y(product) operators are represented as reacting with the same species and rate constants used for SumRO<sub>2</sub>, as with the other types of these operators.
- There are five such reactions for each of the 5 species that are assigned y(Spec) operators, making a total of 25 such reactions (numbers 399-423). Spec-2 is the species representing those formed from disproportion reactions with other peroxy radicals. See the mechanism listing in the electronic supplement for the full list of these reactions. The 5 species of this type, and the Spec-2 species assigned to each are as follows (Spec, Spec-2): (ROOH, KET2), (RUOOH, OLEP), (RAOOH, OLEP), (HPCRB, KET2), and (RPNO<sub>3</sub>, R1NO<sub>3</sub>).
- 51 The z(Product) operator is used primarily to represent the formation of organic nitrates following the reactions of peroxy radicals with NO. These are

Table A-2 (continued)

only used in both the standard and in the full versions of SAPRC-22. The z(product) operators are represented as reacting with the same species and rate constants used for the other types of these operators. They also approximately represent the formation of products from reactions of alkoxy radicals that are formed in the reactions of peroxy radicals with NO<sub>3</sub>, RCO<sub>3</sub>, and (in half molar yields) with RO<sub>2</sub>. A single model species is chosen for each to represent these products of these relatively minor reactions.

There are five such reactions for each of the 9 organic nitrate model species that are assigned such operators, making a total of 45 such reactions (numbers 424-468). Spec-2 is the species representing those formed from reactions other than with NO or HO<sub>2</sub>. See the mechanism listing in the electronic supplement for the full list of these reactions. The 9 nitrate species assigned such operators, and the Spec-2 species assigned to each, are as follows (Spec, Spec-2): (RCNO<sub>3</sub>, KET2), (RHNO<sub>3</sub>, OTH3), (RANO<sub>3</sub>, RUOOH), (RPNO<sub>3</sub>, RUOOH), (RDNO<sub>3</sub>, R1NO<sub>3</sub>), (R1NO<sub>3</sub>, OTH3), (R2NO<sub>3</sub>, OLE1), (RNNO<sub>3</sub>, OTHN), and (PAN2, RCHO).

- 52 Rate constants used for the lumped higher acyl peroxy radicals are the IUPAC (2019) recommendation for the reaction of CH<sub>3</sub>CH<sub>2</sub>C(O)OO· with NO, for the high pressure limit for the reactions of acetyl peroxy radicals with NO<sub>2</sub>, and for reactions of acetyl peroxy radicals with NO<sub>3</sub>, HO<sub>2</sub>, ethyl peroxy, and acetyl peroxy radicals. Products formed are based on MechGen estimates and assignments for the reactions of CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>C(O)OO· or CH<sub>2</sub>=C(CH<sub>3</sub>)C(O)OO·. These in general are based on IUPAC (2019) recommendations.
- 53 The unimolecular rate constants for the unimolecular reactions of these operators, which are added to account for the dependences of product yields on absolute NO concentrations, were derived as discussed in Section 2.4.2. The rate constant for the reaction with NO is the same as used for other peroxy + NO reactions.2.4.2
- 54 Rate constant recommended by Calvert et al (2000).
- 55 Absorption cross sections recommended by IUPAC (2019). Unit quantum yields assumed.
- 56 Absorption cross sections and quantum yields based on IUPAC (2022) recommendations.
- 57 Absorption cross sections recommended by NASA (2015). Unit quantum yields assumed.
- 58 Absorption cross sections from IUPAC (2022). Unit quantum yields are assumed for HCO at wavelengths above ~285 nm, based on data of Chen and Zhu (2001) as discussed by IUPAC (2022).
- 59 Absorption cross-sections and quantum yields recommended by NASA (2015).
- 60 Alkyl ketone absorption cross-sections based on IUPAC (2019) recommendations for methyl ethyl ketone. Overall, wavelength-independent quantum yields adjusted to fit results of ketone - NO<sub>x</sub> chamber experiments, and tend to decrease with carbon number as follows: 0.175, 0.1, 0.1, 0.02 for 4 (MEK), 5, 6, and 7 carbons, respectively. Overall quantum yield for KET2 based on distribution of C<sub>5</sub>+ ketones in the emissions mixture.
- 61 Absorption cross sections recommended by IUPAC (2019). 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.
- 62 The absorption cross sections used are based on those of trans-2-butene 1,4-dial and cis and trans 4-oxo-2-pentenal 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 based on updated estimates of aromatic reactions, but are reasonably representative. The overall absorption cross sections for the photolysis of BUDAL, AFG1, AFG2A, and AFG2B were re-adjusted to minimize biases in predictions of NO oxidation and O<sub>3</sub> formation rates in the aromatic - NO<sub>x</sub> experiments.

Table A-2 (continued)

- 63 The rates of photolyses of these lumped model species are assumed to be the same as those for the simplest compound represented by the model species, as follows: Propionaldehyde for lumped higher aldehydes with no adjacent double bond (RCHO and OLEA2); methacrolein for lumped  $\alpha$ -unsaturated aldehydes (OLEA1); methyl vinyl ketone for lumped  $\alpha$ -unsaturated ketones (LVKS); isopropyl nitrate for lumped organic nitrates without carbonyl or hydroperoxy groups (R1NO3, R2NO3, RHNO3); methyl hydroperoxide for lumped hydroperoxides without carbonyl groups (ROOH, RAOOH, RUOOH)
- 64 Absorption cross sections of peroxyacetic acid given by Orlando and Tyndall (2003) used for lumped peroxy acids.
- 65 Absorption cross sections and quantum yields for lumped  $\alpha$ -keto aldehydes are based on those recommended by IUPAC (2019) for methyl glyoxal. Quantum yield calculated from the expression given for 425 torr N<sub>2</sub>. This "pressure" adjustment was made so the calculated photolysis rates, relative to NO<sub>2</sub>, are consistent with the data of Plum et al (1983) and Klotz et al (2000).
- 66 Absorption cross sections and quantum yields for lumped  $\alpha$ -keto ketones are based on those recommended by IUPAC (2019) for biacetyl. Quantum yield calculated from the expression given by IUPAC (2019) for the pressure and wavelength-dependence quantum yields for methyl glyoxal, but with the effective pressure adjusted so the photolysis rate, relative to that for NO<sub>2</sub>, under ambient conditions is consistent with the data of Plum et al (1983) and Klotz et al (2000).
- 67 Absorption cross sections for carbonyl nitrates from Barnes et al (1993), with primary and secondary nitrates weighed equally. Assume unit quantum yields based on discussions in Barnes et al (1993).
- 68 Compounds with both hydroperoxide and nitrate substituents are assumed to photolyze with the same rate constant assigned for lumped hydroperoxides, based on methyl hydroperoxide, because photolyses of hydroperoxides are faster than those of organic nitrates under atmospheric conditions.
- 69 Absorption cross sections for lumped dinitrates based on averages of absorption cross sections for 1,2-propanediol dinitrate, 1,2-butanediol dinitrate, 2,3-butanediol dinitrate, 3,4-dinitrooxy-1-butene, and 1,4-dinitrooxy-2-butene from Barnes et al (1993). Quantum yields based on discussions in Barnes et al (1993).
- 70 Unsaturated hydroperoxy aldehydes are assumed to have absorption cross sections similar to unsaturated carbonyls, and the absorption cross sections used are averages of the IUPAC (2019)-recommended values for methacrolein and methyl vinyl ketone. Reaction is assumed to be breaking the weakest bond (the O-O bond in hydroperoxy groups) with unit quantum yield.
- 71 Absorption cross section and quantum yields based on NASA (2011) recommendations for PPN (for PAN2) and PAN (for APANS).