



*Supplement of*

## **Derivation of atmospheric reaction mechanisms for volatile organic compounds by the SAPRC mechanism generation system (MechGen)**

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## S1. Chemical Mechanism Assignments and Estimates

### S1.1. Specification of Reactants

MechGen identifies the structure of organic reactants or radicals by specifying "groups" in the molecule, indicating the groups each is bonded to, and the type of bond. Groups are parts of molecules that are treated as units in the system and contain no more than one carbon or nitrogen, and also can contain zero to three hydrogen atoms and zero to three oxygen atoms. These group and molecule designations are used in the tables giving the parameters and assignments since these are how the parameters are assigned. The list of groups that can be used is given in Table S1; illustrative examples are shown in Table S2. Note also the following:

- Neighboring groups in non-branched and non-cyclic structures are separated by either "-", "=", or "#" symbols depending on whether their bonds are single, double, or triple.
- Branched structures are indicated using "(" to show third or fourth groups bonded to groups with more than two neighbors. If the bond between the center group and the 3rd or 4th group is a double or triple bond it is indicated using a "=" or "#" after the "(", as shown for isoprene in Table S2. This is similar to the treatment of branched structure using the SMILES notation (SMILES, 2022). Other examples are also shown in Table S2.
- Monocyclic structures are indicated using "\*" symbols to indicate groups bonded to other groups using single bonds. The "\*" can be before or after the group name, but the standard format is after the name. Bi- and polycyclic structures are indicated using "\*1", "\*2", etc. symbols to indicate groups that are bonded together, and should always be given after the group name but before any bond designation.
- Aromatic structures can be created using "CH" and "C" groups with alternating single or double bonds as with other cyclic polyalkenes. However the standard designation, which reflects the fact that separate groups are used for aromatic carbons, is to designate carbons in aromatic rings using "aCH" or "aC" depending on whether it has a hydrogen or a third group bonded to it, with the aromatic bonds designated as if they were single bonds. See the example for toluene and naphthalene in Table S2.
- Allylic radicals can be created using carbon-centered radical groups and alkene groups to designate one of the resonance structures, and it does not matter which structure is used for this purpose. However the standard designation, which reflects the fact that separate groups are used for such radicals and the radical center is at more than one location, is to designate carbons where the radical center may be located as ".aCH2", "aCH[.]", or "aC[.]" and the other carbons in the allylic structure as if they are aromatic (i.e., alternating double and single bonds). This is only applicable for carbon-centered radicals with conjugated C=C double bonds. See, for example, the structures shown for methyl allyl radicals and the OH+benzene adduct in Table S2.
- Cis and trans isomerization about a double bond are indicated using "^" and "v" symbols, analogous to the use of "\" and "/" symbols in the SMILES notation. Note that specifications of cis-trans isomerization for cyclic compounds are not currently supported, nor are specifications of optical isomers.

As with the SMILES notation, in many cases there can be more than one valid structure designation for a given compound as indicated in Table S2 for many of the compounds. However, MechGen uses an algorithm to derive a single, canonical notation that is unique for each structure. This is necessary for the system to determine whether two structures, derived in different ways (either user input or as a result of a generated reaction) refer to the same compound. The first MechGen structure given in



Table S1. List of groups and group designations used to specify organic reactants.

Non-Radical/Stable Groups [a]			Radical Groups [a]		
Types, names, bonds		Note [b]	Group types, names, bonds		Note [b]
Alkane			Carbon-centered radical groups		
CH4		1	CH3.		
-CH3	CH3-		-CH2.	.CH2-	
-CH2-			-CH[.]-		
-CH()-			-C[.](O)-		
-C(O)-			=CH.	.CH=	
Alkene			=C[.]-	-C[.]=	
=CH2	CH2=		-aCH2.	.aCH2-	2
=CH-	-CH=		-aCH[.]-		2
=C()-	-C()=		-aC[.](O)-		2
=C=			-pC[.]-		6
Alkyne			-CO.	CO[.]-	
#CH	HC#		Peroxy radical groups		
#C-			CH3OO.		1
Aromatic or Allylic			-CH2OO.	.OOCH2-	
-aCH-		2	-CH[OO.]-		
-aC()-		2	-C[OO.](O)-		
Oxygenate			-CO[OO.]	CO[OO.]-	
CO		1	=CHOO.	.OOCH=	
HCHO		1	=C[OO.]-	-C[OO.]=	
CO2		1	-pC[OO.]-		6
-CHO	HCO-		Alkoxy radical groups		
-CO-			CH3O.		1
-OH	HO-		-CH2O.	.OCH2-	
-O-			-CH[O.]-		
Nitrate, nitro, nitroso			-C[O.](O)-		
-ONO2	O2NO-		=CH[O.]	CH[O.]=	
-NO2	NO2-		=C[O.]-	-C[O.]=	
-NO	NO-	3	-CO2.	CO[O.]-	
Amino and stable amine-oxy			-pC[O.]-		6
-NH2	NH2-		N-Containing radicals and excited adducts		
-NH-			-NH.	.NH-	
-N()-			-N[.]-		
-N[O]()-		4	-NH2[O]	NH2[O]-	8
Imine			-NH[O]-		8
=NH	NH=	3	Carbenes		
=N-	-N=	3	-CH[.]-	CH[.]-	
Stabilized Criegee intermediates			-C[.]-		
HCHO2		1	Excited Criegee intermediates		
-CHOO[syn]			HCHO2 {excited}		1, 7
-CHOO[anti]			-CHOO {excited}		7
-C[OO]-			-C[OO]- {excited}		7
-syn-		5			

[a] Reactants are referred to as "radicals" if they have a radical group and as "stable" if they do not. Reactants cannot have more than one radical group. "-", "=", "#" indicate that the group is bonded to

Table S1 (continued)

another group with a single, double, or triple bond, respectively. "-" is also used to designate aromatic bonds or allylic bonds between groups with "a" or "p" prefixes. "()" indicates that the group is bonded to a third or fourth group with a single bond, e.g., "CH<sub>3</sub>-C(CH<sub>3</sub>)(CH<sub>3</sub>)-CH<sub>3</sub> for the "-C()()-" group in neopentane. If two names are given then either form can be used to designate reactants with this type of group.

[b] Additional information and levels of support for reactions of the groups are as follows:

- 1 This is a single molecule group, so has no bonds.
- 2 The "aC" codes are used to indicate carbon centers in aromatic rings and also non-radical unsaturated in allylic groups. The "aC[.]" codes are used to indicate radical centers in allylic groups. For example, allyl radicals are represented by ".aCH<sub>2</sub>-aCH-aCH<sub>2</sub>.", where the groups in the 1 and 3 positions are radical groups and that in the 2 position is a non-radical group. All the groups in benzene ("aCH\*-aCH-aCH-aCH-aCH-aCH\*") are non-radical groups.
- 3 Reactants can be built with this group but either the system cannot generate their reactions, its estimates may not be appropriate, or there are insufficient thermochemical group assignments to support generating many of their reactions. For that reason, discussion of the reactions of compounds with these groups is beyond the scope of this manuscript.
- 4 These are stable amine oxides formed when O<sub>3</sub> reacts with tertiary amines. Unlike amine oxides formed when O<sub>3</sub> reacts with primary or secondary amines, these are assumed to have no rapid reactions in air so are not treated as radical groups.
- 5 Used to indicate which substituent of a disubstituted Criegee intermediate is in the *syn* position. For example, the first CH<sub>3</sub>- group in CH<sub>3</sub>-*syn*-C[OO]-CH<sub>2</sub>-CH<sub>3</sub> is in the *syn* position.
- 6 These are phenyl, phenyl peroxy, or phenoxy radical centers.
- 7 The designation "{excited}" is given at the end of the compound identification and indicates the level of excitation of the intermediate. For Criegee intermediates, it could be "{\*O<sub>3</sub>Ole}" or "{\*O<sub>3</sub>cycOle}" to indicate formation from O<sub>3</sub> + alkene reactions, "{\*O<sub>3</sub>alkyne}" to indicate formation from O<sub>3</sub> + alkyne reactions, and "{\*O<sub>3</sub>carbene}" to indicate formation from carbenes.
- 8 These reactive amine oxide groups are used for intermediates in reactions of O<sub>3</sub> with primary and secondary amines.

the right column of Table S2 is the canonical MechGen designation; the others are valid designations that can be used to create new compounds. However, once created, MechGen uses the canonical structure for it.

Table S2. Examples of designations of selected representative compounds and radicals.

Compound	SMILES [a]	MechGen Structures [a]
propane	CCC	CH3-CH2-CH3
propene	C=CC	CH2=CH-CH3; CH3-CH=CH2
methyl acetylene	C#CC	CH#C-CH3; CH3-C#CH
2-methyl propane	CC(C)C	CH3-CH(CH3)-CH3
3,3-dimethyl pentane	CCC(C)(C)CC	CH3-CH2-C(CH3)(CH3)-CH2-CH3; CH3-C(CH3)(CH2-CH3)-CH2-CH3
isoprene	C=CC(=C)C	CH2=CH-C(=CH2)-CH3; CH2=CH-C(-CH3)=CH2
2-butenes (mixed cis & trans isomers)	CC=CC	CH3-CH=CH-CH3
cis-2-butene	C/C=C\C	CH3-^CH=CH-vCH3; CH3-vCH=CH-^CH3
trans-2-butene	C/C=C/C	CH3-^CH=CH-^CH3; CH3-vCH=CH-vCH3
trans-3-methyl-2-pentene	C/C=C(\C)CC	CH3-^CH=C(vCH3)-CH2-CH3; CH3-CH2-C(^CH3)=CH-^CH3
cyclopropane	C1CC1	CH2*-CH2-CH2*; *CH2-CH2-*CH2
bicyclo [1.1.1] heptane	C1C2CC1C2	CH2*1-CH*2-CH2-CH*1-CH2*2; CH*12-CH2-CH(CH2*1)-CH2*2
spiropentane	C1CC12CC2	CH2*1-CH2-C*12-CH2-CH2*2; C*12(CH2-CH2*1)-CH2-CH2*2
toluene	Cc1ccccc1	CH3-aC*-aCH-aCH-aCH-aCH-aCH*; CH3-C*=CH-CH=CH-CH=CH*
naphthalene	c12ccccc1cccc2	aC*12-aCH-aCH-aCH-aCH-aC*1-aCH-aCH-aCH-aCH*2
2-propyl nitrate	CC(C)ON(=O)=O	CH3-CH(CH3)-ONO2; CH3-CH(ONO2)-CH3
ethylene glycol ethyl ether acetate	CCOCCOC(C)=O	CH3-CH2-O-CH2-CH2-O-CO-CH3
2-propyl radicals	C[CH]C	CH3-CH[.]-CH3
2-propyl peroxy radicals	CC(C)O[O]	CH3-CH[OO.]-CH3
methyl allyl radicals	C=C[CH]C	CH3-aCH[.]-aCH-aCH2; CH3-CH[.]-CH=CH2; or CH3-CH=CH-CH2.
OH+benzene adduct	OC1C=CC=C[CH]1	HO-CH*-aCH[.]-aCH-aCH[.]-aCH-aCH[.]*

[a] The SMILES and first MechGen structure code given are those generated by the system. Subsequent MechGen structures, if given, are alternatives that can be used to create the same compound. Other SMILES or MechGen structures may also be acceptable for creating some of these compounds.

## S1.2. Tables of Parameters for Bimolecular Rate Constant Estimation

The equations used to derive estimated rate constants for reactions of VOCs with OH, NO<sub>3</sub>, O<sub>3</sub>, and O<sup>3</sup>P are given in Table 3 of the main text, and the table numbers with the values of the various parameters are given in Table S3. The tables with the parameter values are given near the end of this document, in Section A5.1, because of the relatively large numbers of parameters. The derivations of these parameters were described by Carter (2021), and most parameters and derivation methods are given there. Although reactions of Cl atoms with organics are beyond the scope of the present work, Carter (2021) included estimates for those reactions and the values of the parameters are included in the Section S5.1 tables for comparison purposes.

Table S3. Table numbers giving the parameters for the various types of reactions of organics with OH, NO<sub>3</sub>, Cl, O<sub>3</sub>, and O<sup>3</sup>P. Table 3 in the main text shows how these parameters are used to estimate rate constants.

Type of Reaction	Parameter	Table (in Section S5)
H-Atom abstractions by OH, NO <sub>3</sub> , or Cl	$kH^{\text{base}}$	Table S37
	$FH^{\text{nbr}}$	Table S38 (OH) Table S39 (NO <sub>3</sub> ) Table S40 (Cl)
	$FH^{\text{ring}}$	Table S42
Additions by OH, NO <sub>3</sub> , or Cl	$kA^{\text{base}}$ $kAro^{\text{base}}$ $kA''^{\text{base}}$	Table S37
	$FA^{\text{nbr}}$	Table S38 (OH) Table S39 (NO <sub>3</sub> ) Table S40 (Cl)
	$FA^{\text{ortho, etc.}}$	Table S41
Additions by O <sub>3</sub> or O <sup>3</sup> P	$kA'^{\text{base}}$ $kA''^{\text{base}}$	Table S43
	$FA'^{\text{nbr}}$ $FA'^{\text{struct}}$ (furan)	Table S44
	$FA'^{\text{struct}}$ (ring)	Table S42

Some of the parameters related to the mechanisms for phenols and related compounds were updated relative to those given by Carter (2021) in order to improve simulation of chamber experiments (Jiang et al, 2023). The affected parameters concern predictions of rate constants for additions of OH or NO<sub>3</sub> and the modified parameters are indicated where applicable in Table S37 through Table S39. The updated rate constant estimates for reactions of OH and NO<sub>3</sub> with phenols are compared with the experimental data used to derive the parameters in Table S4. Although the ability of the estimates to predict the measured total rate constants is not as good as it is for some other types of compounds, it is comparable to the previous estimates of Carter (2021), while giving somewhat better simulations of chamber experiments.

Table S4. Experimental and estimated rate constants for the reactions of OH radicals with phenolic compounds used to derive the estimates of initial branching ratios.

Compound	kOH [a]		Est / Expt	kNO <sub>3</sub> [a]		Est / Expt
	Expt	SAR		Expt	SAR	
Phenol	2.80	1.32	0.5	0.45	1.00	2.2
p-cresol	4.90	2.73	0.6	1.10	1.67	1.5
o-cresol	4.10	2.50	0.6	1.40	1.61	1.2
m-cresol	5.90	5.99	1.0	1.00	1.00	1.0
2,5-dimethylphenol	8.50	7.16	0.8	3.07	1.61	0.5
3,4-dimethylphenol	8.30	7.76	0.9	2.55	1.67	0.7
2,3-dimethylphenol	8.20	9.15	1.1	2.97	1.61	0.5
2,4-dimethylphenol	7.30	9.74	1.3	3.12	5.27	1.7
3,5-dimethylphenol	11.4	12.7	1.1	1.13	1.00	0.9
2,6-dimethylphenol	6.70	5.89	0.9	5.01	4.95	1.0
2,4,6-trimethylphenol	16.7	19.0	1.1			
2,3,6-trimethylphenol	12.7	12.5	1.0			
3,4,5-trimethylphenol	15.5	15.6	1.0			
2,4,5-trimethylphenol	11.0	14.8	1.3			
2,3,5-trimethylphenol	13.7	15.8	1.2			
catechol	10.0	5.8	0.6	9.80	6.79	0.7
3-methylpyrocatechol	20.0	14.0	0.7	17.20	17.96	1.0
4-methylpyrocatechol	15.0	23.7	1.6	14.70	19.03	1.3
5-methyl-2-nitrophenol	0.67	0.59	0.9			
4-methyl-2-nitrophenol	0.36	0.35	1.0			
3-methyl-2-nitrophenol	0.37	0.72	2.0			
2-methyl-6-nitrophenol	0.28	0.33	1.2			

[a] Rate constants are in units of  $10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ . Experimental rate constants from McGillen et al. (2021), as used by Carter (2021). SAR estimates utilize updated parameters, as will be discussed in a separate paper (manuscript in preparation).

### S1.3. Photolysis Sets

Photolysis sets are sets of wavelength-dependent absorption cross sections and quantum yields that are used to calculate rate constants for photolysis reactions, given wavelength-dependent fluxes for the photolyzing light source. Those referenced by MechGen are a subset of those used in the SAPRC-18 (Carter, 2020) and SAPRC-22 (Carter, 2023a) mechanisms, and can be downloaded from the SAPRC mechanism web page (Carter, 2023b). Table S5 lists the set names output by MechGen when generating photolysis reactions so they can be used, in conjunction with an overall wavelength-independent quantum yield (if applicable), to calculate photolysis rate constants for various lighting conditions. The table also indicates which of these contain only absorption cross sections and which also contain wavelength-dependent quantum yields, and has notes or references indicating how they were derived. The table also gives the half-lives relative to photolysis calculated using the data in each set, using unit quantum yields if they are not provided. Note that these rate constant ratios are only applicable if no overall quantum yield or branching ratio factor is applied, as is the case for some types of photolyses (see Section 2.2 of the main text).

Table S5. Summary of photolysis sets referenced by MechGen for calculating photolysis rate constants for various lighting conditions.

Set Name [a]	Half-Life [b]	Has QY? [c]	Based on Compound(s) or Reaction [d]	Source [e]
NO2-06	1.0 min.	yes	$\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}^3\text{P}$	NASA (2006)
AFGS	1.8 min.	no	$\text{HCO-CH}_x=\text{CH}_x\text{CO}_x$ compounds *	See note 1
HPALDS	18 min.	no	Avg of $\sigma$ 's for Methacrolein and MVK *	IUPAC (2023)
BALD-11	21 min.	no	Benzaldehyde *	Calvert et al. (2011)
BACL-11	26 min.	yes	Biacetyl	IUPAC (2023); note 2
MGLY-13	41 min.	yes	Methyl glyoxal	IUPAC (2023); note 3
C2CHOabs	3.3 hours	no	Propionaldehyde ( $\sigma$ 's only)	IUPAC (2023); note 4
CRBNIT	3.8 hours	no	Various carbonyl nitrates	Barnes et al. (1993)
MEK-06	12.0 hours	no	Methyl ethyl ketone *	IUPAC (2023)
GLALD-14	12.5 hours	no	Glycolaldehyde	NASA (2011)
DIONO2	16 hours	no	Various dinitrates	Barnes et al. (1993)
CCHOR-13	25 hours	yes	Acetaldehyde	IUPAC (2023)
COOH	29 hours	no	Methyl hydroperoxide	IUPAC (2023)
MVK-16	36 hours	yes	Methyl vinyl ketone	IUPAC (2023)
IC3ONO2	49 hours	no	Isopropyl nitrate	IUPAC (2023); note 5
ACROL-16	50 hours	yes	Acrolein	NASA (2006); note 6
MACR-06	59 hours	yes	Methacrolein	IUPAC (2023); note 7
PPN-11	101 hours	no	Peroxy proponyl nitrate (PPN)	NASA (2011)
ACET-06	178 hours	yes	Acetone *	IUPAC (2023), note 8
PAN-11	189 hours	no	Peroxy acetyl nitrate (PAN)	NASA (2011)
PAA	192 hours	no	Peroxy acetic acid	Orlando and Tyndall (2003)

[a] Set names refer to names of photolysis (.PHF) files containing wavelength-dependent absorption cross sections and quantum yields also used in the MechGen output and documentation. Photolysis files for inorganics (except  $\text{NO}_2$ ) and small explicit compounds such as formaldehyde and glyoxal are not included. These are ordered by descending photolysis rate constants for ground level conditions.

[b] Half-life relative to the photolysis rate constant calculated for the photolysis sets for direct overhead sun ( $z=0$ ) using the actinic fluxes used in the reactivity scenarios of Carter (1994).

[c] "Yes" means that wavelength-dependent quantum yields are in the file. If "no", all the quantum yields are assumed to be 1 when calculating  $J(\text{photolysis set, light source})$ . An overall quantum yield may be output if it is used, but is not used in all such cases (see next note).

[d] A "\*" indicates that wavelength-independent overall quantum yields are used for most reactions, so the atmospheric half-lives for the individual reactions using this photolysis set will be correspondingly lower than those given in this table for the photolysis set. These overall quantum yields are given in the main text where the various types of reactions are discussed.

[e] Footnotes for specific photolysis sets are given below.

1 "CO<sub>x</sub>" refers to -CO- or -CHO based on absorption cross sections of trans-2-butene-1,4-dial and cis and trans 4-oxo-2-pentenal as provided by Calvert et al. (2002). Cross sections used for lumped species are based on a previous estimate of the distribution of these products from aromatics, giving

31.6% butenedial and 68.4% 4-oxo-2-pentenal. These have not been updated but are reasonably representative. Note, however, that the current IUPAC (2023) recommendation for 4-oxo-2-pentenal give significantly lower photolysis rate constants, but these are not used in the current SAPRC mechanism because they require the use of greater than unit quantum yields for the model to simulate available environmental chamber data. (See Carter (2010a,b) and Carter and Heo (2013) for a discussion of adjustments to the overall quantum yields for aromatic photoreactive products based on chamber data.)

- 2 Absorption cross sections of IUPAC (2023) used. IUPAC gives no recommendation of quantum yields. Quantum yields for the current mechanism were derived in the same way as for SAPRC-07 (Carter, 2010a,b), based on recommendation of pressure-dependence of quantum yields for methyl glyoxal from IUPAC, with pressure dependence adjusted to get same photolysis rates relative to NO<sub>2</sub> as measured by Plum et al. (1983) and Klotz et al. (2000).
- 3 Absorption cross-sections from IUPAC (2023) recommendation for methyl glyoxal. Pressure-dependent quantum yields were derived using the pressure-dependence recommendation given by IUPAC, but derived 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).
- 4 The absorption cross sections of propionaldehyde are used for all aldehydes bonded to an unsaturated carbon-centered group. Although IUPAC (2023) makes no specific recommendations concerning quantum yields or branching ratio, it appears likely that the quantum yield ·CHO formation for λ>~295 nm is near unity, based on the data of Chen and Zhu (2001). MechGen assumes that this is applicable for higher aldehydes of this type as well.
- 5 Isopropyl nitrate has stronger absorption than n-propyl and and lower nitrates, but is chosen as representative of lumped higher nitrates.
- 6 Absorption cross-sections are the NASA (2011) recommendation for acrolein. The quantum yields were derived using the pressure and wavelength-dependent expression given by IUPAC (2023) for methyl vinyl ketone, with the parameter representing total pressure adjusted to yield the NASA-recommended quantum yield of 0.0065 at 313 nm and 1 atm pressure.
- 7 Absorption cross sections used are IUPAC (2023) recommendations for methacrolein. The quantum yields were derived using the pressure and wavelength-dependent expression given by IUPAC (2023) for methyl vinyl ketone, with the total pressure adjusted so that the radical forming photolysis rates for the chamber experiments are the same as those that fit the chamber data for experiments with methacrolein.
- 8 Absorption cross sections and quantum yields based on IUPAC (2023) recommendations for acetone. The absorption cross sections are for T=298 K. Quantum yields are calculated for 1 atm and T=298 K using the complex expression recommended by IUPAC.

## S1.4. Reactions of Carbon-Centered Radicals

### S1.4.1. Rate Constants for O<sub>2</sub> Reactions

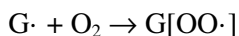
Table S6 gives measured rate constants for the reactions of various types of carbon-centered radicals with O<sub>2</sub>. For estimation purposes, we assume a 298 K rate constant of  $7.5 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ , which corresponds to a pseudo-unimolecular rate constant of  $\sim 3.8 \times 10^7 \text{ sec}^{-1}$  near the surface. This is sufficiently high that O<sub>2</sub> reaction should be the major fate of most carbon-centered radicals under atmospheric conditions. However, as discussed in the main text, this is not the case for all types of carbon-centered radicals that may be formed in the generated mechanisms.

Table S6. Summary of measured O<sub>2</sub> addition rate constants for representative carbon-centered radicals.

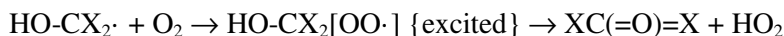
Radical	298 K Rate Constant ( $10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ )	Ref
CH <sub>3</sub> · (high pressure)	1.2	NASA (2011)
CH <sub>3</sub> CH <sub>2</sub> ·	8.0	NASA (2011)
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> ·	8.0	NASA (2011)
CH <sub>3</sub> CH(·)CH <sub>3</sub>	11.0	NASA (2011)
CH <sub>3</sub> C(·)(CH <sub>3</sub> )CH <sub>3</sub>	3.5	Dusanter et al. (2005)
HOCH <sub>2</sub> ·	9.1	NASA (2011)
HC(O)· [a]	5.2	NASA (2011)
CH <sub>3</sub> C(O)·	5.1	NASA (2011)
Used for estimates	7.5	Average of values for 1- and 2-propyl and t-butyl.

### S1.4.2. O<sub>2</sub> Addition Mechanisms

If the carbon-centered radical is not adjacent to any double bonds, then the O<sub>2</sub> reaction involves simply addition to the radical center, forming the corresponding peroxy radical.

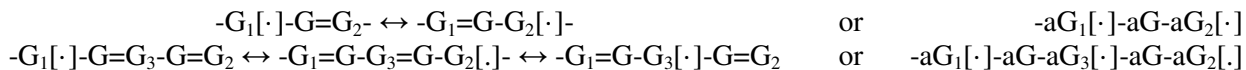


However, the peroxy radicals formed from  $\alpha$ -OH substituted radicals are assumed to rapidly decompose to form HO<sub>2</sub> and the corresponding carbonyl.



MechGen treats these as concerted processes when reactions of  $\alpha$ -OH substituted carbon-centered radicals are generated, since stabilization and other reactions are expected to be unimportant.

If the radical is adjacent to one or more double bond groups, it is assumed to be a resonance structure involving at least one double bond and at least two radical centers, e.g.,





where the "[·]" indicates a radical center and the notation to the right is that used by MechGen for resonance structures. If there are more than two resonance structures, MechGen assumes that the additions occur only at the position that results in conjugated double bonds, which are estimated to be more stable. This means that addition occurs only at one of the two end groups (e.g, G<sub>1</sub> or G<sub>2</sub>, above) because otherwise the double bonds in the O<sub>2</sub> adduct are not conjugated (e.g, addition to G<sub>3</sub> in the second example above).

If one of the radical centers is estimated to have a rapid  $\alpha$ -scission or cyclopropyl ring opening reaction that is estimated to be faster than O<sub>2</sub> addition under atmospheric conditions as discussed in Sections 3.2.1 and 3.2.2 of the main text, it is assumed that those reactions dominate, so there is no O<sub>2</sub> addition.

If there is no rapid reaction at any of the radical centers, then only O<sub>2</sub> addition is assumed to occur and the relative rates of O<sub>2</sub> addition at the two different positions (e.g., G<sub>1</sub> or G<sub>2</sub>) depend on the nature of the two radical groups or their substituents. It is reasonable to expect that the branching ratio might depend on the differences in heats of reaction for O<sub>2</sub> addition at the different positions. Table S7, which gives heats of reactions for various types of allylic radical center groups that may occur in atmospheric mechanisms, shows that this can vary depending on the number and types of substituents. The quantities used for estimation purposes are  $\Delta\Delta\text{Hr}(G)$ , defined as  $\Delta\text{Hr}(G) - \Delta\text{Hr}(\text{prim})$ , where  $\Delta\text{Hr}(G)$  is the heat of reaction for O<sub>2</sub> addition to radical center G, in an allylic radical where the other radical center is primary (-aCH<sub>2</sub>[·]), and  $\Delta\text{Hr}(\text{prim})$  is the heat of reaction for the addition to the primary radical center in that radical. Note that the estimates for heats of addition to the  $\alpha$ -OH substituted radicals are relative to the O<sub>2</sub> adduct initially formed, not the ultimate carbonyl + HO<sub>2</sub> products. The groups substituted by -ONO<sub>2</sub>, -NO<sub>2</sub>, -OOH, or -OOR groups are not considered in this context because they are expected to undergo rapid  $\alpha$ -scission decomposition before O<sub>2</sub> reaction can occur.

Table S7. Estimated heats of reaction for O<sub>2</sub> additions at various types of radical centers in allylic radicals and relative branching ratio factors derived from them.

Radical Center Group (G) [a]		Heats of Reaction [b]			WtF (G) [c]
		$\Delta\text{Hr}(G)$	$\Delta\text{Hr}(\text{prim})$	$\Delta\Delta\text{Hr}(G)$	
-aCH <sub>2</sub> [·]	Primary	-20.09	-20.09	0	1
-aCH[·]-R	Secondary	-21.58	-19.71	-1.87	1.86
-aC[·](R)-R	Tertiary	-19.43	-19.05	-0.38	1.13
-aCH[·]-OX	Sec. $\alpha$ OH	-23.83	-20.29	-3.54	10.52 [d]
-aC[·](R)-OX	Tert. $\alpha$ OH	-23.65	-21.54	-2.11	6.56 [d]
-aCH[·]-CO-X	Sec. $\alpha$ CO	-17.14	-20.29	3.15	0.35
-aC[·](R)-CO-X	Tert. $\alpha$ CO	-16.54	-20.41	3.87	0.28

[a] G is the radical center where the O<sub>2</sub> addition occurs. R is any alkyl group; X is H or alkyl.

[b]  $\Delta\text{Hr}(G)$  and  $\Delta\text{Hr}(\text{prim})$  are heats of reaction (in kcal/mole) for O<sub>2</sub> adding to radical center G and to a primary radical center on the same allylic radical, respectively, and  $\Delta\Delta\text{Hr}$  is  $\Delta\text{Hr}(G) - \Delta\text{Hr}(\text{prim})$ . Heats of reaction are estimated as discussed in Section S2.1.

[c] Branching ratios are calculated from these factors using Equation (3). Factors are calculated using Equation (1) unless indicated otherwise.

[d] Weighting factors corrected for -OH or -OR substitution are calculated using Equation (2).

We are not aware of systematic or comprehensive studies of branching ratios for competitive additions to allylic radicals, but there is information allowing us to make branching ratios in at least two cases. These are as follows:

- Radicals where  $G_1$  is primary and  $G_2$  is secondary occur in the reactions of OH radicals with 1,3-butadiene and isoprene. The product data for these reactions (Calvert et al., 2000) are consistent with addition to the primary radical occurring ~35% of the time. This is consistent with the estimate that the secondary radical is more stable (see Table S7).
- The theoretical calculations of Xu and Wang (2013) on phenol mechanisms and of Yuan et al. (2017) on furan mechanisms both indicate that  $O_2$  preferentially adds to radical centers with -OH or -OR substituents, instead of those with unsubstituted secondary radical centers. This is consistent with our estimates that the  $O_2$  adduct at the -OH or -OR substituted position is more stable. However, if it is assumed that there is no reaction at the non-substituted positions, we found that the mechanisms significantly underpredict reactivities observed in environmental chamber experiments with phenolic compounds (unpublished results). The data are better predicted if it is assumed that  $O_2$  addition to the non-oh OH substituted position occurs approximately 12% of the time. This is highly uncertain, but at least this provides an additional data point allowing a general estimation method to be derived for cases where there is a relatively large difference in heats of reactions.

It should be noted that this treatment is an approximation because  $O_2$  additions to double bonds are believed to be reversible (e.g., Peeters et al, 2014), allowing re-equilibrium between the various peroxy radicals that could be formed. However, it is difficult to derive general estimation rules that take this into account, and chemical mechanisms with rapid equilibrium processes can be difficult to implement for practical modeling because of mathematical "stiffness". It is also difficult to derive SARs for addition reactions that take into account this reversibility. Making the simplification assumption of site-specificity without re-dissociation gives predictions that are consistent with available experimental data, and using a more complex model with highly uncertain dissociation rate constants may not give predictions that are less uncertain.

Based on this approximation of site-specificity and these two data points, the following estimation method is derived:

$$\text{Default weighting factors:} \quad \text{WtF}(G) = e^{-0.331 \times \Delta\Delta\text{Hr}(G)} \quad (1)$$

$$\text{Weighting } G \text{ is -OH or -OR substituted} \quad \text{WtF}(G)^{\text{corr}} = e^{-0.331 \times [\Delta\Delta\text{Hr}(G) - 5.78]} \quad (2)$$

$$\text{Branching ratios:} \quad \alpha(G_1, G_2) = \text{WtF}(G_1) / [\text{WtF}(G_1) + \text{WtF}(G_2)] \quad (3)$$

where  $\alpha(G_1, G_2)$  is the branching ratio for addition to radical center type  $G_1$  while  $G_2$  is the other radical center type,  $\Delta\Delta\text{Hr}(G)$  is from Table S7, and 0.331 and 5.78 kcal/mole are parameters derived to fit

$$\alpha(\text{primary, secondary}) = 0.35 \text{ and} \\ \alpha(\text{secondary, sec. } \alpha\text{-OH}) = 0.12,$$

based on the data discussed above. Plots of these branching ratios against relative heats of reaction, corrected by subtracting the 3.57 kcal/mole for -OH or -OR substituted radicals, where applicable, are shown in Figure S1.

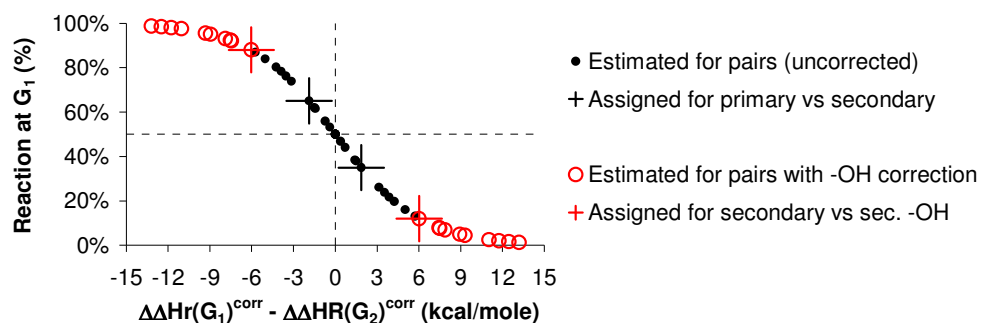


Figure S1. Plots of assigned or estimated fractions of O<sub>2</sub> additions to various radical centers for allylic radicals with various combinations of two radical center types (G<sub>1</sub> and G<sub>2</sub>).

These estimates of branching ratios are quite uncertain both because of the uncertainty in the secondary vs. secondary  $\alpha$ -OH ratio, and because there are no additional data points to verify the appropriateness of the fitting function. These estimates become increasingly uncertain as the magnitudes of the relative heats of reaction increase and should not be used to extrapolate branching ratios for groups other than those listed in Table S7.

#### S1.4.3. Cyclizations of Stabilized Peroxy-Substituted Radicals

Curran et al. (1998) provided estimates for the Arrhenius parameters for estimating rate constants for the decompositions of various QOOH radicals of the type  $\cdot\text{CH}_2(\text{CH}_2)_n\text{OOH}$  as a function of cyclic ether ring size, and these were used as the basis of estimating the importance of these reactions in atmospheric systems. The relevant information is summarized in Table S8, which also includes our heats of reaction ( $\Delta H_r$ ) estimates for these reactions. Plots of the log of the A factor against the ring size and the activation energies against the heats of reaction are shown in Figure S2. Note, however, that this treatment is an approximation because the effective activation energy may not change smoothly with ring size.

Table S8. Data used to estimate rate constants for cyclic ether formation decompositions of radicals with the structure  $\cdot\text{CH}_2(\text{CH}_2)_n\text{OOH}$ .

Ring Size	A [a] (s <sup>-1</sup> )	Ea [a] (kcal/mole)	$\Delta H_r$ [b] (kcal/mole)	k <sub>Isom</sub> [c] (s <sup>-1</sup> )	k <sub>Isom</sub> /kO <sub>2</sub> [d]
3 (n=1)	3.0 x 10 <sup>11</sup>	22.0	-12.81	3 x 10 <sup>-5</sup>	7 x 10 <sup>-13</sup>
4 (n=2)	2.5 x 10 <sup>10</sup>	12.3	-14.48	2 x 10 <sup>-1</sup>	5 x 10 <sup>-9</sup>
5 (n=3)	2.1 x 10 <sup>9</sup>	6.5	-34.32	4 x 10 <sup>4</sup>	1 x 10 <sup>-3</sup>
6 (n=4)	1.5 x 10 <sup>8</sup>	1.8	-39.58	7 x 10 <sup>6</sup>	0.2

[a] From Curran et al. (1998)

[b] Estimated as discussed elsewhere (Carter et al, in preparation, 2022)

[c] Calculated for T=300K using  $k_{\text{Isom}} = A \exp(-E_a/RT)$

[d] Calculated using the pseudo-unimolecular rate constant for O<sub>2</sub> addition of  $3.8 \times 10^7 \text{ sec}^{-1}$ .

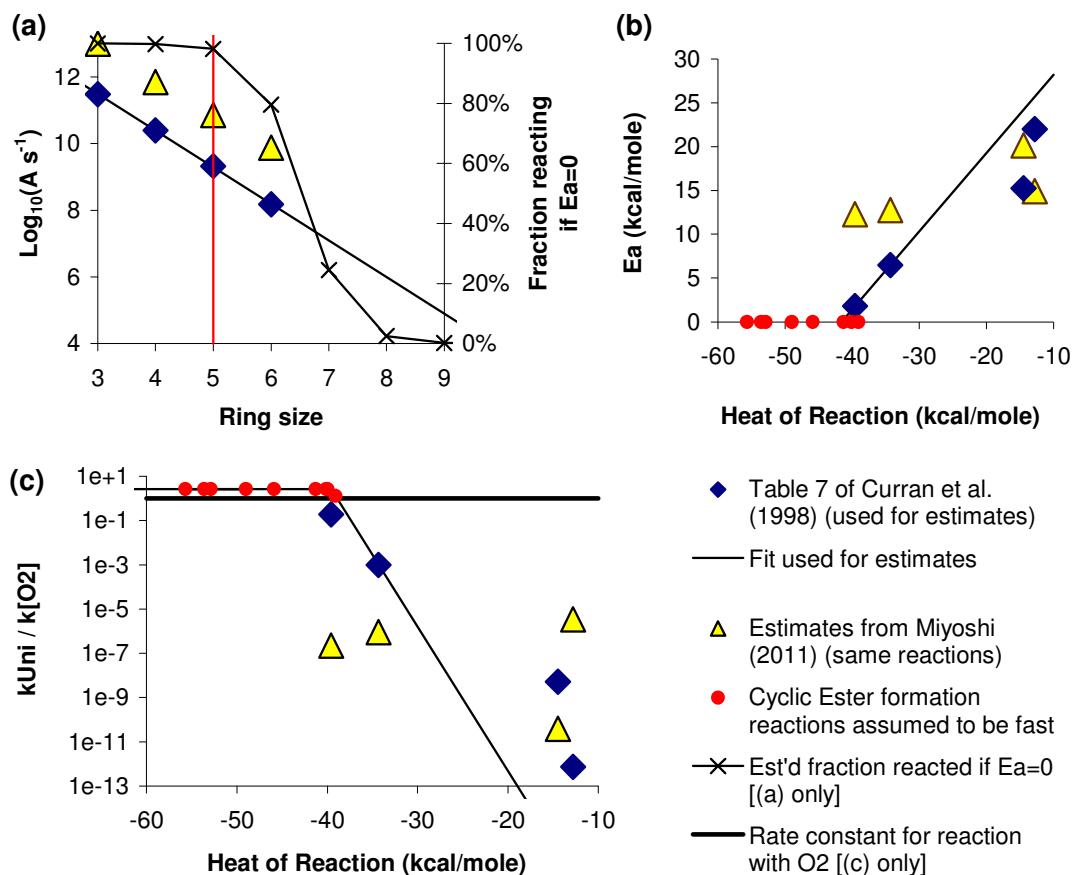


Figure S2. Plots of estimated kinetic parameter data used to derive estimated rate constants for peroxy-substituted radical cyclization decompositions. (a) Plot of estimated A factors against cyclic ether ring size and fractions estimated to react if the activation energy were zero. (b) Plot of estimated activation energies against estimated heats of reactions. (c) Plot of estimated rate constants against heats of reaction.

Table S8 shows that the decompositions of radicals of the type  $\cdot\text{CH}_2(\text{CH}_2)_n\text{OOH}$  are estimated to be slower than  $\text{O}_2$  addition for all ring sizes, though the reaction forming the six member ring may be competitive in some cases. However, these are not the only alkyl radicals that may undergo this type of decomposition, and decompositions for some of these are estimated to be more thermochemically favorable than those listed in Table S8. These are listed in Table S9, along with the estimated heats of reactions for the decompositions forming 5 and 6 member rings, which are estimated to be the most favorable. Note that we are also including reactions involving breaking weak  $\text{O}-\text{NO}_2$  bonds as well as  $\text{O}-\text{O}$  bonds, and reactions of radicals with carbonyl groups and/or carbonyl radicals. Decompositions forming smaller than 5 member rings are less favorable because of ring strain and those forming larger rings are less favorable because of the declining A factor, and are all estimated not to be important.

The rate constants for these reactions are estimated from the data given in Table S8 for radicals of the type  $\cdot\text{CH}_2(\text{CH}_2)_n\text{OOH}$ , assuming that the Arrhenius parameters for the analogous reactions of the radicals of the types listed in Table S9 will have the same dependence on the ring size and heat of reaction. Figure S2 shows that the log of the A factor decreases linearly with size of the ring being

Table S9. Types of cyclization decomposition reactions considered for thermalized carbon-centered radicals. Estimated heats of reaction and estimated ratio of decomposition to O<sub>2</sub> addition are also shown for reactions forming 5- or 6- member rings.

Radical and Reaction Type	$\Delta H_r$ (kcal/mole)		k(isom) / k(R·+O <sub>2</sub> ) [a]	
	Cyc=5	Cyc=6	Cyc=5	Cyc=6
·CH <sub>2</sub> (CH <sub>2</sub> ) <sub>n</sub> OOH → cyc-ether + OH	-34.3	-39.6	0.001	0.2
·CH <sub>2</sub> (CH <sub>2</sub> ) <sub>n</sub> ONO <sub>2</sub> → cyc-ether + NO <sub>2</sub>	-38.2	-43.5	0.3	0.2 - 4 (0.9)
·CH <sub>2</sub> C(O) (CH <sub>2</sub> ) <sub>n</sub> OOH → cyc-β-keto ester + OH	-28.8	-31.7	3x10 <sup>-7</sup>	1x10 <sup>-6</sup>
·CH <sub>2</sub> CH <sub>2</sub> C(O) (CH <sub>2</sub> ) <sub>n-1</sub> OOH → cyc-β-keto ester + OH	-35.3	-38.1	0.004	0.02
·CH <sub>2</sub> (CH <sub>2</sub> ) <sub>n</sub> C(O)OOH → cyc-ester + OH	-41.3	-44.1	3 - 35 (12)	0.2 - 4 (0.9)
·CH <sub>2</sub> (CH <sub>2</sub> ) <sub>n</sub> C(O)OOCH <sub>3</sub> → cyc-ester + CH <sub>3</sub> O.	-45.9	-48.7	3 - 54 (12)	0.2 - 4 (0.9)
·CH <sub>2</sub> (CH <sub>2</sub> ) <sub>n</sub> CO-ONO <sub>2</sub> → cyc-ester + NO <sub>2</sub>	-39.1	-42.0	1.3	0.2 - 4 (0.9)
·CH <sub>2</sub> (CH <sub>2</sub> ) <sub>n</sub> C(O)OONO <sub>2</sub> → cyc-ester + NO <sub>3</sub>	-55.7	-68.3	3 - 54 (12)	0.2 - 4 (0.9)
·CO(CH <sub>2</sub> ) <sub>n</sub> OOH → cyc-ester + OH	-49.0	-51.9	3 - 54 (12)	0.2 - 4 (0.9)
·CO(CH <sub>2</sub> ) <sub>n</sub> OOCH <sub>3</sub> → cyc-ester + CH <sub>3</sub> O.	-53.6	-56.5	3 - 54 (12)	0.2 - 4 (0.9)
·CO(CH <sub>2</sub> ) <sub>n</sub> ONO <sub>2</sub> → cyc-ester + NO <sub>2</sub>	-52.9	-55.7	3 - 54 (12)	0.2 - 4 (0.9)
·CO(CH <sub>2</sub> ) <sub>n</sub> OONO <sub>2</sub> → cyc-ester + NO <sub>3</sub>			Cannot estimate $\Delta H_r$ [c]	
·CO(CH <sub>2</sub> ) <sub>n</sub> C(O)OOH → cyc-anhydride + OH	-40.9	-43.7	3 - 19 (12)	0.2 - 4 (0.9)
·CO(CH <sub>2</sub> ) <sub>n</sub> C(O)OONO <sub>2</sub> → cyc-anhydride + NO <sub>3</sub>	-55.3	-58.2	3 - 54 (12)	0.2 - 4 (0.9)
·CH <sub>2</sub> CH=CH-C(O)OOH → unsat. cyc-ester + OH [b]	-26.0	n/a	4x10 <sup>-9</sup>	n/a
·COCH=CHC(O)OOH → maleic anhydride + OH	-40.1	n/a	3 - 6 (6)	n/a

[a] The rate constant for decomposition is estimated from the ring size and heat of reaction using Equation (S1). The pseudo-unimolecular rate constant for addition of O<sub>2</sub> in the atmosphere is estimated to be 3.8 x 10<sup>7</sup> sec<sup>-1</sup>. If the reaction is estimated to be more endothermic than ~41 kcal/mole the estimated decomposition rate will depend on the minimum activation energy used in Equation (S2). In those cases, three ratios of k(isom)/k(R+O<sub>2</sub>) are given, the first (lowest) ratio being that derived using the upper limit for the minimum activation energy of 1.8 kcal/mole, the second (highest) ratio being that derived using a minimum of zero, and the third (in parentheses) being that derived using a minimum activation energy of 0.9 kcal/mole, half the maximum.

[b] Reaction is much less favorable than the saturated case because of allylic stabilization. Note that this treatment is approximate because it does not take into account the possible reversibility of this reaction in the case of allylic radicals.

[c] Probably even more exothermic than the reaction above, giving similar rate constant estimates.

formed and that the activation energy is correlated with the estimated heat of reaction, with the lines showing the fits used for estimation purposes, as follows:

$$\text{Log}_{10} (A) = 14.78 - 1.10 * \text{ring size} \quad (\text{S1})$$

$$E_a = \max (E_{a_{\min}}, 37.17 + 0.89 * \Delta H_r) \quad (\text{S2})$$

where A is in  $\text{sec}^{-1}$  and  $E_a$  and  $\Delta H_r$  are in kcal/mole. Note that the activation energy estimate uses only the points on Table S8 with the lowest activation energies, because with higher activation energies the rate constant is estimated to be sufficiently slow that the exact magnitude is not relevant. If the estimated heat of reaction is less than around -42 kcal/mole the above equation predicts a negative activation energy, so we must include a minimum activation energy in the estimate. This minimum would be somewhere between 0 and 1.8 kcal/mole, the lowest activation energy listed on Table S8.

Equation (S1) indicates that the estimated A factors for these reactions fall off by more than an order of magnitude with each unit increase in the ring size. This reflects the entropy effects involved with the ring formation reactions. If the activation energy were zero or negligible (or if the radical were highly excited or at a very high temperature) then the rate constant can be approximated by the A factor, i.e., the rate constant if the activation energy were near 0. Figure S2 includes a plot of the reaction estimated to occur via decomposition if the activation energy were near zero regardless of ring size, based on the estimated pseudo-unimolecular rate constant for  $\text{O}_2$  addition as discussed above. It can be seen that even if the energetics were highly favorable, decompositions forming cyclic compounds with more than 7 member rings are unlikely to compete with  $\text{O}_2$  addition, and the possible importance of decompositions forming 6 member depends on uncertainties of the A factor estimates. However, decompositions forming 5-member or smaller rings may be significant if the activation energy were sufficiently low or the excitation were sufficiently high.

Table S9 shows that the reactions of radicals with carbonyl groups or radicals are much more energetically favorable than those of the QOOH radicals whose parameters are given on Table S8, and decomposition is estimated to dominate over addition for the reaction forming the cyclic ester or anhydride with 5-member rings, even with the upper limit minimum activation energy. Cyclizations forming 5-member rings are estimated to be more favorable than cyclizations forming 6 member rings for highly exothermic decompositions because of the higher estimated A factors. For carbonyl radicals whose decompositions form 6-member rings, the estimate of whether decomposition is more important than  $\text{O}_2$  addition depends on the minimum activation energy used in the estimate. The decomposition for these radicals is estimated to be more favorable than  $\text{O}_2$  addition if a zero minimum activation energy is assumed, but it is unlikely that these reactions actually have zero activation energies. If we assume a minimum activation energy of half the minimum shown in Table S8, then the  $\text{O}_2$  addition is estimated to be slightly more favorable, though the relative importance of this reaction in these cases is clearly highly uncertain.

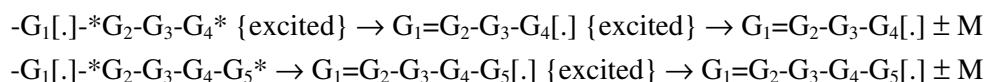
The decompositions of carbon-centered radicals with nitrate groups are estimated to be more favorable than decompositions of carbon-centered hydroperoxy (QOOH) radicals, though not as favorable as decompositions of radicals with carbonyl groups or radicals. However, they are estimated not to be as favorable as  $\text{O}_2$  addition if a minimum activation energy of half the minimum on Table S8 is assumed.

Table S9 also includes some estimates for unsaturated radicals, forming 5-member ring unsaturated cyclic esters or anhydrides. In these cases, the cyclization reaction is estimated to be negligible for  $\alpha$ -unsaturated alkyl radicals because of allylic stabilization, but is estimated to be favorable for  $\alpha$ -unsaturated carbonyl radicals. The latter type of decomposition reactions is predicted to be important in the rapid photolysis reactions of the monounsaturated dicarbonyl products formed in the reactions of aromatics, where radicals of the type  $\cdot\text{C}(\text{O})\text{CH}=\text{CHC}(\text{O})\text{OOH}$  are predicted to be formed

following the O<sub>2</sub> addition and H-shift isomerizations of the initially formed HC(O)CH=CHC(O)· radicals. The decomposition reaction gives rise to OH radicals and maleic anhydride, which is an observed product in the photolyses of these compounds (Calvert et al., 2002, 2011). If O<sub>2</sub> addition dominated, then PAN-type compounds, with significantly different reactivity characteristics, are predicted to be formed instead, and there is no evidence for formation of such products (though they can not entirely be ruled out). This provides additional evidence (albeit indirect) that this type of cyclization reaction occurs in atmospheric systems. Note, however, that Miyoshi (2011) reports results of theoretical calculations of hydroperoxyalkyl rate constants that extrapolate to much lower rate constants at atmospheric temperatures, suggesting that the cyclizations forming 5-member ring esters may not be as fast as estimated using the results of Curran et al. (1998). Therefore, these reactions may only be important for excited radicals. This will need to be re-examined when MechGen is updated, but presently this reaction is still assumed to be fast even for thermalized radicals.

#### S1.4.4. Ring-opening Isomerizations of Excited Radicals

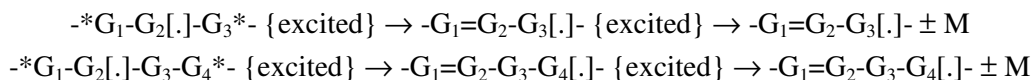
Carbon-centered radicals with 3- or 4-member ring in the β position can also undergo an exothermic ring-opening isomerization, forming a new double bond between what was the radical center and the ring carbon next to it, e.g.,



where "± M" as a product indicates that the radical formed is assumed to be stabilized. Excited radicals of this type can be formed in the reactions of OH with terpenes and other compounds that contain 3- or 4-member rings next to double bonds. For example, Vereecken and Peeters (2012) calculated that the 4-member ring opening reaction of the main radical formed in the reaction of OH radicals with β-pinene occurs ~70% of the time, with ~30% of the radicals formed being stabilized. This is consistent with the observed product data discussed by Vereecken and Peeters (2012) and with theoretical calculations for radicals formed from α-pinene (Peeters et al., 2001) and pinonaldehyde (Fantechi et al., 2002). The fact that at least some stabilization occurs for the excited radical indicates that this sort of decomposition is probably not important once the radicals are stabilized. Analogous ring opening reactions of radicals with 5-member or larger rings are not expected to be important in the atmosphere because they are estimated to be endothermic.

For mechanism generation purposes, we assume that if the radical center is adjacent to a 4-member ring, then the ring opening reaction occurs ~70% of the time, with the remainder being stabilized, as calculated by Vereecken and Peeters (2012) for β-pinene. This is assumed regardless of the size of the radical and substituents involved. Although we are aware of no estimates for analogous ring opening reactions involving 3-member rings, one would expect ring opening to be even more favorable, and we estimate that ring opening dominates over stabilization in these cases.

Similar ring opening reactions can occur if the radical center is in a 3- or 4-member ring, e.g.,



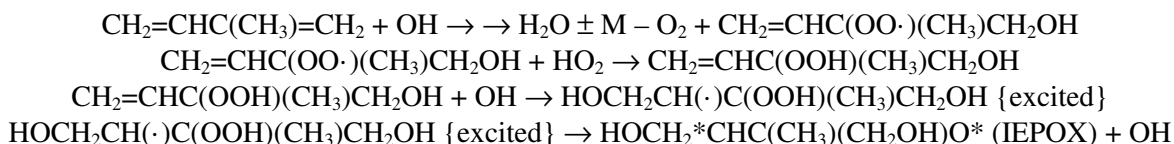
Ring opening of these cyclopropyl radicals occurs not only because it relieves a large ring strain, but also because it forms an allylic stabilized radical. Therefore, for mechanism generation purposes we assume that this ring opening dominates even for thermalized radicals. On the other hand, ring opening of the cyclobutyl radicals relieves less ring strain and also does not form allylic radicals, and we estimate this will not compete with O<sub>2</sub> addition for stabilized species. However, the ring opening of the cyclobutyl

radicals is estimated to have comparable thermochemistry as ring opening of radicals adjacent to cyclobutyl rings, so we assume that excited cyclobutyl radicals undergo ring opening ~70% of the time, consistent with what is assumed for ring opening of radicals adjacent to cyclobutyl rings, as discussed above. Excited radicals like these would be formed following OH addition to cyclopropenes and cyclobutenes, but such compounds are not expected to be important in atmospheric systems, so these estimates for excited radicals probably do not affect generated mechanisms of interest. On the other hand, stabilized  $\alpha$ - radicals of this type may be formed in decomposition reactions, so estimates of their reactions need to be considered when generating mechanisms.

#### S1.4.5. Cyclizations of Excited Peroxy or Nitrate Substituted Radicals

As discussed in the previous section, cyclization of thermalized peroxy-containing carbon-centered radicals forming cyclic compounds with 4-member rings and smaller, or of such radicals not containing carbonyl groups, are estimated to be too slow to compete with O<sub>2</sub> addition because of the effect of ring strain on activation energies. However, the reactions forming the smaller rings would be more favorable for chemically activated radicals and may be sufficiently fast to dominate over stabilization to form thermalized radicals that react primarily with O<sub>2</sub>. On the other hand, as discussed above, reactions forming 7-member or larger rings are estimated not to compete even if the excitation were sufficiently high to make the effective activation energy near zero (see Section S1.4.2). The situation with reactions forming 6-member rings is more uncertain, but as discussed above, these reactions are also assumed not to be important for thermalized radicals, and this is also assumed for excited radicals as well.

Evidence for the importance of enhanced decompositions of chemically activated carbon-centered radicals forming products with 3-member rings (epoxides) comes from the observation of OH-substituted epoxides (IEPOX) in the reactions of isoprene under low-NO<sub>x</sub> conditions. This is attributed to the following types of reactions (Paulot et al., 2009):



Where “ $\pm$  M” indicates stabilization, “{excited}” indicates excitation, and “\*” indicates ring closure. The OH addition reaction has about 30 kcal/mole excess energy, apparently sufficient to overcome the ring strain barrier involved with forming the epoxide and such that the cyclization decomposition of the excited radical competes with stabilization. Note that SPARC-18/22 does not have an “IEPOX” model species and lumps this as ALK5.

Based on this, for mechanism generation purposes, we assume that if a hydroperoxy-substituted carbon-centered radical formed following OH addition to double bonds can undergo a cyclization isomerization to form an epoxide, then the cyclization dominates. Similar reactions are assumed for peroxide, nitrate, and peroxy-nitrate-substituted radicals, since the energetics and transition states are expected to be similar (see Table 6 in the main text). Although stabilization may occur to some extent, for simplicity we assume it is negligible under atmospheric conditions. It is uncertain whether such rapid isomerization of chemically activated radicals also occurs when the isomerization forms 4-member or larger rings, since formation of larger rings becomes less favorable from an entropy standpoint, even though there is less ring strain energy to overcome. We arbitrarily assume that isomerization is not important for chemically activated carbon-centered radicals with peroxy substituents if larger than 3-member rings are formed, since we are not aware of any evidence for such reactions, though they cannot be ruled out. Note that as discussed in the previous section, isomerization may still dominate for some thermalized radicals forming 5-member rings, but not those forming other sized rings.



Note that additions of NO<sub>3</sub> or Cl to double bonds are estimated to form adducts with ~10 kcal/mole less excitation than those formed by OH additions. For that reason, we tentatively assume that this reaction is only important for adducts formed following OH addition. This is uncertain.

If the excited radical can undergo more than one type of 3-member ring cyclization reaction, then it is assumed that all such reactions are equally likely. If the radical or one of its resonance structures can also undergo rapid  $\beta$ -scission decompositions, as discussed in Section 3.2 of the main text, then the  $\beta$ -scission decompositions are assumed to dominate since they are estimated to be more favorable from an entropy standpoint.

Additional decomposition reactions are possible if the peroxy-containing radical has a carbonyl group adjacent to the radical center, such as the radicals formed after OH adds to the unsaturated PAN and the peroxy acid compounds formed as products in organic photooxidation reactions of isoprene and other di- and polyunsaturated compounds. Evidence for decompositions of radicals formed from unsaturated PANs and peroxy acids comes from both experimental data and quantum calculations (Paulot et al., 2009; Kjaergaard et al., 2012; Lin et al., 2013). These were used as the basis for the branching ratio estimates used for mechanism generation that are shown in Table S10. Table S10 summarizes the types of reactions that can occur, including the assumed branching ratios and the analogous reactions and branching ratios for the non-carbonyl containing radicals discussed above. Footnotes indicate how the estimates were derived.

Note that the branching ratio estimates in Table S10 are based on data for a limited number of compounds, and the assumption that they can be generalized to other compounds regardless of size or substituents is uncertain. Also, it is somewhat inconsistent to assume no stabilization for non-carbonyl containing radicals and non-negligible stabilization if a carbonyl group is present. Therefore these branching ratios should be updated once there is sufficient experimental or theoretical data available to make better estimates of how these branching ratios depend on structure.

As discussed in the main text, we assume that all adducts formed following NO<sub>3</sub> or Cl additions to double bonds are all stabilized, based on their lower estimated excitation energy.

## **S1.5. Reactions of Peroxy Radicals**

### **S1.5.1. Bimolecular Rate Constants**

Table S45 (given in Section S5.2 at the end of this document because of its size) gives a summary of the experimental rate constant data for bimolecular reactions of peroxy radicals that served as the basis for the bimolecular rate constant assignments used by MechGen, also in the table (as well as in Table 8 of the main text). Footnotes give the sources of the rate constants and the basis for the various assignments. Note that this does not yet incorporate rate constant measurements or recommendations made available after 2019.

For the reactions of peroxy radicals with NO, NO<sub>2</sub>, and NO<sub>3</sub>, and the reactions of acyl peroxy radicals with HO<sub>2</sub>, the recommended rate constants are based on measurements for ethyl peroxy and either ethyl acyl peroxy if data are available or acetyl peroxy otherwise. High pressure limits are used for rate constants that are pressure dependent (e.g., with NO<sub>2</sub>), since the estimates are generally applied to larger peroxy radicals that are more likely to be stabilized under atmospheric conditions. In most cases these recommended rate constants are reasonably consistent with the available measured values for the higher peroxy radical, though there is some data suggesting that C<sub>6+</sub> compounds may have lower rate constants, as indicated in Figure S3. However, the two C<sub>7+</sub> compounds with the lower rate constants may

Table S10. Branching ratios assumed for reactions of excited radicals formed from the additions of OH to  $\beta$ -peroxy substituted substituents.

Products of reactions of -G <sub>1</sub> (OH)-G <sub>2</sub> [.] -CO-O-OX {OHadd}	Route Designation	Branching Ratios Assumed [b]			Rxn Notes [c]
		X= -H	X= -R	X= -NO <sub>2</sub>	
→ -G <sub>1</sub> (OH)-G <sub>2</sub> [.] -CO-O-OX ± M	Stabilization	82%	40%	20%	1
→ -G <sub>1</sub> (OH)-*G <sub>2</sub> -CO-O* + [.]OX	$\alpha$ -Lactone	14%	45%	60%	2
→ -*G <sub>1</sub> -O-G <sub>2</sub> *-CO-OH + [.]OX	Acid epoxide	5%	15%	20%	3
→ -G <sub>1</sub> (OH)-G <sub>2</sub> =O + CO + ·OX	Ketone CO	~0%	~0%	~0%	4
	Ratio Notes [c]:	5	6	7	

[a] G<sub>1</sub> and G<sub>2</sub> are either -CH<sub>2</sub>- or -CH(-) groups. X is -H, -alkyl (-R) or -NO<sub>2</sub>.

[b] These are the branching ratios used by the mechanism generation system for 1 atmosphere of air, independent of temperature.

[c] Notes on derivations of the branching ratios:

- 1 If the pressure is different from one atmosphere, the branching ratios are recalculated assuming that the stabilization rate is proportional to pressure, with the decomposition fractions normalized to 1. Although stabilization should get more favorable as the size of the molecule increases, this is ignored in the present system.
- 2 This is the same mechanism as the "epoxide" route that is assumed to dominate if no carbonyl group is present.
- 3 This requires that both a  $\alpha$ -carbonyl and  $\beta$ -OH groups are present. The cyclization involves the H from OH migrating to the peroxy oxygen adjacent to the carbonyl group, with the O on the OH adding to the radical center to form the epoxide.
- 4 This could occur by a CO elimination reaction of the initially formed excited  $\alpha$ -lactone. The branching ratios derived by Lin et al. (2013) for X = -NO<sub>2</sub> and by Kjaergaard et al. (2012) for X = -OH suggest that this is a relatively minor pathway, so it is ignored for mechanism generation purposes. However, Kjaergaard et al. (2012) derived higher branching ratios for this route for X = -NO<sub>2</sub>.
- 5 The relative yields for decomposition via the  $\alpha$ -lactone route is the averages of the yields calculated by Kjaergaard et al. (2012) et al. for CH<sub>2</sub>=CHC(O)OOH and CH<sub>2</sub>=C(CH<sub>3</sub>)C(O)OOH. Although they did not consider the acid epoxide route in their calculations, we estimate that the ratio of the acid epoxide to  $\alpha$ -lactone route for X = -OH is the same as derived for X = -NO<sub>2</sub> (see note 7). The ketone CO route may occur to some extent but appears to be minor and is ignored.
- 6 The rate constants relative to stabilization for both the  $\alpha$ -lactone and acid epoxide decompositions were estimated assuming a linear relationship between the decomposition rate constant and the overall heat of reaction starting with OH addition, and using relative rate constants derived for the corresponding reaction of the OH adduct for CH<sub>2</sub>=CHC(O)OOH and CH<sub>3</sub>CHC(O)OONO<sub>2</sub>. A separate linear relationship is used for each type of reaction.
- 7 The branching ratios are based on theoretical and experimental results of Lin et al. (2013) for CH<sub>3</sub>CHC(O)OONO<sub>2</sub>. They estimate a branching ratio of ~3% for the ketone CO route, but this is ignored and the 3% is added to the  $\alpha$ -lactone route. These branching ratios are applied to all carbon-centered radicals of this type.

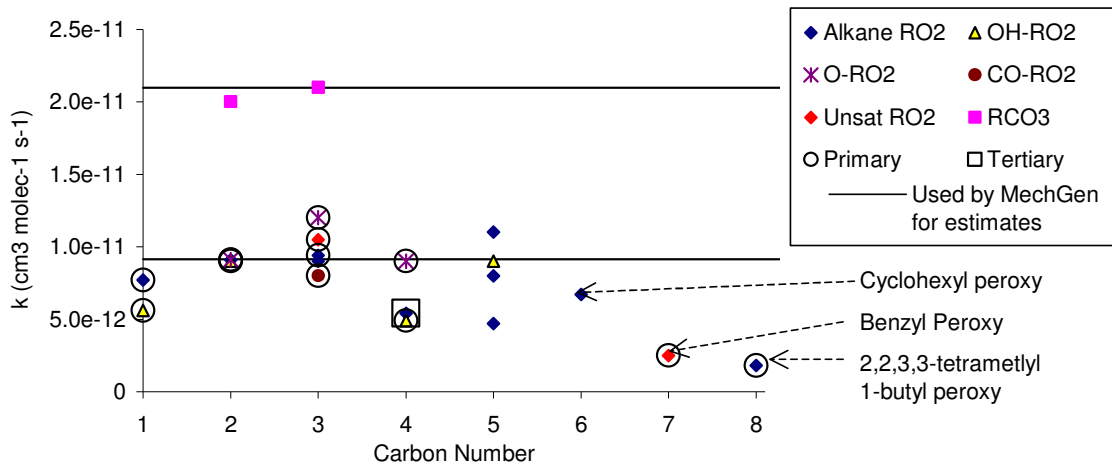


Figure S3. Plots of measured and assigned rate constants for peroxy + NO reactions against the number of carbons in the radical.

not be representative of other types of alkyl peroxy radicals, so we currently retain the approximation that rate constant is independent of molecule size.

In contrast to peroxy radicals, Table S45 indicates that alkyl peroxy + HO<sub>2</sub> rate constants tend to increase with carbon number, as also shown in Figure S4, which plots the measured rate constants against carbon number. They also tend to be somewhat higher for peroxy radicals containing -OH groups for carbon numbers less than about 7, except for benzyl peroxy, which seems to be an outlier (as it is for the NO rate constant, as seen in Figure S3). The available data are reasonably well fitted by:

$$k(\text{RO}_2 + \text{HO}_2) = 10^{-12} \times \min [20.3, 2.48 + (2.48 \times nC)] \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

$$k(\text{HO-RO}_2 + \text{HO}_2) = 10^{-12} \times \min [21.1, 9.37 + (1.68 \times nC)] \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1},$$

where "HO-RO<sub>2</sub>" indicates peroxy radicals with -OH substituents, "RO<sub>2</sub>" are those without -OH, and "nC" is the number of carbons in the radical.

These equations, whose predictions are also plotted in Figure S4, are used by MechGen to estimate the HO<sub>2</sub> rate constants. It is unclear why benzyl peroxy radicals would be an outlier in terms of dependence on carbon number, though the magnitude of the rate constant is very close to that for the C<sub>3</sub> unsaturated peroxy radical in our data set. Data are needed for a wider variety of types of peroxy radicals in order to refine our estimates for these rate constants and how they depend on radical size. Our estimates are based primarily on data for alkane RO<sub>2</sub>'s and those with only one OH substituent, and should be considered to be uncertain by about a factor of 2 for other types of peroxy radicals. This is similar to the level of uncertainty for our estimates for higher acyl peroxy radicals.

Table S45 indicates that the only measured rate constant for the reactions of acyl peroxy radicals is that for acetyl peroxy. Based on this, we use

$$k(\text{RCO}_3 + \text{HO}_2) = 3.14 \times 10^{-12} \exp(-580/T) = 2.2 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

independent of carbon number of substituents.

Table S45 shows that the rate constants for peroxy + peroxy reactions vary by many orders of magnitude, though they tend to be consistent at least to within an order of magnitude for radicals of the same type. The most important factor is whether the radical is primary, secondary, or tertiary, with rate

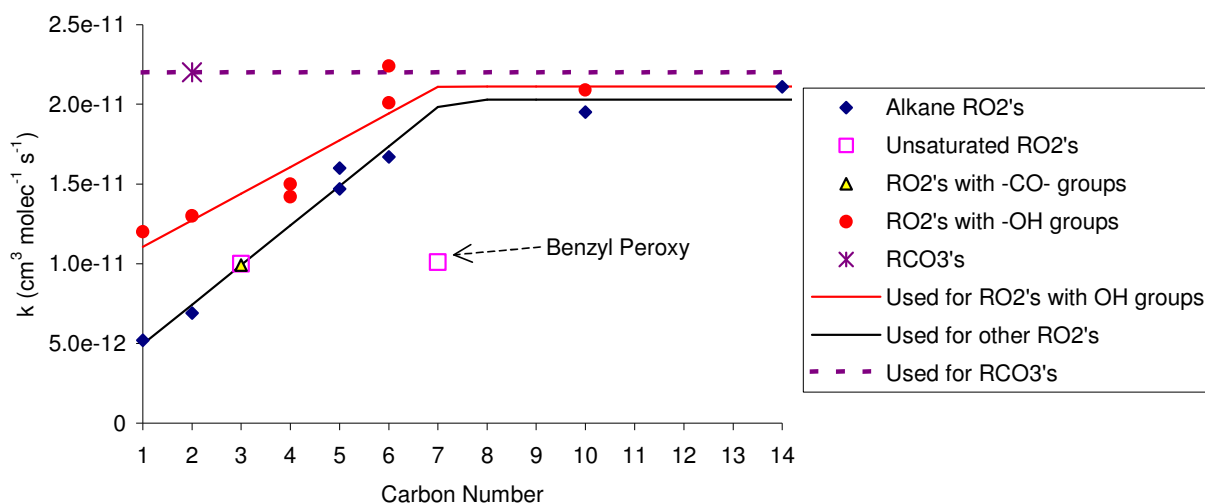


Figure S4. Plots of total rate constants for the reactions of various types of peroxy radical with HO<sub>2</sub>, against the number of carbons in the radical.

constants for tertiary radicals being particularly low. Radicals with -OH substitution also have significantly higher rate constants, especially for tertiary + tertiary reactions. This is shown in Figure S5, which compares the averages and standard deviations of the logs of the rate constants. The rate constants that MechGen assigns for the reactions of the various types of radicals with generic peroxy radicals ("GenRO2") are also shown, where the "error bars" show possible ranges of rate constants for various types of radicals.

Because of the large number of peroxy radicals involved in atmospheric photooxidation mechanisms, it is not practical to include all the peroxy + peroxy combinations in large mechanisms and thus these reactions are generally implemented in explicit mechanisms by reactions of the individual peroxy radicals with generic peroxy radicals. MechGen uses rate constants estimated for secondary peroxy radicals to represent the generic radicals because they are intermediate in magnitude compared to primary or tertiary radicals, and because secondary radicals are expected to be most frequently formed. It is also assumed that the generic peroxy radical is not OH-substituted, though this assumption has not been evaluated. In the case of non-OH substituted reactions, the generic rate constants used are based on geometric means for the peroxy + secondary rate constants. However, there does not appear to be rate constant data for OH-substituted peroxy radicals reacting with non-OH-substituted secondary radicals, so they have to be estimated. We currently estimate these generic rate constants for OH-substituted radicals as follows, where "xOH" refers to the OH-substituted radicals, and "x" can be either primary, secondary, or tertiary.

$$k(xOH+GenRO_2) \approx k(x+GenRO_2) \times \text{SQRT} [ k(xOH+xOH) / k(x+x) ]$$

The appropriateness of this estimate, as well as the other assignments for peroxy + generic peroxy rate constants, is uncertain. However, uncertainties in these estimates are not expected to have large effects on predictions when using the mechanisms for atmospheric simulations because peroxy + peroxy reactions are generally not important loss processes for peroxy radicals compared to reactions with NO<sub>x</sub> species and HO<sub>2</sub>.

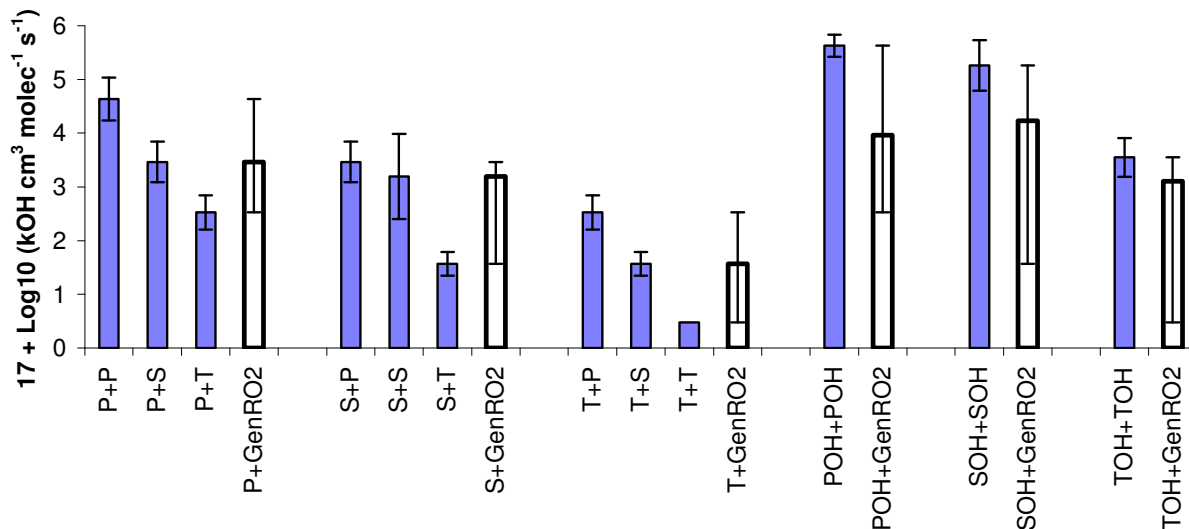
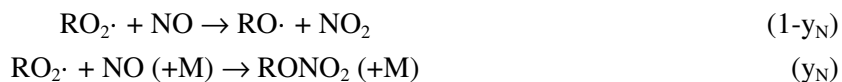


Figure S5. Averages of experimental peroxy + peroxy rate constants of various types, and rate constants assigned by MechGen for peroxy + generic peroxy reactions. Note that the rate constants are multiplied by  $10^{17}$  to give the logs positive magnitudes; "P", "S", and "T" refer to primary, secondary, and tertiary radicals, respectively, that do not have -OH substituent; "POH", "SOH", and "TOH" refer to OH-substituted radicals; "GenRO2" refer to generic peroxy radicals.

### S1.5.2. Nitrate Yields in Peroxy + NO Reactions

Peroxy radicals react with NO via two routes, one being radical propagating and leading to the formation of  $O_3$  in atmospheric systems, and the other being radical terminating, leading to a  $NO_x$  sink. The competing reactions are:



where  $y_N$  is the nitrate yield in the reaction. Because of the importance of peroxy + NO reactions, the nitrate yield is an important parameter affecting simulation results of VOC reactions in atmospheric systems. Note that nitrate formation is not believed to be important in the case of reactions of acyl peroxy radicals ( $RCO_3$ ) with NO.

There have been a number of experimental measurements of nitrate yields from the reactions of NO with various peroxy radicals. In some cases where there are no direct experimental data, the nitrate yields can be estimated by adjustments to fit results of environmental chamber experiments that are sensitive to this parameter. Available data concerning experimentally-derived nitrate yields that were used in deriving estimates for MechGen are summarized in Table S46 through Table S48 in Section S5.2, and the yields measured around 300 K and atmospheric pressure are plotted against carbon number in Figure S6. Figure S7a shows the range of temperatures and pressures for which yield data are available, and shows how well the predicted yields, discussed below, agree with these data. The data indicate that the yields increase with increasing carbon numbers and pressure, and with decreasing temperatures, can potentially vary depending on the structure of the radical and the presence of oxygenated substituents.

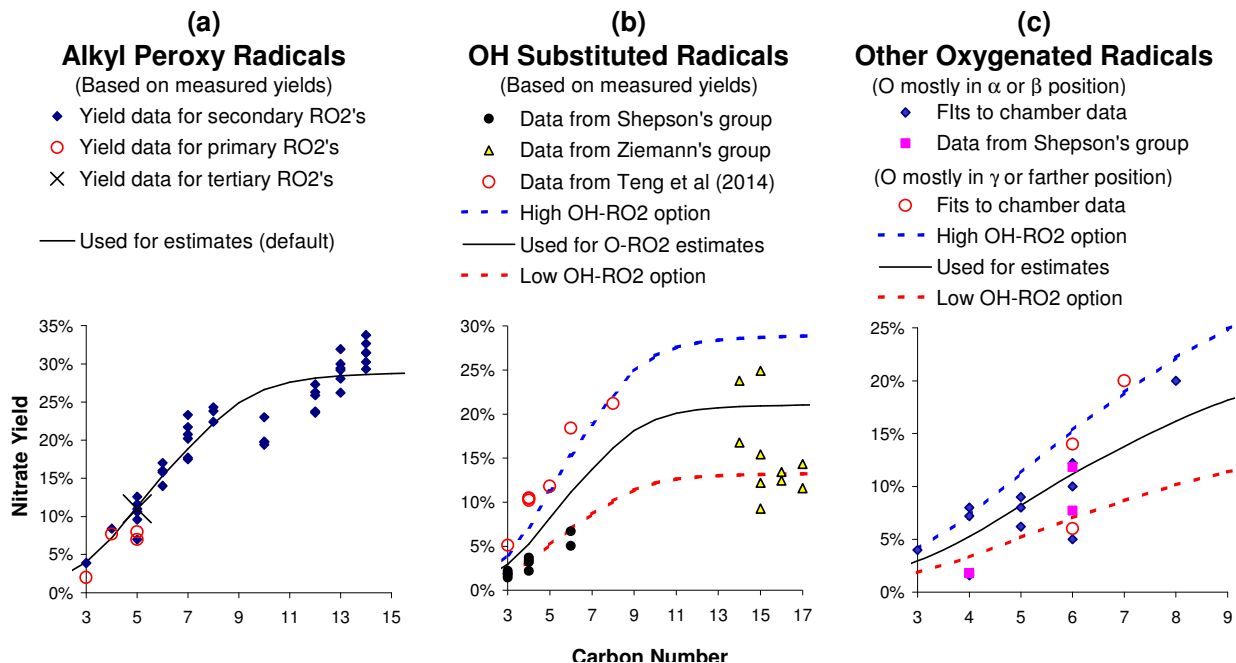


Figure S6. Experimental and estimated nitrate yields against carbon numbers for the reactions of various types of peroxy radicals at  $\sim 298\text{K}$  and 1 atmosphere pressure.

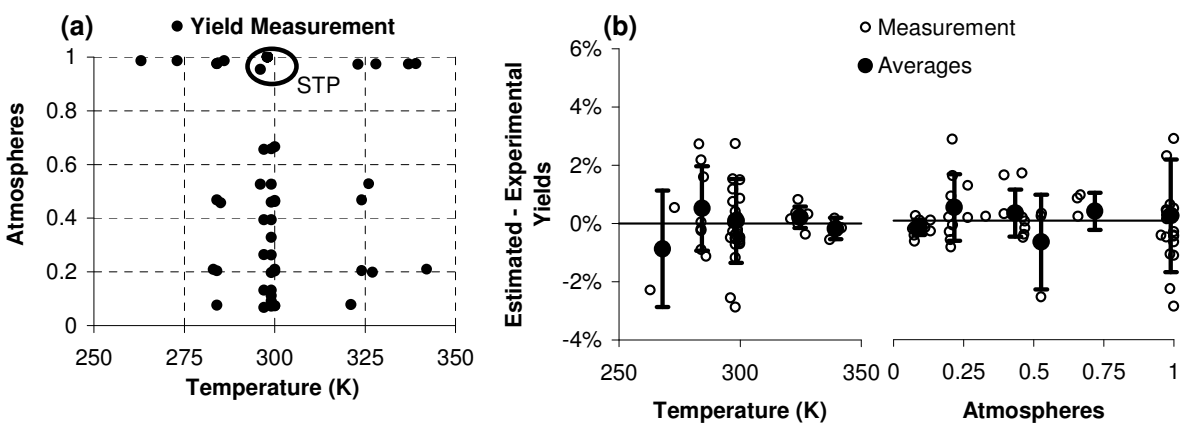
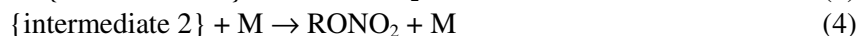
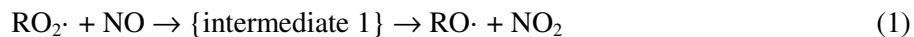


Figure S7. Range of temperatures and pressures where nitrate yield measurements were made for alkyl peroxy radicals and relative differences between experimental and estimated yields as a function of temperature and pressure.

As discussed by Zhang et al. (2004), the general mechanism for RO<sub>2</sub> + NO reaction is believed to be as follows:



where the intermediates refer to different configurations of excited RO<sub>2</sub> + NO adducts. Based on the parameterization first proposed by Atkinson et al. (1983), which in turn was based on the parameterization developed by Troe (1974) for reactions in the pressure fall-off regime, we employ the following equations and parameterization to estimate nitrate yields for various types of radicals as a function of carbon number, temperature, and pressure, revised somewhat to take the above mechanism into account:

$$y_N = \text{Corr} \times \text{fac} \times (k_4/k_3) / [1 + (k_4/k_3)]$$

where  $y_N$  is the nitrate yield, Corr is an adjustment depending on substituents in the radical (with Corr=1 used for alkyl peroxy radicals), fac is an adjustable parameter derived to fit the data for secondary peroxy radicals, and  $(k_3/k_4)$  is an intermediate in the calculation, determined by:

$$(k_4/k_3) = [Y_0 \times M / (1 + Y_r)] \times F^Z$$

$$Y_0 M = \alpha \times e^{\beta nC} \times [T/300] \times m_0 \times P_{\text{atm}}$$

$$Y_r = Y_0 \times M / \{ Y_\infty [(T/300)^{m_\infty}] \}$$

$$Z = 1 / [1 + \log_{10}(Y_r)^2]$$

where  $Y_0 M$ ,  $Y_r$ , and  $Z$ , are also intermediates in the calculation, and  $\alpha$ ,  $\beta$ ,  $Y_\infty$ , and  $m_\infty$  are additional parameters adjusted to fit the data. The inputs are  $nC$ , the carbon number;  $T$ , the temperature in K; and  $P_{\text{atm}}$ , the pressure in atmospheres. The primary difference from parameterizations used for previous SAPRC mechanisms (e.g., Carter, 2010a,b; Carter and Heo, 2013) is the addition of "fac" as an adjustable parameter to incorporate the effect of the two intermediates.

The largest amount of consistent data is available for nitrate yields from secondary peroxy radicals; the data available at ~298K and 1 atmosphere are summarized in Table S46 and the yields at different temperatures and pressures summarized in Table S47. The parameter values derived in this work to fit these data are given in Table S11. Figure S6a shows plots of the experimental and estimated nitrate yields for secondary radicals against carbon number. Figure S7b shows that the estimates fit the data at the different temperatures and pressures about as well as they do at 298 K and 1 atmosphere.

Table S11. Parameter values used to predict nitrate yields in peroxy + NO reactions as a function of carbon number, temperature, pressure, and the presence of non-alkyl groups.

(a) Parameter values [a]				(b) Correction factors	
Parameter	Value	Parameter	Value	Case used for	Corr
Corr	See (b)	$y_\infty$	5.21	Default and high OH-RO <sub>2</sub> option	1
Fac	0.34	$m_0$	-2.05	Used for OH and O-substituted RO <sub>2</sub> 's	0.73
$\alpha$	0.015	$m_\infty$	-14.12	The following used for Figure S8 only	
$\beta$	0.81	F	0.497	Low OH-RO <sub>2</sub> option	0.46

[a] These values are based on units of K for temperature and atmospheres for pressure.

The limited available data for primary and tertiary nitrate yields from alkanes are given at the top of Table S48, and those for ~289 K and 1 atmosphere are included in Figure S6a. The data are insufficient to use different parameters for secondary or tertiary radicals, so, unlike previous parameterizations (e.g., Atkinson et al., 1983), no corrections are made.

It is assumed that substituents more than two carbons away from the carbon bonded to the peroxy group has no effect on the nitrate yield, though this is uncertain. In such case, the parameterizations for unsubstituted alkyl peroxy radicals are used. However, the effects of substituents in the  $\alpha$  or  $\beta$  positions need to be considered. The most important example is  $\beta$ -OH substituted peroxy radicals formed after OH adds to double bonds and then adds O<sub>2</sub>. However, peroxy radicals with other types of substituents in the  $\alpha$  or  $\beta$  position will also be formed in reactions of non-hydrocarbon VOCs, so nitrate yields in their reactions also need to be considered.

There is a fair amount of data on nitrate yields on the  $\beta$  OH-substituted peroxy radicals formed after OH adds to double bonds and then adds O<sub>2</sub>. These data come from four types of sources: (1) data from Shepson's group (Shepson et al., 1985; Muruthamu et al., 1993; O'Brien et al., 1998) where the nitrates were monitored by combination of capillary chromatography and an organic nitrate specific chemiluminescence detector; (2) data from Ziemann's group (Matsunaga and Ziemann, 2009, 2010) where the nitrates were monitored in the particle phase using a thermal desorption particle beam mass spectrometer coupled to a high-performance liquid chromatograph (HPLC) with UV-vis detector for identification and quantification; (3) more recent data from Teng et al. (2014) where gas chromatography with both CF<sub>3</sub>O-CIMS and thermal dissociation NO<sub>2</sub> laser-induced fluorescence was used to quantify the nitrates.

Figure S6b shows that the data from the three methods are not in good agreement. The data from Teng et al. (2014) are in reasonable agreement with the yields predicted by the parameterization that fit the secondary nitrate yields from alkane systems (using Corr = 1), while the data from Shepson's and Ziemann's groups indicate that the nitrate yields are about half that much, being much better fit using Corr = 0.46. Note that hydroxy-substituted nitrates tend to be "sticky" compounds that may be lost to reactor walls, so the measured yields may be low in some experimental systems. The parameterization that fit the latter set of data is referred to as the "Low OH-RO<sub>2</sub>" option on Table S11 and Figure S6, while the parameterization that was derived from the secondary alkyl peroxy data is referred to as the "default" or "High OH-RO<sub>2</sub>" option.

Nitrate yields from  $\beta$ -substituted peroxy radicals are important parameters affecting the effect of alkene reactions on radical levels. It was found that results of alkene-NO<sub>x</sub> chamber experiments are sensitive to this parameter for alkenes larger than propene during the evaluation of SAPRC mechanisms (e.g., Carter, 2000, 2010a). This is not a good way to derive nitrate yields because of uncertainties in other aspects of alkene mechanisms that affect radical levels (particularly Criegee reactions, discussed in Section A2.7), and other uncertainties involved in modeling chamber experiments, but may be useful in determining which option might be best for estimation purposes. Figure S8 shows biases and errors in model simulations of O<sub>3</sub> formation rates calculated using updated versions of the SAPRC-18 mechanism (Carter, 2020) with differing options for the correction factors when calculating nitrate yields from  $\beta$ -substituted peroxy radicals given on Table S11b. The formation rates are measured by rates of change of  $\Delta([O_3]-[NO])$  during the period when O<sub>3</sub> is forming, as discussed by Carter (2010a). About half of the experiments are better simulated using the high OH-RO<sub>2</sub> option, most of the rest are better simulated using the low option. Therefore, fits to the chamber are too variable to use when deciding which option is



better to adopt for estimates, except to indicate that it is likely to be between the low and high option. Using a correction factor between the two extremes significantly reduces the average bias for all compounds studied, and slightly reduces the average error.

Table S48 and Figure S6c show that there are some scattered data concerning nitrate yields from peroxy radicals with ether, carbonyl, or ester substituents (Jenkin et al. 2019 and references therein). They tend to be lower than yields from unsubstituted peroxy radicals, and much lower in a few cases. Most of these data come either from measurements of unspiciated nitrate yields formed in reactions of OH with various oxygenated compounds, or derived from fits of model simulations to environmental chamber data. Use of unspiciated nitrate yields from compounds to estimate yields from specific radicals have uncertainties concerning relative formation rates of various peroxy radical isomers (including those formed following reactions of alkoxy radicals), and also have calibration uncertainties. Yields derived from adjustments of model simulations to chamber data have even more uncertainties, since this is a very indirect method that can be strongly affected by uncertainties in other aspects of the compounds' mechanisms and also uncertainties in characterizations of chamber conditions. These considerations may play a role in the relatively large scatter in the data shown in Figure S6c. However, most of the data are between the high and low estimates used for the OH substituted radicals, though there are cases where nitrate yields below the low estimates are derived.

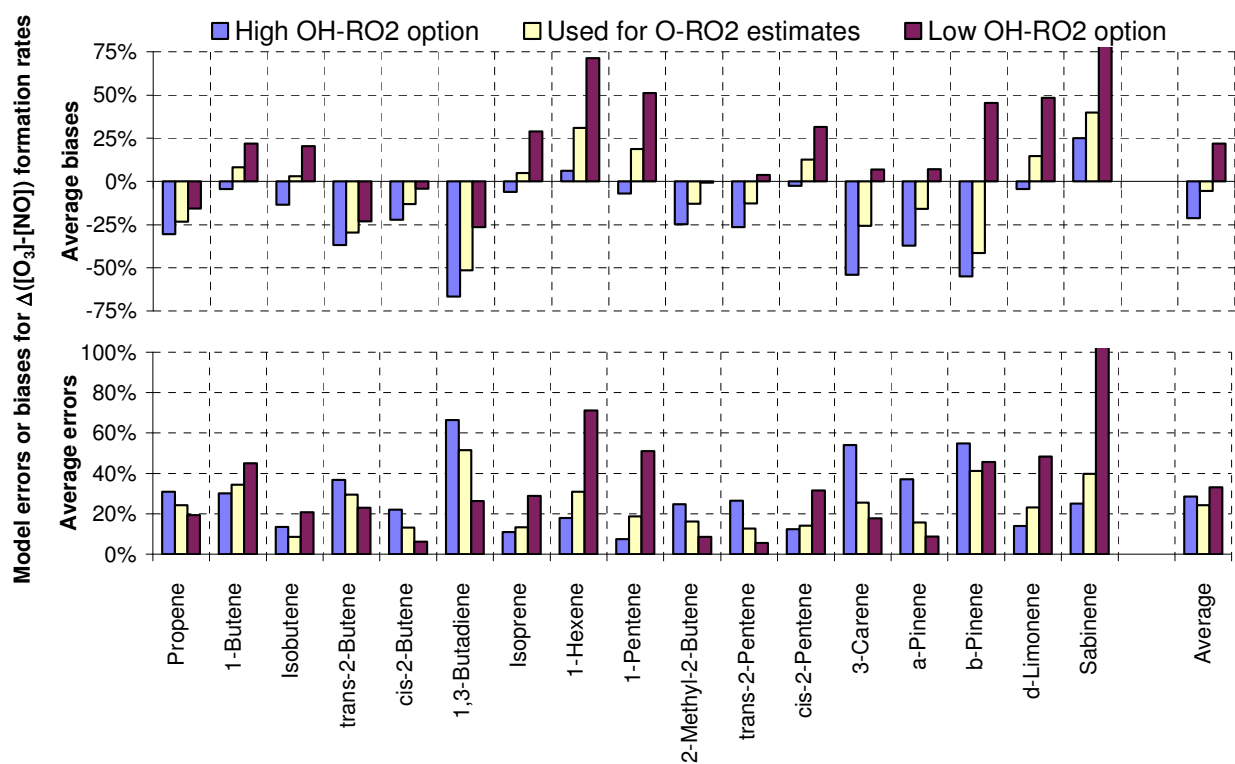


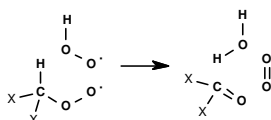
Figure S8. Comparisons of average biases and errors in model simulations of initial rates of change  $\Delta([O_3]-[NO])$  in various alkene -  $NO_x$  chamber experiments used for evaluating SAPRC mechanisms, calculated using various options for estimating nitrate yields from OH-substituted peroxy radicals.

Until this inconsistency in the nitrate yield data for  $\beta$ -hydroxy nitrates is resolved and we have more consistent data on nitrate yields from other  $\alpha$  and  $\beta$ -substituted peroxy radicals, we use a correction

factor halfway between the high and low OH-RO2 options for estimates for all peroxy radicals with oxygen atoms in the  $\alpha$  or  $\beta$  positions, regardless of whether they are or are in alcohol, ether, or ester groups. This is similar to the approach used by Jenkin et al (2019). We also use this correction factor for peroxy radicals with nitrate substituents in the  $\alpha$  or  $\beta$  positions, based on the assumption that their effects are similar to -O- or -OH substitution, and which is also assumed by Jenkin et al (2019). MechGen currently makes no corrections for substituents with only carbonyl groups because this was assumed during the derivation of the SAPRC-22 mechanism (Carter, 2023a), though this will probably be revised when MechGen is updated, especially since Jenkin et al. (2019) uses a correction factor of 0.3 for such compounds. We tentatively assume that nitrate yields with substituents more than two carbons away from the peroxy groups are the same as for unsubstituted peroxy radicals. These estimates must be considered uncertain by at least a factor of two and are more likely to be biased high than low. The estimates are even more uncertain for peroxy radicals with other types of substituents, for which no correction is currently made. Clearly there is a need for additional work on nitrate yields from substituted peroxy radicals.

### S1.5.3. Mechanisms for peroxy + HO<sub>2</sub> reactions

Available data concerning mechanisms for the reactions of various peroxy radicals with HO<sub>2</sub> have been reviewed by IUPAC (2023), and their recommendations are summarized on Table S12. Note that these include only primary peroxy radicals and only one acyl peroxy radical. Because of insufficient data, we assume that the mechanisms for secondary and tertiary peroxy radicals are analogous to those for the primary radicals shown on Table S12 and are independent of substituents other than -OH, -O-, or -CO- on the same carbon as the peroxy group. However, the reaction forming "RCHO + H<sub>2</sub>O + O<sub>2</sub>" involves the intermediacy of a hydrogen shift from the carbon bonded to the peroxy group,



so this type of reaction cannot occur with tertiary peroxy radicals. In those cases where this reaction is predicted to occur for primary and secondary radicals, we add the branching ratio assigned for this reaction to that for the "ROOH + O<sub>2</sub>" route when making predictions for tertiary radicals.

Table S12. Current IUPAC recommendations for the products formed in the reactions of HO<sub>2</sub> with various primary peroxy and acyl peroxy radicals.

Radical	Reaction products and recommended branching ratios [a]			
	ROOH + O <sub>2</sub>	RCHO + H <sub>2</sub> O + O <sub>2</sub>	RO + OH + O <sub>2</sub>	ROH + O <sub>3</sub>
CH <sub>3</sub> OO·	90%	10%		
CH <sub>3</sub> -CH <sub>2</sub> OO·	100%	~0%		
HO-CH <sub>2</sub> OO·	50%	30%	20%	
CH <sub>3</sub> -O-CH <sub>2</sub> OO·	60%	40%		
CH <sub>3</sub> -CO-CH <sub>2</sub> OO·	85%		15%	
CH <sub>3</sub> -CO-OO·	37%		50%	13%

[a] "R" refers to the group bonded to the peroxy O, including CH<sub>3</sub>CO- in the case of acyl peroxy.

The mechanism and branching ratio assignments used by MechGen for peroxy + HO<sub>2</sub> reactions, derived as discussed above, are given on Table 10 in the main text. Note that because of a lack of supporting data, the branching ratio assignments are very uncertain except for primary alkoxy radicals similar to those shown on Table S12.

#### S1.5.4. Mechanisms of organic peroxy + peroxy reactions

Peroxy radicals can react with other organic peroxy radicals under atmospheric conditions, and such reactions may be non-negligible loss processes for peroxy radicals if the NO<sub>x</sub> levels are sufficiently low, though they are calculated to be generally less important than peroxy + HO<sub>2</sub> or NO<sub>3</sub> reactions under daytime or nighttime atmospheric conditions, respectively. They may have an impact on SOA formation if dimer formation occurred, but generally these reactions cannot compete effectively with reactions with NO, NO<sub>3</sub>, and HO<sub>2</sub> except in laboratory experiments carried out at very high concentrations. These reactions can occur via three possible routes, as shown on Table S13. Note that the alkoxy radical and peroxy radical formation routes can occur with any pair of peroxy radicals, while disproportionation requires that at least one of the radicals have an α hydrogen that can be transferred to the other radical. Note that MechGen currently assumes that dimer formation does not occur, in part because it is not able to process cross reactions of different organic radicals.

Table S13. Reaction routes considered for organic peroxy + peroxy reactions

Route label	Reactants	Products
Alkoxy radical formation	ROO· + R'OO·	→ RO· + O <sub>2</sub> + R'O·
	ROO· + R'C(O)OO·	→ RO· + O <sub>2</sub> + R'C(O)O·
	RC(O)OO· + R'C(O)OO·	→ RC(O)O· + O <sub>2</sub> + R'C(O)O·
Disproportionation (if an α H is present in either radical)	ROO· + R'CH <sub>2</sub> OO·	→ ROH + O <sub>2</sub> + R'C(O)H
	ROO· + R'R"CHOO·	→ ROH + O <sub>2</sub> + RC(O)R"
	R'CH <sub>2</sub> OO· + R'C(O)OO·	→ R'C(O)H + O <sub>2</sub> + R'C(O)OH
	RR"CHOO· + R'C(O)OO·	→ R'C(O)R" + O <sub>2</sub> + R'C(O)OH,
Peroxide formation (assumed not to be important)	ROO· + R'OO·	→ ROOR' + O <sub>2</sub>
	ROO· + R'C(O)OO·	→ ROOC(O)R' + O <sub>2</sub>
	RC(O)OO· + R'C(O)OO·	→ RC(O)OOC(O)OR' + O <sub>2</sub>

Table S14 gives a summary of the branching ratios recommended by IUPAC (2023) for peroxy radical pairs for which mechanistic data are available. Note that the table does not include the peroxide channels because there are no radicals on the table where this route is recommended to occur to a significant extent. The fractions for the disproportionation route are divided further into the alcohol and carbonyl routes, corresponding to the product pairs that are formed in these routes. These two routes have to be equal if the radical is reacting with itself, but can differ if a radical is reacting with another radical. An extreme example of this is when a radical with an α hydrogen reacts with a tertiary or acyl radical, where the disproportionation necessarily involves 100% of the carbonyl route for the former, and 100% of the alcohol route for the latter, as indicated on Table S14.

Note that practical atmospheric modeling applications involve the formation and bimolecular reactions of very large numbers of different peroxy radicals, resulting in huge numbers of combinations of peroxy radical + radical reactions. If each were represented explicitly, the entire mechanism would consist mostly of these types of reactions. Fortunately, peroxy + peroxy reactions are generally very

Table S14. Recommended and assigned branching ratios peroxy + peroxy reactions.

Radical 1	Radical 2	Branching ratios [a]			Notes
		Alkoxy	Alcohol	Carbonyl	
CH <sub>3</sub> OO·	CH <sub>3</sub> OO·	37%	(32%)	(32%)	[b, c]
CH <sub>3</sub> CH <sub>2</sub> OO·	CH <sub>3</sub> OO·	(no recommendation)			[b]
CH <sub>3</sub> CH <sub>2</sub> OO·	CH <sub>3</sub> CH <sub>2</sub> OO·	63%	19%	19%	[b]
CH <sub>3</sub> C(O)CH <sub>2</sub> OO·	CH <sub>3</sub> OO·	30%	20%	50%	[b]
CH <sub>3</sub> C(OO·)(CH <sub>3</sub> )CH <sub>3</sub>	CH <sub>3</sub> C(OO·)(CH <sub>3</sub> )CH <sub>3</sub>	100%	-	-	[b]
CH <sub>3</sub> C(OO·)(CH <sub>3</sub> )CH <sub>3</sub>	CH <sub>3</sub> OO·	13%	87%	-	[b]
HOCH <sub>2</sub> OO·	HOCH <sub>2</sub> OO·	90%	6%	6%	[b]
CH <sub>3</sub> C(O)CH <sub>2</sub> OO·	CH <sub>3</sub> C(O)CH <sub>2</sub> OO·	63%	(19%)	(19%)	[b, c]
HOCH <sub>2</sub> CH <sub>2</sub> OO·	HOCH <sub>2</sub> CH <sub>2</sub> OO·	50%	(25%)	(25%)	[b, c]
i-C <sub>3</sub> H <sub>7</sub> OO·	i-C <sub>3</sub> H <sub>7</sub> OO·	56%	22%	22%	[b]
CH <sub>3</sub> C(CH <sub>3</sub> )(OH)CH <sub>2</sub> OO·	CH <sub>3</sub> C(CH <sub>3</sub> )(OH)CH <sub>2</sub> OO·	60%	20%	20%	[b]
CH <sub>3</sub> CH(OH)CH <sub>2</sub> (OO·)CH <sub>3</sub>	CH <sub>3</sub> CH(OH)CH <sub>2</sub> (OO·)CH <sub>3</sub>	18%	41%	41%	[b]
CH <sub>3</sub> C(O)OO·	CH <sub>3</sub> OO·	90%	10%	-	[b]
CH <sub>3</sub> C(O)OO·	CH <sub>3</sub> C(O)CH <sub>2</sub> OO·	50%	50%	-	[b]
CH <sub>3</sub> CH <sub>2</sub> C(O)OO·	CH <sub>3</sub> CH <sub>2</sub> OO·	80%	20%	-	[b]
CH <sub>3</sub> C(O)OO·	CH <sub>3</sub> C(O)OO·	100%	-	-	[b]
Branching ratios assigned for Mechanism Generation					
Primary, Secondary RO <sub>2</sub>	Generic or total RO <sub>2</sub>	50%	25%	25%	[d]
	Generic or total RCO <sub>3</sub>	80%	20%	-	[e]
Tertiary RO <sub>2</sub>	Generic or total RO <sub>2</sub>	50%	50%	-	[f]
	Generic or total RCO <sub>3</sub>	100%	-	-	[g]
Any RCO <sub>3</sub>	Generic or total RO <sub>2</sub>	80%	20%	-	[e]
	Generic or total RCO <sub>3</sub>	100%	-	-	[g]

[a] Ratios for alcohol and carbonyl formation are relative to the product formed from Radical 1. If the radical is reacting with itself, the alcohol and carbonyl routes are represented as being equal. A "-" indicates that this route is not possible for this radical pair.

[b] Branching ratios recommended by IUPAC (2023).

[c] Ratios in parentheses indicate that IUPAC (2023) did not give a specific recommendation for this branching ratio, but it is derived by assuming that only the alkoxy, alcohol, or carbonyl routes are possible, and that the alcohol and carbonyl routes are equal.

[d] Assigned product distribution based roughly on the IUPAC (2023) recommendations for various peroxy + peroxy reactions. The distributions are quite variable depending on the radical pair, but assuming a 50-50 split between alkoxy radical formation and H-shifts is reasonably representative.

[e] The product distribution is estimated based on the data for various acyl peroxy + peroxy reactions. Assuming 80% alkoxy radical formation is within the 50-90% range observed.

[f] The product distribution is estimated. The IUPAC (2023) recommendation for the t-butyl + methyl peroxy reactions suggest that alkoxy radical formation occurs about 13% of the time, but there are no

Table S14 (continued)

data concerning the products of tertiary peroxy + secondary peroxy radicals, which are more representative of generic peroxy radical reactions. Because of lack of data, we assume 50% alkoxy radical formation, as assumed for other types of peroxy radical reactions. H-atom abstraction reactions are not possible for tertiary peroxy radicals.

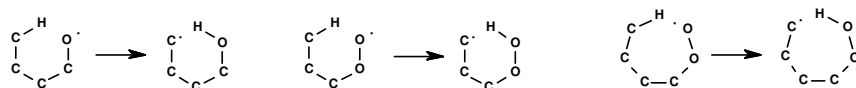
[g] Alkoxy radical formation is the only mechanistic reasonable pathway other than peroxide formation, which is generally not observed.

minor loss processes for peroxy radicals under atmospheric conditions, since reactions with  $\text{NO}_x$  species dominate when  $\text{NO}_x$  is present, reactions with  $\text{HO}_2$  dominate when  $\text{NO}_x$  is low, and reactions with  $\text{NO}_3$  tend to dominate at nighttime. These reactions only need to be considered in very high concentration systems as might occur in laboratory studies of single compounds. Therefore, these reactions are always represented in an approximate manner when modeling reactions in the atmosphere, with even the most explicit mechanisms. For example, the nearly-explicit GECKO-A computer generated mechanisms (Aumont et al., 2005) and the semi-explicit MCM (MCM, 2022, Saunders et al., 2003, Bloss et al., 2005) both represent these as reactions of the individual peroxy radicals with a generic or a set of generic peroxy radical species whose concentration(s) is(are) calculated separately. This approach is also used in the more recent SAPRC mechanisms (Carter, 2016, 2020) when using the output of this mechanism generation system. Note that GECKO-A uses a number of generic peroxy radicals to represent various types, while SAPRC mechanisms, and therefore MechGen, only use two, as discussed below and in Section 4.5 in the main manuscript.

For SAPRC mechanism generation purposes, it is necessary only to assign branching ratios for reactions of individual radicals with generic peroxy or acyl peroxy species. Secondary peroxy radicals are generally formed in higher amounts than primary or tertiary, because abstraction reactions forming primary radicals tend to be slower (see Section S1.5.1), and there are somewhat fewer compounds that form tertiary radicals. Therefore, the branching ratios for reactions with generic peroxy radicals are assigned based on the latter being primary or secondary, rather than tertiary. Table S14 includes branching ratios assigned for mechanism generation purposes. Since there is variability in the branching ratios between alkoxy and alcohol and carbonyl formation, the assumption of a 50-50 split is a simplification that might not be appropriate in all cases. Although there is insufficient information available at present to derive more refined estimates, uncertainties in this branching ratio are not considered to be likely to significantly affect model predictions because these reactions are generally of relatively minor importance.

### S1.5.5. H-Shift Isomerizations

Both alkoxy and peroxy radicals can undergo H-shift isomerization reactions where the radical center abstracts a hydrogen from elsewhere in the molecule, converting the radical group into a group with -OH or -OOH substituents, and forming a carbon centered radical, via a cyclic transition state, e.g.,



This example shows a 1,4-H shift alkoxy and 1,4-H and 1,5-H shift peroxy isomerizations with 6-, 6- or 7-member ring transition states, respectively. (Note that the shifting H is not counted when specifying the span.) H-shift reactions with different ring sizes can also occur, though reactions with more strained or very large rings would be expected to be slower. H-shift isomerizations of alkoxy radicals under atmospheric conditions have been known to be important for longer chain radicals for some time, and are discussed separately below in Section S1.6.3. H-shift isomerizations of peroxy radicals have been known

to be important in combustion systems, but it was only relatively recently realized that these isomerizations may be important for some types of radicals at atmospheric temperatures. The methods used for estimating the rate constants for these peroxy H-shift isomerizations are discussed in this section.

Experimental rate constants for peroxy H-shift isomerizations under atmospheric conditions are limited, but recently Vereecken and Nozière (2020) (VN20), compiled and reviewed results of quantum calculations of H-shift rate constants for a wide variety of types of peroxy radicals, and used these, together with the limited experimental data to derive lookup tables and SARs for predicting their rate constants. The lookup tables utilized combinations of groups with the H-atom that is being abstracted (called "H-groups" in the subsequent discussion) and the type of peroxy radical ("R-groups") to obtain rate constants as a function of transition state ring size. Correction factors were also recommended for when the H-group had  $\beta$ -OH,  $\alpha$ -ONO<sub>2</sub> or  $\beta$ -oxy substituents, with the  $\beta$ -oxy corrections being assumed to depend on ring size. The rate constants in the VN20 lookup tables based on their review of theoretically calculated rate constants are summarized in Table S49 in Section S5.2 (given at the end of this document because of its size), and relevant experimentally measured rate constants, taken from Table 9 of VN20, are summarized on Table S15.

These lookup tables that are the heart of the VN20 SARs give reasonably good coverage of most of the major types of peroxy radicals likely to be formed from reactions of VOCs and their oxidation products in the atmosphere. The types of reactions covered in the lookup tables include the following:

- Abstractions from -CH<sub>3</sub>, -CH<sub>2</sub>-, -CH<, groups without any non-alkyl  $\alpha$  substituents or  $\beta$  double bonds (i.e., a double bond group in the  $\alpha$ -position).
- Abstractions from -CH<sub>2</sub>- or -CH< with  $\alpha$ -OH or -OOH substituents. They recommend assuming that the effect of  $\alpha$ -ether substituent is the same as  $\alpha$ -OH.
- Abstractions from -CH<sub>2</sub>- or -CH< with  $\beta$  double bonds, with separate entries for when the double bond group is within ( $\beta$ -endo) or outside ( $\beta$ -exo) of the transition state. Note that  $\beta$ -endo cases where only one of the double bond groups is in the transition state ring are assigned the same rate constant as those where both are in the ring.
- Abstractions from -C(O)H, with separate entries for when it is next to a double bond group.
- Abstractions by -CH<sub>2</sub>OO·, -CH(OO·)- and -C(OO·)< radical groups.
- Abstractions from hydroperoxy groups, resulting in scrambling of the locations of the peroxy and hydroperoxy groups.
- Transition state ring sizes ranging from 5 to 8 or 9, depending on the H-group, except for those with a  $\beta$ -endo double bond, where the ring sizes ranged from 7 to 8, or abstractions from hydroperoxy groups, where ring sizes varied from 7 to 10.

VN20 did not include reactions of acyl peroxy radicals in their lookup tables, though they did recommend assuming that rate constants for abstractions by this group are a factor of 20 higher than for alkyl peroxy radicals. This is presumably based on the calculations of Møller et al. (2019) of rate constants for several substituted acyl peroxy radicals. Rather than using this somewhat unclear factor of 20 recommendation, the data for acyl peroxy radical rate constants calculated by Møller et al. (2019) were used to extend the lookup tables to include reactions of these radicals, and these are included in Table S49. The other rate constants calculated by Møller et al. (2019) were presumably considered by VN20 when deriving the lookup tables and correction factors for alkyl peroxy radical reactions, so are not considered separately here. However, Seal et al. (2023) recently carried out a theoretical study of H-shift reactions in acyl peroxy reactions whose results were not considered when these SARs were developed. These will need to be examined when MechGen is updated.

Table S15. Experimentally measured rate constants for T = 295-298 K for H-shift isomerization reactions of peroxy radicals.

Reactant [a]	Reacting Groups		Ring Size	k(298) (sec <sup>-1</sup> )		Fac Err [b]	Ref [c]
	H-Group	R-Group		Target	Est'd		
CH <sub>3</sub> <b>CH</b> <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OO·	CH <sub>2</sub>	CH <sub>2</sub> OO·	6	≤5.0e-4	8.1e-4	≥1.6	1
CH <sub>3</sub> <b>CH</b> <sub>2</sub> <b>CH</b> <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OO·	CH <sub>2</sub>	CH <sub>2</sub> OO·	6, 7	2.4e-3	1.7e-3	-1.4	1
CH <sub>3</sub> CH <sub>2</sub> <b>CH</b> <sub>2</sub> <b>CH</b> <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OO·	CH <sub>2</sub>	CH <sub>2</sub> OO·	6, 7	1.7e-3	1.7e-3	±1	1
CH <sub>3</sub> CH <sub>2</sub> <b>CH</b> <sub>2</sub> <b>CH</b> <sub>2</sub> CH( <b>CH</b> <sub>2</sub> CH <sub>3</sub> )CH <sub>2</sub> OO·	CH <sub>2</sub>	CH <sub>2</sub> OO·	6, 7	2.2e-3	2.5e-3	1.1	1
<b>H</b> C(O)C(OO·)(CH <sub>3</sub> )CH <sub>2</sub> OH	CHO	COO·	5	0.50	0.53	1.1	2
CH <sub>3</sub> CH <sub>2</sub> CH(OO·)CH <sub>2</sub> <b>CH</b> (CH <sub>3</sub> )OH	CH-OX	CHOO·	6	0.048	0.068	1.4	3
CH <sub>3</sub> CH <sub>2</sub> CH(OO·)CH <sub>2</sub> CH <sub>2</sub> <b>CH</b> (CH <sub>3</sub> )OH	CH-OX	CHOO·	7	0.14	0.16	1.2	3
CH <sub>3</sub> <b>CH</b> (OH)CH <sub>2</sub> C(OO·)(CH <sub>3</sub> )CH <sub>3</sub>	CH-OX	COO·	6	0.22	0.27	1.2	4
CH <sub>3</sub> <b>CH</b> (OOH)CH <sub>2</sub> C(OO·)(CH <sub>3</sub> )CH <sub>3</sub>	CH-OOH	COO·	6	0.036	0.031	-1.1	4
HO <b>CH</b> <sub>2</sub> C(CH <sub>3</sub> )=CHCH <sub>2</sub> OO·	CH <sub>2</sub> -OxDB/En	CH <sub>2</sub> OO·	7	0.36	1.15	3.2	5
HO <b>CH</b> <sub>2</sub> CH=C(CH <sub>3</sub> )CH <sub>2</sub> OO·	CH <sub>2</sub> -OxDB/En	CH <sub>2</sub> OO·	7	3.70	1.15	-3.2	5

[a] The H that is transferred is shown in bold, underline font. If more than one H is shown, the estimated rate constant is the sum of these reaction routes.

[b] This is either the ratio of Estimated/Target if Estimate is high, or -Target/Estimate if estimate is low.

[c] Sources of the data, which were taken from Table 9 of VN20, are as follows:

- 1 From Nozière and Vereecken (2019). Reaction route not determined.
- 2 From Crouse et al. (2013).
- 3 From Praske et al. (2018).
- 4 From Praske et al. (2019).
- 5 From Teng et al. (2017).

Only data for 296-298 K used.

Unfortunately, these lookup tables and correction factors provided by VN20, together with those that can be added using the data Møller et al. (2019), do not cover all the cases that may be encountered in atmospheric photooxidation systems. These include the following, in the estimated order of importance:

- Most abstractions by acyl peroxy radicals, as discussed above.
- Abstractions from alkyl groups with both -OH (or -Ox) substituents that also have β double bonds. Note that this is one of the cases for which experimental data are available (see Table S15).
- Abstractions from -C(O)H groups with β double bonds.
- Reactions involving β-endo double bonds by the H-group with 6-member transition state rings (as might occur if only one double bond group is in the ring).
- Reactions involving transition state rings larger than 8 or 9.
- Abstractions from -CH< groups with two β double bonds.
- Abstractions from the OH in peroxyacids.
- Reactions of cyclic or bicyclic peroxy radicals.

In order to provide a basis for estimating rate constants, the various factors affecting the rate constants are split up into components that are somewhat more straightforward to estimate, allowing the

lookup tables to be expanded to cover the other cases. The expression used for estimation purposes was as follows:

$$k(T) \approx nH \times A(RS,TS) \times e^{-\{Ea^{HR}(H\text{-group}, R\text{-group}, RS) + Ea^{corr}(\text{subs},RS)\} / RT} \quad (S3)$$

$$Ea^{HR}(H\text{-group},R\text{-group},RS) = Ea^0(H\text{-group},R\text{-Group}) + Ea^{strain}(H\text{-group},R\text{-group},RS) \quad (S4)$$

$$Ea^0(H\text{-group},R\text{-Group}) = \text{Min over } RS=5-8 \{Ea^{HR}(H\text{-group},R\text{-group},RS)\} \quad (S5)$$

$$Ea^{strain}(H\text{-group},R\text{-group},RS) = Ea^{HR}(H\text{-group}, R\text{-group},RS) - Ea^0(H\text{-group},R\text{-Group}) \quad (S6)$$

where T is the temperature, nH is the number of equivalent H atoms that could be abstracted, RS is the ring size of the transition state, HR refers to the combination of H- and R-groups, A is the Arrhenius A factor that is assumed to depend on the ring size and type of transition state (TS),  $Ea^{HR}$  is obtained from lookup tables giving activation energies based on the H- and R-groups and ring size,  $Ea^{corr}(\text{subs})$  are corrections to the activation energies based on applicable  $\alpha$ - or  $\beta$ -substituents,  $Ea^0$  is the activation energy if there were no ring strain and  $\beta$ -subs corrections, and  $Ea^{strain}$  is the ring strain, which is assumed to be at a minimum with the ring size in the 5-8 range, with the minimum value assigned to zero. Note that nH, RS, RH, and subst are determined by the reaction, while the A and Ea values are derived or estimated as discussed below.

Estimation of A Factors and Temperature Dependences. The rate constants for these reactions are expected to be highly temperature dependent, and at least an approximate method to estimate these dependences is required. It is also necessary to simplify the estimation process because it is more straightforward to estimate A and Ea independently. VN20 calculated the rate constants as a function of temperature, and fit the data using the expression:

$$k(T) \approx p1 \times T^{p2} \times e^{-p3/T} \quad (S7)$$

where p1, p2, and p3 are fitting parameters that they tabulated for each type of reaction and are included in Table S49. The p2 values were as high as 28 in some cases, indicating highly non-Arrhenius temperature dependences. However, the three-parameter expression in Equation (S7) is not well suited for general estimation purposes, because it requires more parameters to fit the data, with strong cross-correlation among the parameters, and the parameters are not straightforward to estimate. Therefore, for this work we assume that the temperature dependence can be approximated by an Arrhenius expression in Equation S3, at least for the relatively narrow temperature range used in most model simulations of lower atmospheric conditions. If this is assumed for the atmospheric temperature range of 270-330 K, then the Arrhenius parameters can be derived from the tabulated p1, p2, and p3 values using:

$$Ea \approx \ln(k330/k270) / (1/270 - 1/330); A \approx (k270 \times e^{Ea/270})/nH \quad (S8)$$

where k330 and k270 are rate constants calculated by Equation (S7) for 330 and 270 K, respectively. Although this only approximated the temperature dependence, it fit the data to within  $\pm\sim 10\%$  for this relatively narrow temperature range. The A factors derived using Equation (S8) are included in the tabulations in Table S49.

Figure S9 shows plots of the Arrhenius A factors derived using Equation (S8) from the data provided by VN20 as a function of ring size. For comparison purposes, the figure also uses the A factors as a function of ring size that were used when deriving H-shift isomerization rate constants for alkoxy radicals, as discussed in Section S1.6.3. The results for peroxy radicals indicate that the A factors derived from the temperature-dependence parameters given by VN20 depend on the ring size and type of transition state, but are quite scattered and not consistent in all cases. The data are reasonably consistent for alkyl and HCO transition state types, allowing the data for ring sizes of 5 to 8 or 9 to be used to derive



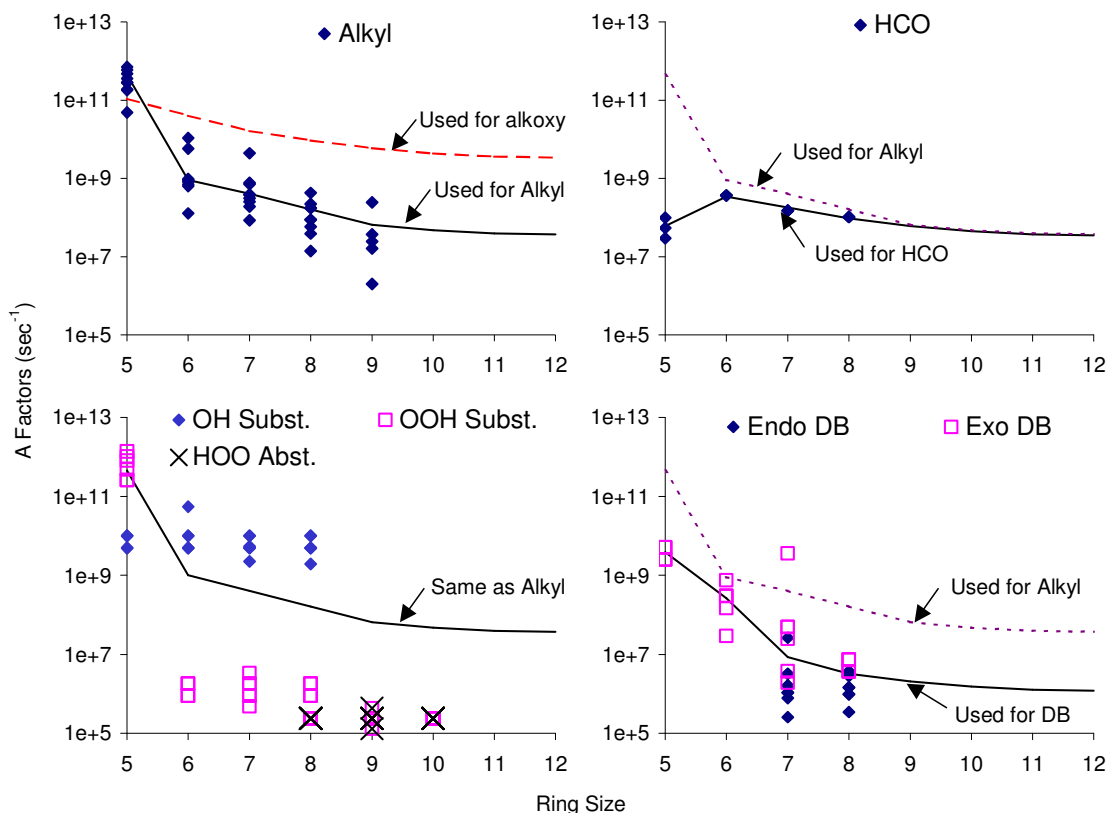


Figure S9. Plots of Arrhenius A factors as a function of ring size for H-shift isomerizations of peroxy radicals derived from the data of Vereecken and Nozière (2020). A factors used in this work to estimate H-shift isomerizations of alkoxy radicals are also shown.

A factors for estimation purposes for these types of reactions. The data for *endo* and *exo* double bond transition state types are more scattered, but suggest that both cases can be approximated by a single curve derived by the averages of data for each ring size. The data for  $\alpha$ -OH or -OOH substituted types, or from abstractions from hydroperoxy groups are inconsistent with each other, and do not appear to be reasonable to use for estimation purposes. Therefore, the A factors derived from the data for alkyl peroxy radicals were used instead for estimation purposes, though this is clearly highly uncertain.

Data are not available for estimating A factors for reactions with transition state rings greater than 8 or 9, so these have to be estimated. These are estimated based on relative changes in A factors assigned for alkoxy radicals, which indicate that the A factors continue to decline as the ring size increases, but eventually level off. For general estimation purposes it is assumed that the decline in A with ring sizes > 12 is small enough that the value estimated for 12-member rings can approximate those for larger rings.

The curves showing how A factors are estimated as a function of ring size for the various types of reactions are included as the solid lines on Figure S9, with dotted lines showing assignments for alkyl types where applicable. The values used are tabulated in Table S16, with footnotes indicating how each value was derived or estimated. However, there can also be cases where the reaction has either an *endo* or *exo* double bond and is also either an abstraction from HCO groups or has an  $\alpha$ -OH or OOH substituent. In those cases, the A factors derived for *endo* or *exo* double bonds alone are used, with the assumption that this is the most important factor affecting the A factor. Note that the combinations of HCO with *exo* double bonds and HCO and  $\alpha$  substituents are not possible. The applicability of these A estimates for  $\alpha$ -

Table S16. Arrhenius A factors used in the estimation of rate constants for H-shift isomerizations of various types of peroxy radicals.

Ring size	Alkyl and $\alpha$ -OX substituent and abstractions from -OOH		Aldehyde (no double bond)		Double bond next to H group	
	A (sec <sup>-1</sup> )	Note	A (sec <sup>-1</sup> )	Note	A (sec <sup>-1</sup> )	Note
5	4.47e+11	1	6.02e+7	1	3.81e+9	4
6	1.01e+9	2	3.36e+8	2	2.60e+8	4
7	4.03e+8	2	1.78e+8	2	8.57e+6	5
8	1.61e+8	2	9.45e+7	2	3.24e+6	5
9	6.47e+7	2	6.07e+7	3	2.08e+6	3
10	4.67e+7	3	4.39e+7	3	1.51e+6	3
11	3.92e+7	3	3.68e+7	3	1.26e+6	3
12	3.68e+7	3	3.46e+7	3	1.19e+6	3

Notes:

- 1 The A factors used were derived using a linear fit through the averages derived for ring sizes from 6 through the maximum with data available.
- 2 Corrections for ring strains through RS=8 were derived from the data of Vereecken and Nozière (2020). The optimized value for RS=9 appears to be an outlier and is not used. Instead, the ring strain for RS=9 is assumed to be the same as that derived for -OH substitution, which is more consistent with the data for smaller ring sizes. For larger ring sizes, it is assumed that the strain for RS=10 is the same as for RS=9, is half that for RS=11 and zero for RS=12, though this is uncertain.
- 3 The A factors used for the larger ring sizes were estimated assuming that the change relative to the value at RS=9 is the same as for the A factors used to estimate alkoxy A factors.
- 4 Use average of logs of values derived for exo double bonds with this ring size.
- 5 Use average of logs of values derived for either endo or exo double bonds with this ring size.

OH,  $\alpha$ -OOH, or hydroperoxy H-groups is particularly uncertain. However, these do not affect estimates of the 298K rate constant, though they significantly affect estimates of how the rate constant changes with temperature.

Estimation of Activation Energies: The  $E_a^{\text{HR}}$  values for the H- and R-group pairs that are covered by the VN20 SARs can be derived directly from the A factors estimated as discussed above and the 298K rate constants in their SAR lookup tables. As indicated by Equations (S4) to (S6) above,  $E_a^{\text{HR}}$  is split up into  $E_a^0$  and  $E_a^{\text{strain}}$ , where  $E_a^0$  is the contribution to the activation energy if there were no ring strain, and  $E_a^{\text{strain}}$  is the contribution due to ring size. It is assumed that the ring strains defined using Equations (S5) and (S6) approach zero but are always positive as the ring sizes become extremely large, so that the minimum strain occurs in the RS=5-8 range, so  $\lim[E_a^{\text{HR}}(\text{RS} \rightarrow \infty)] = E_a^0$ .

Table S17 lists the  $E_a^0$  values derived from these data, and Table S18 gives the  $E_a^{\text{strain}}$  values for the various ring sizes. Estimated values, derived as discussed below, are also included. These are shown graphically in Figure S10 and Figure S11. Footnotes in the tables indicate how these were derived. Those given footnotes "1" or "7" in Table S17 were derived using the rate constants tabulated by VN20, while the others were estimated based on assumed relationships with the tabulated values, as indicated by the other footnotes. The estimates that are expected to be the most significant in terms of atmospheric photooxidations are as follows:

Table S17.  $E_a^0$  values assigned for various pairs of H- and R-groups for estimating peroxy isomerization rate constants, with footnotes indicating how the  $E_a^0$  and  $E_a^{\text{strain}}$  values were derived.

H-Group [a]	Ea0 (kcal/mole) [b]							
	-CH <sub>2</sub> OO.		-CH(OO.)-		-C(OO.)<		-C(O)OO.	
CH <sub>3</sub> [c]	19.74	1	19.06	1	17.85	1	16.42	2,3,4
CH <sub>2</sub> [c]	16.31	1	16.38	1	16.92	1	13.64	2,4
CH	13.55	1	13.32	1	13.93	1	10.64	2,4
CHO	10.05	1,5	7.30	1,5	10.98	1,5	9.66	6,7
CH <sub>2</sub> -Ox	14.94	1	12.84	1,8	15.33	1,9	13.14	7,10
CH-Ox	12.36	1	12.81	1,8	12.34	1,9	10.15	10
CH <sub>2</sub> -OOH	15.58	1,8	16.05	1,8	14.97	1,9	12.79	10
CH-OOH	13.43	1,8	13.77	1,8	13.88	1,9	11.69	10
CH <sub>3</sub> -C=/En	9.42	1,8,11	10.11	1,8,11	11.36	1,9,11	9.65	2,4
CH <sub>2</sub> -C=/En	8.59	1,8,11	8.47	1,8,11	9.36	1,9,11	6.07	2,4
CH-C=/En	4.00	1,8,11	5.40	1,8,11	6.39	1,9,11	4.00	2,4
CH <sub>2</sub> -C=/Ex	8.04	1,8	11.38	1,8	9.00	1,9	5.72	2,4
CH-C=/Ex	9.49	1,8	8.33	1,8	9.38	1,9	6.09	2,4
CHO/En	~ 4	12	~ 4	12	~ 4	12	~ 4	12
CH <sub>2</sub> -OxDB/En	7.39	13,14	6.35	13	8.16	13	5.97	10
CH-OxDB/En	~ 4	13	4.21	13	5.19	13	~ 4	10
CH <sub>2</sub> -OxDB/Ex	6.84	13	7.84	13	7.41	13	5.22	10
CH-OxDB/Ex	8.29	13	7.19	13	8.18	13	5.99	10
CH <sub>2</sub> -C=/EnEx	8.59	9	8.47	9	9.36	9	7.17	2,4
CH-C=/EnEx	~ 4	9	5.40	9	6.39	9	4.20	2,4
CH <sub>2</sub> -OxDB/EnEx	7.39	9	6.35	9	8.16	9	5.97	10
CH-OxDB/EnEx	~ 4	9	4.21	9	5.19	9	~ 4	10
HOO-CH <sub>2</sub>	7.77	1	7.40	1	6.65	1	~ 4	16
HOO-CH	6.83	1	6.66	1	5.65	1	~ 4	16
HOO-C	6.13	1	5.74	1	7.07	1	~ 4	16

[a] The first group is the one with the abstracted H-atom, and if a second group is given it is the one bonded to it, where "-Ox" indicates an -OH or ether group, and -C= indicates a carbon-centered group with a double bond, and -OxDB includes a group with both an -Ox group that also has a  $\beta$  double bond. "/En", "/Ex", and "/EnEx" indicate whether the double bond is within the transition state ( $\beta$ -endo), outside the transition state ( $\beta$ -oxo), or whether there are two  $\beta$  double bonds.

[b] The R-group is shown on the column headers. Footnotes indicate how the  $E_a^0$  and  $E_a^{\text{strain}}$  values were derived or estimated, as follows:

- 1 Except as noted in other footnotes, the  $E_a^{\text{HR}}$  and from them  $E_a^0$  and  $E_a^{\text{strain}}$  values for ring sizes through 8 or 9 were derived from the SARs of VN20.
- 2 Except as indicated by other footnotes, changes in activation energies for abstractions from alkyl H-groups (with or without nearby double bonds) by -CO[OO.] relative to -C[OO.] radicals with ring sizes of 5 or 6 are assumed to be the same as the difference for abstractions from -CH<sub>3</sub> with a ring size of 6, based on quantum calculated rate constants given by Møller et al (2019).
- 3 The  $E_a^{\text{HR}}$  for ring size of 7 was adjusted to fit theoretically calculated rate constant data given by of Møller et al. (2019).
- 4 Changes in  $E_a^{\text{HR}}$  for abstractions from alkyl H-groups (with or without nearby double bonds) by -CO[OO.] relative to -C[OO.] radicals with ring sizes of 7 or greater are assumed to be the same as the difference for abstractions from -CH<sub>3</sub> with ring sizes of 7, based on quantum

Table S17 (continued)

- calculated rate constants given by of Møller et al (2019).
- 5 Assume change in  $E_a^{\text{HR}}$  going from RS=8 to 9 for abstraction from a -CHO group is the same as for abstraction from -CH<sub>3</sub> by the same type of radical. This is because steric effects around -CH<sub>3</sub> are expected to be closer to those around -CHO than is the case for -CH<sub>2</sub>- or -CH<.
  - 6 Changes in  $E_a^{\text{HR}}$  for abstractions from -HCO groups (with or without nearby double bonds) by -CO[OO.] relative to -C[OO.] radicals are assumed to be the same as the difference for abstractions from -CH<sub>3</sub> with a ring size of 6, based on quantum calculated rate constants given by of Møller et al. (2019).
  - 7 The  $E_a^{\text{HR}}$  for ring size of 6 was adjusted to fit rate theoretically calculated rate constant data given by of Møller et al. (2019).
  - 8 Assume change in  $E_a^{\text{RH}}$  going from RS=8 to 9 for abstraction from this group is the same as for abstraction from this group if unsubstituted.
  - 9 Assume change in  $E_a^{\text{RS}}$  going from RS=8 to 9 for abstraction from this group is the same as for abstraction from -CH<sub>2</sub>- groups, since there are no data on abstractions from -CH< groups for RS=9.
  - 10 Changes in  $E_a^{\text{RH}}$  for abstractions from alpha-OH substituted groups (with or without nearby double bonds) by -CO[OO.] relative to -C[OO.] radicals are assumed to be the same as the difference for abstractions from -CH-OH with a ring size of 6, based on quantum calculated rate constants given by of Møller et al. (2019).
  - 11 The ring strains for RS=6 with *endo* gemini double bonds are estimated by assuming that the difference between RS=6 and RS=7 is the same as for abstractions from unsubstituted alkyl groups with the same number of hydrogens. This is very uncertain.
  - 12 It was assumed that the effect on  $E_a^{\text{HR}}$  of the *endo* double bond on abstractions from -CHO is the same as the effect on abstractions from -CH<. However, this yielded unreasonably low  $E_a^0$  values, so the minimum of ~4 kcal/mole was used for  $E_a^0$ , but the estimated strain energies are not changed.
  - 13 It is assumed that the effect of an *endo* or *exo* double bond on  $E_a^{\text{RH}}$  is the same as the effect without -Ox substitution.
  - 14  $E_a^{\text{HR}}$  was adjusted to fit rate constant data of Teng et al. (2017), as tabulated by VN20 for isomerizations of HOCH<sub>2</sub>C(CH<sub>3</sub>)=CHCH<sub>2</sub>OO· and HOCH<sub>2</sub>CH=C(CH<sub>3</sub>)CH<sub>2</sub>-OO·.
  - 15 Assume that  $E_a$  contributions for abstractions from groups with two double bonds are the same as if the group had only an *endo* double bond.
  - 16 These reactions are expected to be very fast, on the basis of high recommended rate constants for abstractions from hydroperoxides and the fact that abstractions from peroxyacids are estimated to be ~10 kcal/mole endothermic. They are assigned the minimum  $E_a^0$  of 4 kcal/mole, and  $E_a(\text{strain})$  values are assumed to be the same as abstractions from HOO-C H-groups with by the same type of radical.
- [c] Peroxy H-shift reactions from unsubstituted -CH<sub>3</sub> or -CH<sub>2</sub>- groups are all estimated to be negligible, so estimates for these reactions are not incorporated into MechGen.

Table S18.  $E_a^{\text{strain}}$  values assigned for various pairs of H- and R-groups and ring sizes through RS=10.

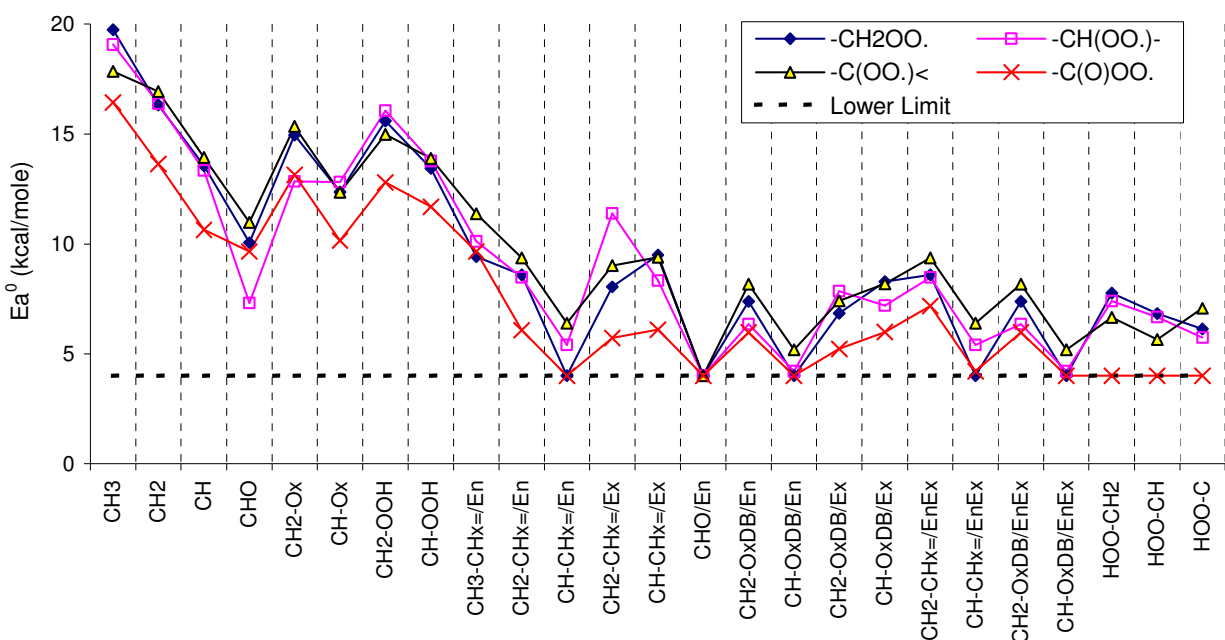
H-Group	$E_a^{\text{strain}}$ (kcal/mole) [a]											
	-CH <sub>2</sub> OO·						-CH(OO·)-					
	5	6	7	8	9	10	5	6	7	8	9	10
CH <sub>3</sub>	11.39	0.06	0	0.27	1.20	1.20	15.17	0.39	0	0.61	5.12	5.12
CH <sub>2</sub>	11.21	0.53	0	0.81	2.92	2.92	14.14	0.21	0	1.65	4.52	4.52
CH	11.59	0.65	0.05	0	7.48	7.48	14.07	0.58	0	1.64	9.12	9.12
CHO	0	0.22	0.25	0.46	1.39	1.39	4.91	1.31	0	4.62	5.55	5.55
CH <sub>2</sub> -Ox	5.45	0.51	0	0.97	2.98	2.98	11.12	2.37	0	3.99	6.87	6.87
CH-Ox	10.46	1.70	0.39	0	3.60	3.60	9.22	1.00	0	0.95	8.43	8.43
CH <sub>2</sub> -OOH	11.11	1.66	0	0.88	1.81	1.81	11.23	0.99	0.18	0	4.51	4.51
CH-OOH		1.81	0	0.33	1.26	1.26		0.71	0.03	0	4.51	4.51
CH <sub>3</sub> -CHx=/En		2.82	2.75	0	0.93	0.93		2.84	2.46	0	4.51	4.51
CH <sub>2</sub> -CHx=/En		2.07	1.53	0	2.11	2.11		1.64	1.42	0	2.87	2.87
CH-CHx=/En		4.51	3.91	0	7.48	7.48		2.01	1.44	0	7.48	7.48
CH <sub>2</sub> -CHx=/Ex	11.99	3.25	1.40	0	2.11	2.11	9.06	2.67	0	0.08	2.95	2.95
CH-CHx=/Ex		2.27	0.14	0	7.48	7.48		2.78	0	0.06	7.54	7.54
CHO/En		3.62	3.65	0	0.93	0.93		1.31	0	1.55	2.47	2.47
CH <sub>2</sub> -OxDB/En		1.88	2.39	0	2.01	2.01		2.37	0	0.92	3.79	3.79
CH-OxDB/En		5.57	4.25	0	3.60	3.60		3.12	2.12	0	7.48	7.48
CH <sub>2</sub> -OxDB/Ex	6.06	3.07	1.23	0	2.01	2.01	6.05	4.83	0	2.42	5.29	5.29
CH-OxDB/Ex	7.93	3.33	0.48	0	3.60	3.60	4.76	3.82	0.62	0	7.48	7.48
CH <sub>2</sub> -CHx=/EnEx		2.07	1.53	0	2.11	2.11		1.64	1.42	0	2.87	2.87
CH-CHx=/EnEx		4.51	3.91	0	7.48	7.48		2.01	1.44	0	7.48	7.48
CH <sub>2</sub> -OxDB/EnEx		1.88	2.39	0	2.01	2.01		2.37	0	0.92	3.79	3.79
CH-OxDB/EnEx		5.57	4.25	0	3.60	3.60		3.12	2.12	0	7.48	7.48
HOO-CH <sub>2</sub>			0.86	0	0.42	2.11			2.43	0	0.43	2.35
HOO-CH			1.02	0	0.25	1.48			0.72	0	0.73	2.41
HOO-C			1.45	0	1.25	2.91			0.36	0	1.91	3.58

H-Group	$E_a^{\text{strain}}$ (kcal/mole) [a]											
	-C(OO·)<						-C(O)OO·					
	5	6	7	8	9	10	5	6	7	8	9	10
CH <sub>3</sub>	16.48	0	2.18	4.65			16.48	0	0.32	2.78		
CH <sub>2</sub>	12.88	0.26	0	1.99			14.75	2.13	0	1.99		
CH	12.02	2.66	0	2.02	9.49	9.49	13.88	4.52	0	2.02	9.49	9.49
CHO	0	1.68	1.02	1.93	2.85	2.85	0	1.68	1.02	1.93	2.85	2.85
CH <sub>2</sub> -Ox	7.35	0.47	0	2.39	5.26	5.26	7.35	0.47	0	2.39	5.26	5.26
CH-Ox	6.49	0.65	0	2.41	9.89	9.89	6.49	0.65	0	2.41	9.89	9.89
CH <sub>2</sub> -OOH	10.11	0	1.34	1.70	6.21	6.21	10.11	0	1.34	1.70	6.21	6.21
CH-OOH		0.38	0.05	0	4.51	4.51		0.38	0.05	0	4.51	4.51
CH <sub>3</sub> -CHx=/En		0	2.18	1.57	6.08	6.08		0.29	0.61	0	4.51	4.51
CH <sub>2</sub> -CHx=/En		1.35	1.08	0	2.87	2.87		3.21	1.08	0	2.87	2.87

Table S18 (continued)

H-Group	Ea <sup>strain</sup> (kcal/mole) [a]											
	-C(OO·)<						-C(O)OO·					
	5	6	7	8	9	10	5	6	7	8	9	10
CH-CH <sub>x</sub> =/En		3.71	1.06	0	7.48	7.48		5.58	1.06	0	7.48	7.48
CH <sub>2</sub> -CH <sub>x</sub> =/Ex	10.73	8.79	0	3.34	6.22	6.22	12.60	10.66	0	3.34	6.22	6.22
CH-CH <sub>x</sub> =/Ex		4.67	3.32	0	7.48	7.48		6.53	3.32	0	7.48	7.48
CHO/En		2.83	2.16	0	0.93	0.93		2.83	2.16	0	0.93	0.93
CH <sub>2</sub> -OxDB/En		1.16	0.69	0	2.87	2.87		1.16	0.69	0	2.87	2.87
CH-OxDB/En		1.31	0.66	0	7.48	7.48		1.31	0.66	0	7.48	7.48
CH <sub>2</sub> -OxDB/Ex	5.20	9.00	0	3.74	6.61	6.61	5.20	9.00	0	3.74	6.61	6.61
CH-OxDB/Ex	0.57	2.27	2.93	0	7.48	7.48	0.57	2.27	2.93	0	7.48	7.48
CH <sub>2</sub> -CH <sub>x</sub> =/EnEx		1.35	1.08	0	2.87	2.87		1.35	1.08	0	2.87	2.87
CH-CH <sub>x</sub> =/EnEx		3.71	1.06	0	7.48	7.48		3.71	1.06	0	7.48	7.48
CH <sub>2</sub> -OxDB/EnEx		1.16	0.69	0	2.87	2.87		1.16	0.69	0	2.87	2.87
CH-OxDB/EnEx		1.31	0.66	0	7.48	7.48		1.31	0.66	0	7.48	7.48
HOO-CH <sub>2</sub>			1.82	0	0.88	2.55			1.82	0	0.88	2.55
HOO-CH			3.36	0	0.73	2.42			3.36	0	0.73	2.42
HOO-C			0	0.17	0.37	2.04			0	0.17	0.37	2.04

[a] See Table S17 for notes indicating how these values were derived for ring sizes through RS=9 and 10. Except as noted, strains for rings larger than 9 estimated by assuming that  $Ea^{\text{strain}}(10) \approx Ea^{\text{strain}}(11) Ea^{\text{strain}}(9)$ ,  $Ea^{\text{strain}}(12) \approx 0.5 \times Ea^{\text{strain}}(11)$ , and  $Ea^{\text{strain}}(13+) \approx 0$  (see Figure S11).

Figure S10. Plots of Ea<sup>0</sup> values assigned to various pairs of H- and R-groups.

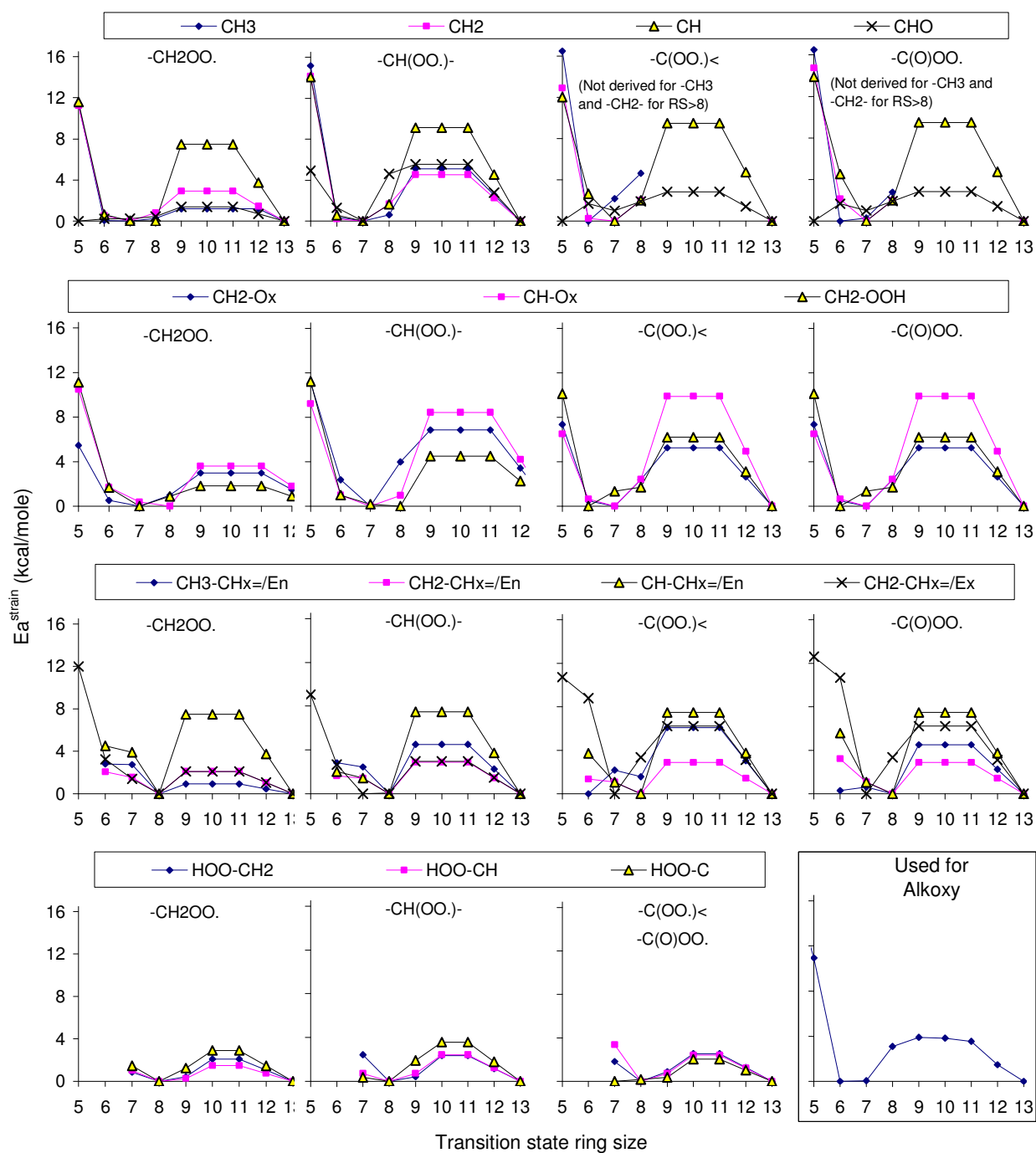


Figure S11. Plots of  $E_a^{\text{strain}}$  values used for H-shift isomerizations of peroxy radicals as a function of ring size for various types of rings. The  $E_a^{\text{strain}}$  values used for alkoxy isomerizations are also shown.

- Acyl peroxy radicals are important in atmospheric photooxidation systems, but reactions of such radicals are not included in the lookup tables given by Vereecken and Nozière (2020). However, they did recommend applying a correction factor of 20 relative to aliphatic unsubstituted radicals, which we presume refers to reactions of  $\text{-C[OO}\cdot\text{]<}$  radicals, which would be the result if the oxy group were removed. Although strictly speaking transition states involved with H-shift reactions of acyl peroxy radicals would have  $\beta$ -oxo substitutions, we assume that these corrections are not intended for acyl peroxy reactions.
- Radicals with double bonds next to  $\text{-HCO}$  groups occur reasonably often in atmospheric photooxidation. Because of lack of information, we roughly assume that the effect of the *endo* double bond on abstractions from  $\text{-CHO}$  is the same as its effect on abstractions from  $\text{-CH<}$ .
- VN20 provided no information about ring strains for ring sizes greater than 9. Based on the ring strains derived for H-shift reactions of alkoxy radicals, discussed in Section S1.6.3, below and shown as a function of ring size in Figure S11, we assume that  $E_a^{\text{strain}}(11) \approx E_a^{\text{strain}}(10) \approx E_a^{\text{strain}}(9)$ , that  $E_a^{\text{strain}}(12) \approx E_a^{\text{strain}}(11)/2$ , and that  $E_a^{\text{strain}}(13+) \approx 0$ .
- Abstractions from hydroperoxy groups by acyl peroxy radicals forming alkyl peroxy radicals with peroxyacid groups are estimated to be exothermic by  $\sim 10$  kcal/mole, while the reactions covered by the VN20 lookup tables are either endothermic, nearly thermoneutral, or exothermic by less than 5 kcal/mole. Therefore, these reactions were assigned the assumed minimum  $E_a^0$  value of 4 kcal/mole (see below), and the  $E_a^{\text{strain}}$  values were assumed to be approximately equal to those derived for abstractions by  $\text{-C[OO}\cdot\text{]<}$  radicals.
- Abstractions from peroxyacid groups by peroxy radicals were not considered because they are estimated to be endothermic by  $\sim 10$  kcal/mole. Abstractions from peroxyacid groups by acyl peroxy radicals, which should be approximately thermoneutral, are also not considered in the current system, though they may be non-negligible.
- Although information was provided on the effects of  $\text{-Ox}$  substitution and of *endo* or *exo* double bonds, information was not provided for cases where H-groups had both types of substituents. In those cases, we assume that the effect on the double bond was the same as is the case for H-groups without  $\text{-Ox}$  substituents. Note that this provides an estimated  $E_a^{\text{strain}}(7)$  of 2.39 kcal/mole. for  $\text{-CH}_2$ -groups with these substituents, while the experimental data in Table S15 are best fit using 1.37 kcal/mole, which is what is used in our estimates in this case. This changes the estimated 298K rate constant by a factor of  $\sim 5.5$ , which indicates the range of uncertainty of these estimates.

Note that in some cases the estimation methods described by footnotes to Table S17 yield very low, and in some cases even slightly negative,  $E_a^0$  estimates. However, the  $E_a^0$  values derived from the SARs of Vereecken and Nozière (2020) were no lower than  $\sim 4$  kcal/mole, so that was taken as the actual lower limit for  $E_a^0$ , and was used whenever the estimated values were lower than that, as indicated in Table S17. Using this lower limit  $E_a^0$  results in 298 K rate constants that are so fast that H-shift isomerization would be the only significant fate of the peroxy radicals involved, so the exact value of these high rate constants, and therefore the upper limit  $E_a^0$  value used, would not have a practical effect on predictions of atmospheric chemical mechanisms unless there is more than one competing "fast" process. In that case, rate constants of competing fast processes are assumed to have the same rate constant.

The  $\alpha$  and  $\beta$  substitution corrections,  $E_a^{\text{corr}}$  were taken directly from effects of relative changes in rate constants caused by these substituents as recommended by VN20, and converted to effects on activation energy based on assuming that these substituents had no effect on the A factors. These substituents may well affect the A factors, but we have insufficient information to estimate such effects. The  $E_a^{\text{corr}}$  values so derived are summarized in Table S19. The recommended  $E_a^{\text{corr}}$  values for  $\beta$ -OH and



$\beta$ -ONO<sub>2</sub> substituents were independent of transition state ring size, but different values for the  $E_a^{\text{corr}}$  values for  $\beta$ -oxo substituents were given for ring sizes up to 8. Note that the recommended  $E_a^{\text{corr}}$  values for *endo*  $\beta$ -oxo were not applied to reactions of acyl peroxy radicals, since these effects are applicable to all such reactions, and are incorporated in the  $E_a^{\text{HR}}$  values used.

Table S19.  $E_a^{\text{corr}}$  values used for various types of  $\alpha$  or  $\beta$  substituents.

Substituent on H-group	$E_a^{\text{corr}}(\text{Subst})$ (kcal/mole)					Note [a]
	RS=5	RS=6	RS=7	RS=8	RS=9+	
$\beta$ -OH			1.09			1
$\alpha$ -ONO <sub>2</sub>			1.89			1
<i>Endo</i> $\beta$ oxo	[b]	0.90	-1.27	-2.38	-2.38	2
<i>Exo</i> $\beta$ oxo	-4.47	-2.28	-1.36	-1.09	-1.09	2

[a] Notes are as follows:

- 1 Ring size independent value from Table 5 of VN20.
- 2  $E_a^{\text{corr}}$  values for RS through 8 from Table 5 of VN20. Values assumed to be constant for ring sizes of 8 or greater.

[b] This reaction requires a ring size of 6 or greater.

H-shift isomerizations are assumed not to occur at significant rates if the radical has an  $\alpha$  substituent other than carbon-centered groups or -OH, -OOH, ether groups, or -ONO<sub>2</sub>, as would be the case if there were  $\alpha$ -halogen substituents, or H-shifts from the HCO in esters. Note that these reactions may well be favored if there were  $\alpha$ -amino substituents, but this is not currently considered by this system.

Note that strain energies should or might be significantly higher in reactions of cyclic peroxy radicals (Vereecken et al., 2021) or those where there is a double bond in the *trans* configuration in the transition state. The mechanism generation system assumes that H-shift isomerizations (for alkoxy as well as peroxy radicals) do not occur if the transition state has a double bond in the *trans* configuration, or has more than one group in the transition state ring that is in another ring. The treatment of *trans* double bonds is reasonable, but some multi-ring configurations may well have low enough strain to allow the reaction to proceed, so our estimates will miss these reactions. No attempt was made in this work to derive separate estimates for H-shift rate constants for cyclic peroxy radicals, or estimate any differences in their A factors. MechGen assumes that the ring strain is the same as in acyclic radicals if no more than two groups in the transition state are in another ring. This may well lead to overestimation of rate constants in some cyclic radicals, while potentially overlooking non-negligible reactions in other cases.

Predicted rate constants. The 298K rate constants predicted using the equations and the parameter values given in this section are essentially the same as those in the lookup tables provided by VN20 and also the rate constants from Møller et al. (2019) that are included in Table S15 because these were used to derive the parameters, and only one example is provided for each H- and R-group pair. Figure S12 plots the experimental vs. estimated rate constants the experimentally measured rate constants that are given in Table S15. This figure does not cover the full range of estimated rate constants (which range from  $\sim 7 \times 10^{-12}$  to  $\sim 7 \times 10^6 \text{ sec}^{-1}$ ), but includes the range where experimental data are available. It can be seen that most of the values agree very well, due to the fact that the lookup tables took these experimental data into account. The one case where there was a factor of three difference was for reactions of two isomers that

had methyl groups in different positions, where the experiments gave a factor of ~10 difference in rate constant, while the SAR predicts that they should have the same rate constant. The estimated rate constant for the reactions of 1-butyl peroxy radicals was greater than the measured upper limit rate by a factor of ~1.6, so the actual error factor is probably greater than this. This

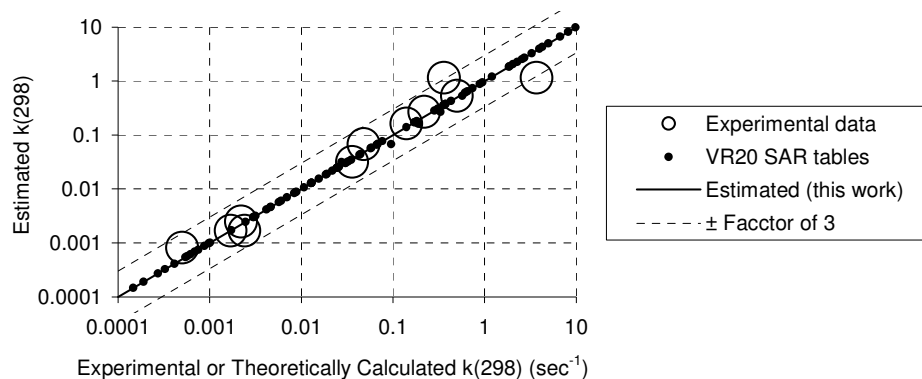


Figure S12. Plots of estimated 298K rate constants for peroxy H-shift isomerizations against the experimental or theoretically calculated values listed in Table S15. The dotted lines show a factor of  $\pm 3$  uncertainty range. Estimated vs. theoretically calculated rate constants in this magnitude range are also shown.

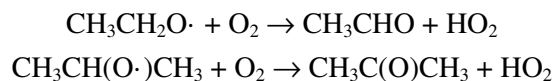
suggests that these estimates are uncertain by at least a factor of 3, though the uncertainty is probably more than an order of magnitude if parameters had to be estimated.

Figure S13 shows the estimated H-shift isomerization rate constants for the most favorable ring size for all the H- and R-group combinations covered by our estimates, excluding  $\alpha$ - and  $\beta$ -substitution corrections. The figure also has lines giving the upper and lower limits of these rate constants used by MechGen when generating peroxy radical reactions -- reactions faster than the upper limit are assumed to be the only fate of the peroxy radical, while those that are below the lower limit are treated as negligible and are not generated. For those with rate constants between these limits there is a competition between unimolecular and bimolecular reactions of these radicals, so the estimated rate constant would have an impact in predicted mechanisms.

## S1.6. Reactions of Alkoxy Radicals

### S1.6.1. Bimolecular Rate Constants

Reaction with  $O_2$ . Alkoxy radicals with  $\alpha$  hydrogens can react with  $O_2$  in the atmosphere by  $O_2$  abstracting the  $\alpha$ -hydrogen, forming  $HO_2$  and the corresponding carbonyl compound. For example,



Alkoxy +  $O_2$  rate constants have been measured for various alkoxy radicals formed from alkanes and were summarized by Atkinson (2007), and Calvert et al. (2008) gave recommendations for methoxy, ethoxy, 1- and 2-propoxy, and 1-butoxy radicals. The recommended values are summarized on Table S20, along with rate constants for 1- and 2-butoxy and 2-pentoxy radicals derived from data summarized by Atkinson (2007). Note that Atkinson (2007) also reported rate constants measured for cyclohexoxy

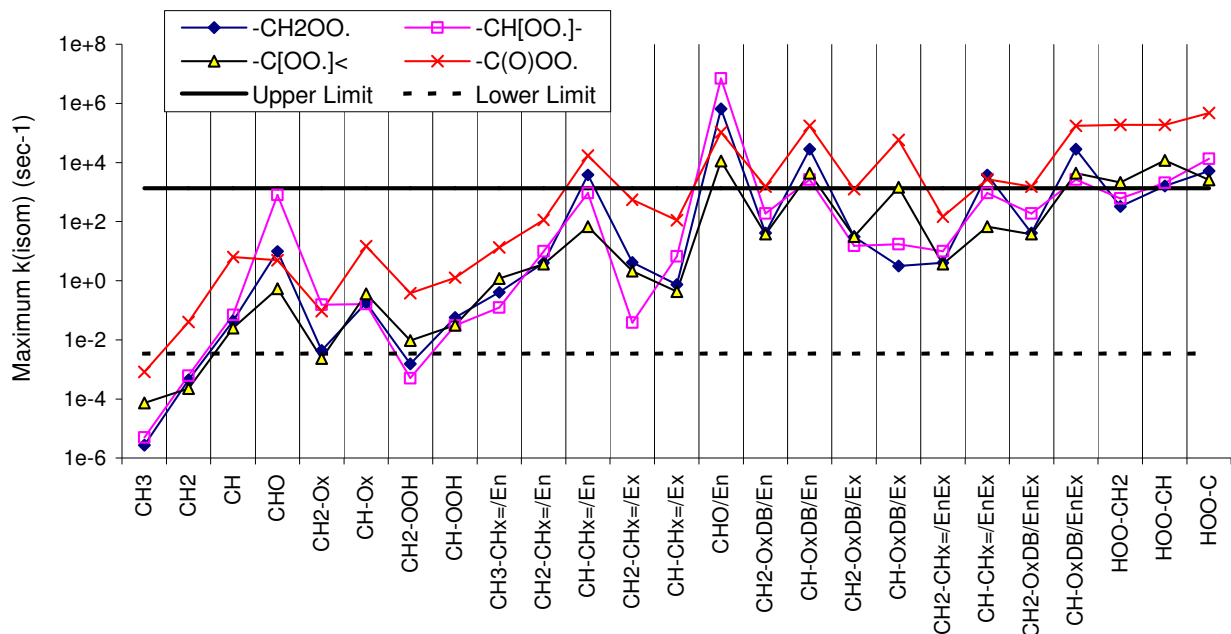


Figure S13. Estimated peroxy H-shift isomerization rate constants for the most favorable ring size for various H- and R-group pairs without  $\beta$ -substitution corrections. Also shown are upper and lower rate constant limits used during mechanism generation.

and 4-methyl cyclohexoxy radicals and other butoxy and pentoxy measurements. However, they are not used for deriving estimation parameters because the temperature dependences reported are not consistent with results for the more well-studied radicals, and may reflect experimental or data analysis problems. Likewise, data reported by Atkinson (2007) for radicals that undergo rapid competing isomerization reactions are also not used because of experimental uncertainties.

Table S20 shows that the rate constants for reactions with  $O_2$  are very similar for  $C_{3+}$  radicals, and so we assume they are the same for all primary alkoxy radicals except methoxy and ethoxy (whose rate constants are assigned for the specific reactions, as shown on Table S56), and they are also the same for all secondary alkoxy radicals. Based on this, we derived the following rate constant expressions for estimation purposes (with the rate constants for methoxy and ethoxy being assigned for these specific cases to the values given in Table S20 as indicated in Section S1.9)

$$k(RCH_2O \cdot + O_2) = 2.38 \times 10^{-14} \exp(-0.38/RT) = 1.25 \times 10^{-14} \text{ at } T=298K,$$

$$k(RCH(O \cdot)R') = 1.95 \times 10^{-14} \exp(-0.59/RT) = 7.27 \times 10^{-15} \text{ at } T=298K,$$

where the units are  $\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  and  $RT$  is the product of temperature and the gas constant. In the case of primary radicals, the 298K rate constant was derived by averaging the recommended values from measurements for n-propoxy and n-butoxy radicals, with the Arrhenius parameters estimated by assuming that the A factor is the same as that given for 1-propoxy. In the case of secondary radicals, the 298K rate constant was derived by averaging the recommended values from measurements for 2-propoxy 2-butoxy, and 3-hexoxy radicals, with the Arrhenius parameters estimated by assuming that the A factor is the same as that given for 2-propoxy.

Table S20. Recommended kinetic parameters for the reactions of alkoxy radicals with O<sub>2</sub>.

Rxn	Radical	From Measurements [a]			Used [b]		Notes [c]
		A	Ea	k(298)	k(298)	Err.	
O <sub>2</sub>	CH <sub>3</sub> O·	7.40e-14	2.27	1.60e-15	As measured		1
O <sub>2</sub>	CH <sub>3</sub> CH <sub>2</sub> O·	5.10e-14	1.09	8.10e-15	As measured		1
O <sub>2</sub>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> O·	2.40e-14	0.46	1.10e-14	1.25e-14	12%	1
O <sub>2</sub>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> O·			1.40e-14	1.25e-14	-12%	2
O <sub>2</sub>	CH <sub>3</sub> C(O·)CH <sub>3</sub>	2.00e-14	0.62	6.90e-15	7.28e-15	5%	1
O <sub>2</sub>	CH <sub>3</sub> CH <sub>2</sub> C(O·)CH <sub>3</sub>			7.80e-15	7.28e-15	-6%	3, 5
O <sub>2</sub>	CH <sub>3</sub> CH <sub>2</sub> C(O·)CH <sub>2</sub> CH <sub>3</sub>			7.20e-15	7.28e-15	1%	4, 5
O <sub>3</sub>	Phenoxy			2.86e-13	As measured		6
NO	Phenoxy			1.88e-12	Reaction ignored		7
NO <sub>2</sub>	Phenoxy			2.08e-12	As measured		7
HO <sub>2</sub>	Phenoxy				1.10e-10		8

[a] Rate constant  $k = A \exp(-E_a/RT)$ , with A and k in  $\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$  and  $E_a$  in kcal/mole.

[b] The first column is the rate constant at 300K used for estimates (in  $\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$ ), and the second is relative difference between the recommended and estimated rate constant for this radical.

[c] Sources of the rate constants and other comments are as follows.

- 1 As recommended by Calvert et al. (2008).
- 2 From Hein et al. (1999), as given by Atkinson (2007).
- 3 Average of room temperature measurements of Hein et al. (1998) and Falgayrac et al. (2004), as cited by Atkinson (2007).
- 4 Data from Hein et al. (2000), as cited by Atkinson (2007).
- 5 Other data tabulated by Atkinson (2007) are not used because the reported Arrhenius parameters are not consistent with data for the more well-studied alkoxy radicals.
- 6 Rate constant from Tao et al. (1999).
- 7 Rate constants from Platz et al. (1998).
- 8 No measurement of this rate constant could be found. It is estimated to be approximately equal to the rate constant for methoxy + HO<sub>2</sub> as measured by Assaf et al. (2018).

Note that alkoxy radicals without  $\alpha$  hydrogens are not expected to react with O<sub>2</sub>. These include tertiary alkoxy radicals (R<sub>3</sub>CO·), acyl oxy radicals (RC(O)O·), and phenoxy radicals (BzO·). Instead, most tertiary alkoxy and all acyl oxy radicals undergo relatively fast decomposition or rearrangement reactions, as discussed below. On the other hand, phenoxy radicals do not have any facile unimolecular reactions, so must be consumed by other bimolecular reactions, as discussed below.

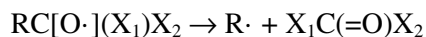
Reactions of Phenoxy Radicals. Phenoxy radicals are formed in the reactions of various aromatics, and are not expected to react with O<sub>2</sub> or undergo unimolecular reactions under atmospheric systems. MechGen assumes that their major atmospheric sinks are either reaction with O<sub>3</sub>, NO<sub>2</sub> or HO<sub>2</sub>. Reactions with NO are ignored, because they are expected to form nitroso compounds or nitrites that would rapidly photolyze to re-form the reactants, and the concentrations of NO<sub>2</sub> are usually higher than NO in the atmosphere. Measured or estimated rate constants for these reactions, including the reaction with NO for comparison, are included in Table S20. Note that the rate constant for the reaction with HO<sub>2</sub>

has not been measured, so it is assumed to be the same as for the reaction of HO<sub>2</sub> with methoxy radicals. These rate constants are also used for reactions of substituted phenoxy radicals, assuming that substituents on the aromatic ring do not affect the bimolecular rate constants.

The mechanisms used by MechGen to represent these bimolecular reactions of phenoxy radical reactions are discussed in Section 6.1 of the main text.

### S1.6.2. $\beta$ Scission Decompositions

Most alkoxy radicals can undergo  $\beta$ -scission reactions, where a bond on the carbon bonded to the alkoxy breaks, forming a radical and a carbonyl group. These can be represented as



where R is any portion of the molecule next to the radical group, and the X's are H's or other portions of the molecule next to the radical group. Depending on the structure and the radical, the reaction energetics can range from highly endothermic to highly exothermic, and the decomposition rate constant can vary from being negligible compared to rates of reaction with O<sub>2</sub> in the atmosphere or other unimolecular reactions, to being the dominant fate for the radical.

Table S51 in Section S5.2 summarizes measured or calculated rate constants for  $\beta$ -scission decompositions of alkoxy radicals that were used as the basis for deriving general decomposition rate constant estimates for this work. The primary source of measurement data is the review of Orlando et al. (2003), but there are also a number of rate constants derived from results of quantum chemical calculations given by Vereecken and Peeters (2009). The data are given in terms of Arrhenius parameters based on the assumption that

$$k(\text{decomp, reaction}) = n \times A(\text{decomp}) \times \exp\{-E_a(\text{reaction})/RT\}$$

where n is the reaction path degeneracy (the number of  $\beta$ -scission decompositions the molecule can undergo that give the same products, which could be up to 3 for tertiary alkoxy radicals with the same substituents), E<sub>a</sub> is the activation energy that depends on the radical and products formed as discussed below, and A(decomp) is a pre-exponential factor that is assumed to be the same for all alkoxy  $\beta$  scission decompositions. Based on a review of the available kinetic data, Orlando et al. (2003) recommended assuming

$$A(\text{decomp}) = 1.0 \times 10^{14} \text{ sec}^{-1}$$

for all decompositions, and that was adopted in this work, and is reflected in the A factors tabulated in Table S51 in Section S5.2. The tabulated activation energies were derived from the measured rate constants and the pre-exponential factors derived from A(decomp) and the reaction path degeneracy, n, for the reaction.

The rate constants and activation energies derived from available experimental data as summarized by Orlando et al. (2003) are insufficient to derive parameters for all types of decomposition reactions of potential interest. With the recent enhancements to quantum calculation tools and computer capabilities, it is now feasible to use quantum calculation results to supplement the experimental database for the purpose of deriving estimation methods. In order to derive general structure-reactivity estimates for alkoxy reactions, Vereecken and Peeters (2009) calculated barrier heights for over 100 decomposition reactions, of which 21 also have experimentally derived activation energies. Those are listed on Table S51, and Figure S14 shows plots of experimentally-derived activation energies against the barrier heights calculated by Vereecken and Peeters (2009) for these 21 compounds. The calculated barrier heights are

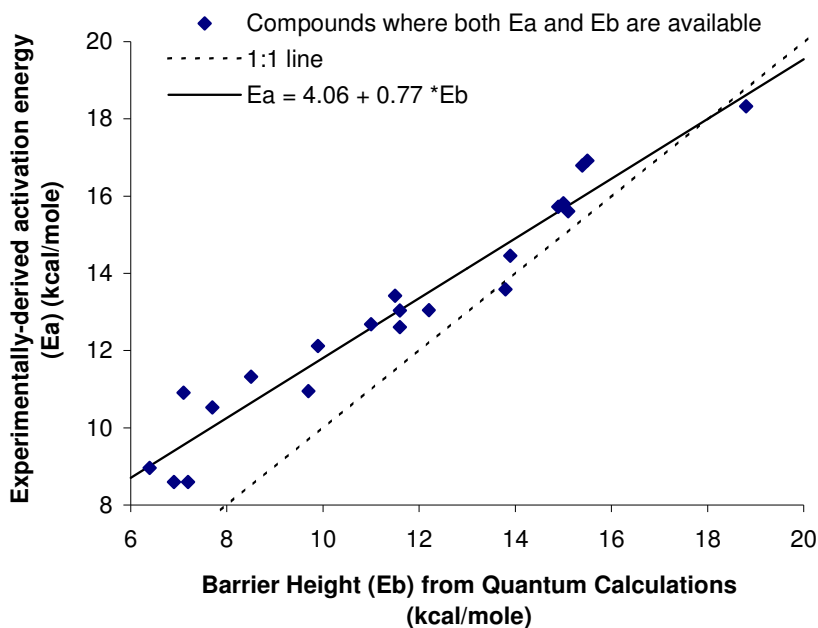


Figure S14. Plots of activation energies for beta-scission decomposition reactions derived from experimental data summarized by Orlando et al. (2003) against barrier heights calculated by Vereecken and Peeters (2009) for the same reactions. The line fit was used to estimate activation energies for reactions where experimental data are not available.

not exactly the same as the activation energies and differ by as much as 4 kcal/mole at the lower barrier heights, but differences are expected because  $E_a$  takes into account temperature-dependent entropic factors while  $E_b$  does not. Nevertheless, the data are well fit by

$$E_a(\text{experimental}) = 4.06 + 0.77 * E_b$$

where  $E_a(\text{experimental})$  is derived from the experimental rate constant given by Orlando et al. (2003) assuming  $A(\text{decomp}) = 1 \times 10^{-14} \text{ sec}^{-1}$ ,  $E_b$  is the barrier height calculated by Vereecken and Peeters (2009), and the units of both are kcal/mole. This equation was used to derive  $E_a$  values for compounds where barrier heights were calculated by Vereecken and Peeters (2009) but for which experimental data are not available. These are included on Table S51 and also used as a basis to derive the parameters for estimating rate constants for these decomposition reactions. Note that Novelli et al. (2020) have updated data relevant to these estimates that will need to be taken into account when MechGen is updated.

Even with the addition of the activation energies for the reactions calculated by Vereecken and Peeters (2009), the available data do not have adequate coverage for some types of alkoxy radical decomposition reactions, particularly decomposition forming smaller alkoxy radicals. In order to include data from such reactions, Table S51 includes reactions whose rate constants and activation energies were derived from relative product yield data, which gives ratios of rate constants relative to another alkoxy radical reaction whose rate constant can be estimated using some other method. These cases are indicated and discussed in footnotes to the table.

In our previous work (Carter, 2000, 2010a), the activation energies for most  $\beta$ -scission decompositions were estimated using

$$E_a(\text{Reaction}) = E_a(\text{FormRad}) + [ E_b \times \Delta H_r(\text{reaction}) ],$$

where EaA depended on the radical formed, EaB was a constant assumed for all alkoxy radicals and was derived from data for reactions forming methyl radicals, and  $\Delta H_r$  was the heat of reaction. However, this did not work well in all cases, correction terms had to be added for some types of reactions, and insufficient information was available for estimating heats of reaction for some reactions. More recently, Vereecken and Peeters (2009) developed a SAR approach where they could estimate activation energies based only on the groups in the molecule near where the reaction is taking place, without having to derive an estimated heat of reaction. In this work, we use a version of this approach, where the activation energy depends only on the types of radicals and products formed in the reaction, and in some cases the substituents on these radicals and products, without the need to derive the heat of reaction, with additional corrections being applied if the radical has rings:

$$Ea(\text{Reaction}) = EaR(\text{FormRad}) + EaP(\text{ProdType}) + EaRc(\text{RadSubst}) + EaPc(\text{ProdSubst}) + \text{RingCorr}(\text{Ring}),$$

where "FormRad" is the type of radical formed in the reaction (methyl, primary, secondary, alkoxy, etc.), and "ProdType" is the type of carbonyl product formed (either formaldehyde, other aldehyde, or ketone), "RadSubst" refers to groups adjacent to the radical center of the radical formed, "ProdSubst" refers to substituents on the carbonyl product formed, and "Ring" refers to the size of the ring that is broken as a result of this decomposition, if applicable (RingCorr=0 if no ring). All these four types of parameters are estimated or derived to be consistent with the data given on Table S51.

The various parameters that MechGen currently uses to estimate activation energies for  $\beta$ -scission decompositions are listed on Table S21 through Table S23, along with footnotes or codes indicating how the parameters were derived. As indicated in these tables, some parameters were optimized to fit the data on Table S51, while others were estimated as discussed below. The adjusted parameters were derived to minimize the sum-of-squares errors in the predicted activation energies, using Excel's "Solver" capabilities. The optimizations were done in three stages. First, the six parameters that determine decomposition rates for unsubstituted acyclic alkoxy radicals (listed first on Table S51) were derived and not adjusted further. Next, the 34 other parameters that affect predicted rates for the other decomposition reactions, mostly for substituted radicals or radicals with unsaturated bonds, were derived to fit the data for the second set of compounds ("Other acyclic alkoxy radicals") listed on Table S51. Finally, the ring correction parameters were derived to fit the data for the decomposition of ring-containing alkoxy radicals, the third set of compounds listed on Table S51.

The EaR parameter gives the dependence of the overall activation energy on the type of radical formed in the decomposition reaction. These parameters are listed on Table S21. The data on Table S51 were not sufficient to derive all these parameters, so many had to be estimated. Various relationships between properties of the radicals and the optimized activation energy parameters were examined, including ionization potentials, but the best correlation was found between the best fit activation energy parameters and the C..H bond dissociation energy (BDE) forming the radical from the corresponding compound where H is added. These estimated BDE values, derived as discussed in Section S2.1, are included on Table S21. Figure S15 gives plots of the optimized activation energy parameters for various types of forming radicals against these bond dissociation energies. The fit is not perfect, but the EaR derived from data for reactions forming alkyl, vinyl, and acyl radicals are approximately fit by

$$EaR(\text{FormRad}) = 0.56 \text{ BDE} - 40.31 \text{ kcal/mole.} \quad (\text{S9})$$

where BDE is the bond dissociation energy in kcal/mole. This was used to derive the estimated EaA parameters listed on Table S21.

The EaP parameter gives the dependence of the activation energy on the general type of carbonyl product formed in the decomposition reaction, relative to the activation energies for reactions forming

Table S21. List of EaR parameters that give dependences of the activation energies of alkoxy radical decompositions on the nature of the radical formed in the decomposition.

Radical Type	BDE [a] (kcal/mole)	EaR (kcal/mole)	Radical Type	BDE [a] (kcal/mole)	EaR (kcal/mole)
Adjusted to fit reactions forming alkyl radicals					
CH <sub>3</sub> (.)	104.98	18.46	>CH(.)	97.82	12.79 [b]
-CH <sub>2</sub> (.)	101.04	15.51 [b]	>C(.)	95.64	10.73 [b]
Adjusted to fit reactions forming other radicals					
HC(O)(.)	88.63	11.44	=CH(.)	110.18	22.23
-CO(.)	89.34	9.27			
Estimated from BDE using Equation (S9)					
=C(.)	106.66	19.04	>CH-OO(.)	85.02	7.00
CH <sub>3</sub> -O(.)	105.16	18.20	>C<OO(.)	85.85	7.46
-CH <sub>2</sub> -O(.)	104.12	17.62	=CH-OO(.)	85.85	7.46
>CH-O(.)	104.98	18.10	=C<OO(.)	85.85	7.46
>C<O(.)	104.12	17.62	-C(O)OO(.)	95.98	13.10
=CH-O(.)	86.46	7.80	NHx(.)	101.84	16.36
=C>O(.)	82.39	5.53	OH	118.83	25.81
-C(O)O(.)	109.53	20.63	Cl	103.15	17.08
HC(O)O(.)	109.91	20.85	Br	87.51	8.38
CH <sub>3</sub> -OO(.)	85.85	7.46	NO <sub>3</sub>	102.05	16.47
-CH <sub>2</sub> OO(.)	85.44	7.23	HO <sub>2</sub>	87.57	8.42

[a] C-H bond dissociation energy associated with forming this type of radical.

[b] Substituent correction factors, EaRc, are applied for these radicals if they contain non-alkyl  $\alpha$  substituents. These are listed in Table S22.

formaldehyde. Note that primary alkoxy radicals give formaldehyde, secondary radicals give higher aldehydes, and tertiary alkoxy radicals give ketones. The data are fit using

$$\begin{aligned} \text{EaP}(\text{formaldehyde}) &= 0 && \text{(assigned)} \\ \text{EaP}(\text{C}_{2+} \text{ aldehydes}) &= -2.23 \text{ kcal/mole} && \text{(adjusted)} \\ \text{EaP}(\text{ketones}) &= -3.89 \text{ kcal/mole} && \text{(adjusted)} \end{aligned}$$

Note that product substituent corrections (EaPc) are applied when aldehydes or ketones are formed with non-alkyl substituents.

The EaRc and EaPc parameters give the corrections to the activation energy due to the presence of substituents on the radical (EaRc) or the aldehyde or ketone products (EaPc) formed. The values that were derived to fit the data and the estimated values for the substituents without available data are summarized on Table S22 and Table S23, respectively. Values for substituents lacking data were estimated using parameters that could be derived from the data, as indicated in the footnotes to the table. Note that the corrections for the halogen or amine substituents are highly uncertain.

There are four types of ring corrections that are applied for decompositions of alkoxy radicals containing ring structures. These are discussed below.



Table S22. List of EaRc parameters that give corrections for the presence of substituents on alkyl radicals for calculating activation energies of alkoxy radical decompositions forming such radicals.

Group	Substituent on -CH <sub>2</sub> .		Substituent on >CH.		Substituent on >CH.	
	Method [a]	EaRc [b]	Method	EaRc	Method	EaRc
-R	Assigned	0	Assigned	0	Assigned	0
-CH <sub>x</sub> =	Adjusted	-5.02	Est 1	-5.02	Est 1	-5.02
-C≡	Est 1	-5.02	Est 1	-5.02	Est 1	-5.02
-CO-	Adjusted	-1.29	Est 2	-1.29	Est 2	-1.29
-OH	Adjusted	-3.60	Adjusted	-3.22	Adjusted	-2.17
-OOH	Adjusted	-4.95	Adjusted	-3.85	Est 3	-3.25
-OOR	Adjusted	-3.33	Adjusted	-2.15	Est 3	-3.25
-O-	Adjusted	-4.33	Adjusted	-3.25	Adjusted	-1.60
-ONO <sub>2</sub>	Adjusted	0.09	Adjusted	0.48	Est 4	0.28
-NO <sub>2</sub>	Adjusted	3.10	Adjusted	2.42	Est 4	0.00
-Cl	Est 5	-3.25	Est 5	-3.25	Est 5	-3.25
-Br	Est 5	-3.25	Est 5	-3.25	Est 5	-3.25
-NH <sub>x</sub>	Est 5	-3.25	Est 5	-3.25	Est 5	-3.25

[a] Method codes: "Assigned": assigned to be zero (not independent of EaR); "Adjusted": adjusted to fit data for alkyl radicals with this substituent; "Est n": estimated as indicated below, where "n" indicates how the estimate was made.

- 1 Estimated to be the same as the correction factor derived from -CH<sub>x</sub>= substitution on -CH<sub>2</sub>-. Because of lack of data, substitution on other alkyl groups and by -C≡ and -Benzyl assumed are assumed to be the same.
- 2 Estimated to be the same as the correction factor derived from -CO- substitution on -CH<sub>2</sub>-. Because of lack of data, substitution on other alkyl groups are assumed to be the same.
- 3 Estimated from the average of the effects of -OH, -OOH, -OOR, and -O substituents on alkyl groups where data are available.
- 4 Derived from the average of the correction factors that fit the data for this substituent on primary and secondary alkyl groups
- 5 The effects of these substituents are unknown. Roughly estimate they are approximately the same as the effects of -OX substituents.

[b] Substituent correction term in units of kcal/mole.

Type 1 corrections are applied to cases where the carbon bonded to the alkoxy group is in a ring and the β-scission reaction breaks the ring. One would expect that the corrections for strained rings to be negative numbers with relatively high magnitudes because the ring strain is relieved. However, the magnitude of the correction is considerably less than the strain in cycloalkane rings of the same size. A plot of the Type 1 ring corrections that were derived to fit the data on Table S51 against cycloalkane ring strains is shown on Figure S16, where it can be seen that the data are reasonably well fit by a straight line. This line was used to estimate Type 1 ring factors for rings where no data is available. The magnitudes of these corrections are indicated on Table S24.

Type 2 corrections are used when the alkoxy group is in a ring but the leaving radical group is not in a ring or is in a different ring, so the reaction does not break any rings. Note that Vereecken and Peeters (2009) found that corrections were also needed in this case. Data on Table S51 are sufficient to derive

Table S23. List of EaPc parameters that give corrections for the presence of substituents on the aldehyde or ketone product formed for calculating activation energies of alkoxy radical decompositions.

Group	Substituents on Aldehyde		Substituents on Ketone	
	Method [a]	EaPc [b]	Method	EaPc
-R	Assigned	0	Assigned	0
-CH <sub>x</sub> -O-	Adjusted	1.07	Est 3	1.07
-CH <sub>x</sub> -OH	Adjusted	-0.18	Adjusted	-0.38
-CH <sub>x</sub> =	Adjusted	-2.03	Est 3	-2.03
-C≡	Est 1	-2.03	Est 3	-2.03
-C(O)- or -CHO	Adjusted	1.30	Adjusted	0.33
-OO-	Adjusted	-4.35	Adjusted	-3.70
-OH	Adjusted	-5.21	Adjusted	-3.63
-O-	Adjusted	-4.94	Adjusted	-3.46
-ONO <sub>2</sub>	Adjusted	-1.06	Est 3	-1.06
-NO <sub>2</sub>	Est 2	-1.06	Est 3	-1.06
-Cl	Est 2	-1.06	Est 3	-1.06
-Br	Est 2	-1.06	Est 3	-1.06
-NH <sub>x</sub>	Est 2	-1.06	Est 3	-1.06
Cyclopropyl ring [c]	Adjusted	-1.49	Est 5	-1.49
Cyclobutyl ring	Adjusted	-0.79	Est 5	-0.79
≥Cyclopentyl ring	Est 4	~0	Est 4	~0

[a] Codes for derivation methods: "Assigned": Assigned to be 0; not independent of EaP; "Adjusted": Adjusted to fit data on Table S51; "Est n": Estimated as indicated below, where "n" is the footnote number.

- 1 No data available to derive the effect of triple-bonded substituents, so it is assumed to have the same effect as a double bonded substituent.
- 2 No data available to derive the effects of these substituents. They are assumed to be the same as the effect of substitution by a nitrate group. This is highly uncertain.
- 3 No data available to derive the effect of this substituent on ketone product. It is assumed to be the same as the effect derived for aldehyde products.
- 4 No data available to estimate effects of larger than cyclobutyl rings. It is assumed that no correction is needed based on the relatively much lower ring strain energies for the larger rings.
- 5 No data available to derive corrections for ring groups bonded to the ketone groups. The correction is estimated to be the same for ring groups bonded to aldehyde groups.

[b] Substituent correction parameter in kcal/mole.

[c] These are "Type 4" ring corrections, used for cases where there is a group in a ring bonded to the aldehyde or ketone group in the carbonyl product formed. Note that the reaction does not break a ring.

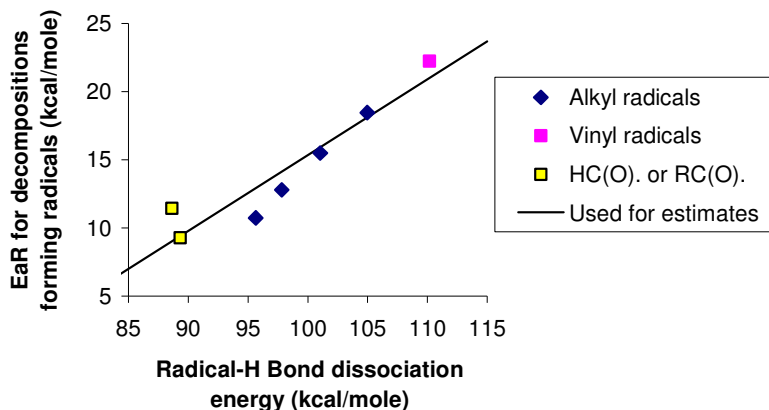


Figure S15. Plots of optimized EaR values for  $\beta$ -scission decompositions forming various types of radicals against the C-H bond dissociation energy that forms the radical. The line that fit the data, used for estimation purposes, is also shown.

corrections for ring sizes of 4-6. These are given in the middle columns of Table S24 along with estimated corrections for other ring sizes. The optimized corrections did not have a strong dependence on ring size, so we estimated the correction for 3-member rings using the correction for 4-member rings and estimated those for 7+ member rings using the correction for 6 member rings. All these corrections were approximately +2 kcal/mole.

Type 3 corrections are used when the alkoxy group is not a ring, but the leaving radical is, so these reactions also do not break a ring. Vereecken and Peeters (2009) also found that these corrections are needed, and data on Table S51 are sufficient to derive corrections for leaving groups in 3-6 member rings. The corrections needed for forming 3-member ring radicals is relatively large, is lower but non-negligible for 4 member rings, and it is relatively small for 5- and 6-member rings. The corrections used for 7+ member rings are estimated to be the same as that that fit the data for 5- and 6-member rings. The magnitudes of these corrections are given in the rightmost columns of Table S24.

Type 4 is when neither the alkoxy group or the radical group formed are in a ring, but the aldehyde or ketone group in the carbonyl product formed is bonded to a group in a ring, which is also not broken during the reaction. Note that MechGen treats Type 4 corrections as substituent corrections on the carbonyl product (EaPc), and the adjusted or estimated values of these corrections are included in the last three rows of Table S23.

The performance of our estimates in predicting the alkoxy radical decomposition activation energies in Table S51 is shown on Figure S17. The activation energies for alkoxy radicals from alkanes and cyclic compounds are reasonably well predicted, while those for most other radicals are generally predicted to within  $\pm 1$  kcal/mole. Note that  $\pm 1$  kcal/mole corresponds to over a factor of 5 uncertainty in the rate constants, which indicates the magnitude of the uncertainties of the estimates. For this reason, the mechanism generation system uses the experimentally-derived values or the values given in Table S51 when available, and only uses estimates as discussed in this section when such data are not available. For example, we could find no data that could be unambiguously used to derive EaR parameters for alkoxy  $\beta$ -scission reactions that form alkoxy radicals, despite the fact that such reactions might occur in the photooxidations of many ethers. Other parameter estimates may be even more uncertain, but most of the reactions involving them are not expected to be very common, except perhaps in multi-generation mechanisms.

Table S24. Correction parameters used when estimating activation energies for beta-scission decompositions for ring-containing alkoxy radicals.

Ring Size	Cycloalkane ring strain (kcal/mole) [a]	1. Alkoxy and Leaving Radical groups in same ring (ring breaking)		2. Alkoxy in a ring; leaving radical group in different or no ring		3. Leaving radical group in a ring but the alkoxy group is not.	
		Method [b]	RingCorr	Method	RingCorr	Method	RingCorr
3	28.20	Est 1	-7.08	Est 2	1.99	Adjusted	7.25
4	26.53	Adjusted	-6.59	Adjusted	1.99	Adjusted	2.14
5	6.69	Adjusted	-2.12	Adjusted	1.80	Adjusted	-0.29
6	0.48	Adjusted	-0.04	Adjusted	1.80	Adjusted	-0.29
7	6.69	Est 1	-1.81	Est 3	1.80	Est 3	-0.29
8	10.28	Est 1	-3.45	Est 3	1.80	Est 3	-0.29
9	13.38	Est 1	-3.39	Est 3	1.80	Est 3	-0.29
10	13.15	Est 1	-3.15	Est 3	1.80	Est 3	-0.29
11	12.19	Est 1	-1.40	Est 3	1.80	Est 3	-0.29
12	5.02	Est 1	-0.25	Est 3	1.80	Est 3	-0.29

[a] From Holmes and Aubry (2012).

[b] Methods codes: "Adjusted": Adjusted to fit data for ring-containing compounds on Table S51; "Est n" Estimated as indicated in note n, given below. Ring correction in kcal/mole.

- 1 Estimated assuming a linear relationship between the ring breaking correction and the cycloalkane ring strain as discussed in the text.
- 2 Assumed to be the same as the correction derived for 4-member rings.
3. Assumed to be the same as derived for 6-member rings.

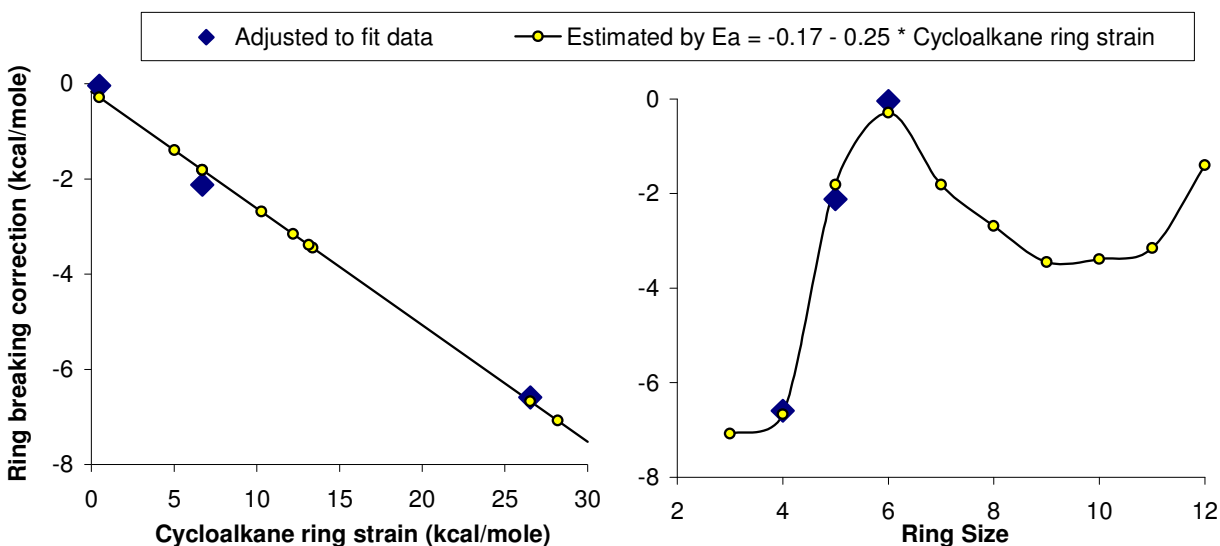


Figure S16. Plots of corrections for ring breaking on activation energies beta scission decompositions of alkoxy radical where both the alkoxy and leaving radical groups are on the same ring against the ring strain for the corresponding cycloalkane and against the ring size.

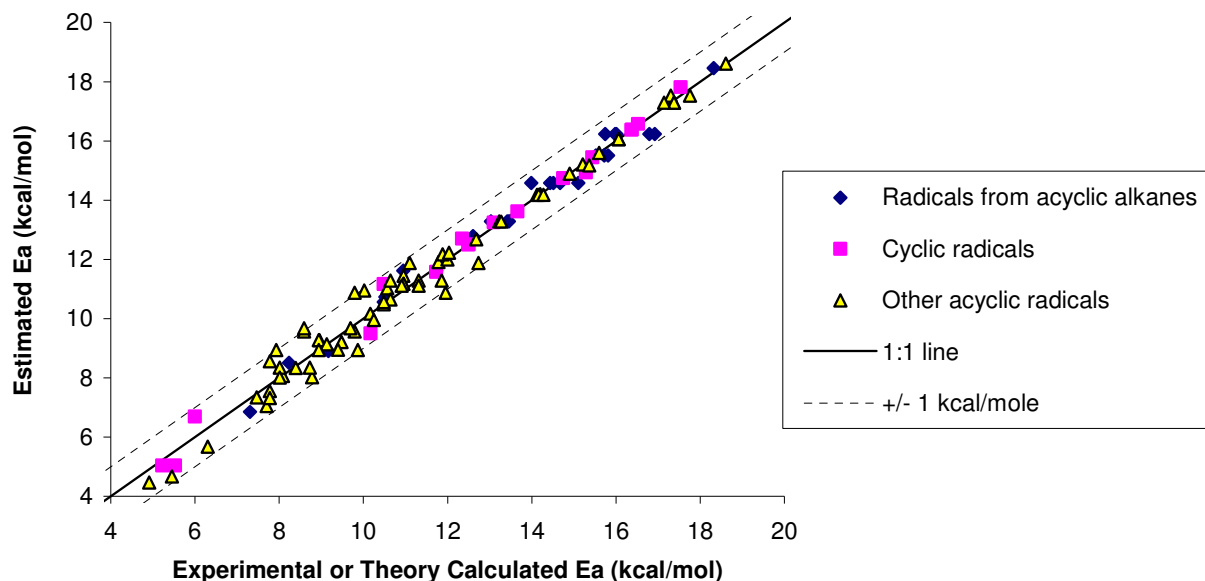
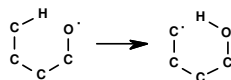


Figure S17. Plots of estimated activation energies for alkoxy radical beta-scission decompositions against the experimentally or theoretically-derived activation energies given in Table S51.

### S1.6.3. H-Shift Isomerization Reactions

As for the peroxy radicals described above (Section S1.5.5), alkoxy radicals can undergo H-shift isomerization reactions where the radical center abstracts a hydrogen from elsewhere in the molecule, converting the radical group into a group with an -OH substituent, and forming a carbon centered radical, via a cyclic transition state, e.g.,



This example shows a 1,4-H shift isomerization with a six-member ring transition state (the H is not counted when specifying the span in these reactions), but reactions with different ring sizes can also occur, though reactions with strained rings would be expected to be slower. H-shift isomerizations of alkoxy radicals under atmospheric conditions have been known to be important for longer chain ( $\approx C_4$  or greater) radicals for some time, and it is necessary to derive estimates for rate constants for this type of reaction for atmospheric conditions. This is discussed in this section.

Table S50 in Section S5.2 gives information concerning measured or theoretically calculated rate constants for H-shift isomerizations of alkoxy radicals that were used in this work to derive estimation methods for these reactions. Note data in this table are limited to data available at the time the estimation methods discussed in this section were developed, so this does not include all the relevant data that may now be available. These will be considered when MechGen is updated. However, the data in Table S50 cover the major types of alkoxy H-shift isomerizations that are needed for mechanisms representing atmospheric photooxidation systems.

The estimation of H-shift rate constants for peroxy radicals discussed in Section S1.5.5 utilized lookup tables derived by Vereecken and Nozière (2020) and extended in this work, but that approach was

not used when estimating these rate constants for alkoxy radicals because insufficient data were available at the time. Instead, the alkoxy hydrogen shift rate constants,  $k^{\text{HS}}$ , are estimated using:

$$k^{\text{HS}}(\text{H-group}, \text{RS}) = n\text{H} \times \text{A}(\text{RS}) \times \exp(-\text{Ea}(\text{H-group}, \text{RS}) / \text{RT}) \quad (\text{S10})$$

$$\text{Ea}(\text{H-group}, \text{RS}) = \text{Ea}^0(\text{H-group}, \text{RS}) + \text{Ea}^{\text{strain}}(\text{RS}) + \text{Ea}^{\text{corr}}(\text{H-group}) \quad (\text{S11})$$

$$\text{Ea}^{\text{corr}}(\text{H-group}) = \sum_{\text{Groups in ring}} \text{Ea}^{\text{InRingCor}}(\text{ring group}) + \sum_{\text{groups } \alpha \text{ to H-group}} \text{Ea}^{\text{corr}}(\text{group}) \quad (\text{S12})$$

where  $k^{\text{HS}}$  is in units of  $\text{min}^{-1}$ ;  $n\text{H}$  is the number of abstractable hydrogens giving the same reaction;  $\text{A}$  and  $\text{Ea}$  are the Arrhenius parameters in units of  $\text{min}^{-1}$  and  $\text{kcal/mole}$ , respectively;  $\text{T}$  is the temperature in degrees  $\text{K}$ ;  $\text{R}$  is the gas constant (0.0019872 in appropriate units); "RS" is the size of the transition state ring; "H-group" is the group from which the H is being abstracted (including substituents on the group and groups between this group and the radical center);  $\text{A}$ ,  $\text{Ea}^0$ ,  $\text{Ea}^{\text{strain}}$ ,  $\text{Ea}^{\text{InRingCor}}$ , and  $\text{Ea}^{\text{corr}}$  are estimated or adjusted parameters used to derive estimated rate constants. Note that unlike estimations for H-shifts in peroxy radicals, there is only one type of radical group ("R-group") used for alkoxy rate constant estimates.

The  $\text{A}$  factors used to estimate H-shift isomerization rate constants are assumed only to depend on the number of equivalent abstractable hydrogens, the type of radical, and ring size. The  $\text{A}$  factors per abstractable hydrogen are given in Table S25. As indicated in the footnotes to the table, these are based on results of theoretical calculations by Vereecken and Peeters (2010) and Davis and Francisco (2010, 2011). These decrease with ring size, making H-shifts over large distances in the molecule decreasingly likely, but not always negligible. These are not treated as adjustable parameters.

The ring strain energies used in part to estimate activation energies of these reactions are not treated as adjustable parameters, and are summarized in Table S25, with footnotes indicating the sources of these values. Note that the ring strain for H-shifts involving 6-member ring transition states are assigned a value of 0, since any strain in these reactions would be accounted for in the  $\text{Ea}^0$  values adjusted to fit the data. The differences in ring strains relative to alkoxy 1,4- are derived from results of theoretical calculations by Davis and Francisco (2011). The strain is high for small rings and also increases with ring size for larger rings. Plots of these ring strains against ring size were shown in Figure S11 in Section S1.5.5, where they are useful for estimating  $\text{A}$  factors for peroxy H-shift reactions.

Figure S18 shows plots of the estimated  $\text{A}$  factors for these reactions against transition state ring size, and also plots of the estimated rate constants against the rate constant for the unstrained ring size of 6, after taking into account the ring strains, but assuming  $\text{Ea}^0$  and the  $\text{Ea}^{\text{corr}}$ 's are the same. It can be seen that the  $\text{A}$  factor decreases slowly with ring size, but because of ring strain effects the reaction is fastest with ring size of 6, is only  $\sim 2.6$  times lower for ring size of 7, and has a minimum at ring size of 9-11 and increases with higher ring sizes. Because we assume strain is 0 for ring sizes greater than 12, the rate constant would decline relatively slowly after that due to the slow decline in  $\text{A}$  factor with ring size at the larger sizes. However, it should be noted that H-shift isomerizations with very long spans are unlikely to be important in most photooxidation mechanisms, since such large alkoxy radicals usually have many other facile reaction routes available to them, such as H-shifts with more favorable ring sizes or  $\beta$ -scission decompositions.

The  $\text{Ea}^0$  parameter can be considered as the base activation energy if there were no ring strain or non-alkyl substituents. They are currently assumed to depend only on the H-group in the case of alkoxy H-shift reactions. The values used for the parameters, and the methods used to derive or estimate them, are given in Table S26. These are either derived by adjustments so estimates fit the data given in Table S50 or are estimated when there are insufficient data available. Note that because of lack of sufficient data for these parameter values, estimated activation energies are particularly uncertain for H-abstractions other than from alkyl or  $-\text{CHO}$  groups.

Table S25. A factors per abstractable hydrogen and ring strain parameters used for estimating H-shift reactions for alkoxy and peroxy radicals.

RS	Shift	A(RS) [a]		Ea <sup>strain</sup> (RS)		k(RS) / k(RS=6) [a]
		sec-1	Note	kcal/mole	Note	
4	1,2-H	2.65e+11	1	18.90	3	9e-14
5	1,3-H	1.09e+11	1	10.95	3	3e-8
6	1,4-H	4.00e+10	2	0	4	1
7	1,5-H	1.63e+10	1	0.05	3	0.4
8	1,7-H	9.24e+9	1	3.10	3	0.0012
9	1,8-H	5.94e+9	1	3.90	3	2e-4
10	1,9-H	4.29e+9	1	3.83	3	2e-4
11	1,10-H	3.60e+9	1	3.55	3	2e-4
12	1,11-H	3.38e+9	1	1.46	3	0.007
13	1,12-H	3.17e+9	3	0	5	0.08

[a] A factor per abstractable hydrogen (nH).

[b] The A factor used for 1,4-H shifts of alkoxy radicals was calculated by Vereecken and Peeters (2010). The A factors for the other ring sizes were derived using the assigned 1,4-H shift factor and the ratios of A factors and Wigner tunneling transmissions calculated by Davis and Francisco (2011).

[c] The ring strains for H-shift reactions with 6-member ring transition states are assigned a value of 0 because any ring strain for these reactions is taken into account in the EaA assignments. Ring strain energies relative to 1,4-H shift (6-member ring transition state) derived from activation energies calculated for various 1-alkoxy radicals by Davis and Francisco (2011).

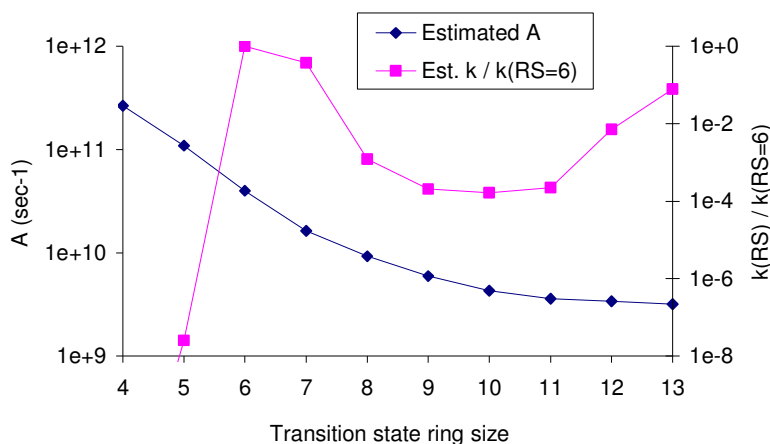


Figure S18. A factors estimated for H-shift reactions of alkoxy radicals, and also relative changes in the rate constants with ring size due to estimated ring strains if all else were equal.

Table S26.  $E_a^0$  parameters used to estimate activation energies for deriving estimated rate constants for H-shift reactions of alkoxy radicals.

H-Group	$E_a^0$ (kcal/mole)	Derivation and Discussion
CH <sub>3</sub> -	7.55	Adjusted to fit activation energies derived from measured or theoretically calculate rate constants for ~298 K and the estimated A factors for the unsubstituted alkoxy radicals given in Table S50.
-CH <sub>2</sub> -	5.97	
-CH<	4.85	
HC(O)-	4.76	Adjusted to fit activation energies derived from measured or theoretically calculate rate constants for ~298 K and the estimated A factors for the HCOCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> O· radical given in Table S50.
HC(O)-O-	No reaction	Abstraction from formate groups are assumed to be negligible based on low group rate constants for reactions of formates with OH radicals (Carter, 2021 and references therein).
HO-	No reaction	It is assumed that H-shifts from -OH groups are not important and are neglected in this work (although this reaction may well be rapid because of hydrogen bonding effects). However, the reaction would be equally rapidly reversed, and even if not, the ultimate products formed would often (but not always) be the same as if the reaction did not occur.
HOO-	4.76	No data are available to estimate H-shift reactions from OOH groups, which are estimated to have similar or lower heats of reaction than abstraction from -CHO. Because of lack of data, the $E_a$ for abstraction from -OOH is assumed to be the same as that assigned for -CHO.

Substituents on the group where the hydrogen is abstracted and non-alkyl groups in the transition state ring can also be expected to affect rate constants for H-shift reactions. The presence of substituents next to the H-group are taken into account as indicated in Table S27, and the presence of non-alkyl groups anywhere in the transition state ring are taken into account as indicated in Table S28, with footnotes indicating how they are derived or estimated. There are sufficient data in Table S50 to derive or estimate correction factors for -CO- or -O- groups in the transition state ring (Table S27) and substitution by -OH or -CH<sub>x</sub>OH groups (Table S28), but effects of other substituents that may also affect H-shift rate constants have to be estimated. For estimation purposes, we assume that the substituent effects for other types of  $\alpha$  substituents for alkoxy H-shift reactions are the same as derived for estimating rate constants for H-abstractions from organics by OH radicals, as given in Table S38, with the activation energy correction estimated by:

$$E_a^{\text{corr}}(\alpha\text{-subst}) = -RT \times \ln(\alpha\text{-subst factor for H-abstractions used for VOC OH reactions})$$

where  $T=298$  K and  $R$  is the gas constant. In a few cases, the OH+VOC substituent correction factor is different for abstractions from the three types of alkyl groups, in which case the average was used when deriving the factors for alkoxy H-shift isomerizations. This is highly uncertain, but is considered to be preferable to ignoring the effects of these substituents entirely.

Figure S19 compares the ~298 K H-shift isomerization rate constants estimated as discussed above with the measured or theoretical values listed in Table S50. The generally excellent agreement is primarily due to the relatively large numbers of adjustable parameters compared to the amount of data



Table S27. Alkoxy H-shift ring strain corrections derived for the presence of carbonyl or ether groups in the transition state ring.

Group	Group Location	H transferred from	E <sub>a</sub> correction [a]	Note [a]
-CO-	Next to H-abstracted group	-CH <sub>2</sub> -, >-CH, -CHO	3.07	1
-CO-	Next to H-abstracted group	-CH <sub>3</sub>	4.31	1
-CO-	Not next to H-abstracted group	Any	0.97	1
O	Anywhere in transition state	Any	≥~4	2

[a] Correction to activation energy due to the presence of the group in the transition state ring in kcal/mole. Derivations of the correction factors are as follows:

- 1 Adjusted so estimates fit k(298) rate constants given in Table S50 for various carbonyl-containing alkoxy radicals.
- 2 Derived to be consistent with the upper limit data for H-shift isomerization rate constants listed in Table S50 for various alkoxy radicals with ether groups in the transition state ring. The correction needs to be at least 4 kcal/mole to be consistent with the upper limit rate constant for CH<sub>3</sub>CH(O·)OCH<sub>2</sub>CH<sub>2</sub>OH.

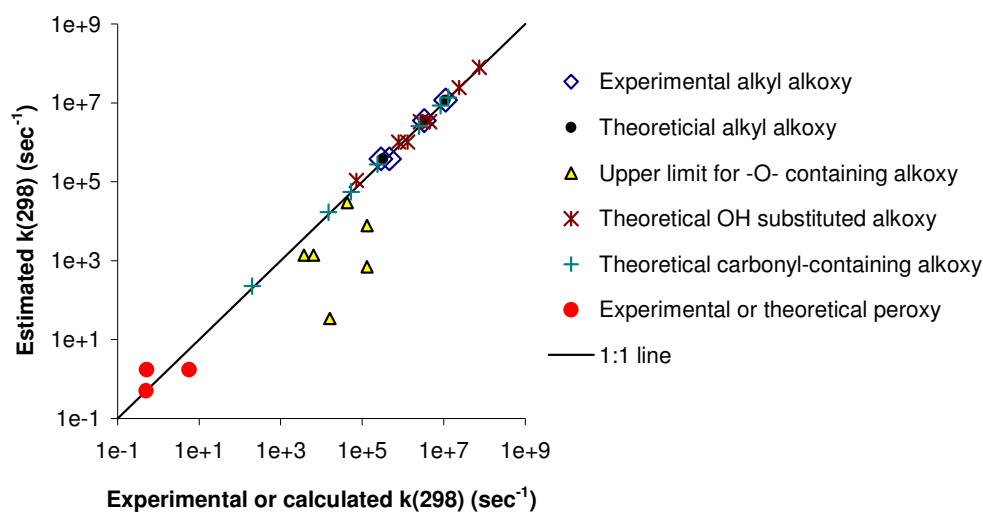


Figure S19. Plot of estimated vs. experimental or theoretically calculated rate constants for H-shift isomerizations of alkoxy or peroxy radicals at 298K.

used to derive the parameters, so this is not necessarily a validation of the estimation method. This is particularly the case for substituent correction factors in the left columns of Table S28, which do not affect predictions of any of the rate constants shown in Table S50 or Figure S19. This is also true for the estimates of the H-shifts for peroxy radicals, where essentially two data points (one being a mean of two somewhat different values for rate constants estimated to be the same) are used to derive the two adjustable parameters. Therefore, more data are needed to verify the H-shift estimates derived for this work, particularly for H-shifts of peroxy radicals.

Table S28. H-abstraction correction terms used for estimating activation energies for H-shift isomerization reactions.

Substituent	OH Abst Fac [a]	Ea <sup>corr</sup> kcal/mole	notes	Substituent	OH Abst Fac [b]	Ea <sup>corr</sup> kcal/mole	notes
<u>OH + Organic abstraction factor used</u>							
-O-	9.1	-1.31	1, 2	-CHx-CO-	3.5	-0.75	1
-O-(OH)	1.23	-0.12	1, 2	-CHx-ONO <sub>2</sub>	0.36	0.61	1
-O-(CO)-	2.0	-0.41	1	-CHx-NO <sub>2</sub>	0.3	0.67	1
-O-(CHO)	0.77	0.16	1	=CHx-	1.00	0	1
-CO-	0.95	0.03	1		<u>Adjusted to fit data</u>		
-CHO	1.00	0	1	-OH	4.130717	-1.15	2
-ONO	1.17	-0.09	1	-CHx-OH	3.66	0.74	2
-ONO <sub>2</sub>	0.14	1.16	1		<u>Estimated</u>		
-CO-OX	0.22	0.89	1	-NO <sub>2</sub>	0	2.00	3

[a] Correction to the estimated 298 K rate constants for OH abstractions for substitution by this group, as given in Table S38. The derivation of these parameters is given by Carter (2021), but the values have since been updated.

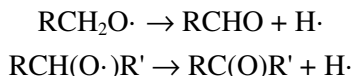
[b] Corrections are given as a factor for the rate constant at 298 K (Fac) (if different than those used for abstractions by OH) and as a contribution to the activation energy (kcal/mole). Notes for derivations of correction factors used are as follows:

- 1 Correction to the activation energy due to this substituent was derived from the correction factor for the effect of this substituent on rate constants for abstractions by OH from various organics, where Ea correction =  $-RT \ln(\text{factor})$ .
- 2 In these cases the correction factor derived from OH abstraction data depends on whether the abstraction is from a -CH<sub>3</sub>, -CH<sub>2</sub>-, or >CH- group. The averages of these factors are given here, and they were used to derive the corrections except when adjusted to fit the isomerization data.
- 3 Adjusted to fit rate constants calculated by Vereecken and Peeters (2010) for H-shift isomerizations for alkoxy radicals with these substituents around the group with the abstracted hydrocarbon.
- 4 Correction to the activation energy due to this substituent is assumed to be large based on the effect of this substituent on rate constants for abstractions by OH from organics with this group. For estimation purposes, it is assumed that this corresponds to an increase in ~2 kcal/mole to the activation energy, which corresponds to a factor of ~0.03.

As indicated above, the data used to derive the estimates for alkoxy H-shift rate constants may not include relevant information that became available after these estimation methods were developed. Therefore, these estimates will likely be updated in the future. But the ability of our current estimates to predict the currently available experimentally measured rate constants suggest that updates to this method may not give significantly different results, at least for the representative types of reactions whose rate constants have been measured.

#### S1.6.4. H-Elimination Decompositions

Primary and secondary alkoxy radicals can also undergo  $\beta$ -scission reactions by H-elimination, forming a carbonyl product and a hydrogen atom.



Available information concerning the rate constants for these reactions are summarized on Table S29. Curran (2006) reviewed information provided H-elimination reactions from several representative alkyl radicals, fitting data to the parameters

$$k(T) = A' \times T^{n'} \times \exp(-E_a/RT).$$

This 3-parameter temperature dependence is not well suited to our estimation methods, so for this work they are re-cast to the 2-parameter expression

$$k(T) = nH \times A/H \times \exp(-E_a/RT),$$

where  $nH$  is the number of H atoms that can be eliminated,  $A/H$  is the A factor per hydrogen, and  $E_a$  is the activation energy parameter used for estimates. The values of  $A/H$  and  $E_a$  are obtained by fitting the rate constants calculated for 270, 300, and 330K. The values of  $A/H$  obtained were 3.8, 2.7, 0.7, and  $3.5 \times 10^{13} \text{ sec}^{-1}$  for methoxy, ethoxy, n-propoxy, and i-propoxy, respectively. If the value for n-propoxy is rejected as an outlier, the other values of  $A/N$  are in reasonably good agreement, so for estimation purposes we use the average for the other three radicals, which is

$$A/nH = 3.3 \times 10^{13} \text{ sec}^{-1}.$$

If this is assumed, then the above equations can be used to derive standard activation energies from their 300K rate constants and the number of hydrogens that can be eliminated.

Figure S20 shows plots of the standard activation energies used for estimation purposes against the estimated heats of reactions for the alkoxy H-atom elimination reactions listed in Table S29. The results show that the data are reasonably well fitted by a straight line, especially if methoxy, which is expected to be somewhat atypical, is eliminated. The best fit to the data, excluding methoxy, is as follows,

$$E_a (\text{standard H-elim}) = 13.50 + 0.52 \times \Delta H_{\text{rxn}} (\text{kcal/mole})$$

and is shown as the solid line on the figure. However, this predicts an H-elimination rate constant that is approximately an order of magnitude lower than the lower limit derived from the product yield data of Wallington et al. (1997) and our estimated rate constant of  $\sim 1.6 \times 10^6 \text{ sec}^{-1}$  for the  $\beta$ -scission decomposition of  $\text{CH}_3\text{OCH}(\text{O}\cdot)\text{OCH}_3$  to  $\text{CH}_3\text{OCHO} + \text{CH}_3\text{O}\cdot$ , as discussed in Section S1.6.2. Note, however, that the  $\beta$ -scission decomposition rate constants have significant uncertainty, so our estimate for the upper limit for H-elimination from  $\text{CH}_3\text{OCH}(\text{O}\cdot)\text{OCH}_3$  is equally uncertain.

These data indicate that the rate constants for H-elimination reactions are much faster for alkoxy- or hydroxy-substituted alkoxy radicals than for alkoxy radicals that do not have such substituents. This could be attributed to lower heats of reactions for H-elimination for O-substituted alkoxy radicals. However, it is possible that if there are two alkoxy and/or hydroxy substituents on the alkoxy radical, then the H-elimination may be even more favorable by the extrapolation from the data from radicals with one or fewer O-substituents. This would explain the apparent overestimate of the activation energy (underestimate of the rate constant) for  $\text{CH}_3\text{OCH}(\text{O}\cdot)\text{OCH}_3$  radicals, the only alkoxy radical listed on Table S29 with two O-substituents (see Figure S20). In order to make appropriate estimates for the products of the reactions of  $\text{CH}_3\text{OCH}(\text{O}\cdot)\text{OCH}_3$  radical, for estimation purposes we assume

$$E_a (\text{XOCH}[\text{O}\cdot]\text{OX}' \text{ H elim}) = E_a (\text{standard H elim}) - 2.0 \text{ kcal/mole},$$

Table S29. Summary of available information concerning rate constants for H-elimination reactions for alkoxy radicals.

Radical	nH	Est $\Delta H_{\text{rxn}}$ [a]	Published Rate Parameters [b]				Std Ea [c]	Notes [d]
			A'	n'	Ea'	k(298)		
CH <sub>3</sub> O·	3	21.2	5.6e+13	-0.39	26.40	7.3e-6	26.08	1
CH <sub>3</sub> CH <sub>2</sub> O·	2	16.5	5.3e+13	-0.69	22.23	5.3e-3	21.95	1
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> O·	2	16.7	3.2e+12	0.75	21.06	2.3e-3	22.44	1
CH <sub>3</sub> CH(O·)CH <sub>3</sub>	1	12.5	5.6e+13	-0.48	20.08	1.1e-1	19.77	1
HOCH <sub>2</sub> O·	2	2.7	1.0e+14	0	14.90	2.3e+3	14.25	2
CH <sub>3</sub> OCH <sub>2</sub> OCH <sub>2</sub> O·	2	1.6				1.1e+3	14.72	3
CH <sub>3</sub> OCH(O·)OCH <sub>3</sub>	1	-5.7				>8e+6	<~9	4

[a] Heat of reaction as estimated by group additivity (see Section S2.1) in kcal/mole.

[b] Rate parameters used to derive the value of k(300) used. Expression is  $k(T) = nH \times A' \times (T/300)^{n'} \times \exp(-Ea'/RT)$ , where nH is the number of H's that can be eliminated, and A' (sec<sup>-1</sup>), n', and Ea' (kcal/mole) are tabulated here.

[c] Activation energy corresponding to k(300) if the temperature dependence of  $k(T) = nH \times \text{Std} \times A \times \exp(-\text{Std} \times Ea/RT)$  is assumed and a general A factor per hydrogen of  $3.3 \times 10^{14} \text{ sec}^{-1}$  is assumed. This is the average of standard A factors per hydrogen for H-eliminations from methoxy, ethoxy, and isopropoxy radicals, which are in reasonably good agreement.

[d] Documentation notes are as follows.

- 1 Rate constant expression recommended by Curran (2006), based on review of available data for the forward and reverse reactions.
- 2 Rate constant expression derived by Veyret et al. (1984) based on modeling data from the photooxidation of formaldehyde.
- 3 Rate constant relative to O<sub>2</sub> reaction derived from the analysis of O<sub>2</sub>-dependent product yield data from dimethoxy methane reported by Wallington et al. (1997). Rate constant placed on an absolute basis using the estimated  $k_{O_2}[O_2]=6.4e+4 \text{ sec}^{-1}$ .
- 4 Lower limit rate constant based on data of Wallington et al. (1997), which indicates that formation of methyl carbonate dominates over decomposition of CH<sub>3</sub>CH(O·)OCH<sub>3</sub>. Lower limit assumed to be ~5 x the rate constant for the decomposition reaction, which is estimated to be  $1.2e+6 \text{ sec}^{-1}$ .

where the choice of -2 kcal/mole as the correction is arbitrary, but sufficient such that the H-atom elimination reaction dominates. This is shown as the dotted line on Figure S20. This is highly uncertain, and better estimates are needed for alkoxy radicals whose H-elimination reactions are exothermic.

Any alkoxy radical that can undergo an H-elimination reaction can also react with O<sub>2</sub> to form the same ultimate products in the presence of O<sub>2</sub>, so if the O<sub>2</sub> reaction is sufficiently fast then the H-elimination reaction can be neglected. As discussed in Section S1.6.1, the rate constants for the O<sub>2</sub> reactions are estimated to be independent of the heat of reaction, and are such that the O<sub>2</sub> reaction would with the same rate constant as the H-elimination reaction if the activation energy for the H-elimination were approximately 12.3 kcal/mole. Figure S20 shows that the O<sub>2</sub> reaction dominates over H-elimination for alkoxy radicals where the H-elimination is endothermic, though it is not entirely negligible if there is a single -OH or -OR substituent. Therefore, uncertainties of estimates for H-elimination rate constants are

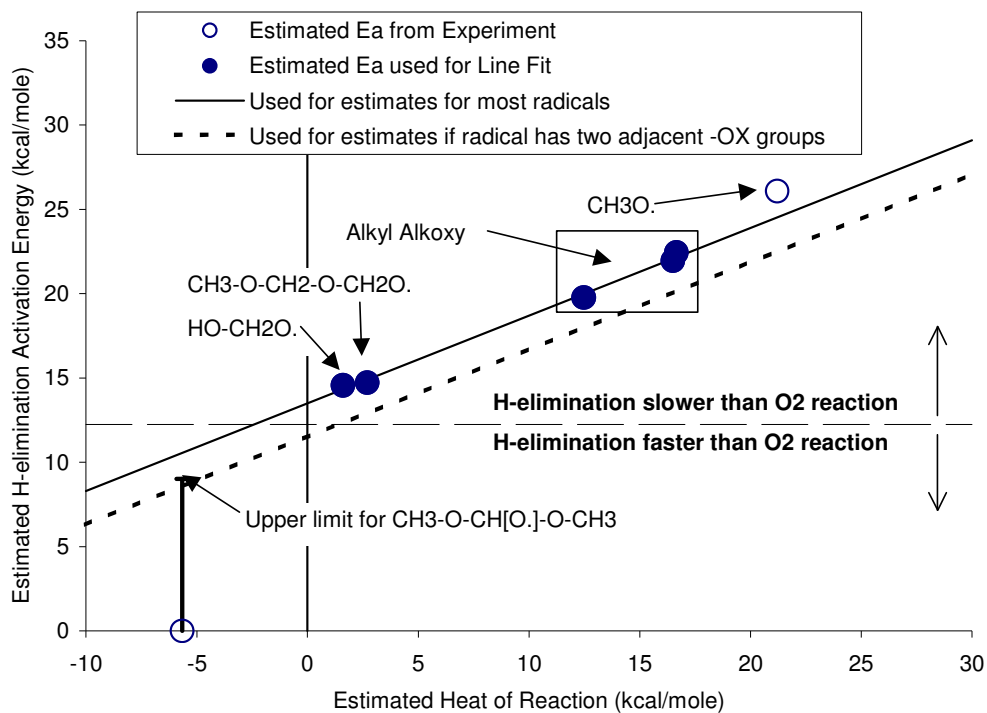
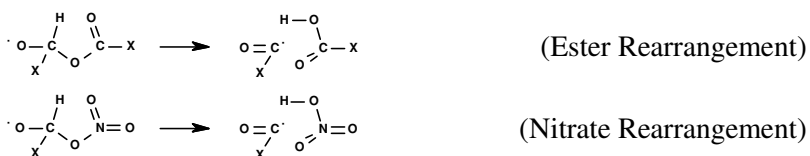


Figure S20. Plots of activation energies derived or estimated for alkoxy H-atom elimination reactions against their estimated heats of reaction.

usually not highly important for such radicals. However, estimates are important if the H-elimination is exothermic, especially if, as is the case for  $\text{CH}_3\text{OCH}(\text{O}\cdot)\text{OCH}_3$  radicals, there is a rapid competing decomposition.

### S1.6.5. Ester and Nitrate Rearrangements

Alkoxy radicals with  $\alpha$  hydrogens that are bonded to  $-\text{O}-\text{CO}-$  or  $-\text{O}-\text{CHO}$ , or nitrate ( $-\text{ONO}_2$ ) groups can also undergo ester or nitrate decomposition reactions, where the  $\alpha$  hydrogen is transferred to a carbonyl group via a 5-member ring cyclic transition state, forming an acid and a carbonyl radical, e.g.



Evidence that the ester rearrangement can be rapid comes from the experimental studies of Tuazon et al. (1988a) and Christensen et al. (2000), who observed the formation of the acid product from this reaction dominating over expected products of competing alkoxy radical reactions, and also the theoretical calculations of Rayez et al. (2002), which are consistent with the experimental data. Evidence that the nitrate rearrangement, forming  $\text{HNO}_3$ , may compete over competing alkoxy radical reactions and may be important at least for excited radicals come from the theoretical calculations of Raghunath et al. (2017). Note that there is no evidence for such reactions in radicals that do not have an oxygen atom between the

alkoxy radical center and the atom with the =O that receives the  $\alpha$  hydrogen. Available information concerning the rate constants for these  $\alpha$  ester and nitrate reactions is summarized on Table S30.

Estimated Rate Parameters. For estimation purposes, we assume that rate constant at temperature T can be given by

$$k(T) = A \times \exp(-E_a/RT),$$

where A and  $E_a$  are assumed to depend only on the type of reaction (ester or nitrate) and type of alkoxy radical (primary or secondary). In each case, the A factor per transferable hydrogen for these reactions are approximately the same as that we assume for 1,4-H shift isomerizations, since both are expected to have similar 5-member ring transition states. Based on the estimated H-shift A factors given in Section S1.6.3, this gives

$$A(\text{ester or nitrate rearrangement}) = nH \times 1.1 \times 10^{-11} \text{ sec}^{-1},$$

Where nH is the number of  $\alpha$  hydrogens at the alkoxy radical, i.e., 2 for primary and 1 for secondary radicals. Table S30 gives the reference activation energies that correspond to the experimental or theoretically calculated  $k(298)$  and these estimated A factors.

Table S30 shows that the rate constants and the corresponding reference activation energies are roughly similar for the ester rearrangements for the two primary alkoxy radicals, but the reaction is much faster and has a lower activation energy for the secondary radical. Table S30 also indicates that the nitrate rearrangement for a primary alkoxy radical is significantly slower and therefore has a much higher activation energy. There is no information concerning effects of substituents on these rate constants and activation energies, so because of lack of data we assume that the A and  $E_a$  parameters are not affected by substituents.

The activation energies used for estimation purposes are included in Table S30, with footnotes indicating how they are derived. There are no reactions on Table S30 that correspond to nitrate rearrangements for secondary alkoxy radicals. So for estimation purposes, we assume that the difference between activation energies for nitrate rearrangements of secondary vs. primary radicals is the same as the estimated difference for ester rearrangements.

Note that these estimates are based on a very limited number of rate constants or theoretical calculations, and more data are needed to evaluate these estimates, and to determine effects of substituents, if any. However, the effects of the uncertainties in these estimates may not be large if the rearrangement is estimated to either dominate or be unimportant. The ester rearrangements are expected to dominate for most secondary alkoxy radicals where this reaction can occur (though some may have very rapid  $\beta$ -scission decompositions that may be competitive -- see Section S1.6.2), though they are estimated to be competitive with reaction with  $O_2$  for primary radicals. For atmospheric  $O_2$  levels, the nitrate rearrangement is estimated to be minor relative to  $O_2$  reaction, though they may become nonnegligible if  $O_2$  were reduced, and the nitrate rearrangement for secondary radicals may be faster than estimated.

### **S1.7. Reactions of adducts from OH + phenolic reactions**

The mechanisms assumed for the reactions of OH radicals with phenolic compounds are generally based on those for aromatic hydrocarbons, with SARs used to predict their rate constants indicating that most of the reaction is by addition to the aromatic ring (Carter, 2021). The subsequent reactions of the OH-phenolic adducts are expected to be analogous to those for aromatic hydrocarbons, but the presence of OH substituents causes some differences. Figure S21 shows possible reactions

Table S30. Available information concerning atmospheric rate constants for ester and nitrate rearrangements.

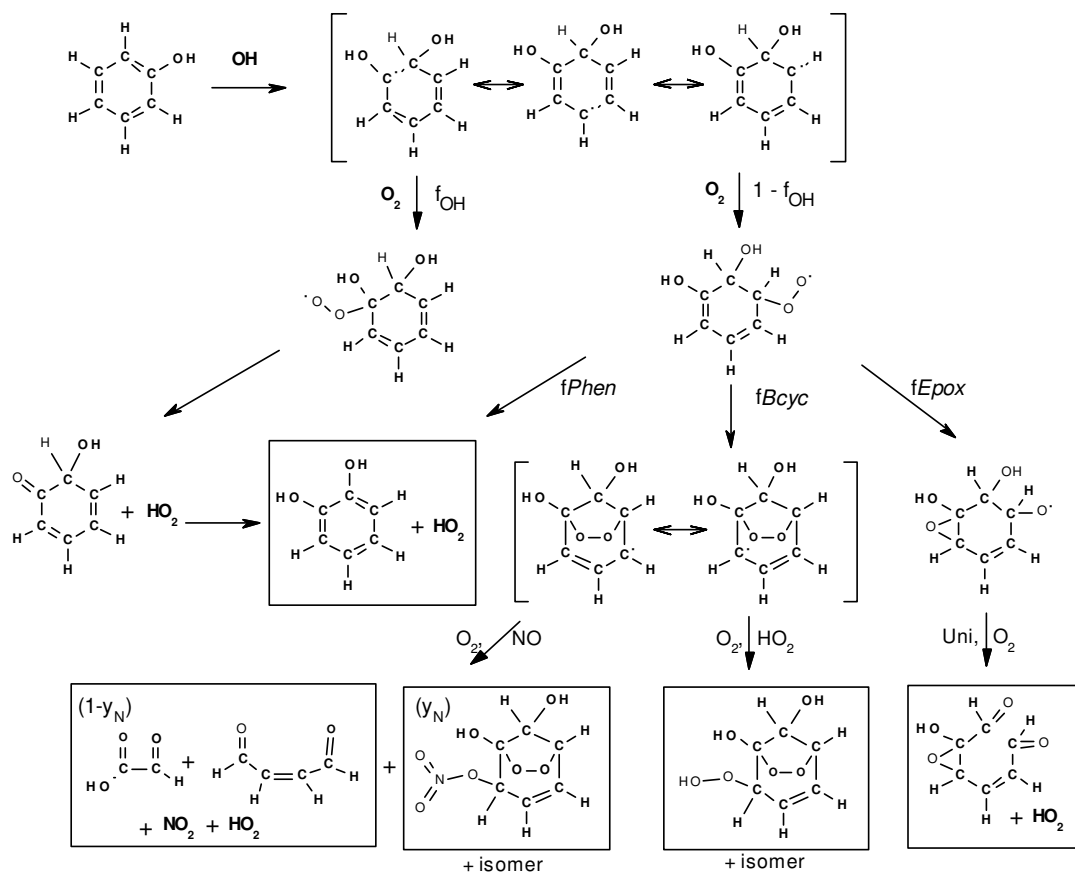
Reaction	Reference [a]		Ref Ea [b]	Estimated		
	k(298)	Note		A	Ea	k(298)
CH <sub>3</sub> C(O)OCH <sub>2</sub> O· → CH <sub>3</sub> C(O)OH + HC(O)·	1.2e+5	1	8.54	2.2e+11	8.94	6.2e+4
HC(O)OCH <sub>2</sub> O· → HCOOH + HC(O)·	3.2e+4	2	9.33	2.2e+11	8.94	6.2e+4
CH <sub>3</sub> C(O)OCH(O·)CH <sub>3</sub> → CH <sub>3</sub> C(O)OH + CH <sub>3</sub> C(O)·	3.7e+7	3	4.74	1.1e+11	4.74	3.7e+7
·OCH <sub>2</sub> ONO <sub>2</sub> → NO <sub>2</sub> OH (HNO <sub>3</sub> ) + HC(O)·	2.2	4	15.00	2.2e+11	15.00	2.2
<u>Assignments used for Mechanism Generation</u>						
RC(O)OCH <sub>2</sub> O· → RC(O)OH + HC(O)·		5, 6		2.2e+11	8.94	6.2e+4
R <sub>1</sub> C(O)OCH(O·)R <sub>2</sub> → R <sub>1</sub> C(O)OH + R <sub>2</sub> C(O)·		5, 7		1.1e+11	4.74	3.7e+7
RCH(O·)ONO <sub>2</sub> → HNO <sub>3</sub> + RC(O)·		5, 8		2.2e+11	10.8	1.3e+3

[a] Experimental or theoretically calculated rate constant around 298K in sec<sup>-1</sup>. Notes giving sources of rate constants are as follows.

- 1 Derived from product yield data for reactions of Cl· with methyl acetate by Christensen et al. (2000). Rate constant placed on an absolute basis using the estimated kO<sub>2</sub>[O<sub>2</sub>]=6.4e+4 sec<sup>-1</sup> (see Section S1.6.1).
- 2 Derived from rate constant relative to O<sub>2</sub> reaction as measured by Wallington et al. (2001). Rate constant placed on an absolute basis using the estimated kO<sub>2</sub>[O<sub>2</sub>]=6.4e+4 sec<sup>-1</sup>.
- 3 Rate constant calculated theoretically for atmospheric conditions by Rayez et al. (2002).
- 4 Rate constant calculated theoretically for atmospheric conditions by Raghunath et al. (2017).
- 5 The A factor per α hydrogen is estimated to be approximately the same as that used for 1,3-H shifts of alkoxy radicals (see Table S25), which is expected to have a similar 5-member ring transition state.
- 6 The activation energy is the average of that given above for CH<sub>3</sub>C(O)OCH<sub>2</sub>O· and HC(O)OCH<sub>2</sub>O·.
- 7 The activation energy is that given above for CH<sub>3</sub>C(O)OCH(O·)CH<sub>3</sub>.
- 8 Estimated from the activation energy given above for ·OCH<sub>2</sub>ONO<sub>2</sub> and the difference in assigned activation energies for secondary and primary alkoxy radicals. Note that it is not necessary to estimate activation energies for nitrate rearrangements for primary alkoxy radicals because ·OCH<sub>2</sub>ONO<sub>2</sub> is the only radical of this type.

[b] Activation energy in kcal/mole derived from the experimental or theoretically calculated k(298) and the estimated A factor.

following OH addition to phenols, using the adduct formed after OH adds to the *ortho* position of o-cresol (estimated to be its major reaction route) as an example. The main differences concern the reactions of adducts with an -OH substituent adjacent to the radical center, while those with the OH substituent in any other position, if they are in fact formed, are assumed to react analogously to those formed in the reactions of unsubstituted aromatics. The same branching ratios (*fPhen*, *fBcyc*, *fEpoxy*), which depend only the substituent at the radical center, are used for those formed from phenols as those from alkylbenzenes, as discussed in Section 3.4 of the main text. Similar products are predicted, including catechols, photoreactive dicarbonyls, dicarbonyl epoxides, and various bicyclic bridged peroxy species. These reactions are shown on the right side of Figure S21.



$f_{OH}$  is the fraction of O<sub>2</sub> addition to the radical center with the  $\alpha$ -OH substituent.

$f_{Phen}$ ,  $f_{Bcyc}$ , and  $f_{Epoxy}$  are branching ratios used for OH + aromatic hydrocarbon adducts.

$y_N$  is the organic nitrate yield in the peroxy + NO reaction.

Figure S21. Reactions following the addition of OH radicals to the *ortho* position of o-cresol.

On the other hand, if the O<sub>2</sub> adds to the radical center adjacent to the -OH substituent, then the reaction would form an  $\alpha$ -hydroxy peroxy adduct that is expected to rapidly decompose to form HO<sub>2</sub> and the corresponding carbonyl, as shown on the left side of Figure S21 and discussed in Section 3.2.1 of the main text. This results in the formation of 5-hydroxy cyclohexadienones, which have not, to our knowledge, been reported as products of reactions of phenols. Instead, relatively high yields of catechols are observed as products from phenols (Calvert et al, 2011, Olariu et al., 2002). In order to account for this, we assume that the 5-hydroxy cyclohexadienones rapidly rearrange to form catechols, as discussed in Section 2.3.2 in the main text and also shown on Figure S21.

The calculations of Xu and Wang (2013) predict the O<sub>2</sub> will add primarily to the radical center with the  $\alpha$ -OH substituent, with addition to the other location being negligible. However, assuming that there is no addition to the other location results in significant underpredictions of O<sub>3</sub> formation, NO oxidation, and phenol consumption in the phenol - NO<sub>x</sub> experiments used to develop previous SAPRC mechanisms (Carter, 2000, 2010a,b). This is shown in Figure S22, which gives plots of selected results of selected phenol - NO<sub>x</sub>, o-cresol - NO<sub>x</sub>, and 1,4-dimethylphenol - NO<sub>x</sub> chamber experiments used to evaluate phenolic mechanisms. The mechanisms shown in the calculation are SAPRC-11, which used simplified mechanisms with parameters optimized for each compound to fit these chamber data (Carter



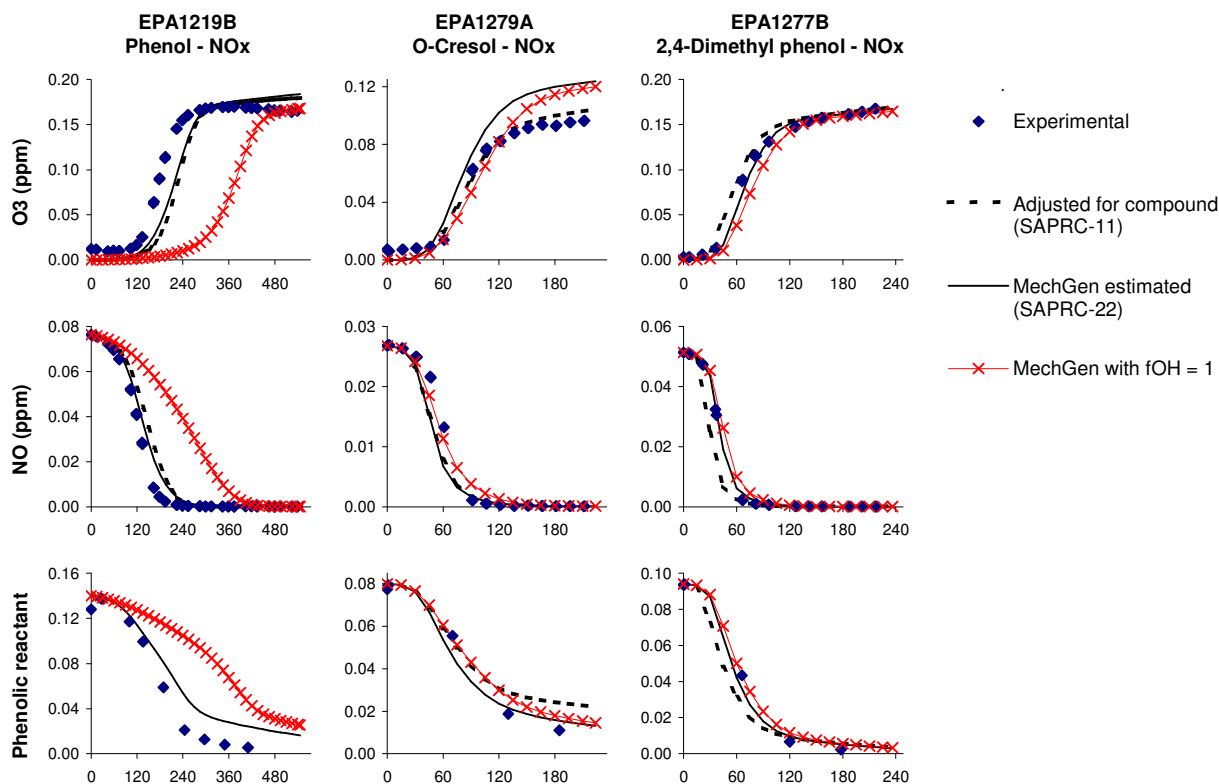


Figure S22. Comparisons of experimental and calculated concentration-time data for  $O_3$ ,  $NO$ , and the reacting phenolic compound for representative phenol, o-cresol, and 2,4-dimethyl phenol -  $NO_x$  experiments.

and Heo, 2013, see also Carter, 2010a), SAPRC-22 (Carter, 2023a), which uses mechanisms derived by the version of MechGen documented in this work with  $f_{OH}$  (see Figure S21) adjusted to be 88% fit the data for the phenol runs, and a version of SAPRC-22 derived from a version of MechGen assuming that all the reaction is at the OH-substituted position ( $f_{OH}=1$ ).

The figure shows that assuming  $f_{OH}=1$  significantly underpredicts reactivities in the phenol experiment shown, while assuming that ~12% of the addition is in the other position fits the data reasonably well. The results for the other phenol -  $NO_x$  experiments are similar, though there is some run-to-run variability. On the other hand, the figure also shows that the o-cresol and 2,4-dimethylphenol experiments are much less sensitive to this parameter. This can be due in part to lower yields of adducts where with both OH-substituted and non-OH-substituted radical centers, and perhaps due to higher yields of photoreactive products from other processes. However, this has not yet been analyzed in detail.

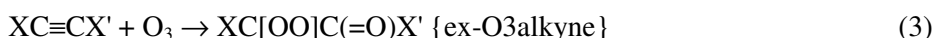
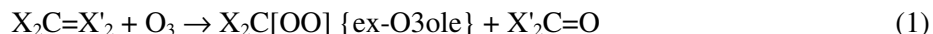
The observation that results of phenol -  $NO_x$  chamber experiments are reasonably well fit by assuming  $f_{OH}=0.88$  for radicals such as shown on Figure S21 was used as input to the general procedure for estimating branching ratios when  $O_2$  adds to allylic radicals, as discussed in Section S1.4.2. Thus, adding to the -OH substituted position is favored, but reaction at the other position is not negligible, at least for phenol. The general method is based on differences in heats of reaction, but a correction is used for -OX substituted radicals to obtain  $f_{OH}=0.88$  for these radicals.

The extent to which the presence of phenolic OH groups will affect the reactions of these phenolic-OH- $O_2$  adducts when the OH is not on the same carbon as the peroxy group is unknown.

However, that the phenolic OH group is not near the reaction site for all adducts of this type shown on the left side of Figure S22, suggesting that its effect on the branching ratios may not be large. Because of lack of data, we assume that OH substitution on the phenolic-OH-O<sub>2</sub> adducts, other than  $\alpha$ -peroxy, does not affect these branching ratios.

### S1.8. Reactions of Criegee Intermediates

Criegee intermediates (CIs) are highly reactive intermediates that have an additional oxygen on a carbonyl oxygen that can be formed in a vibrationally excited state in the reactions of O<sub>3</sub> with alkenes and acetylenes and in the reactions of carbenes with O<sub>2</sub>.



Here X designates H or any group, -C[OO]- designates a Criegee group, {ex-type} indicates excitation from various types of reactions implemented by MechGen, and "\*" indicates ring closure. MechGen keeps track of the type of reaction that form the excited CIs because each type forms intermediates with different amounts of excitation energies. CIs formed from reactions of O<sub>3</sub> with acyclic alkenes should have the least amount of excitation because some of the energy goes to the non-Criegee carbonyl product. CIs formed from the reactions of O<sub>3</sub> with double bonds in rings, reactions of O<sub>3</sub> with alkynes, and reactions of O<sub>2</sub> with carbenes are excited with all the energy of the reaction.

CIs other than CH<sub>2</sub>[OO] can exist in two configurations, designated *syn* and *anti*, as follows:



These are believed to interconvert rapidly if there is any level of excitation, but not to interconvert at a non-negligible rate if the intermediate is stabilized. For that reason, MechGen only specifies the *syn* vs *anti* configuration for stabilized intermediates. MechGen treats *syn* and *anti* isomers differently because most of the possible unimolecular reactions have cyclic transition states involving the [OO] group and a group on the substituent, which would have too much strain unless the substituent is in the *syn* position relative to the Criegee group. This is not a consideration for excited intermediates because of the assumed rapid interconversion.

The various types of reactions of excited and stabilized CIs are discussed in the following sections. Based on these considerations, the types of intermediates can be classified as follows:

#### Excited intermediates

- Excited intermediates with  $\alpha$  carbonyl substituents are predicted to rapidly interconvert by O shifts between the Criegee and adjacent carbonyl group, resulting in an equilibrium involving the two  $\alpha$ -carbonyl Criegee isomers (if they are different). The reactions of each isomer need to be considered when predicting the fates of such intermediates.
- Excited intermediates that have -OH substituents or  $\alpha$ -unsaturated substituents with abstractable allylic hydrogens in the  $\gamma$  position are predicted to undergo extremely fast decomposition reactions that dominate over stabilization. Therefore, intermediates with these substituents are predicted not to be stabilized under atmospheric conditions.

- Excited intermediates that have alkyl substituents with  $\alpha$  hydrogens or have an -H substituent (e.g., RCH[OO]) are predicted to undergo decomposition reactions that compete with stabilization. The amount of stabilization depends on the structure of the intermediate and how it is formed.
- Excited intermediates that do not have substituents listed above are predicted not to undergo unimolecular reactions at sufficient rates that compete with stabilization, so are assumed to be completely stabilized.

#### Stabilized intermediates

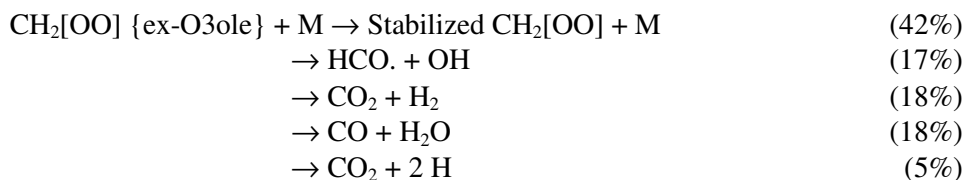
- Stabilized intermediates with -OH or  $\alpha$ -unsaturated substituents with allylic hydrogens in the  $\gamma$  position are not predicted to be formed because initially formed excited intermediate is not predicted to be stabilized. However, if they are specified as the initial reactant, and the reacting substituent is in the *syn* position, they undergo the same reaction as the excited intermediate. They will not react if the reacting substituent is in the *anti* position.
- Other stabilized intermediates, including all that can be formed in reactions of excited intermediates, are assumed not to undergo unimolecular decompositions. Their predicted fates are either isomerization to a dioxirane (3 member ring cyclic peroxide), or reaction with H<sub>2</sub>O.

The various types of reactions, and how MechGen assigns branching ratios for them, are discussed in more detail in the following sections.

#### S1.8.1. Mechanisms for Intermediates formed from O<sub>3</sub> + Simple Alkenes

Available data on the reactions of O<sub>3</sub> with simple alkenes were reviewed in IUPAC (2023), and recommendations or suggestions were made for the reactions of the simplest excited CIs formed in these reactions. These are summarized in Table S31. Table S31 also indicates how the branching ratios used by MechGen were derived based on these data.

In the case of excited CH<sub>2</sub>[OO] formed from ethene, the recommended branching ratios are as follows:



where {ex-O3ole} indicates excitation from O<sub>3</sub> + alkene reactions. These recommendations are adopted by MechGen for reactions of excited CH<sub>2</sub>[OO] radicals formed from any 1-alkene reaction because data are inadequate to assume otherwise. Although the stabilization yield should depend on pressure and the 42% stabilization is only applicable for 1 atmosphere of air, pressure dependences of stabilization yields are ignored in the current version of MechGen.

Data for the reactions of O<sub>3</sub> with propene and the 2-butenes were also reviewed in IUPAC (2023), and suggestions were made for the yields of products from the excited CH<sub>3</sub>CH[OO] formed in these reactions, which are included in Table S31. However, MechGen now predicts that there are secondary sources of OH in the experiments used to measure the OH yields of these reactions (e.g., Atkinson and Aschmann, 1993) that the IUPAC did not take into account in their evaluation, suggesting at least some overestimation of the extent of OH formation from the excited Criegee reactions. Therefore, we needed to make an approximate correction for this predicted secondary OH formation, as discussed below.

Table S31. Summary of IUPAC (2023) suggestions for products formed and branching ratios used by MechGen based on these data.

Products or reaction type	Recommended for O <sub>3</sub> reaction			Used for MechGen	
	Propene	2-Butenes		Yield	Notes [d]
		<i>Cis</i>	<i>trans</i>		
Excited CH <sub>3</sub> CHOO Yield	62%	100%	100%		
Observed OH	48%	33%	60%		1
OH + ·CH <sub>2</sub> CHO (VHP route) [a]	45%	31%	56%	44%	2, 3
Attributed to excited reaction	37%	18%	41%	32%	4
Attributed to syn stabilized reaction	7%	13%	14%	11%	4
"Hot Acid" routes [b]					
CH <sub>3</sub> . + ·CO-OH = CH <sub>3</sub> . + H + CO <sub>2</sub>	-	11%	-	7%	5
CH <sub>2</sub> =CO + H <sub>2</sub> O	6%	7%	4%	-	5
CH <sub>4</sub> + CO <sub>2</sub>	16%	19%	11%	17%	5
CH <sub>3</sub> OH + CO	8%	10%	7%	9%	5
Inferred yields					
Total Stabilization (syn + anti)	23%	38%	43%	35%	3, 6
Stabilization to Syn (33% formation)	7%	13%	14%	11%	4
Stabilization to Anti (67% formation)	15%	25%	29%	23%	4
Total decompositions of excited	68%	65%	63%	65%	7
Relative yields of excited reactions [c]					
OH + ·CH <sub>2</sub> CHO (VHP route)	55%	28%	65%	49%	7, 8
CH <sub>3</sub> . + ·CO-OH = CH <sub>3</sub> . + H + CO <sub>2</sub>	-	17%	-	10%	7, 9
CH <sub>2</sub> =CO + H <sub>2</sub> O	9%	11%	6%	-	7, 9
CH <sub>4</sub> + CO <sub>2</sub>	24%	29%	17%	26%	7, 9
CH <sub>3</sub> OH + CO	12%	15%	11%	14%	7, 9

[a] VHP is the vinyl hydroperoxide route where the OO abstracts an α-H forming an excited hydroperoxide that decomposes.

[b] These are where the H in the CHOO transfers to the O, forming an excited acid that decomposes.

[c] These are the yields if there were no stabilization

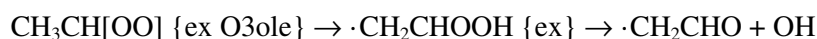
[d] Notes are as follows.

- OH yield from excited CH<sub>3</sub>CHOO recommended by IUPAC (2023).
- The OH yield is adjusted to account for an estimated formation of an additional 0.08 moles of OH due to secondary reactions in the OH yield experiments, as discussed in the text and shown in Table S32.
- MechGen uses the average of the yields recommended for propene and the 2-butenes.
- It is assumed that the observed products and corrected OH correspond to all the reactions of the excited intermediate and the VHP reaction of the intermediate stabilized in the *syn* configuration. Therefore, 1 - the totals for these routes are attributed to the fraction stabilized in the *anti* position, which is not expected to react to form OH or the observed products. Since it is assumed that 35% of the excited intermediates are stabilized (the average of the recommended values from the IUPAC (2023) evaluations of data from propene and the 2-butenes), and that 33% is stabilized in the *syn* configuration (see text), this gives 11% stabilization to the *syn* configuration, which is assumed to react via the VHP route to form OH. The amount of OH attributed to the VHP reaction of the excited intermediate is then derived by subtracting the total OH due to the VHP route from that attributed to the stabilized *syn* isomer.

Table S31 (continued)

- 5 This relatively minor ketene-forming route is not represented explicitly. The yields from the other routes are derived from the averages for propene and the 2-butenes, with half of the average ketene route added to the radical forming route (first reaction), and the other half added to the two non-radical forming routes using the ratios of the averages.
- 6 The total stabilization values are those recommended by IUPAC (2023). The value in the propene column is corrected to remove the recommended 42% stabilization of the excited HCHOO yield formed 38% of the time.
- 7 These are calculated from the total yields for reactions of excited intermediate tabulated in rows above.
- 8 Derived from the OH yield attributed to reactions of the excited radical.
- 9 Derived from the yields of these "hot acid" pathways.

Table S31 indicates that the most important decomposition route for excited  $\text{CH}_3\text{CH}[\text{OO}]$  is the vinyl hydroperoxide (VHP) reaction, where the  $[\text{OO}]$  abstracts an  $\alpha$ -hydrogen on a substituent, forming an excited vinyl hydroperoxide that then decomposes.



This is believed to be the only direct source of OH from this reaction, so the measured OH yields in the  $\text{O}_3$  + alkene systems indicate the extent to which this decomposition occurs. Vereecken et al. (2017) calculated that this reaction is sufficiently rapid that it probably occurs for stabilized as well as excited CIs, though the substituent with the abstractable  $\alpha$  hydrogen must be in the *syn* configuration for this to occur. (Configuration is assumed not to be a factor for the excited intermediates because they are assumed to rapidly interconvert). Therefore, the observed OH yields indicate the extent of formation of the *syn* stabilized isomer, as well as the extent of decomposition of the excited intermediate via the VHP route.

Table S31 shows additional reactions of the excited intermediate via the "hot acid" route, where the H on the monosubstituted Criegee group transfers to the  $[\text{OO}]$  to form excited acetic acid, which then decomposes as shown in the table. These reactions are believed only to occur when the intermediate is excited. Therefore, the *syn* isomer is assumed to react entirely via the VHP route, since this is assumed to be the only route available for the stabilized isomer.

Note that the OH yields recommended in IUPAC (2023) were based on the assumption that the experimentally-derived OH yields were due only to their formation in the VHP reactions (i.e., there were no other sources of OH in the experimental systems employed). The primary experiments used to measure the OH yields in  $\text{O}_3$  + alkene systems consisted of reacting  $\text{O}_3$  with the alkene in air in the dark in the presence of a large excess of cyclohexane, which is the primary sink for the OH formed, and whose measured product yields from the OH reaction are used to derive the extent of OH formation. However, because of H-shift isomerizations of some of the aldehyde-containing peroxy intermediates (see Section S1.6.3), MechGen now predicts that there is at least some OH formation from the subsequent reactions of the  $\cdot\text{CH}_2\text{CHO}$  co-product. The predicted reactions of this intermediate under the conditions of these experiments are given in Table S32, with the "relative rate" column giving the relative amount of reaction through each pathway derived from the model simulations of the experimental system using the SAPRC-18 mechanism updated as discussed in this document. The conditions of the calculations are given in note [a] in the table, but calculations where the initial  $\text{O}_3$  or 2-butene were varied by a factor of two gave essentially the same results. These results indicate that an additional 0.08 moles of OH are formed in these reactions, which means that 1.08 moles of OH are formed per VHP reaction. Although this prediction depends on a number of uncertain branching ratios in several of the competitive reactions

Table S32. Reactions and relative rates of the co-product of the VHP reaction of excited CH<sub>3</sub>CH[OO] intermediates under the conditions of the experiments used to measure OH yields in the reaction of this intermediate

Reaction	Relative Rate
$\cdot\text{CH}_2\text{CHO} + \text{O}_2 \rightarrow \cdot\text{OOCH}_2\text{CHO}$	100%
$\cdot\text{OOCH}_2\text{CHO} + \text{RO}_2 \rightarrow \rightarrow 0.5 \text{HO}_2 + \text{other products [b]}$	35%
$\cdot\text{OOCH}_2\text{CHO} + \text{HO}_2 \rightarrow \rightarrow 0.15 \text{HO}_2 + \text{other products}$	1%
$\cdot\text{OOCH}_2\text{CHO} \rightarrow \text{HOCH}_2\text{C(O)}\cdot$	64%
$\text{HOCH}_2\text{C(O)}\cdot + \text{O}_2 \rightarrow \text{HOCH}_2\text{C(O)OO}\cdot$	64%
$\text{HOCH}_2\text{C(O)OO}\cdot \rightarrow \cdot\text{OOCH}_2\text{C(O)OOH}$	64%
$\cdot\text{OOCH}_2\text{C(O)OOH} + \text{RO}_2 \rightarrow 0.5 \cdot\text{OCH}_2\text{C(O)OOH} + \text{other products}$	55%
$\cdot\text{OOCH}_2\text{C(O)OOH} + \text{HO}_2 \rightarrow \text{HOCH}_2\text{C(O)OOH} + \text{O}_2$	7%
$\rightarrow \mathbf{OH} + \cdot\text{OCH}_2\text{C(O)OOH}$	2%
$\cdot\text{OCH}_2\text{C(O)OOH} \rightarrow \text{HCOC(O)OOH} + \text{HO}_2$	48%
$\rightarrow \text{HCHO} + \text{HOOC(O)}\cdot \rightarrow \text{HCHO} + \text{CO}_2 + \mathbf{OH}$	7%

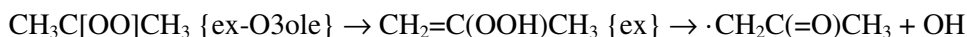
[a] Rate of reaction in model simulation of an experiment with 0.8 ppm *trans*-2-butene, 368 ppm cyclohexane and 0.2 ppm O<sub>3</sub> in 1 atmosphere of NO<sub>x</sub>-free air at 300K.

[b] "RO<sub>2</sub>" is the sum of all the 6 peroxy radicals in the generated mechanisms for O<sub>3</sub> + 2-butenes and OH + cyclohexane. These radicals, and their cross-reactions, are represented explicitly in the simulation.

involved, this correction factor incorporates our best current estimates and is utilized in our analysis of the data, so the OH yield data on Table S31 were corrected to take this into account.

The total amounts of stabilization recommended by IUPAC (2023) for excited CH<sub>3</sub>CH[OO] radicals formed from reactions of O<sub>3</sub> with propene and the 2-butenes averaged 35±10%. We (somewhat arbitrarily) assumed that 1/3 of the stabilization forms the *syn* isomer and the remainder forms the *anti* isomer. This is based on (1) the expectation that stabilization to the *anti* form would be favored based on steric considerations, (2) assumption of a 50-50 distribution tends to result in an overprediction of radical levels from higher monosubstituted CIs based on the assumptions discussed below, and (3) this assumption tends to give somewhat more consistent estimates based on stoichiometry. Based on this assumption, the *syn* isomer is formed with an estimated yield of ~11% , and, since this isomer is assumed to react 100% to form OH, this yield is subtracted from the total (corrected) OH yield to give an ~32% yield for VHP decomposition of the excited isomer. These assumptions are used to derive the branching ratios used by MechGen shown in Table S31.

Data for the reactions of O<sub>3</sub> with 2-methyl propene (isobutene) and 2,3-dimethyl-2-butene were also reviewed by IUPAC (2023), which provide data on the reactions of excited CH<sub>3</sub>C[OO]CH<sub>3</sub> formed in O<sub>3</sub> + alkene reactions under atmospheric conditions. These are all consistent with the VHP reaction being the only fate for this excited intermediate as shown here:



This can occur either while the intermediate is excited or after it is stabilized, since the reaction is expected to be fast even for stabilized intermediates. IUPAC (2023) recommended assuming 39±10%

stabilization of the intermediate formed in the 2,3-dimethyl-2-butene system, but they also reported that the data for reactions of O<sub>3</sub> with 2-methyl propene are more consistent with no stabilization of the excited CH<sub>3</sub>C[OO]CH<sub>3</sub> formed in that system. Because of this discrepancy, we assume that the amount of stabilization of excited CH<sub>3</sub>C[OO]CH<sub>3</sub> is approximately the same as that derived for excited CH<sub>3</sub>CH[OO] as discussed above, which is ~35% (Table S31).

Although it turns out that the extent of stabilization does not affect the overall fate of excited CH<sub>3</sub>C[OO]CH<sub>3</sub> because the VHP reaction can occur either way, it does make a difference in estimates for excited disubstituted intermediates if only one of the substituents has the α hydrogen required for this reaction to occur. The reaction at the reactive group would dominate for the excited intermediate, but would require the reactive group to be in the *syn* position for it to occur once the intermediate is stabilized. MechGen assumes that if the two substituents in the excited intermediate are different, then each group has a 50% chance of being in the *syn* position when the intermediate is stabilized, regardless of the type of substituents. Therefore, if only one substituent has an α hydrogen, then approximately half the stabilized intermediates will not be able to react because the reactive substituent is in the *anti* position.

The above discussion is strictly speaking only applicable to the simplest CIs, containing either no substituents or only methyl groups. Because of lack of data, we assume that the decomposition for other Criegee radicals with alkyl groups in the α position are analogous to those shown in Table S31 for excited CH<sub>3</sub>CH[OO] or as discussed above for excited CH<sub>3</sub>C[OO]CH<sub>3</sub>. Note that the VHP reaction is not possible for tertiary substituents that do not have α hydrogens, so the excited radicals would only react via the hot acid reactions if possible, or only be stabilized if not, and the stabilized radical would not decompose even if it were in the *syn* configuration. The only reactions assumed to be available to it are 1,3 cyclization forming a dioxirane or reaction with H<sub>2</sub>O (see Table 15 in the main manuscript). Based on these considerations, the general reactions of excited intermediates with only alkyl substituents in the α position are as shown in Table S33. The reactions of the stabilized radicals that can undergo the VHP reactions are also shown on the table. The branching ratios for the various reactions are also shown, which depend on the stabilization factor (SF) that may vary with the intermediate as discussed below. The reactions of the stabilized radicals in the *anti* configuration, or those where the VHP reaction is not possible, are discussed separately in Section S1.8.3.

One might expect that the extent of stabilization would increase with the size of the intermediate (Newland et al., 2020), but the extent to which this is the case is uncertain. However, OH yields have been measured in the reactions of O<sub>3</sub> with a number of alkenes, and relevant data summarized by Calvert et al. (2000) are tabulated in Table S34. Note that the yields measured using OH trapping are not corrected for secondary OH sources because these data are being compared with predictions of generated mechanisms that take these reactions into account. The table has three columns of MechGen predictions of these OH yields, made with varying models for how stabilization factors vary with the intermediate, as follows:

- Model "A": Stabilization factors are assumed to be as derived for the analogous methyl-substituted intermediates (~35%) and not to depend on the size of the intermediate or how it is formed.
- Model "B": Stabilization factors are assumed to increase linearly with the number of carbons, being ~35% for methyl-substituted substituents and becoming 100% if they have 12 carbons. The same factors are used regardless of how the intermediate is formed.
- Model "C": Same as Model "B" except that stabilization factors are reduced by a factor of 3 if the Criegee intermediate is formed when O<sub>3</sub> reacts with a double bond in a ring, forming only a single excited intermediate with all the excitation energy. Greater excitation and therefore faster

Table S33. General mechanism for reactions of excited Criegee intermediates formed in the reactions of O<sub>3</sub> with alkenes, applicable to intermediates with α alkyl substituents.

Reaction [a]	Factor [b]	Note
<u>RCH[OO] CIs</u>		
X <sub>2</sub> CHCH[OO] {ex} → ·CX <sub>2</sub> CHO + OH	0.49 x (1 - SF)	1
→ X <sub>2</sub> CH· + ·C(=O)OH	0.10 x (1 - SF)	1
→ X <sub>2</sub> CH <sub>2</sub> + CO <sub>2</sub>	0.26 x (1 - SF)	1
→ CH <sub>3</sub> OH + CO	0.14 x (1 - SF)	1
+ M → X <sub>2</sub> CHCH[OO <i>syn</i> ] + M	0.33 x SF [d]	2
+ M → X <sub>2</sub> CHCH[OO <i>anti</i> ] + M	0.67 x SF	2
X <sub>2</sub> CHCH[OO <i>syn</i> ] → ·CX <sub>2</sub> CHO + OH	100%	
YCH[OO] {ex} → Y· + ·C(=O)OH	0.20 x (1 - SF)	3
→ YH + CO <sub>2</sub>	0.52 x (1 - SF)	3
→ YOH + CO	0.28 x (1 - SF)	3
+ M → YCH[OO <i>syn</i> ] + M	0.33 x SF	2
+ M → YCH[OO <i>anti</i> ] + M	0.67 x SF	2
<u>RC[OO]R' CIs</u>		
X <sub>2</sub> CHC[OO]CHX' <sub>2</sub> {ex} → ·CX <sub>2</sub> C(=O)CHX' <sub>2</sub> + OH	0.5 x (1 - SF)	4
→ CX <sub>2</sub> HC(=O)CX' <sub>2</sub> · + OH	0.5 x (1 - SF)	4
+ M → X <sub>2</sub> CH-syn-C[OO]CHX' <sub>2</sub> + M	0.5 x SF	5
+ M → X <sub>2</sub> CHC[OO]-syn-CHX' <sub>2</sub> + M	0.5 x SF	5
X <sub>2</sub> CHC[OO]Y {ex} → ·CX <sub>2</sub> C(=O)Y + OH	1-SF	4
+ M → X <sub>2</sub> CH-syn-C[OO]Y + M	0.5 x SF	5
+ M → X <sub>2</sub> CHC[OO]-syn-Y + M	0.5 x SF	5
YC[OO]Y' {ex} + M → Y-syn-C[OO]Y' + M	0.5	5, 6
+ M → YC[OO]-syn-Y' + M	0.5	5, 6
X <sub>2</sub> CH-syn-C[OO]R → ·CX <sub>2</sub> C(=O)R + OH	100%	

[a] The notation {ex} indicates excitation by formation in the O<sub>3</sub> + alkene reaction; X and X' are H or any group; and Y and Y' are any group that does not have an α hydrogen, except for groups that have fast reactions that are discussed below in Section S1.8.2

- [b] SF is the stabilization factor, which depends on the intermediate (see text). Notes are as follows:
- 1 Relative branching ratios assumed to be the same as for R = CH<sub>3</sub>, from Table S31.
  - 2 Formation of the *syn* isomer assumed to occur 33% of the time, based on steric and other considerations.
  - 3 Relative branching ratios same as for R = CH<sub>3</sub>, but with the VHP reaction removed and branching ratios for other reactions increased to give 100% total.
  - 4 Assume all possible VHP reactions of excited intermediate occur with equal probability.
  - 5 Equal probability of formation of the two possible *syn* and *anti* isomers, regardless of substituent.
  - 6 No decomposition reaction expected, so 100% stabilization assumed.



Table S34. Summary of predicted, measured, and recommended OH yields in the reactions of O<sub>3</sub> with alkenes.

Compound	OH yields						
	Measured by [a]		IUPAC Review	MechGen Predicted [b]			
	Trapping	LIF		A	B (used)	C	Best [c]
<u>1-Alkenes</u>							
Ethene	12%		17%		17%		Same
Propene	33%		~30%		34%		Same
1-butene	31%		~30%	39%		38%	B=C
1-pentene	37%			38%		37%	B=C
1-hexene	32%			38%		36%	B=C
1-heptene	27%			38%		35%	B=C
1-octene	18%			38%		35%	B=C
<u>Internal alkenes</u>							
cis-2-Butene	41%		33%		51%		Same
trans-2-Butene	64%		60%		51%		Same
2-methyl propene	84%		~64%		65%		Same
2,3-dimethyl-2-butene	90%	70%	~93%		113%		Same
<u>Cycloalkenes</u>							
cyclopentene	61%			94%	86%	101%	B
cyclohexene	68%			60%	54%	63%	C
cycloheptene	46%			59%	52%	62%	B
cyclodecene	35%			59%	48%	61%	B
1-methyl cyclohexene	90%			86%	82%	87%	C
<u>Conjugated dialkenes</u>							
1,3-butadiene	8%				8%		Same
isoprene	27%	50%		28%		27%	B=C
<u>Terpenes</u>							
3-carene	106%			88%	82%	88%	C
limonene	86%			117%	107%	118%	B
a-pinene	85%			91%	86%	92%	B
terpinolene	103%			118%	115%	118%	B
sabinene	26%			53%		42%	B=C
myrcene	115%			56%	81%	43%	B
b-pinene	35%			85%	43%	81%	B
Sum of squares errors:				0.42	0.27	0.42	B

[a] Data from Calvert et al. (2000). "Trapping" refers to the data from Atkinson and co-workers where OH is trapped by adding a cyclohexane tracer. "LIF" refers to data where OH yields were measured directly by laser induced fluorescence. Calvert et al. (2000) gives data using other methods, but results are not as consistent and often disagree with the data shown here.

[b] See text for the description of the models. Note that model "B" is adopted for use by MechGen.

[c] This gives the model that gives the prediction closest to the data. "Same" means all three gave the same predictions, "B=C" means that models "B" and "C" gave the same predictions, which were closer to the data than model "A".

decomposition reactions and less stabilization is expected than if the Criegee intermediate had to share the excitation with a separate carbonyl co-product.

Figure S23 shows plots of predicted vs. experimental OH yields for the three models.

The predicted OH yields for ethene and the alkenes with only CH<sub>3</sub> substituents are the same for each model, and are in fair agreement with the experimental measurements. The estimates also agree very well with the data for 1,3-butadiene and isoprene. Note that in some cases, OH yields of greater than 100% were predicted, indicating that there can be non-negligible OH formation from secondary reactions.

The OH yield predictions for the other compounds depend on the model used to estimate the stabilization factors. The best fits are obtained using model "B", which assumes that the stabilization factor increases with the size of the intermediate but is the same regardless of whether or not it is formed from O<sub>3</sub> addition to a double bond in a ring. Therefore, this is the model adopted for use by MechGen.

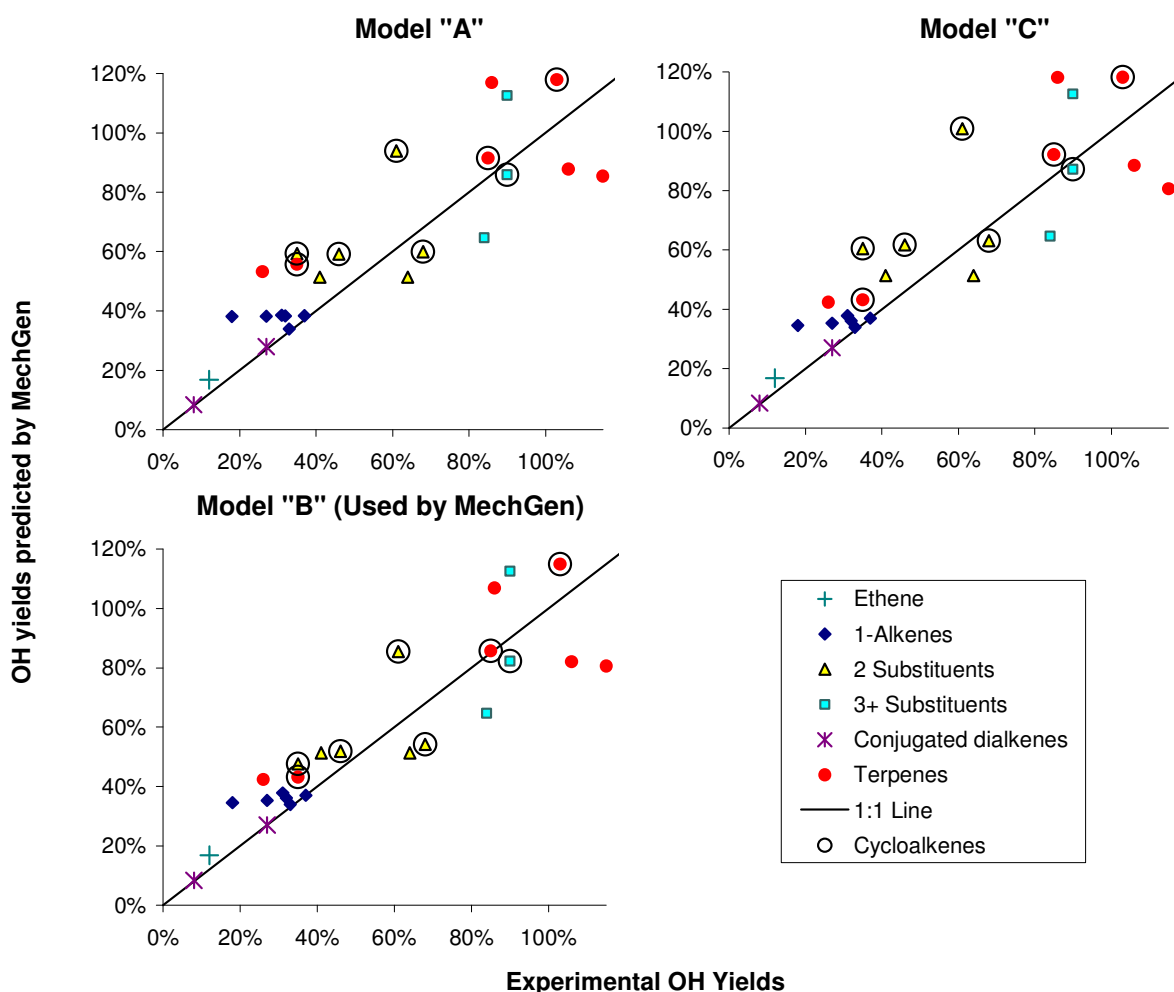


Figure S23. Plots of predicted vs. experimental yields for OH from reactions of O<sub>3</sub> with alkenes in the radical trap experiments summarized by Calvert et al. (2000). The model calculations represented the conditions of the radical trap experiments (no NO<sub>x</sub> present; peroxy radicals react mostly with other peroxy radicals) and used the SAPRC-18 mechanism (Carter, 2020) updated with the Criegee mechanisms derived for this work. The three models are described in the text.

The fact that the apparent stabilization increases with the size of the intermediate is expected, but the fact that it is approximately the same when all the excitation goes to the CI as when it is shared by a separate carbonyl product is surprising, but this is what is indicated by the available OH yield data. There is considerable variability in predictive capability from compound to compound, particularly for the terpenes, which can be attributed to complexities in the mechanisms that our estimates are overlooking or oversimplifying, as well as experimental uncertainties. Although the OH yield predictions are not perfect, this is probably the best that can reasonably be attained using the current estimation approach.

The above discussion is based on considerations of intermediates with only alkyl substituents, but MechGen assumes that non-alkyl substituents in the  $\beta$  or farther position do not affect the mechanism as long as an alkyl (-CH<sub>x</sub>) group is in the  $\alpha$  position. Reactions of intermediates with other types of substituents in the  $\alpha$  position are discussed in the following section.

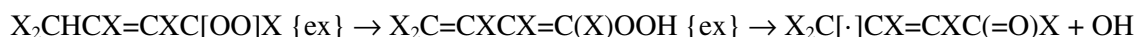
### S1.8.2. Reactions with Non-Alkyl $\alpha$ Substituents

Vereecken et al. (2017) calculated that if a Criegee has an -OH substituent, there is an almost "barrierless" H-shift from the OH to the end carbon of the [OO] group via a 5-member ring, forming a highly excited peroxyacid, which we assume rapidly decomposes under atmospheric conditions as follows:



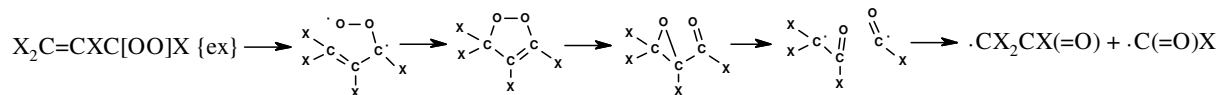
where X is H or any group. These are assumed to dominate over other types of Criegee reactions that might occur, including stabilization or other types of decomposition reactions. Although the reaction of the stabilized intermediate requires that the -OH substituent be in the *syn* position, stabilized substituents with -OH substituents are predicted not to be formed because of the rapid decomposition of the excited intermediate that is initially formed. However, MechGen will generate this reaction with a stabilized intermediate with -OH in the *syn* position if it is manually created by the user.

If the excited intermediate has a double bond group in the  $\alpha$  position, and also has an allylic hydrogen in the  $\gamma$  position relative to the Criegee group, then Vereecken et al. (2017) calculated that an allylic hydroperoxide rearrangement is extremely rapid, and also dominates over stabilization or other possible reactions. This reaction involves the [OO] group abstracting the allylic hydrogen via a 7-member ring transition state to form an excited vinyl hydroperoxide that subsequently decomposes, i.e.,



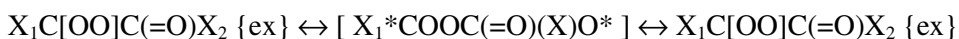
where X is H or any group and {ex} indicates excitation. This reaction also requires that the substituent be in the *syn* position, but it is also assumed to be fast for excited intermediates, and is assumed to be the dominant fate of any Criegee intermediate with at least one substituent of this type, except for those with  $\alpha$ -OH substituents, as discussed above.

On the other hand, if there is no allylic hydrogen in the  $\gamma$  position in the *cis* orientation, then a cyclization rearrangement reaction, where the [OO] adds to the other side of the double bond forming an excited 5-member ring unsaturated cyclic peroxide is still possible. Vereecken et al. (2017) calculated that the reaction forming the cyclic peroxy ether is faster than most VHP decompositions of alkyl-substituted intermediates, but not as fast as the allylic hydroperoxide rearrangement discussed above. This is unlikely to be the final product because it is formed with a high degree of excitation. It is reasonable to expect that such species undergo a highly exothermic rearrangement to form a carbonyl-substituted oxirane, which is even more excited, and might be expected to decompose as shown below.



Since there is no evidence of the formation of either cyclic peroxy ethers or carbonyl-substituted oxiranes in the well-studied isoprene system that forms such CIs, we assume that the subsequent reactions shown above, leading ultimately to decomposition, are fast. However, this is uncertain and speculative.

Vereecken et al. (2017) also considered the reactions of carbonyl-substituted CIs and did not predict any reactions involving -CO- or -HCO substituents to be fast enough to be significant under atmospheric conditions. They considered the possibility of "1,5-oxo-ring closure" of forming a primary ozonide but did not investigate this further, presumably because the ozonide should be unstable and its formation should be rapidly reversed. However, this does not consider the possibility of the ozonide decomposition breaking a different O-O bond than the one that formed it, possibly forming a different carbonyl-Criegee isomer.



Here the X's can be either H or any group, and the reaction only needs to be considered if  $X_1 \neq X_2$ . We assume that this type of O-shift reaction is faster than any competing possible reactions for excited carbonyl-substituted CIs, though theoretical data of Cremer et al. (2021) indicate that this assumption needs to be evaluated when MechGen is updated. In any case, this is not a sink for the CI; it just converts it to different forms whose reactions also need to be considered. MechGen examines both isomers in equilibrium and carries out the decompositions that are estimated to be the fastest, or, if there are no predicted decomposition reactions, will generate stabilization reactions where both types of stabilized isomers are formed in equal yields. If only one isomer has a decomposition reaction, it is assumed to be a net sink for both isomers, with the other isomer rapidly re-forming the reacting isomer by the O-shift reaction until both are consumed.

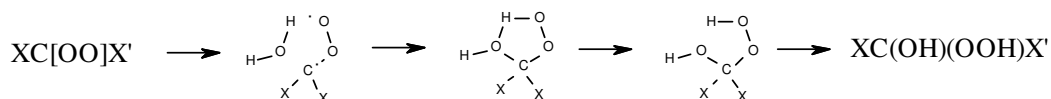
At the present time, we do not consider reactions of CIs with other types of  $\alpha$  substituents besides alkyl, C=C double bond, -OH, or carbonyl groups, and assume that such substituents are not reactive, and thus only react as discussed below in Section S1.8.4. This is primarily applicable for halogen groups, where this is a reasonable assumption. Note that reactions of  $O_3$  with alkenes with other types of  $\alpha$  substituents are not currently supported by MechGen.

### S1.8.3. Mechanisms for Excited Intermediates formed in Other Reactions

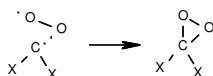
The stabilization fractions discussed above are applicable to excited intermediates formed in  $O_3$  + alkene reactions, but MechGen also predicts formation of excited CIs from reactions of  $O_3$  with alkynes and reactions of  $O_2$  with carbenes. The intermediates formed in the reactions of  $O_3$  probably have similar excitation as those formed when  $O_3$  reacts with double bonds in a ring, since both form single intermediates with all the excitations. Therefore, we assume that the stabilization fractions for intermediates formed from  $O_3$  + alkynes are approximately the same as those derived for excited intermediates formed from  $O_3$  + double bonds in a ring. As discussed above, the available data are more consistent with these stabilization fractions being about the same as those formed from reactions of  $O_3$  with acyclic alkenes, despite the lower expected level of excitation for the CIs. On the other hand, we expect that CIs formed by the addition of  $O_2$  to carbenes have an even higher level of excitation, and tentatively assume that this is sufficient that any favorable decomposition process, such as VHP or hot acid reactions, will dominate over stabilization. Therefore, MechGen uses SF=0 for excited CIs formed from  $O_2$  + carbenes. This is uncertain but carbene formation is generally not predicted by the current version of MechGen, except for a few photolysis reactions (see Section 2.2.1 in the main text).

#### S1.8.4. Reactions of Stabilized Intermediates

Stabilized CIs with groups with alkyl substituents with  $\alpha$  hydrogens in the *syn* position, -OH substituents, or allylic hydrogens in the  $\gamma$  position are assumed to undergo the VHP or other rapid reactions as discussed above. These are referred to as "reactive" substituents in the context of this discussion. Note that stabilized RCH[OO *syn*] intermediates are assumed not to undergo the "hot acid" decompositions that the excited intermediates are assumed to undergo. If the stabilized intermediate cannot undergo any of these reactions, or if the reactive groups are only in the *anti* position, then the fate of the intermediate depends on whether the user has selected the "H<sub>2</sub>O" option, which tells MechGen to generate reactions with H<sub>2</sub>O when applicable. It is set to 1 (true) by default but can be set to 0 (false) to generate reactions for dry conditions. If this option is specified, then these stabilized intermediates are assumed to react with H<sub>2</sub>O to form an  $\alpha$ -hydroxy hydroperoxide, e.g.,



If the H<sub>2</sub>O option is not set, then the stabilized intermediates are assumed to undergo a 1,3-ring closure forming a dioxirane, e.g.



These  $\alpha$ -hydroxy hydroperoxide or cyclic peroxide compounds are treated as stable products for the purposes of mechanism generation. Although Vereecken et al. (2017) and other work cited by them indicate that the rate constant for the reactions with H<sub>2</sub>O or isomerization by 1,3-ring closure can depend on *syn* vs. *anti* configuration and varies significantly depending on the substituents, this is not taken into account in the current version of MechGen. MechGen currently assumes that these reactions are unaffected by whether substituents are in the *syn* or *anti* configuration relative to the stabilized [OO] groups.

#### S1.9. Assigned Rate Constants or Branching Ratios for Specific Reactions

Although MechGen has methods for estimating rate constants and branching ratios for the reactions it can generate, assigned rate constants or branching ratios can be used rather than estimates if data are available. In addition, there are a few unique cases where it is more efficient to use an assignment rather than code for or use parameters for an estimation method that only applies to one case. Table S52 through Table S54 in Section S5.3 give the assigned rate constants and (where available) temperature dependent parameters for the reactions of compounds with OH, O<sub>3</sub>, NO<sub>3</sub>, and O<sup>3</sup>P, respectively. In most cases the rate constants were taken from the compilation of McGillen et al. (2021), which is an update to the originally published rate constant database of McGillen et al. (2020). The main exceptions are rate constants for O<sup>3</sup>P reactions, which were not covered by McGillen et al. (2020, 2021). In addition, Table S56 gives assigned rate constants and temperature dependent parameters for reactions of various radicals or intermediates, and Table S57 gives assigned branching ratios for various reactions of organics or intermediates. Footnotes to the tables give the sources of the rate constants. Because of the size of these tables, they are given at the end of this document in Section S5.

## S2. Estimates of Thermochemistry and Physical Properties

### S2.1. Thermochemical estimates

Several of the SARs used by MechGen require estimates of heats of reactions, so MechGen includes the capability of estimating heats of reactions. These estimates use the Benson (1976) group additivity method, with updated thermochemical group values from Holmes and Aubry (2012) and with additional group values that were estimated when developing MechGen. As discussed by Benson (1976), this method involves assigning heats of reactions to groups of atoms bonded to other atoms, with corrections for ring strain. MechGen assigns heats of formation to each group, which includes contributions of more than one thermochemical group value if the group contains more than one non-H atom. Unfortunately, the group values given by Holmes and Aubry (2012) or found in the literature when MechGen was developed, did not include all the combinations of atoms needed for all products and intermediates that had to be assessed, so a number of group values were estimated, with many if not most estimates being quite uncertain.

The thermochemical group values currently used by MechGen are given in Table S58 through Table S60, with footnotes indicating the sources or estimation methods for the values used. Because of the size of these tables, these are given at the end of this document in Section S5. Table S58 gives the values that were taken from the literature, primarily Holmes and Aubry (2012), but some from NASA (2011) or the NIST structures and properties database program (NIST, 2014). These are considered to be the least uncertain, though relative uncertainties of individual values have not been assessed, and some may well be quite uncertain or need to be updated. The estimated group values are given in Table S59 and Table S60, with the values in Table S59 being judged to have moderate to high uncertainty, and the values in Table S60 to be extremely uncertain and more likely to be inappropriate in some cases. Footnotes to these tables indicate how these estimates were derived. In addition, Table S61 gives the ring strain corrections used from Holmes and Aubry (2012), and heats of formation assigned to specific species primarily from NASA (2006, 2011) that were used.

Most of the thermochemical group values in Table S58 and the assigned heats of formation in Table S62 were obtained in 2014. The currently available literature has not been reviewed to determine if updates are appropriate or additions are available that could reduce the number of estimates that are needed. The estimates in Table S59 are based primarily on assumptions concerning bond dissociation energies, and those in Table S60 are based primarily on assuming speculative relationships between related thermochemical group values. These have not been recently reviewed for consistency and appropriateness, and in many cases should be replaced using more systematic and better documented procedures. In addition, the current ring strain estimates given in Table S61 are limited to monocyclic systems (causing uncertainties in estimates for reactions of many terpenes, for example) and do not consider effects of other groups in the rings besides ketones. However, the current estimates, though uncertain, allow heat of reaction estimates to be made that would otherwise not be possible, allowing assessments of what reactions may or may not occur and allowing use of SARs that are potentially less uncertain than those that do not utilize thermochemical information. In addition, the current thermochemical data are probably sufficient for estimates for the most important species, or are likely not to be the most important uncertainty in the SARs. Therefore, at least up to the present, updating the thermochemical estimates has necessarily been given lower priority than updating the SARs, estimates, and assignments for the many types of reactions needed for mechanism generation.

In any case, it is clear that the thermochemical estimates and group values need to be updated for future versions of MechGen or other mechanism estimation systems that utilize thermochemical estimates. Fortunately, heats of formation can be calculated using quantum chemical methods, and although there may be uncertainties these should be sufficient to improve the most uncertain values given

in Table S60, and probably Table S59 as well. In any case, the entries in these tables indicate where thermochemical work would be most useful for improving SARs and estimates for atmospheric chemistry.

It should be noted that the group additivity methods of Benson are not well suited for cases where there are interactions of non-adjacent groups or atoms in the molecules. Multiple halogen substituents in particular present problems in this regard. Although generated mechanisms for compounds with halogen substituents are beyond the scope of the present document, the MechGen software does have the capability of handling such reactions, but they cannot be implemented because of the lack of sufficient thermochemical estimates.

## S2.2. Volatility and Condensed Fraction Estimates

The example mechanisms discussed in the following section include estimates of equilibrium fractions of products in the particle phase, derived by summing up the yields of each organic product multiplied by the equilibrium fraction of the product in the particle phase in a specified environment. The latter can be estimated using equilibrium partitioning theory (Pankow, 1994), as implemented by Donahue et al. (2006), using the following equations:

$$\begin{aligned} \text{Fraction in particle phase} &= [1 + C^*(\text{compound}, T) / C_{\text{OA}}(\text{environ})]^{-1} && \text{(unitless)} \\ C^*(\text{compound}, T) &= \text{Effective saturation concentration of the compound} && (\mu\text{g}/\text{m}^3) \\ &= P_{\text{vap}}(\text{compound}, T) \times \text{Mwt}(\text{compound}) \times \gamma \times \text{UF} / (R \times T) \\ C_{\text{OA}}(\text{environ}) &= \text{Organic aerosol concentration in the environment} && (\mu\text{g}/\text{m}^3) \\ P_{\text{vap}}(\text{compound}, T) &= \text{Vapor pressure of the compound at temperature T} && (\text{atm}) \\ \text{Mwt}(\text{compound}) &= \text{Molecular weight of the compound} && (\text{g}/\text{mol}) \\ \gamma &= \text{Activity coefficient (unitless) -- approximated as 1.0} && \text{(unitless)} \\ T(\text{environ}) &= \text{Temperature of the environment (deg K)} && (\text{deg K}) \\ R &= \text{Gas constant} = 8.21 \times 10^{-5} && (\text{m}^3 \text{ atm} / \text{degK mol}) \\ \text{UF} &= \text{Units conversion factor} = 10^{-6} && (\text{g}/\mu\text{g}) \end{aligned}$$

The inputs related to the environment include the temperature (T) and the organic aerosol concentration ( $C_{\text{OA}}$ ), and the examples in the following section use  $T = 298 \text{ K}$  and  $C_{\text{OA}} = 50 \mu\text{g}/\text{m}^3$ . The inputs determined by the compound are the molecular weight (Mwt) and the vapor pressure ( $P_{\text{vap}}$ ) at the temperature of the environment. The vapor pressure is estimated from the structure of the molecule as discussed below.

MechGen currently has the capability of estimating heats of formation using either the SIMPOL (Pankow and Asher, 2008) or EVAPORATION (Compernelle et al., 2011) methods. The SIMPOL method is used by default in the examples discussed in this work because it provides estimates for a wider range of compounds. The method of Nannoolal et al. (2008), which is currently used by GECKO-A, has not yet been implemented in MechGen, but may be implemented in future versions. We have not evaluated the optimum method to estimate volatilities, but the use of SIMPOL is considered to be sufficient for example calculations and testing purposes. Further discussion of vapor pressure and SOA estimation methods is beyond the scope of this work, since they do not affect the generated mechanisms as such, only affecting the presentation of the examples.

## S3. Examples of Generated Mechanisms

### S3.1. Methods

The mechanisms of representative compounds were generated using MechGen's "full mechanism generation" procedure (Carter, 2024) where radicals or other highly reactive intermediates formed were also reacted as part of the mechanism generation procedure, but the reactions of stable non-radical products were not generated. Therefore, these mechanisms included reactions of all intermediates formed above a minimum yield, but not the stable products formed. The minimum yield parameters, which determine which of the pathways or intermediates are to be treated as non-negligible, were set at the default values. Further discussion of mechanism generation procedures is given in the corresponding MechGen software manuscript (in preparation).

The generated mechanisms do not, in themselves, give predictions of product yields because competitions between various bimolecular reactions involving the organic species and OH, O<sub>3</sub>, NO, NO<sub>2</sub>, NO<sub>3</sub>, and other peroxy radicals, and between bimolecular, unimolecular, and photolysis reactions, when applicable, affect ultimate yields of products formed. In other words, the yields depend on the environment where the compounds are reacting. However, by defining a set of environmental parameters that specifies the concentrations of the bimolecular co-reactants and the intensity and spectrum of the photolyzing light, yields can be derived for all of the organic products predicted in a generated mechanism. These yields depend on reaction time if the subsequent reactions of the products were taken into account, but for these examples we are considering only reactions leading to the first generation of stable products, and are assuming that the reaction time is sufficient for all the radicals or other reactive intermediates to react.

A comprehensive analysis of product yields in the reactions of organics requires the determination of product yields for a variety of representative atmospheric conditions. However, in this work we only considered one set of conditions for the purpose of providing examples. The conditions are based roughly on results of multi-day dynamic simulations of urban scenarios, representing moderately low NO<sub>x</sub> levels where peroxy + NO reactions are important, but peroxy + peroxy reactions are non-negligible. These conditions represent approximately EBIR (equal benefit incremental reactivity) conditions for ozone reactivity scales (Carter, 1994), where controls of VOCs and NO<sub>x</sub> have approximately the same relative effectiveness in reducing ozone. The characteristics of these conditions are summarized in Table S35. Note that product distributions would be somewhat different for high NO<sub>x</sub>, MIR (maximum incremental reactivity)-like conditions where reactions of peroxy radicals with NO<sub>x</sub> dominate, and quite different from nighttime conditions where NO is near zero and reactions involving NO<sub>3</sub> radicals are much more important. However, further discussion of how product yields vary with environmental conditions is beyond the scope of the present work.

The product yield results were also used to derive a measure of the tendency of the representative compounds to form semi or non-volatile SOA precursors under the specified set of environmental conditions. These are approximated as the sum of the yields of all products multiplied by the fraction of the product estimated to be in the particle phase, calculated as discussed in Section S2.2. Note that this depends on the level of atmospheric aerosol present, which is set at 50 μg/m<sup>3</sup> for the example calculations. Note also that estimates of total particle phase yields are underestimates because they do not account for SOA formed in subsequent generation reactions, which can be a larger source of SOA given sufficient times for the subsequent generation products to react.



Table S35. Oxidant levels and other environmental conditions used to derive product yields for the example mechanisms discussed in this work.

Oxidant or Input	Concentration or Level		Note
	cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup>	Other units	
OH	6.90 x 10 <sup>6</sup>	0.28 ppt	
O <sub>3</sub>	1.96 x 10 <sup>12</sup>	80 ppb	
NO	9.79 x 10 <sup>9</sup>	0.40 ppb	89% of RO <sub>2</sub> reactions
NO <sub>2</sub>	7.25 x 10 <sup>10</sup>	3.0 ppb	
NO <sub>3</sub>	1.58 x 10 <sup>7</sup>	0.65 ppt	0.04% of RO <sub>2</sub> reactions
HO <sub>2</sub>	6.12 x 10 <sup>8</sup>	0.025 ppt	9% of RO <sub>2</sub> reactions
O <sup>3</sup> P	2.61 x 10 <sup>4</sup>		
Total RO <sub>2</sub> 's	4.91 x 10 <sup>8</sup>	20 ppt	Negligible RO <sub>2</sub> reaction
Total RCO <sub>3</sub> 's	8.60 x 10 <sup>7</sup>	3.5 ppt	1% RO <sub>2</sub> reaction
H <sub>2</sub> O	4.20 x 10 <sup>17</sup>	50% RH	
Temperature	298 K		
Light	Direct overhead sun [a]		J(NO <sub>2</sub> ) = 0.723 min <sup>-1</sup>
Atmospheric organic aerosol	C <sub>OA</sub> = 50 µg/m <sup>3</sup>		Moderately high SOA

[a] Actinic fluxes as a function of zenith angle calculated using the actinic fluxes used in the reactivity scenarios of Carter (1994). Half-lives relative to photolysis for the various photolysis sets are given in Table S5.

### S3.2. Example Results

Table S36 lists the example compounds whose mechanisms were generated in this work and gives selected results of our derivations of product yields for the set of environmental conditions given in Table S35. These data were used to derive the figures that are presented in Section 8 of the main manuscript. Because of the large numbers of products formed in all cases, the table gives only totals in terms of yields of compounds with various types of groups on the molecule. Note that yields from multifunctional compounds can contribute to more than one column in that table. The table also gives total yields of multifunctional compounds that have more than one non-alkyl group bonded to a single carbon. These are of interest because estimates for mechanisms of such compounds are particularly uncertain.

Table S36. Representative compounds whose mechanisms were generated for illustrative purposes and a summary of selected results.

Compound	No. Rxns.	No. Prods [a]		Fraction Reacted With [b]				Groups on Products [c]							Cond. [d]	
		All	95%	OH	O3	NO3	HV	-OH	-CHO	-CO-	-O-	-OOH	-ONO2	PANs		Mult.
Propane	31	9	4	100%				0.000	0.265	0.653	-	0.039	0.039	-	-	1e-7
n-Butane	39	12	6	100%				0.092	0.413	0.454	-	0.064	0.074	-	-	6e-6
n-Octane	206	73	28	100%				0.404	0.025	0.580	-	0.419	0.285	-	-	2e-3
n-Dodecane	561	171	58	100%				0.401	0.012	0.515	-	0.382	0.361	-	-	0.05
n-C16	1057	274	84	100%				0.408	0.009	0.508	-	0.376	0.369	-	-	0.16
Isobutane	36	11	5	100%				-	0.079	0.599	-	0.055	0.070	-	-	3e-7
2-Methyl Heptane	1171	266	72	100%				0.445	0.106	0.469	-	0.458	0.301	-	8e-4	0.02
2-Methyl Undecane	3924	578	149	100%				0.471	0.036	0.465	-	0.439	0.380	-	2e-4	0.15
2-Methyl Pentadecane	9304	775	213	100%				0.457	0.028	0.462	-	0.421	0.384	-	1e-4	0.25
2,2-Dimethyl Hexane	401	110	30	100%				0.221	0.204	0.401	-	0.330	0.261	-	1e-5	1e-3
2,3,4-Trimethyl Pentane	1026	141	18	100%				0.053	0.125	0.506	-	0.128	0.254	-	3e-4	3e-3
Ethylcyclohexane	1818	301	71	100%				0.191	0.336	0.481	1e-2	0.344	0.355	0.003	0.024	0.04
1-Butene	161	45	8	94%	6%			0.117	0.646	0.015	-	0.061	0.048	-	0.015	7e-5
1-Octene	1233	265	53	94%	6%			0.631	0.430	0.206	-	0.189	0.192	-	0.175	0.05
1-Dodecene	2286	369	108	96%	4%			0.631	0.358	0.228	-	0.212	0.260	-	0.120	0.21
1-hexadecene	3453	454	160	96%	4%			0.639	0.328	0.245	-	0.222	0.273	-	0.115	0.34
trans-2-Butene	58	15	8	61%	39%			0.077	0.795	0.001	-	0.041	0.030	-	0.050	2e-5
trans-2-octene	730	141	24	66%	34%			0.161	0.702	0.029	-	0.075	0.111	-	0.079	2e-3
Trans-2-Dodecene	1554	251	52	66%	34%			0.186	0.636	0.048	-	0.088	0.152	-	0.110	0.04
Trans-5-Pentadecene	2231	270	66	67%	33%			0.189	0.615	0.059	-	0.094	0.159	-	0.120	0.12
1-Octene	1233	265	53	94%	6%			0.631	0.430	0.206	-	0.189	0.192	-	0.175	0.05
trans-2-octene	730	141	24	66%	34%			0.161	0.702	0.029	-	0.075	0.111	-	0.079	2e-3
2,3-dimethyl-2-hexene	189	44	13	34%	47%	19%		0.077	0.055	0.682	-	0.060	0.141	0.080	0.029	1e-3
1,2-Dimethyl Cyclohexene	829	98	15	70%	27%	3%		0.161	0.121	1.400	5e-4	0.113	0.176	0.064	0.088	4e-3
α-Pinene	1507	216	48	68%	25%	7%		0.311	0.541	0.721	0.070	0.137	0.249	0.024	0.191	0.03
β-Pinene	3322	389	75	93%	5%	3%		0.608	0.318	0.487	0.121	0.232	0.342	0.010	0.177	0.08
d-Limonene	5627	465	467	75%	20%	5%		0.220	0.490	0.686	0.028	0.221	0.180	0.005	0.167	0.07
m-Xylene	98	31	14	100%				0.243	0.809	0.658	0.140	0.063	0.118	-	0.141	4e-3
p-Xylene	59	19	12	100%				0.258	0.954	0.418	0.242	0.049	0.097	-	0.243	3e-3
2,4-dimethyl phenol	108	37	16	72%		28%		0.912	0.156	0.685	0.089	0.054	0.011	-	0.761	0.02
3,6-dimethyl-o-catechol	59	22	9	46%		54%		1.547	0.029	0.759	0.018	0.097	0.003	-	1.067	0.19

Table S36 (continued)

Compound	No. Rxns.	No. Prods [a]		Fraction Reacted With [b]				Groups on Products [c]							Cond. [d]	
		All	95%	OH	O3	NO3	HV	-OH	-CHO	-CO-	-O-	-OOH	-ONO2	PANs		Mult.
Octanal	426	126	36	85%			15%	0.196	0.271	0.132	0.057	0.206	0.124	0.410	0.047	1e-2
2-Octanone	304	96	38	100%				0.286	0.124	1.315	-	0.393	0.264	0.028	0.364	7e-3
n-Hexyl Acetate	935	204	58	100%				0.213	0.267	0.984	0.679	0.335	0.214	0.051	0.180	1e-2
n-Butyl Butyrate	467	116	31	100%				0.010	0.415	0.803	0.691	0.121	0.223	0.036	0.182	1e-3

[a] The "95%" column gives the total number of products whose cumulative yields exceed 95%.

[b] Reactions that amount to less than 0.5% of the total consumption of the VOC for the set of conditions used to determine negligible reactions are not shown, even if mechanisms are generated for them.

[c] This gives the total carbons in products with the indicated groups relative to the amount of carbon reacted. If a compound has more than one group, it contributes to the total given in the column for each of the applicable groups. "Mult" refers to product compounds where there is more than one non-alkyl group on bonded to the same carbon in the molecule.

[c] The "Cond" column gives the total carbons estimated to be in the condensed phase, relative to the carbons reacted. This is calculated from the sum of carbons of all products multiplied by their equilibrium fraction in the particle phase estimated for the representative environmental conditions (as discussed in Section S2.2). Note that this does not include products formed in second and additional generation reactions.

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## S5. Large Tables

### S5.1. Parameters for Estimating Bimolecular rate constants

Table S37. Base rate constant parameters for estimating rate constants for reactions of organics with OH, NO<sub>3</sub>, and Cl.

Parameter	k(298) [a]			Notes [b]
	OH	NO <sub>3</sub>	Cl	
kH <sup>base</sup> for H-Atom abstractions				
-CH <sub>3</sub>	1.30e-13	1.07e-19	2.89e-11	1
-CH <sub>2</sub> -	8.47e-13	9.45e-18	6.54e-11	1
-CH()-	1.93e-12	6.72e-17	5.18e-11	1
-CHO	1.48e-11	2.66e-15	5.72e-11	1
-OH	1.31e-13	0	0	2
-CHO-O-	8.46e-14	0	1.27e-14	2
-HO-O-	5.45e-12	0	0	2
-HO-CO-	6.22e-13	0	0	2
-HO-O-CO-	1.00e-14			2
-HO-aCH or -HO-aC	9.44e-13	8.56e-12	0	2
-CH <sub>2</sub> -OH		1.83e-15		2
-CH()-OH		2.13e-15		2
CH <sub>3</sub> -O-		1.02e-16		2
-CH <sub>2</sub> -O-		1.55e-15		2
-CH()-O-		2.03e-15		2
-CH <sub>3</sub> -CH <sub>x</sub> -O-	(x=0-2)	1.01e-16		2
-CH <sub>2</sub> -CH <sub>x</sub> -O-	(x=0-2)	1.09e-15		2
-CH()-CH <sub>x</sub> -O-	(x=0-2)	2.03e-15		2
kA <sup>base</sup> for Additions to double or triple bonds				
-CH <sub>2</sub> =CH-	2.61e-11	1.16e-14	1.07e-10	3, 4
-CH=CH <sub>2</sub>	4.50e-12	0	1.07e-10	3, 4
-CH=CH-	3.10e-11	1.78e-13	1.37e-10	3, 4
-CH <sub>2</sub> =C()-	5.69e-11	3.31e-13	1.22e-10	3, 4
-C)=CH <sub>2</sub>	4.50e-12	0	1.22e-10	3, 4
-CH=C()-	5.61e-11	6.52e-12	1.47e-10	3, 4
-C)=CH	3.10e-11	0	1.47e-10	3, 4
-C(=C)()-	5.27e-11	2.08e-11	1.47e-10	3, 4
CH <sub>2</sub> =CH-CH <sub>x</sub> =	3.27e-11	5.30e-14	1.95e-10	1, 4, 5
CH(CH <sub>x</sub> )=CH <sub>2</sub>	1.72e-12	0	2.16e-11	1, 4, 5
-CH=CH-CH <sub>x</sub> =	6.90e-11	2.26e-12	1.95e-10	1, 4, 5
CH(CH <sub>x</sub> )=CH-	3.63e-12	0	2.16e-11	1, 4, 5
CH <sub>2</sub> =C()-CH <sub>x</sub> =	5.92e-11	5.94e-13	1.60e-10	1, 4, 5
-C(CH <sub>x</sub> )=CH <sub>2</sub>	3.11e-12	0	1.78e-11	1, 4, 5
-CH=C-CH <sub>x</sub> =	9.66e-11	8.59e-12	1.60e-10	1, 4, 5
-C(CH <sub>x</sub> )=CH	5.08e-12	0	1.78e-11	1, 4, 5
-C)=CH-CH <sub>x</sub> =	9.66e-11	8.59e-12	1.95e-10	1, 4, 5
CH(CH <sub>x</sub> )=C	5.08e-12	0	2.16e-11	1, 4, 5
-C)=C-CH <sub>x</sub> =	1.16e-10	2.08e-11	1.60e-10	1, 4, 5
-C(CH <sub>x</sub> )=C)	6.12e-12	0	1.78e-11	1, 4, 5
CH(CH <sub>x</sub> )=CH-CH <sub>x</sub> = (x=0-1)	6.90e-11	2.26e-12	1.95e-10	2, 5, 6



Table S37 (continued)

Parameter	k(298) [a]			Notes [b]
	OH	NO <sub>3</sub>	Cl	
CH(CH <sub>x</sub> )=C-CH <sub>x</sub> = (x=0-1)	9.66e-11	8.59e-12	1.60e-10	2, 5, 6
-C(CH <sub>x</sub> )=CH-CH <sub>x</sub> = (x=0-1)	9.66e-11	8.59e-12	1.95e-10	2, 5, 6
-C(CH <sub>x</sub> )=C-CH <sub>x</sub> = (x=0-1)	1.16e-10	2.08e-11	1.60e-10	2, 5, 6
C(=CH <sub>2</sub> )=CH-	3.00e-11	6.96e-14	4.38e-10	2
C(=CH <sub>2</sub> )=C()-	5.67e-11	1.74e-12	4.38e-10	2
C(=CH-)=CH-	3.10e-11	8.28e-14	4.38e-10	2
C(=CH-)=C()-	5.61e-11	1.64e-12	4.38e-10	2
C(=C()-)=C()-	5.27e-11	1.21e-12	4.38e-10	2
CH≡C-	5.35e-12	5.06e-16	2.60e-11	1, 6
-C≡CH	5.00e-13	0	2.60e-11	1, 6
-C≡C-	1.34e-11	2.20e-14	2.60e-11	1, 6
kAro <sup>base</sup> for Additions to aromatic groups				
-aCH-	2.04e-13	1.47e-18	2.57e-12	7
-aC()-	2.85e-13	3.78e-17	7.07e-16	7
-aC(aC)-	7.95e-13	3.78e-17	1.19e-11	7
-aC(OH)-		4.75e-13		7
kA <sup>n</sup> base for Additions to amino groups				
-NH <sub>2</sub>	1.75e-11	9.47e-15	2.61e-10	2
-NH-	7.63e-11	2.27e-14	3.31e-10	2
-N()-	8.24e-11	2.37e-14	2.81e-10	2
NH <sub>2</sub> -CO-	6.30e-13	1.32e-15	2.09e-11	2
-NH-CHO or -NH-CO-	5.82e-12	1.37e-15	4.20e-11	2
-N()-CHO or -N()-CO-	1.35e-11	2.92e-14	1.21e-10	2

[a] Rate constants are in units of cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1</sup>. See Carter (2021) for estimated temperature dependence of parameters, which are highly approximate and in many cases also highly uncertain.

[b] Notes are as follows. See Carter (2021) for information on how these parameters were derived.

1. Substituent correction factors for the reactions are given in Table S38, Table S39, or Table S40.
2. Substituent correction factors are not used.
3. Applicable for isolated or separated bonds. Addition is on the first group shown, with the radical center on the other side of the double bond on this group.
4. F<sub>1sub</sub> is the factor for substituents on the first group and F<sub>2sub</sub> is the factor is the group on the other side of the double bond where the addition occurs.
5. Applicable for addition to conjugated double bonds, where addition is on the first group shown, with the radical center on the other side of the double bond on this group.
6. Because of lack of data, the same correction factors are used as used for additions to separated double bonds. This is highly uncertain.
7. Substituent correction factors for groups on various positions of the aromatic ring are given in Table S41. Note that factors are used only the aromatic ring with the reacting group.

Table S38. Substituent correction factors for abstractions or additions by OH radicals.

Neighboring Group (nbr)	Abstraction $FH^{nbr}(\text{nbr}, -\text{CH}_x \text{ or } -\text{CHO})$ [a]				Addition $FA_x^{nbr}(\text{nbr})$ [b]	
	-CH <sub>3</sub>	-CH <sub>2</sub> -	-CH()-	-CHO	x=1	x=2
-CH <sub>3</sub>	1	1	1	1	1	1
-CH <sub>2</sub> -	1.30	1.30	1.30	1.46	1	1
-CH()-	0.99	0.99	0.99	2.02	1	1
-C()()-	1.43	1.43	1.43	1.84	1	1
=CH-	1	1	1	0.52	1	1
=C()-	1	1	1	0.52	1	1
#C-	1	1	1	1	1	1
-aCH= or -aC()=	3.13	1.27	1.27	0.91	0.001	1.36
-OH	5.75	3.95	2.70		1	1
-CHO	1	1	1	0.31	0.46	0.46
-CO-	0.95	0.95	0.95		1.43	0.68
-O-	15.13	9.48	2.68		9.82	1.19
-NO <sub>2</sub>	0.09	0.09	0.09		0.039	0.039
-ONO <sub>2</sub>	0.14	0.14	0.14		0.039	0.039
-Cl	0.27	0.27	0.27		0.16	0.26
-NH <sub>2</sub>	1	1	1		1	1
-NH-	1	1	1	1	1	1
-N()-	1	1	1	1	1	1
-O-OH	1.23	1.23	1.23		1	1
-O-CO-	2.00	2.00	2.00	1	0.001	0.98
-O-CO-O-	1.19	1.19	1.19	1		
-O-CHO	0.77	0.77	0.77		0.001	0.98
-CO-OH	0.22	0.22	0.22		0.54	0.54
-CO-O-	0.22	0.22	0.22	0.79	0.60	0.66
-CO-CO	0.95	0.95	0.95	0.79		
-CO-O-ONO <sub>2</sub>					0.47	0.47
-CH <sub>2</sub> -OH	3.66	3.66	3.66	1.46		
-CH()-OH	3.66	3.66	3.66	2.02		
-C()()-OH	3.66	3.66	3.66	1.84		
-CH <sub>2</sub> -CO-	3.55	3.55	3.55	1.46		
-CH()-CO-	3.55	3.55	3.55	2.02		
-C()()-CO-	3.55	3.55	3.55	1.84		
-CH <sub>2</sub> -NO <sub>2</sub>	0.001	0.001	0.001	1.46	0.40	0.40
-CH()-NO <sub>2</sub>	0.32	0.32	0.32	2.02	0.40	0.40
-C()()-NO <sub>2</sub>	0.32	0.32	0.32	1.84	0.40	0.40
-CH <sub>2</sub> -ONO <sub>2</sub>	0.36	0.36	0.36	1.46	0.54	0.54
-CH()-ONO <sub>2</sub>	0.36	0.36	0.36	2.02	0.54	0.54
-C()()-ONO <sub>2</sub>	0.36	0.36	0.36	1.84	0.54	0.54
-CH <sub>2</sub> -Cl	0.89	0.89	0.89	1.46	1	1
-CH()-Cl	0.89	0.89	0.89	2.02	1	1
-C()()-Cl	0.89	0.89	0.89	1.84	1	1

[a] The first group is the group next to the reaction site. For additions, x=1 refers to substituents on the group where the radical adds, and x=2 to substituents on the group on the other side of the bond.

Table S39. Substituent correction factors for abstractions or additions by NO<sub>3</sub> radicals.

Neighboring Group (nbr)	Abstraction FH <sup>nbr</sup> (nbr,-CH <sub>x</sub> or -CHO) [a]				Addition FA <sub>x</sub> <sup>nbr</sup> (nbr) [a, b]	
	-CH <sub>3</sub>	-CH <sub>2</sub> -	-CH()-	-CHO	x=1	x=2
-CH <sub>3</sub>	1	1	1	1	1	1
-CH <sub>2</sub> -	1.76	1.76	1.76	6.23	1	1
-CH()-	2.06	2.06	2.06	9.54	1	1
-C()()-	2.55	2.55	2.55	9.03	1	1
=CH-	1	1	1	0.39	1	1
=C()-	1	1	1	0.39	1	1
#C-	1	1	1	1	1	1
-aCH= or -aC()=	4.09	4.09	4.09	1	10	77.91
-OH	1	1	1		1	1
-CHO	1.61	1.61	1.61	0.08	0.03	0.01
-CO-	1.55	1.55	1.55		0.02	0.01
-O-	14.74	14.74	14.74		1	123.84
-NO <sub>2</sub>	0.22	0.22	0.22			
-ONO <sub>2</sub>	0.33	0.33	0.33			
-Cl	0.56	0.56	0.56		0.03	0.03
-NH <sub>2</sub>	1	1	1		1	1
-NH-	1	1	1	1	1	1
-N()-	1	1	1	1	1	1
-O-OH	1.90	1.90	1.90		1	1
-O-CO-	2.84	2.84	2.84		10	0.78
-O-CO-O-						
-O-CHO	1.30	1.30	1.30		10	0.78
-CO-OH	0.47	0.47	0.47		0.002	0.009
-CO-O-	0.47	0.47	0.47	0.19	0.002	0.009
-CO-CO	1.55	1.55	1.55	0.19		
-CO-O-ONO <sub>2</sub>					0.0005	0.0005
-CH <sub>2</sub> -OH	4.70	4.70	4.70	6.23		
-CH()-OH	4.70	4.70	4.70	9.54		
-C()()-OH	4.70	4.70	4.70	9.03		
-CH <sub>2</sub> -CO-	4.52	4.52	4.52	6.23		
-CH()-CO-	4.52	4.52	4.52	9.54		
-C()()-CO-	4.52	4.52	4.52	9.03		
-CH <sub>2</sub> -NO <sub>2</sub>	0.006	0.006	0.006	6.23		
-CH()-NO <sub>2</sub>	0.64	0.64	0.64	9.54		
-C()()-NO <sub>2</sub>	0.64	0.64	0.64	9.03		
-CH <sub>2</sub> -ONO <sub>2</sub>	0.70	0.70	0.70	6.23		
-CH()-ONO <sub>2</sub>	0.70	0.70	0.70	9.54		
-C()()-ONO <sub>2</sub>	0.70	0.70	0.70	9.03		
-CH <sub>2</sub> -Cl	1.47	1.47	1.47	6.23	0.012	0.10
-CH()-Cl	1.47	1.47	1.47	9.54	0.012	0.10
-C()()-Cl	1.47	1.47	1.47	9.03	0.012	0.10

[a] The first group is the group next to the reaction site. For additions, x=1 refers to substituents on the group where the radical adds, and x=2 to substituents on the group on the other side of the bond.

[b] An additional correction factor of FA<sup>struct</sup>(nC) is applied for additions by NO<sub>3</sub>, where nC is the number of carbons in the organic and FA<sup>struct</sup>(nC) = {1 - exp(-min(nC, 12) × 0.101)}/{1 - exp(-4 × 0.101)}.

Table S40. Substituent correction factors for abstractions or additions by Cl atoms.

Neighboring Group (nbr)	Abstraction $FH^{nbr}(\text{nbr}, -\text{CH}_x \text{ or } -\text{CHO})$ [a]				Addition $FA_x^{nbr}(\text{nbr})$ [a]	
	-CH <sub>3</sub>	-CH <sub>2</sub> -	-CH()-	-CHO	x=1	x=2
-CH <sub>3</sub>	1	1	1	1	1	1
-CH <sub>2</sub> -	1	1	1	1	1	1
-CH()-	1	1	1	1	1	1
-C()-	1	1	1	1	1	1
=CH-	1	1	1	2.77	1	1
=C()-	1	1	1	2.77	1	1
#C-	1	1	1	1	1	1
-aCH= or -aC()=	0.94	0.94	0.94	1	1	1
-OH	1.77	1.31	0.91		1	1
-CHO	0.79	0.40	0.40	0.31	0.00	0.00
-CO-	0.04	0.60	0.60		0.86	0.86
-O-	3.08	1.17	1.17		1.28	1.28
-NO <sub>2</sub>	0.001	0.001	0.001		1	1
-ONO <sub>2</sub>	0.008	0.067	0.067		1	1
-Cl	0.017	0.081	0.081		0.59	0.59
-NH <sub>2</sub>	1	1	1		1	1
-NH-	1	1	1	1	1	1
-N()-	1	1	1	1	1	1
-O-OH	2.04	1.24	1.24		1	1
-O-CO-	0.005	0.001	0.001	1	1.16	1.16
-O-CO-O-	0.048	0.048	0.048			
-O-CHO	0.048	0.001	0.001		1.16	1.16
-CO-OH	0.001	0.001	0.001		0.86	0.86
-CO-O-	0.097	0.097	0.097	0.87	0.86	0.86
-CO-CO	0.008	0.18	0.18	0.87		
-CO-O-ONO <sub>2</sub>					0.86	0.86
-CH <sub>2</sub> -OH	0.44	0.44	0.44	1		
-CH()-OH	0.55	0.55	0.55	1		
-C()-OH	0.39	0.39	0.39	1		
-CH <sub>2</sub> -CO-	0.20	0.27	0.27	1		
-CH()-CO-	0.54	0.54	0.54	1		
-C()-CO-	0.46	0.46	0.46	1		
-CH <sub>2</sub> -NO <sub>2</sub>	0.004	0.004	0.004	1	1	1
-CH()-NO <sub>2</sub>	0.004	0.004	0.004	1	1	1
-C()-NO <sub>2</sub>	0.004	0.004	0.004	1	1	1
-CH <sub>2</sub> -ONO <sub>2</sub>	0.001	0.001	0.001	1	1	1
-CH()-ONO <sub>2</sub>	0.006	0.006	0.006	1	1	1
-C()-ONO <sub>2</sub>	0.006	0.006	0.006	1	1	1
-CH <sub>2</sub> -Cl	0.17	0.17	0.17	0.14	0.77	0.77
-CH()-Cl	0.17	0.17	0.17	0.14	0.77	0.77
-C()-Cl	0.17	0.17	0.17	0.14	0.77	0.77

[a] The first group is the group next to the reaction site. For additions, x=1 refers to substituents on the group where the radical adds, and x=2 to substituents on the group on the other side of the bond.

Table S41. Substituent correction factors for additions of OH, NO<sub>3</sub> and Cl to aromatic rings.

Rxn	Substituent Group(s)	Aromatic Ring Substituent Correction Factors			
		FA <sup>ortho</sup>	FA <sup>meta</sup>	FA <sup>para</sup>	FA <sup>ipso</sup>
OH	-CH <sub>3</sub>	9.59	1	1	1
	-CH <sub>2</sub> -	9.59	1	1	1
	>CH-	9.59	1	1	1
	>C<	9.59	1	1	1
	=CH-	9.59	1	1	1
	=C<	9.59	1	1	1
	#C-	9.59	1	1	1
	Aro	8.22	1.73	1.68	1
	-OH	25	3.88	1.35	1.05
	-O-	15.3	2.39	0.83	0.65
	-CHO	0.79	0.79	0.79	0.79
	-CO-	0.79	0.79	0.79	0.79
	-NO <sub>2</sub>	0.076	0.076	0.076	0.076
	-ONO <sub>2</sub>	0.076	0.076	0.076	0.076
	-F	0.48	0.48	0.48	0.48
	-Cl	0.62	0.62	0.62	0.62
	-BR	0.70	0.70	0.70	0.70
	-CO-OH	0.79	0.79	0.79	0.79
	-CO-O-	0.79	0.79	0.79	0.79
	-CO-O-ONO <sub>2</sub>	0.79	0.79	0.79	0.79
NO <sub>3</sub>	-CH <sub>3</sub>	5.40	1	5.82	1
	-CH <sub>2</sub> -	5.40	1	5.82	1
	>CH-	5.40	1	5.82	1
	>C<	5.40	1	5.82	1
	=CH-	5.40	1	5.82	1
	=C<	5.40	1	5.82	1
	-OH	18.1	1	2.00	2.96
	-O-	12.1	1	129	1
	-CHO	212	1	176	1
	Cl	-CH <sub>3</sub>	2.80	2.80	2.80
-CH <sub>2</sub> -		2.80	2.80	2.80	1
>CH-		2.80	2.80	2.80	1
>C<		2.80	1	1	1
=CH-		2.80	2.80	2.80	1
=C<		2.80	2.80	2.80	1
Aro		0.73	0.73	0.73	1
-OH		19.3	19.3	19.3	1
-O-		0.87	0.87	0.87	0.87
-CHO		0.47	0.47	0.47	0.47
-NO <sub>2</sub>		0.054	0.054	0.054	0.054
-O-OH		1	1	1	1
-O-CHO		1	1	1	1
-O-CO-		1	1	1	1

Table S42. Correction factors for H-atom abstractions or for additions to groups or bonds in a ring.

Type of Reaction or Double Bond System	Size of Smallest Ring with the Group or with all Groups in the Bond						
	3	4	5	6	7	8	9+
	<u>FH<sup>ring</sup> for H abstraction by OH or NO<sub>3</sub></u>						
Default or only -CHx- in ring	0.018	0.35	0.78	1	1	1	1
-CO- or -CO-O- in ring	0.018	0.17	0.31	0.56	1	1	1
-O- in ring	0.004	0.35	0.78	1	1	1	1
	<u>FH<sup>ring</sup> for H abstraction by Cl</u>						
Any groups in ring	0.001	0.84	0.89	1	1	1	1
	<u>O<sub>3</sub> addition to double bond systems (no ring corrections for O<sup>3</sup>P)</u>						
Isolated double bonds	4.00	4.00	4.00	0.67	2.75	3.45	1
Conjugated double bonds	4.00	4.00	5.98	0.44	1	1	1
Double bonds with α -CO-, -CHO, -O-, or -OH	4.00	4.00	4.00	0.67	2.75	3.45	1

Table S43. Base rate constants for additions of O<sub>3</sub> or O<sup>3</sup>P to bonds or to amine groups. Branching ratios for O<sub>3</sub> reactions are also shown.

Bond or Group	k(298) [a]		O <sub>3</sub> Branching [b]
	O <sub>3</sub>	O <sup>3</sup> P	
	Bonds for kA <sup>base</sup>		
-CH <sub>2</sub> =CH-	9.67e-18	4.44e-12	Both paths equal
-CH <sub>2</sub> =C()-	1.45e-17	1.74e-11	
-CH=CH-	1.59e-16	1.88e-11	
cis -CH=CH-	1.37e-16	(above)	
trans -CH=CH-	1.84e-16	(above)	
-CH=C()-	4.20e-16	5.11e-11	
-C(=C)-	7.46e-16	7.69e-11	
CH <sub>2</sub> =CH-CH=CH-	3.15e-17	5.45e-11	All 4 paths equal
CH <sub>2</sub> =CH-CH=C-	1.94e-16	7.92e-11	
CH <sub>2</sub> =CH-C(=CH)-	6.34e-17	8.70e-11	
CH <sub>2</sub> =CH-C(=C)-	2.94e-16	1.21e-10	
CH <sub>2</sub> =C()-CH=CH <sub>2</sub>	1.28e-17	3.50e-11	
CH <sub>2</sub> =C()-CH=CH-	8.00e-17	8.64e-11	
CH <sub>2</sub> =C()-CH=C()-	2.94e-16	1.34e-10	
CH <sub>2</sub> =C()-C(=CH <sub>2</sub>	2.56e-17	6.71e-11	
CH <sub>2</sub> =C()-C=CH-	9.61e-17	1.34e-10	
CH <sub>2</sub> =C()-C(=C)-	4.46e-16	1.77e-10	
-CH=CH-CH=CH-	3.43e-16	8.35e-11	
-CH=CH-CH=C()-	9.01e-16	1.55e-10	
-CH=CH-C(=C)-	1.37e-15	2.01e-10	
-CH=C()-CH=CH-	2.94e-16	1.55e-10	
-CH=C()-CH=C()-	1.37e-15	2.21e-10	
-CH=C()-C(=CH-	4.46e-16	2.21e-10	
-C(=CH-CH=C()-	3.06e-15	2.37e-10	
-C(=C()-CH=C()-	6.34e-15	2.77e-10	
-C(=C()-C(=C)-	9.62e-15	3.41e-10	
CH <sub>2</sub> =C=CH-	0	6.55e-12	No reactions generated
CH <sub>2</sub> =C=C()-	0	3.00e-11	

Table S43 (continued)

Bond or Group	k(298) [a]		O <sub>3</sub> Branching [b]
	O <sub>3</sub>	O <sub>3</sub> P	
-CH=C=CH-	0	1.60e-11	
-CH=C=C()-	0	8.71e-11	
-C()=C=C()-	0	9.82e-12	
CH <sub>2</sub> =CH-OH	2.76e-16		90% -OH on carbonyl (10% on the Criegee)
CH <sub>2</sub> =C()-OH	1.52e-17		
-CH=CH-OH	7.43e-17		
-CH=C()-OH	2.68e-16		
-C()=CH-OH	1.56e-16		
-C()=C()-OH	5.61e-16		
CH <sub>2</sub> =CH-O-	2.76e-16	1.98e-11	90% -O- on carbonyl
CH <sub>2</sub> =C()-O-	1.52e-17	4.99e-11	
-CH=CH-O-	7.43e-17	9.16e-11	
-CH=C()-O-	2.68e-16	2.02e-10	
-C()=CH-O-	1.56e-16	2.02e-10	
-C()=C()-O-	5.61e-16	3.15e-10	
CH <sub>2</sub> =CH-O-CHO	3.82e-18		90% -O-CHO on carbonyl
CH <sub>2</sub> =C()-O-CHO	3.93e-18		
-CH=CH-O-CHO	1.88e-18		
-CH=C()-O-CHO	7.00e-19		
-C()=CH-O-CHO	6.76e-18		
-C()=C()-O-CHO	1.42e-17		
CH <sub>2</sub> =CH-O-CO-	3.82e-18	1.38e-12	90% -O-CO- on carbonyl
CH <sub>2</sub> =C()-O-CO-	3.93e-18	2.77e-12	
-CH=CH-O-CO-	1.88e-18	4.29e-12	
-CH=C()-O-CO-	7.00e-19	1.52e-11	
-C()=CH-O-CO-	6.76e-18	2.10e-11	
-C()=C()-O-CO-	1.42e-17	1.48e-11	
CH <sub>2</sub> =CH-CHO	2.80e-19	4.00e-13	90% -CHO on carbonyl
CH <sub>2</sub> =C()-CHO	1.20e-18	1.04e-12	
-CH=CH-CHO	1.86e-18	2.49e-12	
-CH=C()-CHO	3.91e-18	2.89e-12	
-C()=CH-CHO	1.82e-18	9.24e-12	
-C()=C()-CHO	9.47e-18	7.12e-12	
CH <sub>2</sub> =CH-CO-	5.40e-18	1.15e-12	90% -CO- on carbonyl
CH <sub>2</sub> =C()-CO-	1.19e-17	7.57e-12	
-CH=CH-CO-	4.18e-17	2.04e-11	
-CH=C()-CO-	4.31e-17	2.26e-11	
-C()=CH-CO-	8.29e-18	2.54e-11	
-C()=C()-CO-	4.38e-17	4.10e-11	
CH <sub>2</sub> =CH-CO-OH	7.05e-19	5.71e-13	90% -CO-OH on carbonyl
CH <sub>2</sub> =C()-CO-OH	2.99e-18	2.88e-12	
-CH=CH-CO-OH	2.07e-18	2.95e-12	
-CH=C()-CO-OH	7.47e-18	6.51e-12	
-C()=CH-CO-OH	4.35e-18	6.51e-12	
-C()=C()-CO-OH	1.57e-17	1.02e-11	
CH <sub>2</sub> =CH-CO-O-	1.13e-18	4.08e-13	90% -CO-O- on carbonyl
CH <sub>2</sub> =C()-CO-O-	8.97e-18	5.45e-12	
-CH=CH-CO-O-	7.88e-18	5.40e-12	
-CH=C()-CO-O-	8.78e-18	6.24e-12	

Table S43 (continued)

Bond or Group	k(298) [a]		O <sub>3</sub> Branching [b]
	O <sub>3</sub>	O <sup>3</sup> P	
-C(=CH-CO-O-	2.51e-17	2.44e-11	
-C(=C()-CO-O-	6.99e-17	1.20e-11	
CH <sub>2</sub> =CH-CO-CO <sub>x</sub>	5.40e-18		90% -CO-CO <sub>x</sub> on carbonyl (-CO <sub>x</sub> is -CO- or -CHO)
CH <sub>2</sub> =C()-CO-CO <sub>x</sub>	1.19e-17		
-CH=CH-CO-CO <sub>x</sub>	4.18e-17		
-CH=C()-CO-CO <sub>x</sub>	4.31e-17		
-C(=CH-CO-CO <sub>x</sub>	8.29e-18		
-C(=C()-CO-CO <sub>x</sub>	4.38e-17		
CO <sub>x</sub> -CH <sub>y</sub> =CH <sub>y</sub> -CO <sub>x</sub>	3.27e-18	3.99e-13	Both paths equal (y=0 or 1)
	Groups for kA <sup>n</sup> base		
CH#C-	1.68e-20	8.97e-13	Both paths equal
-C#C-	1.68e-20	8.60e-12	
-NH <sub>2</sub>	7.40e-21	8.54e-13	Only one reaction
-NH-	1.67e-18	6.00e-12	
-N()-	7.84e-18	2.18e-11	

[a] Rate constant in units of cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1</sup>. See Carter (2021) for estimated temperature dependences, which are uncertain and highly approximate.

[b] See text in main manuscript for a discussion of O<sup>3</sup>P branching ratios.



Table S44. Correction factors for additions of O<sub>3</sub> to double bond systems.

Group or Structure	FA <sup>nbr</sup> (subst)		
	Isolated	Conjugated	α-Subst [a]
	<u>FA<sup>nbr</sup>(subst)</u>		
-aro	1.87	1.37	1.00
-OH	[b]		0.31
-O-	[b]	0.56	1.00
-CO-	[b]	0.024	1.00
-CHO	[b]	0.024	
-NO <sub>2</sub>	0.007	0.082	
-ONO <sub>2</sub>	0.007	0.082	
-F	0.076	0.27	
-Cl	0.014	0.118	1.00
-O-CO-	[b]		1.00
-O-CO-O-	[b]		
-CH <sub>x</sub> -OH [c]	1.25	1.12	
-CH <sub>x</sub> -O-	0.34	0.58	
-CH <sub>x</sub> -CHO	0.34	0.59	
-CH <sub>x</sub> -CO-	0.26	0.51	
-CH <sub>x</sub> -O-CO-	0.34	0.58	
-CH <sub>x</sub> -NO <sub>2</sub>	0.042	0.21	
-CH <sub>x</sub> -ONO <sub>2</sub>	0.042	0.21	
-CH <sub>x</sub> -F	0.099	0.31	
-CH <sub>x</sub> -Cl	0.20	0.44	
	<u>FA<sup>struct</sup>(site) for furan structures [d]</u>		
1 subst. on furan		0.017	
2 subst. on furan		0.034	
3 subst. on furan		0.050	
4 subst. on furan		0.066	
	<u>Corrections nβ = number of non-H β-substituents by reaction site</u>		
	FA <sup>struct</sup> (nβ) = 1 - (0.268 × {(min [4, max(1, nβ)] - 1}),		

- [a] Isolated double bonds with -CHO, -CO-, -OH, or -O- substituents.
- [b] No correction is applied because the effect of this substituent is incorporated into the base rate constant for bonds with these substituents.
- [c] "-CH<sub>x</sub>" is either -CH<sub>3</sub>, -CH<sub>2</sub>-, -CH()-, or -C()()-.
- [d] The base rate constant is for the double bond structure if there were no ring. A ring correction factor of 4.0 is also applied (see Table S42).

## S5.2. Radical Rate Constants and Branching Ratios

Table S45. Experimental and estimated rate constants for the bimolecular reactions of peroxy radicals under atmospheric conditions.

Radical	Rate Constant (cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup> )			
	k(298)	A	Ea/T	Note [a]
	<u>RO<sub>2</sub> + NO</u>			
<u>Used for MechGen Estimates</u>	9.13e-12	2.55e-12	-380	1
CH <sub>3</sub> OO·	7.7e-12	2.3e-12	-360	2
CH <sub>3</sub> CH <sub>2</sub> OO·	9.1e-12	2.6e-12	-380	2
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OO·	9.4e-12	2.9e-12	-350	2
CH <sub>3</sub> C(CH <sub>3</sub> ) <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> OO·	1.8e-12			3
CH <sub>3</sub> CH(OO·)CH <sub>3</sub>	9.0e-12	2.7e-12	-360	2
CH <sub>3</sub> C(CH <sub>3</sub> )(CH <sub>3</sub> )CH <sub>2</sub> OO·	4.7e-12			3
CH <sub>2</sub> *-CH <sub>2</sub> CH <sub>2</sub> CH(OO·)CH <sub>2</sub> *	1.1e-11			3
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH(OO·)CH <sub>3</sub>	8.0e-12			3
CH <sub>2</sub> *(CH <sub>2</sub> ) <sub>2</sub> CH(OO·)CH <sub>2</sub> CH <sub>2</sub> *	6.7e-12			3
CH <sub>3</sub> C(OO·)(CH <sub>3</sub> )CH <sub>3</sub>	5.4e-12			3
CH <sub>2</sub> =CH-CH <sub>2</sub> OO·	1.1e-11			3
Phenyl-CH <sub>2</sub> OO·	2.5e-12			3
.OOCH <sub>2</sub> OH	5.6e-12			2
CH <sub>3</sub> C(CH <sub>3</sub> )(CH <sub>2</sub> OO·)OH	4.9e-12			3
CH <sub>2</sub> =C(CH <sub>3</sub> )CH(OO·)CH <sub>2</sub> OH	9.0e-12			3
.OOCH <sub>2</sub> CH <sub>2</sub> OH	5.6e-12			3
CH <sub>3</sub> OCH <sub>2</sub> OO·	9.1e-12			3
CH <sub>3</sub> C(O)CH <sub>2</sub> OO·	1.2e-11			3
CH <sub>3</sub> OCH(OCH <sub>3</sub> )OCH <sub>2</sub> OO·	9.0e-12			3
CH <sub>3</sub> C(O)CH <sub>2</sub> OO·	8.0e-12			2
	<u>RCO<sub>3</sub> + NO</u>			
<u>Used for MechGen Estimates</u>	2.10e-11	6.70e-12	-340	4
CH <sub>3</sub> C(O)OO·	2.0e-11	7.5e-12	-290	2
CH <sub>3</sub> CH <sub>2</sub> C(O)OO·	2.1e-11	6.7e-12	-340	2
	<u>RO<sub>2</sub> + NO<sub>2</sub></u>			
<u>Used for MechGen Estimates</u>	8.8e-12			5
CH <sub>3</sub> OO·	4.0e-12	Pressure dependent		2
	high pressure->	1.8e-11		2
CH <sub>3</sub> CH <sub>2</sub> OO·	5.1e-12	Pressure dependent		2
	high pressure ->	8.8e-11		2
CH <sub>3</sub> C(O)CH <sub>2</sub> OO·	6.4e-12			2
	<u>RCO<sub>3</sub> + NO<sub>2</sub></u>			
<u>Used for MechGen Estimates</u>	7.7e-12			6
CH <sub>3</sub> C(O)OO·	8.9e-12	Pressure dependent		2
	high pressure ->	1.8e-11		2
CH <sub>3</sub> CH <sub>2</sub> C(O)OO·	7.4e-12	Pressure dependent		7
	high pressure ->	7.7e-12		7
	<u>RO<sub>2</sub> + NO<sub>3</sub></u>			

Table S45 (continue)

Radical	Rate Constant ( $\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$ )			
	k(298)	A	Ea/T	Note [a]
<u>Used for MechGen Estimates</u>	2.3e-12			8
CH <sub>3</sub> OO·	1.2e-12			2
CH <sub>3</sub> CH <sub>2</sub> OO·	2.3e-12			2
	<u>RCO<sub>3</sub> + NO<sub>3</sub></u>			
<u>Used for MechGen Estimates</u>	4.00e-12			9
CH <sub>3</sub> C(O)OO·	4.00e-12			2
	<u>RO<sub>2</sub> + HO<sub>2</sub></u>			
<u>Used for MechGen Estimates</u>				
Non-OH RO <sub>2</sub> + HO <sub>2</sub>	10 <sup>-12</sup> min	[20.3, 2.48 + (2.48 nC)]		See text
OH-RO <sub>2</sub> + HO <sub>2</sub>	10 <sup>-12</sup> min	[21.1, 9.37 + (1.68 nC)]		See text
<u>Alkane RO<sub>2</sub> + HO<sub>2</sub></u>				
CH <sub>3</sub> OO·	5.2e-12	3.80e-13	-780	2
CH <sub>3</sub> CH <sub>2</sub> OO·	6.9e-12	6.40e-13	-710	2
CH <sub>3</sub> C(CH <sub>3</sub> )(CH <sub>3</sub> )CH <sub>2</sub> OO·	1.5e-11			10
*CH <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> CH(OO·)CH <sub>2</sub> CH <sub>2</sub> *	1.7e-11			10
*CH <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> CH(OO·)CH <sub>2</sub> *	1.6e-11			10
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> CH <sub>2</sub> OO·	2.0e-11			10
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>12</sub> CH <sub>2</sub> OO·	2.1e-11			10
<u>Unsaturated RO<sub>2</sub> + HO<sub>2</sub></u>				
CH <sub>2</sub> =CHCH <sub>2</sub> OO·	1.0e-11			10
Phenyl-CH <sub>2</sub> OO·	1.0e-11			10
<u>OH-RO<sub>2</sub> + HO<sub>2</sub></u>				
.OOCH <sub>2</sub> OH	1.2e-11	5.60e-15	-2300	2
.OOCH <sub>2</sub> CH <sub>2</sub> OH	1.3e-11			2
CH <sub>3</sub> C(CH <sub>3</sub> )(CH <sub>2</sub> OO·)OH	1.4e-11			10
CH <sub>3</sub> CH(OO·)CH(CH <sub>3</sub> )OH	1.5e-11			10
CH <sub>3</sub> C(OO·)(CH <sub>3</sub> )C(CH <sub>3</sub> )(CH <sub>3</sub> )OH	2.0e-11			10
HO-(cyc-C6)-O <sub>2</sub>	2.2e-11			10
HO-(a-pinene)-O <sub>2</sub>	2.1e-11			10
<u>CO-RO<sub>2</sub> + HO<sub>2</sub></u>				
CH <sub>3</sub> C(O)CH <sub>2</sub> OO·	9.0e-12			2
	<u>RCO<sub>3</sub> + HO<sub>2</sub></u>			
<u>Used for MechGen Estimates</u>	<u>2.2e-11</u>	<u>3.14e-12</u>	<u>-580</u>	<u>9</u>
CH <sub>3</sub> C(O)OO·	2.2e-11	3.14e-12	-580	2
	<u>Non-OH-substituted RO<sub>2</sub> + RO<sub>2</sub> [b]</u>			
<u>Used for MechGen Estimates</u>				
Primary RO <sub>2</sub> + Generic RO <sub>2</sub>	2.9e-14			11
Secondary RO <sub>2</sub> + Generic RO <sub>2</sub>	1.6e-14			11
Tertiary RO <sub>2</sub> + Generic RO <sub>2</sub>	3.7e-16			11
<u>Primary RO<sub>2</sub> + Primary RO<sub>2</sub></u>				
Geometric mean of data below	4.3e-13			
CH <sub>3</sub> OO· + (self)	4.6e-13			2
CH <sub>3</sub> CH <sub>2</sub> OO· + MeO <sub>2</sub>	2.0e-13			12
CH <sub>3</sub> CH <sub>2</sub> OO· + (self)	7.0e-14			12
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OO· + MeO <sub>2</sub>	5.6e-13			13
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OO· + EtO <sub>2</sub>	9.3e-14			13
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OO· + (self)	3.0e-13			12

Table S45 (continue)

Radical	Rate Constant (cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup> )			
	k(298)	A	Ea/T	Note [a]
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OO· + MeO <sub>2</sub>	7.8e-13			13
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OO· + EtO <sub>2</sub>	1.3e-13			13
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OO· + nC <sub>3</sub> O <sub>2</sub>	5.0e-13			13
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OO· + (self)	6.9e-13			13
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OO· + MeO <sub>2</sub>	1.5e-12			12
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OO· + EtO <sub>2</sub>	5.3e-13			12
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OO· + (self)	3.9e-13			12
CH <sub>3</sub> C(CH <sub>3</sub> )(CH <sub>3</sub> )CH <sub>2</sub> OO· + MeO <sub>2</sub>	1.5e-12			12
CH <sub>2</sub> =CH-CH <sub>2</sub> OO· + (self)	7.0e-13			12
CH <sub>3</sub> C(CH <sub>3</sub> )(CH <sub>3</sub> )CH <sub>2</sub> OO· + (self)	1.2e-12			12
<u>Primary RO<sub>2</sub> + Secondary RO<sub>2</sub></u>				
Geometric mean of data below	2.9e-14			
CH <sub>3</sub> CH(OO·)CH <sub>3</sub> + MeO <sub>2</sub>	3.1e-14			13
CH <sub>3</sub> CH(OO·)CH <sub>3</sub> + EtO <sub>2</sub>	5.1e-15			13
CH <sub>3</sub> CH(OO·)CH <sub>3</sub> + nC <sub>3</sub> O <sub>2</sub>	2.0e-14			13
CH <sub>3</sub> CH(OO·)CH <sub>3</sub> + nC <sub>4</sub> O <sub>2</sub>	2.7e-14			13
CH <sub>3</sub> CH <sub>2</sub> CH(OO·)CH <sub>3</sub> + MeO <sub>2</sub>	6.2e-14			13
CH <sub>3</sub> CH <sub>2</sub> CH(OO·)CH <sub>3</sub> + EtO <sub>2</sub>	1.0e-14			13
CH <sub>3</sub> CH <sub>2</sub> CH(OO·)CH <sub>3</sub> + nC <sub>3</sub> O <sub>2</sub>	4.0e-14			13
CH <sub>3</sub> CH <sub>2</sub> CH(OO·)CH <sub>3</sub> + nC <sub>4</sub> O <sub>2</sub>	5.6e-14			13
CH <sub>2</sub> *(CH <sub>2</sub> ) <sub>2</sub> CH(OO·)CH <sub>2</sub> CH <sub>2</sub> * + MeO <sub>2</sub>	9.0e-14			12
CH <sub>2</sub> *(CH <sub>2</sub> ) <sub>2</sub> CH(OO·)CH <sub>2</sub> CH <sub>2</sub> * + EtO <sub>2</sub>	4.0e-14			12
<u>Primary RO<sub>2</sub> + Tertiary RO<sub>2</sub></u>				
Geometric mean of data below	3.3e-15			
CH <sub>3</sub> C(OO·)(CH <sub>3</sub> )CH <sub>3</sub> + MeO <sub>2</sub>	3.1e-15			12
CH <sub>3</sub> C(OO·)(CH <sub>3</sub> )CH <sub>3</sub> + EtO <sub>2</sub>	1.3e-15			13
CH <sub>3</sub> C(OO·)(CH <sub>3</sub> )CH <sub>3</sub> + nC <sub>3</sub> O <sub>2</sub>	4.8e-15			13
CH <sub>3</sub> C(OO·)(CH <sub>3</sub> )CH <sub>3</sub> + nC <sub>4</sub> O <sub>2</sub>	6.7e-15			13
<u>Secondary RO<sub>2</sub> + Secondary RO<sub>2</sub></u>				
Geometric mean of data below	1.6e-14			
CH <sub>3</sub> CH(OO·)CH <sub>3</sub> + (self)	1.1e-15			12
CH <sub>3</sub> CH <sub>2</sub> CH(OO·)CH <sub>3</sub> + sC <sub>3</sub> O <sub>2</sub>	2.2e-15			13
CH <sub>3</sub> CH <sub>2</sub> CH(OO·)CH <sub>3</sub> + (self)	2.6e-15			12
CH <sub>2</sub> *CH <sub>2</sub> CH(OO·)CH <sub>2</sub> CH <sub>2</sub> * + (self)	4.5e-14			12
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH(OO·)CH <sub>3</sub> + (self)	3.3e-14			12
CH <sub>2</sub> *(CH <sub>2</sub> ) <sub>2</sub> CH(OO·)CH <sub>2</sub> CH <sub>2</sub> * + (self)	4.2e-14			12
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> CH(OO·)CH <sub>3</sub> + (self)	8.2e-14			12
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>9</sub> CH(OO·)CH <sub>3</sub> + (self)	1.1e-13			12
<u>Secondary RO<sub>2</sub> + Tertiary RO<sub>2</sub></u>				
Geometric mean of data below	3.7e-16			
CH <sub>3</sub> C(OO·)(CH <sub>3</sub> )CH <sub>3</sub> + sC <sub>3</sub> O <sub>2</sub>	2.6e-16			13
CH <sub>3</sub> C(OO·)(CH <sub>3</sub> )CH <sub>3</sub> + sC <sub>4</sub> O <sub>2</sub>	5.3e-16			13
<u>Tertiary RO<sub>2</sub> + Tertiary RO<sub>2</sub></u>				
CH <sub>3</sub> C(OO·)(CH <sub>3</sub> )CH <sub>3</sub> + (self)	3.0e-17			12
<u>OH-substituted RO<sub>2</sub> + RO<sub>2</sub></u>				
Used for MechGen Estimates				14
Primary OH-RO <sub>2</sub> + Generic RO <sub>2</sub>	9.1e-14			14
Secondary OH-RO <sub>2</sub> + Generic RO <sub>2</sub>	1.7e-13			14

Table S45 (continue)

Radical	Rate Constant (cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup> )			
	k(298)	A	Ea/T	Note [a]
Tertiary OH-RO <sub>2</sub> + Generic RO <sub>2</sub>	1.3e-14			
<u>Self-reactions of primary OH-substituted RO<sub>2</sub></u>				
Geometric mean of data below	4.3e-12			
.OOCH <sub>2</sub> CH <sub>2</sub> OH + (self)	6.2e-12			12
.OOCH <sub>2</sub> OH + (self)	2.3e-12			12
CH <sub>3</sub> C(CH <sub>3</sub> )(CH <sub>2</sub> OO·)OH + (self)	4.8e-12			12
CH <sub>3</sub> C(O)CH <sub>2</sub> OO· + (self)	8.0e-12			12
.OOCH <sub>2</sub> CH=CH-CH <sub>2</sub> OH + (self)	2.8e-12			12
CH <sub>3</sub> C(CH <sub>2</sub> OO·)=C(CH <sub>3</sub> )CH <sub>2</sub> OH + (self)	3.9e-12			12
<u>Self-reactions of secondary OH-substituted RO<sub>2</sub></u>				
Geometric mean of data below	1.8e-12			
HOCH*CH <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> CH(OO·)* + (self)	1.6e-12			12
CH <sub>3</sub> CH(OO·)CH(CH <sub>3</sub> )OH + (self)	6.6e-13			12
CH <sub>2</sub> =CH-CH(OO·)CH <sub>2</sub> OH + (self)	5.7e-12			12
<u>Self-reactions of tertiary OH-substituted RO<sub>2</sub></u>				
Geometric mean of data below	3.5e-14			
CH <sub>3</sub> C(OO·)(CH <sub>3</sub> )CH <sub>2</sub> OH + (self)	1.5e-14			12
CH <sub>3</sub> C(OO·)(CH <sub>3</sub> )C(CH <sub>3</sub> )(CH <sub>3</sub> )OH + (self)	7.5e-14			12
CH <sub>2</sub> =C(CH <sub>3</sub> )C(OO·)(CH <sub>3</sub> )CH <sub>2</sub> OH + (self)	6.9e-14			12
CH <sub>3</sub> C(OO·)*-(CH <sub>2</sub> ) <sub>4</sub> CH*OH + (self)	2.0e-14			12
	<u>RO<sub>2</sub> + RCO<sub>3</sub></u>			
<u>Used for MechGen Estimates</u>	1.6e-11			15
CH <sub>3</sub> C(O)OO· + MeO <sub>2</sub>	1.1e-11			2
CH <sub>3</sub> C(O)OO· + EtO <sub>2</sub>	1.6e-11			2
	<u>RCO<sub>3</sub> + RCO<sub>3</sub></u>			
<u>Used for MechGen Estimates</u>	1.4e-11			16
CH <sub>2</sub> *(CH <sub>2</sub> ) <sub>2</sub> CH(OO·)CH <sub>2</sub> CH <sub>2</sub> * + MeCO <sub>3</sub>	1.0e-11			12
CH <sub>3</sub> C(O)OO· + (self)	1.6e-11			2
CH <sub>3</sub> CH <sub>2</sub> C(O)OO· + (self)	1.7e-11			2
Phenyl-C(O)OO· + (self)	1.4e-11			12

[a] Sources of tabulated rate constants are as follows. Note that the year given with the IUPAC citation is the date of the evaluation, not the date on the reference list. IUPAC evaluations are available at IUPAC (2023).

- 1 Rate constant for ethyl peroxy is used for estimation purposes.
- 2 IUPAC (2018) recommendation.
- 3 Experimental value from Table 1 of King and Thompson (2003).
- 4 Rate constant for CH<sub>3</sub>CH<sub>2</sub>C(O)OO· is used for estimation purposes.
- 5 IUPAC (2018) recommendation for the high pressure rate constant for ethyl peroxy + NO<sub>2</sub>.
- 6 NASA (2011) recommendation for the high pressure rate constant for CH<sub>3</sub>CH<sub>2</sub>C(O)OO· + NO<sub>2</sub>.
- 7 NASA (2011) recommendation.
- 8 IUPAC (2018) recommendation for ethyl peroxy.
- 9 IUPAC (2018) recommendation for acetyl peroxy.
- 10 Experimental value from Table 1 of Johnson et al. (2004).
- 11 Use the geometric mean for the reactions of this type of peroxy radical with secondary peroxy radicals.
- 12 Experimental value from Table 2 and 3 of Johnson et al. (2004).
- 13 Estimated rate constant as given in Table 4 or 5 of Johnson et al. (2004)

Table S45 (continue)

- 14 Estimated using the recommended rate constant for non-OH substituted RO<sub>2</sub>'s + generic RO<sub>2</sub> × the square root of the ratio of the geometric mean of the self-reaction of OH-substituted RO<sub>2</sub>'s of this type to the recommended rate constant for the reactions of non-OH substituted RO<sub>2</sub>'s of this type with other radicals of this type.
- 15 Use the rate constant for acetyl peroxy + ethyl peroxy.
- 16 Geometric mean of the data for the specific RCO<sub>3</sub> + RCO<sub>3</sub> reactions on this table.
- [b] Codes for second reactant in peroxy + peroxy reactions are as follows: (self) = self reaction; MeO2 = methyl peroxy; nC3O2 = n-propyl peroxy; nC4O2 = n-butyl peroxy; sC3O2 = isopropyl peroxy; SC4O2 = 2-butyl peroxy; and MeCO3 = Acetyl peroxy.

Table S46. Summary of experimental and calculated nitrate yields for secondary peroxy radicals at standard temperature and pressure (T ~ 300 K, P ~ 1 atm.).

nC	Ref	Experimental Data [a]						Estimate Used [b]		
		2	3	4	5	6	7	Expt.	Calc	Err
3	1	3.9%						3.9%	4.0%	0.1%
4	1	8.4%						7.7%	7.2%	-0.5%
4	2	7.0%								
5	1	11%	13%					11%	11%	0.2%
5	3	11%								
5	4	10%	12%							
6	1	14%	16%					16%	15%	-0.4%
6 (cyc)	2	17%						17%	15%	-1.2%
6	5	16%								
7	1	18%	20%	18%				18%	19%	0.4%
8	1	22%	24%	24%				23%	22%	-0.5%
8	6	23%	22%	21%						
10	6	23%	19%	20%	20%			20%	27%	6.1%
12	6	27%	24%	24%	26%	26%		25%	28%	2.7%
13	6	32%	29%	26%	28%	30%	29%	29%	28%	-0.7%
14	6	29%	34%	31%	33%	31%	30%	31%	29%	-2.9%

[a] Experimental nitrate yields, where the number indicates the individual isomer. Codes for references for data are as follows.

- |   |                                    |   |                        |
|---|------------------------------------|---|------------------------|
| 1 | From table 2 in Arey et al. (2001) | 4 | Aschmann et al. (2006) |
| 2 | Espada et al. (2005)               | 5 | Aschmann et al. (2011) |
| 3 | Cassanelli et al. (2007)           | 6 | Yeh and Ziemann (2014) |

[b] "Expt" is the average of the experimental measurements for the various isomers. "Calc" is the nitrate yield estimated as discussed in the text. "Err" = calculated - experimental yields (absolute error).

Table S47. Summary of experimental and calculated nitrate yields for secondary peroxy radicals at varying temperature and pressure.

nC [a]	T (K)	P (atm)	Ref	Experimental Data [b]				Estimate Used [c]		
				1	2	3	4	Expt.	Calc	Err
3	299	0.07	1		0.6%			0.6%	0.4%	(-0%)
	299	0.09		0.5%		0.5%	0.5%	(0%)		
	299	0.11		0.8%		0.8%	0.6%	(-0%)		
	299	0.13		1.0%		1.0%	0.7%	(-0%)		
	299	0.20		0.9%		0.9%	1.0%	(0%)		
	299	0.26		1.2%		1.2%	1.3%	(0%)		
	299	0.33		1.4%		1.4%	1.6%	(0%)		
	299	0.39		1.6%		1.6%	1.8%	(0%)		
	299	0.46		2.0%		2.0%	2.1%	(0%)		
	299	0.53		2.2%		2.2%	2.4%	(0%)		
	299	0.66		2.7%		2.7%	2.9%	(0%)		
5	263	1	2		18.0%			18.0%	15.7%	(-2%)
	273	1		14.0%		14.0%	14.5%	(1%)		
	286	1		14.0%		14.0%	12.9%	(-1%)		
5	297	0.07	3		1.9%			1.9%	1.6%	(-0%)
	297	0.13		2.9%		2.9%	2.9%	(0%)		
	297	0.26		3.9%		3.9%	5.1%	(1%)		
	297	0.39		5.2%		5.2%	6.7%	(2%)		
	297	0.66		7.8%	9.1%	8.5%	9.2%	(1%)		
5	300	0.07	4		2.4%	2.4%		2.4%	1.7%	(-1%)
	327	0.20		3.1%	3.5%	3.3%	2.9%	(-0%)		
	300	0.20		4.7%	4.6%	4.7%	4.0%	(-1%)		
	284	0.20		5.3%	5.9%	5.6%	4.7%	(-1%)		
	300	0.46		7.5%	8.1%	7.8%	7.2%	(-1%)		
	284	0.47		8.3%	9.4%	8.9%	8.6%	(-0%)		
	326	0.53		5.0%	5.2%	5.1%	5.3%	(0%)		
	300	0.67		7.8%	8.4%	8.1%	8.9%	(1%)		
	337	0.97		6.2%	6.4%	6.3%	5.7%	(-1%)		
	328	0.97		6.4%	6.6%	6.5%	6.8%	(0%)		
	284	0.98		12.4%	13.6%	13.0%	13.1%	(0%)		
5 [d]	262	1	2	14%				14%	16%	(2%)
	263	1		13%		13%	16%	(3%)		
	267	1		13%		13%	15%	(2%)		
	268	1		10%		10%	15%	(5%)		
	273	1		11%		11%	15%	(4%)		
	273	1		12%		12%	15%	(3%)		
	283	1		9%		9%	13%	(4%)		
	290	1		7%		7%	12%	(5%)		
	5 [e]	261		1	2		24%			24%
273		1	14%			14%	15%	(1%)		
305		1	12%			12%	10%	(-2%)		
6 [f]	296	0.53	5	15%				15%	12%	(-3%)
	296	0.95	6	16%				16%	16%	(-0%)
7	300	0.07	4		6.2%	7.5%	6.5%	6.7%	6.2%	(-0%)

Table S47 (continued)

nC [a]	T (K)	P (atm)	Ref	Experimental Data [b]				Estimate Used [c]		
				1	2	3	4	Expt.	Calc	Err
	284	0.08			7.1%	8.7%	7.4%	7.7%	7.5%	( -0% )
	321	0.08			4.4%	5.4%	4.5%	4.8%	4.9%	( 0% )
	324	0.21			6.4%	7.5%	6.3%	6.7%	7.5%	( 1% )
	283	0.21			10.0%	12.0%	10.8%	11.0%	13.7%	( 3% )
	300	0.21			9.0%	10.9%	9.4%	9.8%	11.3%	( 2% )
	342	0.21			5.5%	5.9%	5.2%	5.5%	5.4%	( -0% )
	285	0.46			15%	18%	16%	16%	18%	( 2% )
	300	0.47			14%	18%	15%	16%	15%	( -0% )
	324	0.47			10%	11%	10%	10%	10%	( -0% )
	323	0.97			13%	14%	12%	13%	13%	( 0% )
	339	0.97			9.8%	10.6%	9.4%	9.9%	10.1%	( 0% )
	284	0.98			18%	22%	19%	20%	22%	( 2% )

[a] Carbon number. These all have straight-chain structures unless indicated differently in the footnote.

[b] Experimental nitrate yields, where the number indicates the individual isomer. Codes for references for data are as follows.

- |   |                           |   |                        |
|---|---------------------------|---|------------------------|
| 1 | Butkovskaya et al. (2010) | 4 | Atkinson et al. (1983) |
| 2 | Cassanelli et al. (2007)  | 5 | Orlando et al. (2000)  |
| 3 | Aschmann et al. (2006)    | 6 | Platz et al. (1999)    |

[c] "Expt" is the average of the experimental measurements for the various isomers. "Calc" is the nitrate yield estimated as discussed in the text. "Err" = calculated - experimental yields.

[d] Data for neopentyl peroxy radicals (primary peroxy).

[e] Data for 2-methyl-2 butyl peroxy radicals (tertiary peroxy).

[f] Data for cyclohexyl peroxy radicals.



Table S48. Summary of experimental and calculated nitrate yields for primary and tertiary peroxy radicals from alkanes and for peroxy radicals with non-alkyl groups.

Peroxy Radical or Primary Reactant	nC	Experimental [a]			Estimates	
		T (K)	Yield	Ref	Yield	Err
Primary unsubstituted RO <sub>2</sub> 's [b]						
1-Propyl	3		2%	1	4%	( 2% )
1-Butyl	4		8%	2	7%	( -0% )
Neopentyl	5	263	13%	3	16%	( 3% )
Neopentyl	5	267	13%	3	15%	( 2% )
Neopentyl	5	268	10%	3	15%	( 5% )
Neopentyl	5	273	11%	3	15%	( 4% )
Neopentyl	5	273	12%	3	15%	( 3% )
Neopentyl	5	283	9%	3	13%	( 4% )
Neopentyl	5	290	7%	3	12%	( 5% )
Neopentyl	5		8%	3	11%	( 3% )
Neopentyl	5		7%	3	11%	( 4% )
Tertiary unsubstituted RO <sub>2</sub> 's [b]						
2-Methyl-2-butyl	5	261	24%	3	16%	( -8% )
2-Methyl-2-butyl	5	273	14%	3	15%	( 1% )
2-Methyl-2-butyl	5		11%	3	11%	( 0% )
2-Methyl-2-butyl	5	305	12%	3	10%	( -2% )
$\beta$ Hydroxy substituted RO <sub>2</sub> yields measured for specific isomers [c]						
2-hydroxy-1-ethyl	2		1%	5	2%	( 1% )
2-hydroxy-1-propyl	3		2%	5	3%	( 1% )
2-hydroxy-1-propyl	3		2%	6	3%	( 1% )
1-hydroxy-2-propyl	3		1%	5	3%	( 2% )
1-hydroxy-2-propyl	3		2%	6	3%	( 1% )
2-hydroxy-1-butyl	4		3%	5	5%	( 2% )
1-hydroxy-2-butyl	4		2%	5	5%	( 3% )
3-hydroxy-2-butyl	4		3%	5	5%	( 2% )
3-hydroxy-2-butyl	4		4%	7	5%	( 2% )
2-hydroxy-1-hexyl	6		7%	5	11%	( 4% )
1-hydroxy-2-hexyl	6		5%	5	11%	( 6% )
1-hydroxy-2-tetradecyl	14		17%	8	21%	( 4% )
1-hydroxy-2-methyl-2-tridecyl	14		24%	9	21%	( -3% )
1-hydroxy-2-pentadecyl	15		15%	8	21%	( 6% )
2-hydroxy-1-pentadecyl	15		9%	8	21%	( 12% )
1-hydroxy-2-methyl-2-tetradecyl	15		25%	9	21%	( -4% )
2-hydroxy-2-methyl-1-tetradecyl	15		12%	9	21%	( 9% )
1-hydroxy-2-hexadecyl	16		13%	8	21%	( 8% )
2-hydroxy-1-hexadecyl	16		12%	8	21%	( 9% )
1-hydroxy-2-heptadecyl	17		14%	8	21%	( 7% )
2-hydroxy-1-heptadecyl	17		12%	8	21%	( 9% )

Table S48 (continued)

Peroxy Radical or Primary Reactant	Experimental [a]				Estimates	
	nC	T (K)	Yield	Ref	Yield	Err
Unspecified RO <sub>2</sub> isomers from OH + Alkenes [c, d]						
ethene	2		2%	9	2%	(-1%)
propene	3		5%	9	3%	(-2%)
1-butene	4		11%	9	5%	(-5%)
cis-2-butene	4		10%	9	5%	(-5%)
Isobutene	4		10%	9	5%	(-5%)
2-methyl-2-Butene	5		12%	9	8%	(-4%)
1-hexene	6		18%	9	16%	(-2%)
1-octene	8		21%	9	24%	(3%)
Unspecified RO <sub>2</sub> isomers from ethers or alcohol ethers with O mostly in the $\alpha$ or $\beta$ positions [c, d]						
Diethyl Ether	4		7%	10	5%	(-2%)
methoxy propane	4		2%	11	5%	(3%)
2-Ethoxyethanol	4		8%	10	5%	(-3%)
1-Methoxy-2-Propanol	4		2%	10	5%	(4%)
1-methoxy-2-propanol [d]	4		2%	11	5%	(3%)
Methyl t-Butyl Ether	5		9%	10	8%	(-1%)
ethoxy butane	6		8%	11	11%	(3%)
2-Butoxyethanol	6		10%	10	11%	(1%)
2-(2-Ethoxyethoxy) Ethanol	6		12%	10	11%	(-1%)
2-butoxyethanol [d]	6		12%	11	11%	(-1%)
2-(2-Butoxyethoxy)-Ethanol	8		20%	10	16%	(-4%)
Unspecified RO <sub>2</sub> isomers from esters with O mostly in the $\alpha$ or $\beta$ position [c, d]						
Methyl Acetate	3		4%	10	3%	(-1%)
Isopropyl Acetate	5		8%	10	9%	(1%)
Methyl Isopropyl Carbonate	5		6%	10	9%	(3%)
Dimethyl Succinate	6		5%	10	11%	(6%)
			3%	12	11%	(8%)
Unspecified RO <sub>2</sub> isomers from esters with O mostly not in the $\alpha$ or $\beta$ position [b, d]						
Methyl Pivalate	6		6%	10	21%	(15%)
t-Butyl Acetate	6		14%	10	18%	(4%)
2-Butoxy Ethanol	6		10%	13	5%	(-3%)
Dimethyl Glutarate	7		20%	10	17%	(-3%)
			15%	14	17%	(2%)
Peroxy radicals from ketones						
3-Oxo-2-Butyl [b]	4		<1%	16	2%	(2%)
Methyl Vinyl Ketone	4		4%	15	5%	(1%)
(sum of two isomers) [c]						

[a] Footnotes for sources of experimental data are as follows.

- |                                |                                     |
|--------------------------------|-------------------------------------|
| 1 Atkinson et al. (1982)       | 2 Espada et al. (2005)              |
| 3 Cassanelli et al. (2007)     | 4 O'Brien et al. (1998)             |
| 5 Shepson et al. (1985)        | 6 Muruthamu et al. (1993)           |
| 7 Matsunaga and Ziemann (2009) | 8 Matsunaga and Ziemann (2010)      |
| 9 Teng et al. (2014)           | 10 Adjusted to fit chamber data [e] |
| 11 Espada and Shepson (2005)   | 12 Cavalli et al. (2001)            |
| 13 Tuazon et al. (1998b)       | 14 Tuazon et al. (1999)             |

Table S48 (continued)

15 Praske et al. (2015)

16 Lightfoot et al. (1992)

- [b] Yields are estimated using the default parameterization based on alkyl peroxy radicals.
- [c] Yields are estimated using the parameterization employed for radicals with O-substituents in the  $\alpha$  or  $\beta$  position (Corr = 0.73).
- [d] Estimates of total unspiciated nitrate yields depend on branching ratios for formations of the various peroxy radicals formed, which were estimated by MechGen as discussed elsewhere in this document.
- [e] Environmental chamber experiments with various compounds carried out using SAPRC indoor chambers (Carter et al, 1995, 2005) are reported in various project reports by Carter and co-workers, most of which are available at <https://intra.engr.ucr.edu/~carter/pubs>. The results of these experiments were simulated using various versions of the SAPRC mechanism with nitrate yields adjusted to optimize fits of model predictions of experimental O<sub>3</sub> and NO data. Data for these experiments and inputs for modeling them, are available at <https://intra.engr.ucr.edu/~carter/SAPRC/SAPRCfiles.htm>.

Table S49. Recommended rate constants provided by in the lookup tables of Vereecken and Nozière (2020) based on their review of theoretical calculations of hydrogen shift rate constants for peroxy radicals with various pairs of reacting groups and ring sizes, and estimated A factors and activation energies derived in this work. Selected relevant data from theoretical calculations of Møller et al (2019) are also included.

Properties of Radicals				Quantum Calculation Data					Estimated in this work [a]	
Reacting Groups		RS	nH	k(298) (sec <sup>-1</sup> )	k(T)=p1 * p2 <sup>T</sup> * exp(-p3)			Derived A	A	Ea
H-Group	R-Group				p1	p2	p3			
<u>Data from Vereecken and Nozière (2020)</u>										
CH3	CH2OO.	5	3	1.98e-11	1.21e+7	1.40	14,586	4.8e+10	4.5e+11	31.13
CH3	CH2OO.	6	3	8.22e-6	1.01e-32	13.94	5,195	1.3e+8	9.1e+8	19.80
CH3	CH2OO.	7	3	4.06e-6	5.66e-17	8.59	7,137	1.9e+8	4.0e+8	19.74
CH3	CH2OO.	8	3	1.03e-6	1.47e-16	8.21	7,186	3.9e+7	1.6e+8	20.01
CH3	CH2OO.	9	3	8.60e-8	3.89e-27	11.40	6,083	2.0e+6	6.5e+7	20.94
CH3	CHOO.	5	6	2.13e-13	2.74e+10	0.55	16,790	1.8e+11	4.5e+11	34.23
CH3	CHOO.	6	3	1.50e-5	1.31e-27	12.46	6,010	8.1e+8	9.1e+8	19.44
CH3	CHOO.	7	3	1.28e-5	2.22e-22	10.52	6,353	3.1e+8	4.0e+8	19.06
CH3	CHOO.	8	3	1.82e-6	4.57e-25	10.98	5,873	1.4e+7	1.6e+8	19.67
CH3	CHOO.	9	3	3.60e-10	7.49e-17	8.18	9,307	1.6e+7	6.5e+7	24.18
CH3	COO.	5	9	2.68e-13	3.01e+10	0.60	16,835	1.9e+11	4.5e+11	34.33
CH3	COO.	6	3	2.22e-4	7.45e-23	10.79	5,650	6.3e+8	9.1e+8	17.85
CH3	COO.	7	3	2.48e-6	3.47e-18	9.05	7,235	2.5e+8	4.0e+8	20.03
CH3	COO.	8	3	1.54e-8	2.52e-16	8.19	8,561	5.8e+7	1.6e+8	22.50
CH2	CH2OO.	5	2	5.86e-9	1.43e+10	0.55	13,551	2.9e+11	4.5e+11	27.52
CH2	CH2OO.	6	2	8.10e-4	5.00e-20	9.81	5,534	8.9e+8	9.1e+8	16.84
CH2	CH2OO.	7	2	8.83e-4	1.68e-12	7.19	6,223	7.1e+8	4.0e+8	16.31
CH2	CH2OO.	8	2	9.08e-5	3.72e-5	4.59	7,535	4.3e+8	1.6e+8	17.11
CH2	CH2OO.	9	2	1.03e-6	6.83e-1	3.04	9,150	2.4e+8	6.5e+7	19.22
CH2	CHOO.	5	2	3.72e-11	2.70e+10	0.45	15,078	2.8e+11	4.5e+11	30.52
CH2	CHOO.	6	2	1.23e-3	2.95e-24	11.26	4,966	8.8e+8	9.1e+8	16.59
CH2	CHOO.	7	2	7.83e-4	3.47e-18	9.05	5,519	3.8e+8	4.0e+8	16.38
CH2	CHOO.	8	2	1.93e-5	2.52e-16	8.19	6,435	8.7e+7	1.6e+8	18.03
CH2	CHOO.	9	2	6.04e-8	7.49e-17	8.18	7,769	2.4e+7	6.5e+7	20.90
CH2	COO.	5	2	1.23e-10	6.85e+10	0.35	14,829	3.6e+11	4.5e+11	29.81
CH2	COO.	6	2	4.49e-4	7.45e-23	10.79	5,440	9.5e+8	9.1e+8	17.19
CH2	COO.	7	2	3.12e-4	3.47e-18	9.05	5,793	3.8e+8	4.0e+8	16.92
CH2	COO.	8	2	4.32e-6	2.52e-16	8.19	6,882	8.7e+7	1.6e+8	18.92
CH	CH2OO.	5	1	1.62e-7	4.01e+10	0.40	12,614	5.9e+11	4.5e+11	25.14
CH	CH2OO.	6	1	0.035	1.77e-3	4.39	6,563	1.1e+10	9.1e+8	14.20
CH	CH2OO.	7	1	0.043	1.88e-3	4.25	6,285	4.4e+9	4.0e+8	13.60
CH	CH2OO.	8	1	1.86e-2	1.61e-18	8.98	4,218	2.2e+8	1.6e+8	13.55
CH	CH2OO.	9	1	2.44e-8	1.58e-22	10.09	7,395	3.7e+7	6.5e+7	21.03
CH	CHOO.	5	1	3.61e-9	6.35e+10	0.30	13,715	4.7e+11	4.5e+11	27.40
CH	CHOO.	6	1	0.058	1.64e-35	14.99	2,420	7.0e+8	9.1e+8	13.90
CH	CHOO.	7	1	0.068	1.28e-35	14.71	1,831	8.4e+7	4.0e+8	13.32
CH	CHOO.	8	1	1.72e-3	2.52e-16	8.19	5,097	1.7e+8	1.6e+8	14.96
CH	COO.	5	1	4.17e-8	1.84e+11	0.20	13,133	7.0e+11	4.5e+11	25.95
CH	COO.	6	1	6.20e-4	2.24e-16	8.73	6,280	5.8e+9	9.1e+8	16.59
CH	COO.	7	1	0.025	3.47e-18	9.05	4,493	7.6e+8	4.0e+8	13.93
CH	COO.	8	1	3.26e-4	2.52e-16	8.19	5,593	1.7e+8	1.6e+8	15.95
CHO	CH2OO.	5	1	2.56	5.24e-65	24.74	-2,379	5.4e+7	6.0e+7	10.05
CHO	CH2OO.	6	1	9.84	3.66e-37	15.46	0,573	3.7e+8	3.4e+8	10.27
CHO	CH2OO.	7	1	4.98	2.03e-41	16.79	0,101	1.5e+8	1.8e+8	10.30
CHO	CH2OO.	8	1	1.84	2.91e-30	12.90	1,458	1.0e+8	9.4e+7	10.51

Table S49 (continued)

Properties of Radicals				Quantum Calculation Data				Estimated in this work [a]		
Reacting Groups		RS	nH	k(298) (sec <sup>-1</sup> )	k(T)=p1 * p2 <sup>T</sup> * exp(-p3)			Derived A	A	Ea
H-Group	R-Group				p1	p2	p3			
CHO	CHOO.	5	1	0.066	1.08e-66	25.23	-1,616	3.0e+7	6.0e+7	12.21
CHO	CHOO.	6	1	162	3.66e-37	15.46	-0,271	3.7e+8	3.4e+8	8.61
CHO	CHOO.	7	1	790	2.03e-41	16.79	-1,405	1.5e+8	1.8e+8	7.30
CHO	CHOO.	8	1	0.171	2.91e-30	12.90	2,167	1.0e+8	9.4e+7	11.92
CHO	COO.	5	1	0.570	2.54e-63	24.25	-1,605	9.8e+7	6.0e+7	10.94
CHO	COO.	6	1	0.174	3.66e-37	15.46	1,775	3.7e+8	3.4e+8	12.66
CHO	COO.	7	1	0.284	2.03e-41	16.79	0,958	1.5e+8	1.8e+8	12.00
CHO	COO.	8	1	0.032	2.91e-30	12.90	2,663	1.0e+8	9.4e+7	12.91
CH2-OX	CH2OO.	5	2	9.79e-4	8.05e-2	3.81	7,790	4.9e+9	4.5e+11	20.40
CH2-OX	CH2OO.	6	2	8.39e-3	8.05e-2	3.81	7,150	4.9e+9	9.1e+8	15.46
CH2-OX	CH2OO.	7	2	8.84e-3	8.05e-2	3.81	7,134	4.9e+9	4.0e+8	14.94
CH2-OX	CH2OO.	8	2	6.86e-4	8.05e-2	3.81	7,896	4.9e+9	1.6e+8	15.92
CH2-OX	CHOO.	5	2	2.40e-6	8.05e-2	3.81	9,581	4.9e+9	4.5e+11	23.96
CH2-OX	CHOO.	6	2	1.27e-2	8.05e-2	3.81	7,026	4.9e+9	9.1e+8	15.21
CH2-OX	CHOO.	7	2	0.310	3.41e+7	0.86	6,972	5.4e+9	4.0e+8	12.84
CH2-OX	CHOO.	8	2	1.46e-4	8.05e-2	3.81	8,358	4.9e+9	1.6e+8	16.83
CH2-OX	COO.	5	2	2.06e-5	8.05e-2	3.81	8,941	4.9e+9	4.5e+11	22.69
CH2-OX	COO.	6	2	4.65e-3	8.05e-2	3.81	7,326	4.9e+9	9.1e+8	15.81
CH2-OX	COO.	7	2	4.58e-3	8.05e-2	3.81	7,330	4.9e+9	4.0e+8	15.33
CH2-OX	COO.	8	2	3.26e-5	8.05e-2	3.81	8,804	4.9e+9	1.6e+8	17.72
CH-OX	CH2OO.	5	1	8.25e-6	8.05e-2	3.81	9,213	9.9e+9	4.5e+11	22.82
CH-OX	CH2OO.	6	1	0.044	5.54e-2	4.12	7,059	5.4e+10	9.1e+8	14.06
CH-OX	CH2OO.	7	1	0.182	8.05e-2	3.81	6,233	9.9e+9	4.0e+8	12.74
CH-OX	CH2OO.	8	1	0.140	1.17e-1	3.51	5,907	1.9e+9	1.6e+8	12.36
CH-OX	CHOO.	5	1	3.13e-5	8.05e-2	3.81	8,816	9.9e+9	4.5e+11	22.03
CH-OX	CHOO.	6	1	0.096	8.05e-2	3.81	6,425	9.9e+9	9.1e+8	13.61
CH-OX	CHOO.	7	1	0.188	3.03e-1	3.39	5,905	2.2e+9	4.0e+8	12.72
CH-OX	CHOO.	8	1	1.30e-2	8.05e-2	3.81	7,019	9.9e+9	1.6e+8	13.76
CH-OX	COO.	5	1	6.97e-3	8.05e-2	3.81	7,205	9.9e+9	4.5e+11	18.83
CH-OX	COO.	6	1	0.331	8.05e-2	3.81	6,055	9.9e+9	9.1e+8	12.87
CH-OX	COO.	7	1	0.360	8.05e-2	3.81	6,030	9.9e+9	4.0e+8	12.34
CH-OX	COO.	8	1	2.46e-3	8.05e-2	3.81	7,515	9.9e+9	1.6e+8	14.75
CH2-OOH	CH2OO.	5	2	2.37e-8	1.96e+7	1.61	12,969	4.8e+11	4.5e+11	26.69
CH2-OOH	CH2OO.	6	2	4.13e-4	2.01e-52	19.91	0,654	9.0e+5	9.1e+8	17.24
CH2-OOH	CH2OO.	7	2	3.01e-3	2.01e-52	19.91	0,062	9.0e+5	4.0e+8	15.58
CH2-OOH	CH2OO.	8	2	2.72e-4	2.01e-52	19.91	0,778	9.0e+5	1.6e+8	16.46
CH2-OOH	CHOO.	5	2	8.77e-9	2.38e+4	2.69	13,103	8.0e+11	4.5e+11	27.28
CH2-OOH	CHOO.	6	2	5.70e-4	2.01e-52	19.91	0,558	9.0e+5	9.1e+8	17.05
CH2-OOH	CHOO.	7	2	1.01e-3	3.77e-40	15.89	1,981	3.4e+6	4.0e+8	16.23
CH2-OOH	CHOO.	8	2	5.44e-4	2.01e-52	19.91	0,572	9.0e+5	1.6e+8	16.05
CH2-OOH	COO.	5	2	3.56e-7	2.04e+5	2.45	12,228	1.4e+12	4.5e+11	25.09
CH2-OOH	COO.	6	2	1.89e-2	2.01e-52	19.91	-0,484	9.0e+5	9.1e+8	14.97
CH2-OOH	COO.	7	2	8.77e-4	2.01e-52	19.91	0,430	9.0e+5	4.0e+8	16.31
CH2-OOH	COO.	8	2	1.90e-4	2.01e-52	19.91	0,886	9.0e+5	1.6e+8	16.68
CH-OOH	CH2OO.	5	1	2.33e-7	7.83e+4	2.24	11,716	2.6e+11	4.5e+11	24.93
CH-OOH	CH2OO.	6	1	5.99e-3	2.01e-52	19.91	-0,143	1.8e+6	9.1e+8	15.24
CH-OOH	CH2OO.	7	1	0.057	1.07e-64	23.93	-2,406	4.8e+5	4.0e+8	13.43
CH-OOH	CH2OO.	8	1	1.30e-2	2.01e-52	19.91	-0,374	1.8e+6	1.6e+8	13.76
CH-OOH	CHOO.	5	1	1.39e-6	1.22e+5	2.38	11,559	1.0e+12	4.5e+11	23.87

Table S49 (continued)

Properties of Radicals				Quantum Calculation Data				Estimated in this work [a]		
Reacting Groups		RS	nH	k(298) (sec <sup>-1</sup> )	k(T)=p1 * p2 <sup>T</sup> * exp(-p3)			Derived A	A	Ea
H-Group	R-Group				p1	p2	p3			
CH-OOH	CHOO.	6	1	0.022	2.01e-52	19.91	-0,527	1.8e+6	9.1e+8	14.48
CH-OOH	CHOO.	7	1	0.030	2.01e-52	19.91	-0,627	1.8e+6	4.0e+8	13.80
CH-OOH	CHOO.	8	1	1.29e-2	2.01e-52	19.91	-0,371	1.8e+6	1.6e+8	13.77
CH-OOH	COO.	5	1	5.30e-7	9.91e+5	1.86	11,587	2.6e+11	4.5e+11	24.44
CH-OOH	COO.	6	1	0.028	2.01e-52	19.91	-0,597	1.8e+6	9.1e+8	14.34
CH-OOH	COO.	7	1	0.025	2.01e-52	19.91	-0,563	1.8e+6	4.0e+8	13.93
CH-OOH	COO.	8	1	1.07e-2	2.01e-52	19.91	-0,315	1.8e+6	1.6e+8	13.88
CH3-CHx=/En	CH2OO.	7	3	0.030	4.65e-75	27.56	-3,167	2.6e+5	8.6e+6	12.17
CH3-CHx=/En	CH2OO.	8	3	1.20	8.54e-60	22.36	-2,615	3.4e+5	3.2e+6	9.42
CH3-CHx=/En	CHOO.	7	3	1.55e-2	3.42e-67	25.07	-1,803	1.1e+6	8.6e+6	12.57
CH3-CHx=/En	CHOO.	8	3	0.372	3.95e-52	19.88	-1,227	9.6e+5	3.2e+6	10.11
CH3-CHx=/En	COO.	7	3	2.99e-3	3.42e-67	25.07	-1,313	1.1e+6	8.6e+6	13.55
CH3-CHx=/En	COO.	8	3	3.16e-3	3.95e-52	19.88	0,194	9.6e+5	3.2e+6	12.94
CH2-CHx=/En	CH2OO.	7	2	0.650	7.21e-70	25.88	-3,373	7.7e+5	8.6e+6	10.12
CH2-CHx=/En	CH2OO.	8	2	3.28	1.83e-44	17.39	-0,836	3.8e+6	3.2e+6	8.59
CH2-CHx=/En	CHOO.	7	2	0.946	3.42e-67	25.07	-3,028	1.6e+6	8.6e+6	9.90
CH2-CHx=/En	CHOO.	8	2	3.96	3.95e-52	19.88	-1,932	1.4e+6	3.2e+6	8.47
CH2-CHx=/En	COO.	7	2	0.377	3.42e-67	25.07	-2,754	1.6e+6	8.6e+6	10.44
CH2-CHx=/En	COO.	8	2	0.885	3.95e-52	19.88	-1,486	1.4e+6	3.2e+6	9.36
CH-CHx=/En	CH2OO.	7	1	13.7	1.20e-56	21.76	-2,204	2.6e+7	8.6e+6	7.90
CH-CHx=/En	CH2OO.	8	1	3.80e+3	3.95e-52	19.88	-3,978	2.9e+6	3.2e+6	4.00
CH-CHx=/En	CHOO.	7	1	82.3	3.42e-67	25.07	-4,359	3.2e+6	8.6e+6	6.84
CH-CHx=/En	CHOO.	8	1	353	3.95e-52	19.88	-3,270	2.9e+6	3.2e+6	5.40
CH-CHx=/En	COO.	7	1	29.6	3.42e-67	25.07	-4,054	3.2e+6	8.6e+6	7.45
CH-CHx=/En	COO.	8	1	66.8	3.95e-52	19.88	-2,774	2.9e+6	3.2e+6	6.39
CH2-CHx=/Ex	CH2OO.	5	2	1.56e-5	9.82e+1	2.65	9,172	2.5e+9	3.8e+9	20.03
CH2-CHx=/Ex	CH2OO.	6	2	2.71	5.52e-47	18.56	-0,525	2.9e+7	2.6e+8	11.29
CH2-CHx=/Ex	CH2OO.	7	2	2.04	8.49e-55	20.84	-1,928	1.9e+6	8.6e+6	9.44
CH2-CHx=/Ex	CH2OO.	8	2	8.22	4.62e-48	18.62	-1,503	3.6e+6	3.2e+6	8.04
CH2-CHx=/Ex	CHOO.	5	2	7.72e-6	9.82e+1	2.65	9,382	2.5e+9	3.8e+9	20.45
CH2-CHx=/Ex	CHOO.	6	2	0.026	6.10e-25	11.23	3,540	1.5e+8	2.6e+8	14.05
CH2-CHx=/Ex	CHOO.	7	2	0.077	7.71e-37	15.05	1,531	2.5e+7	8.6e+6	11.38
CH2-CHx=/Ex	CHOO.	8	2	0.026	4.62e-48	18.62	0,219	3.6e+6	3.2e+6	11.46
CH2-CHx=/Ex	COO.	5	2	2.55e-5	9.82e+1	2.65	9,026	2.5e+9	3.8e+9	19.74
CH2-CHx=/Ex	COO.	6	2	4.60e-5	6.74e-3	3.90	8,104	7.6e+8	2.6e+8	17.80
CH2-CHx=/Ex	COO.	7	2	4.27	7.72e-46	17.86	-1,061	3.7e+6	8.6e+6	9.00
CH2-CHx=/Ex	COO.	8	2	5.70e-3	4.62e-48	18.62	0,665	3.6e+6	3.2e+6	12.35
CH-CHx=/Ex	CH2OO.	5	1	9.52e-5	9.82e+1	2.65	8,634	5.1e+9	3.8e+9	18.55
CH-CHx=/Ex	CH2OO.	6	1	0.615	6.10e-25	11.23	2,595	3.0e+8	2.6e+8	11.76
CH-CHx=/Ex	CH2OO.	7	1	0.739	7.71e-37	15.05	0,857	4.9e+7	8.6e+6	9.63
CH-CHx=/Ex	CH2OO.	8	1	0.356	4.62e-48	18.62	-0,568	7.3e+6	3.2e+6	9.49
CH-CHx=/Ex	CHOO.	5	1	7.50e-4	9.82e+1	2.65	8,019	5.1e+9	3.8e+9	17.32
CH-CHx=/Ex	CHOO.	6	1	1.87	6.10e-25	11.23	2,263	3.0e+8	2.6e+8	11.10
CH-CHx=/Ex	CHOO.	7	1	6.69	7.71e-37	15.05	0,200	4.9e+7	8.6e+6	8.33
CH-CHx=/Ex	CHOO.	8	1	2.27	4.62e-48	18.62	-1,120	7.3e+6	3.2e+6	8.39
CH-CHx=/Ex	COO.	5	1	8.66e-3	9.82e+1	2.65	7,290	5.1e+9	3.8e+9	15.88
CH-CHx=/Ex	COO.	6	1	1.30e-2	6.10e-25	11.23	3,744	3.0e+8	2.6e+8	14.05
CH-CHx=/Ex	COO.	7	1	4.17e-3	6.99e-10	6.43	6,275	3.6e+9	8.6e+6	12.70

Table S49 (continued)

Properties of Radicals				Quantum Calculation Data				Estimated in this work [a]		
Reacting Groups		RS	nH	k(298) (sec <sup>-1</sup> )	k(T)=p1 * p2 <sup>T</sup> * exp(-p3)			Derived A	A	Ea
H-Group	R-Group				p1	p2	p3			
CH-CHx=/Ex	COO.	8	1	0.430	4.62e-48	18.62	-0,624	7.3e+6	3.2e+6	9.38
HOO-CH2	CH2OO.	7	1	190					4.0e+8	8.63
HOO-CH2	CH2OO.	8	1	326	5.64e-20	8.46	-0,566	2.4e+5	1.6e+8	7.77
HOO-CH2	CH2OO.	9	1	64.2	5.64e-20	8.46	-0,082	2.4e+5	6.5e+7	8.19
HOO-CH2	CH2OO.	10	1	2.68	5.64e-20	8.46	0,864	2.4e+5	4.7e+7	9.87
HOO-CH2	CHOO.	7	1	25.1					4.0e+8	9.83
HOO-CH2	CHOO.	8	1	607	5.64e-20	8.46	-0,751	2.4e+5	1.6e+8	7.40
HOO-CH2	CHOO.	9	1	118	9.14e-15	6.76	0,423	4.3e+5	6.5e+7	7.83
HOO-CH2	CHOO.	10	1	3.34	5.64e-20	8.46	0,791	2.4e+5	4.7e+7	9.74
HOO-CH2	COO.	7	1	247					4.0e+8	8.47
HOO-CH2	COO.	8	1	2.13e+3	5.64e-20	8.46	-1,126	2.4e+5	1.6e+8	6.65
HOO-CH2	COO.	9	1	192	5.64e-20	8.46	-0,408	2.4e+5	6.5e+7	7.54
HOO-CH2	COO.	10	1	8.30	5.64e-20	8.46	0,528	2.4e+5	4.7e+7	9.20
HOO-CH	CH2OO.	7	1	705					4.0e+8	7.85
HOO-CH	CH2OO.	8	1	1.59e+3	5.64e-20	8.46	-1,038	2.4e+5	1.6e+8	6.83
HOO-CH	CH2OO.	9	1	417	3.48e-25	10.16	-1,327	1.3e+5	6.5e+7	7.08
HOO-CH	CH2OO.	10	1	37.9	5.64e-20	8.46	0,075	2.4e+5	4.7e+7	8.31
HOO-CH	CHOO.	7	1	1.54e+3					4.0e+8	7.39
HOO-CH	CHOO.	8	1	2.09e+3	5.64e-20	8.46	-1,119	2.4e+5	1.6e+8	6.66
HOO-CH	CHOO.	9	1	246	5.64e-20	8.46	-0,482	2.4e+5	6.5e+7	7.39
HOO-CH	CHOO.	10	1	10.3	5.64e-20	8.46	0,464	2.4e+5	4.7e+7	9.08
HOO-CH	COO.	7	1	100					4.0e+8	9.01
HOO-CH	COO.	8	1	1.16e+4	5.64e-20	8.46	-1,630	2.4e+5	1.6e+8	5.65
HOO-CH	COO.	9	1	1.36e+3	5.64e-20	8.46	-0,991	2.4e+5	6.5e+7	6.38
HOO-CH	COO.	10	1	56.7	5.64e-20	8.46	-0,045	2.4e+5	4.7e+7	8.07
HOO-C	CH2OO.	7	1	1.10e+3					4.0e+8	7.59
HOO-C	CH2OO.	8	1	5.14e+3	5.64e-20	8.46	-1,388	2.4e+5	1.6e+8	6.13
HOO-C	CH2OO.	9	1	251	5.64e-20	8.46	-0,489	2.4e+5	6.5e+7	7.38
HOO-C	CH2OO.	10	1	10.9	5.64e-20	8.46	0,448	2.4e+5	4.7e+7	9.04
HOO-C	CHOO.	7	1	1.34e+4					4.0e+8	6.11
HOO-C	CHOO.	8	1	9.92e+3	5.64e-20	8.46	-1,584	2.4e+5	1.6e+8	5.74
HOO-C	CHOO.	9	1	158	5.64e-20	8.46	-0,350	2.4e+5	6.5e+7	7.65
HOO-C	CHOO.	10	1	6.82	5.64e-20	8.46	0,586	2.4e+5	4.7e+7	9.32
HOO-C	COO.	7	1	2.62e+3					4.0e+8	7.07
HOO-C	COO.	8	1	784	5.64e-20	8.46	-0,827	2.4e+5	1.6e+8	7.25
HOO-C	COO.	9	1	225	5.64e-20	8.46	-0,456	2.4e+5	6.5e+7	7.44
HOO-C	COO.	10	1	9.72	5.64e-20	8.46	0,481	2.4e+5	4.7e+7	9.11
<u>Data from Møller et al (2019)</u>										
Structure Calculated										
CH3	CO[OO.]	6	3	4.40e-4	HOCH <sub>2</sub> C(CH <sub>3</sub> )(OH)C(O)OO·				9.1e+8	17.44
CH3	CO[OO.]	6	3	3.50e-4	HC(O)C(CH <sub>3</sub> )(OH)C(O)OO·				9.1e+8	17.58
CH3	CO[OO.]	7	3	5.50e-3	CH <sub>3</sub> C(O)CH(OH)C(O)OO·				4.0e+8	15.47
CHO	CO[OO.]	6	1	0.26	HC(O)C(CH <sub>3</sub> )(OH)C(O)OO·				3.4e+8	12.42
CH2-Ox	CO[OO.]	6	2	0.030	HOCH <sub>2</sub> C(CH <sub>3</sub> )(OH)C(O)OO·				9.1e+8	14.70

[a] Estimated rate constants from this work are not shown because they are the same as the theoretically calculated rate constants on this table.

Table S50. Available information concerning rate constants for H-shift reactions of alkoxy radicals, and Arrhenius parameters derived for estimating these rate constants.

Reaction [a]	Used as Standard [b,c,d]			Estimated [e]		
	k(~298)	Ea	Note	A	Ea	k(298)
k (298) derived from evaluated experimental data (IUPAC, 2022, Atkinson, 2007)						
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{O}\cdot \rightarrow \cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	2.9e+5	7.66	1	1.2e+11	7.55	3.8e+5
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{O}\cdot)\text{CH}_3 \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_2\cdot$	4.6e+5	7.38	2	1.2e+11	7.55	3.8e+5
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}\cdot \rightarrow \text{CH}_3\text{CH}(\cdot)\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	3.3e+6	5.97	2	8.0e+10	5.97	3.5e+6
$\text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_3 \rightarrow$ $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{C}(\cdot)(\text{CH}_3)\text{CH}_3$	1.1e+7	4.85	2	4.0e+10	4.85	1.2e+7
k(298) derived from theoretical calculations of Vereecken and Peeters (2010)						
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{O}\cdot \rightarrow \cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	3.2e+5	7.60	3	1.2e+11	7.55	3.8e+5
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}\cdot \rightarrow \text{CH}_3\text{CH}(\cdot)\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	3.3e+6	5.98	3	8.0e+10	5.97	3.5e+6
$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{O}\cdot \rightarrow$ $\text{CH}_3\text{C}(\cdot)(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	1.1e+7	4.86	3	4.0e+10	4.85	1.2e+7
$\text{HCOCH}_2\text{CH}_2\text{CH}_2\text{O}\cdot \rightarrow \text{CO}(\cdot)\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	1.3e+7	4.76	3	4.0e+10	4.76	1.4e+7
$\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{O}\cdot \rightarrow \cdot\text{CH}_2\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{OH}$	2.0e+2	11.97	3	1.2e+11	11.97	2.3e+2
$\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{O}\cdot \rightarrow \text{CH}_3\text{CH}(\cdot)\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{OH}$	1.5e+4	9.17	3	8.0e+10	9.16	1.7e+4
$\text{CH}_3\text{CH}(\text{CH}_3)\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{O}\cdot \rightarrow$ $\text{CH}_3\text{C}(\cdot)(\text{CH}_3)\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{OH}$	5.3e+4	8.01	3	4.0e+10	8.03	5.6e+4
$\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{CH}_2\text{O}\cdot \rightarrow \cdot\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{CH}_2\text{OH}$	2.4e+5	7.77	3	1.2e+11	7.73	2.8e+5
$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{CH}_2\text{O}\cdot \rightarrow \text{CH}_3\text{CH}(\cdot)\text{CH}_2\text{C}(\text{O})\text{CH}_2\text{OH}$	2.5e+6	6.14	3	8.0e+10	6.16	2.6e+6
$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{C}(\text{O})\text{CH}_2\text{O}\cdot \rightarrow$ $\text{CH}_3\text{C}(\cdot)(\text{CH}_3)\text{CH}_2\text{C}(\text{O})\text{CH}_2\text{OH}$	8.4e+6	5.01	3	4.0e+10	5.04	8.6e+6
$\cdot\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \rightarrow \text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}(\cdot)\text{OH}$	2.4e+7	4.80	3	8.0e+10	4.82	2.4e+7
$\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_2\text{O}\cdot \rightarrow$ $\text{CH}_3\text{C}(\cdot)(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	7.5e+7	3.72	3	4.0e+10	3.70	8.1e+7
$\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{O}\cdot \rightarrow \cdot\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{OH}$	7.3e+4	8.48	3	1.2e+11	8.29	1.1e+5
$\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{O}\cdot \rightarrow$ $\text{CH}_3\text{CH}(\cdot)\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{OH}$	7.8e+5	6.83	3	8.0e+10	6.72	1.0e+6
$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{O}\cdot \rightarrow$ $\text{CH}_3\text{C}(\cdot)(\text{CH}_3)\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{OH}$	2.7e+6	5.69	3	4.0e+10	5.59	3.4e+6
$\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}\cdot \rightarrow$ $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\cdot)\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	1.3e+6	6.53	3	8.0e+10	6.72	1.0e+6
$\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{O}\cdot \rightarrow$ $\text{CH}_3\text{CH}(\text{OH})\text{C}(\cdot)(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	4.5e+6	5.38	3	4.0e+10	5.59	3.4e+6
Upper limit k(298) derived from results of various product studies (see notes)						
$\text{CH}_3\text{CH}(\text{O}\cdot)\text{OC}(\text{CH}_3)(\text{CH}_3)\text{CH}_3 \rightarrow$ $\text{CH}_3\text{CH}(\text{OH})\text{OC}(\text{CH}_3)(\text{CH}_3)\text{CH}_2\cdot$	<3.7e+3	>10.9	4	3.6e+11	11.5	1.4e+3
$\text{CH}_3\text{C}(\text{CH}_3)(\text{CH}_3)\text{OCH}_2\text{O}\cdot \rightarrow$ $\text{CH}_3\text{C}(\text{CH}_3)(\text{CH}_2\cdot)\text{OCH}_2\text{OH}$	<6.4e+3	>10.6	5	3.6e+11	11.5	1.4e+3
$\text{CH}_3\text{CH}(\text{O}\cdot)\text{OCH}_2\text{CH}_2\text{OH} \rightarrow$ $\text{CH}_3\text{CH}(\text{OH})\text{OCH}_2\text{CH}(\cdot)\text{OH}$	<4.3e+4	>8.5	6	8.0e+10	8.8	3.0e+4



Table S50 (continued)

Reaction [a]	Used as Standard [b,c,d]			Estimated [e]		
	k(~298)	Ea	Note	A	Ea	k(298)
$\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{OCH}(\text{O}\cdot)\text{CH}_3 \rightarrow$ $\text{CH}_3\text{C}(\text{O})\text{OCH}(\cdot)\text{CH}_2\text{OCH}(\text{CH}_3)\text{OH}$	<1.3e+5	>7.9	7	8.0e+10	9.6	7.8e+3
$\text{CH}_3\text{CH}_2\text{OC}(\text{O})\text{CH}_2\text{CH}_2\text{OCH}(\text{O}\cdot)\text{CH}_3 \rightarrow$ $\text{CH}_3\text{CH}_2\text{OC}(\text{O})\text{CH}(\cdot)\text{CH}_2\text{OCH}(\text{CH}_3)\text{OH}$	<1.3e+5	>7.9	8	8.0e+10	11.1	690
$\text{CH}_3\text{CH}_2\text{OC}(\text{O})\text{CH}_2\text{O}\cdot \rightarrow \cdot\text{CH}_2\text{CH}_2\text{OC}(\text{O})\text{CH}_2\text{OH}$	<1.6e+4	>8.8	9	4.9e+10	9.1	34

[a] The hydrogen that is shifted is shown in bold.

[b] k(~298) is the measured, theoretically calculated, or upper limit rate constant derived from experimental product yield data in  $\text{sec}^{-1}$ , at or near 298 K.

[c] Ea is the activation energy, in kcal/mole, corresponding to the tabulated rate constant at 298 K if the estimated A factor is assumed is assumed.

[d] Footnotes for the derivation of the data used as the standard are as follows. Dates for IUPAC citations are the date of the evaluation. Current IUPAC evaluations are at IUPAC (2023).

- 1 As recommended by IUPAC (2016).
- 2 As recommended by Atkinson (2007).
- 3 Derived from quantum calculations by Vereecken and Peeters (2010) for the various types of reactions. The k(298) values shown are taken from averages for representative compounds, as given in Table 6 of Vereecken and Peeters (2010). The simplest representatives of each of the types of reactions are shown on the table and were used to derive the best-fit estimated activation energies.
- 4 The yields of t-butyl formate and t-butyl acetate from ethyl t-butyl ether measured by Smith et al. (1992), assuming that  $\text{CH}_3\text{CH}(\text{O}\cdot)\text{OC}(\text{CH}_3)(\text{CH}_3)\text{CH}_3$  reactions are the only sources of these products, suggest that isomerization should be slower than the  $\text{O}_2$  reaction, which is estimated to have a rate constant of  $k_{\text{O}_2}[\text{O}_2]=4.9\text{e}+4 \text{ sec}^{-1}$  (see Section S1.6.1). The only way to account for the ~70% yield of t-butyl formate in the reaction of OH with MTBE (Calvert et al, 2011) is to assume that the  $\text{CH}_3\text{C}(\text{CH}_3)(\text{CH}_3)\text{OCH}_2\text{O}\cdot$  radical, formed in estimated 63% yield, must react mostly with  $\text{O}_2$ , and dominate over isomerization. Upper limit rate constant placed on an absolute basis using the estimated  $k_{\text{O}_2}[\text{O}_2]=4.9\text{e}+4 \text{ sec}^{-1}$ .
- 6 The most reasonable way to account for the ~36% yield of  $\text{HCOOCH}_2\text{CH}_2\text{OH}$  and ~8% yield of  $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{OH}$  from OH + ethoxyethanol observed by Stemmler et al. (1996) is to assume that the  $\text{CH}_3\text{CH}(\text{O}\cdot)\text{OCH}_2\text{CH}_2\text{OH}$  radical, predicted to be formed ~32% of the time, reacts by decomposition and (to a lesser extent) with  $\text{O}_2$ , with isomerization minor. Upper limit isomerization rate constant placed on an absolute basis using the estimated  $k_{\text{O}_2}[\text{O}_2]=4.9\text{e}+4 \text{ s}^{-1}$  and the decomposition/ $\text{O}_2$  rate constant ratio derived from the ratios of yields of these two products.
- 7 The relatively high yields of  $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{OCHO}$  from 2-ethoxyethyl acetate (Wells et al., 1996) means that decomposition must dominate over isomerization for this radical. The upper limit isomerization rate constant is placed on an absolute basis using the estimated decomposition rate constant.
- 8 The most reasonable explanation for the observation of ~30% of  $\text{CH}_3\text{CH}_2\text{OC}(\text{O})\text{CH}_2\text{CH}_2\text{OCHO}$  from ethyl 3-ethoxypropionate (Baxley et al., 1997) is to assume that this radical decomposes to form this product to a significant extent. This radical is predicted to be formed ~30% of the time. Upper limit rate constant placed on an absolute basis using estimated rate constant of the decomposition.

Table S50 (continued)

- 9 The most reasonable explanation for the observation of ~25% of  $\text{CH}_3\text{CH}_2\text{OC(O)CHO}$  from ethyl 3-ethoxypropionate (Baxley et al., 1997) is to assume that this radical reacts with  $\text{O}_2$  to a significant extent. This radical is predicted to be formed ~30% of the time.
- [e] The A factors and activation energies are estimated as discussed in the text, and  $k(298)$  is the corresponding rate constant at 298 K. The units of A and  $k(298)$  are  $\text{sec}^{-1}$  and the units of  $E_a$  are kcal/mole.

Table S51. Measured rate constants or rate constants derived from results of quantum calculations for  $\beta$ -scission decompositions of alkoxy radicals that were used for deriving parameters for estimating  $\beta$ -scission decomposition rate constants.

Reaction	$\Delta H_r$	Used for Optimizations [a]				Estimated [b]			
		k(298)	n × A	Ea	Ref	k(298)	Ratio	Ea	Diff.
<u>Acyclic alkyl alkoxy radicals</u>									
CH <sub>3</sub> CH <sub>2</sub> O· → HCHO + CH <sub>3</sub> ·	13.18	3.6e+0	1e+14	18.33	1	2.9e+0	0.8	18.46	0.13
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> O· → HCHO + CH <sub>3</sub> CH <sub>2</sub> ·	11.83	3.0e+2	1e+14	15.72	1	4.2e+2	1.4	15.51	-0.21
CH <sub>3</sub> CH(O·)CH <sub>3</sub> → CH <sub>3</sub> CHO + CH <sub>3</sub> ·	7.63	3.6e+2	2e+14	16.01	1	2.5e+2	0.7	16.23	0.22
CH <sub>3</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> O· → HCHO + CH <sub>3</sub> CH(·)CH <sub>3</sub>	10.34	5.7e+4	1e+14	12.60	1	4.2e+4	0.7	12.79	0.19
CH <sub>3</sub> CH <sub>2</sub> CH(O·)CH <sub>3</sub> → CH <sub>3</sub> CHO + CH <sub>3</sub> CH <sub>2</sub> ·	6.47	2.8e+4	1e+14	13.04	1	1.8e+4	0.7	13.28	0.25
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> O· → HCHO + CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> ·	12.14	2.5e+2	1e+14	15.81	1	4.2e+2	1.7	15.51	-0.30
CH <sub>3</sub> C(O·)(CH <sub>3</sub> )CH <sub>3</sub> → CH <sub>3</sub> C(O)CH <sub>3</sub> + CH <sub>3</sub> ·	4.28	2.5e+3	3e+14	15.11	1	6.2e+3	2.5	14.57	-0.53
CH <sub>3</sub> CH <sub>2</sub> CH(O·)CH <sub>3</sub> → CH <sub>3</sub> CH <sub>2</sub> CHO + CH <sub>3</sub> ·	7.97	3.9e+1	1e+14	16.92	1	1.2e+2	3.2	16.23	-0.69
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> O· → HCHO + CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> ·	12.08	4.2e+2	1e+14	15.51	2	4.2e+2	1.0	15.51	0.00
CH <sub>3</sub> CH(O·)CH(CH <sub>3</sub> )CH <sub>3</sub> → CH <sub>3</sub> CHO + CH <sub>3</sub> CH(·)CH <sub>3</sub>	4.98	1.7e+6	1e+14	10.59	2	1.8e+6	1.0	10.57	-0.03
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH(O·)CH <sub>3</sub> → CH <sub>3</sub> CHO + CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> ·	6.78	1.5e+4	1e+14	13.42	1	1.8e+4	1.2	13.28	-0.13
CH <sub>3</sub> CH <sub>2</sub> CH(O·)CH <sub>2</sub> CH <sub>3</sub> → CH <sub>3</sub> CH <sub>2</sub> CHO + CH <sub>3</sub> CH <sub>2</sub> ·	6.81	2.7e+4	2e+14	13.45	1	3.6e+4	1.3	13.28	-0.17
CH <sub>3</sub> C(CH <sub>3</sub> )(CH <sub>3</sub> )CH <sub>2</sub> O· → HCHO + CH <sub>3</sub> C(·)(CH <sub>3</sub> )CH <sub>3</sub>	9.28	1.9e+6	1e+14	10.53	1	1.3e+6	0.7	10.73	0.20
CH <sub>3</sub> CH(O·)CH(CH <sub>3</sub> )CH <sub>3</sub> → CH <sub>3</sub> CH(CH <sub>3</sub> )CHO + CH <sub>3</sub> ·	8.60	2.0e+2	1e+14	15.96	2	1.2e+2	0.6	16.23	0.27
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH(O·)CH <sub>3</sub> → CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CHO + CH <sub>3</sub> ·	7.63	4.9e+1	1e+14	16.79	1	1.2e+2	2.6	16.23	-0.56
CH <sub>3</sub> CH <sub>2</sub> C(O·)(CH <sub>3</sub> )CH <sub>3</sub> → CH <sub>3</sub> CH <sub>2</sub> C(O)CH <sub>3</sub> + CH <sub>3</sub> ·	4.05	1.1e+4	2e+14	13.99	1	4.1e+3	0.4	14.57	0.58
CH <sub>3</sub> CH <sub>2</sub> C(O·)(CH <sub>3</sub> )CH <sub>3</sub> → CH <sub>3</sub> C(O)CH <sub>3</sub> + CH <sub>3</sub> CH <sub>2</sub> ·	3.12	9.4e+5	1e+14	10.95	1	3.0e+5	0.3	11.62	0.68
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> C(O·)(CH <sub>3</sub> )CH <sub>3</sub> → CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> C(O)CH <sub>3</sub> + CH <sub>3</sub> ·	4.05	3.5e+3	2e+14	14.67	2	4.1e+3	1.2	14.57	-0.10
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> C(O·)(CH <sub>3</sub> )CH <sub>3</sub> → CH <sub>3</sub> C(O)CH <sub>3</sub> + CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> ·	3.43	2.2e+5	1e+14	11.80	2	3.0e+5	1.3	11.62	-0.18
CH <sub>3</sub> CH(CH <sub>3</sub> )C(O·)(CH <sub>3</sub> )CH <sub>3</sub> → CH <sub>3</sub> C(O)CH(CH <sub>3</sub> )CH <sub>3</sub> + CH <sub>3</sub> ·	5.02	5.1e+3	2e+14	14.45	2	4.1e+3	0.8	14.57	0.13
CH <sub>3</sub> CH(O·)C(CH <sub>3</sub> )(CH <sub>3</sub> )CH <sub>3</sub> → CH <sub>3</sub> CHO + CH <sub>3</sub> C(·)(CH <sub>3</sub> )CH <sub>3</sub>	3.92	6.9e+7	1e+14	8.40	2	5.8e+7	0.8	8.51	0.11
CH <sub>3</sub> CH(CH <sub>3</sub> )C(O·)(CH <sub>3</sub> )CH <sub>3</sub> → CH <sub>3</sub> C(O)CH <sub>3</sub> + CH <sub>3</sub> CH(·)CH <sub>3</sub>	1.63	1.5e+7	1e+14	9.31	2	2.9e+7	2.0	8.91	-0.40
CH <sub>3</sub> CH(O·)C(CH <sub>3</sub> )(CH <sub>3</sub> )CH <sub>3</sub> → CH <sub>3</sub> C(CH <sub>3</sub> )(CH <sub>3</sub> )CHO + CH <sub>3</sub> ·	9.56	2.9e+2	1e+14	15.73	2	1.2e+2	0.4	16.23	0.50
CH <sub>3</sub> C(O·)(CH <sub>3</sub> )C(CH <sub>3</sub> )(CH <sub>3</sub> )CH <sub>3</sub> → CH <sub>3</sub> C(O)C(CH <sub>3</sub> )(CH <sub>3</sub> )CH <sub>3</sub> + CH <sub>3</sub> ·	5.98	4.5e+3	2e+14	14.52	2	4.1e+3	0.9	14.57	0.05
CH <sub>3</sub> C(O·)(CH <sub>3</sub> )C(CH <sub>3</sub> )(CH <sub>3</sub> )CH <sub>3</sub> → CH <sub>3</sub> C(O)CH <sub>3</sub> + CH <sub>3</sub> C(·)(CH <sub>3</sub> )CH <sub>3</sub>	0.57	3.2e+8	1e+14	7.49	2	9.5e+8	3.0	6.85	-0.64
<u>Other acyclic alkoxy radicals</u>									
CH <sub>2</sub> =CHCH(O·)CH <sub>3</sub> → CH <sub>2</sub> =CHCHO + CH <sub>3</sub> ·	5.00	3.7e+3	1e+14	14.22	2	3.8e+3	1.0	14.20	-0.02
CH <sub>2</sub> =CHCH <sub>2</sub> CH <sub>2</sub> O· → HCHO + ·CH <sub>2</sub> =CHCH <sub>2</sub> ·	-2.43	1.7e+6	1e+14	10.59	2	2.0e+6	1.2	10.49	-0.10
CH <sub>2</sub> =CHCH(O·)CH <sub>3</sub> → CH <sub>3</sub> CHO + CH <sub>2</sub> =CH·	18.60	2.6e-1	1e+14	19.89	2	2.1e-1	0.8	20.01	0.12
·OCH <sub>2</sub> CH <sub>2</sub> OH → HCHO + ·CH <sub>2</sub> OH	9.72	2.3e+5	1e+14	11.78	3	1.8e+5	0.8	11.91	0.13
CH <sub>3</sub> CH(O·)OH → HC(O)OH + CH <sub>3</sub> ·	-5.87	1.5e+6	1e+14	10.67	2	8.3e+5	0.5	11.02	0.36

Table S51 (continued)

Reaction	$\Delta H_r$	Used for Optimizations [a]				Estimated [b]			
		k(298)	$n \times A$	Ea	Ref	k(298)	Ratio	Ea	Diff.
HC(O)CH <sub>2</sub> O· → HCHO + HCO·	6.88	7.9e+5	1e+14	11.04	2	4.1e+5	0.5	11.44	0.40
CH <sub>3</sub> CH(O·)CH <sub>2</sub> OH → HC(O)CH <sub>2</sub> OH + CH <sub>3</sub> ·	7.18	1.7e+2	1e+14	16.04	2	1.7e+2	1.0	16.05	0.02
CH <sub>3</sub> CH <sub>2</sub> CH(O·)OH → HC(O)OH + CH <sub>3</sub> CH <sub>2</sub> ·	-7.03	9.0e+7	1e+14	8.25	2	1.2e+8	1.3	8.07	-0.17
CH <sub>3</sub> CH(O·)OCH <sub>3</sub> → CH <sub>3</sub> OCHO + CH <sub>3</sub> ·	-5.10	1.3e+6	1e+14	10.74	2	5.2e+5	0.4	11.29	0.55
CH <sub>3</sub> C(O·)(CH <sub>3</sub> )OH → CH <sub>3</sub> C(O)OH + CH <sub>3</sub> ·	-12.85	7.4e+6	2e+14	10.14	2	1.9e+6	0.3	10.94	0.81
CH <sub>3</sub> CH(O·)CH <sub>2</sub> OH → CH <sub>3</sub> CHO + ·CH <sub>2</sub> OH	4.36	5.0e+7	1e+14	8.59	1	7.9e+6	0.2	9.68	1.09
CH <sub>3</sub> CH(O·)CHO → HC(O)CHO + CH <sub>3</sub> ·	12.44	2.3e+1	1e+14	17.25	2	1.4e+1	0.6	17.53	0.29
CH <sub>3</sub> CH(O·)CHO → CH <sub>3</sub> CHO + HCO·	-1.10	9.0e+6	1e+14	9.61	2	1.7e+7	1.9	9.21	-0.39
CH <sub>3</sub> C(O)CH <sub>2</sub> O· → HCHO + CH <sub>3</sub> C(O)·	6.30	2.7e+7	1e+14	8.96	1	1.6e+7	0.6	9.27	0.32
CH <sub>3</sub> CH(O·)CH(CH <sub>3</sub> )OH → CH <sub>3</sub> CH(CHO)OH + CH <sub>3</sub> ·	11.47	1.7e+2	1e+14	16.04	2	1.7e+2	1.0	16.05	0.02
CH <sub>3</sub> C(O·)(CH <sub>3</sub> )CH <sub>2</sub> OH → CH <sub>3</sub> C(O)CH <sub>2</sub> OH + CH <sub>3</sub> ·	2.88	8.5e+3	2e+14	14.14	2	7.8e+3	0.9	14.19	0.04
CH <sub>3</sub> CH(O·)CH <sub>2</sub> OCH <sub>3</sub> → CH <sub>3</sub> OCH <sub>2</sub> CHO + CH <sub>3</sub> ·	8.85	2.0e+1	1e+14	17.32	2	2.1e+1	1.0	17.30	-0.02
CH <sub>3</sub> CH <sub>2</sub> OCH(O·)CH <sub>3</sub> → CH <sub>3</sub> CH <sub>2</sub> OCHO + CH <sub>3</sub> ·	-5.67	5.0e+5	1e+14	11.32	1	5.2e+5	1.0	11.29	-0.03
CH <sub>3</sub> CH(O·)CH(CH <sub>3</sub> )OH → CH <sub>3</sub> CHO + CH <sub>3</sub> CH(·)OH	4.06	2.5e+8	1e+14	7.64	2	4.1e+8	1.7	7.34	-0.30
CH <sub>3</sub> OC(O·)(CH <sub>3</sub> )CH <sub>3</sub> → CH <sub>3</sub> C(O)OCH <sub>3</sub> + CH <sub>3</sub> ·	-11.94	1.0e+6	2e+14	11.32	1	1.4e+6	1.4	11.11	-0.21
CH <sub>3</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> O· → HCHO + CH <sub>3</sub> CH <sub>2</sub> OCH <sub>2</sub> ·	9.89	7.9e+5	1e+14	11.04	2	6.4e+5	0.8	11.18	0.13
CH <sub>3</sub> CH <sub>2</sub> CH(O·)OCH <sub>3</sub> → CH <sub>3</sub> OCHO + CH <sub>3</sub> CH <sub>2</sub> ·	-6.26	1.0e+8	1e+14	8.17	2	7.6e+7	0.7	8.34	0.17
CH <sub>3</sub> CH(O·)CH <sub>2</sub> OCH <sub>3</sub> → CH <sub>3</sub> CHO + CH <sub>3</sub> OCH <sub>2</sub> ·	5.03	1.0e+7	1e+14	9.53	2	2.7e+7	2.7	8.95	-0.58
CH <sub>3</sub> C(O·)(CH <sub>3</sub> )CH <sub>2</sub> OH → CH <sub>3</sub> C(O)CH <sub>3</sub> + ·CH <sub>2</sub> OH	1.01	2.8e+7	1e+14	8.93	2	1.3e+8	4.6	8.02	-0.90
CH <sub>3</sub> C(O·)(CH <sub>3</sub> )CHO → CH <sub>3</sub> C(O)CHO + CH <sub>3</sub> ·	5.75	2.4e+3	2e+14	14.90	2	2.4e+3	1.0	14.90	0.00
CH <sub>3</sub> C(O·)(CH <sub>3</sub> )CHO → CH <sub>3</sub> C(O)CH <sub>3</sub> + HCO·	-6.37	1.5e+8	1e+14	7.94	2	2.9e+8	1.9	7.55	-0.39
CH <sub>3</sub> C(O)CH(O·)CH <sub>3</sub> → CH <sub>3</sub> C(O)CHO + CH <sub>3</sub> ·	11.25	1.0e+1	1e+14	17.70	2	1.4e+1	1.3	17.53	-0.17
CH <sub>3</sub> CH <sub>2</sub> C(O)CH <sub>2</sub> O· → HCHO + CH <sub>3</sub> CH <sub>2</sub> C(O)·	5.32	2.2e+7	1e+14	9.08	2	1.6e+7	0.7	9.27	0.20
CH <sub>3</sub> C(O)CH(O·)CH <sub>3</sub> → CH <sub>3</sub> CHO + CH <sub>3</sub> C(O)·	-1.68	1.7e+8	1e+14	7.87	2	6.8e+8	4.0	7.05	-0.82
CH <sub>3</sub> OC(CH <sub>3</sub> )(CH <sub>3</sub> )CH <sub>2</sub> O· → HCHO + CH <sub>3</sub> OC(·)(CH <sub>3</sub> )CH <sub>3</sub>	7.92	2.0e+7	1e+14	9.13	1	2.0e+7	1.0	9.13	0.00
CH <sub>3</sub> CH(CH <sub>3</sub> )CH(O·)CH <sub>2</sub> OH → CH <sub>3</sub> CH(CH <sub>3</sub> )CHO + ·CH <sub>2</sub> OH	5.33	7.8e+6	1e+14	9.69	4	7.9e+6	1.0	9.68	-0.01
CH <sub>3</sub> CH(OH)C(O·)(CH <sub>3</sub> )CH <sub>3</sub> → CH <sub>3</sub> C(O)CH(CH <sub>3</sub> )OH + CH <sub>3</sub> ·	7.89	7.9e+3	2e+14	14.18	2	7.8e+3	1.0	14.19	0.01
CH <sub>3</sub> CH(O·)CH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub> → CH <sub>3</sub> CHO + CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> ·	6.72	2.0e+4	1e+14	13.23	1	1.8e+4	0.9	13.28	0.06
CH <sub>3</sub> CH <sub>2</sub> C(O·)(CH <sub>3</sub> )OCH <sub>3</sub> → CH <sub>3</sub> CH <sub>2</sub> C(O)OCH <sub>3</sub> + CH <sub>3</sub> ·	-12.20	1.0e+6	1e+14	10.91	1	7.1e+5	0.7	11.11	0.21
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH(O·)OCH <sub>3</sub> → CH <sub>3</sub> OCHO + CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> ·	-5.95	4.0e+7	1e+14	8.72	1	7.6e+7	1.9	8.34	-0.38
CH <sub>3</sub> CH(OH)C(O·)(CH <sub>3</sub> )CH <sub>3</sub> → CH <sub>3</sub> C(O)CH <sub>3</sub> + CH <sub>3</sub> CH(·)OH	0.71	1.7e+9	1e+14	6.51	2	6.8e+9	4.0	5.68	-0.83
CH <sub>3</sub> C(O)CH <sub>2</sub> CH(O·)CH <sub>3</sub> → CH <sub>3</sub> CHO + CH <sub>3</sub> C(O)CH <sub>2</sub> ·	1.49	1.6e+5	1e+14	12.00	5	1.6e+5	1.0	12.00	0.00
CH <sub>3</sub> C(O·)(CH <sub>3</sub> )C(CH <sub>3</sub> )(CH <sub>3</sub> )OH → CH <sub>3</sub> C(O)C(CH <sub>3</sub> )(CH <sub>3</sub> )OH + CH <sub>3</sub> ·	9.81	6.6e+3	2e+14	14.30	2	7.8e+3	1.2	14.19	-0.11
CH <sub>3</sub> CH(O·)OC(CH <sub>3</sub> )(CH <sub>3</sub> )CH <sub>3</sub> → CH <sub>3</sub> C(CH <sub>3</sub> )(CH <sub>3</sub> )OCHO + CH <sub>3</sub> ·	-4.77	2.0e+5	1e+14	11.86	1	5.2e+5	2.6	11.29	-0.57
CH <sub>3</sub> C(O·)(CH <sub>3</sub> )C(CH <sub>3</sub> )(CH <sub>3</sub> )OH → CH <sub>3</sub> C(O)CH <sub>3</sub> + CH <sub>3</sub> C(·)(CH <sub>3</sub> )OH	-0.79	6.9e+9	1e+14	5.68	2	3.7e+10	5.4	4.67	-1.00

Table S51 (continued)

Reaction	$\Delta H_r$	Used for Optimizations [a]				Estimated [b]			
		k(298)	n × A	Ea	Ref	k(298)	Ratio	Ea	Diff.
$\cdot\text{OCH}_2\text{CH}_2\text{OOH} \rightarrow \text{HCHO} + \cdot\text{CH}_2\text{OOH}$	10.65	1.7e+6	1e+14	10.59	2	1.8e+6	1.1	10.55	-0.04
$\text{CH}_3\text{CH}(\text{O}\cdot)\text{OOH} \rightarrow \text{HC}(\text{O})\text{OOH} + \text{CH}_3\cdot$	0.66	6.2e+5	1e+14	11.20	2	1.9e+5	0.3	11.88	0.69
$\text{HOCH}_2\text{CH}(\text{O}\cdot)\text{OH} \rightarrow \text{HC}(\text{O})\text{OH} + \cdot\text{CH}_2\text{OH}$	-9.14	1.7e+10	1e+14	5.15	2	5.3e+10	3.1	4.47	-0.68
$\text{CH}_3\text{C}(\text{O}\cdot)(\text{OH})\text{OH} \rightarrow \text{HOC}(\text{O})\text{OH} + \text{CH}_3\cdot$	-14.81	1.5e+8	1e+14	7.94	2	4.3e+8	2.9	7.32	-0.63
$\text{CH}_3\text{CH}(\text{CH}_2\text{O}\cdot)\text{OOH} \rightarrow \text{HCHO} + \text{CH}_3\text{CH}(\cdot)\text{OOH}$	9.61	2.2e+7	1e+14	9.08	2	2.8e+7	1.3	8.94	-0.14
$\text{CH}_3\text{CH}(\text{O}\cdot)\text{OOCH}_3 \rightarrow \text{CH}_3\text{OOCHO} + \text{CH}_3\cdot$	1.21	4.2e+4	1e+14	12.78	2	1.9e+5	4.6	11.88	-0.90
$\text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}_2\text{OOH} \rightarrow \text{CH}_3\text{CHO} + \cdot\text{CH}_2\text{OOH}$	5.29	5.4e+7	1e+14	8.55	2	7.8e+7	1.5	8.33	-0.22
$\text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}_2\text{OOH} \rightarrow \text{HC}(\text{O})\text{CH}_2\text{OOH} + \text{CH}_3\cdot$	8.85	2.0e+1	1e+14	17.32	2	2.1e+1	1.0	17.30	-0.02
$\text{CH}_3\text{OOCH}_2\text{CH}_2\text{O}\cdot \rightarrow \text{HCHO} + \text{CH}_3\text{OOCH}_2\cdot$	14.37	1.7e+5	1e+14	11.95	2	1.2e+5	0.7	12.18	0.23
$\text{CH}_3\text{CH}_2\text{CH}(\text{O}\cdot)\text{OOH} \rightarrow \text{HC}(\text{O})\text{OOH} + \text{CH}_3\text{CH}_2\cdot$	-0.50	1.2e+8	1e+14	8.10	2	2.8e+7	0.2	8.93	0.84
$\text{CH}_3\text{C}(\text{O}\cdot)(\text{CH}_3)\text{OOH} \rightarrow \text{CH}_3\text{C}(\text{O})\text{OOH} + \text{CH}_3\cdot$	-5.96	1.1e+7	2e+14	9.91	2	2.1e+6	0.2	10.87	0.96
$\text{CH}_3\text{OOCH}(\text{CH}_3)\text{CH}_2\text{O}\cdot \rightarrow \text{HCHO} + \text{CH}_3\text{CH}(\cdot)\text{OOCH}_3$	9.61	1.3e+6	1e+14	10.74	2	1.6e+6	1.2	10.64	-0.10
$\text{CH}_3\text{OOC}(\text{O}\cdot)(\text{CH}_3)\text{CH}_3 \rightarrow \text{CH}_3\text{C}(\text{O})\text{OOCH}_3 + \text{CH}_3\cdot$	-5.96	3.0e+5	2e+14	12.03	2	2.1e+6	7.0	10.87	-1.15
$\text{CH}_3\text{CH}_2\text{CH}(\text{O}\cdot)\text{OOCH}_3 \rightarrow \text{CH}_3\text{OOCHO} + \text{CH}_3\text{CH}_2\cdot$	0.05	4.7e+6	1e+14	9.99	2	2.8e+7	5.9	8.93	-1.05
$\text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}_2\text{OOCH}_3 \rightarrow \text{CH}_3\text{OOCH}_2\text{CHO} + \text{CH}_3\cdot$	8.85	2.9e+1	1e+14	17.09	2	2.1e+1	0.7	17.30	0.20
$\text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}_2\text{OOCH}_3 \rightarrow \text{CH}_3\text{CHO} + \text{CH}_3\text{OOCH}_2\cdot$	9.01	2.5e+6	1e+14	10.36	2	5.0e+6	2.0	9.95	-0.41
$\cdot\text{OCH}_2\text{CH}_2\text{NO}_2 \rightarrow \text{HCHO} + \cdot\text{CH}_2\text{NO}_2$	17.44	2.6e+0	1e+14	18.53	2	2.2e+0	0.9	18.61	0.08
$\text{CH}_3\text{CH}(\text{CH}_2\text{O}\cdot)\text{NO}_2 \rightarrow \text{HCHO} + \text{CH}_3\text{CH}(\cdot)\text{NO}_2$	11.29	7.1e+2	1e+14	15.20	2	7.0e+2	1.0	15.21	0.01
$\cdot\text{OCH}_2\text{CH}_2\text{ONO}_2 \rightarrow \text{HCHO} + \cdot\text{CH}_2\text{ONO}_2$	10.65	3.7e+2	1e+14	15.58	2	3.7e+2	1.0	15.60	0.01
$\text{CH}_3\text{CH}(\text{O}\cdot)\text{ONO}_2 \rightarrow \text{HC}(\text{O})\text{ONO}_2 + \text{CH}_3\cdot$	-4.77	5.5e+2	1e+14	15.35	2	7.4e+2	1.4	15.17	-0.18
$\text{CH}_3\text{CH}(\text{CH}_2\text{O}\cdot)\text{ONO}_2 \rightarrow \text{HCHO} + \text{CH}_3\text{CH}(\cdot)\text{ONO}_2$	9.62	1.7e+4	1e+14	13.31	2	1.8e+4	1.1	13.27	-0.04
$\text{CH}_3\text{CH}_2\text{CH}(\text{O}\cdot)\text{ONO}_2 \rightarrow \text{HC}(\text{O})\text{ONO}_2 + \text{CH}_3\text{CH}_2\cdot$	-5.93	1.3e+5	1e+14	12.10	2	1.1e+5	0.8	12.22	0.12
<u>Cyclic alkoxy radicals</u>									
$\cdot\text{OCH}_2\text{CH}^*\text{CH}_2\text{CH}_2^* \rightarrow \text{HCHO} + \text{CH}_2^*\text{CH}_2\text{CH}(\cdot)^*$	10.28	1.5e-1	1e+14	20.19	2	2.0e-1	1.3	20.04	-0.16
$\text{CH}_2^*\text{CH}_2\text{CH}(\text{O}\cdot)\text{CH}_2^* \rightarrow \text{HC}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\cdot$	-19.81	5.6e+9	2e+14	6.20	2	2.5e+9	0.4	6.69	0.49
$\text{CH}_3\text{C}(\text{O}\cdot)^*\text{CH}_2\text{CH}_2\text{CH}_2^* \rightarrow \text{CH}_2^*\text{CH}_2\text{C}(\text{O})\text{CH}_2^* + \text{CH}_3\cdot$	2.36	8.1e+1	1e+14	16.49	2	7.1e+1	0.9	16.57	0.08
$\text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}^*\text{CH}_2\text{CH}_2^* \rightarrow \text{CH}_3\text{CHO} + \text{CH}_2^*\text{CH}_2\text{CH}(\cdot)^*$	4.92	1.5e+1	1e+14	17.47	2	8.7e+0	0.6	17.81	0.34
$\cdot\text{OCH}_2\text{CH}^*\text{CH}_2\text{CH}_2\text{CH}_2^* \rightarrow \text{HCHO} + \text{CH}_2^*\text{CH}_2\text{CH}(\cdot)\text{CH}_2^*$	10.28	6.2e+2	1e+14	15.28	2	1.1e+3	1.8	14.93	-0.35
$\text{CH}_3\text{C}(\text{O}\cdot)^*\text{CH}_2\text{CH}_2\text{CH}_2^* \rightarrow \text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\cdot$	-23.39	1.2e+10	2e+14	5.75	2	4.1e+10	3.4	5.03	-0.72
$\text{CH}_2^*\text{CH}_2\text{CH}_2\text{CH}(\text{O}\cdot)\text{CH}_2^* \rightarrow \text{HC}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot$	0.03	3.4e+6	2e+14	10.59	2	1.3e+6	0.4	11.16	0.57
$\text{CH}_2^*\text{CH}_2\text{CH}_2\text{CH}(\text{O}\cdot)\text{CH}_2\text{CH}_2^* \rightarrow \text{HC}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot$	6.24	5.0e+4	2e+14	13.09	1	3.9e+4	0.8	13.24	0.15
$\cdot\text{OCH}_2\text{CH}^*\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2^* \rightarrow \text{HCHO} + \text{CH}_2^*\text{CH}_2\text{CH}_2\text{CH}(\cdot)\text{CH}_2^*$	10.28	6.2e+4	1e+14	12.56	2	6.8e+4	1.1	12.50	-0.06
$\text{CH}_3\text{C}(\text{O}\cdot)^*\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2^* \rightarrow \text{CH}_2^*\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{CH}_2^* + \text{CH}_3\cdot$	2.84	1.0e+2	1e+14	16.34	2	9.9e+1	0.9	16.37	0.03
$\text{CH}_3\text{CH}_2\text{C}(\text{O}\cdot)^*\text{CH}_2\text{CH}_2\text{CH}_2^* \rightarrow \text{CH}_2^*\text{CH}_2\text{C}(\text{O})\text{CH}_2^* + \text{CH}_3\text{CH}_2\cdot$	1.20	9.1e+3	1e+14	13.69	2	1.0e+4	1.1	13.62	-0.07

Table S51 (continued)

Reaction	$\Delta H_r$	Used for Optimizations [a]				Estimated [b]			
		k(298)	n × A	Ea	Ref	k(298)	Ratio	Ea	Diff.
$\text{CH}_3\text{CH}_2\text{C}(\text{O}\cdot)^*\text{CH}_2\text{CH}_2\text{CH}_2^* \rightarrow \text{CH}_3\text{CH}_2\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\cdot$	-23.65	2.0e+10	2e+14	5.45	2	4.1e+10	2.0	5.03	-0.42
$\text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}^*\text{CH}_2\text{CH}_2\text{CH}_2^* \rightarrow \text{CH}_3\text{CHO} + \text{CH}_2^*\text{CH}_2\text{CH}(\cdot)\text{CH}_2^*$	4.92	8.0e+4	1e+14	12.41	2	4.8e+4	0.6	12.70	0.30
$\text{CH}_3\text{C}(\text{O}\cdot)^*\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2^* \rightarrow \text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot$	-3.55	5.7e+6	2e+14	10.29	2	2.1e+7	3.8	9.50	-0.79
$\text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}^*\text{CH}_2\text{CH}_2\text{CH}_2^* \rightarrow \text{HC}(\text{O})\text{CH}^*\text{CH}_2\text{CH}_2\text{CH}_2^* + \text{CH}_3\cdot$	8.60	4.8e+2	1e+14	15.43	2	4.7e+2	1.0	15.44	0.01
$\text{CH}_3\text{C}(\text{O}\cdot)^*\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2^* \rightarrow \text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot$	2.66	4.4e+5	2e+14	11.80	2	6.4e+5	1.5	11.58	-0.22
$\cdot\text{OCH}_2\text{CH}^*(\text{CH}_2)_5^* \rightarrow \text{HCHO} + \text{CH}_2^*\text{CH}_2\text{CH}_2\text{CH}(\cdot)\text{CH}_2\text{CH}_2^*$	10.28	6.2e+4	1e+14	12.56	2	6.8e+4	1.1	12.50	-0.06
$\text{CH}_3\text{C}(\text{O}\cdot)^*(\text{CH}_2)_5^* \rightarrow \text{CH}_2^*\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{CH}_2\text{CH}_2^* + \text{CH}_3\cdot$	6.18	1.0e+2	1e+14	16.34	2	9.9e+1	0.9	16.37	0.03
$\text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}^*\text{CH}_2\text{CH}_2^* \rightarrow \text{HC}(\text{O})\text{CH}^*\text{CH}_2\text{CH}_2^* + \text{CH}_3\cdot$	8.60	1.5e+3	1e+14	14.75	2	1.5e+3	1.0	14.74	-0.01

[a] Rate constants and A factors are in units of  $\text{sec}^{-1}$  and activation energies are in units of kcal/mole. The A factor is set at  $1.0 \times 10^{-14} \text{ sec}^{-1} \times$  the reaction path degeneracy. The rate constant is derived as discussed in the footnote given in the "Ref" column. The activation energy is derived from the rate constant and A factor, where  $k(T) = A \exp(-E_a/RT)$ . Footnotes giving sources of the rate constants are as follows:

- 1 Average of estimated 298 K rate constants tabulated in Tables 1 and 2 by Orlando et al. (2003). Data from previous studies that disagreed with more recent data are not used in the averages, nor are data for radicals estimated to have non-negligible isomerization reactions.
- 2 The activation energies were derived from  $E_b(\text{DFT})$  values tabulated in Table 2 of Vereecken and Peeters (2009), calculated using the B3LYP/6-31G(d,p) level of theory. These were used to estimate activation energies by using a linear fit between the activation energies derived from the data tabulated by Orlando et al. (2003) as discussed in the text. The 298 K rate constants were derived from the estimated activation energies and A factors.
- 3 Based on yield ratios of formaldehyde / glycolaldehyde formed from OH + ethene as recommended by Calvert et al. (2000). It is assumed that reactions of  $\cdot\text{HOCH}_2\text{CH}_2\text{O}\cdot$  forming these products are the only significant reactions. Rate constant placed on an absolute basis using the estimated rate constant for the  $\text{O}_2$  reaction.
- 4 Derived from the ratios of yields of 2-propanal / glycolaldehyde observed from OH + 3-methyl-1-butene measured by Atkinson et al. (1998), assuming that the formation of both products are from decompositions of  $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}(\text{O}\cdot)\text{CH}_2\text{OH}$ , and placed on an absolute basis using the estimated rate constant for the reaction forming  $\text{CH}_3\text{CH}(\cdot)\text{CH}_3 + \text{HC}(\text{O})\text{CH}_2\text{OH}$ .
- 5 Derived from the ratio of acetaldehyde to  $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{C}(\text{O})\text{CH}_3$  yields from 2-pentanone as reported by Atkinson et al. (2000), assuming they both only come from  $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}(\text{O}\cdot)\text{CH}_3$ , and using the estimated rate constant for the  $\text{O}_2$  reaction.

[b] Estimated values, with rate constants in  $\text{sec}^{-1}$  and activation energies in kcal/mole. Estimated A factor derived as discussed in the text, with the rate constant derived from the estimated rate constant and activation energy. "Ratio" is the ratio of estimated to target rate constant and "Diff" is the difference between the estimated and target activation energy.

### S5.3. Tables of Assignments

Table S52. Assigned rate constants for the reactions of compounds with OH radicals.

Name	k(298)	A	Ea	B	Ref
Methylamine	2.20e-11	1.02e-11	-0.455		1
Methanol	8.79e-13	2.32e-13	-0.799	2.72	1
Formic Acid	4.50e-13				1
Methyl Hydroperoxide	1.00e-11	5.30e-12	-0.378		1
Ethane	2.49e-13	1.51e-12	1.059	1.92	1
Acetylene	7.47e-13		Falloff		2
Ethene	7.90e-12		Falloff		3
Dimethyl Amine	6.82e-11	2.98e-11	-0.490		1
Ethyl Amine	2.77e-11	1.47e-11	-0.375		1
Ethanol	3.33e-12	4.42e-13	-1.204	2.29	1
Dimethyl Ether	2.83e-12	1.02e-12	-0.612	2.09	1
Ethylene Oxide	9.08e-14	1.63e-12	1.701	2	1
Acetaldehyde	1.49e-11	2.40e-12	-1.085	0.77	1
Ethanolamine	7.94e-11				1
Ethylene Glycol	1.45e-11				1
Methyl Formate	1.76e-13	2.68e-14	-1.129	3.76	1
Acetic Acid	7.49e-13	8.97e-15	-2.627	2	1
Glycolaldehyde	1.10e-11				1
Glyoxal	9.22e-12	1.83e-12	-0.960	0.79	1
Ethyl hydroperoxide	6.00e-12				1
peroxyacetic acid	3.00e-14				1
Peroxyacetyl nitrate	3.00e-14				1
Propane	1.11e-12	2.00e-12	0.342	1.76	1
Cyclopropane	7.64e-14	6.00e-12	2.583		1
Propene	2.44e-11	1.20e-11	-0.417	-0.62	1
1,2-propadiene (allene)	9.82e-12	7.66e-12	-0.147		1
Methyl Acetylene	5.40e-12				1
Trimethyl Amine	5.59e-11	2.40e-11	-0.500		1
Isopropyl Alcohol	5.24e-12	7.21e-13	-1.180	1.41	1
n-Propyl Alcohol	5.86e-12	9.98e-13	-1.055	1.86	1
Trimethylene Oxide	1.03e-11				1
Propylene Oxide	4.67e-13				1
Propionaldehyde	2.00e-11	6.63e-13	-2.023	1.99	1
Acrolein	2.17e-11	7.10e-12	-0.662		1
Acetone	1.87e-13	1.97e-14	-1.347	3.88	1
Propylene Glycol	2.10e-11				1
1,3-dioxolane	1.00e-11				1
Dimethoxy methane	4.55e-12	2.74e-14	-3.044	4.62	1
2-Methoxyethanol	1.24e-11	5.40e-13	-1.864	2	1
Ethyl Formate	8.76e-13	8.10e-14	-1.417	2	1
Methyl Acetate	3.36e-13	6.05e-15	-2.395	4.47	1
Acrylic Acid	1.70e-11				1
Propionic Acid	1.20e-12				1
Methyl Glyoxal	1.19e-11	2.27e-13	-2.351	2	1
Hydroxy Acetone	5.88e-12	1.44e-13	-2.206	2.63	1
1-nitropropane	3.62e-13	3.80e-12	1.391		1
2-nitropropane	2.51e-13	2.20e-12	1.284		1
Dimethyl Carbonate	3.26e-13	5.68e-14	-1.043	2	1

Table S52 (continued)

Name	k(298)	A	Ea	B	Ref
isopropyl nitrate	2.86e-13	6.20e-13	0.457		1
n-Butane	2.38e-12	2.09e-12	-0.083	1.82	1
Isobutane	2.11e-12	6.28e-13	-0.727	2.39	1
Cyclobutane	2.00e-12	1.11e-11	1.013		1
1-Butene	3.14e-11	6.60e-12	-0.924		1
Isobutene	5.13e-11	9.40e-12	-1.004		1
cis-2-Butene	5.28e-11	3.80e-12	-1.558		1
trans-2-Butene	6.31e-11	6.06e-12	-1.387		1
1,2-Butadiene	2.60e-11				1
1,3-Butadiene	6.64e-11	1.12e-11	-1.053		1
Ethyl Acetylene	7.50e-12				1
2-Butyne	2.70e-11				1
1-buten-3-yne (vinyl acetylene)	3.27e-11	6.40e-12	-0.966		1
t-butyl amine	1.01e-11				1
Isobutyl Alcohol	9.71e-12	1.72e-13	-2.399	3	1
n-Butyl Alcohol	9.15e-12	2.94e-13	-2.046	2.88	1
s-Butyl Alcohol	8.70e-12	3.88e-13	-1.850	2.25	1
t-Butyl Alcohol	1.08e-12	6.74e-14	-1.653	3.46	1
Tetrahydrofuran	1.70e-11	9.40e-12	-0.352		1
Diethyl Ether	1.27e-11	4.21e-13	-2.027	2.72	1
1,2-Epoxybutane	1.90e-12				1
Furan	3.84e-11	9.67e-12	-0.816		1
2-Methylpropanal	2.57e-11	6.70e-12	-0.795		1
Butanal	2.37e-11	2.75e-13	-2.649	2.65	1
Crotonaldehyde	3.59e-11	6.00e-12	-1.059		1
Methacrolein	2.86e-11	8.00e-12	-0.755		1
Cyclobutanone	8.70e-13				1
Methyl Ethyl Ketone	1.05e-12	5.42e-14	-1.767	3.57	1
Methylvinyl ketone	2.01e-11	2.60e-12	-1.212		1
Morpholine	1.10e-10	1.52e-11	-1.172		1
2-Amino-2-Methyl-1-Propanol	2.80e-11				1
Dimethylaminoethanol	7.00e-11				1
1,3-Butanediol	2.99e-11				1
1,2-Butanediol	2.43e-11				1
1,4-Butanediol	3.67e-11				1
2,3-Butanediol	2.12e-11				1
1,4-dioxane	1.16e-11	6.80e-12	-0.316		1
1-Methoxy-2-Propanol	2.00e-11				1
2-Ethoxyethanol	1.95e-11				1
3-methoxy-1-propanol	2.15e-11				1
gamma- butyrolactone	2.90e-12				1
Ethyl Acetate	1.67e-12	1.69e-13	-1.357		1
Methyl Propionate	9.44e-13	4.29e-14	-1.844	3.58	1
n-Propyl Formate	1.86e-12	2.17e-13	-1.278	2	1
Isopropyl Formate	2.13e-12	3.13e-13	-1.135		1
isobutyric acid	2.10e-12				1
butanoic acid	1.80e-12				1
3H-furan-2-one	4.90e-11				1
Methyl Acrylate	1.29e-11	2.00e-12	-1.105		1
Vinyl Acetate	2.50e-11	4.77e-12	-0.980		1
Biacetyl	2.36e-13	1.23e-13	-0.393	2	1
2-butene-1,4-dial	5.29e-11				1
Methoxy Acetone	6.59e-12				1



Table S52 (continued)

Name	k(298)	A	Ea	B	Ref
T-butyl hydroperoxide	3.57e-12	7.00e-13	-0.964		1
Propylene Carbonate	2.52e-12				1
Methyl Lactate	2.48e-12				1
Maleic anhydride	3.91e-13	1.55e-12	0.815		1
2-butyl nitrate	8.60e-13				1
isobutyl nitrate	1.38e-12				1
Methacrolein's PAN	2.90e-11				1
n-Pentane	3.76e-12	2.58e-12	-0.230	1.83	1
Neopentane	9.10e-13	1.30e-12	0.203	2.1	1
Iso-Pentane	3.74e-12	1.01e-11	0.588		1
Cyclopentane	4.77e-12	1.84e-12	-0.572	2.13	1
1-Pentene	3.23e-11	1.06e-13	-3.398	3.08	1
3-Methyl-1-Butene	3.18e-11	5.32e-12	-1.059		1
2-Methyl-1-Butene	6.10e-11				1
2-Methyl-2-Butene	8.69e-11	1.92e-11	-0.894		1
cis-2-Pentene	6.50e-11				1
trans-2-Pentene	6.70e-11				1
Cyclopentene	6.70e-11				1
Trans 1,3-Pentadiene	1.16e-10	1.41e-11	-1.248		1
1,4-Pentadiene	5.43e-11	1.04e-11	-0.978		1
1,2-Pentadiene	3.60e-11				1
3-Methyl-1,2-Butadiene	5.70e-11				1
Isoprene	1.00e-10	2.70e-11	-0.775		1
Cyclopentanol	1.10e-11				1
2-Pentanol	1.10e-11				1
3-Pentanol	1.30e-11				1
Pentyl Alcohol	1.10e-11				1
isoamyl alcohol (3-methyl-1-butanol)	1.40e-11	1.50e-12	-1.320		1
2-methyl-2-butanol; t-amyl alcohol	3.42e-12	2.00e-12	-0.318		1
3-methyl-2-butanol	1.19e-11	2.50e-12	-0.922		1
Alpha-Methyltetrahydrofuran	2.46e-11	2.57e-12	-1.337		1
Tetrahydropyran	1.23e-11	7.80e-12	-0.270		1
Methyl n-Butyl Ether	1.45e-11	1.01e-11	-0.213		1
Methyl t-Butyl Ether	3.10e-12	1.87e-13	-1.675	3.34	1
2-Methyl-3-Butene-2-ol	6.28e-11	8.10e-12	-1.212		1
2-methyl furan	7.00e-11				1
3-methyl furan	9.54e-11	3.37e-11	-0.616		1
2,2-Dimethylpropanal (pivaldehyde)	2.78e-11	5.30e-12	-0.982		1
3-Methylbutanal (Isovaleraldehyde)	2.59e-11				1
Pentanal (Valeraldehyde)	2.66e-11	8.60e-12	-0.668		1
Cyclopentanone	2.90e-12				1
2-Pentanone	4.05e-12	3.80e-13	-1.401		1
3-Pentanone	2.00e-12				1
Methyl Isopropyl Ketone	3.02e-12	1.45e-12	-0.435		1
Ethyl vinyl ketone	2.62e-11	4.77e-12	-1.008		1
2,2-Dimethoxy Propane	4.13e-12	3.73e-12	-0.060		1
2-Propoxyethanol	1.73e-11				1
3-Ethoxy-1-Propanol	2.20e-11				1
3-Methoxy-1-Butanol	2.36e-11				1
Ethyl Propionate	2.10e-12				1
Isopropyl Acetate	3.80e-12	4.10e-14	-2.689	2	1
Methyl Butyrate	3.37e-12	1.22e-13	-1.973	2	1
Methyl Isobutyrate	1.70e-12				1

Table S52 (continued)

Name	k(298)	A	Ea	B	Ref
n-Butyl Formate	3.69e-12	4.46e-13	-1.258	2	1
Propyl Acetate	3.44e-12	1.31e-13	-1.943	2	1
Ethyl Acrylate	1.60e-11	2.50e-12	-1.097		1
Methyl Methacrylate	4.08e-11	2.68e-12	-1.612		1
Glutaraldehyde	2.38e-11				1
2,4-pentanedione	8.26e-11	5.20e-12	-1.637		1
PROD2 Species #1	1.55e-11				1
4-oxo-2-penteneal	6.20e-11				1
2-Methoxyethyl Acetate	8.18e-12	2.90e-12	-0.614		1
Ethyl Lactate	3.51e-12				1
Methyl Isopropyl Carbonate	2.55e-12				1
Unsaturated organic nitrate isoprene product 2	3.90e-11				1
Unsaturated organic nitrate isoprene product 6	1.10e-10				1
Unsaturated organic nitrate isoprene product 10	3.40e-11				1
Unsaturated organic nitrate isoprene product 11	6.60e-11				1
n-Hexane	4.96e-12	1.52e-12	-0.709	2.12	1
2,2-Dimethyl Butane	2.23e-12	3.37e-11	1.608		1
2,3-Dimethyl Butane	5.87e-12	6.38e-13	-1.323	2.47	1
2-Methyl Pentane	5.25e-12	1.77e-11	0.719		1
3-Methylpentane	5.54e-12	1.80e-11	0.698		1
Cyclohexane	6.69e-12	3.35e-12	-0.417	1.86	1
Isopropyl Cyclopropane	2.61e-12				1
Methylcyclopentane	7.57e-12	1.67e-12	-0.903	2.1	1
1-Hexene	3.70e-11				1
3,3-Dimethyl-1-Butene	2.90e-11				1
2-Methyl-1-Pentene	6.14e-11				1
2,3-Dimethyl-2-Butene	1.10e-10				1
2-Methyl-2-Pentene	8.90e-11				1
Cis-3-Hexene	6.27e-11				1
Trans 4-Methyl-2-Pentene	6.10e-11				1
Trans-2-Hexene	6.08e-11				1
Cyclohexene	6.77e-11				1
Trans 1,4-Hexadiene	9.10e-11				1
trans-1,3-hexadiene	1.12e-10				1
Benzene	1.21e-12	2.30e-12	0.378		1
Triethyl Amine	9.28e-11				1
Cyclohexanol	1.70e-11				1
1-Hexanol	1.30e-11				1
2-Hexanol	1.20e-11				1
4-methyl-2-pentanol (methyl isobutyl carbinol)	1.70e-11				1
Di n-Propyl Ether	1.99e-11	1.03e-11	-0.391		1
Ethyl n-Butyl Ether	2.22e-11	6.60e-12	-0.719		1
Ethyl t-Butyl Ether	8.70e-12	3.40e-12	-0.556		1
Methyl t-Amyl Ether	5.58e-12	3.13e-12	-0.342		1
diisopropyl ether	9.97e-12	2.97e-12	-0.717		1
cis-3-hexen-1-ol	1.08e-10	1.54e-11	-1.153		1
2,5-dimethyl furan	1.15e-10	1.12e-12	-2.749	1.61	1
2-ethyl furan	1.16e-10				1
Hexanal	2.85e-11	4.28e-12	-1.123		1
Cyclohexanone	6.40e-12				1
4-Methyl-2-Pentanone	1.34e-11	1.18e-12	-1.440		1
Methyl n-Butyl Ketone	7.55e-12	8.40e-13	-1.300		1
Methyl t-Butyl Ketone	1.21e-12				1

Table S52 (continued)

Name	k(298)	A	Ea	B	Ref
3-hexanone; ethyl n-propyl ketone	6.40e-12				1
mesityl oxide (2-methyl-2-penten-4-one)	8.41e-11				1
Phenol	2.82e-11	4.70e-13	-2.424		1
2-Methyl-2,4-Pentanediol	1.36e-11				1
ethylene glycol diethyl ether; 1,2-diethoxyethane	5.66e-11	5.22e-13	-2.782	2	1
2-Butoxyethanol	3.00e-11				1
3 methoxy -3 methyl-Butanol	1.64e-11				1
Ethyl Butyrate	4.50e-12				1
Isobutyl Acetate	6.48e-12	1.35e-13	-2.299	2	1
Methyl Pivalate	1.21e-12	1.11e-15	-4.165	6.95	1
n-Butyl Acetate	5.68e-12	2.73e-13	-1.804	2	1
n-Propyl Propionate	4.00e-12				1
s-Butyl Acetate	6.11e-12	9.63e-14	-2.464	2	1
t-Butyl Acetate	5.75e-13	2.87e-13	-0.419	2	1
methyl pentanoate; methyl valerate	5.26e-12	1.69e-13	-2.043	2	1
Ethyl Methacrylate	4.30e-11				1
Diacetone Alcohol	4.50e-12	5.42e-13	-1.253		1
PROD2 Species #6	2.20e-11				1
PROD2 Species #7	1.70e-11				1
3-hexene-2,5-dione	7.20e-11				4
2-(2-Ethoxyethoxy) Ethanol	5.72e-11				1
1-Methoxy-2-Propyl Acetate	1.45e-11	2.01e-12	-1.168		1
2-Ethoxyethyl Acetate	1.21e-11	1.40e-12	-1.276		1
Dimethyl Succinate	1.64e-12				1
Ethylene Glycol Diacetate	2.16e-12				1
n-Heptane	6.24e-12	3.84e-12	-0.294	1.79	1
2,2,3-Trimethyl Butane	3.81e-12				1
2,2-Dimethyl Pentane	3.40e-12				1
2,3-Dimethyl Pentane	6.56e-12	1.53e-11	0.501		1
2,4-Dimethyl Pentane	5.76e-12	2.70e-11	0.914		1
2-Methyl Hexane	6.66e-12	2.55e-12	-0.574	1.56	1
3-Methyl Hexane	6.66e-12	6.13e-12	-0.052	0.74	1
Cycloheptane	9.96e-12	5.57e-12	-0.352	2	1
Methylcyclohexane	9.26e-12	1.54e-12	-1.071	2.26	1
1-Heptene	3.88e-11				1
2,3-dimethyl-1-pentene	5.70e-11				1
2-methyl-1-hexene	6.50e-11				1
2,3-Dimethyl-2-Pentene	1.03e-10				1
Trans-2-Heptene	6.80e-11				1
Trans 4,4-dimethyl-2-Pentene	5.50e-11				1
1-Methyl Cyclohexene	9.40e-11				1
Toluene	5.64e-12	1.80e-12	-0.676		1
1-Heptanol	1.30e-11				1
Heptanal	2.96e-11				1
Benzaldehyde	1.26e-11	5.90e-12	-0.447		1
2-Heptanone	8.17e-12	3.17e-13	-1.932	2.27	1
Di-Isopropyl Ketone	4.90e-12				1
5-Methyl-2-Hexanone	1.20e-11	1.25e-12	-1.339		1
m-cresol	5.88e-11	2.30e-12	-1.918		1
p-cresol	4.94e-11	1.90e-12	-1.928		1
o-Cresol	4.16e-11	1.60e-12	-1.928		1
Benzyl alcohol	2.70e-11				1
Methoxybenzene; Anisole	2.04e-11	5.06e-12	-0.825		1

Table S52 (continued)

Name	k(298)	A	Ea	B	Ref
n-Butoxy-2-Propanol (Propylene Glycol n-Butyl Ether)	3.80e-11				1
Butyl Propionate	6.01e-12	2.98e-12	-0.415		1
Amyl Acetate	7.40e-12	3.34e-13	-1.842	2	1
n-Propyl Butyrate	6.00e-12				1
methyl hexanoate	7.39e-12	3.00e-13	-1.904	2	1
n-butyl acrylate	1.95e-11	3.74e-13	-2.339		1
3-methyl-3-hexene-2,5-dione	9.40e-11				1
PROD2 Species #3	1.60e-11				1
PROD2 Species #10	1.90e-11				1
Ethyl 3-Ethoxy Propionate	2.20e-11				1
Dimethyl Glutarate	2.24e-12				1
n-Octane	8.48e-12	2.49e-12	-0.733	1.99	1
2,2,3,3-Tetramethyl Butane	9.88e-13	1.79e-12	0.344	2	1
2,2,4-Trimethyl Pentane	3.34e-12				1
2,2-Dimethyl Hexane	4.80e-12				1
2,3,4-Trimethyl Pentane	6.60e-12				1
Cyclooctane	1.39e-11	3.33e-11	0.519		1
Ethylcyclohexane	1.34e-11				1
1-Octene	3.44e-11	7.01e-13	-2.305		1
2-Methyl-1-heptene	6.71e-11				1
trans-2-octene	7.23e-11				1
Trans-4-Octene	6.90e-11				1
Ethyl Benzene	7.00e-12				1
m-Xylene	2.31e-11				1
o-Xylene	1.36e-11				1
p-Xylene	1.21e-11	4.14e-12	-0.634		1
Styrene	5.81e-11	9.80e-12	-1.053		1
1,4-dimethylcyclohexane	1.40e-11				5
1-Octanol	1.30e-11				1
2-Ethyl-1-Hexanol	1.13e-11				1
2-Octanol	2.52e-11				1
3-Octanol	3.14e-11				1
4-Octanol	2.87e-11				1
Di-Isobutyl Ether	2.60e-11				1
Di-n-butyl Ether	2.85e-11	4.50e-12	-1.093		1
2-Octanone	1.10e-11				1
2,3-dimethyl phenol	8.20e-11				1
2,4-dimethyl phenol	7.30e-11				1
2,5-dimethyl phenol	8.50e-11				1
2,6-dimethyl phenol	6.70e-11				1
3,4-dimethyl phenol	8.30e-11				1
n-Butyl Butyrate	9.80e-12	5.35e-12	-0.358		1
Butyl Methacrylate	6.59e-11	2.44e-12	-1.951		1
Isobutyl Methacrylate	5.42e-11	5.53e-12	-1.351		1
cis-3-hexenyl acetate	7.74e-11				1
2-(2-Butoxyethoxy)-Ethanol	7.44e-11				1
Dimethyl Adipate	3.65e-12				1
n-Nonane	1.02e-11	2.34e-12	-0.882	2.19	1
2,3,5-Trimethyl Hexane	7.90e-12				1
2-Methyl Octane	1.01e-11				1
3,3-Diethyl Pentane	4.80e-12				1
4-Methyl Octane	9.70e-12				1
1,3,5-trimethylcyclohexane	1.77e-11				1

Table S52 (continued)

Name	k(298)	A	Ea	B	Ref
1,1,3-Trimethyl Cyclohexane	8.70e-12				1
Propyl Cyclohexane	1.32e-11	2.25e-11	0.316		1
1-Nonene	4.32e-11				1
n-Propyl Benzene	5.80e-12				1
Isopropyl Benzene (cumene)	6.30e-12				1
m-Ethyl Toluene	2.04e-11	1.05e-12	-1.756		1
o-Ethyl Toluene	1.23e-11				1
p-Ethyl Toluene	1.23e-11				1
1,2,3-Trimethyl Benzene	3.27e-11				1
1,2,4-Trimethyl Benzene	3.25e-11				1
1,3,5-Trimethyl Benzene	5.86e-11				1
Indene	7.80e-11				1
Indane	1.90e-11				1
b-Methyl Styrene	5.70e-11				1
$\alpha$ -methyl styrene	5.10e-11				1
Cis-hydrindane; Bicyclo[4.3.0]nonane	1.63e-11				6
2-Nonanone	1.22e-11				1
Di-isobutyl ketone (2,6-dimethyl-4-heptanone)	2.50e-11				1
2,3,5-trimethyl phenol	1.37e-10				1
2,3,6-trimethyl phenol	1.27e-10				1
butylal; dibutoxymethane	3.65e-11	5.20e-12	-1.153		1
n-Decane	1.31e-11	2.53e-12	-0.982	2	1
2,6-Dimethyl Octane	1.29e-11				1
2-Methyl Nonane	1.28e-11				1
3,4-Diethyl Hexane	6.92e-12				1
Butyl Cyclohexane	1.47e-11				1
1-Decene	4.61e-11				1
3-Carene	8.45e-11	2.55e-11	-0.709		1
a-Pinene	5.31e-11	1.34e-11	-0.815		1
b-Pinene	7.59e-11	1.62e-11	-0.914		1
d-Limonene	1.65e-10	3.41e-11	-0.934		1
Sabinene	1.17e-10				1
Beta-myrcene	2.15e-10				1
beta-ocimene (cis and trans)	2.52e-10				1
Terpinolene	2.20e-10				1
Camphene	5.19e-11	4.13e-12	-1.498		1
t-Butyl Benzene	4.50e-12				1
1-methyl-4-isopropylbenzene (p-cymene)	1.40e-11	1.82e-12	-1.206		1
1,2,3,4-tetramethyl benzene	6.56e-11	4.18e-12	-1.630		1
1,2,4,5-tetramethyl benzene	5.63e-11	1.31e-12	-2.226		1
1,2,3,5-tetramethyl benzene	6.27e-11	2.07e-11	-0.656		1
Tetralin	3.40e-11				1
Naphthalene	2.30e-11	1.55e-11	-0.233		1
Menthol	1.48e-11				1
Di-n-Pentyl Ether	3.30e-11	7.80e-12	-0.853		1
Citronellol (3,7-dimethy-6-octen-1-ol)	1.70e-10				1
a-terpineol	1.90e-10				1
Linalool	1.79e-10				1
Geraniol	2.30e-10				1
Camphor	4.10e-12				1
2-Decanone	1.32e-11				1
1,2-Diacetyl benzene	4.00e-12				1
n-Undecane	1.19e-11				1

Table S52 (continued)

Name	k(298)	A	Ea	B	Ref
1-Undecene	4.79e-11				1
pentamethyl benzene	1.07e-10	3.97e-12	-1.947		1
1-methyl naphthalene	4.70e-11				1
2-methyl naphthalene	5.05e-11				1
n-Dodecane	1.31e-11				1
Hexyl Cyclohexane	1.78e-11				1
1-Dodecene	5.03e-11				1
hexamethyl benzene	1.40e-10	2.07e-11	-1.133		1
2,3-Dimethyl Naphthalene	6.80e-11				1
1-ethyl naphthalene	3.50e-11				1
n-Tridecane	1.51e-11				1
1-Tridecene	5.09e-11				1
n-Tetradecane	1.67e-11				1
1-Tetradecene	4.96e-11				1
n-Pentadecane	1.92e-11				1
alpha-farnesene (mixed isomers)	2.20e-10				1
beta-farnesene (mixed isomers)	2.30e-10				1
beta-caryophyllene	2.00e-10				1
n-C16	2.16e-11				1

Temperature dependence, if assigned, given by  $k(T) = A \times \exp(-E_a/RT) \times (T/300)^B$ , where  $R=0.0019872$ . Units of  $k$  and  $A$  are  $\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$ . Units of  $E_a$  are kcal/mole and  $B$  is unitless. The "ref" column gives the sources for the rate constants, as follows:

- 1 From McGillen et al. (2020, 2021).
- 2 Falloff parameters:  $A_\infty=8.30\text{e-}13$ ,  $E_{a_\infty}=0\text{K}$ ,  $B_\infty=2.00$ ,  $A_0=5.50\text{e-}30$ ,  $E_{a_0}=0\text{K}$ ,  $B_0=0$ ,  $F=0.60$ ,  $N=1$ , based on the NASA (2015) evaluation.
- 3 Falloff parameters:  $A_\infty=8.40\text{e-}12$ ,  $E_{a_\infty}=0\text{K}$ ,  $B_\infty=-1.75$ ,  $A_0=1.10\text{e-}28$ ,  $E_{a_0}=0\text{K}$ ,  $B_0=-3.5$ ,  $F=0.60$ ,  $N=1$ , based on the NASA (2015) evaluation.
- 4 Rate constant used is that for the cis isomer since this is the isomer most likely to be formed. Rate constant from the compilation of McGillen et al. (2020, 2021).
- 5 Average of values for the cis and trans isomer from the compilation of McGillen et al. (2020, 2021).
- 6 Average of data for the cis and trans isomer from the compilation of McGillen et al. (2020, 2021).

Table S53. Assigned rate constants for the reactions of compounds with ozone.

Name	k(298)	A	Ea	B	Ref
Methylamine	7.40e-21				1
Ethene	1.54e-18	6.82e-15	4.968		1
Acetylene	1.00e-20				1
Dimethyl Amine	1.67e-18				1
Propene	1.05e-17	5.77e-15	3.736		1
1,2-propadiene (allene)	1.84e-19	1.54e-15	5.346		1
Methyl Acetylene	1.43e-20				1
Trimethyl Amine	7.84e-18				1
Acrolein	2.80e-19				1
Acrylic Acid	7.05e-19				1
1-Butene	9.96e-18	3.55e-15	3.478		1
Isobutene	1.15e-17	2.92e-15	3.279		1
cis-2-Butene	1.30e-16	3.37e-15	1.928		1
trans-2-Butene	1.99e-16	7.00e-15	2.106		1
1,3-Butadiene	6.28e-18	1.34e-14	4.537		1
Ethyl Acetylene	1.97e-20				1
Furan	2.40e-18				1
Methacrolein	1.21e-18	1.40e-15	4.173		1
Methylvinyl ketone	5.16e-18	8.50e-16	3.021		1
Dimethylaminoethanol	6.80e-18				1
Methacrylic Acid	3.00e-18				1
2-butene-1,4-dial	1.60e-18				1
Methacrolein's PAN	8.20e-18				1
1-Pentene	1.06e-17	2.13e-15	3.140		1
3-Methyl-1-Butene	7.30e-18	7.24e-14	5.447		1
2-Methyl-1-Butene	1.36e-17	6.18e-15	3.621		1
2-Methyl-2-Butene	4.03e-16	6.51e-15	1.647		1
cis-2-Pentene	1.28e-16	3.70e-15	1.991		1
trans-2-Pentene	1.59e-16	7.10e-15	2.250		1
Cyclopentene	5.59e-16	1.78e-15	0.686		1
1,4-Pentadiene	1.45e-17				1
Isoprene	1.27e-17	1.05e-14	3.974		1
2-Methyl-3-Butene-2-ol	1.00e-17				1
3-methyl furan	2.00e-17				1
4-oxo-2-penteneal	4.80e-18				1
1-Hexene	1.14e-17	2.30e-15	3.140		1
3,3-Dimethyl-1-Butene	3.77e-18	2.68e-15	3.887		1
3-Methyl-1-Pentene	3.80e-18				1
4-Methyl-1-Pentene	8.48e-18	4.72e-15	3.742		1
2,3-Dimethyl-1-Butene	1.00e-17				1
2-Ethyl-1-Butene	1.30e-17				1
2-Methyl-1-Pentene	1.60e-17				1
2,3-Dimethyl-2-Butene	1.10e-15	3.00e-15	0.596		1
Cis-2-Hexene	1.05e-16	3.20e-15	2.021		1
Cis-3-Hexene	1.44e-16				1
Cis-3-Methyl-2-Pentene	4.50e-16				1
Trans 3-Methyl-2-Pentene	5.60e-16				1
Trans-2-Hexene	1.53e-16	7.60e-15	2.311		1
Trans-3-Hexene	1.57e-16				1
1-Methyl cyclopentene	6.64e-16	1.80e-15	0.590		1
Cyclohexene	8.10e-17				1
cis-3-hexen-1-ol	7.21e-17				1
2,5-dimethyl furan	4.20e-16				1

Table S53 (continued)

Name	k(298)	A	Ea	B	Ref
3-hexene-2,5-dione	1.80e-18				2
1-Heptene	1.15e-17	4.20e-15	3.490		1
2,3,3-trimethyl-1-Butene	7.80e-18				1
1-Methyl Cyclohexene	1.46e-16	4.79e-15	2.067		1
4-Methyl Cyclohexene	7.31e-17				1
1-Octene	1.01e-17				1
3-Methyl-2-Isopropyl-1-Butene	3.00e-18				1
Cis-4-Octene	9.00e-17				1
Trans 2,5-Dimethyl 3-Hexene	3.80e-17				1
Trans-4-Octene	1.31e-16				1
Trans 2,2-Dimethyl 3-Hexene	4.00e-17				1
2,4,4-trimethyl-2-Pentene	1.32e-16				1
1,2-Dimethyl Cyclohexene	2.07e-16				1
Styrene	1.60e-17				1
cis-3-hexenyl acetate	5.84e-17				1
Indene	1.65e-16				1
1-Decene	1.11e-17				1
3,4-Diethyl-2-Hexene	4.00e-18				1
Cis-5-Decene	1.14e-16				1
3-Carene	4.80e-17				1
a-Pinene	9.58e-17	8.22e-16	1.272		1
b-Pinene	1.89e-17	1.39e-15	2.544		1
d-Limonene	2.19e-16	2.91e-15	1.530		1
Sabinene	8.30e-17				1

Temperature dependence, if assigned, given by  $k(T) = A \times \exp(-E_a/RT) \times (T/300)^B$ , where  $R=0.0019872$ . Units of k and A are  $\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$ . Units of Ea are kcal/mole and B is unitless. The "ref" column gives the sources for the rate constants, as follows:

- 1 From the compilation of McGillen et al. (2020, 2021).
- 2 Rate constant used is that for the cis isomer since this is the isomer most likely to be formed. Rate constant from the compilation of McGillen et al. (2020, 2021).



Table S54. Assigned rate constants for the reactions of compounds with NO<sub>3</sub> radicals.

Name	k(298)	A	Ea	B
Methanol	1.29e-16	9.40e-13	5.266	
Ethene	2.09e-16	3.30e-12	5.723	
Dimethyl Ether	1.86e-16	8.99e-13	5.020	
Acetaldehyde	2.72e-15	1.40e-12	3.696	
Glyoxal	4.00e-16			
Propane	9.20e-18			
Propene	9.52e-15	4.60e-13	2.295	
Methyl Acetylene	2.03e-16	1.25e-11	6.526	
Isopropyl Alcohol	1.40e-15			
Propionaldehyde	6.30e-15			
Acrolein	1.10e-15			
Methyl Glyoxal	5.00e-16			
n-Butane	1.50e-17			
Isobutane	1.04e-16	2.14e-12	5.880	
1-Butene	1.32e-14	3.20e-13	1.888	
Isobutene	3.40e-13			
cis-2-Butene	3.50e-13			
trans-2-Butene	3.90e-13			
1,3-Butadiene	1.10e-13			
Ethyl Acetylene	4.63e-16	3.21e-11	6.598	
2-Butyne	6.90e-14			
n-Butyl Alcohol	1.87e-15			
s-Butyl Alcohol	2.00e-15			
Tetrahydrofuran	5.76e-15	2.00e-9	7.551	
Diethyl Ether	3.22e-15	4.95e-12	4.344	
Furan	1.21e-12	1.15e-13	-1.391	
2-Methylpropanal	1.24e-14	1.67e-12	2.901	
Butanal	1.10e-14	1.70e-12	2.981	
Crotonaldehyde	5.62e-15			
Methacrolein	3.40e-15			
Methylvinyl ketone	1.30e-16			
1-Methoxy-2-Propanol	1.60e-15			
2-Ethoxyethanol	9.16e-15			
3H-furan-2-one	1.76e-13			
Methyl Acrylate	1.10e-16			
Vinyl Acetate	9.00e-15			
Methacrolein's PAN	1.60e-16			
n-Pentane	8.30e-17			
Iso-Pentane	1.70e-16	1.50e-12	5.379	
Cyclopentane	1.45e-16			
1-Pentene	1.50e-14			
3-Methyl-1-Butene	1.40e-14			
2-Methyl-1-Butene	5.00e-13			
2-Methyl-2-Butene	9.40e-12			
cis-2-Pentene	6.80e-13			
trans-2-Pentene	3.90e-13			
Cyclopentene	4.80e-13			
Trans 1,3-Pentadiene	1.80e-12			
1,4-Pentadiene	2.30e-14			
Isoprene	6.51e-13	2.95e-12	0.894	
isoamyl alcohol (3-methyl-1-butanol)	2.28e-15			
2-methyl-1-butanol	2.39e-15			
Methyl n-Butyl Ether	1.88e-15			

Table S54 (continued)

Name	k(298)	A	Ea	B
Methyl t-Butyl Ether	7.04e-16	2.50e-12	4.839	
2-Methyl-3-Butene-2-ol	1.20e-14	4.60e-14	0.795	
2-methyl furan	2.57e-11			
3-methyl furan	1.26e-11			
2,2-Dimethylpropanal (pivaldehyde)	2.40e-14			
3-Methylbutanal (Isovaleraldehyde)	2.17e-14	4.90e-11	4.571	
Pentanal (Valeraldehyde)	1.62e-14			
Ethyl vinyl ketone	9.90e-17			
Propyl Acetate	5.00e-17			
Ethyl Acrylate	1.60e-16			
Methyl Methacrylate	3.29e-15			
n-Hexane	1.10e-16			
2,3-Dimethyl Butane	4.24e-16			
2-Methyl Pentane	1.70e-16			
3-Methylpentane	2.05e-16			
Cyclohexane	1.35e-16			
1-Hexene	1.80e-14			
3,3-Dimethyl-1-Butene	1.50e-14			
3-Methyl-1-Pentene	1.30e-14			
4-Methyl-1-Pentene	1.30e-14			
2-Ethyl-1-Butene	4.50e-13			
2-Methyl-1-Pentene	4.40e-13			
2,3-Dimethyl-2-Butene	5.70e-11			
2-Methyl-2-Pentene	8.50e-12			
Cis-2-Hexene	5.50e-13			
Cis-3-Hexene	4.50e-13			
Cis-3-Methyl-2-Pentene	8.50e-12			
Trans 3-Methyl-2-Pentene	8.10e-12			
Trans-2-Hexene	3.90e-13			
Trans-3-Hexene	3.70e-13			
Cyclohexene	5.60e-13	5.83e-12	1.387	
Di n-Propyl Ether	6.05e-15	3.20e-12	3.712	
Ethyl t-Butyl Ether	8.54e-15	1.92e-12	3.205	
Methyl t-Amyl Ether	2.18e-15	1.06e-12	3.662	
diisopropyl ether	5.14e-15	1.97e-12	3.521	
cis-3-hexen-1-ol	2.70e-13			
2,5-dimethyl furan	5.80e-11			
Hexanal	1.61e-14			
mesityl oxide (2-methyl-2-penten-4-one)	1.44e-13			
Phenol	4.50e-12			
2-Butoxyethanol	3.10e-15			
Ethyl Methacrylate	4.79e-15			
n-Heptane	1.40e-16			
2,2,3-Trimethyl Butane	2.20e-16			
2,4-Dimethyl Pentane	1.45e-16			
1-Heptene	2.00e-14			
3,4-dimethyl-1-pentene	1.40e-14			
3-methyl-1-hexene	1.60e-14			
2-methyl-1-hexene	5.30e-13			
3,3-dimethyl-1-pentene	1.40e-14			
1-Methyl Cyclohexene	9.31e-12	9.69e-13	-1.339	
Toluene	6.60e-17			
Heptanal	1.97e-14			
Benzaldehyde	4.00e-15			

Table S54 (continued)

Name	k(298)	A	Ea	B
m-cresol	1.00e-11			
p-cresol	1.10e-11			
o-Cresol	1.40e-11			
Benzyl alcohol	4.00e-15			
Methoxybenzene; Anisole	1.50e-16			
n-butyl acrylate	1.90e-16			
n-Octane	1.90e-16			
2,2,4-Trimethyl Pentane	7.50e-17			
1-Octene	2.50e-14			
1,2-Dimethyl Cyclohexene	5.10e-12			
m-Xylene	2.30e-16			
o-Xylene	3.90e-16			
p-Xylene	4.60e-16			
Styrene	1.50e-12			
2-Ethyl-1-Hexanol	2.93e-15			
Octanal	1.80e-14			
2,3-dimethyl phenol	2.97e-11			
2,4-dimethyl phenol	3.12e-11			
2,5-dimethyl phenol	3.07e-11			
2,6-dimethyl phenol	5.01e-11			
3,4-dimethyl phenol	2.55e-11			
Butyl Methacrylate	5.71e-15			
Isobutyl Methacrylate	6.02e-15			
cis-3-hexenyl acetate	2.46e-13			
n-Nonane	2.20e-16			
p-Ethyl Toluene	8.00e-16			
1,2,3-Trimethyl Benzene	1.76e-15			
1,2,4-Trimethyl Benzene	1.72e-15			
1,3,5-Trimethyl Benzene	8.20e-16			
Indene	4.10e-12			
Indane	7.40e-15			
n-Decane	2.60e-16			
1-Decene	2.60e-14			
3-Carene	9.00e-12			
a-Pinene	6.22e-12	1.20e-12	-0.974	
b-Pinene	2.50e-12			
d-Limonene	1.20e-11			
Sabinene	1.00e-11			
Beta-myrcene	1.10e-11			
beta-ocimene (cis and trans)	2.20e-11			
Terpinolene	9.70e-11			
Camphene	6.60e-13			
1-methyl-4-isopropylbenzene (p-cymene)	1.00e-15			
Tetralin	1.11e-14			
Citronellol (3,7-dimethy-6-octen-1-ol)	1.15e-11			
a-terpineol	1.60e-11			
Linalool	1.10e-11			
Geraniol	1.60e-11			
1-Dodecene	2.80e-14			
1-Tetradecene	2.80e-14			
beta-caryophyllene	1.90e-11			

Table S54 (continued)

Temperature dependence, if assigned, given by  $k(T) = A \times \exp(-E_a/RT) \times (T/300)^B$ , where  $R=0.0019872$ . Units of  $k$  and  $A$  are  $\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$ . Units of  $E_a$  are kcal/mole and  $B$  is unitless. All rate constants are from McGillen et al. (2020, 2021).

Table S55. Assigned rate constants for the reactions of compounds with O<sup>3</sup>P.

Name	k(298)	A	Ea	Ref
Methylamine	5.56e-13	9.02e-12	1.649	1
Acetylene	1.40e-13	3.01e-11	3.180	2
Ethene	7.29e-13	1.07e-11	1.590	3
Dimethyl Amine	6.00e-12	1.52e-11	0.550	1
Ethyl Amine	1.31e-12	1.13e-11	1.276	1
1,2-propadiene (allene)	1.20e-12	2.72e-11	1.848	3
Methyl Acetylene	8.96e-13	2.66e-11	2.007	2
Propene	3.98e-12	1.02e-11	0.556	3
Acrolein	3.99e-13	2.32e-11	2.405	4
Trimethyl Amine	2.18e-11	1.08e-11	-0.415	1
1,2-Butadiene	5.80e-12			3
1,3-Butadiene	1.98e-11	2.26e-11	0.079	3
2-Butyne	8.60e-12			2
1-Butene	4.14e-12	1.34e-11	0.696	3
Isobutene	1.69e-11	1.14e-11	-0.233	3
cis-2-Butene	1.76e-11	1.10e-11	-0.278	3
trans-2-Butene	1.99e-11	1.09e-11	-0.358	3
Isoprene	3.50e-11			3
Cyclopentene	2.10e-11	2.40e-11	0.079	3
1,2-Pentadiene	7.40e-12			3
2,3-Pentadiene	1.60e-11			3
1-Pentene	4.65e-12	1.78e-11	0.795	3
3-Methyl-1-Butene	4.16e-12	1.03e-11	0.537	3
2-Methyl-1-Butene	1.80e-11			3
2-Methyl-2-Butene	5.11e-11	2.44e-11	-0.437	3
cis-2-Pentene	1.71e-11	1.14e-11	-0.238	3
trans-2-Pentene	2.10e-11	1.15e-11	-0.358	3
Cyclohexene	2.00e-11	2.21e-11	0.060	3
3,3-Dimethyl-1-Butene	4.80e-12			3
2,3-Dimethyl-2-Butene	7.69e-11	2.81e-11	-0.596	3
1-Hexene	4.98e-12	1.51e-11	0.656	3
1-Methyl Cyclohexene	9.00e-11			5
3-Carene	3.20e-11			3
a-Pinene	3.20e-11			3
b-Pinene	2.70e-11			3
d-Limonene	7.20e-11			3

Temperature dependence, if assigned, given by  $k(T) = A \times \exp(-E_a/RT)$ , where  $R=0.0019872$ . Units of  $k$  and  $A$  are  $\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$ . Units of  $E_a$  are kcal/mole. The "ref" column gives the sources for the rate constants, as follows:

- 1 From Atkinson and Pitts (1978).
- 2 From NIST (2014) database.
- 3 Rate constant recommended by Calvert et al. (2000).
- 4 From Calvert et al. (2011).
- 5 Rate constant from Atkinson (1997). Temperature dependence is expected to be small.

Table S56. Rate constants assigned for the reactions of radicals.

Reaction	k(298)	A	Ea	Ref
$\text{CH}_3\text{O}\cdot + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2\cdot$	1.59e-15	7.37e-14	2.271	1
$\text{CH}_3\text{CH}_2\text{O}\cdot \rightarrow \text{HCHO} + \text{CH}_3\cdot$	3.58e+0	5.00e+13	17.915	2
$\text{CH}_3\text{CH}_2\text{O}\cdot + \text{O}_2 \rightarrow \text{CH}_3\text{CHO} + \text{HO}_2\cdot$	8.09e-15	5.13e-14	1.093	1
$\text{HC(O)CH}_2\text{O}\cdot \rightarrow \text{HCHO} + \text{HCO}\cdot$	9.22e+5	5.00e+13	10.541	3
$\text{CH}_3\text{CH(O}\cdot\text{)OH} \rightarrow \text{HC(O)OH} + \text{CH}_3\cdot$	1.77e+6	5.00e+13	10.154	3
$\text{CH}_3\text{C(O}\cdot\text{)(OH)OH} \rightarrow \text{HOC(O)OH} + \text{CH}_3\cdot$	1.97e+8	5.00e+13	7.367	3
$\text{CH}_3\text{CH(O}\cdot\text{)OOH} \rightarrow \text{HC(O)OOH} + \text{CH}_3\cdot$	7.09e+5	5.00e+13	10.696	3
$\text{HOCH}_2\text{CH(O}\cdot\text{)OH} \rightarrow \text{HC(O)OH} + \cdot\text{CH}_2\text{OH}$	2.48e+10	5.00e+13	4.503	3
$\cdot\text{OCH}_2\text{CH}_2\text{OOH} \rightarrow \text{HCHO} + \cdot\text{CH}_2\text{OOH}$	2.02e+6	5.00e+13	10.076	3
$\cdot\text{OCH}_2\text{CH}_2\text{-NO}_2 \rightarrow \text{HCHO} + \cdot\text{CH}_2\text{-NO}_2$	2.20e+0	5.00e+13	18.204	3
$\text{CH}_3\text{CH(O}\cdot\text{)ONO}_2 \rightarrow \text{HCO-ONO}_2 + \text{CH}_3\cdot$	5.34e+2	5.00e+13	14.953	3
$\cdot\text{OCH}_2\text{CH}_2\text{ONO}_2 \rightarrow \text{HCHO} + \cdot\text{CH}_2\text{ONO}_2$	3.61e+2	5.00e+13	15.185	3
$\text{CH}_3\text{CH(O}\cdot\text{)CH}_3 \rightarrow \text{CH}_3\text{CHO} + \text{CH}_3\cdot$	3.58e+2	1.00e+14	15.599	2
$\text{CH}_3\text{CH(O}\cdot\text{)CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{C(O)CH}_3 + \text{HO}_2\cdot$	6.89e-15	1.95e-14	0.616	1
$\text{CH}_3\text{CH}_2\text{CH}_2\text{O}\cdot \rightarrow \text{HCHO} + \text{CH}_3\text{CH}_2\cdot$	2.91e+2	5.00e+13	15.312	2
$\text{CH}_3\text{CH}_2\text{CH}_2\text{O}\cdot + \text{O}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CHO} + \text{HO}_2\cdot$	1.10e-14	2.38e-14	0.457	1
$\text{CH}_3\text{CH(O}\cdot\text{)CHO} \rightarrow \text{HC(O)CHO} + \text{CH}_3\cdot$	2.03e+1	5.00e+13	16.888	3
$\text{CH}_3\text{CH(O}\cdot\text{)CHO} \rightarrow \text{CH}_3\text{CHO} + \text{HCO}\cdot$	1.11e+7	5.00e+13	9.070	3
$\text{CH}_3\text{C(O)CH}_2\text{O}\cdot \rightarrow \text{HCHO} + \text{CH}_3\text{C(O)}\cdot$	2.68e+7	5.00e+13	8.546	2
$\text{CH}_3\text{C(O}\cdot\text{)(CH}_3\text{)OH} \rightarrow \text{CH}_3\text{C(O)OH} + \text{CH}_3\cdot$	8.86e+6	1.00e+14	9.612	3
$\text{CH}_3\text{CH(O}\cdot\text{)OCH}_3 \rightarrow \text{CH}_3\text{OCHO} + \text{CH}_3\cdot$	1.56e+6	5.00e+13	10.231	3
$\text{CH}_3\text{CH(O}\cdot\text{)CH}_2\text{OH} \rightarrow \text{HC(O)CH}_2\text{OH} + \text{CH}_3\cdot$	1.64e+2	5.00e+13	15.650	3
$\text{CH}_3\text{CH(O}\cdot\text{)CH}_2\text{OH} \rightarrow \text{CH}_3\text{CHO} + \cdot\text{CH}_2\text{OH}$	4.97e+7	5.00e+13	8.181	2
$\text{CH}_3\text{CH}_2\text{CH(O}\cdot\text{)OH} \rightarrow \text{HC(O)OH} + \text{CH}_3\text{CH}_2\cdot$	1.16e+8	5.00e+13	7.677	3
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{O}\cdot \rightarrow \text{HCHO} + \text{CH}_3\text{OCH}_2\cdot$	9.22e+5	5.00e+13	10.541	3
$\text{CH}_3\text{CH(CH}_2\text{O}\cdot\text{)OH} \rightarrow \text{HCHO} + \text{CH}_3\text{CH}(\cdot\text{)OH}$	4.97e+7	5.00e+13	8.181	2
$\text{CH}_3\text{CH(O}\cdot\text{)OOCH}_3 \rightarrow \text{CH}_3\text{OOCHO} + \text{CH}_3\cdot$	4.56e+4	5.00e+13	12.321	3
$\text{CH}_3\text{CH(O}\cdot\text{)CH}_2\text{OOH} \rightarrow \text{HC(O)CH}_2\text{OOH} + \text{CH}_3\cdot$	1.78e+1	5.00e+13	16.966	3
$\text{CH}_3\text{CH(O}\cdot\text{)CH}_2\text{OOH} \rightarrow \text{CH}_3\text{CHO} + \cdot\text{CH}_2\text{OOH}$	6.91e+7	5.00e+13	7.986	3
$\text{CH}_3\text{CH}_2\text{CH(O}\cdot\text{)OOH} \rightarrow \text{HC(O)OOH} + \text{CH}_3\text{CH}_2\cdot$	1.51e+8	5.00e+13	7.522	3
$\text{CH}_3\text{OOCH}_2\text{CH}_2\text{O}\cdot \rightarrow \text{HCHO} + \text{CH}_3\text{OOCH}_2\cdot$	1.92e+5	5.00e+13	11.470	3
$\text{CH}_3\text{CH(CH}_2\text{O}\cdot\text{)OOH} \rightarrow \text{HCHO} + \text{CH}_3\text{CH}(\cdot\text{)OOH}$	2.76e+7	5.00e+13	8.528	3
$\text{CH}_3\text{C(O}\cdot\text{)(CH}_3\text{)OOH} \rightarrow \text{CH}_3\text{C(O)OOH} + \text{CH}_3\cdot$	1.31e+7	1.00e+14	9.380	3
$\text{CH}_3\text{CH(CH}_2\text{O}\cdot\text{)NO}_2 \rightarrow \text{HCHO} + \text{CH}_3\text{CH}(\cdot\text{)NO}_2$	6.93e+2	5.00e+13	14.798	3
$\text{CH}_3\text{CH}_2\text{CH(O}\cdot\text{)ONO}_2 \rightarrow \text{HCO-ONO}_2 + \text{CH}_3\text{CH}_2\cdot$	1.48e+5	5.00e+13	11.625	3
$\text{CH}_3\text{CH(CH}_2\text{O}\cdot\text{)ONO}_2 \rightarrow \text{HCHO} + \text{CH}_3\text{CH}(\cdot\text{)ONO}_2$	1.82e+4	5.00e+13	12.863	3
$\text{CH}_2=\text{CH-CH(O}\cdot\text{)CH}_3 \rightarrow \text{CH}_2=\text{CH-CHO} + \text{CH}_3\cdot$	3.79e+3	5.00e+13	13.792	3
$\text{CH}_2=\text{CH-CH(O}\cdot\text{)CH}_3 \rightarrow \text{CH}_3\text{CHO} + \text{CH}_2=\text{CH}\cdot$	2.08e-1	5.00e+13	19.598	3
$\text{CH}_2=\text{CH-CH}_2\text{CH}_2\text{O}\cdot \rightarrow \text{HCHO} + \text{CH}_2=\text{CH-CH}_2\cdot$	2.02e+6	5.00e+13	10.076	3
$\text{CH}_2^*\text{CH}_2\text{CH(O}\cdot\text{)CH}_2^* \rightarrow \cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$	7.95e+9	1.00e+14	5.587	3

Table S56 (continued)

Reaction	k(298)	A	Ea	Ref
$\cdot\text{OCH}_2\text{CH}^*\text{CH}_2\text{CH}_2^* \rightarrow \text{HCHO} + \text{CH}_2^*\text{CH}_2\text{CH}(\cdot)^*$	1.24e-1	5.00e+13	19.907	3
$\text{CH}_3\text{CH}_2\text{CH}(\text{O}\cdot)\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CHO} + \text{CH}_3\cdot$	3.84e+1	5.00e+13	16.510	2
$\text{CH}_3\text{CH}_2\text{CH}(\text{O}\cdot)\text{CH}_3 \rightarrow \text{CH}_3\text{CHO} + \text{CH}_3\text{CH}_2\cdot$	2.72e+4	5.00e+13	12.626	2
$\text{CH}_3\text{CH}_2\text{CH}(\text{O}\cdot)\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{CH}_2\text{C}(\text{O})\text{CH}_3 + \text{HO}_2\cdot$	7.75e-15			4
$\text{CH}_3\text{C}(\text{O}\cdot)(\text{CH}_3)\text{CH}_3 \rightarrow \text{CH}_3\text{C}(\text{O})\text{CH}_3 + \text{CH}_3\cdot$	2.47e+3	1.50e+14	14.697	2
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{O}\cdot \rightarrow \text{HCHO} + \text{CH}_3\text{CH}_2\text{CH}_2\cdot$	2.50e+2	5.00e+13	15.402	2
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{O}\cdot + \text{O}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CHO} + \text{HO}_2\cdot$	1.40e-14			5
$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{O}\cdot \rightarrow \text{HCHO} + \text{CH}_3\text{CH}(\cdot)\text{CH}_3$	5.65e+4	5.00e+13	12.194	2
$\text{CH}_3\text{C}(\text{O}\cdot)(\text{CH}_3)\text{CHO} \rightarrow \text{CH}_3\text{C}(\text{O})\text{CHO} + \text{CH}_3\cdot$	2.34e+3	1.00e+14	14.489	3
$\text{CH}_3\text{C}(\text{O}\cdot)(\text{CH}_3)\text{CHO} \rightarrow \text{CH}_3\text{C}(\text{O})\text{CH}_3 + \text{HCO}\cdot$	1.97e+8	5.00e+13	7.367	3
$\text{CH}_3\text{C}(\text{O})\text{CH}(\text{O}\cdot)\text{CH}_3 \rightarrow \text{CH}_3\text{C}(\text{O})\text{CHO} + \text{CH}_3\cdot$	9.25e+0	5.00e+13	17.353	3
$\text{CH}_3\text{C}(\text{O})\text{CH}(\text{O}\cdot)\text{CH}_3 \rightarrow \text{CH}_3\text{CHO} + \text{CH}_3\text{C}(\text{O})\cdot$	2.24e+8	5.00e+13	7.290	3
$\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{CH}_2\text{O}\cdot \rightarrow \text{HCHO} + \text{CH}_3\text{CH}_2\text{C}(\text{O})\cdot$	2.76e+7	5.00e+13	8.528	3
$\text{CH}_3\text{CH}_2\text{OCH}(\text{O}\cdot)\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{OCHO} + \text{CH}_3\cdot$	4.96e+5	5.00e+13	10.908	2
$\text{CH}_3\text{C}(\text{O}\cdot)(\text{CH}_3)\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{C}(\text{O})\text{CH}_2\text{OH} + \text{CH}_3\cdot$	8.64e+3	1.00e+14	13.715	3
$\text{CH}_3\text{C}(\text{O}\cdot)(\text{CH}_3)\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{C}(\text{O})\text{CH}_3 + \cdot\text{CH}_2\text{OH}$	3.59e+7	5.00e+13	8.373	3
$\text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}(\text{CH}_3)\text{OH} \rightarrow \text{CH}_3\text{CH}(\text{CHO})\text{OH} + \text{CH}_3\cdot$	1.64e+2	5.00e+13	15.650	3
$\text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}(\text{CH}_3)\text{OH} \rightarrow \text{CH}_3\text{CHO} + \text{CH}_3\text{CH}(\cdot)\text{OH}$	3.32e+8	5.00e+13	7.057	3
$\text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}_2\text{OCH}_3 \rightarrow \text{CH}_3\text{OCH}_2\text{CHO} + \text{CH}_3\cdot$	1.78e+1	5.00e+13	16.966	3
$\text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}_2\text{OCH}_3 \rightarrow \text{CH}_3\text{CHO} + \text{CH}_3\text{OCH}_2\cdot$	1.26e+7	5.00e+13	8.993	3
$\text{CH}_3\text{CH}_2\text{CH}(\text{O}\cdot)\text{OCH}_3 \rightarrow \text{CH}_3\text{OCHO} + \text{CH}_3\text{CH}_2\cdot$	1.33e+8	5.00e+13	7.599	3
$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}\cdot \rightarrow \text{HCHO} + \text{CH}_3\text{CH}_2\text{OCH}_2\cdot$	9.22e+5	5.00e+13	10.541	3
$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_2\text{O}\cdot)\text{OH} \rightarrow \text{HCHO} + \text{CH}_3\text{CH}_2\text{CH}(\cdot)\text{OH}$	6.55e+6	5.00e+13	9.380	3
$\text{CH}_3\text{C}(\text{CH}_3)(\text{CH}_2\text{O}\cdot)\text{OH} \rightarrow \text{HCHO} + \text{CH}_3\text{C}(\cdot)(\text{CH}_3)\text{OH}$	1.97e+8	5.00e+13	7.367	3
$\text{CH}_3\text{C}(\text{O}\cdot)(\text{CH}_3)\text{OCH}_3 \rightarrow \text{CH}_3\text{C}(\text{O})\text{OCH}_3 + \text{CH}_3\cdot$	9.92e+5	1.00e+14	10.908	2
$\text{CH}_3\text{CH}(\text{CH}_2\text{O}\cdot)\text{OCH}_3 \rightarrow \text{HCHO} + \text{CH}_3\text{CH}(\cdot)\text{OCH}_3$	1.33e+8	5.00e+13	7.599	3
$\text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}_2\text{OOCH}_3 \rightarrow \text{CH}_3\text{OOCH}_2\text{CHO} + \text{CH}_3\cdot$	2.64e+1	5.00e+13	16.733	3
$\text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}_2\text{OOCH}_3 \rightarrow \text{CH}_3\text{CHO} + \text{CH}_3\text{OOCH}_2\cdot$	2.99e+6	5.00e+13	9.844	3
$\text{CH}_3\text{CH}_2\text{CH}(\text{O}\cdot)\text{OOCH}_3 \rightarrow \text{CH}_3\text{OOCHO} + \text{CH}_3\text{CH}_2\cdot$	5.75e+6	5.00e+13	9.457	3
$\text{CH}_3\text{C}(\text{O}\cdot)(\text{CH}_3)\text{OOCH}_3 \rightarrow \text{CH}_3\text{C}(\text{O})\text{OOCH}_3 + \text{CH}_3\cdot$	3.37e+5	1.00e+14	11.547	3
$\text{CH}_3\text{CH}(\text{CH}_2\text{O}\cdot)\text{OOCH}_3 \rightarrow \text{HCHO} + \text{CH}_3\text{CH}(\cdot)\text{OOCH}_3$	1.56e+6	5.00e+13	10.231	3
$\text{CH}_3\text{C}(\text{O}\cdot)^*\text{CH}_2\text{CH}_2\text{CH}_2^* \rightarrow \text{CH}_2^*\text{CH}_2\text{C}(\text{O})\text{CH}_2^* + \text{CH}_3\cdot$	7.51e+1	5.00e+13	16.114	3
$\text{CH}_3\text{C}(\text{O}\cdot)^*\text{CH}_2\text{CH}_2\text{CH}_2^* \rightarrow \text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\cdot$	1.74e+10	1.00e+14	5.122	3
$\text{CH}_2^*\text{CH}_2\text{CH}_2\text{CH}(\text{O}\cdot)\text{CH}_2^* \rightarrow \cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$	4.04e+6	1.00e+14	10.076	3
$\text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}^*\text{CH}_2\text{CH}_2^* \rightarrow \text{CH}_3\text{CHO} + \text{CH}_2^*\text{CH}_2\text{CH}(\cdot)^*$	1.37e+1	5.00e+13	17.121	3
$\cdot\text{OCH}_2\text{CH}^*\text{CH}_2\text{CH}_2\text{CH}_2^* \rightarrow \text{HCHO} + \text{CH}_2^*\text{CH}_2\text{CH}(\cdot)\text{CH}_2^*$	6.08e+2	5.00e+13	14.876	3
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{O}\cdot)\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CHO} + \text{CH}_3\cdot$	4.78e+1	5.00e+13	16.381	2
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{O}\cdot)\text{CH}_3 \rightarrow \text{CH}_3\text{CHO} + \text{CH}_3\text{CH}_2\text{CH}_2\cdot$	1.43e+4	5.00e+13	13.005	2
$\text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}(\text{CH}_3)\text{CH}_3 \rightarrow \text{CH}_3\text{CH}(\text{CH}_3)\text{CHO} + \text{CH}_3\cdot$	1.88e+2	5.00e+13	15.572	3
$\text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}(\text{CH}_3)\text{CH}_3 \rightarrow \text{CH}_3\text{CHO} + \text{CH}_3\text{CH}(\cdot)\text{CH}_3$	2.02e+6	5.00e+13	10.076	3
$\text{CH}_3\text{CH}_2\text{C}(\text{O}\cdot)(\text{CH}_3)\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{C}(\text{O})\text{CH}_3 + \text{CH}_3\cdot$	1.09e+4	1.00e+14	13.579	2
$\text{CH}_3\text{CH}_2\text{C}(\text{O}\cdot)(\text{CH}_3)\text{CH}_3 \rightarrow \text{CH}_3\text{C}(\text{O})\text{CH}_3 + \text{CH}_3\text{CH}_2\cdot$	9.31e+5	5.00e+13	10.535	2
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}\cdot \rightarrow \text{HCHO} + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\cdot$	4.11e+2	5.00e+13	15.108	3

Table S56 (continued)

Reaction	k(298)	A	Ea	Ref
$\text{CH}_3\text{CH}_2\text{CH}(\text{O}\cdot)\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CHO} + \text{CH}_3\text{CH}_2\cdot$	2.69e+4	1.00e+14	13.042	2
$\text{CH}_3\text{CH}_2\text{CH}(\text{O}\cdot)\text{CH}_2\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{CH}_2\text{C}(\text{O})\text{CH}_2\text{CH}_3 + \text{HO}_2\cdot$	7.20e-15			6
$\text{CH}_3\text{C}(\text{CH}_3)(\text{CH}_3)\text{CH}_2\text{O}\cdot \rightarrow \text{HCHO} + \text{CH}_3\text{C}(\cdot)(\text{CH}_3)\text{CH}_3$	1.88e+6	5.00e+13	10.118	2
$\text{CH}_3\text{CH}_2\text{C}(\text{O}\cdot)(\text{CH}_3)\text{OCH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{C}(\text{O})\text{OCH}_3 + \text{CH}_3\cdot$	9.91e+5	5.00e+13	10.498	2
$\text{CH}_3\text{CH}(\text{OH})\text{C}(\text{O}\cdot)(\text{CH}_3)\text{CH}_3 \rightarrow \text{CH}_3\text{C}(\text{O})\text{CH}(\text{CH}_3)\text{OH} + \text{CH}_3\cdot$	8.11e+3	1.00e+14	13.753	3
$\text{CH}_3\text{CH}(\text{OH})\text{C}(\text{O}\cdot)(\text{CH}_3)\text{CH}_3 \rightarrow \text{CH}_3\text{C}(\text{O})\text{CH}_3 + \text{CH}_3\text{CH}(\cdot)\text{OH}$	2.36e+9	5.00e+13	5.896	3
$\text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}_2\text{CH}_2\text{OCH}_3 \rightarrow \text{CH}_3\text{CHO} + \text{CH}_3\text{OCH}_2\text{CH}_2\cdot$	1.98e+4	5.00e+13	12.815	2
$\text{CH}_3\text{C}(\text{CH}_3)(\text{CH}_2\text{O}\cdot)\text{OCH}_3 \rightarrow \text{HCHO} + \text{CH}_3\text{C}(\cdot)(\text{CH}_3)\text{OCH}_3$	1.99e+7	5.00e+13	8.724	2
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{O}\cdot)\text{OCH}_3 \rightarrow \text{CH}_3\text{OCHO} + \text{CH}_3\text{CH}_2\text{CH}_2\cdot$	3.98e+7	5.00e+13	8.313	2
$\text{CH}_3\text{C}(\text{O}\cdot)^*\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2^* \rightarrow \text{CH}_2^*\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{CH}_2^* + \text{CH}_3\cdot$	9.75e+1	5.00e+13	15.959	3
$\text{CH}_3\text{C}(\text{O}\cdot)^*\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2^* \rightarrow \text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot$	6.82e+6	1.00e+14	9.767	3
$\text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}^*\text{CH}_2\text{CH}_2\text{CH}_2^* \rightarrow \text{HC}(\text{O})\text{CH}^*\text{CH}_2\text{CH}_2\text{CH}_2^* + \text{CH}_3\cdot$	4.68e+2	5.00e+13	15.031	3
$\text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}^*\text{CH}_2\text{CH}_2\text{CH}_2^* \rightarrow \text{CH}_3\text{CHO} + \text{CH}_2^*\text{CH}_2\text{CH}(\cdot)\text{CH}_2^*$	8.76e+4	5.00e+13	11.934	3
$\text{CH}_2^*\text{CH}_2\text{CH}_2\text{CH}(\text{O}\cdot)\text{CH}_2\text{CH}_2^* \rightarrow \cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$	4.95e+4	1.00e+14	12.682	2
$\text{CH}_3\text{CH}_2\text{C}(\text{O}\cdot)^*\text{CH}_2\text{CH}_2\text{CH}_2^* \rightarrow \text{CH}_2^*\text{CH}_2\text{C}(\text{O})\text{CH}_2^* + \text{CH}_3\text{CH}_2\cdot$	9.48e+3	5.00e+13	13.250	3
$\text{CH}_3\text{CH}_2\text{C}(\text{O}\cdot)^*\text{CH}_2\text{CH}_2\text{CH}_2^* \rightarrow \text{CH}_3\text{CH}_2\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\cdot$	2.94e+10	1.00e+14	4.813	3
$\cdot\text{OCH}_2\text{CH}^*\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2^* \rightarrow \text{HCHO} + \text{CH}_2^*\text{CH}_2\text{CH}_2\text{CH}(\cdot)\text{CH}_2^*$	6.74e+4	5.00e+13	12.089	3
$\text{CH}_3\text{CH}(\text{O}\cdot)\text{C}(\text{CH}_3)(\text{CH}_3)\text{CH}_3 \rightarrow \text{CH}_3\text{C}(\text{CH}_3)(\text{CH}_3)\text{CHO} + \text{CH}_3\cdot$	2.78e+2	5.00e+13	15.340	3
$\text{CH}_3\text{CH}(\text{O}\cdot)\text{C}(\text{CH}_3)(\text{CH}_3)\text{CH}_3 \rightarrow \text{CH}_3\text{CHO} + \text{CH}_3\text{C}(\cdot)(\text{CH}_3)\text{CH}_3$	8.96e+7	5.00e+13	7.832	3
$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{O}\cdot)(\text{CH}_3)\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{CH}_3 + \text{CH}_3\cdot$	3.47e+3	1.00e+14	14.256	3
$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{O}\cdot)(\text{CH}_3)\text{CH}_3 \rightarrow \text{CH}_3\text{C}(\text{O})\text{CH}_3 + \text{CH}_3\text{CH}_2\text{CH}_2\cdot$	2.49e+5	5.00e+13	11.315	3
$\text{CH}_3\text{CH}(\text{CH}_3)\text{C}(\text{O}\cdot)(\text{CH}_3)\text{CH}_3 \rightarrow \text{CH}_3\text{C}(\text{O})\text{CH}(\text{CH}_3)\text{CH}_3 + \text{CH}_3\cdot$	5.13e+3	1.00e+14	14.024	3
$\text{CH}_3\text{CH}(\text{CH}_3)\text{C}(\text{O}\cdot)(\text{CH}_3)\text{CH}_3 \rightarrow \text{CH}_3\text{C}(\text{O})\text{CH}_3 + \text{CH}_3\text{CH}(\cdot)\text{CH}_3$	1.87e+7	5.00e+13	8.760	3
$\text{CH}_3\text{C}(\text{O}\cdot)(\text{CH}_3)\text{C}(\text{CH}_3)(\text{CH}_3)\text{OH} \rightarrow \text{CH}_3\text{C}(\text{O})\text{C}(\text{CH}_3)(\text{CH}_3)\text{OH} + \text{CH}_3\cdot$	6.66e+3	1.00e+14	13.869	3
$\text{CH}_3\text{C}(\text{O}\cdot)(\text{CH}_3)\text{C}(\text{CH}_3)(\text{CH}_3)\text{OH} \rightarrow \text{CH}_3\text{C}(\text{O})\text{CH}_3 + \text{CH}_3\text{C}(\cdot)(\text{CH}_3)\text{OH}$	9.94e+9	5.00e+13	5.045	3
$\text{CH}_3\text{CH}(\text{O}\cdot)\text{OC}(\text{CH}_3)(\text{CH}_3)\text{CH}_3 \rightarrow \text{CH}_3\text{C}(\text{CH}_3)(\text{CH}_3)\text{OCHO} + \text{CH}_3\cdot$	1.98e+5	5.00e+13	11.451	2
$\text{CH}_3\text{C}(\text{O}\cdot)^*\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2^* \rightarrow \text{CH}_2^*\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{CH}_2\text{CH}_2^* + \text{CH}_3\cdot$	9.75e+1	5.00e+13	15.959	3
$\text{CH}_3\text{C}(\text{O}\cdot)^*\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2^* \rightarrow \text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot$	4.99e+5	1.00e+14	11.315	3
$\cdot\text{OCH}_2\text{CH}^*\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2^* \rightarrow \text{HCHO} + \text{CH}_2^*\text{CH}_2\text{CH}_2\text{CH}(\cdot)\text{CH}_2\text{CH}_2^*$	6.74e+4	5.00e+13	12.089	3
$\text{CH}_3\text{C}(\text{O}\cdot)(\text{CH}_3)\text{C}(\text{CH}_3)(\text{CH}_3)\text{CH}_3 \rightarrow \text{CH}_3\text{C}(\text{O})\text{C}(\text{CH}_3)(\text{CH}_3)\text{CH}_3 + \text{CH}_3\cdot$	4.50e+3	1.00e+14	14.102	3
$\text{CH}_3\text{C}(\text{O}\cdot)(\text{CH}_3)\text{C}(\text{CH}_3)(\text{CH}_3)\text{CH}_3 \rightarrow \text{CH}_3\text{C}(\text{O})\text{CH}_3 + \text{CH}_3\text{C}(\cdot)(\text{CH}_3)\text{CH}_3$	4.30e+8	5.00e+13	6.903	3

Temperature dependence, if assigned, given by  $k(T) = A \times \exp(-E_a/RT)$ , where  $R=0.0019872$ . Units of  $k$  and  $A$  are  $\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$ . Units of  $E_a$  are kcal/mole. The "ref" column gives the sources for the rate constants, as follows:

- 1 Rate constant parameters from Calvert et al. (2008).
- 2 Average of estimated 298K rate constants tabulated in Tables 1 and 2 by Orlando et al. (2003). Data from previous studies that disagreed with more recent data are not used in the averages, nor are data for radicals estimated to have non-negligible isomerization reactions. A factors are estimated to be  $5 \times 10^{-13} \text{sec}^{-1} \times$  reaction degeneracy, as recommended by Atkinson (2007).
- 3 Derived from Eb(DFT) values tabulated in Table 2 of Vereecken and Peeters (2009), calculated using the B3LYP/6-31G(d,p) level of theory. These are used to estimate activation energies by using a linear fit between the activation energies derived from the data tabulated by Orlando et al. (2003) assuming an A factor of  $5 \times 10^{-13} \text{sec}^{-1} \times$  the reaction degeneracy recommended by Atkinson (2007). The 298 K rate constant is derived from these estimated activation energies and A factors.
- 4 Rate constant is average of room temperature measurements of Hein et al. (1998) and Falgayrac et al. (2004), as cited by Atkinson (2007). Other data tabulated by Atkinson (2007) are not used because the reported Arrhenius



Table S56 (continued)

parameters are not consistent with data for the more well-studied alkoxy radicals.

5 Rate constant parameters from Hein et al. (1999).

6 Rate constant from Hein et al. (2000), as cited by Atkinson (2007). Other data tabulated by Atkinson (2007) are not used because the reported Arrhenius parameters are not consistent with data for the more well-studied alkoxy radicals.

Table S57. Branching ratios assigned for various reactions.

Reactants [a]	Products	Fraction	Ref [b]
CH <sub>3</sub> OH + OH	H <sub>2</sub> O + .CH <sub>2</sub> OH	0.85	1
	H <sub>2</sub> O + CH <sub>3</sub> O·	0.15	
HC(O)OH + OH	H <sub>2</sub> O + HCO <sub>2</sub> ·	1	2
HC#CH + OH	CH=CHOH	1	3
	CH <sub>2</sub> CHO	0	
CH <sub>2</sub> =CH <sub>2</sub> + O <sub>3</sub> P	CH <sub>2</sub> *CH <sub>2</sub> O*	0.1	4
	CH <sub>3</sub> CHO	0.1	
	CH <sub>2</sub> CHO + H.	0.29	
	HCO· + CH <sub>3</sub> ·	0.51	
CH=CHOH + O <sub>2</sub>	HC(O)OH + HCO·	0.33	3
	HC(O)CHO + OH	0.67	
CH <sub>3</sub> CHO + OH	H <sub>2</sub> O + CH <sub>3</sub> C(O)·	0.95	1
	H <sub>2</sub> O + .CH <sub>2</sub> CHO	0.05	
CH <sub>3</sub> CH <sub>2</sub> OH + OH	H <sub>2</sub> O + CH <sub>3</sub> CH(·)OH	0.9	1
	H <sub>2</sub> O + CH <sub>3</sub> CH <sub>2</sub> O·	0.05	
	H <sub>2</sub> O + .CH <sub>2</sub> CH <sub>2</sub> OH	0.05	
CH <sub>3</sub> C(O)OH + OH	H <sub>2</sub> O + .CH <sub>2</sub> C(O)OH	0.3	1
	H <sub>2</sub> O + CH <sub>3</sub> C(O)O·	0.7	
HC(O)CH <sub>2</sub> OH + OH	H <sub>2</sub> O + CO(·)CH <sub>2</sub> OH	0.8	1
	H <sub>2</sub> O + HC(O)CH(·)OH	0.2	
HC(O)CH <sub>2</sub> OH + HV	CH <sub>2</sub> OH + HCO·	0.83	
	CH <sub>3</sub> OH + CO	0.1	
	CH <sub>2</sub> CHO + OH	0.07	
HC(O)C(O)O-ONO <sub>2</sub>	CO <sub>2</sub> + HCO· + NO <sub>3</sub>	1	5
CH <sub>2</sub> =CHCHO + OH	H <sub>2</sub> O + CH <sub>2</sub> =CHC(O)·	0.68	6
	HC(O)CH(·)CH <sub>2</sub> OH	0.26	
	CH <sub>2</sub> CH(CH(O)OH)	0.06	
CH <sub>3</sub> C(·)=CHOH + O <sub>2</sub>	HC(O)OH + CO + CH <sub>3</sub> ·	0.3	7
	CH <sub>3</sub> C(O)CHO + OH	0.7	
CH <sub>3</sub> OCH <sub>2</sub> OCH <sub>3</sub> + OH	H <sub>2</sub> O + CH <sub>3</sub> OCH <sub>2</sub> OCH <sub>2</sub> ·	0.67	8
	H <sub>2</sub> O + CH <sub>3</sub> OCH(·)OCH <sub>3</sub>	0.33	
CH*=CHOCH=CH* + OH	HOCH*CH(·)CH=CH-O*	0.24	9
	HC(O)CH(·)CH=CHOH	0.76	
CH*=CHOCH=CH* + NO <sub>3</sub>	O <sub>2</sub> NOCH*CH(·)CH=CH-O*	1	10
CH <sub>2</sub> =C(CH <sub>3</sub> )CHO + O <sub>3</sub>	HCHO + CH <sub>3</sub> C[OO]-CHO { *O <sub>3</sub> Ole }	0.1	11
	CH <sub>3</sub> C(O)CHO + CH <sub>2</sub> OO { *O <sub>3</sub> Ole }	0.9	
CH <sub>2</sub> =CHC(O)CH <sub>3</sub> + OH	CH <sub>3</sub> C(O)CH(·)CH <sub>2</sub> OH	0.7	12
	CH <sub>3</sub> C(O)CH(CH <sub>2</sub> ·)OH	0.3	
CH <sub>2</sub> =CHC(O)CH <sub>3</sub> + O <sub>3</sub>	HCHO + CH <sub>3</sub> C(O)CHOO { *O <sub>3</sub> Ole }	0.05	11
	CH <sub>3</sub> C(O)CHO + CH <sub>2</sub> OO { *O <sub>3</sub> Ole }	0.95	
CH <sub>3</sub> C(·)=C(CH <sub>3</sub> )OH + O <sub>2</sub>	CH <sub>3</sub> C(O)OH + CO + CH <sub>3</sub> ·	0.26	7
	CH <sub>3</sub> C(O)COCH <sub>3</sub> + OH	0.74	
HOCH*CH(·)CH=CH-O* { *OHadd }	HOCH*CH(·)CH=CH-O*	0.24	9
	HC(O)CH(·)CH=CHOH	0.76	
CO*C(O)COOCO*	CO <sub>2</sub> + CO + CO + CO	1	13

Table S57 (continued)

Reactants [a]	Products	Fraction	Ref [b]
CH <sub>2</sub> =CHC(=CH <sub>2</sub> )CH <sub>3</sub> + O <sub>3</sub>	HCHO + CH <sub>2</sub> =CHC[OO]-CH <sub>3</sub> { *O <sub>3</sub> Ole }	0.2	14
	HCHO + CH <sub>2</sub> =C(CH <sub>3</sub> )CHOO { *O <sub>3</sub> Ole }	0.2	
	CH <sub>2</sub> =C(CH <sub>3</sub> )CHO + CH <sub>2</sub> OO { *O <sub>3</sub> Ole }	0.39	
	CH <sub>2</sub> =CHC(O)CH <sub>3</sub> + CH <sub>2</sub> OO { *O <sub>3</sub> Ole }	0.16	
	CH <sub>2</sub> =CHC*(CH <sub>3</sub> )CH <sub>2</sub> O* + O <sub>2</sub>	0.025	
	CH <sub>2</sub> =C(CH <sub>3</sub> )CH*CH <sub>2</sub> O* + O <sub>2</sub>	0.025	
CH <sub>2</sub> =CHC(=CH <sub>2</sub> )CH <sub>3</sub> + O <sub>3</sub> P	CH <sub>2</sub> =CHC*(CH <sub>3</sub> )CH <sub>2</sub> O*	0.5	15
	CH <sub>2</sub> =C(CH <sub>3</sub> )CH*CH <sub>2</sub> O*	0.25	
	CH <sub>2</sub> =CHC(O)CH <sub>2</sub> · + CH <sub>3</sub> ·	0.25	
CH <sub>2</sub> =CHC(=CH <sub>2</sub> )CH <sub>3</sub> + NO <sub>3</sub>	CH <sub>2</sub> =CHC(·)(CH <sub>3</sub> )CH <sub>2</sub> ONO <sub>2</sub>	1	14
CH <sub>2</sub> =CHC(=CH <sub>2</sub> )CH <sub>3</sub> + Cl·	CH <sub>3</sub> C(CH <sub>2</sub> ·)=CHCH <sub>2</sub> Cl	0.42	16
	CH <sub>2</sub> =C(CH <sub>3</sub> )CH(CH <sub>2</sub> ·)Cl	0.07	
	CH <sub>2</sub> =CHC(CH <sub>3</sub> )(CH <sub>2</sub> ·)Cl	0.02	
	CH <sub>2</sub> =CHC(·)(CH <sub>3</sub> )CH <sub>2</sub> Cl	0.34	
	HCl + CH <sub>2</sub> =C(CH <sub>2</sub> ·)CH=CH <sub>2</sub>	0.15	
CH <sub>2</sub> =CHC(=CH <sub>2</sub> )CH <sub>3</sub> + OH	CH <sub>3</sub> C(CH <sub>2</sub> ·)=CHCH <sub>2</sub> OH	0.386	17
	CH <sub>2</sub> =CHC(·)(CH <sub>3</sub> )CH <sub>2</sub> OH	0.557	
	CH <sub>2</sub> =C(CH <sub>3</sub> )CH(CH <sub>2</sub> ·)OH	0.028	
	CH <sub>2</sub> =CHC(CH <sub>3</sub> )(CH <sub>2</sub> ·)OH	0.028	
CH <sub>3</sub> C*=CHCH=CH-O* + OH	CH <sub>3</sub> C*(OH)CH(·)CH=CH-O*	0.3	9
	CH <sub>3</sub> C(·)*CH=CHCH(OH)O*	0.26	
	CH <sub>3</sub> C(·)(OH)CH=CHCHO	0.18	
	CH <sub>3</sub> C(O)CH(·)CH=CHOH	0.26	
CH <sub>3</sub> C*=CHCH=CH-O* + NO <sub>3</sub>	CH <sub>3</sub> C*(ONO <sub>2</sub> )CH(·)CH=CH-O*	0.536	18
	CH <sub>3</sub> C(·)*CH=CHCH(ONO <sub>2</sub> )O*	0.464	
CH <sub>3</sub> C*=CHOCH=CH* + OH	CH <sub>3</sub> C(·)*CH=CHOCH*OH	0.63	9
	CH <sub>3</sub> C*=CHCH(OH)OCH(·)*	0.1	
	CH <sub>3</sub> C(=CHOH)CH(·)CHO	0.18	
	CH <sub>3</sub> C(·)(CHO)CH=CHOH	0.09	
CH <sub>3</sub> C*=CHOCH=CH* + NO <sub>3</sub>	CH <sub>3</sub> C(·)*CH=CHOCH*ONO <sub>2</sub>	0.863	18
	CH <sub>3</sub> C*=CHCH(ONO <sub>2</sub> )OCH(·)*	0.137	
CH <sub>2</sub> =CHC(CH <sub>3</sub> )(CH <sub>3</sub> )OH + OH	CH <sub>3</sub> C(CH <sub>3</sub> )(OH)CH(·)CH <sub>2</sub> OH	0.667	19
	CH <sub>3</sub> C(CH <sub>3</sub> )(OH)CH(CH <sub>2</sub> ·)OH	0.333	
CH <sub>2</sub> =CHC(CH <sub>3</sub> )(CH <sub>3</sub> )OH + O <sub>3</sub>	HCHO + CH <sub>3</sub> C(CH <sub>3</sub> )(CHO)OH { *O <sub>3</sub> Ole }	0.3	20
	CH <sub>3</sub> C(CH <sub>3</sub> )(CHO)OH + CH <sub>2</sub> OO { *O <sub>3</sub> Ole }	0.7	
CH <sub>3</sub> C(CH <sub>3</sub> )(CH <sub>3</sub> )OCH <sub>3</sub> + OH	H <sub>2</sub> O + CH <sub>3</sub> C(CH <sub>3</sub> )(CH <sub>3</sub> )OCH <sub>2</sub> ·	0.8	21
	H <sub>2</sub> O + CH <sub>3</sub> C(CH <sub>3</sub> )(CH <sub>2</sub> ·)OCH <sub>3</sub>	0.2	
CH <sub>3</sub> C*(OH)CH(·)CH=CH-O* { *OHadd }	CH <sub>3</sub> C(·)(OH)CH=CHCHO	0.375	9
	CH <sub>3</sub> C*(OH)CH(·)CH=CH-O*	0.625	
CH <sub>3</sub> C(·)*CH=CHCH(OH)O* { *OHadd }	CH <sub>3</sub> C(O)CH(·)CH=CHOH	0.5	9
	CH <sub>3</sub> C(·)*CH=CHCH(OH)O*	0.5	
CH <sub>3</sub> C(·)*CH=CHOCH*OH { *OHadd }	CH <sub>3</sub> C(=CHOH)CH(·)CHO	0.222	9
	CH <sub>3</sub> C(·)*CH=CHOCH*OH	0.778	
CH <sub>3</sub> C*=CHCH(OH)OCH(·)* { *OHadd }	CH <sub>3</sub> C(·)(CHO)CH=CHOH	0.474	9
	CH <sub>3</sub> C*=CHCH(OH)OCH(·)*	0.526	
CH <sub>3</sub> C*=CHCH=C(CH <sub>3</sub> )O* + OH	CH <sub>3</sub> C(O)CH(·)CH=C(CH <sub>3</sub> )OH	0.28	9
	CH <sub>3</sub> C(·)*CH=CHC(CH <sub>3</sub> )(OH)O*	0.72	
CH <sub>3</sub> C*=CHCH=C(CH <sub>3</sub> )O* + NO <sub>3</sub>	CH <sub>3</sub> C(·)*CH=CHC(CH <sub>3</sub> )(ONO <sub>2</sub> )O*	1	10

Table S57 (continued)

Reactants [a]	Products	Fraction	Ref [b]
CH <sub>3</sub> C(·)*CH=CHC(CH <sub>3</sub> )(OH)O* { *OHadd }	CH <sub>3</sub> C(O)CH(·)CH=C(CH <sub>3</sub> )OH	0.28	9
	CH <sub>3</sub> C(·)*CH=CHC(CH <sub>3</sub> )(OH)O*	0.72	
CH <sub>3</sub> OC(O)CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> C(O)OCH <sub>3</sub> + OH	H <sub>2</sub> O + CH <sub>3</sub> OC(O)CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> C(O)OCH <sub>2</sub> ·	0.39	22
	H <sub>2</sub> O + CH <sub>3</sub> OC(O)CH <sub>2</sub> CH <sub>2</sub> CH(·)C(O)OCH <sub>3</sub>	0.2	
	H <sub>2</sub> O + CH <sub>3</sub> OC(O)CH <sub>2</sub> CH(·)CH <sub>2</sub> C(O)OCH <sub>3</sub>	0.41	

[a] "{\*OHadd} indicates a radical that is excited by the addition of OH radicals to a double bond.

[b] Sources of branching ratio assignments are as follows:

- 1 Branching ratios recommended by IUPAC (2023).
- 2 Believed to be the major reaction route.
- 3 Estimated mechanism is based on the data of Hatakeyama et al. (1986) and modeling acetylene environmental chamber runs Carter et al. (1997b).
- 4 Radical fragmentation distribution as recommended by Calvert et al. (2000), ignoring H<sub>2</sub> + ketene route. Although Calvert et al. (2000) recommends assuming 95% fragmentation, it is necessary to assume ~20% stabilization to remove biases in model simulations of ethene.
- 5 It is assumed that this compound decomposes to these products based on the observations of Orlando and Tyndall (2001) in the reactions of glyoxal with OH in the presence of NO<sub>2</sub>, where N<sub>2</sub>O<sub>5</sub> is observed but no PAN compound. However, these products may be formed in the reaction of HC(O)COC(O)· with O<sub>2</sub> without the intermediacy of HC(O)C(O)COONO<sub>2</sub>·.
- 6 Based on Orlando and Tyndall (2002).
- 7 Based on yields of methylglyoxal and biacetyl from methyl acetylene as reported by Lockhart et al. (2013). They also conclude that acetyl radicals are formed with sufficient excitation that they decompose before reaction with O<sub>2</sub>, so this is incorporated in the competing reaction where it is formed.
- 8 Based on ratio of yields of CH<sub>3</sub>OCH<sub>2</sub>OCHO relative to CH<sub>3</sub>OC(O)OCH<sub>3</sub> + CH<sub>3</sub>OCHO given by Sidebottom et al. (1997), which is consistent with product data of Wallington et al. (1997).
- 9 Branching ratios based on quantum calculations for the reactions of furans by Yuan et al. (2017). These represent the net effects of adducts that then decompose before stabilization.
- 10 This represents the effects of NO<sub>3</sub> addition followed by stabilization. Decomposition such as occurs with the OH adduct is assumed to be less important because of lower excitation energy of the adduct.
- 11 Based on product yields of Grosjean et al. (1993), as assumed by Carter and Atkinson (1996).
- 12 Based on product distribution of Tuazon and Atkinson (1989), as discussed by Carter and Atkinson (1996).
- 13 Assumed to rapidly undergo this exothermic decomposition.
- 14 As assumed by Carter and Atkinson (1996).
- 15 As assumed by Carter and Atkinson (1996). Products represented by epoxides. Most of the reaction is assumed to occur at the more substituted position.
- 16 Branching ratios based on mechanism of Fan and Zhang (2004).
- 17 Adjusted to minimize errors in predictions of methacrolein, MVK, formaldehyde, and 3-methylfuran yields as assumed by Carter and Atkinson (1996). Note that it is also necessary to adjust branching ratios for reaction of initially formed allylic radicals with O<sub>2</sub>· additions that do not form allylic radicals are assumed to be equally probable.
- 18 This represents the effects of NO<sub>3</sub> addition followed by stabilization. Branching ratios for the two O<sub>2</sub> addition routes is assumed to be the same as estimated for the OH addition, except that decomposition such as occurs with the OH adduct is assumed to be less important because of lower excitation energy of the adduct.
- 19 Based on product data reported by Alvarado et al. (1999). The corresponding alkoxy radical is estimated to decompose form glycolaldehyde and the precursor to acetone, both observed products.
- 20 Based on product data of Alvarado et al. (1999).
- 21 Branching ratios based on product studies of Tuazon et al. (1991) and Smith et al. (1991), with overall yields increased to account for 100% reaction.
- 22 Based on yield of CH<sub>3</sub>OC(O)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C(O)OH observed by Tuazon et al. (1999).

## S5.4. Thermochemical Group Data

Table S58. Thermochemical group values (kcal/mole) that were taken from the literature.

Group [a]	Value	Ref	Additional Reference Info. [b]	Group	Value	Ref	Additional Reference Info.
C_(C)	-10.04	1		C_(C)(C)	-5.00	1	
C_(C)(C)(C)	-1.67	1		C_(C)(C)(C)(C)	0.48	1	
C_(C)(C)(C)(C*)	0.48	2		C_(C)(C)(C)(Cb)	2.63	1	
C_(C)(C)(C)(Cd)	1.43	1		C_(C)(C)(C)(Cd*)	1.43	2	
C_(C)(C)(C)(CO)	2.15	1		C_(C)(C)(C)(CO*)	2.15	2	
C_(C)(C)(C)(Ct)	1.31	1		C_(C)(C)(C)(N)	-3.11	1	
C_(C)(C)(C)(NO2)	-12.21	3	CH3C(C)(NO2)CH3	C_(C)(C)(C)(O)	-5.02	1	
C_(C)(C)(C)(O*)	-5.02	2		C_(C)(C)(C)(ONO2)	-24.18	4	C_(C)(C)(C)(O) + O_(C)(NO2)
C_(C)(C)(C*)	-1.67	2		C_(C)(C)(C*)(C*)	0.48	2	
C_(C)(C)(C*)(Cb)	2.63	2		C_(C)(C)(C*)(Cd)	1.43	2	
C_(C)(C)(C*)(Cd*)	1.43	2		C_(C)(C)(C*)(CO)	2.15	2	
C_(C)(C)(C*)(CO*)	2.15	2		C_(C)(C)(C*)(Ct)	1.31	2	
C_(C)(C)(C*)(N)	-3.11	2		C_(C)(C)(C*)(NO2)	-12.21	2	
C_(C)(C)(C*)(O)	-5.02	2		C_(C)(C)(C*)(O*)	-5.02	2	
C_(C)(C)(C*)(ONO2)	-24.18	2		C_(C)(C)(Cb)	-0.96	1	
C_(C)(C)(Cb)(CO*)	4.78	2		C_(C)(C)(Cb)(N)	-1.43	1	
C_(C)(C)(Cb)(O*)	-6.90	2		C_(C)(C)(Cd)	-1.67	1	
C_(C)(C)(Cd)(CO*)	2.41	2		C_(C)(C)(Cd)(O*)	-3.39	2	
C_(C)(C)(Cd*)	-1.67	2		C_(C)(C)(Cd*)(O)	-3.39	2	
C_(C)(C)(Cd*)(ONO2)	-19.85	2		C_(C)(C)(CO)	-0.96	1	
C_(C)(C)(CO)(CO*)	5.02	2		C_(C)(C)(CO)(O*)	0.48	2	
C_(C)(C)(CO*)	-0.96	2		C_(C)(C)(CO*)(Ct)	5.26	2	
C_(C)(C)(CO*)(N)	-1.67	2		C_(C)(C)(CO*)(NO2)	-11.25	2	
C_(C)(C)(CO*)(O)	0.48	2		C_(C)(C)(CO*)(ONO2)	-18.68	2	
C_(C)(C)(Ct)	-1.55	1		C_(C)(C)(Ct)(O*)	-5.30	2	
C_(C)(C)(N)	-4.30	1		C_(C)(C)(N)(O*)	-17.33	2	
C_(C)(C)(NO2)	-14.34	1		C_(C)(C)(NO2)(O*)	-21.53	2	
C_(C)(C)(O)	-6.21	1		C_(C)(C)(O)(O)	-11.47	1	
C_(C)(C)(O)(O*)	-11.47	2		C_(C)(C)(O)(ONO2)	-30.63	4	C_(C)(C)(O)(O) + O_(C)(NO2)
C_(C)(C)(O*)	-6.21	2		C_(C)(C)(O*)(O*)	-11.47	2	
C_(C)(C)(O*)(ONO2)	-30.63	2		C_(C)(C)(ONO2)	-25.38	4	C_(C)(C)(O) + O_(C)(NO2)
C_(C)(C*)	-5	2		C_(C)(C*)(C*)	-1.67	2	

Table S58 (continued)

Group [a]	Value	Ref	Additional Reference Info. [b]	Group	Value	Ref	Additional Reference Info.
C_(C)(C*)(Cb)	-0.96	2		C_(C)(C*)(Cb)(CO)	4.78	2	
C_(C)(C*)(Cb)(N)	-1.43	2		C_(C)(C*)(Cb)(O)	-6.9	2	
C_(C)(C*)(Cd)	-1.67	2		C_(C)(C*)(Cd)(CO)	2.41	2	
C_(C)(C*)(Cd)(NO2)	-7.15	2		C_(C)(C*)(Cd)(O)	-3.39	2	
C_(C)(C*)(Cd)(ONO2)	-19.85	2		C_(C)(C*)(Cd*)	-1.67	2	
C_(C)(C*)(CO)	-0.96	2		C_(C)(C*)(CO)(CO)	5.02	2	
C_(C)(C*)(CO)(Ct)	5.26	2		C_(C)(C*)(CO)(N)	-1.67	2	
C_(C)(C*)(CO)(NO2)	-11.25	2		C_(C)(C*)(CO)(O)	0.48	2	
C_(C)(C*)(CO)(ONO2)	-18.68	2		C_(C)(C*)(CO*)	-0.96	2	
C_(C)(C*)(Ct)	-1.55	2		C_(C)(C*)(Ct)(O)	-5.3	2	
C_(C)(C*)(Ct)(ONO2)	-21.79	2		C_(C)(C*)(N)	-4.3	2	
C_(C)(C*)(N)(N)	-15.41	2		C_(C)(C*)(N)(O)	-17.33	2	
C_(C)(C*)(N)(ONO2)	-30.4	2		C_(C)(C*)(NO2)	-14.34	2	
C_(C)(C*)(NO2)(NO2)	-7.76	2		C_(C)(C*)(NO2)(O)	-21.53	2	
C_(C)(C*)(O)	-6.21	2		C_(C)(C*)(O)(O)	-11.47	2	
C_(C)(C*)(O)(O*)	-11.47	2		C_(C)(C*)(O)(ONO2)	-30.63	2	
C_(C)(C*)(O*)	-6.21	2		C_(C)(C*)(ONO2)	-25.38	2	
C_(C)(C*)(ONO2)(ONO2)	-51.47	2		C_(C)(Cb)	-4.78	1	
C_(C)(Cb)(CO*)	1.67	2		C_(C)(Cb)(N)	-3.59	1	
C_(C)(Cb)(O)	-8.1	5		C_(C)(Cb)(O*)	-8.1	2	
C_(C)(Cd)	-4.8	1		C_(C)(Cd)(Cd)	-1.67	1	
C_(C)(Cd)(Cd)(O*)	-1.91	2		C_(C)(Cd)(Cd*)	-1.67	2	
C_(C)(Cd)(CO)(CO*)	5.02	2		C_(C)(Cd)(CO)(O*)	0.48	2	
C_(C)(Cd)(CO*)	-0.69	2		C_(C)(Cd)(CO*)(NO2)	-10.28	2	
C_(C)(Cd)(CO*)(O)	0.48	2		C_(C)(Cd)(CO*)(ONO2)	-18.68	2	
C_(C)(Cd)(NO2)(O*)	-20.55	2		C_(C)(Cd)(O)	-6.5	5	
C_(C)(Cd)(O)(O*)	-12.43	2		C_(C)(Cd)(O*)	-6.5	2	
C_(C)(Cd)(O*)(ONO2)	-31.59	2		C_(C)(Cd*)	-4.8	2	
C_(C)(Cd*)(O)	-6.5	2		C_(C)(Cd*)(ONO2)	-22.96	2	
C_(C)(CN)	-5.02	1		C_(C)(CO)	-5.26	1	
C_(C)(CO)(CO)(CO*)	6.69	2		C_(C)(CO)(CO)(O*)	0.48	2	
C_(C)(CO)(CO*)	1.91	2		C_(C)(CO)(CO*)(NO2)	-7.65	2	
C_(C)(CO)(CO*)(O)	0.48	2		C_(C)(CO)(CO*)(ONO2)	-18.68	2	
C_(C)(CO)(N)	-2.87	1		C_(C)(CO)(NO2)(O*)	-20.81	2	
C_(C)(CO)(O)(O*)	-13.62	2		C_(C)(CO)(O*)	-2.63	2	
C_(C)(CO)(O*)(ONO2)	-32.79	2		C_(C)(CO*)	-5.26	2	
C_(C)(CO*)(Ct)	2.15	2		C_(C)(CO*)(N)	-2.87	2	
C_(C)(CO*)(NO2)	-13.38	2		C_(C)(CO*)(NO2)(NO2)	-28.94	2	
C_(C)(CO*)(NO2)(O)	-20.81	2		C_(C)(CO*)(O)	-2.63	2	

Table S58 (continued)

Group [a]	Value	Ref	Additional Reference Info. [b]	Group	Value	Ref	Additional Reference Info.
C_(C)(CO*)(O)(O)	-13.62	2		C_(C)(CO*)(O)(ONO2)	-32.79	2	
C_(C)(CO*)(ONO2)	-21.79	2		C_(C)(CO*)(ONO2)(ONO2)	-51.95	2	
C_(C)(Ct)	-4.78	1		C_(C)(Ct)(O)	-6.5	5	
C_(C)(Ct)(O*)	-6.5	2		C_(C)(N)	-0.48	1	
C_(C)(N)(O*)	-18.52	2		C_(C)(NO2)	-14.34	1	
C_(C)(NO2)(NO2)	-9.9	5		C_(C)(NO2)(NO2)(O*)	-39.93	2	
C_(C)(NO2)(O)(O*)	-31.8	2		C_(C)(NO2)(O*)	-23.66	2	
C_(C)(O)	-7.89	1		C_(C)(O)(O)	-15.54	1	
C_(C)(O)(O)(O)	-25.1	1		C_(C)(O)(O)(O*)	-25.1	2	
C_(C)(O)(O)(ONO2)	-44.26	4	C_(C)(O)(O)(O) + O_(C)(NO2)	C_(C)(O)(O*)	-15.54	2	
C_(C)(O)(O*)(O*)	-25.1	2		C_(C)(O)(O*)(ONO2)	-44.26	2	
C_(C)(O)(ONO2)	-34.7	4	C_(C)(O)(O) + O_(C)(NO2)	C_(C)(O*)	-7.89	2	
C_(C)(O*)(O*)	-15.54	2		C_(C)(O*)(ONO2)	-34.7	2	
C_(C)(O*)(ONO2)(ONO2)	-62.94	2		C_(C)(ONO2)	-27.05	4	C_(C)(O) + O_(C)(NO2)
C_(C*)	-10.04	2		C_(C*)(C*)	-5	2	
C_(C*)(Cb)	-4.78	2		C_(C*)(Cb)(CO)	1.67	2	
C_(C*)(Cb)(N)	-3.59	2		C_(C*)(Cb)(O)	-8.1	2	
C_(C*)(Cd)	-4.8	2		C_(C*)(Cd)(Cd)	-1.67	2	
C_(C*)(Cd)(CO)	-0.69	2		C_(C*)(Cd)(CO)(CO)	5.02	2	
C_(C*)(Cd)(CO)(NO2)	-10.28	2		C_(C*)(Cd)(CO)(O)	0.48	2	
C_(C*)(Cd)(CO)(ONO2)	-18.68	2		C_(C*)(Cd)(NO2)	-10.25	2	
C_(C*)(Cd)(NO2)(NO2)	-6.79	2		C_(C*)(Cd)(NO2)(O)	-20.55	2	
C_(C*)(Cd)(O)	-6.5	2		C_(C*)(Cd)(O)(O)	-12.43	2	
C_(C*)(Cd)(O)(ONO2)	-31.59	2		C_(C*)(Cd)(ONO2)	-22.96	2	
C_(C*)(Cd)(ONO2)(ONO2)	-49.56	2		C_(C*)(Cd*)	-4.8	2	
C_(C*)(CO)	-5.26	2		C_(C*)(CO)(CO)	1.91	2	
C_(C*)(CO)(CO)(CO)	6.69	2		C_(C*)(CO)(CO)(NO2)	-7.65	2	
C_(C*)(CO)(CO)(O)	0.48	2		C_(C*)(CO)(CO)(ONO2)	-18.68	2	
C_(C*)(CO)(Ct)	2.15	2		C_(C*)(CO)(N)	-2.87	2	
C_(C*)(CO)(NO2)	-13.38	2		C_(C*)(CO)(NO2)(NO2)	-28.94	2	
C_(C*)(CO)(NO2)(O)	-20.81	2		C_(C*)(CO)(O)	-2.63	2	
C_(C*)(CO)(O)(O)	-13.62	2		C_(C*)(CO)(O)(ONO2)	-32.79	2	
C_(C*)(CO)(ONO2)	-21.79	2		C_(C*)(CO)(ONO2)(ONO2)	-51.95	2	
C_(C*)(CO*)	-5.26	2		C_(C*)(Ct)	-4.78	2	
C_(C*)(Ct)(O)	-6.5	2		C_(C*)(Ct)(ONO2)	-22.99	2	
C_(C*)(N)	-0.48	2		C_(C*)(N)(N)	-16.6	2	
C_(C*)(N)(O)	-18.52	2		C_(C*)(N)(ONO2)	-31.59	2	
C_(C*)(NO2)	-14.34	2		C_(C*)(NO2)(NO2)	-9.9	2	
C_(C*)(NO2)(NO2)(O)	-39.93	2		C_(C*)(NO2)(O)	-23.66	2	

Table S58 (continued)

Group [a]	Value	Ref	Additional Reference Info. [b]	Group	Value	Ref	Additional Reference Info.
C_(C*)(NO2)(O)(O)	-31.8	2		C_(C*)(O)	-7.89	2	
C_(C*)(O)(O)	-15.54	2		C_(C*)(O)(O)(O)	-25.1	2	
C_(C*)(O)(O)(O*)	-25.1	2		C_(C*)(O)(O)(ONO2)	-44.26	2	
C_(C*)(O)(O*)	-15.54	2		C_(C*)(O)(ONO2)	-34.7	2	
C_(C*)(O)(ONO2)(ONO2)	-62.94	2		C_(C*)(O*)	-7.89	2	
C_(C*)(ONO2)	-27.05	2		C_(C*)(ONO2)(ONO2)	-52.66	2	
C_(Cb)	-10.04	1		C_(Cb)(Cb)	-4.78	1	
C_(Cb)(Cb)(Cb)	-0.96	1		C_(Cb)(Cb)(Cb)(Cb)	7.41	1	
C_(Cb)(Cd)	-4.3	1		C_(Cb)(Cd*)	-4.3	2	
C_(Cb)(CO)	-2.63	1		C_(Cb)(CO*)	-2.63	2	
C_(Cb)(N)	-6.21	1		C_(Cb)(O)	-6.21	1	
C_(Cb)(O*)	-6.21	2		C_(Cb)(ONO2)	-25.38	4	C_(Cb)(O) + O_(C)(NO2)
C_(Cd)	-10.04	1		C_(Cd)(Cd)	-4.3	1	
C_(Cd)(Cd)(CO)	-2.87	1		C_(Cd)(Cd)(CO*)	-2.87	2	
C_(Cd)(Cd)(O)	-5.02	1		C_(Cd)(Cd)(O*)	-5.02	2	
C_(Cd)(Cd)(ONO2)	-24.18	4	C_(Cd)(Cd)(O) + O_(C)(NO2)	C_(Cd)(Cd*)	-4.3	2	
C_(Cd)(Cd*)(CO)	-2.87	2		C_(Cd)(Cd*)(O)	-5.02	2	
C_(Cd)(CN)	-5.5	1		C_(Cd)(CO)	-3.82	1	
C_(Cd)(CO)(CO*)	1.91	2		C_(Cd)(CO)(O)(O*)	-12.67	2	
C_(Cd)(CO)(O*)	-2.63	2		C_(Cd)(CO*)	-3.82	2	
C_(Cd)(CO*)(NO2)	-13.38	2		C_(Cd)(CO*)(O)	-2.63	2	
C_(Cd)(CO*)(ONO2)	-21.79	2		C_(Cd)(NO2)(O*)	-23.66	2	
C_(Cd)(O)	-6.93	1		C_(Cd)(O)(O*)	-15.54	2	
C_(Cd)(O*)	-6.93	2		C_(Cd)(O*)(ONO2)	-34.7	2	
C_(Cd)(ONO2)	-26.09	4	C_(Cd)(O) + O_(C)(NO2)	C_(Cd*)	-10.04	2	
C_(Cd*)(CO)	-3.82	2		C_(Cd*)(O)	-6.93	2	
C_(Cd*)(O)(O)	-15.54	2		C_(Cd*)(O*)	-6.93	2	
C_(Cd*)(ONO2)	-26.09	4	C_(Cd*)(O) + O_(C)(NO2)	C_(CN)(O)	25.1	1	
C_(CO)	-10.04	1		C_(CO)(CO)	-2.39	1	
C_(CO)(CO)(CO)(CO*)	8.37	2		C_(CO)(CO)(CO)(O*)	1.2	2	
C_(CO)(CO)(CO*)(O)	1.2	2		C_(CO)(CO)(CO*)(ONO2)	-17.97	2	
C_(CO)(CO)(O)(O*)	-11.95	2		C_(CO)(CO)(O*)	-2.63	2	
C_(CO)(CO)(O*)(ONO2)	-31.11	2		C_(CO)(CO*)	-2.39	2	
C_(CO)(CO*)(NO2)	-10.76	2		C_(CO)(CO*)(O)	-2.63	2	
C_(CO)(CO*)(O)(O)	-11.95	2		C_(CO)(CO*)(O)(ONO2)	-31.11	2	
C_(CO)(CO*)(ONO2)	-21.79	2		C_(CO)(Ct)	-2.15	1	
C_(CO)(N)	-5.02	1		C_(CO)(NO2)(NO2)(O*)	-38.26	2	
C_(CO)(NO2)(O*)	-22.94	2		C_(CO)(O)	-6.93	1	
C_(CO)(O)(O)(O*)	-23.42	2		C_(CO)(O)(O*)	-14.82	2	



Table S58 (continued)

Group [a]	Value	Ref	Additional Reference Info. [b]	Group	Value	Ref	Additional Reference Info.
C_(CO)(O)(O*)(ONO2)	-42.58	2		C_(CO)(O*)	-6.93	2	
C_(CO)(O*)(ONO2)	-33.98	2		C_(CO)(O*)(ONO2)(ONO2)	-61.75	2	
C_(CO)(ONO2)	-26.09	4	C_(CO)(O) + O_(C)(NO2)	C_(CO*)	-10.04	2	
C_(CO*)(Ct)	-2.15	2		C_(CO*)(N)	-5.02	2	
C_(CO*)(NO2)	-13.38	2		C_(CO*)(NO2)(NO2)	-31.07	2	
C_(CO*)(NO2)(NO2)(O)	-38.26	2		C_(CO*)(NO2)(O)	-22.94	2	
C_(CO*)(O)	-6.93	2		C_(CO*)(O)(O)	-14.82	2	
C_(CO*)(O)(O)(O)	-23.42	2		C_(CO*)(O)(O)(ONO2)	-42.58	2	
C_(CO*)(O)(ONO2)	-33.98	2		C_(CO*)(O)(ONO2)(ONO2)	-61.75	2	
C_(CO*)(ONO2)	-26.09	2		C_(CO*)(ONO2)(ONO2)	-53.14	2	
C_(Ct)(O)	-5.5	1		C_(Ct)(O*)	-5.5	2	
C_(Ct)(ONO2)	-24.66	4	C_(Ct)(O) + O_(C)(NO2)	C_(N)	-10.04	1	
C_(N)(N)	-12.78	5		C_(N)(O)	-14.7	5	
C_(N)(O*)	-14.7	2		C_(N*)	-10.04	2	
C_(NO2)	-17.76	6	CH3NO2	C_(NO2)(NO2)(O*)	-42.07	2	
C_(NO2)(O)(O*)	-33.94	2		C_(NO2)(O*)	-22.47	2	
C_(O)	-10.04	1		C_(O)(O)	-16.01	1	
C_(O)(O)(O)	-25.81	1		C_(O)(O)(O)(O)	-38.72	1	
C_(O)(O)(O)(O*)	-38.72	2		C_(O)(O)(O)(ONO2)	-57.88	4	C_(O)(O)(O)(O) + O_(C)(NO2)
C_(O)(O)(O*)	-25.81	2		C_(O)(O)(O*)(O*)	-38.72	2	
C_(O)(O)(O*)(ONO2)	-57.88	2		C_(O)(O)(ONO2)	-44.97	4	C_(O)(O)(O) + O_(C)(NO2)
C_(O)(O*)	-16.01	2		C_(O)(O*)(O*)	-25.81	2	
C_(O)(O*)(ONO2)	-44.97	2		C_(O)(ONO2)	-35.18	4	C_(O)(O) + O_(C)(NO2)
C_(O*)	-10.04	2		C_(O*)(O*)	-16.01	2	
C_(O*)(ONO2)	-35.18	2		C_(O*)(ONO2)(ONO2)	-64.14	2	
C_(ONO2)	-29.2	4	C_(O) + O_(C)(NO2)	C*_(C)	39.19	7	N-C3H7, C3H8
C*_(C)(C)	40.72	7	I-C3H7, C3H8	C*_(C)(C)(C)	41.87	3	tert-butyl, Isobutane
C*_(C)(C)(ONO2)	15.85	4	C*_(C)(C)(O) + O_(C*)(NO2)	C*_(C)(O)	35.51	7	7
C*_(C)(ONO2)	16.35	4	C*_(C)(O) + O_(C*)(NO2)	C*_(Cd)	24.88	7	C3H5, C3H6
C*_(Cd)(CO)(ONO2)	7.44	4	C*_(Cd)(CO)(O) + O_(C*)(NO2)	C*_(Cd)(O)(O)	30.88	9	8
C*_(CO)	33.72	7	CH3C(O)CH2, CH3C(O)CH3	C*_(CO)(O)(ONO2)	9.78	4	C*_(CO)(O)(O) + O_(C*)(NO2)
C*_(N)	31.17	7	CH2NH2, CH3NH2	C*_(O)	34.87	7	CH3OCH2, CH3OCH3
C*_(ONO2)	15.71	4	C*_(O) + O_(C*)(NO2)	Ca_(Cd)(Cd)	33.7	1	
Cb_(C)(Cb)(Cb)	5.5	1		Cb_(C)(Cb)(Cb*)	5.5	2	
Cb_(C*)(Cb)(Cb)	5.5	2		Cb_(Cb)(Cb)	3.3	1	
Cb_(Cb)(Cb)(Cb)	5.02	1		Cb_(Cb)(Cb)(Cd)	6.45	1	
Cb_(Cb)(Cb)(CN)	8.37	1		Cb_(Cb)(Cb)(CO)	4.3	1	
Cb_(Cb)(Cb)(CO*)	4.3	2		Cb_(Cb)(Cb)(Ct)	0	1	
Cb_(Cb)(Cb)(N)	5.98	1		Cb_(Cb)(Cb)(NO2)	-1.2	1	

Table S58 (continued)

Group [a]	Value	Ref	Additional Reference Info. [b]	Group	Value	Ref	Additional Reference Info.
Cb_(Cb)(Cb)(O)	5.98	1		Cb_(Cb)(Cb)(O*)	5.98	2	
Cb_(Cb)(Cb*)	3.3	2		Cb_(Cb)(Cb*)(CO)	4.3	2	
Cb_(Cb)(Cb*)(O)	5.98	2		Cd_(C)(C)(Cd)	10.18	1	
Cd_(C)(C)(Cd*)	10.18	2		Cd_(C)(C*)(Cd)	10.18	2	
Cd_(C)(Cb)(Cd)	8.6	1		Cd_(C)(Cd)	8.56	1	
Cd_(C)(Cd)(Cd)	8.77	1		Cd_(C)(Cd)(Cd*)	8.77	2	
Cd_(C)(Cd)(CO)	7.41	1		Cd_(C)(Cd)(CO*)	7.41	2	
Cd_(C)(Cd)(Ct)	9.56	1		Cd_(C)(Cd)(N)	9.8	1	
Cd_(C)(Cd)(O)	10.28	1		Cd_(C)(Cd*)	8.56	2	
Cd_(C)(Cd*)(CO)	7.41	2		Cd_(C)(Cd*)(O)	10.28	2	
Cd_(C*)(Cd)	8.56	2		Cd_(C*)(Cd)(Cd)	8.77	2	
Cd_(C*)(Cd)(CO)	7.41	2		Cd_(C*)(Cd)(O)	10.28	2	
Cd_(C*)(Cd)(ONO2)	-13.4	2		Cd_(Cb)(Cb)(Cd)	11.95	1	
Cd_(Cb)(Cd)	6.69	1		Cd_(Cd)	6.26	1	
Cd_(Cd)(Cd)	6.79	1		Cd_(Cd)(Cd)(Cd)	12.67	1	
Cd_(Cd)(Cd)(CN)	39.67	1		Cd_(Cd)(Cd)(CO)	9.08	1	
Cd_(Cd)(Cd)(CO*)	9.08	2		Cd_(Cd)(Cd)(O)	8.84	1	
Cd_(Cd)(Cd*)	6.79	2		Cd_(Cd)(Cd*)(CO)	9.08	2	
Cd_(Cd)(CO)	5.02	1		Cd_(Cd)(CO)(O)	11.71	1	
Cd_(Cd)(CO)(ONO2)	-13.43	4	Cd_(Cd)(CO)(O) + O_(Cd)(NO2)	Cd_(Cd)(CO*)	5.02	2	2
Cd_(Cd)(CO*)(O)	11.71	2		Cd_(Cd)(Ct)	8.6	1	
Cd_(Cd)(Ct)(O)	8.84	1		Cd_(Cd)(N)	8.6	1	
Cd_(Cd)(NO2)	7.1	5		Cd_(Cd)(O)	8.6	1	
Cd_(Cd)(O)(O)	12.26	6	CH3CF2	Cd_(Cd)(O*)	8.6	2	
Cd_(Cd)(ONO2)	-16.53	4	Cd_(Cd)(O) + O_(Cd)(NO2)	Cd_(Cd*)	6.26	2	
Cd_(Cd*)(CO)	5.02	2		Cd_(Cd*)(CO)(CO)	3.87	2	
Cd_(Cd*)(CO)(O)	11.71	2		Cd_(Cd*)(O)	8.6	2	
Cd*__(Cd)	64.34	7	C2H3, C2H4	CN_(C)	27.49	1	
CN_(Cb)	27.49	1		CN_(Cd)	27.49	1	
CN_(Ct)	27.49	1		CO_(C)	-29.4	1	
CO_(C)(C)	-31.79	1		CO_(C)(C*)	-31.79	2	
CO_(C)(Cb)	-31.07	1		CO_(C)(Cd)	-29.4	1	
CO_(C)(Cd*)	-29.4	2		CO_(C)(CO)	-28.92	1	
CO_(C)(CO*)	-28.92	2		CO_(C)(Ct)	-27.01	1	
CO_(C)(N)	-32.5	1		CO_(C)(O)	-35.13	1	
CO_(C)(O*)	-35.13	2		CO_(C)(ONO2)	-73.66	4	CO_(C)(O) + O_(CO)(NO2)
CO_(C*)	-29.4	2		CO_(C*)(Cb)	-31.07	2	
CO_(C*)(Cd)	-29.4	2		CO_(C*)(CO)	-28.92	2	
CO_(C*)(Ct)	-27.01	2		CO_(C*)(O)	-35.13	2	

Table S58 (continued)

Group [a]	Value	Ref	Additional Reference Info. [b]	Group	Value	Ref	Additional Reference Info.
CO_(C*)(ONO2)	-73.66	2		CO_(Ca)	-9.56	1	
CO_(Cb)	-29.16	1		CO_(Cb)(Cb)	-28.2	1	
CO_(Cb)(CO)	-26.29	1		CO_(Cb)(N)	-30.59	1	
CO_(Cb)(O)	-34.18	1		CO_(Cb)(O*)	-34.18	2	
CO_(Cd)	-27.01	1		CO_(Cd)(Cd)	-27.01	1	
CO_(Cd)(O)	-32.03	1		CO_(Cd)(O*)	-32.03	2	
CO_(Cd*)	-27.01	2		CO_(Cd*)(O)	-32.03	2	
CO_(CO)	-25.33	1		CO_(CO)(CO*)	-26.05	2	
CO_(CO)(O)	-29.4	1		CO_(CO)(O*)	-29.4	2	
CO_(CO*)	-25.33	2		CO_(CO*)(O)	-29.4	2	
CO_(Ct)	-25.57	1		CO_(Ct)(O)	-27.49	1	
CO_(Ct)(O*)	-27.49	2		CO_(N)	-30.59	1	
CO_(N)(N)	-30.07	6	(NH2)2CO	CO_(O)	-32.03	1	
CO_(O)(O)	-30.83	1		CO_(O)(O*)	-30.83	2	
CO_(O)(ONO2)	-69.35	4	CO_(O)(O) + O_(CO)(NO2)	CO_(O*)	-32.03	2	
CO_(O*)(ONO2)	-69.35	2		CO_(ONO2)	-70.55	4	CO_(O) + O_(CO)(NO2)
CO*__(C)	6.3	7	C2H5CO, C2H5CHO	CO*__(CO)	10.37	7	C2H5CO, C2H5CHO
CO*__(ONO2)	-27.65	4	CO*__(O) + O_(CO*)(NO2)	Ct_(C)	27.49	1	
Ct_(C)(Ct)	27.55	5		Ct_(C*)(Ct)	27.55	2	
Ct_(Cb)	29.88	1		Ct_(Cb)(Ct)	24.67	5	
Ct_(Cd)	30.11	1		Ct_(Cd)(Ct)	29.2	5	
Ct_(CN)	29.4	1		Ct_(CO)	28.68	1	
Ct_(Ct)	28.2	1		Ct_(Ct)(Ct)	25.6	5	
Ct_(O)	43.02	1		N_(C)	4.3	1	
N_(C)(C)	15.54	1		N_(C)(C)(C)	24.38	1	
N_(C)(C)(C*)	24.38	2		N_(C)(C)(Cb)	26.2	5	
N_(C)(C)(Cd)	24.4	5		N_(C)(C)(CO)	4.06	1	
N_(C)(C)(N)	29.2	5		N_(C)(C)(NO2)	18.8	5	
N_(C)(C*)	15.54	2		N_(C)(Cb)	14.9	5	
N_(C)(Cd)	9.8	1		N_(C)(Cd)(N)	30	5	
N_(C)(CO)	-4.78	1		N_(C)(CO)(CO)	-5.9	5	
N_(C)(N)	20.9	5		N_(C*)	4.3	2	
N_(Cb)	-2.63	1		N_(Cb)(Cb)	16.3	5	
N_(Cb)(CO)	0.4	5		N_(Cb)(CO)(CO)	-0.5	5	
N_(Cb)(N)	22.1	5		N_(Cd)	0	1	
N_(Cd)(Cd)	4.54	1		N_(Cd)(N)	21.5	5	
N_(CO)	-14.34	1		N_(CO)(CO)	-18.5	5	
N_(CO)(CO)(CO)	-2.6	5		N_(N)	11.4	5	
NC_(C)	50.19	1		NO2_(C)	0	5	

Table S58 (continued)

Group [a]	Value	Ref	Additional Reference Info. [b]	Group	Value	Ref	Additional Reference Info.
NO2_(C*)	0	2		NO2_(Ca)	0	9	
NO2_(Cb)	0	5		NO2_(Cd)	0	9	
NO2_(CO)	0	9		NO2_(CO*)	0	2	
NO2_(Ct)	0	9		NO2_(N)	0	9	
NO2_(O)	0	9		NO2_(O*)	0	2	
NO2_(ONO2)	0	9		O_(C)	-38	1	
O_(C)(C)	-23.66	1		O_(C)(C*)	-23.66	2	
O_(C)(Cb)	-29.64	1		O_(C)(Cd)	-29.64	1	
O_(C)(CO)	-43.02	1		O_(C)(CO*)	-43.02	2	
O_(C)(Ct)	-33.7	1		O_(C)(NO2)	-19.16	3	CH3-ONO2
O_(C)(O)	-5.74	1		O_(C)(O*)	-5.74	2	
O_(C*)	-38	2		O_(C*)(Cb)	-29.64	2	
O_(C*)(Cd)	-29.64	2		O_(C*)(CO)	-43.02	2	
O_(C*)(Ct)	-33.7	2		O_(C*)(NO2)	-19.16	2	
O_(C*)(O)	-5.74	2		O_(Cb)	-45.41	1	
O_(Cb)(Cb)	-32.5	1		O_(Cb)(Cd)	-25	5	
O_(Cb)(CO)	-43.5	1		O_(Cb)(CO*)	-43.5	2	
O_(Cb)(O*)	-11.71	2		O_(Cb*)	-45.41	2	
O_(Cd)	-45.41	1		O_(Cd)(Cd)	-32.74	1	
O_(Cd)(CO)	-44.69	1		O_(Cd)(CO*)	-44.69	2	
O_(Cd)(Ct)	-35.85	1		O_(Cd)(O*)	-11.71	2	
O_(Cd*)	-45.41	2		O_(Cd*)(O)	-11.71	2	
O_(CO)	-58.08	1		O_(CO)(CO)	-48.28	1	
O_(CO)(CO*)	-48.28	2		O_(CO)(O)	-19.12	1	
O_(CO)(O*)	-8.99	3	CH3C(O)O2	O_(CO)(ONO2)	-12.21	6	CH3C(O)O2NO2
O_(CO*)	-58.08	2		O_(CO*)(NO2)	-38.52	2	
O_(CO*)(O)	-19.12	2		O_(CO*)(ONO2)	-12.21	2	
O_(Ct)	-48.04	1		O_(NO2)	-32.1	7	HONO2
O_(NO2)(NO2)	3.18	7	N2O5	O_(NO2)(O)	4	5	
O_(NO2)(O*)	4	2		O_(O)	-16.49	1	
O_(O)(O)	14.7	5		O_(O)(O*)	14.7	2	
O_(O*)	-16.49	2		O_(ONO2)	-12.91	7	HO2NO2
O*_(C)	14.02	7	C2H5O, C2H5OH	O*_(CO)	-0.65	7	CH3C(O)O, CH3C(O)OH
O*_(O)	17.26	7	CH3O2, CH3OOH	ONO2_(C)	0	9	
ONO2_(C*)	0	2		ONO2_(Ca)	0	9	
ONO2_(Cb)	0	9		ONO2_(Cd)	0	9	
ONO2_(CO)	0	9		ONO2_(CO*)	0	2	
ONO2_(Ct)	0	9		ONO2_(N)	0	9	
ONO2_(NO2)	3.18	7	N2O5	ONO2_(O)	0	9	

Table S58 (continued)

Group [a]	Value	Ref	Additional Reference Info. [b]	Group	Value	Ref	Additional Reference Info.
ONO2_(O*)	0	2		ONO_(C)	-5.98	1	

[a] Group designation format: center\_(neighbor 1)(neighbor 2), etc. Radical center indicated by "\*". C, N, or O refer to atoms. Cd, Ct, Ca, and Cb refer to double bonded, triple bonded, allene bonded, and aromatic bonded carbons, respectively. CO, NO2, ONO2, and ONO refer to carbonyl, nitro, nitrate, or nitrite groups, respectively. CN and NC refer to C≡N and N≡C groups, respectively.

[b] Reference notes are as follows:

- 1 Holmes and Aubry (2012).
- 2 Set to be the same as the corresponding group without the radical center because the effect of forming the radical is accounted for using other radical groups.
- 3 Derived from the heat of formation for the indicated compound, from the NIST structures and properties database program (NIST, 2014).
- 4 Derived from other thermochemical group values as indicated.
- 5 Obtained from the NIST structures and properties database program (NIST, 2014).
- 6 Derived from the heat of formation for the indicated compound from NASA (2011).
- 7 Derived from the heats of formation for the indicated compounds from NASA (2011).
- 8 Derived based on heat of formation of resonance structure and C\*\_(Cd) and Cd(Cd)(O)(O).
- 9 Single valence center groups set to zero.

Table S59. Thermochemical group values (kcal/mole) that were assigned when developing MechGen and that are judged to have a moderate to high level of uncertainty.

Group [a]	Value	Ref	Additional Reference Info. [b]
C_(C)(C)(Cb)(CO)	4.78	1	C_(C)(Cb)(CO) + C_(C)(C)(C)(CO) - C_(C)(C)(CO)
C_(C)(C)(Cb)(O)	-6.90	1	C_(C)(Cb)(O) + C_(C)(C)(C)(O) - C_(C)(C)(O)
C_(C)(C)(Cd)(CO)	2.41	1	C_(C)(Cd)(CO) + C_(C)(C)(C)(Cd) - C_(C)(C)(Cd)
C_(C)(C)(Cd)(NO2)	-7.15	1	C_(C)(Cd)(NO2) + C_(C)(C)(C)(Cd) - C_(C)(C)(Cd)
C_(C)(C)(Cd)(O)	-3.39	1	C_(C)(Cd)(O) + C_(C)(C)(C)(Cd) - C_(C)(C)(Cd)
C_(C)(C)(Cd)(ONO2)	-19.85	1	C_(C)(Cd)(ONO2) + C_(C)(C)(C)(Cd) - C_(C)(C)(Cd)
C_(C)(C)(CO)(CO)	5.02	1	C_(C)(CO)(CO) + C_(C)(C)(C)(CO) - C_(C)(C)(CO)
C_(C)(C)(CO)(Ct)	5.26	1	C_(C)(CO)(Ct) + C_(C)(C)(C)(CO) - C_(C)(C)(CO)
C_(C)(C)(CO)(N)	-1.67	1	C_(C)(CO)(N) + C_(C)(C)(C)(N) - C_(C)(C)(N)
C_(C)(C)(CO)(NO2)	-11.25	1	C_(C)(CO)(NO2) + C_(C)(C)(C)(NO2) - C_(C)(C)(NO2)
C_(C)(C)(CO)(O)	0.48	1	C_(C)(CO)(O) + C_(C)(C)(C)(CO) - C_(C)(C)(CO)
C_(C)(C)(Ct)(O)	-5.30	1	C_(C)(Ct)(O) + C_(C)(C)(C)(O) - C_(C)(C)(O)
C_(C)(C)(Ct)(ONO2)	-21.79	1	C_(C)(Ct)(ONO2) + C_(C)(C)(C)(ONO2) - C_(C)(C)(ONO2)
C_(C)(C)(N)(N)	-15.41	1	C_(C)(N)(N) + C_(C)(C)(C)(N) - C_(C)(C)(N)
C_(C)(C)(N)(O)	-17.33	1	C_(C)(N)(O) + C_(C)(C)(C)(N) - C_(C)(C)(N)
C_(C)(C)(N)(ONO2)	-30.40	1	C_(C)(N)(ONO2) + C_(C)(C)(C)(N) - C_(C)(C)(N)
C_(C)(C)(NO2)(NO2)	-7.76	1	C_(C)(NO2)(NO2) + C_(C)(C)(C)(NO2) - C_(C)(C)(NO2)
C_(C)(C)(NO2)(O)	-21.53	1	C_(C)(NO2)(O) + C_(C)(C)(C)(NO2) - C_(C)(C)(NO2)
C_(C)(C)(ONO2)(ONO2)	-51.47	1	C_(C)(ONO2)(ONO2) + C_(C)(C)(C)(ONO2) - C_(C)(C)(ONO2)
C_(C)(Cb)(CO)	1.67	1	C_(Cb)(CO) + C_(C)(C)(CO) - C_(C)(CO)
C_(C)(Cd)(Cd)(O)	-1.91	1	C_(Cd)(Cd)(O) + C_(C)(C)(C)(Cd) - C_(C)(C)(Cd)
C_(C)(Cd)(Cd)(ONO2)	-18.37	2	
C_(C)(Cd)(CO)	-0.69	1	C_(Cd)(CO) + C_(C)(C)(Cd) - C_(C)(Cd)
C_(C)(Cd)(CO)(CO)	5.02	1	C_(Cd)(CO)(CO) + C_(C)(C)(C)(Cd) - C_(C)(C)(Cd)
C_(C)(Cd)(CO)(NO2)	-10.28	1	C_(Cd)(CO)(NO2) + C_(C)(C)(C)(Cd) - C_(C)(C)(Cd)
C_(C)(Cd)(CO)(O)	0.48	1	C_(Cd)(CO)(O) + C_(C)(C)(C)(Cd) - C_(C)(C)(Cd)
C_(C)(Cd)(CO)(ONO2)	-18.68	1	C_(Cd)(CO)(ONO2) + C_(C)(C)(C)(Cd) - C_(C)(C)(Cd)
C_(C)(Cd)(NO2)	-10.25	1	C_(Cd)(NO2) + C_(C)(C)(Cd) - C_(C)(Cd)
C_(C)(Cd)(NO2)(NO2)	-6.79	1	C_(Cd)(NO2)(NO2) + C_(C)(C)(C)(Cd) - C_(C)(C)(Cd)
C_(C)(Cd)(NO2)(O)	-20.55	1	C_(Cd)(NO2)(O) + C_(C)(C)(C)(Cd) - C_(C)(C)(Cd)
C_(C)(Cd)(O)(O)	-12.43	1	C_(Cd)(O)(O) + C_(C)(C)(C)(Cd) - C_(C)(C)(Cd)
C_(C)(Cd)(O)(ONO2)	-31.59	1	C_(Cd)(O)(ONO2) + C_(C)(C)(C)(Cd) - C_(C)(C)(Cd)
C_(C)(Cd)(ONO2)	-22.96	1	C_(Cd)(ONO2) + C_(C)(C)(Cd) - C_(C)(Cd)
C_(C)(Cd)(ONO2)(ONO2)	-49.56	1	C_(Cd)(ONO2)(ONO2) + C_(C)(C)(C)(Cd) - C_(C)(C)(Cd)
C_(C)(Cd*)(CO)	-0.69	3	CH2=C(..H)-CH(CH3)-CHO, CH2=C(..H)-CH(CH3)-CH3
C_(C)(Cd*)(CO)(O)	0.48	3	CH2=C(..H)-C(CH3)(CHO)-OH, CH2=C(..H)-C(CH3)(CH3)-OH
C_(C)(CO)(CO)	1.91	1	C_(CO)(CO) + C_(C)(C)(CO) - C_(C)(CO)
C_(C)(CO)(CO)(NO2)	-7.65	1	C_(CO)(CO)(NO2) + C_(C)(C)(C)(CO) - C_(C)(C)(CO)
C_(C)(CO)(CO)(O)	0.48	1	C_(CO)(CO)(O) + C_(C)(C)(C)(CO) - C_(C)(C)(CO)
C_(C)(CO)(Ct)	2.15	1	C_(CO)(Ct) + C_(C)(C)(CO) - C_(C)(CO)
C_(C)(CO)(NO2)	-13.38	1	C_(CO)(NO2) + C_(C)(C)(NO2) - C_(C)(NO2)
C_(C)(CO)(NO2)(NO2)	-28.94	1	C_(CO)(NO2)(NO2) + C_(C)(C)(C)(NO2) - C_(C)(C)(NO2)
C_(C)(CO)(NO2)(O)	-20.81	1	C_(CO)(NO2)(O) + C_(C)(C)(C)(NO2) - C_(C)(C)(NO2)
C_(C)(CO)(O)	-2.63	1	C_(CO)(O) + C_(C)(C)(CO) - C_(C)(CO)
C_(C)(CO)(O)(O)	-13.62	1	C_(CO)(O)(O) + C_(C)(C)(C)(O) - C_(C)(C)(O)
C_(C)(CO)(ONO2)(ONO2)	-51.95	1	C_(CO)(ONO2)(ONO2) + C_(C)(C)(C)(ONO2) - C_(C)(C)(ONO2)
C_(C)(Ct)(ONO2)	-22.99	1	C_(Ct)(ONO2) + C_(C)(C)(ONO2) - C_(C)(ONO2)
C_(C)(N)(N)	-16.6	1	C_(N)(N) + C_(C)(C)(N) - C_(C)(N)
C_(C)(N)(O)	-18.52	1	C_(N)(O) + C_(C)(C)(N) - C_(C)(N)
C_(C)(N)(ONO2)	-31.59	1	C_(N)(ONO2) + C_(C)(C)(N) - C_(C)(N)

Table S59 (continued)

Group [a]	Value	Ref	Additional Reference Info. [b]
C_(C)(NO2)(NO2)(O)	-39.93	1	C_(NO2)(NO2)(O) + C_(C)(C)(C)(NO2) - C_(C)(C)(NO2)
C_(C)(NO2)(O)(O)	-31.8	1	C_(NO2)(O)(O) + C_(C)(C)(C)(NO2) - C_(C)(C)(NO2)
C_(C)(O)(ONO2)(ONO2)	-62.94	1	C_(O)(ONO2)(ONO2) + C_(C)(C)(C)(ONO2) - C_(C)(C)(ONO2)
C_(C)(ONO2)(ONO2)	-52.66	1	C_(ONO2)(ONO2) + C_(C)(C)(ONO2) - C_(C)(ONO2)
C_(Cd)(CO)(CO)(O*)	17.12	3	CH2=CH-C(O..H)(CHO)-CHO, CH2=CH-C(O..H)(CH3)-CHO
C_(Cd)(CO)(CO*)(O)	3.08	3	CH2=CH-C(OH)(CHO)-CO..H CH2=CH-CH(CHO)-CO..H
C_(Cd)(CO*)(O)(O)	-12.67	3	CH2=C(OH)-CH=CH..H, CH2=CH-CH=CH..H
C_(Cd)(O)(O)(O*)	-23.47	3	=C-C(O)(O)(O..H), =C-C(C)(O)(O..H)
C_(Cd)(O)(O*)(ONO2)	-42.63	3	CH2=CH-C(O..H)(ONO2)-OH, CH2=CH-C(OH)(OH)-O..H
C_(Cd*)(CO)(O)	-2.63	3	H..Cd(CO)(O), H..Cd(C)(O)
C_(Cd*)(O)(O)(O)	-23.47	3	CH2=CH-C(OH)(OH)-OH, CH2=CH-CH(OH)-OH.
C_(CO)(CO)(CO*)	2.63	4	
C*_(C)(C)(Cd)	27.56	5	C_(Cd)..H + C_(C)(C)(C)..H - C_(C)..H
C*_(C)(C)(CO)	37.12	5	C_(CO)..H + C_(C)(C)(C)..H - C_(C)..H
C*_(C)(C)(Ct)	27.68	5	C_(Ct)..H + C_(C)(C)(C)..H - C_(C)..H
C*_(C)(C)(N)	31.22	5	C_(N)..H + C_(C)(C)(C)..H - C_(C)..H
C*_(C)(C)(O)	35.01	5	C_(C)(O)..H + C_(C)(C)(C)..H - C_(C)(C)..H
C*_(C)(Cd)	26.6	5	C_(Cd)..H + C_(C)(C)..H - C_(C)..H
C*_(C)(Cd)(Cd)	25.62	6	CH2=CH-C[.](CH3)-CH=CH2 = CH2=CH-C[.](CH3)-CH=CH2.
C*_(C)(Cd)(CO)	28.54	5	C_(C)(C)(Cd)..H
C*_(C)(Cd)(O)	22.74	5	C_(C)(C)(Cd)..H
C*_(C)(Cd)(ONO2)	6.27	5	C_(C)(C)(Cd)..H
C*_(C)(CO)	34.99	5	C_(CO)..H + C_(C)(C)..H - C_(C)..H
C*_(C)(CO)(CO)	43.5	5	C_(CO)(CO)..H + C_(C)(C)(C)..H - C_(C)(C)..H
C*_(C)(CO)(O)	38.96	5	C_(CO)(O)..H + C_(C)(C)(C)..H - C_(C)(C)..H
C*_(C)(CO)(ONO2)	19.8	5	C_(CO)(ONO2)..H + C_(C)(C)(C)..H - C_(C)(C)..H
C*_(C)(Ct)	26.63	5	C_(Ct)..H + C_(C)(C)..H - C_(C)..H
C*_(C)(N)	37.21	5	C_(N)..H + C_(C)(C)..H - C_(C)..H
C*_(C)(O)(O)	27.2	5	C_(O)(O)..H + C_(C)(C)(C)..H - C_(C)(C)..H
C*_(C)(O)(ONO2)	6.89	5	C_(O)(ONO2)..H + C_(C)(C)(C)..H - C_(C)(C)..H
C*_(Cd)(Cd)	27.1	5	C_(C)(Cd)..H
C*_(Cd)(Cd)(O)	24.22	5	C_(C)(C)(Cd)..H
C*_(Cd)(Cd)(ONO2)	0.89	3	CH2=CH-C(..H)(ONO2)-CH=CH2, CH2=CH-C(..H)(OH)-CH=CH2
C*_(Cd)(CO)	27.58	5	C_(C)(Cd)..H
C*_(Cd)(CO)(CO)	27.27	6	CH2=CH-C[.](CO-CH3)-CO-CH3 = CH2=CH-C[.](CO-CH3)-CO-CH3.
C*_(Cd)(CO)(O)	26.61	5	C_(C)(C)(Cd)..H
C*_(Cd)(O)	24.47	5	C_(C)(Cd)..H
C*_(Cd)(O)(ONO2)	-1.66	6	CH2=CH-C[.](OH)-ONO2 = CH2=CH-C[.](OH)-ONO2.
C*_(Cd)(ONO2)	5.31	5	C_(C)(Cd)..H
C*_(CO)(CO)	41.37	5	C_(CO)..H
C*_(CO)(CO)(O)	41.17	5	C_(CO)..H
C*_(CO)(O)	36.83	5	C_(CO)..H
C*_(CO)(O)(O)	28.94	5	C_(CO)..H
C*_(CO)(ONO2)	17.67	5	C_(CO)..H
C*_(Ct)	24.88	5	C_(Cd)..H
C*_(O)(O)	28.9	5	C_(O)..H
C*_(O)(O)(O)	16.93	3	H..C(O)(O)(O), H..C(C)(O)(O)
C*_(O)(ONO2)	8.59	5	C_(CO)..H
Cd_(Cd)(Cd)(Cd*)	12.67	3	CH2=C(CH=CH2)-CH=CH..H, CH2=CH-C(CH3)=CH..H
Cd_(Cd)(Cd)(O*)	4.77	3	CH2=C(O..H)-CH=CH2, CH2=C(O..H)-CH3
Cd_(Cd)(Cd)(ONO2)	-17.73	3	CH2=CH-C(..H)(ONO2)-CH=CH2, CH2=CH-C(..H)(OH)-CH=CH2
Cd_(Cd)(Cd*)(O)	8.84	3	CH2=C(OH)-CH=CH..H, CH2=CH-CH=CH..H
Cd_(Cd)(Cd*)(ONO2)	-17.73	3	CH2=CH-C(OONO2)=CH..H, CH2=CH-C(CH3)=CH..H
Cd_(Cd)(CO)(CO*)	3.83	7	

Table S59 (continued)

Group [a]	Value	Ref	Additional Reference Info. [b]
Cd_(Cd)(CO)(O*)	7.64	3	=C(CO)(O..H), =C(C)(O..H)
Cd_(Cd)(CO*)(ONO2)	-13.43	3	CH2=C(ONO2)-CO..H, CH2=C(OH)-CO..H
Cd_(Cd)(O)(O*)	8.19	3	=C(O)(O..H), =C(C)(O..H)
Cd_(Cd*)(O)(O)	12.26	3	H..CH=C(O)(O), H..CH=C(C)(O)
Cd*(C)(Cd)	63.12	5	Cd_(Cd)..H + C_(C)(C)..H - C_(C)..H
Cd*(Cd)(Cd)	61.35	3	n CH2=C(..H)-CH=CH2, CH2=C(..H)-CH3
Cd*(Cd)(CO)	59.58	3	n CH2=C(..H)-CO-CH3, CH2=C(..H)-CH3
Cd*(Cd)(O)	63.16	3	n CH2=C(..H)-OH, CH2=C(..H)-CH3
Cd*(Cd)(ONO2)	38.03	3	CH2=C(..H)-ONO2, CH2=C(..H)-OH
CO_(Cd)(CO*)	-26.53	3	CH3=CH-CO-CO..H, CH3-CO-CO..H
CO_(Cd*)(CO)	-26.53	3	CH2=C(..H)-CO-CHO, CH2=C(..H)-CO-CH3
CO*(Cb)	6.5	8	
CO*(Cd)	8.69	5	CO_(C)..H
CO*(O)	10.87	9	
N*(C)(C)	58.44	10	
O_(C)(Cd*)	-29.64	3	CH2=C(..H)-O-CH3, CH2=C(..H)-CH3
O_(Cd*)(CO)	-44.69	3	CH2=C(..H)-O-CHO, CH2=C(..H)-CH3

[a] Group designation format: center\_(neighbor 1)(neighbor 2), etc. Radical center indicated by "\*". C, N, or O refer to atoms. Cd, Ct, Ca, and Cb refer to double bonded, triple bonded, allene bonded, and aromatic bonded carbons, respectively. CO, NO2, ONO2, and ONO refer to carbonyl, nitro, nitrate, or nitrite groups, respectively. CN and NC refer to C#N and N#C groups, respectively.

[b] Reference notes are as follows:

- 1 Derived from groups with fewer substituents as indicated.
- 2 Derived assuming that the heat of formation of  $\text{CH}_3\text{C}(\text{CH}=\text{CH}_2)(\text{CH}=\text{CH}_2)\text{OH} + \text{CH}_3\text{C}(\text{CH}=\text{CH}_2)(\text{CH}_3)\text{-ONO}_2$  is the same as  $\text{CH}_3\text{C}(\text{CH}=\text{CH}_2)(\text{CH}=\text{CH}_2)\text{ONO}_2 + \text{CH}_3\text{C}(\text{CH}=\text{CH}_2)(\text{CH}_3)\text{OH}$ .
- 3 Indicated bond dissociation energies assumed to be the same.
- 4 Derived assuming that beta-substitution by -CHO does not affect the CO..H bond dissociation energy.
- 5 Estimated from other bond dissociation energies as indicated.
- 6 Derived assuming equal heats of formation as indicated.
- 7 Assume same CO..H bond dissociation energy in  $\text{CH}_2=\text{C}(\text{CHO})\text{CHO}$  as  $\text{CH}_2=\text{C}(\text{CH}_3)\text{CHO}$ .
- 8 Assume same CO..H bond dissociation energy in aromatic aldehydes as normal aldehydes.
- 9 Derived assuming the bond dissociation energy for CO\_(O)-H is 95.0 kcal/mole, which is estimated based on an assumed correlation between bond the dissociation energy and CO-H + OH rate constants.
- 10 Derived assuming a N-H bond dissociation energy of ~95 kcal/mole based on tabulations in Lalevee et al. (2002).



Table S60. Thermochemical group values (kcal/mole) that were assigned when developing MechGen and that are judged to have a very high level of uncertainty.

Group [a]	Value	Ref	Additional Reference Info. [b]
C_(C)(C)(Cb)(ONO2)	-18.66	1	C_(C)(C)(Cd)(ONO2) + C_(Cb)(CO) - C_(Cd)(CO)
C_(C)(C)(CO)(ONO2)	-18.68	1	C_(C)(C)(CO)(O) + C_(C)(C)(C)(ONO2) - C_(C)(C)(C)(O)
C_(C)(C*)(Cb)(ONO2)	-18.66	1	C_(C)(C)(Cd)(ONO2) + C_(Cb)(CO) - C_(Cd)(CO)
C_(C)(Cb)(O)(O)	-10.76	1	C_(C)(C)(O)(O) + C_(C)(C)(Cb) - C_(C)(C)(C)
C_(C)(Cb)(ONO2)	-22.24	1	C_(C)(Cd)(ONO2) + C_(Cb)(ONO2) - C_(Cd)(ONO2)
C_(C)(CO)(CO)(CO)	6.69	1	C_(C)(C)(CO)(CO) + C_(C)(C)(C)(CO) - C_(C)(C)(C)(C)
C_(C)(CO)(CO)(ONO2)	-18.68	2	C_(C)(CO)(CO)(O) + C_(C)(C)(C)(ONO2)
C_(C)(CO)(O)(ONO2)	-32.79	1	C_(C)(CO)(O)(O) + C_(C)(C)(C)(ONO2) - C_(C)(C)(C)(O)
C_(C)(CO)(ONO2)	-21.79	1	C_(C)(CO)(O) + C_(C)(C)(ONO2) - C_(C)(C)(O)
C_(C)(NO2)(O)	-23.66	1	C_(C)(O)(O) + C_(C)(C)(NO2) - C_(C)(C)(O)
C_(C*)(Cb)(ONO2)	-22.94	1	C_(C*)(Cd)(ONO2) + C_(C*)(Cb) - C_(C*)(Cd)
C_(C*)(Cd)(Cd)(O)	-1.91	3	
C_(C*)(Cd)(Cd)(ONO2)	-18.37	3	
C_(Cb)(CO)(O)	-1.91	1	C_(C)(CO)(O) + C_(C)(C)(Cb) - C_(C)(C)(C)
C_(Cb)(CO)(ONO2)	-20.60	1	C_(Cd)(CO)(ONO2) + C_(Cb)(CO) - C_(Cd)(CO)
C_(Cd)(CO)(CO)	1.91	1	C_(C)(CO)(CO) + C_(C)(C)(Cd) - C_(C)(C)(C)
C_(Cd)(CO)(CO)(O)	3.08	1	C_(C)(Cd)(CO)(O) + C_(Cd)(CO)(CO) - C_(C)(Cd)(CO)
C_(Cd)(CO)(CO)(ONO2)	-17.51	1	C_(C)(Cd)(CO)(ONO2) + C_(C)(Cd)(CO)(ONO2) - C_(C)(C)(Cd)(ONO2)
C_(Cd)(CO)(NO2)	-13.38	1	C_(C)(CO)(NO2) + C_(C)(C)(Cd) - C_(C)(C)(C)
C_(Cd)(CO)(O)	-2.63	1	C_(C)(CO)(O) + C_(C)(C)(Cd) - C_(C)(C)(C)
C_(Cd)(CO)(O)(O)	-12.67	1	C_(C)(CO)(O)(O) + C_(C)(C)(C)(Cd) - C_(C)(C)(C)(C)
C_(Cd)(CO)(ONO2)	-21.79	1	C_(C)(CO)(ONO2) + C_(C)(C)(Cd) - C_(C)(C)(C)
C_(Cd)(NO2)	-13.38	1	C_(Cd)(O) + C_(C)(NO2) - C_(C)(O)
C_(Cd)(NO2)(NO2)	-9.90	1	C_(C)(NO2)(NO2) + C_(C)(C)(Cd) - C_(C)(C)(C)
C_(Cd)(NO2)(O)	-23.66	1	C_(C)(NO2)(O) + C_(C)(C)(Cd) - C_(C)(C)(C)
C_(Cd)(O)(O)	-15.54	1	C_(C)(O)(O) + C_(C)(C)(Cd) - C_(C)(C)(C)
C_(Cd)(O)(O)(O)	-23.47	1	C_(C)(O)(O)(O) + C_(C)(C)(Cd)(O) - C_(C)(C)(C)(O)
C_(Cd)(O)(O)(ONO2)	-42.63	1	C_(Cd)(O)(O)(O) + C_(O)(ONO2) - C_(O)(O)
C_(Cd)(O)(ONO2)	-34.70	1	C_(C)(O)(ONO2) + C_(C)(C)(Cd) - C_(C)(C)(C)
C_(Cd)(ONO2)(ONO2)	-52.66	1	C_(C)(ONO2)(ONO2) + C_(C)(C)(Cd) - C_(C)(C)(C)
C_(CO)(CO)(CO)	2.63	1	C_(C)(CO)(CO) + C_(C)(C)(CO) - C_(C)(C)(C)
C_(CO)(CO)(CO)(CO)	8.37	1	C_(C)(CO)(CO)(CO) + C_(C)(C)(C)(CO) - C_(C)(C)(C)(C)
C_(CO)(CO)(CO)(O)	1.2	1	C_(C)(CO)(CO)(CO) + C_(C)(C)(C)(O) - C_(C)(C)(C)(C)
C_(CO)(CO)(CO)(ONO2)	-17.97	1	C_(CO)(CO)(CO)(O) + C_(C)(C)(C)(ONO2) - C_(C)(C)(C)(O)
C_(CO)(CO)(NO2)	-10.76	1	C_(CO)(CO)(O) + C_(C)(C)(NO2) - C_(C)(C)(O)
C_(CO)(CO)(O)	-2.63	1	C_(C)(CO)(CO) + C_(C)(C)(O) - C_(C)(C)(C)
C_(CO)(CO)(O)(O)	-11.95	1	C_(C)(CO)(O)(O) + C_(C)(C)(C)(CO) - C_(C)(C)(C)(C)
C_(CO)(CO)(O)(ONO2)	-31.11	1	C_(CO)(CO)(O)(O) + C_(C)(C)(C)(ONO2) - C_(C)(C)(C)(O)
C_(CO)(CO)(ONO2)	-21.79	1	C_(CO)(CO)(O) + C_(C)(C)(ONO2) - C_(C)(C)(O)
C_(CO)(NO2)	-13.38	1	C_(CO)(O) + C_(C)(NO2) - C_(C)(O)
C_(CO)(NO2)(NO2)	-31.07	1	C_(CO)(NO2)(O) + C_(C)(C)(NO2) - C_(C)(C)(O)
C_(CO)(NO2)(NO2)(O)	-38.26	1	C_(C)(NO2)(NO2)(O) + C_(C)(C)(C)(CO) - C_(C)(C)(C)(C)
C_(CO)(NO2)(O)	-22.94	1	C_(CO)(O)(O) + C_(C)(C)(NO2) - C_(C)(C)(O)
C_(CO)(O)(O)	-14.82	1	C_(C)(O)(O) + C_(C)(C)(CO) - C_(C)(C)(C)
C_(CO)(O)(O)(O)	-23.42	1	C_(C)(O)(O)(O) + C_(C)(C)(C)(CO) - C_(C)(C)(C)(C)
C_(CO)(O)(O)(ONO2)	-42.58	1	C_(CO)(O)(O)(O) + C_(C)(C)(C)(ONO2) - C_(C)(C)(C)(O)
C_(CO)(O)(ONO2)	-33.98	1	C_(CO)(O)(O) + C_(C)(C)(ONO2) - C_(C)(C)(O)
C_(CO)(O)(ONO2)(ONO2)	-61.75	1	C_(CO)(O)(O)(ONO2) + C_(C)(C)(C)(ONO2) - C_(C)(C)(C)(O)
C_(CO)(ONO2)(ONO2)	-53.14	1	C_(CO)(O)(ONO2) + C_(C)(C)(ONO2) - C_(C)(C)(O)
C_(Ct)	-10.04	4	C_(C)

Table S60 (continued)

Group [a]	Value	Ref	Additional Reference Info. [b]
C_(Ct)(O)(O)	-15.54	1	C_(Cd)(O)(O) + C_(Ct) - C_(Cd)
C_(N)(ONO2)	-27.77	1	C_(O)(ONO2) + C_(C)(N) - C_(C)(O)
C_(NO2)(NO2)	-28.92	1	C_(NO2)(O) + C_(C)(NO2) - C_(C)(O)
C_(NO2)(NO2)(O)	-42.07	1	C_(NO2)(O)(O) + C_(C)(C)(NO2) - C_(C)(C)(O)
C_(NO2)(O)	-22.47	1	C_(O)(O) + C_(C)(NO2) - C_(C)(O)
C_(NO2)(O)(O)	-33.94	1	C_(O)(O)(O) + C_(C)(C)(NO2) - C_(C)(C)(O)
C_(O)(ONO2)(ONO2)	-64.14	1	C_(O)(O)(ONO2) + C_(C)(C)(ONO2) - C_(C)(C)(O)
C_(ONO2)(ONO2)	-54.34	1	C_(O)(ONO2) + C_(C)(ONO2) - C_(C)(O)
C*_(C)(C)(Cb)	31.69	5	
C*_(C)(Cb)	30.04	6	
C*_(C)(Cb)(O)	24.56	7	
C*_(C)(Cb)(ONO2)	12.58	8	
C*_(C)(N)(O)	28.52	1	C*_(C)(O)(O) + C_(N)(O) - C_(O)(O)
C*_(C)(NO2)	29.06	1	C*_(C)(O) + C_(NO2)(O) - C_(O)(O)
C*_(Cb)	28.3	9	
C*_(Cb)(O)	23.95	10	
C*_(Cb)(ONO2)	12.96	8	
C*_(Cd)(Cd)(CO)	18.14	11	CH2=CH-C[.] (CHO)-CH=CH2 = CH2=CH-C(CHO)=CH-CH2.
C*_(CO)(CO)(CO)	49.02	12	HCO-C[.] (CHO)-CHO + HCO-CH2. --> 2 HCO-CH[.] -CHO
C*_(CO)(CO)(ONO2)	21.12	1	C*_(C)(CO)(ONO2) + C*_(CO)(ONO2) - C*_(C)(ONO2)
C*_(Ct)(O)	24.47	1	C*_(Cd)(O) + C*_(Ct) - C*_(Cd)
C*_(N)(O)	30.21	1	C*_(O)(O) + C_(N)(O) - C_(O)(O)
C*_(O)(O)(ONO2)	-2.23	1	C*_(O)(O)(O) + C_(O)(ONO2) - C_(O)(O)
Cb*_(Cb)(Cb)	61.38	13	
Cd_(C)(C)(Ca)	8.77	14	Cd_(C)(Cd)(Cd)
Cd_(C)(Ca)	8.56	14	Cd_(C)(Cd)
Cd_(C)(Cd)(O*)	6.21	15	
Cd_(C)(Cd)(ONO2)	-13.4	2	Cd_(Cd)(ONO2) + C_(C)(C)(Cd)
Cd_(Ca)	6.26	14	Cd_(Cd)
Cd_(Cd)(CO)(CO)	3.87	2	Cd_(C)(Cd)(CO) + Cd_(Cd)(CO)
Cd_(Cd)(O)(ONO2)	-12.87	12	CH2=C(OH)-OH + CH2=CH-ONO2 --> CH2=C(OH)-ONO2 + CH2=CH-OH
CO_(Cd)(CO)	-26.53	1	CO_(C)(Cd) + CO_(C)(CO) - CO_(C)(C)
CO_(Cd)(ONO2)	-51.19	1	CO_(Cd)(O) + C_(O)(ONO2) - C_(O)(O)
CO_(CO)(CO)	-26.05	1	CO_(C)(CO) + CO_(C)(CO) - CO_(C)(C)
CO_(CO)(ONO2)	-67.74	12	CH3-CO-CO-OH + CH3-CO-ONO2 --> CH3-CO-CO-ONO2 + CH3-CO-OH
Ct_(CO)(Ct)	24.01	1	Ct_(C)(Ct) + Cd_(Cd)(CO) - Cd_(C)(Cd)
O_(Cb)(O)	-11.71	1	O_(C)(O) + O_(C)(Cb) - O_(C)(C)
O_(Cd)(Cd*)	-32.74	4	Cb_(Cb)(Cb)(CO)
O_(Cd)(NO2)	-25.14	1	O_(Cd)(O) + O_(C)(NO2) - O_(C)(O)
O_(Cd)(O)	-11.71	1	O_(C)(O) + O_(C)(Cd) - O_(C)(C)
O_(CO)(NO2)	-38.52	1	O_(C)(NO2) + O_(C)(CO) - O_(C)(C)
O*_(Cb)	-11.05	16	
O*_(Cd)	-11.05	17	
ONO2_(Cd*)	0	4	ONO2_(CO)

[a] Group designation format: center\_(neighbor 1)(neighbor 2), etc. Radical center indicated by "\*". C, N, or O refer to atoms. Cd, Ct, Ca, and Cb refer to double bonded, triple bonded, allene bonded, and aromatic bonded carbons, respectively. CO, NO2, ONO2, and ONO refer to carbonyl, nitro, nitrate, or nitrite groups, respectively. CN and NC refer to C#N and N#C groups, respectively.

[b] Reference notes are as follows:

- 1 Rough estimate derived from effect of replacing one substituent group with another as indicated.
- 2 Rough estimate derived from other thermochemical group values as indicated.
- 3 Assumed that -OX substitution on the other side of the double bond from the radical center does not affect

Table S60 (continued)

- the C..H bond dissociation forming the radical.
- 4 Assumed to be the same as assigned for another group.
  - 5 Derived to yield a  $\text{CH}_3\text{C}(\cdot\text{H})(\text{CH}_3)\text{Ph}$  bond dissociation energy of 84.75, which is estimated based on those for  $\text{Ph-CH}_2\cdot\text{H}$ ,  $\text{CH}_2=\text{CH-CH}_2\cdot\text{H}$  and  $\text{CH}_2=\text{CH-C}(\cdot\text{H})(\text{CH}_3)\text{CH}_3$ .
  - 6 Derived to yield a  $\text{CH}_3\text{CH}(\cdot\text{H})\text{Ph}$  bond dissociation energy of 86.92, which is estimated based on those for  $\text{Ph-CH}_2\cdot\text{H}$ ,  $\text{CH}_2=\text{CH-CH}_2\cdot\text{H}$  and  $\text{CH}_2=\text{CH-CH}(\cdot\text{H})\text{CH}_3$ .
  - 7 Derived to yield a  $\text{CH}_3\text{C}(\cdot\text{H})(\text{OH})\text{Ph}$  bond dissociation energy of 84.76, which is estimated based on those for  $\text{Ph-CH}_2\cdot\text{H}$ ,  $\text{CH}_2=\text{CH-CH}_2\cdot\text{H}$  and  $\text{CH}_2=\text{CH-C}(\cdot\text{H})(\text{OH})\text{CH}_3$ .
  - 8 Rough estimate assuming that alpha- $\text{ONO}_2$  substitution in benzyl type radicals does not affect C..H bond dissociation energy. This is highly uncertain since effects on  $-\text{ONO}_2$  substitution does not seem to be consistent for other cases.
  - 9 Derived to yield the  $\text{Ph-CH}_2\cdot\text{H}$  bond dissociation energy of 90.44 kcal/mole (reference citation not found).
  - 10 Derived to yield a  $\text{HOCH}(\cdot\text{H})\text{Ph}$  bond dissociation energy of 82.26, which is estimated based on those for  $\text{Ph-CH}_2\cdot\text{H}$ ,  $\text{CH}_2=\text{CH-CH}_2\cdot\text{H}$  and  $\text{CH}_2=\text{CH-CH}(\cdot\text{H})\text{OH}$ .
  - 11 Derived assuming equal heats of formation as indicated.
  - 12 Derived assuming zero heat of reaction for the indicated reaction.
  - 13 Assumed same C..H bond dissociation energy for benzene as for ethene.
  - 14 Cd\_(Ca) represented as Cd\_(Cd).
  - 15 Estimated assuming heats of formation for  $\text{CX}_2=\text{C}(\text{O}\cdot)\text{CH}_3$  are similar to those derived for  $(\cdot)\text{CHXC}(\text{O})\text{CH}_3$ , where  $\text{X} = \text{H}$  or  $\text{CH}_3$ . Uncertainty is at least 0.5 kcal/mole.
  - 16 Assumed same  $\text{Ph-O}\cdot\text{H}$  bond dissociation energy as estimated for  $\text{CH}_2=\text{CH-O}\cdot\text{H}$ .
  - 17 Estimated assuming heats of formation for  $\text{CX}_2=\text{CH}(\text{O}\cdot)$  are similar to those derived for  $(\cdot)\text{CHX-CHO}$ , where  $\text{X} = \text{H}$  or  $\text{CH}_3$ . Uncertainty is at least 0.5 kcal/mole.

Table S61. Ring strain corrections (kcal/mole) from Holmes and Aubry (2011) used for thermochemical estimates.

Ring Size	Default	Cyclic Ketones
3	28.20	43.74
4	26.53	25.10
5	6.69	5.74
6	0.48	2.87
7	6.69	3.35
8	10.28	2.39
9	13.38	5.26
10	13.15	4.30
11	12.19	
12	5.02	
13	1.00	

Table S62. Heats of formation (kcal/mole) assigned to specific species.

Stable species [a]	$\Delta H_f$	Ref [b]	Radical species	$\Delta H_f$	Ref
H <sub>2</sub>	0	1	H.	52.10	2
N <sub>2</sub>	0	1	O <sub>3</sub> P	59.57	2
H <sub>2</sub> O	-57.80	2	OH	8.93	2
HNO	26.10	2	CH <sub>3</sub> ·	35.06	2
NO	21.76	2	·CH <sub>2</sub> -NH <sub>2</sub>	35.61	2
O <sub>2</sub>	0	1	CH <sub>3</sub> -NH.	44.00	2
HO <sub>2</sub> ·	2.94	2	HCO·	10.55	2
HOOH	-32.48	2	·CH <sub>2</sub> OH	-4.06	2
NO <sub>2</sub>	8.12	2	CH <sub>3</sub> O·	5.02	2
O <sub>3</sub>	33.87	2	CO(·)OH	-46.13	2
HOOOH	-21.51	2	CH <sub>3</sub> OO·	2.15	2
NO <sub>3</sub>	17.85	2	·CH <sub>2</sub> -NO <sub>2</sub>	35.21	2
HNO <sub>3</sub>	-32.10	2	NO <sub>2</sub> CH(·)NO <sub>2</sub>	40.39	2
NO <sub>2</sub> OH	-32.10	2	CH <sub>2</sub> =CH.	70.60	2
HOOOOH	-10.61	2	CH <sub>3</sub> CH <sub>2</sub> ·	28.90	2
HO-ONO <sub>2</sub>	-12.91	2	CH <sub>3</sub> C(O)·	-2.46	2
NO <sub>2</sub> ONO <sub>2</sub>	3.18	2	CH <sub>3</sub> CH(·)OH	-12.72	2
CH <sub>4</sub>	-17.82	2	CH <sub>3</sub> CH <sub>2</sub> O·	-4.10	3
CO	-26.42	2	CH <sub>3</sub> OCH <sub>2</sub> ·	0.91	2
HCHO	-25.98	2	·CH <sub>2</sub> C(O)OH	-60.47	2
CH <sub>3</sub> OH	-48.04	2	CH <sub>3</sub> C(O)O·	-46.01	2
HCO-NH <sub>2</sub>	-46.34	2	CH <sub>3</sub> -OC(O)·	-41.54	2
NH <sub>2</sub> C(O)NH <sub>2</sub>	-58.75	2	CO(·)CH <sub>2</sub> OH	-36.81	2
HC(O)OH	-90.49	2	HC(O)OCH <sub>2</sub> ·	-37.09	2
CH <sub>3</sub> OOH	-31.60	2	CH <sub>3</sub> CH <sub>2</sub> OO·	-6.55	2
HOCH <sub>2</sub> OH	-73.90	2	CH <sub>3</sub> OOCH <sub>2</sub> ·	17.07	2
CO <sub>2</sub>	-94.05	2	CH <sub>3</sub> C(O)OO·	-36.90	2
CH <sub>3</sub> -NO <sub>2</sub>	-17.76	2	CH <sub>2</sub> =CH-CH <sub>2</sub> ·	39.70	2
HC(O)OOH	-68.19	2	CH <sub>3</sub> CH(·)CH <sub>3</sub>	20.70	2
CH <sub>3</sub> -ONO <sub>2</sub>	-29.21	2	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> ·	24.21	2
CH <sub>2</sub> =CH <sub>2</sub>	12.52	2	CH <sub>3</sub> CH <sub>2</sub> C(O)·	-8.70	2
CH <sub>3</sub> CH <sub>3</sub>	-20.04	2	CH <sub>3</sub> C(O)CH <sub>2</sub> ·	-8.13	2
CH <sub>3</sub> CH <sub>2</sub> -NH <sub>2</sub>	-11.35	2	CH <sub>3</sub> CH <sub>2</sub> OCH <sub>2</sub> ·	-7.48	2
CH <sub>3</sub> CHO	-39.70	3	CH <sub>3</sub> CH <sub>2</sub> OC(O)·	-46.51	2
CH <sub>3</sub> CH <sub>2</sub> OH	-56.12	2	CH <sub>3</sub> C(O)OCH <sub>2</sub> ·	-50.33	2
CH <sub>3</sub> OCH <sub>3</sub>	-44.00	2	CH <sub>3</sub> CH(OO·)CH <sub>3</sub>	-15.60	3
HC(O)CHO	-50.67	2			
CH <sub>2</sub> =C(OH)OH	-72.30	2			
CH <sub>3</sub> C(O)OH	-103.44	2			
CH <sub>3</sub> OCHO	-85.42	2			
HC(O)CH <sub>2</sub> OH	-76.00	2			
CH <sub>3</sub> CH <sub>2</sub> OOH	-39.89	2			
HOCH <sub>2</sub> CH <sub>2</sub> OH	-93.74	2			
HC(O)CH(OH)OH	-118.55	2			
HOCH <sub>2</sub> C(O)OH	-139.34	2			
HOC(O)COOH	-174.90	2			
HOCH <sub>2</sub> OOCH <sub>2</sub> OH	-136.64	2			
CH <sub>3</sub> C(O)O-ONO <sub>2</sub>	-57.39	2			
CH <sub>2</sub> =CH-CH <sub>3</sub>	4.78	2			
CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	-25.02	2			
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> -NH <sub>2</sub>	-16.92	2			
CH <sub>3</sub> -N(CH <sub>3</sub> )CH <sub>3</sub>	-5.64	2			
CH <sub>2</sub> =CH-CHO	-17.76	2			

Stable species [a]	$\Delta H_f$	Ref [b]	Radical species	$\Delta H_f$	Ref
CH <sub>3</sub> CH <sub>2</sub> CHO	-44.36	2			
CH <sub>3</sub> C(O)CH <sub>3</sub>	-51.90	3			
CH <sub>3</sub> CH(CH <sub>3</sub> )OH	-65.15	2			
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	-60.97	2			
CH <sub>3</sub> CH <sub>2</sub> OCH <sub>3</sub>	-51.72	2			
CH <sub>3</sub> CH <sub>2</sub> OCHO	-93.88	2			
CH <sub>3</sub> C(O)CH <sub>2</sub> OH	-89.15	2			
CH <sub>3</sub> OCH <sub>2</sub> OCH <sub>3</sub>	-83.29	2			
CH <sub>3</sub> C(CHO)(OH)OH	-131.64	2			
HOCH <sub>2</sub> CH(OH)CH <sub>2</sub> OH	-138.12	2			
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	-30.03	2			
CH <sub>3</sub> C(O)OOC(O)CH <sub>3</sub>	-119.50	2			

[a] Species designations are as used by MechGen. Ordered by carbon, oxygen, and nitrogen numbers.

[b] Sources of data are as follows:

- 1 Zero by convention
- 2 NASA (2011)
- 3 NASA (2006)