SUPPLEMENTAL INFORMATION

Derivation of Atmospheric Reaction Mechanisms for Volatile Organic Compounds by the SAPRC Mechanism Generation System (MechGen)

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A1.1. 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 A-1; illustrative examples are shown in Table A-2. 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 A-2. This is similar to the treatment of branched structure using the SMILES notation (SMILES, 2022). Other examples are also shown in Table A-2.
- 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 A-2.
- 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 A-2.
- 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.

Table A-1. List of groups and group designations used to specify organic reactants.

Non-Radical/Stable Groups [a]		
Types, names, bonds		Note [b]
Alkane		
CH4		1
-CH3	CH3-	
-CH2-		
-CH()-		
-C()()-		
Alkene		
=CH2	CH2=	
=CH-	-CH=	
=C()-	-C()=	
=C=		
Alkyne		
#CH	HC#	
#C-		
Aromatic or Allylic		
-aCH-		2
-aC()-		2
Oxygenate		
CO		1
HCHO		1
CO2		1
-CHO	HCO-	
-CO-		
-OH	HO-	
-O-		
Nitrate, nitro, nitroso		
-ONO2	O2NO-	
-NO2	NO2-	
-NO	NO-	3
Amino and stable amine-oxy		
-NH2	NH2-	
-NH-		
-N()-		
-N[O]()-		4
Imine		
=NH	NH=	3
=N-	-N=	3
Stabilized Criegee intermediates		
HCHO2		1
-CHOO[syn]		
-CHOO[anti]		
-C[OO]-		
-syn-		5

Radical Groups [a]		
Group types, names, bonds		Note [b]
Carbon-centered radical groups		
CH3.		
-CH2.	.CH2-	
-CH[.]-		
-C[.]()-		
=CH.	.CH=	
=C[.]-	-C[.]=	
-aCH2.	.aCH2-	2
-aCH[.]-		2
-aC[.]()-		2
-pC[.]-		6
-CO.	CO[.]-	
Peroxy radical groups		
CH3OO.		1
-CH2OO.	.OOCH2-	
-CH[OO.]-		
-C[OO.]()-		
-CO[OO.]	CO[OO.]-	
=CHOO.	.OOCH=	
=C[OO.]-	-C[OO.]=	
-pC[OO.]-		6
Alkoxy radical groups		
CH3O.		1
-CH2O.	.OCH2-	
-CH[O.]-		
-C[O.]()-		
=CH[O.]	CH[O.]=	
=C[O.]-	-C[O.]=	
-CO2.	CO[O.]-	
-pC[O.]-		6
N-Containing radicals and excited adducts		
-NH.	.NH-	
-N[.]-		
-NH2[O]	NH2[O]-	8
-NH[O]-		8
Carbenes		
-CH[..]	CH[..]-	
-C[..]-		
Excited Criegee intermediates		
HCHO2 {excited}		1, 7
-CHOO {excited}		7
-C[OO]- {excited}		7

[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 A-1 (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., "CH3-C(CH3)(CH3)-CH3 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 ".aCH2-aCH-aCH2.", 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_3 reacts with tertiary amines. Unlike amine oxides formed when O_3 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_3- group in CH3-syn-C[OO]-CH2-CH3 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 "{*O3Ole}" or "{*O3cycOle}" to indicate formation from O_3 + alkene reactions, "{*O3alkyne}" to indicate formation from O_3 + alkyne reactions, and {*O3carbene}" to indicate formation from carbenes.

8 These reactive amine oxide groups are used for intermediates in reactions of O_3 with primary and secondary amines.

Table A-2. 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.

A1.2. Tables of Parameters for Bimolecular Rate Constant Estimation

The equations used to derive estimated rate constants for reactions of VOCs with OH, NO_3, O_3, and O^3P are given in Table 3 of the main text, and the table numbers with the values of the various parameters are given in Table A-3. 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 A5.1 tables for comparison purposes.

Table A-3. Table numbers giving the parameters for the various types of reactions of organics with OH, NO_3, Cl, O_3, and O^3P. Table 3 in the main text shows how these parameters are used to estimate rate constants.

Type of Reaction	Parameter	Table (in Section A5)
H-Atom abstractions by OH, NO_3, or Cl	kH^{base}	Table A-37
	FH^{nbr}	Table A-38 (OH) Table A-39 (NO_3) Table A-40 (Cl)
	FH^{ring}	Table A-42
Additions by OH, NO_3, or Cl	kA^{base} $kAro^{base}$ $kA''^{\,base}$	Table A-37
	FA^{nbr}	Table A-38 (OH) Table A-39 (NO_3) Table A-40 (Cl)
	$FA^{ortho,\ etc.}$	Table A-41
Additions by O_3 or O^3P	$kA'^{\,base}$ $kA''^{\,base}$	Table A-43
	$FA'^{\,nbr}$ $FA'^{\,struct}$ (furan)	Table A-44
	$FA'^{\,struct}$ (ring)	Table A-42

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_3 and the modified parameters are indicated where applicable in Table A-37 through Table A-39. The updated rate constant estimates for reactions of OH and NO_3 with phenols are compared with the experimental data used to derive the parameters in Table A-4. 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 A-4. 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 /	kNO_3 [a]		Est /
	Expt	SAR	Expt	Expt	SAR	Expt
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} cm^3 $molec^{-1}$ 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).

A1.3. 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 A-5 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 A-5. 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	$NO_2 + h\nu \rightarrow NO + O^3P$	NASA (2006)
AFGS	1.8 min.	no	$HCO\text{-}CH_x\text{=}CH_xCO_x$ compounds *	See note 1
HPALDS	18 min.	no	Avg of σ'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 (σ'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 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(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_x" 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_2 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_2. This "pressure" adjustment was made so the calculated photolysis rates relative to NO_2 are consistent with the data of Plum et al. (1983) and Klotz et al. (2000).

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=29 8K. Quantum yields are calculated for 1 atm and T=298 K using the complex expression recommended by IUPAC.

A1.4. Reactions of Carbon-Centered Radicals

A1.4.1. Rate Constants for O_2 Reactions

Table A-6 gives measured rate constants for the reactions of various types of carbon-centered radicals with O_2. For estimation purposes, we assume a 298 K rate constant of 7.5×10^{-12} cm^3 $molec^{-1}$ s^{-1}, which corresponds to a pseudo-unimolecular rate constant of $\sim 3.8 \times 10^7$ sec^{-1} near the surface. This is sufficiently high that O_2 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 A-6. Summary of measured O_2 addition rate constants for representative carbon-centered radicals.

Radical	298 K Rate Constant (10^{-12} cm3 $molec^{-1}$ s^{-1})	Ref
$CH_3\cdot$ (high pressure)	1.2	NASA (2011)
$CH_3CH_2\cdot$	8.0	NASA (2011)
$CH_3CH_2CH_2\cdot$	8.0	NASA (2011)
$CH_3CH(\cdot)CH_3$	11.0	NASA (2011)
$CH_3C(\cdot)(CH_3)CH_3$	3.5	Dusanter et al. (2005)
$HOCH_2\cdot$	9.1	NASA (2011)
$HC(O)\cdot$ [a]	5.2	NASA (2011)
$CH_3C(O)\cdot$	5.1	NASA (2011)
Used for estimates	7.5	Average of values for 1- and 2-propyl and t-butyl.

A1.4.2. O_2 Addition Mechanisms

If the carbon-centered radical is not adjacent to any double bonds, then the O_2 reaction involves simply addition to the radical center, forming the corresponding peroxy radical.

$$G\cdot + O_2 \rightarrow G[OO\cdot]$$

However, the peroxy radicals formed from α-OH substituted radicals are assumed to rapidly decompose to form HO_2 and the corresponding carbonyl.

$$HO\text{-}CX_2\cdot + O_2 \rightarrow HO\text{-}CX_2[OO\cdot]\ \{excited\} \rightarrow XC(=O)=X + HO_2$$

MechGen treats these as concerted processes when reactions of α-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.,

$$-G_1[\cdot]\text{-}G{=}G_2\text{-} \leftrightarrow -G_1{=}G\text{-}G_2[\cdot]\text{-} \quad \text{or} \quad -aG_1[\cdot]\text{-}aG\text{-}aG_2[\cdot]$$

$$-G_1[\cdot]\text{-}G{=}G_3\text{-}G{=}G_2 \leftrightarrow -G_1{=}G\text{-}G_3{=}G\text{-}G_2[.]\text{-} \leftrightarrow -G_1{=}G\text{-}G_3[\cdot]\text{-}G{=}G_2 \quad \text{or} \quad -aG_1[\cdot]\text{-}aG\text{-}aG_3[\cdot]\text{-}aG\text{-}aG_2[.]$$

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_1 or G_2, above) because otherwise the double bonds in the O_2 adduct are not conjugated (e.g, addition to G_3 in the second example above).

If one of the radical centers is estimated to have a rapid α-scission or cyclopropyl ring opening reaction that is estimated to be faster than O_2 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_2 addition.

If there is no rapid reaction at any of the radical centers, then only O_2 addition is assumed to occur and the relative rates of O_2 addition at the two different positions (e.g., G_1 or G_2) 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_2 addition at the different positions. Table A-7, 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 ΔΔHr(G), defined as ΔHr(G) - ΔHr(prim), where ΔHr(G) is the heat of reaction for O_2 addition to radical center G, in an allylic radical where the other radical center is primary (-aCH_2[·]), and ΔHr(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 α-OH substituted radicals are relative to the O_2 adduct initially formed, not the ultimate carbonyl + HO_2 products. The groups substituted by -ONO_2, -NO_2, -OOH, or -OOR groups are not considered in this context because they are expected to undergo rapid α-scission decomposition before O_2 reaction can occur.

Table A-7. Estimated heats of reaction for O_2 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] ΔHr (G)	ΔHr (prim)	ΔΔHr (G)	WtF (G) [c]
-aCH_2[·]	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. αOH	-23.83	-20.29	-3.54	10.52 [d]
-aC[·](R)-OX	Tert. αOH	-23.65	-21.54	-2.11	6.56 [d]
-aCH[·]-CO-X	Sec. αCO	-17.14	-20.29	3.15	0.35
-aC[·](R)-CO-X	Tert. αCO	-16.54	-20.41	3.87	0.28

[a] G is the radical center where the O_2 addition occurs. R is any alkyl group; X is H or alkyl.

[b] ΔHr(G) and ΔHr(prim) are heats of reaction (in kcal/mole) for O_2 adding to radical center G and to a primary radical center on the same allylic radical, respectively, and ΔΔHr is ΔHr(G) - ΔHr(prim). Heats of reaction are estimated as discussed in Section A2.1.

[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 A-7).
- 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-OH 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.

Based on these two data points, the following estimation method is derived:

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

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

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

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, $\Delta\Delta$Hr(G) is from Table A-7, 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 A-1.

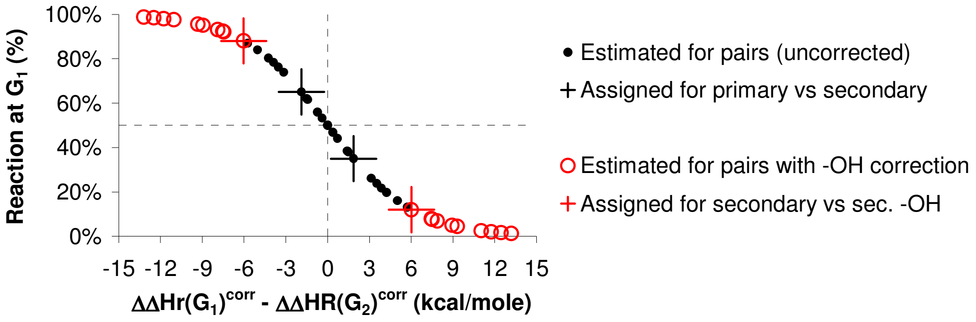


Figure A-1. Plots of assigned or estimated fractions of O_2 additions to various radical centers for allylic radicals with various combinations of two radical center types (G_1 and G_2).

These estimates of branching ratios are quite uncertain both because of the uncertainty in the secondary vs. secondary α-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 A-7.

A1.4.3. 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 $\cdot CH_2(CH_2)nOOH$ 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 A-8, which also includes our heats of reaction (ΔHr) 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 A-2.

Table A-8. Data used to estimate rate constants for cyclic ether formation decompositions of radicals with the structure $\cdot CH_2(CH_2)_nOOH$.

Ring Size	A [a] (s^{-1})	Ea [a] (kcal/mole)	ΔH_r [b] (kcal/mole)	kIsom [c] (s^{-1})	kIsom/kO_2 [d]
3 (n=1)	3.0×10^{11}	22.0	-12.81	3×10^{-5}	7×10^{-13}
4 (n=2)	2.5×10^{10}	12.3	-14.48	2×10^{-1}	5×10^{-9}
5 (n=3)	2.1×10^{9}	6.5	-34.32	4×10^{4}	1×10^{-3}
6 (n=4)	1.5×10^{8}	1.8	-39.58	7×10^{6}	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 kIsom = A exp(-Ea/RT)

[d] Calculated using the pseudo-unimolecular rate constant for O_2 addition of 3.8×10^7 sec^{-1}.

Table A-8 shows that the decompositions of radicals of the type $\cdot CH_2(CH_2)_nOOH$ are estimated to be slower than 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 A-8. These are listed in Table A-9, 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 O-NO_2 bonds as well as O-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 A-8 for radicals of the type $\cdot CH_2(CH_2)_nOOH$, assuming that the Arrhenius parameters for the analogous reactions of the radicals of the types listed in Table A-9 will have the same dependence on the ring size and heat of reaction. Figure A-2 shows that the log of the A factor decreases linearly with size of the ring being

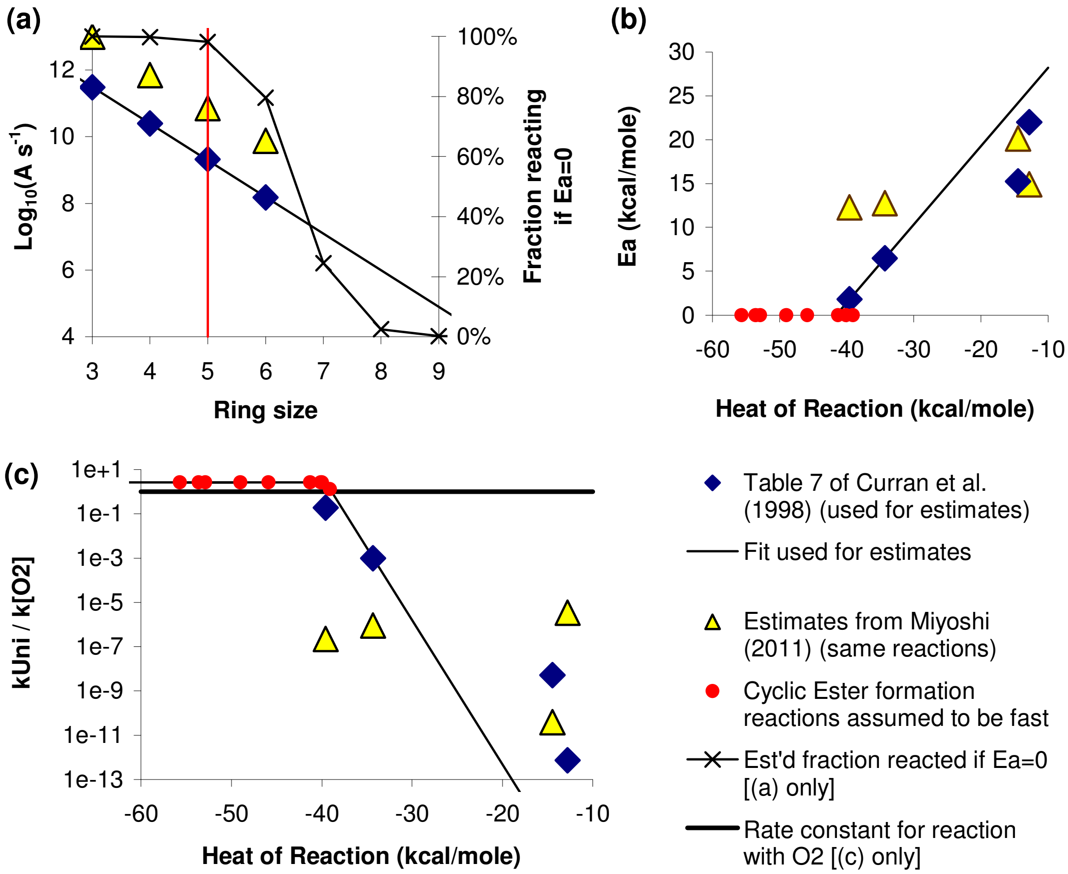


Figure A-2. Plots of estimated kinetic parameter data used to derive estimated rate constants for peroxy-substituted radical cyclization decompositions. (a) Plot of estimated A factors against cyclic ether ring size and fractions estimated to react if the activation energy were zero. (b) Plot of estimated activation energies against estimated heats of reactions. (c) Plot of estimated rate constants against heats of reaction.

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:

$$\mathrm{Log}_{10}\,(\mathrm{A}) = 14.78 - 1.10 * \text{ring size} \tag{I}$$

$$\mathrm{Ea} = \max\,(\mathrm{Ea}_{\min}\,,\; 37.17 + 0.89 * \Delta\mathrm{H}_r) \tag{II}$$

where A is in sec^{-1} and Ea and ΔH_r are in kcal/mole. Note that the activation energy estimate uses only the points on Table A-8 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 A-8.

Equation (I) 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

Table A-9. Types of cyclization decomposition reactions considered for thermalized carbon-centered radicals. Estimated heats of reaction and estimated ratio of decomposition to O_2 addition are also shown for reactions forming 5- or 6- member rings.

Radical and Reaction Type	ΔH_r (kcal/mole)		k(isom) / k($R\cdot+O_2$) [a]	
	Cyc=5	Cyc=6	Cyc=5	Cyc=6
$\cdot CH_2(CH_2)_nOOH \rightarrow$ cyc-ether + OH	-34.3	-39.6	0.001	0.2
$\cdot CH_2(CH_2)_nONO_2 \rightarrow$ cyc-ether + NO_2	-38.2	-43.5	0.3	0.2 - 4 (0.9)
$\cdot CH_2C(O)\ (CH_2)_nOOH \rightarrow$ cyc-β-keto ester + OH	-28.8	-31.7	$3x10^{-7}$	$1x10^{-6}$
$\cdot CH_2CH_2C(O)\ (CH_2)_{n-1}OOH \rightarrow$ cyc-β-keto ester + OH	-35.3	-38.1	0.004	0.02
$\cdot CH_2(CH_2)_nC(O)OOH \rightarrow$ cyc-ester + OH	-41.3	-44.1	3 - 35 (12)	0.2 - 4 (0.9)
$\cdot CH_2(CH_2)_nC(O)OOCH_3 \rightarrow$ cyc-ester + CH_3O.	-45.9	-48.7	3 - 54 (12)	0.2 - 4 (0.9)
$\cdot CH_2(CH_2)_nCO\text{-}ONO_2 \rightarrow$ cyc-ester + NO_2	-39.1	-42.0	1.3	0.2 - 4 (0.9)
$\cdot CH_2(CH_2)_nC(O)OONO_2 \rightarrow$ cyc-ester + NO_3	-55.7	-68.3	3 - 54 (12)	0.2 - 4 (0.9)
$\cdot CO(CH_2)_nOOH \rightarrow$ cyc-ester + OH	-49.0	-51.9	3 - 54 (12)	0.2 - 4 (0.9)
$\cdot CO(CH_2)_nOOCH_3 \rightarrow$ cyc-ester + CH_3O.	-53.6	-56.5	3 - 54 (12)	0.2 - 4 (0.9)
$\cdot CO(CH_2)_nONO_2 \rightarrow$ cyc-ester + NO_2	-52.9	-55.7	3 - 54 (12)	0.2 - 4 (0.9)
$\cdot CO(CH_2)_nOONO_2 \rightarrow$ cyc-ester + NO_3	Cannot estimate ΔH_r [c]			
$\cdot CO(CH_2)_nC(O)OOH \rightarrow$ cyc-anhydride + OH	-40.9	-43.7	3 - 19 (12)	0.2 - 4 (0.9)
$\cdot CO(CH_2)_nC(O)OONO_2 \rightarrow$ cyc-anhydride + NO_3	-55.3	-58.2	3 - 54 (12)	0.2 - 4 (0.9)
$.CH_2CH{=}CH\text{-}C(O)OOH \rightarrow$ unsat. cyc-ester + OH	-26.0 [b]	n/a	$4x10^{-9}$	n/a
$.COCH{=}CHC(O)OOH \rightarrow$ 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 (I). The pseudo-unimolecular rate constant for addition of O_2 in the atmosphere is estimated to be 3.8×10^7 sec^{-1}. 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 (II). In those cases, three ratios of k(isom)/k($R+O_2$) 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.

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

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 A-2 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 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 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 A-9 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 A-8, 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 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 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 A-8, then the 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 O_2 addition if a minimum activation energy of half the minimum on Table A-8 is assumed.

Table A-9 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 α-unsaturated alkyl radicals because of allylic stabilization, but is estimated to be favorable for α-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 ·C(O)CH=CHC(O)OOH are predicted to be formed following the O_2 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_2 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.

A1.4.4. 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.,

$$\text{-}G_1[.]\text{-*}G_2\text{-}G_3\text{-}G_4\text{*}\ \{\text{excited}\} \rightarrow G_1{=}G_2\text{-}G_3\text{-}G_4[.]\ \{\text{excited}\} \rightarrow G_1{=}G_2\text{-}G_3\text{-}G_4[.] \pm M$$

$$\text{-}G_1[.]\text{-*}G_2\text{-}G_3\text{-}G_4\text{-}G_5\text{*} \rightarrow G_1{=}G_2\text{-}G_3\text{-}G_4\text{-}G_5[.]\ \{\text{excited}\} \rightarrow G_1{=}G_2\text{-}G_3\text{-}G_4\text{-}G_5[.] \pm M$$

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.,

$$-{*}G_1\text{-}G_2[.]\text{-}G_3{*}\text{-}\ \{\text{excited}\} \rightarrow -G_1{=}G_2\text{-}G_3[.]\text{-}\ \{\text{excited}\} \rightarrow -G_1{=}G_2\text{-}G_3[.]\text{-}\ \pm \text{M}$$

$$-{*}G_1\text{-}G_2[.]\text{-}G_3\text{-}G_4{*}\text{-}\ \{\text{excited}\} \rightarrow -G_1{=}G_2\text{-}G_3\text{-}G_4[.]\text{-}\ \{\text{excited}\} \rightarrow -G_1{=}G_2\text{-}G_3\text{-}G_4[.]\text{-}\ \pm \text{M}$$

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_2 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 α- radicals of this type may be formed in decomposition reactions, so estimates of their reactions need to be considered when generating mechanisms.

A1.4.5. 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_2 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_2. 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 A1.4.2). 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_x conditions. This is attributed to the following types of reactions (Paulot et al., 2009):

$$\mathrm{CH_2{=}CHC(CH_3){=}CH_2 + OH \rightarrow \rightarrow H_2O \pm M - O_2 + CH_2{=}CHC(OO\cdot)(CH_3)CH_2OH}$$
$$\mathrm{CH_2{=}CHC(OO\cdot)(CH_3)CH_2OH + HO_2 \rightarrow CH_2{=}CHC(OOH)(CH_3)CH_2OH}$$
$$\mathrm{CH_2{=}CHC(OOH)(CH_3)CH_2OH + OH \rightarrow HOCH_2CH(\cdot)C(OOH)(CH_3)CH_2OH\ \{excited\}}$$
$$\mathrm{HOCH_2CH(\cdot)C(OOH)(CH_3)CH_2OH\ \{excited\} \rightarrow HOCH_2{*}CHC(CH_3)(CH_2OH)O{*}\ (IEPOX) + OH}$$

Where "± 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 peroxynitrate-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_3 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 β-scission decompositions, as discussed in Section 3.2 of the main text, then the β-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 A-10. Table A-10 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.

Table A-10. Branching ratios assumed for reactions of excited radicals formed from the additions of OH to β-peroxy substituted substituents.

Products of reactions of -G$_1$(OH)-G$_2$[.]-CO-O-OX {OHadd}	Route Designation	Branching Ratios Assumed [b]			Rxn Notes [c]
		X= -H	X= -R	X= -NO$_2$	
→ -G$_1$(OH)-G$_2$[.]-CO-O-OX ± M	Stabilization	82%	40%	20%	1
→ -G$_1$(OH)-*G$_2$-CO-O* + [.]OX	α-Lactone	14%	45%	60%	2
→ -*G$_1$-O-G$_2$*-CO-OH + [.]OX	Acid epoxide	5%	15%	20%	3
→ -G1(OH)-G2=O + CO + ·OX	Ketone CO	~0%	~0%	~0%	4
	Ratio Notes [c]:	5	6	7	

[a] G$_1$ and G$_2$ are either -CH$_2$- or -CH()- groups. X is -H, -alkyl (-R) or -NO$_2$.

[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 α-carbonyl and β-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 α-lactone. The branching ratios derived by Lin et al. (2013) for X = -NO$_2$ 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$_2$.

5 The relative yields for decomposition via the α-lactone route is the averages of the yields calculated by Kjaergaard et al. (2012) et al. for CH_2=CHC(O)OOH and CH_2=C(CH_3)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 α-lactone route for X = -OH is the same as derived for X = -NO$_2$ (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 α-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_2=CHC(O)OOH and CH_3CHC(O)OONO$_2$. 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_3CHC(O)OONO$_2$. They estimate a branching ratio of ~3% for the ketone CO route, but this is ignored and the 3% is added to the α-lactone route. These branching ratios are applied to all carbon-centered radicals of this type.

Note that the branching ratio estimates in Table A-10 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_3 or Cl additions to double bonds are all stabilized, based on their lower estimated excitation energy.

A1.5. Reactions of Peroxy Radicals

A1.5.1. Bimolecular Rate Constants

Table A-45 (given in Section A5.2 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_2, and NO_3, and the reactions of acyl peroxy radicals with HO_2, 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_2), 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_{6+} compounds may have lower rate constants, as indicated in Figure A-3. However, the two C_{7+} compounds with the lower rate constants may not be representative of other types of alkyl peroxy radicals, so we currently retain the approximation that rate constant is independent of molecule size.

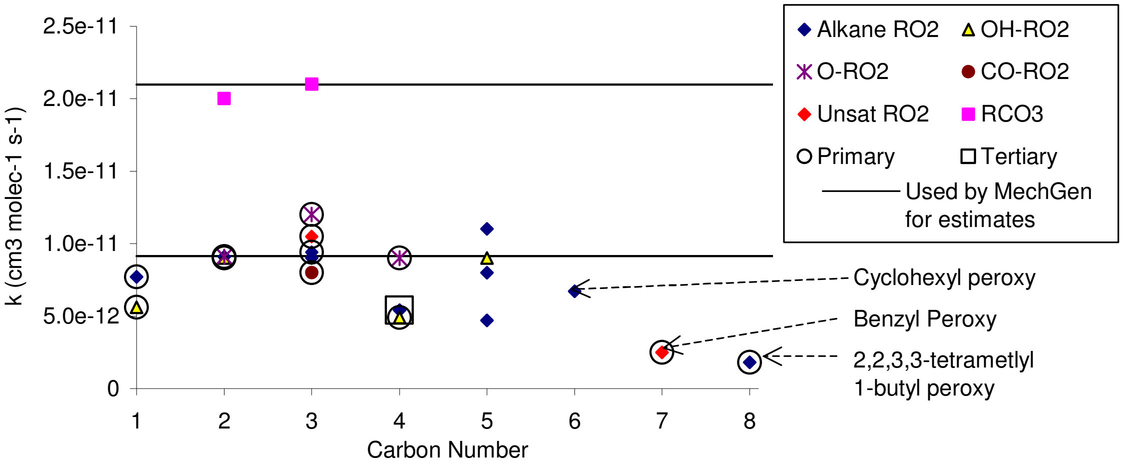


Figure A-3. Plots of measured and assigned rate constants for peroxy + NO reactions against the number of carbons in the radical.

In contrast to peroxy radicals, Table A-45 indicates that alkyl peroxy + HO_2 rate constants tend to increase with carbon number, as also shown in Figure A-4, 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 A-3). The available data are reasonably well fitted by:

$$k(RO_2 + HO_2) = 10^{-12} \text{ x min } [20.3, 2.48 + (2.48 \text{ x nC})] \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

$$k(HO\text{-}RO_2 + HO_2) = 10^{-12} \text{ x min } [21.1, 9.37 + (1.68 \text{ x nC})]] \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1},$$

where "HO-RO_2" indicates peroxy radicals with -OH substituents, "RO_2" are those without -OH, and "nC" is the number of carbons in the radical.

These equations, whose predictions are also plotted in Figure A-4, are used by MechGen to estimate the HO_2 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_3 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_2'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.

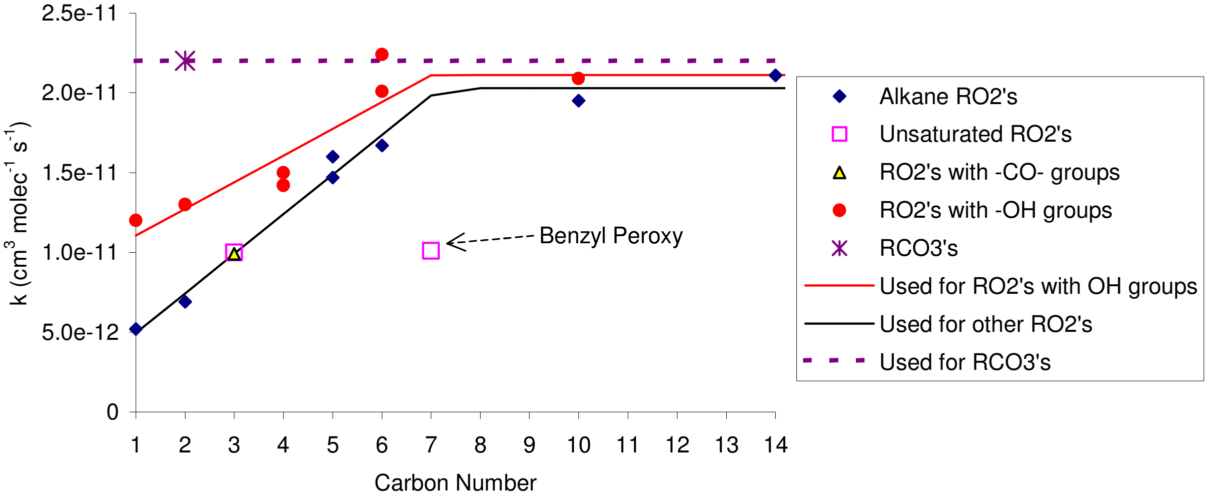


Figure A-4. Plots of total rate constants for the reactions of various types of peroxy radical with HO_2, against the number of carbons in the radical.

Table A-45 indicates that the only measured rate constant for the reactions of acyl peroxy radicals is that for acetyl peroxy. Based on this, we use

$$k(RCO_3 + HO_2) = 3.14 \text{ x } 10^{-12} \exp(-580/T) = 2.2 \text{ x } 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

independent of carbon number of substituents.

Table A-45 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 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 A-5, 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 assumes 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 "*x*OH" refers to the OH-substituted radicals, and "*x*" can be either primary, secondary, or tertiary.

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

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

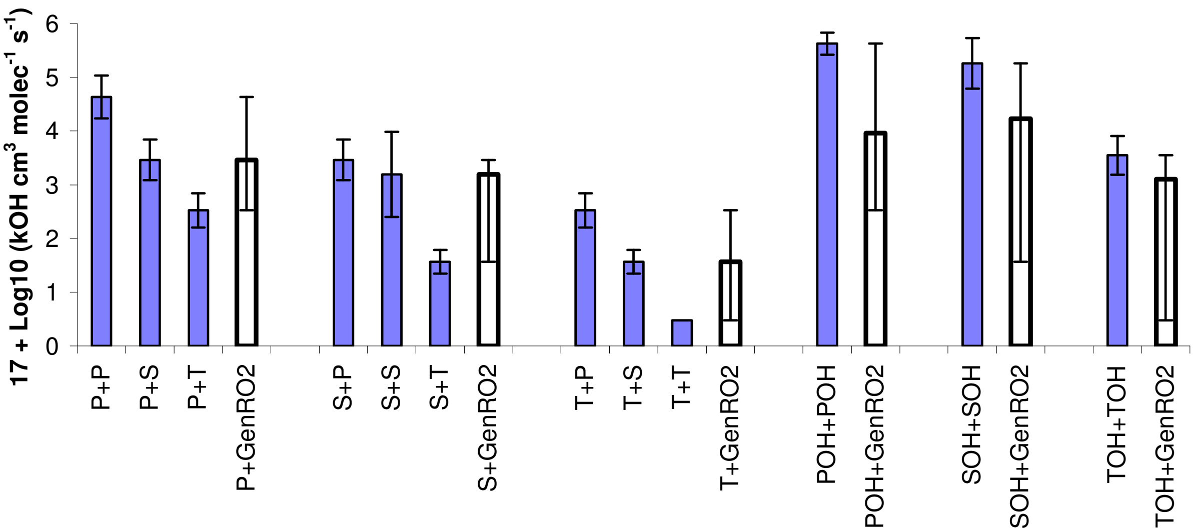


Figure A-5. Averages of experimental peroxy + peroxy rate constants of various types, and rate constants assigned by MechGen for peroxy + generic peroxy reactions. Note that the rate constants are multiplied by 10^{17} to give the logs positive magnitudes; "P", "S", and "T" refer to primary, secondary, 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.

reactions are generally not important loss processes for peroxy radicals compared to reactions with NO_x species and HO_2.

A1.5.2. 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:

$$RO_2\cdot + NO \rightarrow RO\cdot + NO_2 \qquad (1\text{-}y_N)$$

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

where yN 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 A-46 through Table A-48 in Section A5.2, and the yields measured around 300K and atmospheric pressure are plotted against carbon number in Figure A-6. Figure A-7a 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.

As discussed by Zhang et al. (2004), the general mechanism for RO_2 + NO reaction is believed to be as follows:

$$RO_2\cdot + NO \rightarrow \{\text{intermediate 1}\} \rightarrow RO\cdot + NO_2 \qquad (1)$$

$$\rightarrow \{\text{intermediate 2}\} \qquad (2)$$

$$\{\text{intermediate 2}\} \rightarrow RO\cdot + NO_2 \qquad (3)$$

$$\{\text{intermediate 2}\} + M \rightarrow RONO_2 + M \qquad (4)$$

where the intermediates refer to different configurations of excited RO_2 + 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:

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

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:

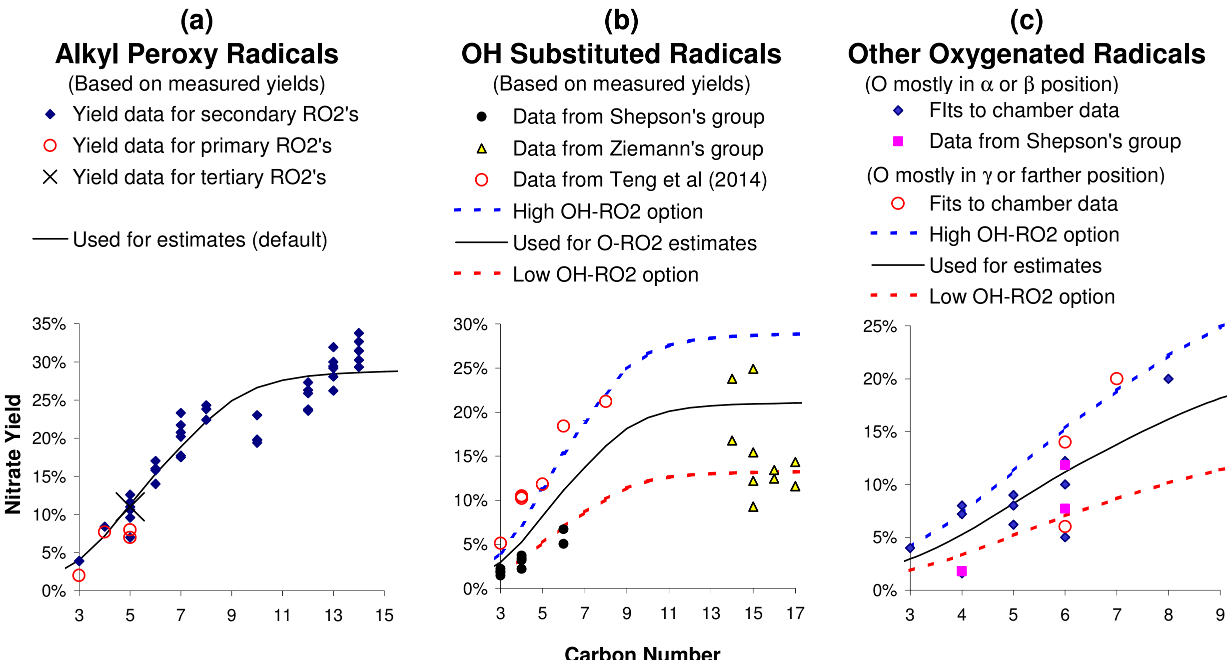


Figure A-6. Experimental and estimated nitrate yields against carbon numbers for the reactions of various types of peroxy radicals at ~298K and 1 atmosphere pressure.

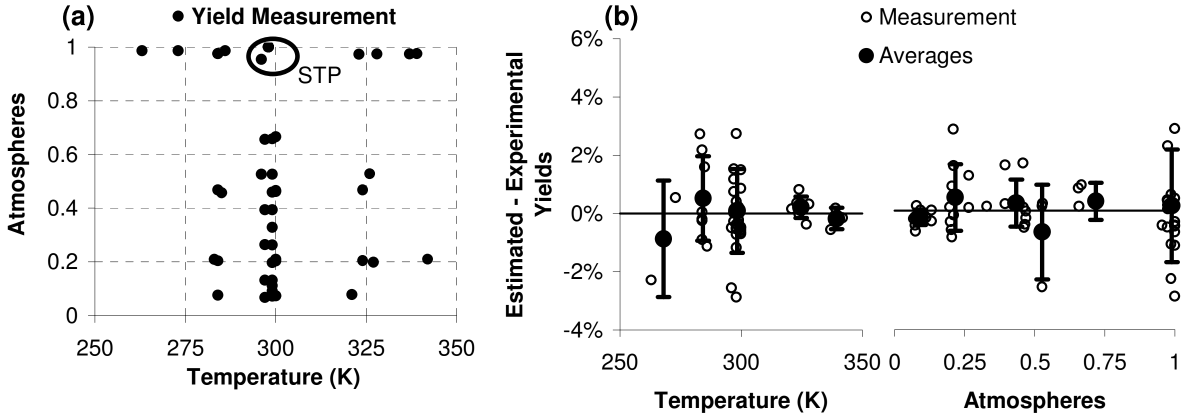


Figure A-7. Range of temperatures and pressures where nitrate yield measurements were made for alkyl peroxy radicals and relative differences between experimental and estimated yields as a function of temperature and pressure.

$$(k_4/k_3) = [Y_0 \text{ x } M / (1 + Y_r)] \text{ x } F^Z$$
$$Y_0M = \alpha \text{ x } e^{\beta \text{ nC}} \text{ x } [T/300] \text{ x } m_0 \text{ x } P_{atm}$$
$$Y_r = Y_0 \text{ x } M / \{ Y_\infty [(T/300)^{m_\infty}] \}$$
$$Z = 1 / [1 + \log_{10}(Y_r)^2]$$

where Y_0M, Y_r, and Z, are also intermediates in the calculation, and α, β, Y_∞ , and m_∞ are additional parameters adjusted to fit the data. The inputs are nC, the carbon number; T, the temperature in K; and P_{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 A-46 and the yields at different temperatures and pressures summarized in Table A-47. The parameter values derived in this work to fit these data are given in Table A-11. Figure A-6a shows plots of the experimental and estimated nitrate yields for secondary radicals against carbon number. Figure A-7b 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 A-11. 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]			
Parameter	Value	Parameter	Value
Corr	See (b)	y_∞	5.21
Fac	0.34	m_0	-2.05
α	0.015	m_∞	-14.12
β	0.81	F	0.497

(b) Correction factors	
Case used for	Corr
Default and high OH-RO_2 option	1
Used for OH and O-substituted RO_2's	0.73
The following used for Figure A-8 only	
Low OH-RO_2 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 A-48, and those for ~289K and 1 atmosphere are included in Figure A-6a. 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 α or β positions need to be considered. The most important example is β-OH substituted peroxy radicals formed after OH adds to double bonds and then adds O_2. However, peroxy radicals with other types of substituents in the α or β 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 β OH-substituted peroxy radicals formed after OH adds to double bonds and then adds O_2. 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_3O-CIMS and thermal dissociation NO_2 laser-induced fluorescence was used to quantify the nitrates.

Figure A-6b 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_2" option on Table A-11 and Figure A-6, while the parameterization that was derived from the secondary alkyl peroxy data is referred to as the "default" or "High OH-RO_2" option.

Nitrate yields from β-substituted peroxy radicals are important parameters affecting the effect of alkene reactions on radical levels. It was found that results of alkene-NO_x 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 A-8 shows biases and errors in model simulations of O_3 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 β-substituted peroxy radicals given on Table A-11b. The formation rates are measured by rates of change of Δ([O3]-[NO]) during the period when O_3 is forming, as discussed by Carter (2010a). About half of the experiments are better simulated using the high OH-RO_2 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 A-48 and Figure A-6c 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 unspeciated nitrate yields from formed in reactions of OH with various oxygenated compounds, or derived from fits of model simulations to environmental chamber data. Use of unspeciated 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 adjustements 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 A-6c. 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.

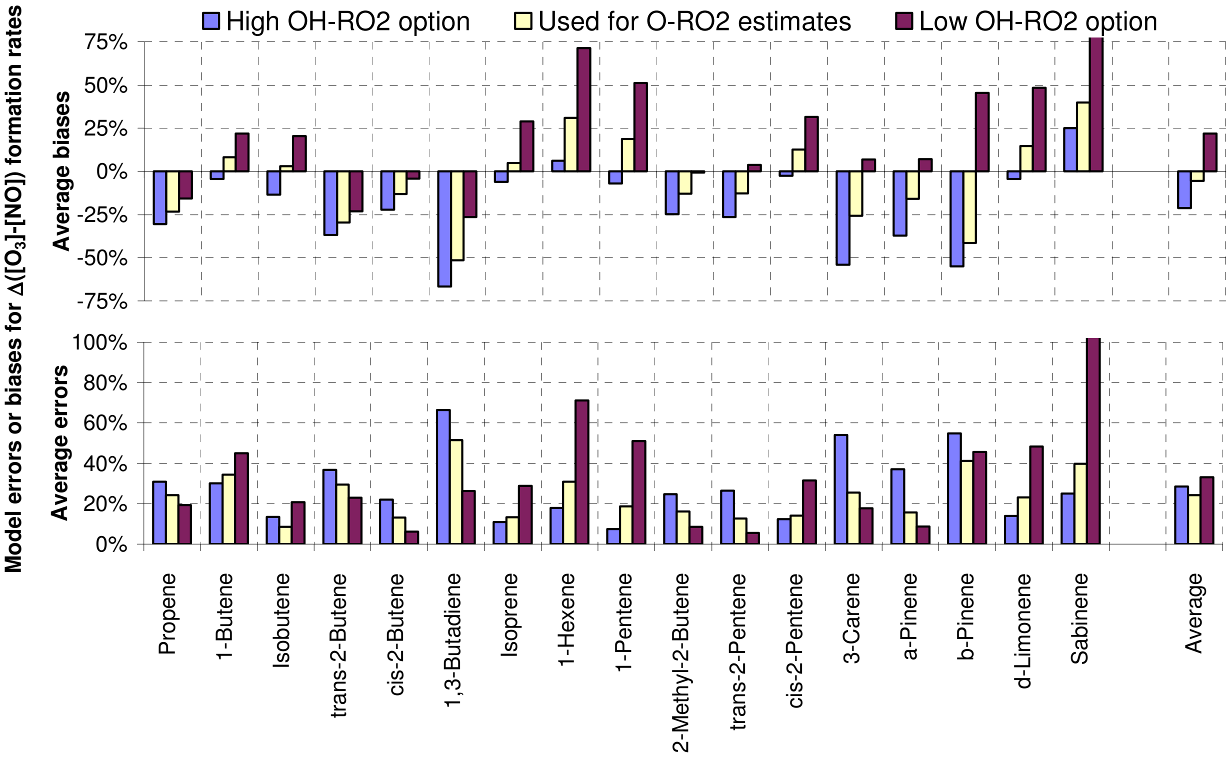


Figure A-8. Comparisons of average biases and errors in model simulations of initial rates of change $\Delta([O_3]-[NO])$ in various alkene - NO_x chamber experiments used for evaluating SAPRC mechanisms, calculated using various options for estimating nitrate yields from OH-substituted peroxy radicals.

Until this inconsistency in the nitrate yield data for β-hydroxy nitrates is resolved and we have more consistent data on nitrate yields from other α and β-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 α or β 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 α or β 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 conrrections 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.

A1.5.3. Mechanisms for peroxy + HO_2 reactions

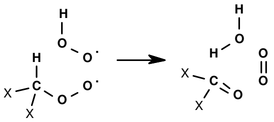
Available data concerning mechanisms for the reactions of various peroxy radicals with HO_2 have been reviewed by IUPAC (2023), and their recommendations are summarized on Table A-12. Note that these include only primary peroxy radicals and only one acyl peroxy radical. Because of insufficient

Table A-12. Current IUPAC recommendations for the products formed in the reactions of HO_2 with various primary peroxy and acyl peroxy radicals.

Radical	Reaction products and recommended branching ratios [a]			
	$ROOH + O_2$	$RCHO + H_2O + O_2$	$RO + OH + O_2$	$ROH + O_3$
$CH_3OO.$	90%	10%		
CH_3-$CH_2OO.$	100%	~0%		
HO-$CH_2OO.$	50%	30%	20%	
CH_3-O-$CH_2OO.$	60%	40%		
CH_3-CO-$CH_2OO.$	85%		15%	
CH_3-CO-OO.	37%		50%	13%

[a] "R" refers to the group bonded to the peroxy O, including CH_3CO- in the case of acyl peroxy.

data, we assume that the mechanisms for secondary and tertiary peroxy radicals are analogous to those for the primary radicals shown on Table A-12 and are independent of substituents other than -OH, -O-, or -CO- on the same carbon as the peroxy group. However, the reaction forming "$RCHO + H_2O + O_2$" 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 "$ROOH + O_2$" route when making predictions for tertiary radicals.

The mechanism and branching ratio assignments used by MechGen for peroxy + HO_2 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 A-12.

A1.5.4. 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_x levels are sufficiently low, though they are calculated to be generally less important than peroxy + HO_2 or NO_3 reactions under daytime or nighttime atmospheric conditions, respectively. These reactions can occur via three possible routes, as shown on Table A-13. 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.

Table A-14 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 disproportion 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,

Table A-13. Reaction routes considered for organic peroxy + peroxy reactions

Route label	Reactants	Products
Alkoxy radical formation	ROO· + R'OO·	→ RO· + O_2 + R'O·
	ROO· + R'C(O)OO·	→ RO· + O_2 + R'C(O)O·
	RC(O)OO· + R'C(O)OO·	→ RC(O)O· + O_2 + R'C(O)O·
Disproportionation (if an α H is present in either radical)	ROO· + R'CH2OO·	→ ROH + O_2 + R'C(O)H
	ROO· + R'R"CHOO·	→ ROH + O_2 + RC(O)R"
	$R'CH_2OO·$ + R'C(O)OO·	→ R'C(O)H + O_2 + R'C(O)OH
	RR"CHOO· + R'C(O)OO·	→ R'C(O)R" + O_2 + R'C(O)OH,
Peroxide formation (assumed not to be important)	ROO· + R'OO·	→ ROOR'· + O_2
	ROO· + R'C(O)OO·	→ ROOC(O)R'· + O_2
	RC(O)OO· + R'C(O)OO·	→ RC(O)OOC(O)OR'· + O_2

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 A-14.

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 minor loss processes for peroxy radicals under atmospheric conditions, since reactions with NO_x species dominate when NO_x is present, reactions with HO_2 dominate when NO_x is low, and reactions with 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 A1.5.1), 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 A-14 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.

Table A-14. Recommended and assigned branching ratios peroxy + peroxy reactions.

Radical 1	Radical 2	Branching ratios [a]			
		Alkoxy	Alcohol	Carbonyl	Notes
$CH_3OO\cdot$	$CH_3OO\cdot$	37%	(32%)	(32%)	[b, c]
$CH_3CH_2OO\cdot$	$CH_3OO\cdot$	(no recommendation)			[b]
$CH_3CH_2OO\cdot$	$CH_3CH_2OO\cdot$	63%	19%	19%	[b]
$CH_3C(O)CH_2OO\cdot$	$CH_3OO\cdot$	30%	20%	50%	[b]
$CH_3C(OO\cdot)(CH_3)CH_3$	$CH_3C(OO\cdot)(CH_3)CH_3$	100%	-	-	[b]
$CH_3C(OO\cdot)(CH_3)CH_3$	$CH_3OO\cdot$	13%	87%	-	[b]
$HOCH_2OO\cdot$	$HOCH_2OO\cdot$	90%	6%	6%	[b]
$CH_3C(O)CH_2OO\cdot$	$CH_3C(O)CH_2OO\cdot$	63%	(19%)	(19%)	[b, c]
$HOCH_2CH_2OO\cdot$	$HOCH_2CH_2OO\cdot$	50%	(25%)	(25%)	[b, c]
$i\text{-}C_3H_7OO\cdot$	$i\text{-}C_3H_7OO\cdot$	56%	22%	22%	[b]
$CH_3C(CH_3)(OH)CH_2OO\cdot$	$CH_3C(CH_3)(OH)CH_2OO\cdot$	60%	20%	20%	[b]
$CH_3CH(OH)CH_2(OO\cdot)CH_3$	$CH_3CH(OH)CH_2(OO\cdot)CH_3$	18%	41%	41%	[b]
$CH_3C(O)OO\cdot$	$CH_3OO\cdot$	90%	10%	-	[b]
$CH_3C(O)OO\cdot$	$CH_3C(O)CH_2OO\cdot$	50%	50%	-	[b]
$CH_3CH_2C(O)OO\cdot$	$CH_3CH_2OO\cdot$	80%	20%	-	[b]
$CH_3C(O)OO\cdot$	$CH_3C(O)OO\cdot$	100%	-	-	[b]
Branching ratios assigned for Mechanism Generation					
Primary, Secondary RO_2	Generic or total RO_2	50%	25%	25%	[d]
	Generic or total RCO_3	80%	20%	-	[e]
Tertiary RO_2	Generic or total RO_2	50%	50%	-	[f]
	Generic or total RCO_3	100%	-	-	[g]
Any RCO_3	Generic or total RO_2	80%	20%	-	[e]
	Generic or total RCO_3	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

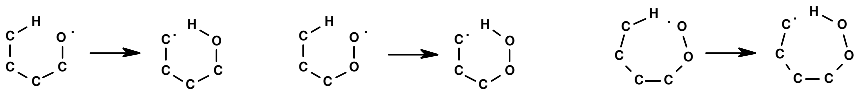
Table A-14 (continued)

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.

A1.5.5. 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 A1.6.3. 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 β-OH, α-ONO_2 or β-oxy substituents, with the β-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 A-49 in Section A5.2 (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 A-15

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_3, -CH_2-, -CH<, groups without any non-alkyl α substituents or β double bonds (i.e., a double bond group in the α-position).
- Abstractions from -CH_2- or -CH< with α-OH or -OOH substituents. They recommend assuming that the effect of α-ether substituent is the same as α-OH.

Table A-15. Experimentally measured rate constants for T = 295-298 K for H-shift isomerization reactions of peroxy radicals.

Reactant [a]	Reacting Groups		Ring	k(298) (sec^{-1})		Fac	Ref
	H-Group	R-Group	Size	Target	Est'd	Err [b]	[c]
$CH_3C\underline{\mathbf{H}}_2CH_2CH_2OO\cdot$	CH_2	$CH_2OO.$	6	≤5.0e-4	8.1e-4	≥1.6	1
$CH_3C\underline{\mathbf{H}}_2C\underline{\mathbf{H}}_2CH_2CH_2OO\cdot$	CH_2	$CH_2OO.$	6, 7	2.4e-3	1.7e-3	-1.4	1
$CH_3CH_2C\underline{\mathbf{H}}_2C\underline{\mathbf{H}}_2CH_2CH_2OO\cdot$	CH_2	$CH_2OO.$	6, 7	1.7e-3	1.7e-3	±1	1
$CH_3CH_2C\underline{\mathbf{H}}_2C\underline{\mathbf{H}}_2CH(C\underline{\mathbf{H}}_2CH_3)CH_2OO\cdot$	CH_2	$CH_2OO.$	6, 7	2.2e-3	2.5e-3	1.1	1
$\underline{\mathbf{H}}C(O)C(OO\cdot)(CH_3)CH_2OH$	CHO	COO.	5	0.50	0.53	1.1	2
$CH_3CH_2CH(OO\cdot)CH_2C\underline{\mathbf{H}}(CH_3)OH$	CH-OX	CHOO.	6	0.048	0.068	1.4	3
$CH_3CH_2CH(OO\cdot)CH_2CH_2C\underline{\mathbf{H}}(CH_3)OH$	CH-OX	CHOO.	7	0.14	0.16	1.2	3
$CH_3C\underline{\mathbf{H}}(OH)CH_2C(OO\cdot)(CH_3)CH_3$	CH-OX	COO.	6	0.22	0.27	1.2	4
$CH_3C\underline{\mathbf{H}}(OOH)CH_2C(OO\cdot)(CH_3)CH_3$	CH-OOH	COO.	6	0.036	0.031	-1.1	4
$HOC\underline{\mathbf{H}}_2C(CH_3){=}CHCH_2OO\cdot$	CH_2-OxDB/En	$CH_2OO.$	7	0.36	1.15	3.2	5
$HOC\underline{\mathbf{H}}_2CH{=}C(CH_3)CH_2OO\cdot$	CH_2-OxDB/En	$CH_2OO.$	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 the either 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 Crounse 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.

- Abstractions from -CH_2- or -CH< with β double bonds, with separate entries for when the double bond group is within (β-*endo*) or outside (β-*exo*) of the transition state. Note that β-*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 $-CH_2OO\cdot$, $-CH(OO\cdot)$- and $-C(OO\cdot)$< 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 β-*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 A-

49. 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.

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 A-15).
- 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:

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

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

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

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

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}(subs) are corrections to the activation energies based on applicable α- or β-substituents, Ea^{0} is the activation energy if there were no ring strain and β-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:

$$k(T) \approx p1 \text{ x } T^{p2} \text{ x } e^{-p3/T} \qquad \text{(III)}$$

where p1, p2, and p3 are fitting parameters that they tabulated for each type of reaction and are included in Table A-49. The p2 values were as high as 28 in some cases, indicating highly non-Arrhenius temperature dependences. However, the three-parameter expression in Equation (III) is not well suited for general estimation purposes, so for this work we assume that the temperature dependence can be approximated by an Arrhenius expression in Equation (I), 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:

$$\mathrm{Ea} \approx \ln\,(\mathrm{k330}/\mathrm{k270}) \,/\, (1/270 - 1/330); \quad \mathrm{A} \approx (\mathrm{k270} \times e^{\mathrm{Ea}/270})/\mathrm{nH} \qquad \text{(IV)}$$

where k330 and k270 are rate constants calculated by Equation (III) for 330 and 270 K, respectively. Although this only approximated the temperature dependence, it fit the data to within ±~10% for this relatively narrow temperature range. The A factors derived using Equation (IV) are included in the tabulations in Table A-49.

Figure A-9 shows plots of the Arrhenius A factors derived using Equation (IV) 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

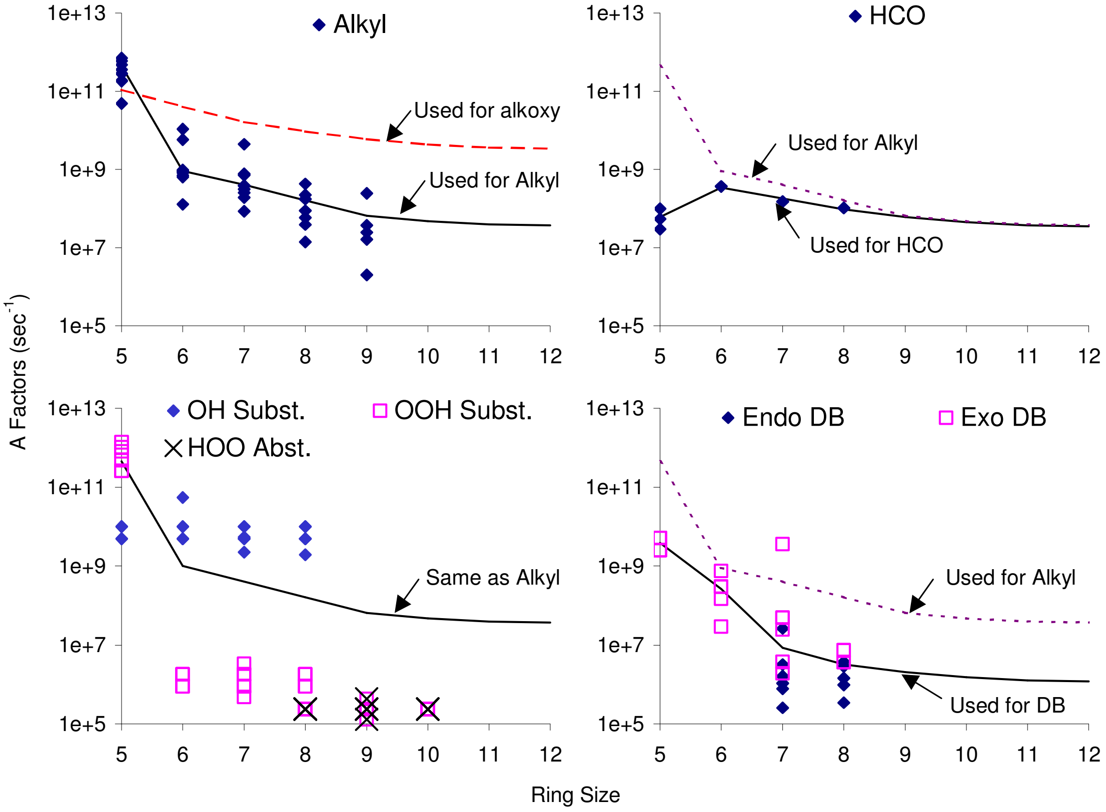


Figure A-9. Plots of Arrhenius A factors as a function of ring size for H-shift isomerizations of peroxy radicals derived from the data of Vereecken and Nozière (2020). A factors used in this work to estimate H-shift isomerizations of alkoxy radicals are also shown.

radicals, as discussed in Section A1.6.3. 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 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 α -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 A-9, with dotted lines showing assignments for alkyl types where applicable. The values used are tabulated in Table A-16, with footnotes indicating how each

Table A-16. Arrhenius A factors used in the estimation of rate constants for H-shift isomerizations of various types of peroxy radicals.

Ring size	Alkyl and α-OX substituent and abstractions from -OOH		Aldehyde (no double bond)		Double bond next to H group	
	A (sec^{-1})	Note	A (sec^{-1})	Note	A (sec^{-1})	Note
5	4.47e+11	1	6.02e+7	1	1.80e+10	4
6	1.01e+9	2	3.36e+8	2	2.11e+9	4
7	4.03e+8	2	1.78e+8	2	4.40e+8	5
8	1.61e+8	2	9.45e+7	2	1.32e+8	5
9	6.47e+7	2	6.07e+7	3	5.05e+7	3
10	4.67e+7	3	4.39e+7	3	2.29e+7	3
11	3.92e+7	3	3.68e+7	3	1.17e+7	3
12	3.68e+7	3	3.46e+7	3	6.55e+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.

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 α-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 α substituents are not possible. The applicability of these A estimates for α-OH, α-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 Ea^{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 (II) to (IV) above, Ea^{HR} is split up into Ea^0 and Ea^{strain}, where Ea^0 is the contribution to the activation energy if there were no ring strain, and Ea^{strain} is the contribution due to ring size. It is assumed that the ring strains defined using Equations (III) and (IV) 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 $\lim[Ea^{HR}(RS\rightarrow\infty)] = Ea^0$.

Table A-17 lists the Ea^0 values derived from these data, and Table A-18 gives the Ea^{strain} values for the various ring sizes. Estimated values, derived as discussed below, are also included. These are shown graphically in Figure A-10 and Figure A-11. Footnotes in the tables indicate how these were derived. Those given footnotes "1" or "7" in Table A-17 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:

- 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 -C[OO·]< 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 β-oxo substitutions, we assume that these corrections are not intended for acyl peroxy reactions.
- Radicals with double bonds next to -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 -CHO is the same as its effect on abstractions from -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 A1.6.3, below and shown as a function of ring size in Figure A-11, we assume that $Ea^{strain}(11) \approx Ea^{strain}(10) \approx Ea^{strain}(9)$, that $Ea^{strain}(12) \approx Ea^{strain}(11)/2$, and that $Ea^{strain}(13+) \approx 0$.
- Abstractions from hydroperoxy groups by acyl peroxy radicals forming alkyl peroxy radicals with peroxyacid groups are estimated to be exothermic by ~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 Ea^0 value of 4 kcal/mole (see below), and the Ea^{strain} values were assumed to be approximately equal to those derived for abstractions by -C[OO·]< radicals.
- Abstractions from peroxyacid groups by peroxy radicals were not considered because they are estimated to be endothermic by ~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.

Table A-17. Ea^0 values assigned for various pairs of H- and R-groups for estimating peroxy isomerization rate constants, with footnotes indicating how the Ea^0 and Ea^{strain} values were derived.

H-Group [a]	Ea0 (kcal/mole) [b]							
	-CH$_2$OO.		-CH(OO.)-		-C(OO.)<		-C(O)OO.	
CH$_3$ [c]	19.74	1	19.06	1	17.85	1	16.42	2,3,4
CH$_2$ [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$_2$-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$_2$-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$_3$-C=/En	9.42	1,8,11	10.11	1,8,11	11.36	1,9,11	9.65	2,4
CH$_2$-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$_2$-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$_2$-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$_2$-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$_2$-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$_2$-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$_2$	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 β double bond. "/En", "/Ex", and "/EnEx" indicate whether the double bond group is within the transition state (β-*endo*), outside the transition state (β-*oxo*), or whether there are two β double bonds.

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

1 Except as noted in other footnotes, the Ea^{HR} and from them Ea^0 and Ea^{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$_3$ with a ring size of 6, based on quantum calculated rate constants given by Møller et al (2019).

3 The Ea^{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 Ea^{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 -CH3 with ring sizes of 7, based on quantum

Table A-17 (continued)

calculated rate constants given by of Møller et al (2019).

5 Assume change in Ea^{HR} going from RS=8 to 9 for abstraction from a -CHO group is the same as for abstraction from -CH_3 by the same type of radical. This is because steric effects around -CH_3 are expected to be closer to those around -CHO than is the case for -CH_2- or -CH<.

6 Changes in Ea^{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_3 with a ring size of 6, based on quantum calculated rate constants given by of Møller et al. (2019).

7 The Ea^{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 Ea^{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 Ea^{RS} going from RS=8 to 9 for abstraction from this group is the same as for abstraction from -CH_2- groups, since there are no data on abstractions from -CH< groups for RS=9.

10 Changes in Ea^{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 Ea^{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 Ea^0 values, so the minimum of ~4 kcal/mole was used for Ea^0, but the estimated strain energies are not changed.

13 It is assumed that the effect of an *endo* or *exo* double bond on Ea^{RH} is the same as the effect without -Ox substitution.

14 Ea^{HR} was adjusted to fit rate constant data of Teng et al. (2017), as tabulated by VN20 for isomerizations of $HOCH_2C(CH_3){=}CHCH_2OO\cdot$ and $HOCH_2CH{=}C(CH_3)CH_2\text{-}OO\cdot$.

15 Assume that Ea 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 Ea0 of 4 kcal/mole, and Ea(strain) values are asumed 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_3 or -CH_2- groups are all estimated to be negligible, so estimates for these reactions are not incorporated into MechGen.

Table A-18. Ea^{strain} values assigned for various pairs of H- and R-groups and ring sizes through RS=10.

	Ea^{strain} (kcal/mole) [a]											
H-Group	-$CH_2OO\cdot$						-CH(OO·)-					
	5	6	7	8	9	10	5	6	7	8	9	10
CH_3	11.39	0.06	0	0.27	1.20	1.20	15.17	0.39	0	0.61	5.12	5.12
CH_2	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_2-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_2-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_3-CHx=/En		2.82	2.75	0	0.93	0.93		2.84	2.46	0	4.51	4.51
CH_2-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_2-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_2-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_2-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_2-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_2-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_2			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

	Ea^{strain} (kcal/mole) [a]											
H-Group	-C(OO·)<						-C(O)OO·					
	5	6	7	8	9	10	5	6	7	8	9	10
CH_3	16.48	0	2.18	4.65			16.48	0	0.32	2.78		
CH_2	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_2-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_2-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_3-CHx=/En		0	2.18	1.57	6.08	6.08		0.29	0.61	0	4.51	4.51
CH_2-CHx=/En		1.35	1.08	0	2.87	2.87		3.21	1.08	0	2.87	2.87

Table A-18 (continued)

H-Group	Ea^{strain} (kcal/mole) [a]											
	-C(OO·)<						-C(O)OO·					
	5	6	7	8	9	10	5	6	7	8	9	10
CH-CHx=/En		3.71	1.06	0	7.48	7.48		5.58	1.06	0	7.48	7.48
CH_2-CHx=/Ex	10.73	8.79	0	3.34	6.22	6.22	12.60	10.66	0	3.34	6.22	6.22
CH-CHx=/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_2-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_2-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_2-CHx=/EnEx		1.35	1.08	0	2.87	2.87		1.35	1.08	0	2.87	2.87
CH-CHx=/EnEx		3.71	1.06	0	7.48	7.48		3.71	1.06	0	7.48	7.48
CH_2-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_2			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 A-17 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 $Ea^{strain}(10) \approx Ea^{strain}(11)$ $Ea^{strain}(9)$, $Ea^{strain}(12) \approx 0.5 \times Ea^{strain}(11)$, and $Ea^{strain}(13+) \approx 0$ (see Figure A-11).

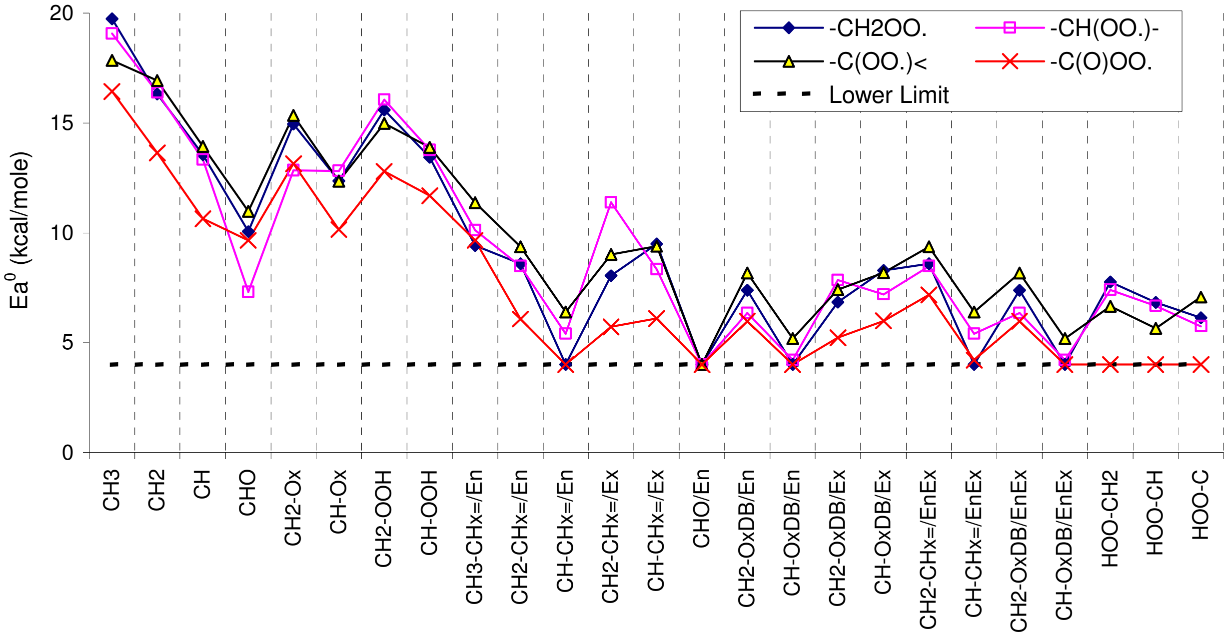


Figure A-10. Plots of Ea^0 values assigned to various pairs of H- and R-groups.

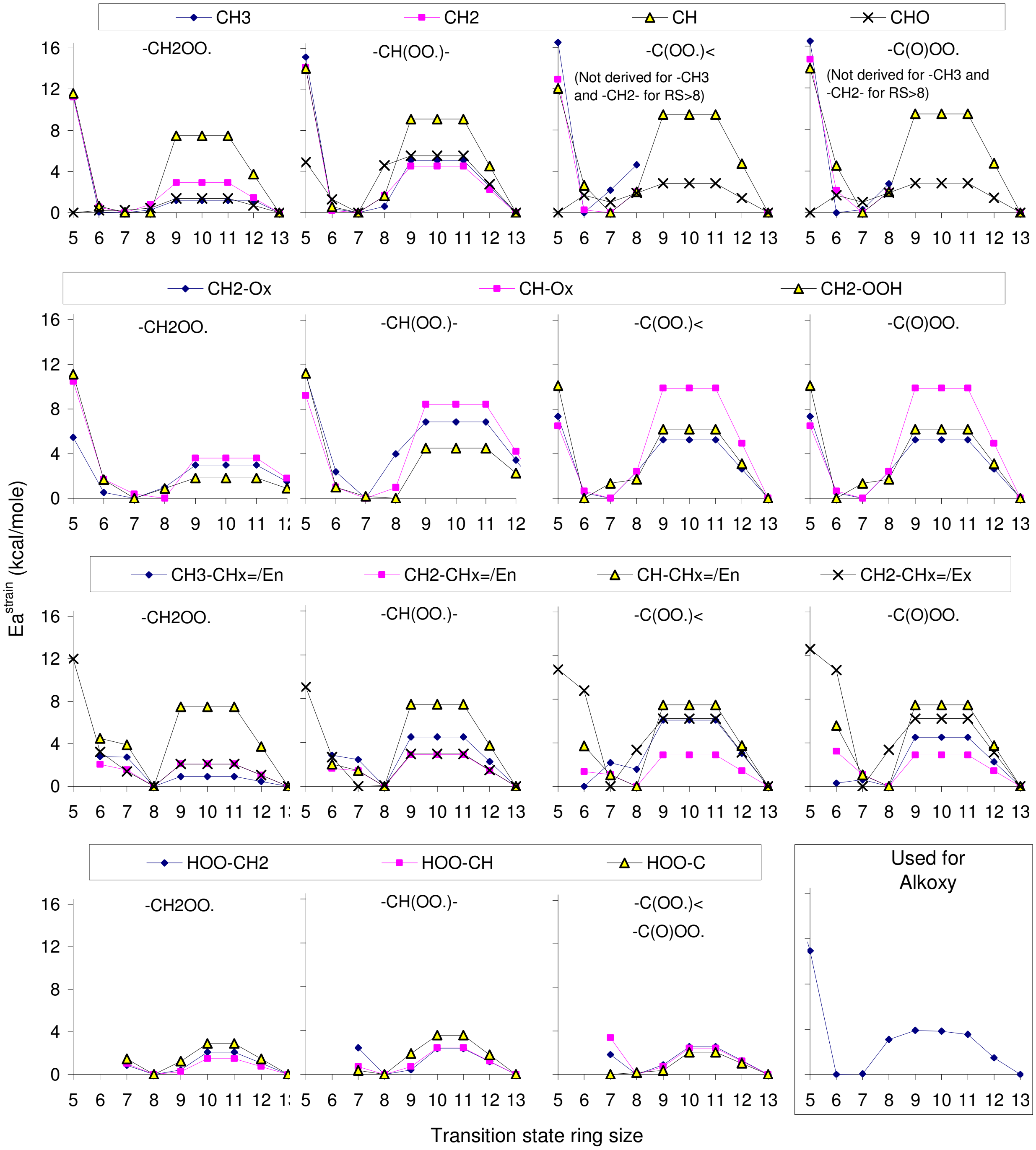


Figure A-11. Plots of Ea^{strain} values used for H-shift isomerizations of peroxy radicals as a function of ring size for various types of rings. The Ea^{strain} values used for alkoxy isomerizations are also shown.

- Although information was provided on the effects of -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 -Ox substituents. Note that this provides an estimated $Ea^{strain(}(7)$ of 2.39 kcal/mole. for $-CH_2-$ groups with these substituents, while the experimental data in Table A-15 are best fit using 1.37 kca/mole, which is what is used in our estimates in this case. This changes the estimated 298K rate constant by a factor of ~5.5, which indicates the range of uncertainty of these estimates.

Note that in some cases the estimation methods described by footnotes to Table A-17 yield very low, and in some cases even slightly negative, Ea^0 estimates. However, the Ea^0 values derived from the SARs of Vereecken and Nozière (2020) were no lower than ~4 kcal/mole, so that was taken as the actual lower limit for Ea^0, and was used whenever the estimated values were lower than that, as indicated in Table A-17. Using this lower limit Ea^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 Ea^0 value used, would not have a practical effect on predictions of atmospheric chemical mechanisms.

The α and β substitution corrections, Ea^{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 Ea^{corr} values so derived are summarized in Table A-19. The recommended Ea^{corr} values for β-OH and β-ONO_2 substituents were independent of transition state ring size, but different values for the Ea^{corr} values for β-oxo substituents were given for ring sizes up to 8. Note that the recommended Ea^{corr} values for *endo* β-oxo were not applied to reactions of acyl peroxy radicals, since these effects are applicable to all such reactions, and are incorporated in the Ea^{HR} values used.

Table A-19. Ea^{corr} values used for various types of α or β substituents.

Substituent on H-group	Ea^{corr}(Subst) (kcal/mole) RS=5	RS=6	RS=7	RS=8	RS=9+	Note [a]
β-OH			1.09			1
α-ONO2			1.89			1
Endo β oxo	[b]	0.90	-1.27	-2.38	-2.38	2
Exo β 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 Ea^{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 α substituent other than carbon-centered groups or -OH, -OOH, ether groups, or $-ONO_2$, as would be the case if there were α-halogen substituents, or H-shifts from the HCO in esters. Note that these reactions may well be favored if there were α-amino substituents, but this is not currently considered by this system.

Note that strain energies should or might be significantly different in reactions of cyclic peroxy radicals 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.

<u>Predicted rate constants</u>. 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 A-15 because these were used to derive the parameters, and only one example is provided for each H- and R-group pair. Figure A-12 plots the experimental vs. estimated rate constants the experimentally measured rate constants that are given in Table A-15. This figure does not cover the full range of estimated rate constants (which range from ~7 x 10^{-12} to ~7 x 10^{6} 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 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.

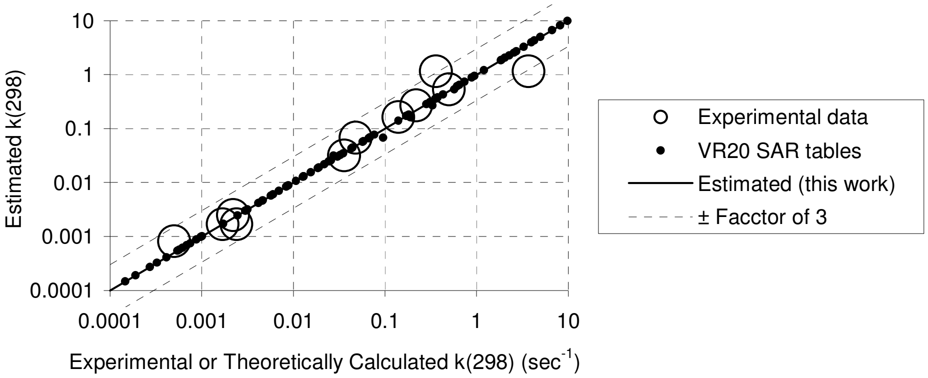


Figure A-12. Plots of estimated 298K rate constants for peroxy H-shift isomerizations against the experimental or theoretically calculated values listed in Table A-15. The dotted lines show a factor of ±3 uncertainty range. Estimated vs. theoretically calculated rate constants in this magnitude range are also shown.

Figure A-13 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 α- and β-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.

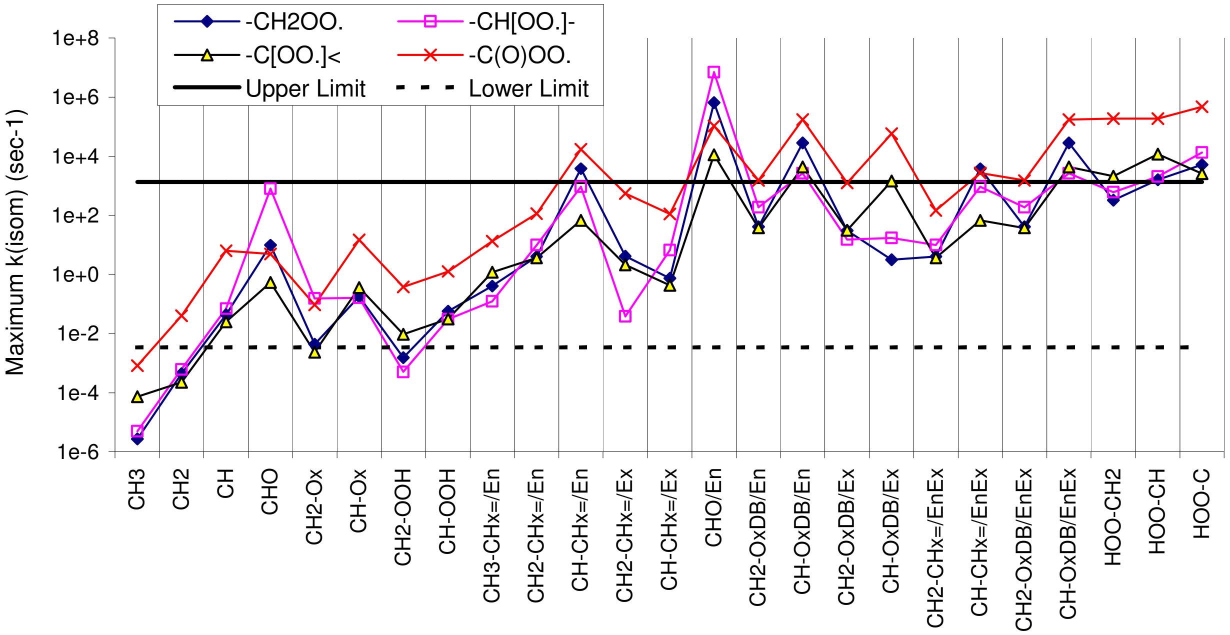


Figure A-13. Estimated peroxy H-shift isomerization rate constants for the most favorable ring size for various H- and R-group pairs without β-substitution corrections. Also shown are upper and lower rate constant limits used during mechanism generation

A1.6. Reactions of Alkoxy Radicals

A1.6.1. Bimolecular Rate Constants

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

$$CH_3CH_2O\cdot + O_2 \rightarrow CH_3CHO + HO_2$$

$$CH_3CH(O\cdot)CH_3 + O_2 \rightarrow CH_3C(O)CH_3 + HO_2$$

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 A-20, 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 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.

Table A-20. Recommended kinetic parameters for the reactions of alkoxy radicals with O_2.

Rxn	Radical	From Measurements [a]			Used [b]		Notes
		A	Ea	k(298)	k(298)	Err.	[c]
O_2	$CH_3O\cdot$	7.40e-14	2.27	1.60e-15	As measured		1
O_2	$CH_3CH_2O\cdot$	5.10e-14	1.09	8.10e-15	As measured		1
O_2	$CH_3CH_2CH_2O\cdot$	2.40e-14	0.46	1.10e-14	1.25e-14	12%	1
O_2	$CH_3CH_2CH_2CH_2O\cdot$			1.40e-14	1.25e-14	-12%	2
O_2	$CH_3C(O\cdot)CH_3$	2.00e-14	0.62	6.90e-15	7.28e-15	5%	1
O_2	$CH_3CH_2C(O\cdot)CH_3$			7.80e-15	7.28e-15	-6%	3, 5
O_2	$CH_3CH_2C(O\cdot)CH_2CH_3$			7.20e-15	7.28e-15	1%	4, 5
O_3	Phenoxy			2.86e-13	As measured		6
NO	Phenoxy			1.88e-12	Reaction ignored		7
NO_2	Phenoxy			2.08e-12	As measured		7
HO_2	Phenoxy				1.10e-10		8

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

[b] The first column is the rate constant at 300K used for estimates (in cm^3 $molec^{-1}$ 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_2 as measured by Assaf et al. (2018).

Likewise, data reported by Atkinson (2007) for radicals that undergo rapid competing isomerization reactions are also not used because of experimental uncertainties.

Table A-20 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 A-56), 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 A-20 as indicated in Section A1.9)

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

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

where the units are $cm^3\ molec^{-1}\ s^{-1}$ 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.

Note that alkoxy radicals without α hydrogens are not expected to react with O_2. These include tertiary alkoxy radicals ($R_3CO\cdot$), acyl oxy radicals ($RC(O)O\cdot$), and phenoxy radicals ($BzO\cdot$). 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_2 or undergo unimolecular reactions under atmospheric systems. MechGen assumes that their major atmospheric sinks are either reaction with O_3, NO_2 or HO_2. 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_2 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 A-20. Note that the rate constant for the reaction with HO_2 has not been measured, so it is assumed to be the same as for the reaction of HO_2 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.

A1.6.2. β Scission Decompositions

Most alkoxy radicals can undergo β-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

$$RC[O\cdot](X_1)X_2 \rightarrow R\cdot + X_1C(=O)X_2$$

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_2 in the atmosphere or other unimolecular reactions, to being the dominant fate for the radical.

Table A-51 in Section A5.2 summarizes measured or calculated rate constants for β-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

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

where n is the reaction path degeneracy (the number of β-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), Ea 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 β scission decompositions. Based on a review of the available kinetic data, Orlando et al. (2003) recommended assuming

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

for all decompositions, and that was adopted in this work, and is reflected in the A factors tabulated in Table A-51 in Section A5.2. 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 A-51, and Figure A-14 shows plots of experimentally-derived activation energies against the barrier heights calculated by Vereecken and Peeters (2009) for these 21 compounds. Although the calculated barrier heights are not exactly the same as the activation energies, and differ by as much as 4 kcal/mole at the lower barrier heights, the data are well fit by

$$Ea(experimental) = 4.06 + 0.77 * Eb$$

where Ea(experimental) is derived from the experimental rate constant given by Orlando et al. (2003) assuming $A(decomp)=1 \times 10^{-14} sec^{-1}$, Eb is the barrier height calculated by Vereecken and Peeters (2009), and the units of both are kcal/mole. This equation was used to derive Ea 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 A-51 and also used as a basis to derive the parameters for estimating rate constants for these decomposition reactions.

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 A-51 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 β-scission decompositions were estimated using

$$Ea(Reaction) = EaA(FormRad) + [\ EaB \times \Delta H_r\ (reaction)\ ],$$

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 ΔH_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

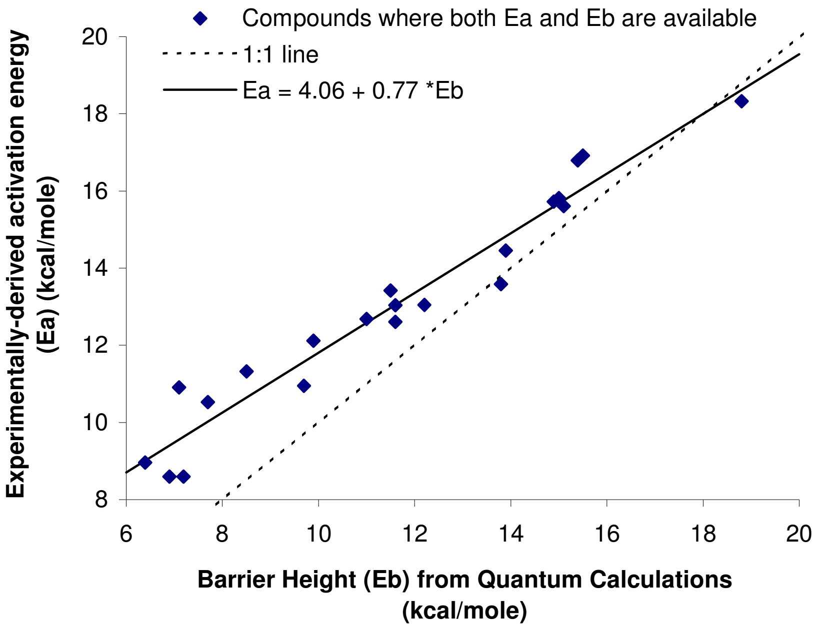


Figure A-14. Plots of activation energies for beta-scission decomposition reactions derived from experimental data summarized by Orlando et al. (2003) against barrier heights calculated by Vereecken and Peeters (2009) for the same reactions. The line fit was used to estimate activation energies for reactions where experimental data are not available.

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:

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

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 A-51.

The various parameters that MechGen currently uses to estimate activation energies for β-scission decompositions are listed on Table A-21 through Table A-23, 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 A-51, 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 A-51) 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 A-51.

Table A-21. List of EaR parameters that give dependences of the activation energies of alkoxy radial 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_3(.)	104.98	18.46	>CH(.)	97.82	12.79 [b]
-CH_2(.)	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 (III)					
=C(.)	106.66	19.04	>CH-OO(.)	85.02	7.00
CH_3-O(.)	105.16	18.20	>C<OO(.)	85.85	7.46
-CH_2-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_3-OO(.)	85.85	7.46	NO3	102.05	16.47
-CH_2OO(.)	85.44	7.23	HO2	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 α substituents. These are listed in Table A-22.

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 A-51.

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 A-21. The data on Table A-51 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 A2.1, are included on Table A-21. Figure A-15 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

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

where BDE is the bond dissociation energy in kcal/mole. This was used to derive the estimated EaA parameters listed on Table A-21.

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 A-22. 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_2. Method [a]	EaRc [b]	Substituent on >CH. Method	EaRc	Substituent on >CH. Method	EaRc
-R	Assigned	0	Assigned	0	Assigned	0
-CHx=	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_2	Adjusted	0.09	Adjusted	0.48	Est 4	0.28
-NO_2	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
-NHx	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_x= substitution on -CH_2-. 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_2-. Because of lack of data, substitution on other alkyl broups 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.

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

$$\text{EaP(formaldehyde)} = 0 \qquad \text{(assigned)}$$
$$\text{EaP}(C_{2+}\text{ aldehydes}) = -2.23 \text{ kcal/mole} \qquad \text{(adjusted)}$$
$$\text{EaP(ketones)} = -3.89 \text{ kcal/mole} \qquad \text{(adjusted)}$$

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

Table A-23. 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
-CHx-O-	Adjusted	1.07	Est 3	1.07
-CHx-OH	Adjusted	-0.18	Adjusted	-0.38
-CHx=	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_2	Adjusted	-1.06	Est 3	-1.06
-NO_2	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
-NHx	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 A-51; "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 group ketone products formed. The correction is estimated to be the same for ring groups bonded to aldehyde products.

[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

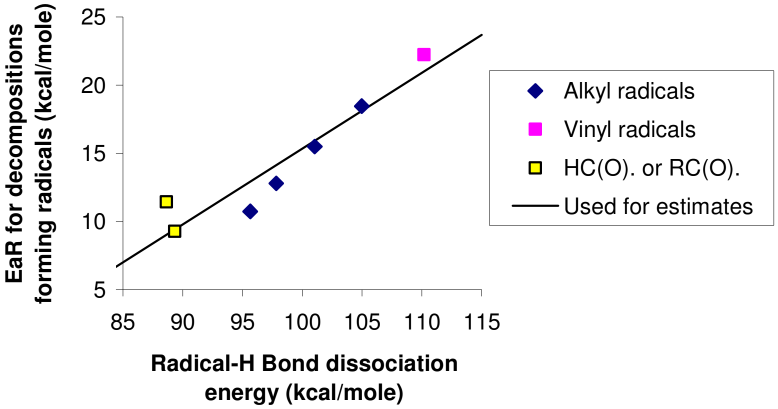


Figure A-15. Plots of optimized EaR values for β-scission decompositions forming various types of radicals against the C-H bond dissociation energy that forms the radical. The line that fit the data, used for estimation purposes, is also shown.

summarized on Table A-22 and Table A-23, 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.

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 A-51 against cycloalkane ring strains is shown on Figure A-16, 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 A-24.

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 A-51 are sufficient to derive corrections for ring sizes of 4-6. These are given in the middle columns of Table A-24 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 A-51 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 A-24.

Table A-24. 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 Aurby (2012)

[b] Methods codes: "Adjusted": Adjusted to fit data for ring-containing compounds on Table A-51; "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.

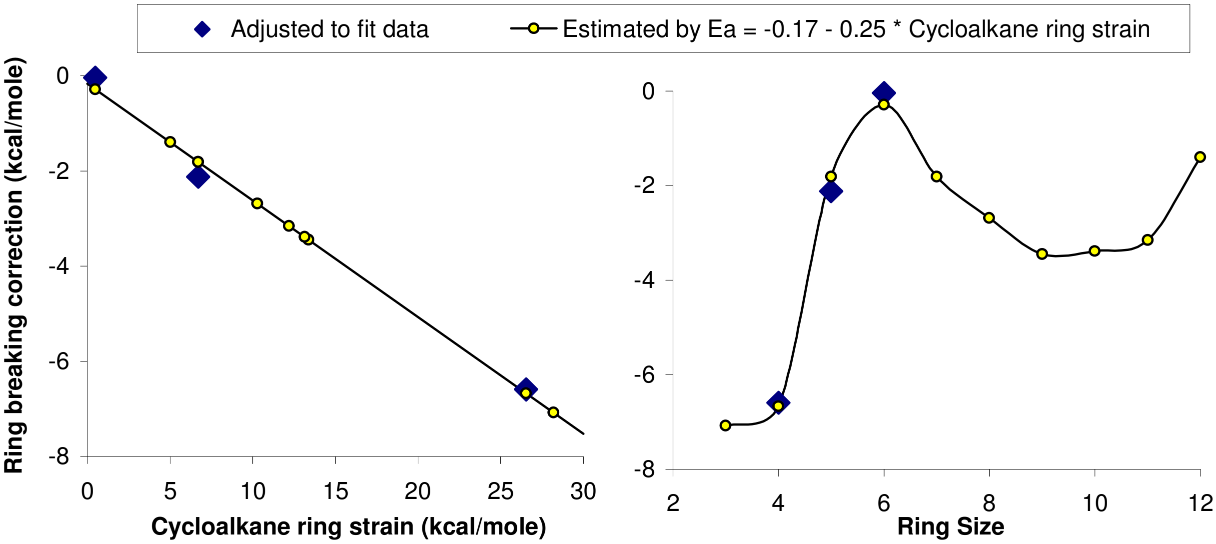


Figure A-16. Plots of corrections for ring breaking on activation energies beta scission decompositions of alkoxy radical where both the alkoxy and leaving radical groups are on the same ring against the ring strain for the corresponding cycloalkane and against the ring size.

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 A-23.

The performance of our estimates in predicting the alkoxy radical decomposition activation energies in Table A-51 is shown on Figure A-17. 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 ±1 kcal/mole. Note that ±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 A-51 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 β-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.

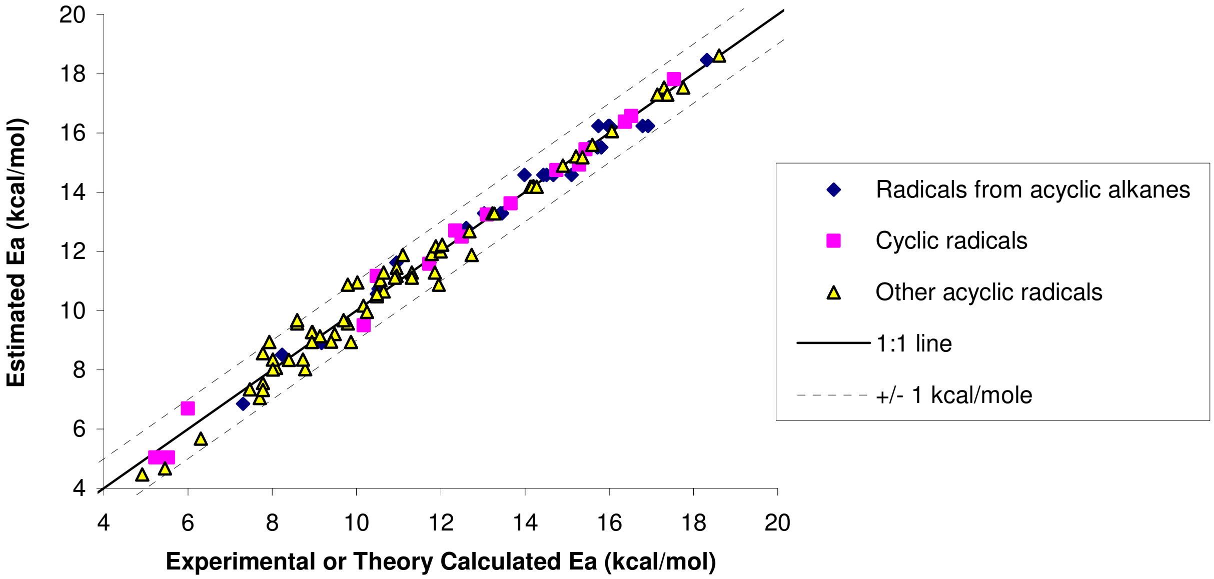
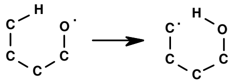


Figure A-17. Plots of estimated activation energies for alkoxy radical beta-scission decompositions against the experimentally or theoretically-derived activation energies given in Table A-51.

A1.6.3. H-Shift Isomerization Reactions

As for the peroxy radicals described above (Section A1.5.5), 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 (≈C4 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 A-50 in Section A5.2 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 A-50 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 A1.5.5 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^{HS}, are estimated using:

$$k^{HS}(\text{H-group, RS}) = \text{nH x A(RS) x exp(-Ea(H-group, RS) / RT)} \qquad \text{(I)}$$

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

$$\text{Ea}^{\text{corr}}\text{(H-group)} = \Sigma_{\text{Groups in ring}}\ \text{Ea}^{\text{InRingCor}}\text{(ring group)} + \Sigma_{\text{groups }\alpha\text{ to H-group}}\ \text{Ea}^{\text{corr}}\text{(group)} \qquad \text{(III)}$$

where k^{HS} is in units of min^{-1}; nH is the number of abstractable hydrogens giving the same reaction; A and Ea are the Arrhenius parameters in units of min^{-1} and kcal/mole, respectively; T is the temperature in degrees K; 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); A, Ea^{0}, $\text{Ea}^{\text{strain}}$, $\text{Ea}^{\text{InRingCor}}$, and Ea^{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 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 A factors per abstractable hydrogen are given in Table A-25. 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 A-25, 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 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

Table A-25. 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^{strain}(RS)		k(RS) /
		sec-1	Note	kcal/mole	Note	k(RS=6) [a]
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).

size for larger rings. Plots of these ring strains against ring size were shown in Figure A-11 in Section A1.5.5, where they are useful for estimating A factors for peroxy H-shift reactions.

Figure A-18 shows plots of the estimated 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 Ea^{0} and the Ea^{corr}'s are the same. It can be seen that the A factor decreases slowly with ring size, but because of ring strain effects the reaction is fastest with ring size of 6, is only ~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 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 β-scission decompositions.

The 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 A-26. These are either derived by adjustments so estimates fit the data given in Table A-50 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 -CHO groups.

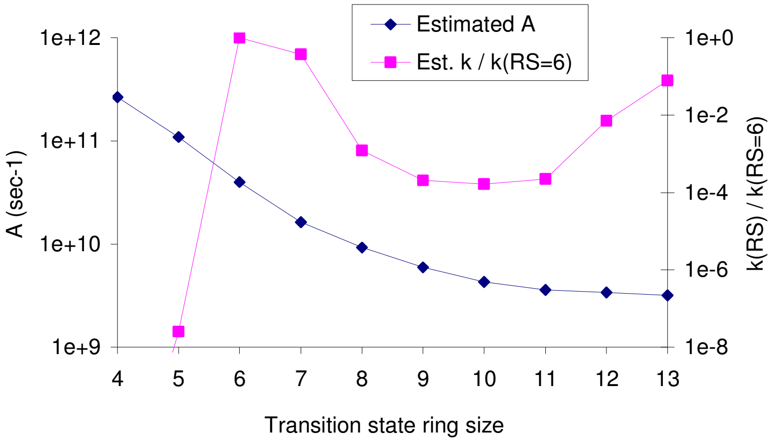


Figure A-18. A factors estimated for H-shift reactions of alkoxy radicals, and also relative changes in the rate constants with ring size due to estimated ring strains if all else were equal.

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Table A-26. Ea^0 parameters used to estimate activation energies for deriving estimated rate constants for H-shift reactions of alkoxy radicals.

H-Group	Ea^0 (kcal/mole)	Derivation and Discussion
CH_3-	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 A-50.
-CH_2-	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 $HCOCH_2CH_2CH_2O$· radical given in Table A-50.
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 EaA 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 A-27, and the presence of non-alkyl groups anywhere in the transition state ring are taken into account as indicated in Table A-28, with footnotes indicating how they are derived or estimated. There are sufficient data in Table A-50 to derive or estimate correction factors for -CO- or -O- groups in the transition state ring (Table A-27) and substitution by -OH or $-CH_xOH$ groups (Table A-28), 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 α 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 A-38, with the activation energy correction estimated by:

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

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.

Table A-27. 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	Ea correction [a]	Note [a]
-CO-	Next to H-abstracted group	$-CH_2-$, >-CH, -CHO	3.07	1
-CO-	Next to H-abstracted group	$-CH_3$	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 A-50 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 A-50 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 $CH_3CH(O\cdot)OCH_2CH_2OH$.

Figure A-19 compares the ~298 K H-shift isomerization rate constants estimated as discussed above with the measured or theoretical values listed in Table A-50. The generally excellent agreement is primarily due to the relatively large numbers of adjustable parameters compared to the amount of data 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 A-28, which do not affect predictions of any of the rate constants shown in Table A-50 or Figure A-19. 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

Table A-28. H-abstraction correction terms used for estimating activation energies for H-shift isomerization reactions.

Substituent	OH Abst Fac [a]	Ea^{corr} kcal/mole	notes	Substituent	OH Abst Fac [b]	Ea^{corr} kcal/mole	notes
OH + Organic abstraction factor used							
-O-	9.1	-1.31	1, 2	-CHx-CO-	3.5	-0.75	1
-O-(OH)	1.23	-0.12	1, 2	-CHx-ONO_2	0.36	0.61	1
-O-(CO)-	2.0	-0.41	1	-CHx-NO_2	0.3	0.67	1
-O-(CHO)	0.77	0.16	1	=CHx-	1.00	0	1
-CO-	0.95	0.03	1		Adjusted to fit data		
-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_2	0.14	1.16	1		Estimated		
-CO-OX	0.22	0.89	1	-NO_2	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 A-38. 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 298K (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(factor).

2 In these cases the correction factor derived from OH abstraction data depends on whether the abstraction is from a -CH_3, -CH_2-, 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.

adjustable parameters. Therefore, more data are needed to verify the H-shift estimates derived for this work, particularly for H-shifts of peroxy radicals.

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.

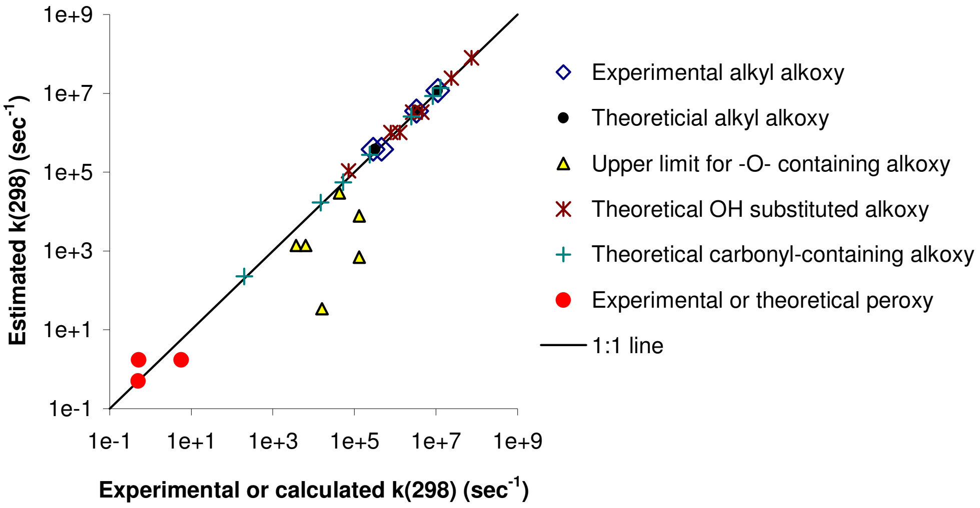


Figure A-19. Plot of estimated vs. experimental or theoretically calculated rate constants for H-shift isomerizations of alkoxy or peroxy radicals at 298K.

A1.6.4. H-Elimination Decompositions

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

$$RCH_2O\cdot \rightarrow RCHO + H\cdot$$

$$RCH(O\cdot)R' \rightarrow RC(O)R' + H\cdot$$

Available information concerning the rate constants for these reactions are summarized on Table A-29. Curran (2006) reviewed information provided H-elimination reactions from several representative alkyl radicals, fitting data to the parameters

$$k(T) = A' \text{ x } T^{n'} \text{ x } \exp(-Ea'/RT).$$

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

$$k(T) = nH \text{ x } A/H \text{ x } \exp(-Ea/RT),$$

where nH is the number of H atoms that can be eliminated, A/H is the A factor per hydrogen, and Ea is the activation energy parameter used for estimates. The values of A/H and Ea 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 x 10^{-13} 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

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

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.

Table A-29. Summary of available information concerning rate constants for H-elimination reactions for alkoxy radicals.

Radical	nH	Est	Published Rate Parameters [b]				Std	Notes
		ΔH_{rxn} [a]	A'	n'	Ea'	k(298)	Ea [c]	[d]
$CH_3O\cdot$	3	21.2	5.6e+13	-0.39	26.40	7.3e-6	26.08	1
$CH_3CH_2O\cdot$	2	16.5	5.3e+13	-0.69	22.23	5.3e-3	21.95	1
$CH_3CH_2CH_2O\cdot$	2	16.7	3.2e+12	0.75	21.06	2.3e-3	22.44	1
$CH_3CH(O\cdot)CH_3$	1	12.5	5.6e+13	-0.48	20.08	1.1e-1	19.77	1
$HOCH_2O\cdot$	2	2.7	1.0e+14	0	14.90	2.3e+3	14.25	2
$CH_3OCH_2OCH_2O\cdot$	2	1.6				1.1e+3	14.72	3
$CH_3OCH(O\cdot)OCH_3$	1	-5.7				>8e+6	<~9	4

[a] Heat of reaction as estimated by group additivity (see Section A2.1) in kcal/mole.

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

[c] Activation energy corresponding to k(300) if the temperature dependence of k(T) = nH x Std A x exp(-Std Ea/RT) is assumed and a general A factor per hydrogen of 3.3×10^{14} 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_2 reaction derived from the analysis of O_2-dependent product yield data from dimethoxy methane reported by Wallington et al. (1997). Rate constant placed on an absolute basis using the estimated $kO_2[O_2]$=6.4e+4 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 $CH_3CH(O.)OCH_3$. Lower limit assumed to be ~5 x the rate constant for the decomposition reaction, which is estimated to be 1.2e+6 sec^{-1}.

Figure A-20 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 A-29. 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,

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

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 $\sim 1.6 \times 10^6$ sec^{-1} for the β-scission decomposition of $CH_3OCH(O\cdot)OCH_3$ to $CH_3OCHO + CH_3O\cdot$, as discussed in Section A1.6.2. Note,

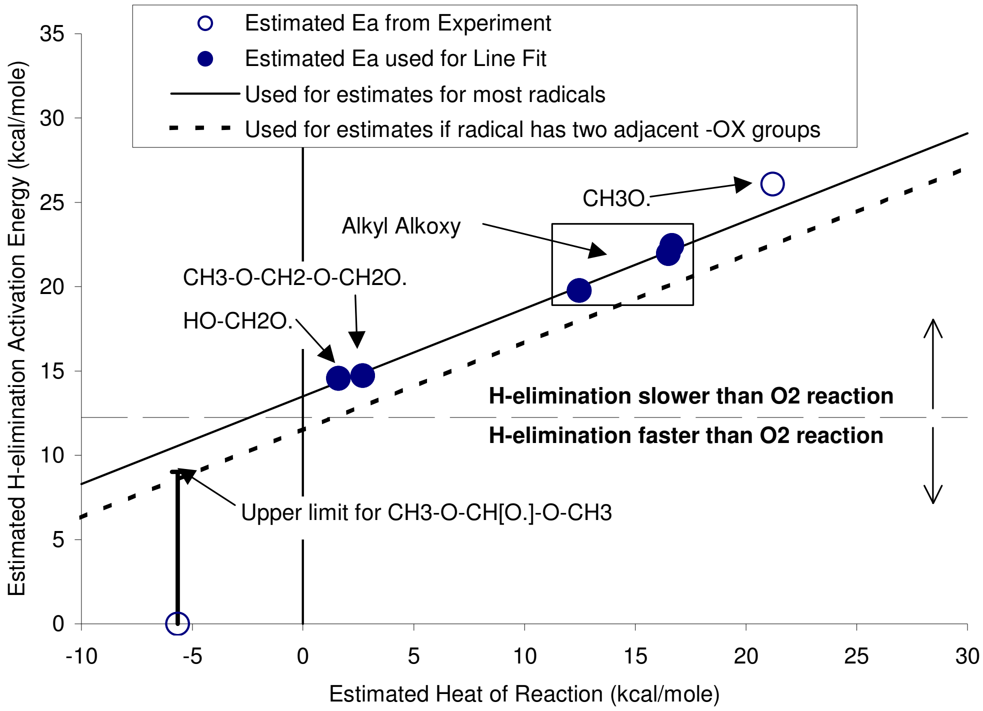


Figure A-20. Plots of activation energies derived or estimated for alkoxy H-atom elimination reactions against their estimated heats of reaction.

however, that the β-scission decomposition rate constants have significant uncertainty, so our estimate for the upper limit for H-elimination from $CH_3OCH(O\cdot)OCH_3$ 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 $CH_3OCH(O\cdot)OCH_3$ radicals, the only alkoxy radical listed on Table A-29 with two O-substituents (see Figure A-20). In order to make appropriate estimates for the products of the reactions of $CH_3OCH(O\cdot)OCH_3$ radical, for estimation purposes we assume

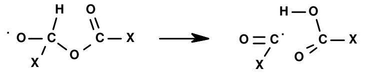
$$\text{Ea (XOCH[O}\cdot\text{]OX' H elim)} = \text{Ea (standard H elim)} - 2.0\ \text{kcal/mole},$$

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 A-20. This is highly uncertain, and better estimates are needed for alkoxy radicals whose H-elimination reactions are exothermic.

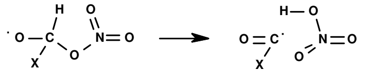
Any alkoxy radical that can undergo an H-elimination reaction can also react with O_2 to form the same ultimate products in the presence of O_2, so if the O_2 reaction is sufficiently fast then the H-elimination reaction can be neglected. As discussed in Section A1.6.1, the rate constants for the O_2 reactions are estimated to be independent of the heat of reaction, and are such that the O_2 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 A-20 shows that the O_2 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 usually not highly important for such radicals. However, estimates are important if the H-elimination is exothermic, especially if, as is the case for $CH_3OCH(O\cdot)OCH_3$ radicals, there is a rapid competing decomposition.

A1.6.5. Ester and Nitrate Rearrangements

Alkoxy radicals with α hydrogens that are bonded to -O-CO- or -O-CHO, or nitrate ($-ONO_2$) groups can also undergo ester or nitrate decomposition reactions, where the α hydrogen is transferred to a carbonyl group via a 5-member ring cyclic transition state, forming an acid and a carbonyl radical, e.g.



(Ester Rearrangement)



(Nitrate Rearrangement)

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 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 α hydrogen. Available information concerning the rate constants for these α ester and nitrate reactions is summarized on Table A-30.

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

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

where A and Ea 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 A1.6.3, this gives

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

Where nH is the number of α hydrogens at the alkoxy radical, i.e., 2 for primary and 1 for secondary radicals. Table A-30 gives the reference activation energies that correspond to the experimental or theoretically calculated k(298) and these estimated A factors.

Table A-30 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 A-30 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

Table A-30. Available information concerning atmospheric rate constants for ester and nitrate rearrangements.

Reaction	Reference [a]		Ref	Estimated		
	k(298)	Note	Ea [b]	A	Ea	k(298)
$CH_3C(O)OCH_2O\cdot \rightarrow CH_3C(O)OH + HC(O)\cdot$	1.2e+5	1	8.54	2.2e+11	8.94	6.2e+4
$HC(O)OCH_2O\cdot \rightarrow HCOOH + HC(O)\cdot$	3.2e+4	2	9.33	2.2e+11	8.94	6.2e+4
$CH_3C(O)OCH(O\cdot)CH_3 \rightarrow CH_3C(O)OH + CH_3C(O)\cdot$	3.7e+7	3	4.74	1.1e+11	4.74	3.7e+7
$.OCH_2ONO_2 \rightarrow NO_2OH\ (HNO_3) + HC(O)\cdot$	2.2	4	15.00	2.2e+11	15.00	2.2
Assignments used for Mechanism Generation						
$RC(O)OCH_2O\cdot \rightarrow RC(O)OH + HC(O)\cdot$		5, 6		2.2e+11	8.94	6.2e+4
$R_1C(O)OCH(O\cdot)R_2 \rightarrow R_1C(O)OH + R_2C(O)\cdot$		5, 7		1.1e+11	4.74	3.7e+7
$RCH(O\cdot)ONO_2 \rightarrow HNO_3 + RC(O)\cdot$		5, 8		2.2e+11	10.8	1.3e+3

[a] Experimental or theoretically calculated rate constant around 298K in sec^{-1}. 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 $kO_2[O_2]$=6.4e+4 sec^{-1} (see Section A1.6.1).

2 Derived from rate constant relative to O_2 reaction as measured by Wallington et al. (2001). Rate constant placed on an absolute basis using the estimated $kO_2[O_2]$=6.4e+4 sec^{-1}.

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 A-25), which is expected to have a similar 5-member ring transition state.

6 The activation energy is the average of that given above for $CH_3C(O)OCH_2O\cdot$ and $HC(O)OCH_2O\cdot$.

7 The activation energy is that given above for $CH_3C(O)OCH(O\cdot)CH_3$.

8 Estimated from the activation energy given above for $\cdot OCH_2ONO_2$ 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 $\cdot OCH_2ONO_2$ 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.

activation energies, so because of lack of data we assume that the A and Ea parameters are not affected by substituents.

The activation energies used for estimation purposes are included in Table A-30, with footnotes indicating how they are derived. There are no reactions on Table A-30 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.

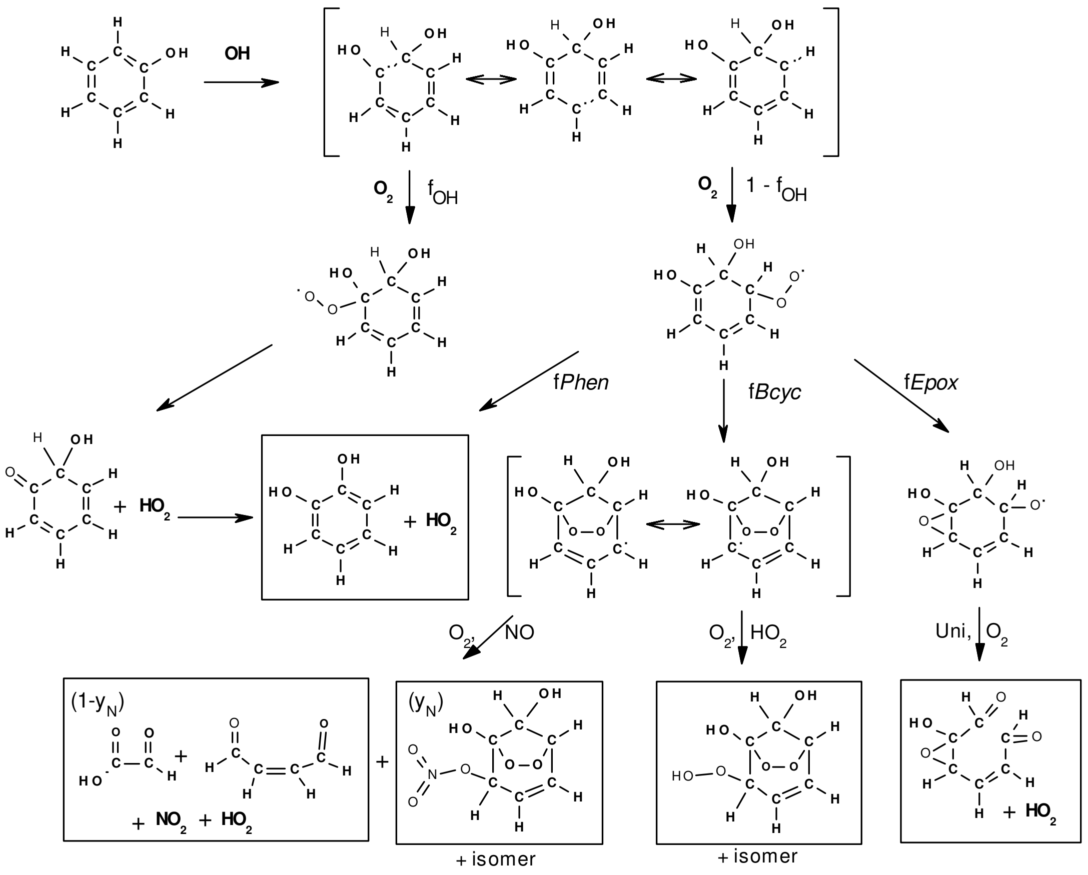
Note that these estimates are based on a very limited number of rate constants or theoretical calculations, and more data are needed to evaluate these estimates, and to determine effects of substituents, if any. However, the effects of the uncertainties in these estimates may not be large if the rearrangement 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 β-scission decompositions that may be competitive -- see Section A1.6.2), 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.

A1.7. 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 A-21 shows possible reactions 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 (f*Phen*, f*Bcyc*, f*Epox*), 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 A-21.

On the other hand, if the O_2 adds to the radical center adjacent to the -OH substituent, then the reaction would form an α-hydroxy peroxy adduct that is expected to rapidly decompose to form HO_2 and the corresponding carbonyl, as shown on the left side of Figure A-21 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 A-21.

The calculations of Xu and Wang (2013) predict the O_2 will add primarily to the radical center with the α-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_3 formation, NO oxidation, and phenol consumption in the phenol - NO_x experiments used to develop previous SAPRC mechanisms (Carter, 2000, 2010a,b). This is shown in Figure A-22, which gives plots of selected results of selected phenol - NO_x, o-cresol - NO_x, and 1,4-dimethylphenol - NO_x 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 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 A-21) 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).



f_{OH} is the fraction of O_2 addition to the radical center with the α-OH substituent.
f*Phen*, f*Bcyc*, and f*Epox* are branching ratios used for OH + aromatic hydrocarbon adducts
y_N is the organic nitrate yield in the peroxy + NO reaction

Figure A-21. Reactions following the addition of OH radicals to the *ortho* position of o-cresol.

The figure shows that assuming fOH=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 A-21 was used as input to the general procedure for estimating branching ratios when O_2 adds to allylic radicals, as discussed in Section A1.4.2. 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

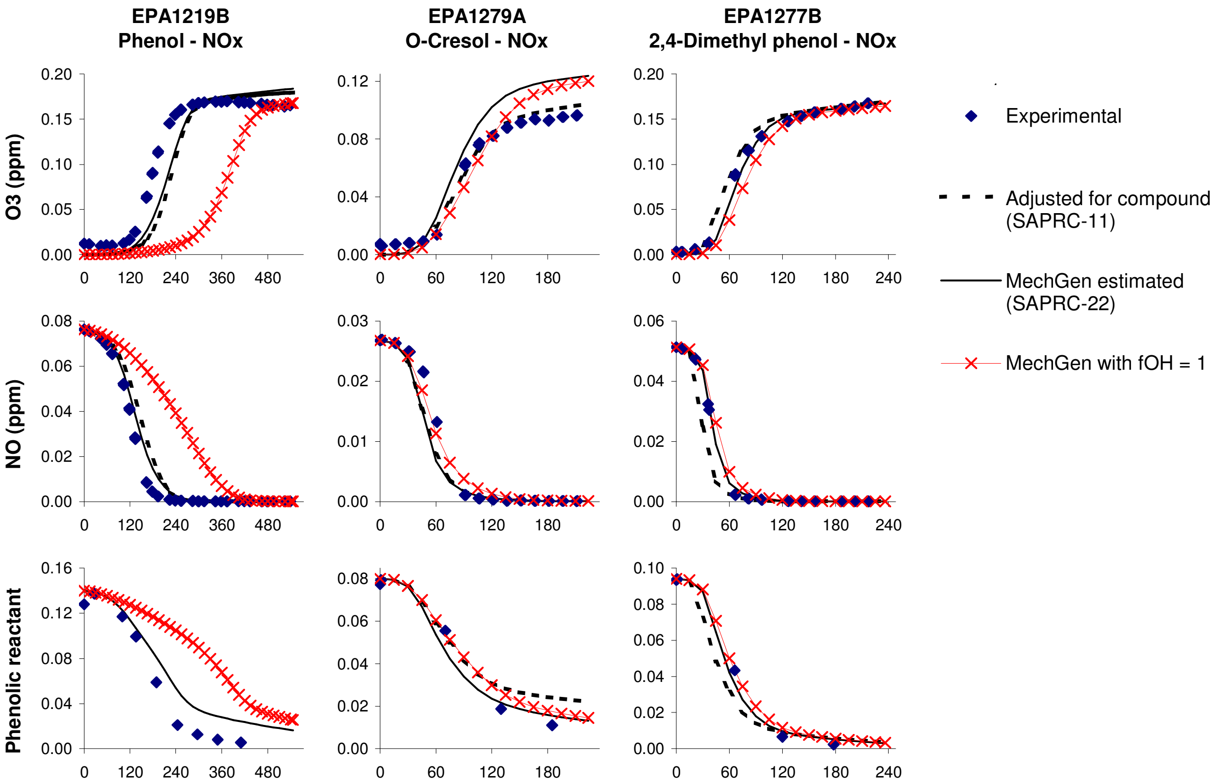


Figure A-22. Comparisons of experimental and calculated concentration-time data for O_3, NO, and the reacting phenolic compound for representative phenol, o-cresol, and 2,4-dimethyl phenol - NO_x experiments.

left side of Figure A-22, 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_2 adducts, other than α-peroxy, does not affect these branching ratios.

A1.8. 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_3 with alkenes and acetylenes and in the reactions of carbenes with O_2.

$$X_2C{=}X'_2 + O_3 \rightarrow X_2C[OO]\ \{\text{ex-O3ole}\} + X'_2C{=}O \tag{1}$$

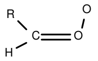
$$*(G)_nC(X){=}C(X')* + O_3 \rightarrow X'C({=}O)(G)_nC[OO]X\ \{\text{ex-O3cycole}\} \tag{2}$$

$$XC{\equiv}CX' + O_3 \rightarrow XC[OO]C({=}O)X'\ \{\text{ex-O3alkyne}\} \tag{3}$$

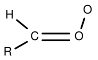
$$X_2C{:} + O_2 \rightarrow X_2C[OO]\ \{\text{ex-O2carbene}\} \tag{4}$$

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 Criegees because each type forms intermediates with different amounts of excitation energies. CIs formed from reactions of O_3 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_3 with double bonds in rings, reactions of O_3 with alkynes, and reactions of O_2 with carbenes are excited with all the energy of the reaction.

CIs other than $CH_2[OO]$ can exist in two configurations, designated *syn* and *anti*, as follows:



Syn



Anti

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 α carbonyl substituents are predicted to rapidly interconvert by O shifts between the Criegee and adjacent carbonyl group, resulting in an equilibrium involving the two α-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 α-unsaturated substituents with abstractable allylic hydrogens in the γ 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 α 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 α-unsaturated substituents with allylic hydrogens in the γ 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_2O.

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

A1.8.1. Mechanisms for Intermediates formed from O_3 + Simple Alkenes

Available data on the reactions of O_3 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 A-31. Table A-31 also indicates how the branching ratios used by MechGen were derived based on these data.

In the case of excited $CH_2[OO]$ formed from ethene, the recommended branching ratios are as follows:

$$
\begin{aligned}
CH_2[OO]\ \{\text{ex-O3ole}\} + M &\rightarrow \text{Stabilized } CH_2[OO] + M && (42\%)\\
&\rightarrow HCO. + OH && (17\%)\\
&\rightarrow CO_2 + H_2 && (18\%)\\
&\rightarrow CO + H_2O && (18\%)\\
&\rightarrow CO_2 + 2\ H && (5\%)
\end{aligned}
$$

where {ex-O3ole} indicates excitation from O_3 + alkene reactions. These recommendations are adopted by MechGen for reactions of excited $CH_2[OO]$ 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_3 with propene and the 2-butenes were also reviewed in IUPAC (2023), and suggestions were made for the yields of products from the excited $CH_3CH[OO]$ formed in these reactions, which are included in Table A-31. 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 A-31 indicates that the most important decomposition route for excited $CH_3CH[OO]$ is the vinyl hydroperoxide (VHP) reaction, where the [OO] abstracts an α-hydrogen on a substituent, forming an excited vinyl hydroperoxide that then decomposes.

$$CH_3CH[OO]\ \{\text{ex O3ole}\} \rightarrow \cdot CH_2CHOOH\ \{\text{ex}\} \rightarrow \cdot CH_2CHO + OH$$

This is believed to be the only direct source of OH from this reaction, so the measured OH yields in the 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 α 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 A-31 shows additional reactions of the excited intermediate via the "hot acid" route, where the H on the monosubstituted Criegee group transfers to the [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

Table A-31. 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_3 reaction			Used for MechGen	
	Propene	2-Butenes		Yield	Notes [d]
		cis	*trans*		
Excited CH_3CHOO Yield	62%	100%	100%		
Observed OH	48%	33%	60%		1
OH + ·CH_2CHO (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_3. + ·CO-OH = CH_3. + H + CO_2	-	11%	-	7%	5
CH_2=CO + H_2O	6%	7%	4%	-	5
CH_4 + CO_2	16%	19%	11%	17%	5
CH_3OH + 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
Stabilazation 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_2CHO (VHP route)	55%	28%	65%	49%	7, 8
CH3. + ·CO-OH = CH_3. + H + CO_2	-	17%	-	10%	7, 9
CH_2=CO + H_2O	9%	11%	6%	-	7, 9
CH_4 + CO_2	24%	29%	17%	26%	7, 9
CH_3OH + 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.

1 OH yield from excited CH_3CHOO recommended by IUPAC (2023).

2 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 A-32.

3 MechGen uses the average of the yields recommended for propene and the 2-butenes.

4 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 A-31 (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.

no other sources of OH in the experimental systems employed). The primary experiments used to measure the OH yields in O_3 + alkene systems consisted of reacting 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 A1.6.3), MechGen now predicts that there is at least some OH formation from the subsequent reactions of the $\cdot CH_2CHO$ co-product. The predicted reactions of this intermediate under the conditions of these experiments are given in Table A-32, 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 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 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 A-31 were corrected to take this into account.

The total amounts of stabilization recommended by IUPAC (2023) for excited $CH_3CH[OO]$ radicals formed from reactions of O_3 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 A-31.

Data for the reactions of O_3 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 $CH_3C[OO]CH_3$ formed in O_3 + alkene reactions under atmospheric conditions. These are all consistent with the VHP reaction being the only fate for this excited intermediate as shown here:

$$CH_3C[OO]CH_3\ \{ex\text{-}O3ole\} \rightarrow CH_2{=}C(OOH)CH_3\ \{ex\} \rightarrow \cdot CH_2C({=}O)CH_3 + OH$$

Table A-32. Reactions and relative rates of the co-product of the VHP reaction of excited $CH_3CH[OO]$ intermediates under the conditions of the experiments used to measure OH yields in the reaction of this intermediate

Reaction		Relative Rate
$\cdot CH_2CHO + O_2$	$\rightarrow \cdot OOCH_2CHO$	100%
$\cdot OOCH_2CHO + RO_2$	$\rightarrow \rightarrow 0.5\ HO_2$ + other products [b]	35%
$\cdot OOCH_2CHO + HO_2$	$\rightarrow \rightarrow 0.15\ HO_2$ + other products	1%
$\cdot OOCH_2CHO$	$\rightarrow HOOCH_2C(O)\cdot$	64%
$HOOCH_2C(O)\cdot + O_2$	$\rightarrow HOOCH_2C(O)OO\cdot$	64%
$HOOCH_2C(O)OO\cdot$	$\rightarrow \cdot OOCH_2C(O)OOH$	64%
$\cdot OOCH_2C(O)OOH + RO_2$	$\rightarrow 0.5\ .OCH_2C(O)OOH$ + other products	55%
$\cdot OOCH_2C(O)OOH + HO_2$	$\rightarrow HOOCH_2C(O)OOH + O_2$	7%
	$\rightarrow$ **OH** + $\cdot OCH_2C(O)OOH$	**2%**
$.OCH_2C(O)OOH$	$\rightarrow HCOC(O)OOH + HO_2$	48%
	$\rightarrow HCHO + HOOC(O)\cdot \rightarrow HCHO + CO_2 +$ **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_3 in 1 atmosphere of NO_x-free air at 300K.

[b] "RO_2" is the sum of all the 6 peroxy radicals in the generated mechanisms for O_3 + 2-butenes and OH + cyclohexane. These radicals, and their cross-reactions, are represented explicitly in the simulation.

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_3 with 2-methyl propene are more consistent with no stabilization of the excited $CH_3C[OO]CH_3$ formed in that system. Because of this discrepancy, we assume that the amount of stabilization of excited $CH_3C[OO]CH_3$ is approximately the same as that derived for excited $CH_3C[OO]$ as discussed above, which is ~35% (Table A-31).

Although it turns out that the extent of stabilization does not affect the overall fate of excited $CH_3C[OO]CH_3$ 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 A-31 for excited $CH_3CH[OO]$ or as discussed above for excited $CH_3C[OO]CH_3$. 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. Based on these considerations, the general reactions of excited intermediates with only alkyl substituents in the α position are as shown in Table A-33. 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 A1.8.3.

One might expect that the extent of stabilization would increase with the size of the intermediate, but the extent to which this is the case is uncertain. However, OH yields have been measured in the reactions of O_3 with a number of alkenes, and relevant data summarized by Calvert et al. (2000) are tabulated in Table A-34. 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_3 reacts with a double bond in a ring, forming only a single excited intermediate with all the excitation energy. Greater excitation and therefore faster decomposition reactions and less stabilization is expected than if the Criegee intermediate had to share the excitation with a separate carbonyl co-product.

Figure A-23 shows plots of predicted vs. experimental OH yields for the three models.

The predicted OH yields for ethene and the alkenes with only CH_3 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_3 addition to a double bond in a ring. Therefore, this is the model adopted for use by MechGen. 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 β or farther position do not affect the mechanism as

Table A-33. General mechanism for reactions of excited Criegee intermediates formed in the reactions of O_3 with alkenes, applicable to intermediates with α alkyl substituents.

Reaction [a]		Factor [b]	Note
	<u>RCH[OO] Criegees</u>		
$X_2CHCH[OO]$ {ex}	$\rightarrow \cdot CX_2CHO + OH$	0.49 x (1 - SF)	1
	$\rightarrow X_2CH\cdot + \cdot C(=O)OH$	0.10 x (1 - SF)	1
	$\rightarrow X_2CH_2 + CO_2$	0.26 x (1 - SF)	1
	$\rightarrow CH_3OH + CO$	0.14 x (1 - SF)	1
	$+ M \rightarrow X_2CHCH[OO$ *syn*$] + M$	0.33 x SF [d]	2
	$+ M \rightarrow X_2CHCH[OO$ *anti*$] + M$	0.67 x SF	2
$X_2CHCH[OO$ *syn*$]$	$\rightarrow \cdot CX_2CHO + OH$	100%	
$YCH[OO]$ {ex}	$\rightarrow Y\cdot + \cdot C(=O)OH$	0.20 x (1 - SF)	3
	$\rightarrow YH + CO_2$	0.52 x (1 - SF)	3
	$\rightarrow YOH + CO$	0.28 x (1 - SF)	3
	$+ M \rightarrow YCH[OO$ *syn*$] + M$	0.33 x SF	2
	$+ M \rightarrow YCH[OO$ *anti*$] + M$	0.67 x SF	2
	<u>RC[OO]R' Criegees</u>		
$X_2CHC[OO]CHX'_2$ {ex}	$\rightarrow \cdot CX_2C(=O)CHX'_2 + OH$	0.5 x (1 - SF)	4
	$\rightarrow CX_2HC(=O)CX'_2\cdot + OH$	0.5 x (1 - SF)	4
	$+ M \rightarrow X_2CH\text{-syn-}C[OO]CHX'_2 + M$	0.5 x SF	5
	$+ M \rightarrow X_2CHC[OO]\text{-syn-}CHX'_2 + M$	0.5 x SF	5
$X_2CHC[OO]Y$ {ex}	$\rightarrow \cdot CX_2C(=O)Y + OH$	1-SF	4
	$+ M \rightarrow X_2CH\text{-syn-}C[OO]Y + M$	0.5 x SF	5
	$+ M \rightarrow X_2CHC[OO]\text{-syn-}Y + M$	0.5 x SF	5
$YC[OO]Y'$ {ex}	$+ M \rightarrow Y\text{-syn-}C[OO]Y' + M$	0.5	5, 6
	$+ M \rightarrow YC[OO]\text{-syn-}Y' + M$	0.5	5, 6
$X_2CH\text{-syn-}C[OO]R$	$\rightarrow \cdot CX_2C(=O)R + OH$	100%	

[a] The notation {ex} indicates excitation by formation in the O_3 + 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 A1.8.2

[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_3, from Table A-31.
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_3, 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 A-34. Summary of predicted, measured, and recommended OH yields in the reactions of O_3 with alkenes.

Compound	OH yields						
	Measured by [a]		IUPAC Review	MechGen Predicted [b]			
	Trapping	LIF		A	B (used)	C	Best [c]
			1-Alkenes				
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
			Internal alkenes				
cis-2-Butene	41%		33%		51%		Same
trans-2-Butene	64%		60%		51%		Same
2-methyl propene	84%		~64%		65%		Same
2,3-dimethtyl-2-butene	90%	70%	~93%		113%		Same
			Cycloalkenes				
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
			Conjugated dialkenes				
1,3-butadiene	8%				8%		Same
isoprene	27%	50%		28%	27%		B=C
			Terpenes				
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 (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 (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".

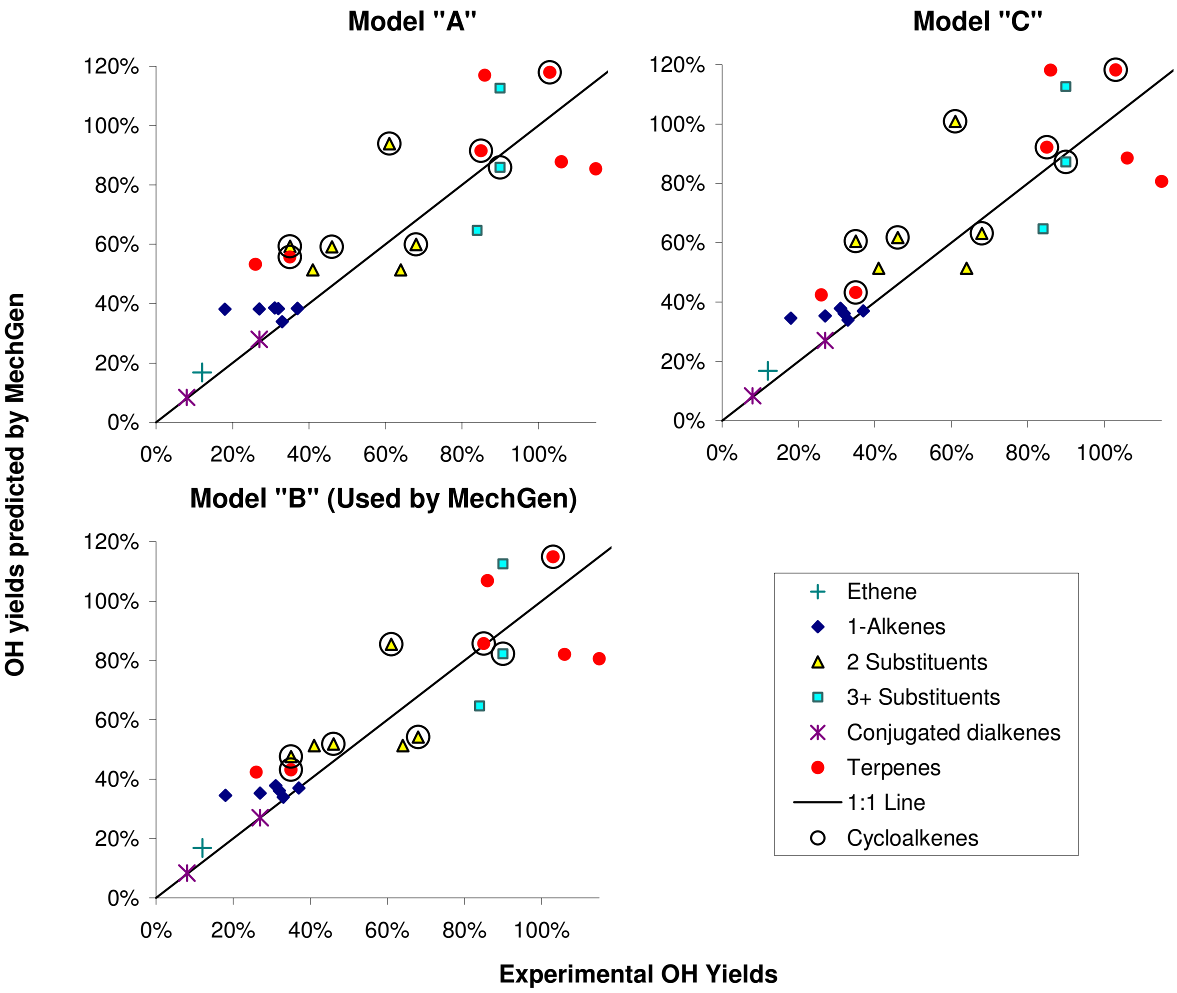


Figure A-23. Plots of predicted vs. experimental yields for OH from reactions of O_3 with alkenes in the radical trap experiments summarized by Calvert et al. (2000). The model calculations represented the conditions of the radical trap experiments (no NO_x present; peroxy radicals react mostly with 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.

long as an alkyl ($-CH_x$) group is in the α position. Reactions of intermediates with other types of substituents in the α position are discussed in the following section.

A1.8.2. Reactions with Non-Alkyl α 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:

$$\text{HOC[OO]X } \{\textit{syn} \text{ or excited}\} \rightarrow \text{XC(=O)OOH } \{\text{ex}\} \rightarrow \text{XC(=O)O}\cdot + \text{OH} \rightarrow \text{X}\cdot + \text{CO}_2 + \text{OH}$$

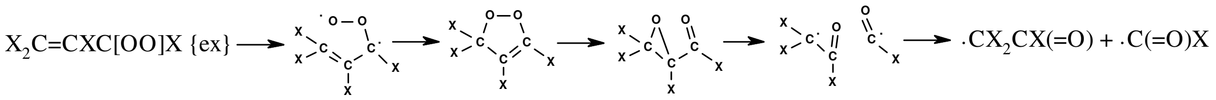
where X is H or any group. These are assumed to dominate over other types of Criegee reactions that might occur, including stabilization or other types of decomposition reactions. Although the reaction of the stabilized intermediate requires that the -OH substituent be in the *syn* position, stabilized 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 α position, and also has an allylic hydrogen in the γ 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.,

$$X_2CHCX{=}CXC[OO]X\ \{ex\} \rightarrow X_2C{=}CXCX{=}C(X)OOH\ \{ex\} \rightarrow X_2C[\cdot]CX{=}CXC({=}O)X + OH$$

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 α-OH substituents, as discussed above.

On the other hand, if there is no allylic hydrogen in the γ 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, but Vereecken et al. (2017) apparently did not consider subsequent reactions of this excited species. 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 Criegees 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.

$$X_1C[OO]C({=}O)X_2\ \{ex\} \leftrightarrow [\ X_1{*}COOC({=}O)(X)O{*}\ ] \leftrightarrow X_1C[OO]C({=}O)X_2\ \{ex\}$$

Here the X's can be either H or any group, and the reaction only needs to be considered if $X_1 \neq X_2$. Although this needs to be investigated, we assume that this type of O-shift reaction is faster than any competing possible reactions for excited carbonyl-substituted Criegees. However, 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.

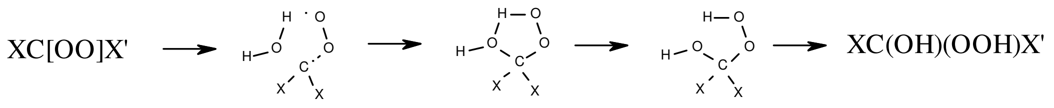
At the present time, we do not consider reactions of CIs with other types of α substituents besides alkyl, C=C double bond, -OH, or carbonyl groups, and assume that such substituents are not reactive, and thus only react as discussed below in Section A1.8.4. This is primarily applicable for halogen groups, where this is a reasonable assumption. Note that reactions of O_3 with alkenes with other types of α substituents are not currently supported by MechGen.

A1.8.3. Mechanisms for Excited Intermediates formed in Other Reactions

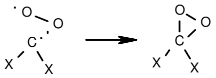
The stabilization fractions discussed above are applicable to excited intermediates formed in O_3 + alkene reactions, but MechGen also predicts formation of excited CIs from reactions of O_3 with alkynes and reactions of O_2 with carbenes. The intermediates formed in the reactions of O_3 probably have 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 Criegees 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).

A1.8.4. Reactions of Stabilized Intermediates

Stabilized CIs with groups with alkyl substituents with α hydrogens in the *syn* position, -OH substituents, or allylic hydrogens in the γ 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_2O" option, which tells MechGen to generate reactions with H_2O 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_2O to form an α-hydroxy hydroperoxide, e.g.,



If the H_2O option is not set, then the stabilized intermediates are assumed to undergo a 1,3-ring closure forming a dioxirane, e.g.



These α-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_2O 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.

A1.9. 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 A-52 through Table A-54 in Section A5.3 give the assigned rate constants and (where available) temperature dependent parameters for the reactions of compounds with OH, O_3, NO_3, and O^3P, 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^3P reactions, which were not covered by McGillen et al. (2020, 2021). In addition, Table A-56 gives assigned rate constants and temperature dependent parameters for reactions of various radicals or intermediates, and Table A-57 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 A5.

A2. Estimates of Thermochemistry and Physical Properties

A2.1. 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 A-58 through Table A-60, 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 A5. Table A-58 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 A-59 and Table A-60, with the values in Table A-59 being judged to have moderate to high uncertainty, and the values in Table A-60 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 A-61 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 A-58 and the assigned heats of formation in Table A-62 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 A-59 are based primarily on assumptions concerning bond dissociation energies, and those in Table A-60 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 A-61 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 A-60, and probably Table A-59 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.

A2.2. 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:

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

The inputs related to the environment include the temperature (T) and the organic aerosol concentration (C_{OA}), and the examples in the following section use T = 298 K and C_{OA} = 50 $\mu g/m^3$. The inputs determined by the compound are the molecular weight (Mwt) and the vapor pressure (P_{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 (Compernolle 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.

A3.Examples of Generated Mechanisms

A3.1. Methods

The mechanisms of representative compounds were generated using MecGen's "full mechanism generation" procedure (Carter, in prep.) 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 parameter, which determines which of the pathways for a given reaction are treated as non-negligible, was set at the default value of 0.5% except as noted otherwise. Further discussion of mechanism generation procedures is given in the MechGen software documentation (Carter, in prep.).

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_3, NO, NO_2, NO_3, 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_x 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_x have approximately the same relative effectiveness in reducing ozone. The characteristics of these conditions are summarized in Table A-35. Note that product distributions would be somewhat different for high NO_x, MIR (maximum incremental reactivity)-like conditions where reactions of peroxy radicals with NO_x dominate, and quite different from nighttime conditions where NO is near zero and reactions involving NO_3 radicals are much more important. However, further discussion of how product yields vary with environmental conditions is beyond the scope of the present work.

Although kinetic model simulations can be employed to derive product yields given a generated mechanism and set of environmental conditions, this is not necessary if (1) the steady state approximation is applied to all reactive intermediates and (2) there are no cases where reactions of a given reactive intermediate result in formation, in one step or several, of the same intermediate. The first requirement is reasonably well satisfied in one-generation mechanisms if subsequent reactions of non-radical products are not generated, since the radicals and other reactive intermediates are essentially in a steady state on the time scale of atmospheric transformations. The second requirement is more restrictive, but is also satisfied in most cases with mechanisms generated by the current system, provided that the formation of rapidly reacting alkyl peroxy nitrates (see Section 2.3.1 of the main text) is not included. The two exceptions applicable to the example mechanisms concern those where phenoxy radicals or hydroperoxy-substituted peroxy radicals are predicted to be formed.

Table A-35. 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 cm^3 $molec^{-1}$ s^{-1}	 Other units	Note
OH	6.90 x 10^6	0.28 ppt	
O_3	1.96 x 10^{12}	80 ppb	
NO	9.79 x 10^9	0.40 ppb	89% of RO_2 reactions
NO_2	7.25 x 10^{10}	3.0 ppb	
NO_3	1.58 x 10^7	0.65 ppt	0.04% or RO_2 reactions
HO_2	6.12 x 10^8	0.025 ppt	9% of RO_2 reactions
O^3P	2.61 x 10^4		
Total RO_2's	4.91 x 10^8	20 ppt	Negligible RO_2 reaction
Total RCO_3's	8.60 x 10^7	3.5 ppt	1% RO_2 reaction
H_2O	4.20 x 10^{17}	50% RH	
Temperature	298 K		
Light	Direct overhead sun [a]		$J(NO_2) = 0.723\ min^{-1}$
Atmospheric organic aerosol	$C_{OA} = 50\ \mu g/m^3$		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 A-5.

The interconversions of phenoxy and phenyl peroxy radicals are attributed to the formation of phenoxy radicals when phenyl peroxy radicals react with NO and the regeneration of phenyl peroxy phenoxy radicals when phenoxy radicals react with O_3 (see Section 6.1 of the main text). However, these reactions do not amount to a net sink for either type of radical, and only affect relative yields of phenols and nitrophenols. Peroxy radicals with hydroperoxy groups are predicted to rapidly scramble the location of the hydroperoxy hydrogen (see Section A1.5.5), resulting in the formation of different isomers from unsymmetrical radicals when they are ultimately consumed by other reactions. Although such reactions are expected to occur at least to some extent in mechanisms of many VOCs, they are expected to be usually fairly minor and primarily affect predictions of distributions of isomers of low-yield hydroperoxy-containing products. To simplify the analysis of product yields, the phenoxy + O_3 and the peroxy/hydroperoxy scrambling reactions were disabled when generating the example mechanisms for this work.

The algorithm used for deriving product yields from a generated mechanism for a given set of conditions that is incorporated into MechGen is as follows:

1. The species concentrations defined by the set of environmental conditions are used to convert all bimolecular reactions involving those species to pseudo-unimolecular reactions. In addition, rate constants for photolysis reactions are calculated using the actinic fluxes defined by the set of conditions. All unimolecular or pseudo-unimolecular reactions of the same species are combined.
2. The "yield" of the initially reacting compound is set to unity. The yields of products in this initial reaction are their yields in the combined pseudo-unimolecular reaction of this initially reacting compound. This is used to initialize the list of intermediate or product species and their yields. The list of stable products is initialized as an empty list.
3. The following procedure is carried out on the list of intermediate or product species until it is empty.

4. Each entry that is a non-radical product (i.e., has no reactions in the generated mechanism) is removed from the intermediate species list and either added to the stable product list, along with its yield, or its yield is added to the yield of the product if it is already on this list.
5. Each entry that has reactions is also removed from the list, and its unimolecular or pseudo-unimolecular reaction derived in Step 1 is examined to determine yields of products that it forms. The yields of these products, multiplied by the yields of the reactant forming it taken from the intermediate list, is then either added to the list of products and intermediates, or its cumulative yield is added to the yield of the product or intermediated if it is already on the list.
6. The process is completed once the list of intermediates and products is empty. Note that this will not occur if there are intermediates that form themselves after one or more steps, and the process is aborted if this is found to be the case.
7. The stable products formed, and their yields for the given set of environmental conditions, are then given in the list of stable products. Note that this product list does not include any of the intermediates that have reactions in the one-generation mechanisms.

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 A2.2. Note that this depends on the level of atmospheric aerosol present, which is set at 50 $\mu g/m^3$ 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.

A3.2. Example Results

Table A-36 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 A-35. 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 A-36. Representative compounds whose mechanisms were generated for illustrative purposes and a summary of selected results.

Compound	No.	No. Prods [a]		Fraction Reacted With [b]				Groups on Products [c]								Cond.
	Rxns.	All	95%	OH	O3	NO3	HV	-OH	-CHO	-CO-	-O-	-OOH	-ONO2	PANs	Mult.	[d]
Propane	39	9	4	100%				0.000	0.265	0.653	-	0.039	0.039	-	-	1e-7
n-Butane	50	12	6	100%				0.092	0.412	0.454	-	0.064	0.074	-	-	6e-6
n-Octane	253	59	28	100%				0.402	0.025	0.579	-	0.418	0.285	-	-	1e-3
n-Dodecane	733	108	59	100%				0.389	0.011	0.509	-	0.378	0.359	-	-	0.04
n-C16	1229	140	85	100%				0.383	0.008	0.496	-	0.369	0.366	-	-	0.15
Isobutane	46	11	5	100%				-	0.079	0.599	-	0.055	0.070	-	-	3e-7
2-Methyl Heptane	770	142	66	100%				0.476	0.115	0.453	-	0.393	0.303	-	2e-3	0.02
2-Methyl Undecane	1956	229	139	100%				0.479	0.044	0.441	-	0.377	0.380	-	3e-5	0.12
2-Methyl Pentadecane	3589	273	202	100%				0.439	0.032	0.436	-	0.366	0.380	-	2e-5	0.21
1-Butene	165	39	9	94%	6%			0.117	0.644	0.015	-	0.061	0.047	-	0.015	7e-5
1-Octene	1361	143	61	94%	6%			0.633	0.419	0.195	-	0.168	0.194	-	0.174	0.05
1-Dodecene	2118	226	124	96%	4%			0.627	0.351	0.216	-	0.192	0.263	-	0.120	0.21
1-hexadecene	2882	291	190	96%	4%			0.633	0.322	0.232	-	0.204	0.275	-	0.114	0.33
trans-2-Butene	63	13	8	61%	39%			0.077	0.794	0.001	-	0.041	0.030	-	0.050	2e-5
trans-2-octene	737	101	23	66%	34%			0.160	0.704	0.022	-	0.069	0.107	-	0.076	2e-3
Trans-2-Dodecene	958	137	50	66%	34%			0.183	0.638	0.038	-	0.078	0.144	-	0.107	0.04
Trans-5-Pentadecene	1184	170	64	67%	33%			0.186	0.617	0.048	-	0.084	0.152	-	0.118	0.11
n-Octane	253	59	28	100%				0.402	0.025	0.579	-	0.418	0.285	-	-	1e-3
2-Methyl Heptane	770	142	66	100%				0.476	0.115	0.453	-	0.393	0.303	-	2e-3	0.02
2,2-Dimethyl Hexane	543	84	32	100%				0.219	0.203	0.400	-	0.329	0.261	-	-	1e-3
2,3,4-Trimethyl Pentane	573	72	16	100%				0.045	0.124	0.507	-	0.124	0.254	-	8e-5	2e-3
Ethylcyclohexane	2910	190	73	100%				0.182	0.335	0.475	6e-3	0.340	0.354	0.003	0.021	0.04
1-Octene	1361	143	61	94%	6%			0.633	0.419	0.195	-	0.168	0.194	-	0.174	0.05
trans-2-octene	737	101	23	66%	34%			0.160	0.704	0.022	-	0.069	0.107	-	0.076	2e-3
2,3-dimethyl-2-hexene	196	35	13	34%	47%	19%		0.077	0.055	0.681	-	0.060	0.141	0.080	0.029	8e-4
1,2-Dimethyl Cyclohexene	1486	85	16	70%	27%	3%		0.162	0.113	1.397	1e-3	0.110	0.178	0.064	0.088	5e-3
m-Xylene	106	28	14	100%				0.243	0.800	0.651	0.132	0.063	0.118	-	0.134	4e-3
p-Xylene	66	19	12	100%				0.258	0.953	0.418	0.242	0.049	0.097	-	0.243	3e-3
2,4-dimethyl phenol	92	27	14	78%		30%		0.931	0.155	0.755	0.085	0.006	0.011	-	0.829	0.02
3,6-dimethyl-o-catechol	56	17	8	54%		63%		1.480	0.024	0.958	0.008	0.002	0.004	-	1.347	0.22
Octanal	872	102	35	85%			15%	0.194	0.266	0.130	0.057	0.203	0.123	0.411	0.046	1e-2
2-Octanone	416	87	38	100%				0.284	0.123	1.317	-	0.394	0.264	0.027	0.364	7e-3
n-Hexyl Acetate	660	138	59	100%				0.197	0.293	0.904	0.653	0.314	0.217	0.051	0.176	9e-3

Table A-36 (continued)

Compound	No.	No. Prods [a]		Fraction Reacted With [b]				Groups on Products [c]								Cond.
	Rxns.	All	95%	OH	O3	NO3	HV	-OH	-CHO	-CO-	-O-	-OOH	-ONO2	PANs	Mult.	[d]
n-Butyl Butyrate	438	98	30	100%				0.009	0.420	0.783	0.682	0.116	0.224	0.037	0.178	1e-3
2-[2-(2-Ethoxyethoxy) ethoxy] Ethanol	649	117	57	100%				0.549	0.739	0.046	2.179	0.521	0.139	-	0.906	0.20
a-Pinene	1935	130	49	68%	25%	7%		0.310	0.537	0.714	0.070	0.135	0.245	0.023	0.186	0.03
b-Pinene	5553	181	78	93%	5%	3%		0.600	0.315	0.468	0.119	0.222	0.340	0.009	0.160	0.07
d-Limonene	7705	172	174	75%	20%	5%		0.224	0.410	0.649	0.022	0.147	0.185	0.005	0.135	0.03

[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 A2.2). Note that this does not include products formed in second and additional generation reactions.

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A5. Large Tables

A5.1. Parameters for Estimating Bimolecular rate constants

Table A-37. Base rate constant parameters for estimating rate constants for reactions of organics with OH, NO$_3$, and Cl.

Parameter	k(298) [a]			Notes [b]
	OH	NO$_3$	Cl	
kH^{base} for H-Atom abstractions				
-CH$_3$	1.30e-13	1.07e-19	2.89e-11	1
-CH$_2$-	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$_2$-OH		1.83e-15		2
-CH()-OH		2.13e-15		2
CH$_3$-O-		1.02e-16		2
-CH$_2$-O-		1.55e-15		2
-CH()-O-		2.03e-15		2
-CH$_3$-CH$_x$-O- (x=0-2)		1.01e-16		2
-CH$_2$-CH$_x$-O- (x=0-2)		1.09e-15		2
-CH()-CH$_x$-O- (x=0-2)		2.03e-15		2
kA^{base} for Additions to double or triple bonds				
-CH$_2$=CH-	2.61e-11	1.16e-14	1.07e-10	3, 4
-CH=CH$_2$	4.50e-12	0	1.07e-10	3, 4
-CH=CH-	3.10e-11	1.78e-13	1.37e-10	3, 4
-CH$_2$=C()-	5.69e-11	3.31e-13	1.22e-10	3, 4
-C()=CH$_2$	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$_2$=CH-CH$_x$=	3.27e-11	5.30e-14	1.95e-10	1, 4, 5
CH(CH$_x$=)=CH$_2$	1.72e-12	0	2.16e-11	1, 4, 5
-CH=CH-CH$_x$=	6.90e-11	2.26e-12	1.95e-10	1, 4, 5
CH(CH$_x$=)=CH-	3.63e-12	0	2.16e-11	1, 4, 5
CH2=C()-CH$_x$=	5.92e-11	5.94e-13	1.60e-10	1, 4, 5
-C(CH$_x$=)=CH$_2$	3.11e-12	0	1.78e-11	1, 4, 5
-CH=C-CH$_x$=	9.66e-11	8.59e-12	1.60e-10	1, 4, 5
-C(CH$_x$=)=CH	5.08e-12	0	1.78e-11	1, 4, 5
-C()=CH-CH$_x$=	9.66e-11	8.59e-12	1.95e-10	1, 4, 5
CH(CH$_x$=)=C	5.08e-12	0	2.16e-11	1, 4, 5
-C()=C-CH$_x$=	1.16e-10	2.08e-11	1.60e-10	1, 4, 5
-C(CH$_x$=)=C)	6.12e-12	0	1.78e-11	1, 4, 5
CH(CH$_x$=)=CH-CH$_x$= (x=0-1)	6.90e-11	2.26e-12	1.95e-10	2, 5, 6

Table A-37 (continued)

Parameter		k(298) [a]			Notes [b]
		OH	NO_3	Cl	
$CH(CH_x=)=C-CH_x=$	(x=0-1)	9.66e-11	8.59e-12	1.60e-10	2, 5, 6
$-C(CH_x=)=CH-CH_x=$	(x=0-1)	9.66e-11	8.59e-12	1.95e-10	2, 5, 6
$-C(CH_x=)=C-CH_x=$	(x=0-1)	1.16e-10	2.08e-11	1.60e-10	2, 5, 6
$C(=CH_2)=CH-$		3.00e-11	6.96e-14	4.38e-10	2
$C(=CH_2)=C()-$		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
		$kAro^{base}$ 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''^{base} for Additions to amino groups			
$-NH_2$		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_2-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^3 $molec^{-1}$ s^{-1}. 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 A-38, Table A-39, or Table A-40.
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_1sub is the factor for substituents on the first group and F_2sub 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 A-41. Note that factors are used only the aromatic ring with the reacting group.

Table A-38. Substituent correction factors for abstractions or additions by OH radicals.

Neighboring	Abstraction FH^{nbr}(nbr,-CHx or -CHO) [a]				Addition FA$_x^{nbr}$(nbr) [b]	
Group (nbr)	-CH$_3$	-CH$_2$-	-CH()-	-CHO	x=1	x=2
-CH$_3$	1	1	1	1	1	1
-CH$_2$-	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$_2$	0.09	0.09	0.09		0.039	0.039
-ONO$_2$	0.14	0.14	0.14		0.039	0.039
-Cl	0.27	0.27	0.27		0.16	0.26
-NH$_2$	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$_2$					0.47	0.47
-CH$_2$-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$_2$-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$_2$-NO$_2$	0.001	0.001	0.001	1.46	0.40	0.40
-CH()-NO$_2$	0.32	0.32	0.32	2.02	0.40	0.40
-C()()-NO$_2$	0.32	0.32	0.32	1.84	0.40	0.40
-CH$_2$-ONO$_2$	0.36	0.36	0.36	1.46	0.54	0.54
-CH()-ONO$_2$	0.36	0.36	0.36	2.02	0.54	0.54
-C()()-ONO$_2$	0.36	0.36	0.36	1.84	0.54	0.54
-CH$_2$-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 A-39. Substituent correction factors for abstractions or additions by NO$_3$ radicals.

Neighboring Group (nbr)	Abstraction FH^{nbr}(nbr,-CHx or -CHO) [a]				Addition FA$_x^{nbr}$(nbr) [a]	
	-CH$_3$	-CH$_2$-	-CH()-	-CHO	x=1	x=2
-CH$_3$	1	1	1	1	1	1
-CH$_2$-	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$_2$	0.22	0.22	0.22			
-ONO$_2$	0.33	0.33	0.33			
-Cl	0.56	0.56	0.56		0.03	0.03
-NH$_2$	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$_2$					0.0005	0.0005
-CH$_2$-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$_2$-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$_2$-NO$_2$	0.006	0.006	0.006	6.23		
-CH()-NO$_2$	0.64	0.64	0.64	9.54		
-C()()-NO$_2$	0.64	0.64	0.64	9.03		
-CH$_2$-ONO$_2$	0.70	0.70	0.70	6.23		
-CH()-ONO$_2$	0.70	0.70	0.70	9.54		
-C()()-ONO$_2$	0.70	0.70	0.70	9.03		
-CH$_2$-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.

Table A-40. Substituent correction factors for abstractions or additions by Cl atoms.

Neighboring Group	Abstraction FH^{nbr}(nbr,-CHx or -CHO) [a]				Addition FA_x^{nbr}(nbr) [a]	
(nbr)	$-CH_3$	$-CH_2-$	-CH()-	-CHO	x=1	x=2
$-CH_3$	1	1	1	1	1	1
$-CH_2-$	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
$-NO_2$	0.001	0.001	0.001		1	1
$-ONO_2$	0.008	0.067	0.067		1	1
-Cl	0.017	0.081	0.081		0.59	0.59
$-NH_2$	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		
$-CO-O-ONO_2$					0.86	0.86
$-CH_2-OH$	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		
$-CH_2-CO-$	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		
$-CH_2-NO_2$	0.004	0.004	0.004	1	1	1
$-CH()-NO_2$	0.004	0.004	0.004	1	1	1
$-C()()-NO_2$	0.004	0.004	0.004	1	1	1
$-CH_2-ONO_2$	0.001	0.001	0.001	1	1	1
$-CH()-ONO_2$	0.006	0.006	0.006	1	1	1
$-C()()-ONO_2$	0.006	0.006	0.006	1	1	1
$-CH_2-Cl$	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 A-41. Substituent correction factors for additions of OH, NO_3 and Cl to aromatic rings.

Rxn	Substituent Group(s)	Aromatic Ring Substituent Correction Factors FA^{ortho}	FA^{meta}	FA^{para}	FA^{ipso}
OH	$-CH_3$	9.59	1	1	1
	$-CH_2-$	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
	$-NO_2$	0.076	0.076	0.076	0.076
	$-ONO_2$	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
	$-CO-O-ONO_2$	0.79	0.79	0.79	0.79
NO3	$-CH_3$	5.40	1	5.82	1
	$-CH_2-$	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	$-CH_3$	2.80	2.80	2.80	1
	$-CH_2-$	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
	$-NO_2$	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 A-42. Correction factors for H-atom abstractions or for additions to groups or bonds in a ring.

Type of Reaction or Double Bond	Size of Smallest Ring with the Group or with all Groups in the Bond						
System	3	4	5	6	7	8	9+
H abstraction by OH or NO_3							
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
H abstraction by Cl							
Any groups in ring	0.001	0.84	0.89	1	1	1	1
O_3 addition to double bond systems (no ring corrections for O^3P)							
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 A-43. Base rate constants for additions of O_3 or O^3P to bonds or to amine groups. Branching ratios for O_3 reactions are also shown.

Bond or Group	k(298) [a]		O_3 Branching [b]
	O_3	O^3P	
	Bonds for kA^{base}		
-CH$_2$=CH-	9.67e-18	4.44e-12	Both paths equal
-CH$_2$=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$_2$=CH-CH=CH-	3.15e-17	5.45e-11	All 4 paths equal
CH$_2$=CH-CH=C-	1.94e-16	7.92e-11	
CH$_2$=CH-C()=CH-	6.34e-17	8.70e-11	
CH$_2$=CH-C()=C()-	2.94e-16	1.21e-10	
CH$_2$=C()-CH=CH$_2$	1.28e-17	3.50e-11	
CH$_2$=C()-CH=CH-	8.00e-17	8.64e-11	
CH$_2$=C()-CH=C()-	2.94e-16	1.34e-10	
CH$_2$=C()-C()=CH$_2$	2.56e-17	6.71e-11	
CH$_2$=C()-C=CH-	9.61e-17	1.34e-10	
CH$_2$=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$_2$=C=CH-	0	6.55e-12	No reactions generated
CH$_2$=C=C()-	0	3.00e-11	

Table A-43 (continued)

Bond or Group	k(298) [a]		O_3 Branching [b]
	O_3	O^3P	
-CH=C=CH-	0	1.60e-11	
-CH=C=C()-	0	8.71e-11	
-C()=C=C()-	0	9.82e-12	
CH_2=CH-OH	2.76e-16		90% -OH on carbonyl (10% on the Criegee)
CH_2=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_2=CH-O-	2.76e-16	1.98e-11	90% -O- on carbonyl
CH_2=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_2=CH-O-CHO	3.82e-18		90% -O-CHO on carbonyl
CH_2=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_2=CH-O-CO-	3.82e-18	1.38e-12	90% -O-CO- on carbonyl
CH_2=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_2=CH-CHO	2.80e-19	4.00e-13	90% -CHO on carbonyl
CH_2=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_2=CH-CO-	5.40e-18	1.15e-12	90% -CO- on carbonyl
CH_2=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_2=CH-CO-OH	7.05e-19	5.71e-13	90% -CO-OH on carbonyl
CH_2=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_2=CH-CO-O-	1.13e-18	4.08e-13	90% -CO-O- on carbonyl
CH_2=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 A-43 (continued)

Bond or Group	k(298) [a]		O$_3$ Branching [b]
	O$_3$	O^{3}P	
-C()=CH-CO-O-	2.51e-17	2.44e-11	
-C()=C()-CO-O-	6.99e-17	1.20e-11	
CH$_2$=CH-CO-CO$_x$	5.40e-18		90% -CO-COx on carbonyl
CH$_2$=C()-CO-CO$_x$	1.19e-17		(-CO$_x$ is -CO- or -CHO)
-CH=CH-CO-CO$_x$	4.18e-17		
-CH=C()-CO-CO$_x$	4.31e-17		
-C()=CH-CO-CO$_x$	8.29e-18		
-C()=C()-CO-CO$_x$	4.38e-17		
COx-CHy=CHy-COx	3.27e-18	3.99e-13	Both paths equal (y=0 or 1)
Groups for kA''^{base}			
CH#C-	1.68e-20	8.97e-13	Both paths equal
-C#C-	1.68e-20	8.60e-12	
-NH2	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^3 molec^{-1} s^{-1}. See Carter (2021) for estimated temperature dependences, which are uncertain and highly approximate.

[b] See text in main manuscript for a discussion of O^{3}P branching ratios.

Table A-44. Correction factors for additions of O_3 to double bond systems.

Group or Structure	fA'^{nbr}(subst)		
	Isolated	Conjugated	α-Subst [a]
	fA'^{nbr}(subst)		
-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	
-NO2	0.007	0.082	
-ONO2	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$_x$-OH [c]	1.25	1.12	
-CH$_x$-O-	0.34	0.58	
-CH$_x$-CHO	0.34	0.59	
-CH$_x$-CO-	0.26	0.51	
-CH$_x$-O-CO-	0.34	0.58	
-CH$_x$-NO_2	0.042	0.21	
-CH$_x$-ONO_2	0.042	0.21	
-CH$_x$-F	0.099	0.31	
-CH$_x$-Cl	0.20	0.44	
	FA'^{struct}(site) for furan structures [d]		
1 subst. on furan		0.017	
2 subst. on furan		0.034	
3 subst. on furan		0.050	
4 subst. on furan		0.066	

[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$_x$" is either -CH_3, -CH_2-, -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 A-42).

A5.2. Radical Rate Constants and Branching Ratios

Table A-45. Experimental and estimated rate constants for the bimolecular reactions of peroxy radicals under atmospheric conditions.

Radical	Rate Constant (cm^3 $molec^{-1}$ s^{-1})			
	k(298)	A	Ea/T	Note [a]
	<u>RO_2 + NO</u>			
<u>Used for MechGen Estimates</u>	9.13e-12	2.55e-12	-380	1
$CH_3OO\cdot$	7.7e-12	2.3e-12	-360	2
$CH_3CH_2OO\cdot$	9.1e-12	2.6e-12	-380	2
$CH_3CH_2CH_2OO\cdot$	9.4e-12	2.9e-12	-350	2
$CH_3C(CH_3)_2C(CH_3)_2CH_2OO\cdot$	1.8e-12			3
$CH_3CH(OO\cdot)CH_3$	9.0e-12	2.7e-12	-360	2
$CH_3C(CH_3)(CH_3)CH_2OO\cdot$	4.7e-12			3
CH2*-CH2CH2CH(OO·)CH2*	1.1e-11			3
$CH_3CH_2CH_2CH(OO\cdot)CH_3$	8.0e-12			3
CH2*(CH2)2CH(OO·)CH2CH2*	6.7e-12			3
$CH_3C(OO\cdot)(CH_3)CH_3$	5.4e-12			3
CH_2=CH-$CH_2OO\cdot$	1.1e-11			3
Phenyl-$CH_2OO\cdot$	2.5e-12			3
.$OOCH_2OH$	5.6e-12			2
$CH_3C(CH_3)(CH_2OO\cdot)OH$	4.9e-12			3
CH_2=$C(CH_3)CH(OO\cdot)CH_2OH$	9.0e-12			3
.$OOCH_2CH_2OH$	5.6e-12			3
$CH_3OCH_2OO\cdot$	9.1e-12			3
CH3C(O)CH2OO·	1.2e-11			3
$CH_3OCH(OCH_3)OCH_2OO\cdot$	9.0e-12			3
$CH_3C(O)CH_2OO\cdot$	8.0e-12			2
	<u>RCO_3 + NO</u>			
<u>Used for MechGen Estimates</u>	2.10e-11	6.70e-12	-340	4
$CH_3C(O)OO\cdot$	2.0e-11	7.5e-12	-290	2
$CH_3CH_2C(O)OO\cdot$	2.1e-11	6.7e-12	-340	2
	<u>RO_2 + NO_2</u>			
<u>Used for MechGen Estimates</u>	8.8e-12			5
$CH_3OO\cdot$	4.0e-12	Pressure dependent		2
high pressure->	1.8e-11			2
$CH_3CH_2OO\cdot$	5.1e-12	Pressure dependent		2
high pressure ->	8.8e-11			2
$CH_3C(O)CH_2OO\cdot$	6.4e-12			2
	<u>RCO_3 + NO_2</u>			
<u>Used for MechGen Estimates</u>	7.7e-12			6
$CH_3C(O)OO\cdot$	8.9e-12	Pressure dependent		2
high pressure ->	1.8e-11			2
$CH_3CH_2C(O)OO\cdot$	7.4e-12	Pressure dependent		7
high pressure ->	7.7e-12			7
	<u>RO_2 + NO_3</u>			

Table A-45 (continue)

Radical	Rate Constant (cm^3 $molec^{-1}$ s^{-1})			
	k(298)	A	Ea/T	Note [a]
Used for MechGen Estimates	2.3e-12			8
$CH_3OO\cdot$	1.2e-12			2
$CH_3CH_2OO\cdot$	2.3e-12			2
	$RCO_3 + NO_3$			
Used for MechGen Estimates	4.00e-12			9
$CH_3C(O)OO\cdot$	4.00e-12			2
	$RO_2 + HO_2$			
Used for MechGen Estimates				
Non-OH $RO_2 + HO_2$	10^{-12} min [20.3, 2.48 + (2.48 nC)]			See text
OH-$RO_2 + HO_2$	10^{-12} min [21.1, 9.37 + (1.68 nC)]			See text
Alkane $RO_2 + HO_2$				
$CH_3OO\cdot$	5.2e-12	3.80e-13	-780	2
$CH_3CH_2OO\cdot$	6.9e-12	6.40e-13	-710	2
$CH_3C(CH_3)(CH_3)CH_2OO\cdot$	1.5e-11			10
$*CH_2(CH_2)_2CH(OO\cdot)CH_2CH_2*$	1.7e-11			10
$*CH_2(CH_2)_2CH(OO\cdot)CH_2*$	1.6e-11			10
$CH_3(CH_2)_8CH_2OO\cdot$	2.0e-11			10
$CH_3(CH_2)_{12}CH_2OO\cdot$	2.1e-11			10
Unsaturated $RO_2 + HO_2$				
$CH_2=CHCH_2OO\cdot$	1.0e-11			10
Phenyl-$CH_2OO\cdot$	1.0e-11			10
OH-$RO_2 + HO_2$				
$.OOCH_2OH$	1.2e-11	5.60e-15	-2300	2
$.OOCH_2CH_2OH$	1.3e-11			2
$CH_3C(CH_3)(CH_2OO\cdot)OH$	1.4e-11			10
$CH_3CH(OO\cdot)CH(CH_3)OH$	1.5e-11			10
$CH_3C(OO\cdot)(CH_3)C(CH_3)(CH_3)OH$	2.0e-11			10
HO–(cyc-C6)–O2	2.2e-11			10
HO–(a-pinene)–O2	2.1e-11			10
CO-$RO_2 + HO_2$				
$CH_3C(O)CH_2OO\cdot$	9.0e-12			2
	$RCO_3 + HO_2$			
Used for MechGen Estimates	2.2e-11	3.14e-12	-580	9
$CH_3C(O)OO\cdot$	2.2e-11	3.14e-12	-580	2
	Non-OH-substituted $RO_2 + RO_2$ [b]			
Used for MechGen Estimates				
Primary RO_2 + Generic RO_2	2.9e-14			11
Secondary RO_2 + Generic RO_2	1.6e-14			11
Tertiary RO_2 + Generic RO_2	3.7e-16			11
Primary RO_2 + Primary RO_2				
Geometric mean of data below	4.3e-13			
$CH_3OO\cdot$ + (self)	4.6e-13			2
$CH_3CH_2OO\cdot$ + MeO_2	2.0e-13			12
$CH_3CH_2OO\cdot$ + (self)	7.0e-14			12
$CH_3CH_2CH_2OO\cdot$ + MeO_2	5.6e-13			13
$CH_3CH_2CH_2OO\cdot$ + EtO_2	9.3e-14			13
$CH_3CH_2CH_2OO\cdot$ + (self)	3.0e-13			12

Table A-45 (continue)

Radical	Rate Constant (cm^3 $molec^{-1}$ s^{-1})			
	k(298)	A	Ea/T	Note [a]
$CH_3CH_2CH_2CH_2OO\cdot$ + MeO_2	7.8e-13			13
$CH_3CH_2CH_2CH_2OO\cdot$ + EtO_2	1.3e-13			13
$CH_3CH_2CH_2CH_2OO\cdot$ + $nC3O_2$	5.0e-13			13
$CH_3CH_2CH_2CH_2OO\cdot$ + (self)	6.9e-13			13
$CH_3CH_2CH_2CH_2CH_2OO\cdot$ + MeO_2	1.5e-12			12
$CH_3CH_2CH_2CH_2CH_2OO\cdot$ + EtO_2	5.3e-13			12
$CH_3CH_2CH_2CH_2CH_2OO\cdot$ + (self)	3.9e-13			12
$CH_3C(CH_3)(CH_3)CH_2OO\cdot$ + MeO_2	1.5e-12			12
$CH_2{=}CH\text{-}CH_2OO\cdot$ + (self)	7.0e-13			12
$CH_3C(CH_3)(CH_3)CH_2OO\cdot$ + (self)	1.2e-12			12
Primary RO_2 + Secondary RO_2				
Geometric mean of data below	2.9e-14			
$CH_3CH(OO\cdot)CH_3$ + MeO_2	3.1e-14			13
$CH_3CH(OO\cdot)CH_3$ + EtO_2	5.1e-15			13
$CH_3CH(OO\cdot)CH_3$ + $nC3O_2$	2.0e-14			13
$CH_3CH(OO\cdot)CH_3$ + $nC4O_2$	2.7e-14			13
$CH_3CH_2CH(OO\cdot)CH_3$ + MeO_2	6.2e-14			13
$CH_3CH_2CH(OO\cdot)CH_3$ + EtO_2	1.0e-14			13
$CH_3CH_2CH(OO\cdot)CH_3$ + $nC3O_2$	4.0e-14			13
$CH_3CH_2CH(OO\cdot)CH_3$ + $nC4O_2$	5.6e-14			13
$CH_2*(CH_2)2CH(OO\cdot)CH_2CH_2*$ + MeO_2	9.0e-14			12
$CH_2*(CH_2)2CH(OO\cdot)CH_2CH_2*$ + EtO_2	4.0e-14			12
Primary RO_2 + Tertiary RO_2				
Geometric mean of data below	3.3e-15			
$CH_3C(OO\cdot)(CH_3)CH_3$ + MeO_2	3.1e-15			12
$CH_3C(OO\cdot)(CH_3)CH_3$ + EtO_2	1.3e-15			13
$CH_3C(OO\cdot)(CH_3)CH_3$ + $nC3O_2$	4.8e-15			13
$CH_3C(OO\cdot)(CH_3)CH_3$ + $nC4O_2$	6.7e-15			13
Secondary RO_2 + Secondary RO_2				
Geometric mean of data below	1.6e-14			
$CH_3CH(OO\cdot)CH_3$ + (self)	1.1e-15			12
$CH_3CH_2CH(OO\cdot)CH_3$ + $sC3O_2$	2.2e-15			13
$CH_3CH_2CH(OO\cdot)CH_3$ + (self)	2.6e-15			12
$CH_2*CH_2CH(OO\cdot)CH_2CH_2*$ + (self)	4.5e-14			12
$CH_3CH_2CH_2CH(OO\cdot)CH_3$ + (self)	3.3e-14			12
$CH_2*(CH_2)_2CH(OO\cdot)CH_2CH_2*$ + (self)	4.2e-14			12
$CH_3(CH_2)_7CH(OO\cdot)CH_3$ + (self)	8.2e-14			12
$CH_3(CH_2)_9CH(OO\cdot)CH_3$ + (self)	1.1e-13			12
Secondary RO_2 + Tertiary RO_2				
Geometric mean of data below	3.7e-16			
$CH_3C(OO\cdot)(CH_3)CH_3$ + $sC3O_2$	2.6e-16			13
$CH_3C(OO\cdot)(CH_3)CH_3$ + $sC4O_2$	5.3e-16			13
Tertiary RO_2 + Tertiary RO_2				
$CH_3C(OO\cdot)(CH_3)CH_3$ + (self)	3.0e-17			12
OH-substituted RO_2 + RO_2				
Used for MechGen Estimates				14
Primary OH-RO_2 + Generic RO_2	9.1e-14			14
Secondary OH-RO_2 + Generic RO_2	1.7e-13			14

Table A-45 (continue)

Radical	Rate Constant (cm^3 $molec^{-1}$ s^{-1})			
	k(298)	A	Ea/T	Note [a]
Tertiary OH-RO_2 + Generic RO_2	1.3e-14			
<u>Self-reactions of primary OH-substituted RO_2</u>				
Geometric mean of data below	4.3e-12			
$.OOCH_2CH_2OH$ + (self)	6.2e-12			12
$.OOCH_2OH$ + (self)	2.3e-12			12
$CH_3C(CH_3)(CH_2OO\cdot)OH$ + (self)	4.8e-12			12
$CH_3C(O)CH_2OO\cdot$ + (self)	8.0e-12			12
$.OOCH_2CH=CH\text{-}CH_2OH$ + (self)	2.8e-12			12
$CH_3C(CH_2OO\cdot)=C(CH_3)CH_2OH$ + (self)	3.9e-12			12
<u>Self-reactions of secondary OH-substituted RO_2</u>				
Geometric mean of data below	1.8e-12			
$HOCH*CH_2(CH_2)3CH(OO\cdot)*$ + (self)	1.6e-12			12
$CH_3CH(OO\cdot)CH(CH_3)OH$ + (self)	6.6e-13			12
$CH_2=CH\text{-}CH(OO\cdot)CH_2OH$ + (self)	5.7e-12			12
<u>Self-reactions of tertiary OH-substituted RO_2</u>				
Geometric mean of data below	3.5e-14			
$CH_3C(OO\cdot)(CH_3)CH_2OH$ + (self)	1.5e-14			12
$CH_3C(OO\cdot)(CH_3)C(CH_3)(CH_3)OH$ + (self)	7.5e-14			12
$CH_2=C(CH_3)C(OO\cdot)(CH_3)CH_2OH$ + (self)	6.9e-14			12
$CH_3C(OO\cdot)*\text{-}(CH_2)4CH*OH$ + (self)	2.0e-14			12
	<u>RO_2 + RCO_3</u>			
<u>Used for MechGen Estimates</u>	1.6e-11			15
$CH_3C(O)OO\cdot$ + MeO_2	1.1e-11			2
$CH_3C(O)OO\cdot$ + EtO_2	1.6e-11			2
	<u>RCO_3 + RCO_3</u>			
<u>Used for MechGen Estimates</u>	1.4e-11			16
$CH_2*(CH_2)_2CH(OO\cdot)CH_2CH_2*$ + $MeCO_3$	1.0e-11			12
$CH_3C(O)OO\cdot$ + (self)	1.6e-11			2
$CH_3CH_2C(O)OO\cdot$ + (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 $CH_3CH_2C(O)OO\cdot$ is used for estimation purposes.
5 IUPAC (2018) recommendation for the high pressure rate constant for ethyl peroxy + NO_2.
6 NASA (2011) recommendation for the high pressure rate constant for $CH_3CH_2C(O)OO.$ + NO_2.
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 A-45 (continue)

14 Estimated using the recommended rate constant for non-OH substituted RO_2's + generic RO_2 × the square root of the ratio of the geometric mean of the self-reaction of OH-substituted RO_2's of this type to the recommended rate constant for the reactions of non-OH substituted RO_2'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_3 +RCO_3 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 A-46. Summary of experimental and calculated nitrate yields for secondary peroxy radicals at standard temperature and pressure (T ~ 300 K, P ~ 1 atm.).

nC		Experimental Data [a]						Estimate Used [b]		
	Ref	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 A-47. Summary of experimental and calculated nitrate yields for secondary peroxy radicals at varying temperature and pressure.

nC	T	P		Experimental Data [b]				Estimate Used [c]		
[a]	(K)	(atm)	Ref	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%	16%	(-8%)
	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 A-47 (continued)

nC	T	P		Experimental Data [b]				Estimate Used [c]		
[a]	(K)	(atm)	Ref	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)
2 Cassanelli et al. (2007)
3 Aschmann et al. (2006)
4 Atkinson et al. (1983)
5 Orlando et al. (2000)
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 A-48. Summary of experimental and calculated nitrate yields for primary and tertiary peroxy radicals from alkanes and for peroxy radials with non-alkyl groups.

Peroxy Radical or Primary Reactant	nC	Experimental [a] T (K)	Yield	Ref	Estimates Yield	Err
		Primary unsubstituted RO_2'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_2'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%)
		β Hydroxy substituted RO_2 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 A-48 (continued)

Peroxy Radical or		Experimental [a]			Estimates	
Primary Reactant	nC	T (K)	Yield	Ref	Yield	Err
Unspecified RO_2 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_2 isomers from ethers or alcohol ethers with O mostly in the α or β 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_2 isomers from esters with O mostly in the α or β 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_2 isomers from esters with O mostly not in the α or β 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 (sum of two isomers) [c]	4		4%	15	5%	(1%)

[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 A-48 (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 α or β position (Corr = 0.73).

[d] Estimates of total unspeciated 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_3 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 A-49. 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)	$k(T)=p1 * p2^T * exp(-p3)$			Derived		
H-Group	R-Group			(sec^{-1})	p1	p2	p3	A	A	Ea
Data from Vereeckin and Nozière (2020)										
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 A-49 (continued)

Properties of Radicals					Quantum Calculation Data				Estimated in this work [a]	
Reacting Groups				k(298)	k(T)=p1 * p2^T * exp(-p3)			Derived		
H-Group	R-Group	RS	nH	(sec^{-1})	p1	p2	p3	A	A	Ea
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 A-49 (continued)

Properties of Radicals Reacting Groups		RS	nH	k(298) (sec^{-1})	Quantum Calculation Data k(T)=p1 * p2^{T} * exp(-p3)			Derived	Estimated in this work [a]	
H-Group	R-Group				p1	p2	p3	A	A	Ea
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 A-49 (continued)

Properties of Radicals					Quantum Calculation Data				Estimated in this work [a]	
Reacting Groups				k(298)	$k(T)=p1 * p2^T * \exp(-p3)$			Derived		
H-Group	R-Group	RS	nH	(sec^{-1})	p1	p2	p3	A	A	Ea
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
				Data from Møller et al (2019)						
					Structure Calculated					
CH3	CO[OO.]	6	3	4.40e-4	$HOCH_2C(CH_3)(OH)C(O)OO\cdot$				9.1e+8	17.44
CH3	CO[OO.]	6	3	3.50e-4	$HC(O)C(CH_3)(OH)C(O)OO\cdot$				9.1e+8	17.58
CH3	CO[OO.]	7	3	5.50e-3	$CH_3C(O)CH(OH)C(O)OO\cdot$				4.0e+8	15.47
CHO	CO[OO.]	6	1	0.26	$HC(O)C(CH_3)(OH)C(O)OO\cdot$				3.4e+8	12.42
CH2-Ox	CO[OO.]	6	2	0.030	$HOCH_2C(CH_3)(OH)C(O)OO\cdot$				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 A-50. 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)						
$\mathbf{CH}_3CH_2CH_2CH_2O\cdot \rightarrow .CH_2CH_2CH_2CH_2\mathbf{OH}$	2.9e+5	7.66	1	1.2e+11	7.55	3.8e+5
$\mathbf{CH}_3CH_2CH_2CH(O\cdot)CH_3 \rightarrow CH_3CH(\mathbf{OH})CH_2CH_2CH_2\cdot$	4.6e+5	7.38	2	1.2e+11	7.55	3.8e+5
$CH_3\mathbf{CH}_2CH_2CH_2CH_2O\cdot \rightarrow CH_3CH(\cdot)CH_2CH_2CH_2\mathbf{OH}$	3.3e+6	5.97	2	8.0e+10	5.97	3.5e+6
$CH_3CH(O\cdot)CH_2CH_2\mathbf{CH}(CH_3)CH_3 \rightarrow$ $CH_3CH(\mathbf{OH})CH_2CH_2C(\cdot)(CH_3)CH_3$	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)						
$\mathbf{CH}_3CH_2CH_2CH_2O\cdot \rightarrow .CH_2CH_2CH_2CH_2\mathbf{OH}$	3.2e+5	7.60	3	1.2e+11	7.55	3.8e+5
$CH_3\mathbf{CH}_2CH_2CH_2CH_2O\cdot \rightarrow CH_3CH(\cdot)CH_2CH_2CH_2\mathbf{OH}$	3.3e+6	5.98	3	8.0e+10	5.97	3.5e+6
$CH_3\mathbf{CH}(CH_3)CH_2CH_2CH_2O\cdot \rightarrow$ $CH_3C(\cdot)(CH_3)CH_2CH_2CH_2\mathbf{OH}$	1.1e+7	4.86	3	4.0e+10	4.85	1.2e+7
$\mathbf{H}COCH_2CH_2CH_2O\cdot \rightarrow CO(\cdot)CH_2CH_2CH_2\mathbf{OH}$	1.3e+7	4.76	3	4.0e+10	4.76	1.4e+7
$\mathbf{CH}_3C(O)CH_2CH_2O\cdot \rightarrow .CH_2C(O)CH_2CH_2\mathbf{OH}$	2.0e+2	11.97	3	1.2e+11	11.97	2.3e+2
$CH_3\mathbf{CH}_2C(O)CH_2CH_2O\cdot \rightarrow CH_3CH(\cdot)C(O)CH_2CH_2\mathbf{OH}$	1.5e+4	9.17	3	8.0e+10	9.16	1.7e+4
$CH_3\mathbf{CH}(CH_3)C(O)CH_2CH_2O\cdot \rightarrow$ $CH_3C(\cdot)(CH_3)C(O)CH_2CH_2\mathbf{OH}$	5.3e+4	8.01	3	4.0e+10	8.03	5.6e+4
$\mathbf{CH}_3CH_2C(O)CH_2O\cdot \rightarrow .CH_2CH_2C(O)CH_2\mathbf{OH}$	2.4e+5	7.77	3	1.2e+11	7.73	2.8e+5
$CH_3\mathbf{CH}_2CH_2C(O)CH_2O\cdot \rightarrow CH_3CH(\cdot)CH_2C(O)CH_2\mathbf{OH}$	2.5e+6	6.14	3	8.0e+10	6.16	2.6e+6
$CH_3\mathbf{CH}(CH_3)CH_2C(O)CH_2O\cdot \rightarrow$ $CH_3C(\cdot)(CH_3)CH_2C(O)CH_2\mathbf{OH}$	8.4e+6	5.01	3	4.0e+10	5.04	8.6e+6
$.OCH_2CH_2CH_2\mathbf{CH}_2OH \rightarrow \mathbf{H}OCH_2CH_2CH_2CH(\cdot)OH$	2.4e+7	4.80	3	8.0e+10	4.82	2.4e+7
$CH_3\mathbf{CH}(OH)CH_2CH_2CH_2O\cdot \rightarrow$ $CH_3C(\cdot)(OH)CH_2CH_2CH_2\mathbf{OH}$	7.5e+7	3.72	3	4.0e+10	3.70	8.1e+7
$\mathbf{CH}_3CH(OH)CH_2CH_2O\cdot \rightarrow .CH_2CH(OH)CH_2CH_2\mathbf{OH}$	7.3e+4	8.48	3	1.2e+11	8.29	1.1e+5
$CH_3\mathbf{CH}_2CH(OH)CH_2CH_2O\cdot \rightarrow$ $CH_3CH(\cdot)CH(OH)CH_2CH_2\mathbf{OH}$	7.8e+5	6.83	3	8.0e+10	6.72	1.0e+6
$CH_3\mathbf{CH}(CH_3)CH(OH)CH_2CH_2O\cdot \rightarrow$ $CH_3C(\cdot)(CH_3)CH(OH)CH_2CH_2\mathbf{OH}$	2.7e+6	5.69	3	4.0e+10	5.59	3.4e+6
$CH_3CH(OH)\mathbf{CH}_2CH_2CH_2CH_2O\cdot \rightarrow$ $CH_3CH(OH)CH(\cdot)CH_2CH_2CH_2\mathbf{OH}$	1.3e+6	6.53	3	8.0e+10	6.72	1.0e+6
$CH_3CH(OH)\mathbf{CH}(CH_3)CH_2CH_2CH_2O\cdot \rightarrow$ $CH_3CH(OH)C(\cdot)(CH_3)CH_2CH_2CH_2\mathbf{OH}$	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)						
$CH_3CH(O\cdot)OC(CH_3)(CH_3)C\mathbf{H}_3 \rightarrow$ $CH_3CH(\mathbf{OH})OC(CH_3)(CH_3)CH_2\cdot$	<3.7e+3	>10.9	4	3.6e+11	11.5	1.4e+3
$CH_3C(C\mathbf{H}_3)(CH_3)OCH_2O\cdot \rightarrow$ $CH_3C(CH_3)(CH_2\cdot)OCH_2O\mathbf{H}$	<6.4e+3	>10.6	5	3.6e+11	11.5	1.4e+3
$CH_3CH(O\cdot)OCH_2C\mathbf{H}_2OH \rightarrow$ $CH_3CH(O\mathbf{H})OCH_2CH(\cdot)OH$	<4.3e+4	>8.5	6	8.0e+10	8.8	3.0e+4

Table A-50 (continued)

Reaction [a]	Used as Standard [b,c,d]			Estimated [e]		
	k(~298)	Ea	Note	A	Ea	k(298)
$CH_3C(O)OC\mathbf{H}_2CH_2OCH(O\cdot)CH_3 \rightarrow CH_3C(O)OCH(\cdot)CH_2OCH(CH_3)O\mathbf{H}$	<1.3e+5	>7.9	7	8.0e+10	9.6	7.8e+3
$CH_3CH_2OC(O)C\mathbf{H}_2CH_2OCH(O\cdot)CH_3 \rightarrow CH_3CH_2OC(O)CH(\cdot)CH_2OCH(CH_3)O\mathbf{H}$	<1.3e+5	>7.9	8	8.0e+10	11.1	690
$C\mathbf{H}_3CH_2OC(O)CH_2O\cdot \rightarrow \cdot CH_2CH_2OC(O)CH_2O\mathbf{H}$	<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 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 $CH_3CH(O\cdot)OC(CH_3)(CH_3)CH_3$ reactions are the only sources of these products, suggest that isomerization should be slower than the O_2 reaction, which is estimated to have a rate constant of $kO_2[O_2]$=4.9e+4 sec-1 (see Section A1.6.1). 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 $CH_3C(CH_3)(CH_3)OCH_2O\cdot$ radical, formed in estimated 63% yield, must react mostly with O_2, and dominate over isomerization. Upper limit rate constant placed on an absolute basis using the estimated $kO_2[O_2]$=4.9e+4 sec-1.

6 The most reasonable way to account for the ~36% yield of $HCOOCH_2CH_2OH$ and ~8% yield of $CH_3C(O)OCH_2CH_2OH$ from OH + ethoxyethanol observed by Stemmler et al. (1996) is to assume that the $CH_3CH(O\cdot)OCH_2CH_2OH$ radical, predicted to be formed ~32% of the time, reacts by decomposition and (to a lesser extent) with O_2, with isomerization minor. Upper limit isomerization rate constant placed on an absolute basis using the estimated $kO_2[O_2]$=4.9e+4 s^{-1} and the decomposition/O_2 rate constant ratio derived from the ratios of yields of these two products.

7 The relatively high yields of $CH_3C(O)OCH_2CH_2OCHO$ 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 $CH_3CH_2OC(O)CH_2CH_2OCHO$ 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 A-50 (continued)

9 The most reasonable explanation for the observation of ~25% of $CH_3CH_2OC(O)CHO$ from ethyl 3-ethoxypropionate (Baxley et al., 1997) is to assume that this radical reacts with O_2 to a significant extent. This radical is predicted to be formed ~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 sec^{-1} and the units of Ea are kcal/mole.

Table A-51. Measured rate constants or rate constants derived from results of quantum calculations for β-scission decompositions of alkoxy radicals that were used for deriving parameters for estimating β-scission decomposition rate constants.

Reaction	ΔH_r	Used for Optimizations [a]				Estimated [b]			
		k(298)	n × A	Ea	Ref	k(298)	Ratio	Ea	Diff.
Acyclic alkyl alkoxy radicals									
$CH_3CH_2O\cdot \rightarrow HCHO + CH_3\cdot$	13.18	3.6e+0	1e+14	18.33	1	2.9e+0	0.8	18.46	0.13
$CH_3CH_2CH_2O\cdot \rightarrow HCHO + CH_3CH_2\cdot$	11.83	3.0e+2	1e+14	15.72	1	4.2e+2	1.4	15.51	-0.21
$CH_3CH(O\cdot)CH_3 \rightarrow CH_3CHO + CH_3\cdot$	7.63	3.6e+2	2e+14	16.01	1	2.5e+2	0.7	16.23	0.22
$CH_3CH(CH_3)CH_2O\cdot \rightarrow HCHO + CH_3CH(\cdot)CH_3$	10.34	5.7e+4	1e+14	12.60	1	4.2e+4	0.7	12.79	0.19
$CH_3CH_2CH(O\cdot)CH_3 \rightarrow CH_3CHO + CH_3CH_2\cdot$	6.47	2.8e+4	1e+14	13.04	1	1.8e+4	0.7	13.28	0.25
$CH_3CH_2CH_2CH_2O\cdot \rightarrow HCHO + CH_3CH_2CH_2\cdot$	12.14	2.5e+2	1e+14	15.81	1	4.2e+2	1.7	15.51	-0.30
$CH_3C(O\cdot)(CH_3)CH_3 \rightarrow CH_3C(O)CH_3 + CH_3\cdot$	4.28	2.5e+3	3e+14	15.11	1	6.2e+3	2.5	14.57	-0.53
$CH_3CH_2CH(O\cdot)CH_3 \rightarrow CH_3CH_2CHO + CH_3\cdot$	7.97	3.9e+1	1e+14	16.92	1	1.2e+2	3.2	16.23	-0.69
$CH_3CH_2CH_2CH_2CH_2O\cdot \rightarrow HCHO + CH_3CH_2CH_2CH_2\cdot$	12.08	4.2e+2	1e+14	15.51	2	4.2e+2	1.0	15.51	0.00
$CH_3CH(O\cdot)CH(CH_3)CH_3 \rightarrow CH_3CHO + CH_3CH(\cdot)CH_3$	4.98	1.7e+6	1e+14	10.59	2	1.8e+6	1.0	10.57	-0.03
$CH_3CH_2CH_2CH(O\cdot)CH_3 \rightarrow CH_3CHO + CH_3CH_2CH_2\cdot$	6.78	1.5e+4	1e+14	13.42	1	1.8e+4	1.2	13.28	-0.13
$CH_3CH_2CH(O\cdot)CH_2CH_3 \rightarrow CH_3CH_2CHO + CH_3CH_2\cdot$	6.81	2.7e+4	2e+14	13.45	1	3.6e+4	1.3	13.28	-0.17
$CH_3C(CH_3)(CH_3)CH_2O\cdot \rightarrow HCHO + CH_3C(\cdot)(CH_3)CH_3$	9.28	1.9e+6	1e+14	10.53	1	1.3e+6	0.7	10.73	0.20
$CH_3CH(O\cdot)CH(CH_3)CH_3 \rightarrow CH_3CH(CH_3)CHO + CH_3\cdot$	8.60	2.0e+2	1e+14	15.96	2	1.2e+2	0.6	16.23	0.27
$CH_3CH_2CH_2CH(O\cdot)CH_3 \rightarrow CH_3CH_2CH_2CHO + CH_3\cdot$	7.63	4.9e+1	1e+14	16.79	1	1.2e+2	2.6	16.23	-0.56
$CH_3CH_2C(O\cdot)(CH_3)CH_3 \rightarrow CH_3CH_2C(O)CH_3 + CH_3\cdot$	4.05	1.1e+4	2e+14	13.99	1	4.1e+3	0.4	14.57	0.58
$CH_3CH_2C(O\cdot)(CH_3)CH_3 \rightarrow CH_3C(O)CH_3 + CH_3CH_2\cdot$	3.12	9.4e+5	1e+14	10.95	1	3.0e+5	0.3	11.62	0.68
$CH_3CH_2CH_2C(O\cdot)(CH_3)CH_3 \rightarrow CH_3CH_2CH_2C(O)CH_3 + CH_3\cdot$	4.05	3.5e+3	2e+14	14.67	2	4.1e+3	1.2	14.57	-0.10
$CH_3CH_2CH_2C(O\cdot)(CH_3)CH_3 \rightarrow CH_3C(O)CH_3 + CH_3CH_2CH_2\cdot$	3.43	2.2e+5	1e+14	11.80	2	3.0e+5	1.3	11.62	-0.18
$CH_3CH(CH_3)C(O\cdot)(CH_3)CH_3 \rightarrow CH_3C(O)CH(CH_3)CH_3 + CH_3\cdot$	5.02	5.1e+3	2e+14	14.45	2	4.1e+3	0.8	14.57	0.13
$CH_3CH(O\cdot)C(CH_3)(CH_3)CH_3 \rightarrow CH_3CHO + CH_3C(\cdot)(CH_3)CH_3$	3.92	6.9e+7	1e+14	8.40	2	5.8e+7	0.8	8.51	0.11
$CH_3CH(CH_3)C(O\cdot)(CH_3)CH_3 \rightarrow CH_3C(O)CH_3 + CH_3CH(\cdot)CH_3$	1.63	1.5e+7	1e+14	9.31	2	2.9e+7	2.0	8.91	-0.40
$CH_3CH(O\cdot)C(CH_3)(CH_3)CH_3 \rightarrow CH_3C(CH_3)(CH_3)CHO + CH_3\cdot$	9.56	2.9e+2	1e+14	15.73	2	1.2e+2	0.4	16.23	0.50
$CH_3C(O\cdot)(CH_3)C(CH_3)(CH_3)CH_3 \rightarrow CH_3C(O)C(CH_3)(CH_3)CH_3 + CH_3\cdot$	5.98	4.5e+3	2e+14	14.52	2	4.1e+3	0.9	14.57	0.05
$CH_3C(O\cdot)(CH_3)C(CH_3)(CH_3)CH_3 \rightarrow CH_3C(O)CH_3 + CH_3C(\cdot)(CH_3)CH_3$	0.57	3.2e+8	1e+14	7.49	2	9.5e+8	3.0	6.85	-0.64
Other acyclic alkoxy radicals									
$CH_2{=}CHCH(O\cdot)CH_3 \rightarrow CH_2{=}CHCHO + CH_3\cdot$	5.00	3.7e+3	1e+14	14.22	2	3.8e+3	1.0	14.20	-0.02
$CH_2{=}CHCH_2CH_2O\cdot \rightarrow HCHO + .CH_2{=}CHCH_2\cdot$	-2.43	1.7e+6	1e+14	10.59	2	2.0e+6	1.2	10.49	-0.10
$CH_2{=}CHCH(O\cdot)CH_3 \rightarrow CH_3CHO + CH_2{=}CH.$	18.60	2.6e-1	1e+14	19.89	2	2.1e-1	0.8	20.01	0.12
$.OCH_2CH_2OH \rightarrow HCHO + .CH_2OH$	9.72	2.3e+5	1e+14	11.78	3	1.8e+5	0.8	11.91	0.13
$CH_3CH(O\cdot)OH \rightarrow HC(O)OH + CH_3\cdot$	-5.87	1.5e+6	1e+14	10.67	2	8.3e+5	0.5	11.02	0.36

Table A-51 (continued)

Reaction	ΔH_r	Used for Optimizations [a]				Estimated [b]			Diff.
		k(298)	n × A	Ea	Ref	k(298)	Ratio	Ea	
$HC(O)CH_2O\cdot \rightarrow HCHO + HCO\cdot$	6.88	7.9e+5	1e+14	11.04	2	4.1e+5	0.5	11.44	0.40
$CH_3CH(O\cdot)CH_2OH \rightarrow HC(O)CH_2OH + CH_3\cdot$	7.18	1.7e+2	1e+14	16.04	2	1.7e+2	1.0	16.05	0.02
$CH_3CH_2CH(O\cdot)OH \rightarrow HC(O)OH + CH_3CH_2\cdot$	-7.03	9.0e+7	1e+14	8.25	2	1.2e+8	1.3	8.07	-0.17
$CH_3CH(O\cdot)OCH_3 \rightarrow CH_3OCHO + CH_3\cdot$	-5.10	1.3e+6	1e+14	10.74	2	5.2e+5	0.4	11.29	0.55
$CH_3C(O\cdot)(CH_3)OH \rightarrow CH_3C(O)OH + CH_3\cdot$	-12.85	7.4e+6	2e+14	10.14	2	1.9e+6	0.3	10.94	0.81
$CH_3CH(O\cdot)CH_2OH \rightarrow CH_3CHO + .CH_2OH$	4.36	5.0e+7	1e+14	8.59	1	7.9e+6	0.2	9.68	1.09
$CH_3CH(O\cdot)CHO \rightarrow HC(O)CHO + CH_3\cdot$	12.44	2.3e+1	1e+14	17.25	2	1.4e+1	0.6	17.53	0.29
$CH_3CH(O\cdot)CHO \rightarrow CH_3CHO + HCO\cdot$	-1.10	9.0e+6	1e+14	9.61	2	1.7e+7	1.9	9.21	-0.39
$CH_3C(O)CH_2O\cdot \rightarrow HCHO + CH_3C(O)\cdot$	6.30	2.7e+7	1e+14	8.96	1	1.6e+7	0.6	9.27	0.32
$CH_3CH(O\cdot)CH(CH_3)OH \rightarrow CH_3CH(CHO)OH + CH_3\cdot$	11.47	1.7e+2	1e+14	16.04	2	1.7e+2	1.0	16.05	0.02
$CH_3C(O\cdot)(CH_3)CH_2OH \rightarrow CH_3C(O)CH_2OH + CH_3\cdot$	2.88	8.5e+3	2e+14	14.14	2	7.8e+3	0.9	14.19	0.04
$CH_3CH(O\cdot)CH_2OCH_3 \rightarrow CH_3OCH_2CHO + CH_3\cdot$	8.85	2.0e+1	1e+14	17.32	2	2.1e+1	1.0	17.30	-0.02
$CH_3CH_2OCH(O\cdot)CH_3 \rightarrow CH_3CH_2OCHO + CH_3\cdot$	-5.67	5.0e+5	1e+14	11.32	1	5.2e+5	1.0	11.29	-0.03
$CH_3CH(O\cdot)CH(CH_3)OH \rightarrow CH_3CHO + CH_3CH(\cdot)OH$	4.06	2.5e+8	1e+14	7.64	2	4.1e+8	1.7	7.34	-0.30
$CH_3OC(O\cdot)(CH_3)CH_3 \rightarrow CH_3C(O)OCH_3 + CH_3\cdot$	-11.94	1.0e+6	2e+14	11.32	1	1.4e+6	1.4	11.11	-0.21
$CH_3CH_2OCH_2CH_2O\cdot \rightarrow HCHO + CH_3CH_2OCH_2\cdot$	9.89	7.9e+5	1e+14	11.04	2	6.4e+5	0.8	11.18	0.13
$CH_3CH_2CH(O\cdot)OCH_3 \rightarrow CH_3OCHO + CH_3CH_2\cdot$	-6.26	1.0e+8	1e+14	8.17	2	7.6e+7	0.7	8.34	0.17
$CH_3CH(O\cdot)CH_2OCH_3 \rightarrow CH_3CHO + CH_3OCH_2\cdot$	5.03	1.0e+7	1e+14	9.53	2	2.7e+7	2.7	8.95	-0.58
$CH_3C(O\cdot)(CH_3)CH_2OH \rightarrow CH_3C(O)CH_3 + .CH_2OH$	1.01	2.8e+7	1e+14	8.93	2	1.3e+8	4.6	8.02	-0.90
$CH_3C(O\cdot)(CH_3)CHO \rightarrow CH_3C(O)CHO + CH_3\cdot$	5.75	2.4e+3	2e+14	14.90	2	2.4e+3	1.0	14.90	0.00
$CH_3C(O\cdot)(CH_3)CHO \rightarrow CH_3C(O)CH_3 + HCO\cdot$	-6.37	1.5e+8	1e+14	7.94	2	2.9e+8	1.9	7.55	-0.39
$CH_3C(O)CH(O\cdot)CH_3 \rightarrow CH_3C(O)CHO + CH_3\cdot$	11.25	1.0e+1	1e+14	17.70	2	1.4e+1	1.3	17.53	-0.17
$CH_3CH_2C(O)CH_2O\cdot \rightarrow HCHO + CH_3CH_2C(O)\cdot$	5.32	2.2e+7	1e+14	9.08	2	1.6e+7	0.7	9.27	0.20
$CH_3C(O)CH(O\cdot)CH_3 \rightarrow CH_3CHO + CH_3C(O)\cdot$	-1.68	1.7e+8	1e+14	7.87	2	6.8e+8	4.0	7.05	-0.82
$CH_3OC(CH_3)(CH_3)CH_2O\cdot \rightarrow HCHO + CH_3OC(\cdot)(CH_3)CH_3$	7.92	2.0e+7	1e+14	9.13	1	2.0e+7	1.0	9.13	0.00
$CH_3CH(CH_3)CH(O\cdot)CH_2OH \rightarrow CH_3CH(CH_3)CHO + .CH_2OH$	5.33	7.8e+6	1e+14	9.69	4	7.9e+6	1.0	9.68	-0.01
$CH_3CH(OH)C(O\cdot)(CH_3)CH_3 \rightarrow CH_3C(O)CH(CH_3)OH + CH_3\cdot$	7.89	7.9e+3	2e+14	14.18	2	7.8e+3	1.0	14.19	0.01
$CH_3CH(O\cdot)CH_2CH_2OCH_3 \rightarrow CH_3CHO + CH_3OCH_2CH_2\cdot$	6.72	2.0e+4	1e+14	13.23	1	1.8e+4	0.9	13.28	0.06
$CH_3CH_2C(O\cdot)(CH_3)OCH_3 \rightarrow CH_3CH_2C(O)OCH_3 + CH_3\cdot$	-12.20	1.0e+6	1e+14	10.91	1	7.1e+5	0.7	11.11	0.21
$CH_3CH_2CH_2CH(O\cdot)OCH_3 \rightarrow CH_3OCHO + CH_3CH_2CH_2\cdot$	-5.95	4.0e+7	1e+14	8.72	1	7.6e+7	1.9	8.34	-0.38
$CH_3CH(OH)C(O\cdot)(CH_3)CH_3 \rightarrow CH_3C(O)CH_3 + CH_3CH(\cdot)OH$	0.71	1.7e+9	1e+14	6.51	2	6.8e+9	4.0	5.68	-0.83
$CH_3C(O)CH_2CH(O\cdot)CH_3 \rightarrow CH_3CHO + CH_3C(O)CH_2\cdot$	1.49	1.6e+5	1e+14	12.00	5	1.6e+5	1.0	12.00	0.00
$CH_3C(O\cdot)(CH_3)C(CH_3)(CH_3)OH \rightarrow CH_3C(O)C(CH_3)(CH_3)OH + CH_3\cdot$	9.81	6.6e+3	2e+14	14.30	2	7.8e+3	1.2	14.19	-0.11
$CH_3CH(O\cdot)OC(CH_3)(CH_3)CH_3 \rightarrow CH_3C(CH_3)(CH_3)OCHO + CH_3\cdot$	-4.77	2.0e+5	1e+14	11.86	1	5.2e+5	2.6	11.29	-0.57
$CH_3C(O\cdot)(CH_3)C(CH_3)(CH_3)OH \rightarrow CH_3C(O)CH_3 + CH_3C(\cdot)(CH_3)OH$	-0.79	6.9e+9	1e+14	5.68	2	3.7e+10	5.4	4.67	-1.00

Table A-51 (continued)

Reaction	ΔH_r	Used for Optimizations [a]				Estimated [b]			
		k(298)	n × A	Ea	Ref	k(298)	Ratio	Ea	Diff.
$.OCH_2CH_2OOH \rightarrow HCHO + .CH_2OOH$	10.65	1.7e+6	1e+14	10.59	2	1.8e+6	1.1	10.55	-0.04
$CH_3CH(O\cdot)OOH \rightarrow HC(O)OOH + CH_3\cdot$	0.66	6.2e+5	1e+14	11.20	2	1.9e+5	0.3	11.88	0.69
$HOCH_2CH(O\cdot)OH \rightarrow HC(O)OH + .CH_2OH$	-9.14	1.7e+10	1e+14	5.15	2	5.3e+10	3.1	4.47	-0.68
$CH_3C(O\cdot)(OH)OH \rightarrow HOC(O)OH + CH_3\cdot$	-14.81	1.5e+8	1e+14	7.94	2	4.3e+8	2.9	7.32	-0.63
$CH_3CH(CH_2O\cdot)OOH \rightarrow HCHO + CH_3CH(\cdot)OOH$	9.61	2.2e+7	1e+14	9.08	2	2.8e+7	1.3	8.94	-0.14
$CH_3CH(O\cdot)OOCH_3 \rightarrow CH_3OOCHO + CH_3\cdot$	1.21	4.2e+4	1e+14	12.78	2	1.9e+5	4.6	11.88	-0.90
$CH_3CH(O\cdot)CH_2OOH \rightarrow CH_3CHO + .CH_2OOH$	5.29	5.4e+7	1e+14	8.55	2	7.8e+7	1.5	8.33	-0.22
$CH_3CH(O\cdot)CH_2OOH \rightarrow HC(O)CH_2OOH + CH_3\cdot$	8.85	2.0e+1	1e+14	17.32	2	2.1e+1	1.0	17.30	-0.02
$CH_3OOCH_2CH_2O\cdot \rightarrow HCHO + CH_3OOCH_2\cdot$	14.37	1.7e+5	1e+14	11.95	2	1.2e+5	0.7	12.18	0.23
$CH_3CH_2CH(O\cdot)OOH \rightarrow HC(O)OOH + CH_3CH_2\cdot$	-0.50	1.2e+8	1e+14	8.10	2	2.8e+7	0.2	8.93	0.84
$CH_3C(O\cdot)(CH_3)OOH \rightarrow CH_3C(O)OOH + CH_3\cdot$	-5.96	1.1e+7	2e+14	9.91	2	2.1e+6	0.2	10.87	0.96
$CH_3OOCH(CH_3)CH_2O\cdot \rightarrow HCHO + CH_3CH(\cdot)OOCH_3$	9.61	1.3e+6	1e+14	10.74	2	1.6e+6	1.2	10.64	-0.10
$CH_3OOC(O\cdot)(CH_3)CH_3 \rightarrow CH_3C(O)OOCH_3 + CH_3\cdot$	-5.96	3.0e+5	2e+14	12.03	2	2.1e+6	7.0	10.87	-1.15
$CH_3CH_2CH(O\cdot)OOCH_3 \rightarrow CH_3OOCHO + CH_3CH_2\cdot$	0.05	4.7e+6	1e+14	9.99	2	2.8e+7	5.9	8.93	-1.05
$CH_3CH(O\cdot)CH_2OOCH_3 \rightarrow CH_3OOCH_2CHO + CH_3\cdot$	8.85	2.9e+1	1e+14	17.09	2	2.1e+1	0.7	17.30	0.20
$CH_3CH(O\cdot)CH_2OOCH_3 \rightarrow CH_3CHO + CH_3OOCH_2\cdot$	9.01	2.5e+6	1e+14	10.36	2	5.0e+6	2.0	9.95	-0.41
$.OCH_2CH_2NO_2 \rightarrow HCHO + .CH_2NO_2$	17.44	2.6e+0	1e+14	18.53	2	2.2e+0	0.9	18.61	0.08
$CH_3CH(CH_2O\cdot)NO_2 \rightarrow HCHO + CH_3CH(\cdot)NO_2$	11.29	7.1e+2	1e+14	15.20	2	7.0e+2	1.0	15.21	0.01
$.OCH_2CH_2ONO_2 \rightarrow HCHO + .CH_2ONO_2$	10.65	3.7e+2	1e+14	15.58	2	3.7e+2	1.0	15.60	0.01
$CH_3CH(O\cdot)ONO_2 \rightarrow HC(O)ONO_2 + CH_3\cdot$	-4.77	5.5e+2	1e+14	15.35	2	7.4e+2	1.4	15.17	-0.18
$CH_3CH(CH_2O\cdot)ONO_2 \rightarrow HCHO + CH_3CH(\cdot)ONO_2$	9.62	1.7e+4	1e+14	13.31	2	1.8e+4	1.1	13.27	-0.04
$CH_3CH_2CH(O\cdot)ONO_2 \rightarrow HC(O)ONO_2 + CH_3CH_2\cdot$	-5.93	1.3e+5	1e+14	12.10	2	1.1e+5	0.8	12.22	0.12
<u>Cyclic alkoxy radicals</u>									
$.OCH_2CH*CH_2CH_2* \rightarrow HCHO + CH_2*CH_2CH(\cdot)*$	10.28	1.5e-1	1e+14	20.19	2	2.0e-1	1.3	20.04	-0.16
$CH_2*CH_2CH(O\cdot)CH_2* \rightarrow HC(O)CH_2CH_2CH_2\cdot$	-19.81	5.6e+9	2e+14	6.20	2	2.5e+9	0.4	6.69	0.49
$CH_3C(O\cdot)*CH_2CH_2CH_2* \rightarrow CH_2*CH_2C(O)CH_2* + CH_3\cdot$	2.36	8.1e+1	1e+14	16.49	2	7.1e+1	0.9	16.57	0.08
$CH_3CH(O\cdot)CH*CH_2CH_2* \rightarrow CH_3CHO + CH_2*CH_2CH(\cdot)*$	4.92	1.5e+1	1e+14	17.47	2	8.7e+0	0.6	17.81	0.34
$.OCH_2CH*CH_2CH_2CH_2* \rightarrow HCHO + CH_2*CH_2CH(\cdot)CH_2*$	10.28	6.2e+2	1e+14	15.28	2	1.1e+3	1.8	14.93	-0.35
$CH_3C(O\cdot)*CH_2CH_2CH_2* \rightarrow CH_3C(O)CH_2CH_2CH_2\cdot$	-23.39	1.2e+10	2e+14	5.75	2	4.1e+10	3.4	5.03	-0.72
$CH_2*CH_2CH_2CH(O\cdot)CH_2* \rightarrow HC(O)CH_2CH_2CH_2CH_2\cdot$	0.03	3.4e+6	2e+14	10.59	2	1.3e+6	0.4	11.16	0.57
$CH_2*CH_2CH_2CH(O\cdot)CH_2CH_2* \rightarrow HC(O)CH_2CH_2CH_2CH_2CH_2\cdot$	6.24	5.0e+4	2e+14	13.09	1	3.9e+4	0.8	13.24	0.15
$.OCH_2CH*CH_2CH_2CH_2CH_2* \rightarrow HCHO + CH_2*CH_2CH_2CH(\cdot)CH_2*$	10.28	6.2e+4	1e+14	12.56	2	6.8e+4	1.1	12.50	-0.06
$CH_3C(O\cdot)*CH_2CH_2CH_2CH_2* \rightarrow CH_2*CH_2CH_2C(O)CH_2* + CH_3\cdot$	2.84	1.0e+2	1e+14	16.34	2	9.9e+1	0.9	16.37	0.03
$CH_3CH_2C(O\cdot)*CH_2CH_2CH_2* \rightarrow CH_2*CH_2C(O)CH_2* + CH_3CH_2\cdot$	1.20	9.1e+3	1e+14	13.69	2	1.0e+4	1.1	13.62	-0.07

Table A-51 (continued)

Reaction	ΔH_r	Used for Optimizations [a]				Estimated [b]			
		k(298)	n × A	Ea	Ref	k(298)	Ratio	Ea	Diff.
$CH_3CH_2C(O\cdot)*CH_2CH_2CH_2* \rightarrow CH_3CH_2C(O)CH_2CH_2CH_2\cdot$	-23.65	2.0e+10	2e+14	5.45	2	4.1e+10	2.0	5.03	-0.42
$CH_3CH(O\cdot)CH*CH_2CH_2CH_2* \rightarrow CH_3CHO + CH_2*CH_2CH(\cdot)CH_2*$	4.92	8.0e+4	1e+14	12.41	2	4.8e+4	0.6	12.70	0.30
$CH_3C(O\cdot)*CH_2CH_2CH_2CH_2* \rightarrow CH_3C(O)CH_2CH_2CH_2CH_2\cdot$	-3.55	5.7e+6	2e+14	10.29	2	2.1e+7	3.8	9.50	-0.79
$CH_3CH(O\cdot)CH*CH_2CH_2CH_2* \rightarrow HC(O)CH*CH_2CH_2CH_2* + CH_3\cdot$	8.60	4.8e+2	1e+14	15.43	2	4.7e+2	1.0	15.44	0.01
$CH_3C(O\cdot)*CH_2CH_2CH_2CH_2CH_2* \rightarrow CH_3C(O)CH_2CH_2CH_2CH_2CH_2\cdot$	2.66	4.4e+5	2e+14	11.80	2	6.4e+5	1.5	11.58	-0.22
$.OCH_2CH*(CH_2)_5* \rightarrow HCHO + CH_2*CH_2CH_2CH(\cdot)CH_2CH_2*$	10.28	6.2e+4	1e+14	12.56	2	6.8e+4	1.1	12.50	-0.06
$CH_3C(O\cdot)*(CH_2)_5* \rightarrow CH_2*CH_2CH_2C(O)CH_2CH_2* + CH_3\cdot$	6.18	1.0e+2	1e+14	16.34	2	9.9e+1	0.9	16.37	0.03
$CH_3CH(O\cdot)CH*CH_2CH_2* \rightarrow HC(O)CH*CH_2CH_2* + CH_3\cdot$	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 sec^{-1} and activation energies are in units of kcal/mole. The A factor is set at 1.0 x 10^{-14} sec^{-1} × 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(-Ea/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 Eb(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 $.HOCH_2CH_2O\cdot$ forming these products are the only significant reactions. Rate constant placed on an absolute basis using the estimated rate constant for the 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 $CH_3CH(CH_3)CH(O.)CH_2OH$, and placed on an absolute basis using the estimated rate constant for the reaction forming $CH_3CH(.)CH_3 + HC(O)CH_2OH$.

5 Derived from the ratio of acetaldehyde to $CH_3C(O)CH_2C(O)CH_3$ yields from 2-pentanone as reported by Atkinson et al. (2000), assuming they both only come from $CH_3C(O)CH_2CH(O.)CH_3$, and using the estimated rate constant for the O_2 reaction.

[b] Estimated values, with rate constants in 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.

A5.3. Tables of Assignments

Table A-52. 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 A-52 (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-Butandiol	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 A-52 (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 A-52 (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 A-52 (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 A-52 (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 A-52 (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
α-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 A-52 (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 x exp(-Ea/RT) x (T/300)^B, where R=0.0019872. Units of k and A are cm^3 $molec^{-1}$ 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 McGillen et al. (2020, 2021).

2 Falloff parameters: A_∞=8.30e-13, Ea_∞=0K, B_∞=2.00, A_0=5.50e-30, Ea_0=0K, B_0=0, F=0.60, N=1, based on the NASA (2015) evaluation.

3 Falloff parameters: A_∞=8.40e-12, Ea_∞=0K, B_∞==-1.75, A_0=1.10e-28, Ea_0=0K, 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 A-53. 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 A-53 (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 x exp(-Ea/RT) x (T/300)^B, where R=0.0019872. Units of k and A are cm^3 $molec^{-1}$ 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 A-54. Assigned rate constants for the reactions of compounds with NO_3 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 A-54 (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 A-54 (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 A-54 (continued)

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

Table A-55. Assigned rate constants for the reactions of compounds with O^3P.

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 x exp(-Ea/RT), where R=0.0019872. Units of k and A are cm^3 $molec^{-1}$ s^{-1}. Units of Ea 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 A-56. Rate constants assigned for the reactions of radicals.

Reaction	k(298)	A	Ea	Ref
$CH_3O\cdot + O_2 \rightarrow HCHO + HO_2\cdot$	1.59e-15	7.37e-14	2.271	1
$CH_3CH_2O\cdot \rightarrow HCHO + CH_3\cdot$	3.58e+0	5.00e+13	17.915	2
$CH_3CH_2O\cdot + O_2 \rightarrow CH_3CHO + HO_2\cdot$	8.09e-15	5.13e-14	1.093	1
$HC(O)CH_2O\cdot \rightarrow HCHO + HCO\cdot$	9.22e+5	5.00e+13	10.541	3
$CH_3CH(O\cdot)OH \rightarrow HC(O)OH + CH_3\cdot$	1.77e+6	5.00e+13	10.154	3
$CH_3C(O\cdot)(OH)OH \rightarrow HOC(O)OH + CH_3\cdot$	1.97e+8	5.00e+13	7.367	3
$CH_3CH(O\cdot)OOH \rightarrow HC(O)OOH + CH_3\cdot$	7.09e+5	5.00e+13	10.696	3
$HOCH_2CH(O\cdot)OH \rightarrow HC(O)OH + .CH_2OH$	2.48e+10	5.00e+13	4.503	3
$.OCH_2CH_2OOH \rightarrow HCHO + .CH_2OOH$	2.02e+6	5.00e+13	10.076	3
$.OCH_2CH_2\text{-}NO_2 \rightarrow HCHO + .CH_2\text{-}NO_2$	2.20e+0	5.00e+13	18.204	3
$CH_3CH(O\cdot)ONO_2 \rightarrow HCO\text{-}ONO_2 + CH_3\cdot$	5.34e+2	5.00e+13	14.953	3
$.OCH_2CH_2ONO_2 \rightarrow HCHO + .CH_2ONO_2$	3.61e+2	5.00e+13	15.185	3
$CH_3CH(O\cdot)CH_3 \rightarrow CH_3CHO + CH_3\cdot$	3.58e+2	1.00e+14	15.599	2
$CH_3CH(O\cdot)CH_3 + O_2 \rightarrow CH_3C(O)CH_3 + HO_2\cdot$	6.89e-15	1.95e-14	0.616	1
$CH_3CH_2CH_2O\cdot \rightarrow HCHO + CH_3CH_2\cdot$	2.91e+2	5.00e+13	15.312	2
$CH_3CH_2CH_2O\cdot + O_2 \rightarrow CH_3CH_2CHO + HO_2\cdot$	1.10e-14	2.38e-14	0.457	1
$CH_3CH(O\cdot)CHO \rightarrow HC(O)CHO + CH_3\cdot$	2.03e+1	5.00e+13	16.888	3
$CH_3CH(O\cdot)CHO \rightarrow CH_3CHO + HCO\cdot$	1.11e+7	5.00e+13	9.070	3
$CH_3C(O)CH_2O\cdot \rightarrow HCHO + CH_3C(O)\cdot$	2.68e+7	5.00e+13	8.546	2
$CH_3C(O\cdot)(CH_3)OH \rightarrow CH_3C(O)OH + CH_3\cdot$	8.86e+6	1.00e+14	9.612	3
$CH_3CH(O\cdot)OCH_3 \rightarrow CH_3OCHO + CH_3\cdot$	1.56e+6	5.00e+13	10.231	3
$CH_3CH(O\cdot)CH_2OH \rightarrow HC(O)CH_2OH + CH_3\cdot$	1.64e+2	5.00e+13	15.650	3
$CH_3CH(O\cdot)CH_2OH \rightarrow CH_3CHO + .CH_2OH$	4.97e+7	5.00e+13	8.181	2
$CH_3CH_2CH(O\cdot)OH \rightarrow HC(O)OH + CH_3CH_2\cdot$	1.16e+8	5.00e+13	7.677	3
$CH_3OCH_2CH_2O\cdot \rightarrow HCHO + CH_3OCH_2\cdot$	9.22e+5	5.00e+13	10.541	3
$CH_3CH(CH_2O\cdot)OH \rightarrow HCHO + CH_3CH(\cdot)OH$	4.97e+7	5.00e+13	8.181	2
$CH_3CH(O\cdot)OOCH_3 \rightarrow CH_3OOCHO + CH_3\cdot$	4.56e+4	5.00e+13	12.321	3
$CH_3CH(O\cdot)CH_2OOH \rightarrow HC(O)CH_2OOH + CH_3\cdot$	1.78e+1	5.00e+13	16.966	3
$CH_3CH(O\cdot)CH_2OOH \rightarrow CH_3CHO + .CH_2OOH$	6.91e+7	5.00e+13	7.986	3
$CH_3CH_2CH(O\cdot)OOH \rightarrow HC(O)OOH + CH_3CH_2\cdot$	1.51e+8	5.00e+13	7.522	3
$CH_3OOCH_2CH_2O\cdot \rightarrow HCHO + CH_3OOCH_2\cdot$	1.92e+5	5.00e+13	11.470	3
$CH_3CH(CH_2O\cdot)OOH \rightarrow HCHO + CH_3CH(\cdot)OOH$	2.76e+7	5.00e+13	8.528	3
$CH_3C(O\cdot)(CH_3)OOH \rightarrow CH_3C(O)OOH + CH_3\cdot$	1.31e+7	1.00e+14	9.380	3
$CH_3CH(CH_2O\cdot)NO_2 \rightarrow HCHO + CH_3CH(\cdot)NO_2$	6.93e+2	5.00e+13	14.798	3
$CH_3CH_2CH(O\cdot)ONO_2 \rightarrow HCO\text{-}ONO_2 + CH_3CH_2\cdot$	1.48e+5	5.00e+13	11.625	3
$CH_3CH(CH_2O\cdot)ONO_2 \rightarrow HCHO + CH_3CH(\cdot)ONO_2$	1.82e+4	5.00e+13	12.863	3
$CH_2{=}CH\text{-}CH(O\cdot)CH_3 \rightarrow CH_2{=}CH\text{-}CHO + CH_3\cdot$	3.79e+3	5.00e+13	13.792	3
$CH_2{=}CH\text{-}CH(O\cdot)CH_3 \rightarrow CH_3CHO + CH_2{=}CH.$	2.08e-1	5.00e+13	19.598	3
$CH_2{=}CH\text{-}CH_2CH_2O\cdot \rightarrow HCHO + CH_2{=}CH\text{-}CH_2\cdot$	2.02e+6	5.00e+13	10.076	3
$CH_2{*}CH_2CH(O\cdot)CH_2{*} \rightarrow .CH_2CH_2CH_2CHO$	7.95e+9	1.00e+14	5.587	3

Table A-56 (continued)

Reaction	k(298)	A	Ea	Ref
$.OCH_2CH*CH_2CH_2* \rightarrow HCHO + CH_2*CH_2CH(\cdot)*$	1.24e-1	5.00e+13	19.907	3
$CH_3CH_2CH(O\cdot)CH_3 \rightarrow CH_3CH_2CHO + CH_3\cdot$	3.84e+1	5.00e+13	16.510	2
$CH_3CH_2CH(O\cdot)CH_3 \rightarrow CH_3CHO + CH_3CH_2\cdot$	2.72e+4	5.00e+13	12.626	2
$CH_3CH_2CH(O\cdot)CH_3 + O_2 \rightarrow CH_3CH_2C(O)CH_3 + HO_2\cdot$	7.75e-15			4
$CH_3C(O\cdot)(CH_3)CH_3 \rightarrow CH_3C(O)CH_3 + CH_3\cdot$	2.47e+3	1.50e+14	14.697	2
$CH_3CH_2CH_2CH_2O\cdot \rightarrow HCHO + CH_3CH_2CH_2\cdot$	2.50e+2	5.00e+13	15.402	2
$CH_3CH_2CH_2CH_2O\cdot + O_2 \rightarrow CH_3CH_2CH_2CHO + HO_2\cdot$	1.40e-14			5
$CH_3CH(CH_3)CH_2O\cdot \rightarrow HCHO + CH_3CH(\cdot)CH_3$	5.65e+4	5.00e+13	12.194	2
$CH_3C(O\cdot)(CH_3)CHO \rightarrow CH_3C(O)CHO + CH_3\cdot$	2.34e+3	1.00e+14	14.489	3
$CH_3C(O\cdot)(CH_3)CHO \rightarrow CH_3C(O)CH_3 + HCO\cdot$	1.97e+8	5.00e+13	7.367	3
$CH_3C(O)CH(O\cdot)CH_3 \rightarrow CH_3C(O)CHO + CH_3\cdot$	9.25e+0	5.00e+13	17.353	3
$CH_3C(O)CH(O\cdot)CH_3 \rightarrow CH_3CHO + CH_3C(O)\cdot$	2.24e+8	5.00e+13	7.290	3
$CH_3CH_2C(O)CH_2O\cdot \rightarrow HCHO + CH_3CH_2C(O)\cdot$	2.76e+7	5.00e+13	8.528	3
$CH_3CH_2OCH(O\cdot)CH_3 \rightarrow CH_3CH_2OCHO + CH_3\cdot$	4.96e+5	5.00e+13	10.908	2
$CH_3C(O\cdot)(CH_3)CH_2OH \rightarrow CH_3C(O)CH_2OH + CH_3\cdot$	8.64e+3	1.00e+14	13.715	3
$CH_3C(O\cdot)(CH_3)CH_2OH \rightarrow CH_3C(O)CH_3 + .CH_2OH$	3.59e+7	5.00e+13	8.373	3
$CH_3CH(O\cdot)CH(CH_3)OH \rightarrow CH_3CH(CHO)OH + CH_3\cdot$	1.64e+2	5.00e+13	15.650	3
$CH_3CH(O\cdot)CH(CH_3)OH \rightarrow CH_3CHO + CH_3CH(\cdot)OH$	3.32e+8	5.00e+13	7.057	3
$CH_3CH(O\cdot)CH_2OCH_3 \rightarrow CH_3OCH_2CHO + CH_3\cdot$	1.78e+1	5.00e+13	16.966	3
$CH_3CH(O\cdot)CH_2OCH_3 \rightarrow CH_3CHO + CH_3OCH_2\cdot$	1.26e+7	5.00e+13	8.993	3
$CH_3CH_2CH(O\cdot)OCH_3 \rightarrow CH_3OCHO + CH_3CH_2\cdot$	1.33e+8	5.00e+13	7.599	3
$CH_3CH_2OCH_2CH_2O\cdot \rightarrow HCHO + CH_3CH_2OCH_2\cdot$	9.22e+5	5.00e+13	10.541	3
$CH_3CH_2CH(CH_2O\cdot)OH \rightarrow HCHO + CH_3CH_2CH(\cdot)OH$	6.55e+6	5.00e+13	9.380	3
$CH_3C(CH_3)(CH_2O\cdot)OH \rightarrow HCHO + CH_3C(\cdot)(CH_3)OH$	1.97e+8	5.00e+13	7.367	3
$CH_3C(O\cdot)(CH_3)OCH_3 \rightarrow CH_3C(O)OCH_3 + CH_3\cdot$	9.92e+5	1.00e+14	10.908	2
$CH_3CH(CH_2O\cdot)OCH_3 \rightarrow HCHO + CH_3CH(\cdot)OCH_3$	1.33e+8	5.00e+13	7.599	3
$CH_3CH(O\cdot)CH_2OOCH_3 \rightarrow CH_3OOCH_2CHO + CH_3\cdot$	2.64e+1	5.00e+13	16.733	3
$CH_3CH(O\cdot)CH_2OOCH_3 \rightarrow CH_3CHO + CH_3OOCH_2\cdot$	2.99e+6	5.00e+13	9.844	3
$CH_3CH_2CH(O\cdot)OOCH_3 \rightarrow CH_3OOCHO + CH_3CH_2\cdot$	5.75e+6	5.00e+13	9.457	3
$CH_3C(O\cdot)(CH_3)OOCH_3 \rightarrow CH_3C(O)OOCH_3 + CH_3\cdot$	3.37e+5	1.00e+14	11.547	3
$CH_3CH(CH_2O\cdot)OOCH_3 \rightarrow HCHO + CH_3CH(\cdot)OOCH_3$	1.56e+6	5.00e+13	10.231	3
$CH_3C(O\cdot)*CH_2CH_2CH_2* \rightarrow CH_2*CH_2C(O)CH_2* + CH_3\cdot$	7.51e+1	5.00e+13	16.114	3
$CH_3C(O\cdot)*CH_2CH_2CH_2* \rightarrow CH_3C(O)CH_2CH_2CH_2\cdot$	1.74e+10	1.00e+14	5.122	3
$CH_2*CH_2CH_2CH(O\cdot)CH_2* \rightarrow .CH_2CH_2CH_2CH_2CHO$	4.04e+6	1.00e+14	10.076	3
$CH_3CH(O\cdot)CH*CH_2CH_2* \rightarrow CH_3CHO + CH_2*CH_2CH(\cdot)*$	1.37e+1	5.00e+13	17.121	3
$.OCH_2CH*CH_2CH_2CH_2* \rightarrow HCHO + CH_2*CH_2CH(\cdot)CH_2*$	6.08e+2	5.00e+13	14.876	3
$CH_3CH_2CH_2CH(O\cdot)CH_3 \rightarrow CH_3CH_2CH_2CHO + CH_3\cdot$	4.78e+1	5.00e+13	16.381	2
$CH_3CH_2CH_2CH(O\cdot)CH_3 \rightarrow CH_3CHO + CH_3CH_2CH_2\cdot$	1.43e+4	5.00e+13	13.005	2
$CH_3CH(O\cdot)CH(CH_3)CH_3 \rightarrow CH_3CH(CH_3)CHO + CH_3\cdot$	1.88e+2	5.00e+13	15.572	3
$CH_3CH(O\cdot)CH(CH_3)CH_3 \rightarrow CH_3CHO + CH_3CH(\cdot)CH_3$	2.02e+6	5.00e+13	10.076	3
$CH_3CH_2C(O\cdot)(CH_3)CH_3 \rightarrow CH_3CH_2C(O)CH_3 + CH_3\cdot$	1.09e+4	1.00e+14	13.579	2
$CH_3CH_2C(O\cdot)(CH_3)CH_3 \rightarrow CH_3C(O)CH_3 + CH_3CH_2\cdot$	9.31e+5	5.00e+13	10.535	2
$CH_3CH_2CH_2CH_2CH_2O\cdot \rightarrow HCHO + CH_3CH_2CH_2CH_2\cdot$	4.11e+2	5.00e+13	15.108	3

Table A-56 (continued)

Reaction	k(298)	A	Ea	Ref
$CH_3CH_2CH(O\cdot)CH_2CH_3 \rightarrow CH_3CH_2CHO + CH_3CH_2\cdot$	2.69e+4	1.00e+14	13.042	2
$CH_3CH_2CH(O\cdot)CH_2CH_3 + O_2 \rightarrow CH_3CH_2C(O)CH_2CH_3 + HO_2\cdot$	7.20e-15			6
$CH_3C(CH_3)(CH_3)CH_2O\cdot \rightarrow HCHO + CH_3C(\cdot)(CH_3)CH_3$	1.88e+6	5.00e+13	10.118	2
$CH_3CH_2C(O\cdot)(CH_3)OCH_3 \rightarrow CH_3CH_2C(O)OCH_3 + CH_3\cdot$	9.91e+5	5.00e+13	10.498	2
$CH_3CH(OH)C(O\cdot)(CH_3)CH_3 \rightarrow CH_3C(O)CH(CH_3)OH + CH_3\cdot$	8.11e+3	1.00e+14	13.753	3
$CH_3CH(OH)C(O\cdot)(CH_3)CH_3 \rightarrow CH_3C(O)CH_3 + CH_3CH(\cdot)OH$	2.36e+9	5.00e+13	5.896	3
$CH_3CH(O\cdot)CH_2CH_2OCH_3 \rightarrow CH_3CHO + CH_3OCH_2CH_2\cdot$	1.98e+4	5.00e+13	12.815	2
$CH_3C(CH_3)(CH_2O\cdot)OCH_3 \rightarrow HCHO + CH_3C(\cdot)(CH_3)OCH_3$	1.99e+7	5.00e+13	8.724	2
$CH_3CH_2CH_2CH(O\cdot)OCH_3 \rightarrow CH_3OCHO + CH_3CH_2CH_2\cdot$	3.98e+7	5.00e+13	8.313	2
$CH_3C(O\cdot)*CH_2CH_2CH_2CH_2* \rightarrow CH_2*CH_2CH_2C(O)CH_2* + CH_3\cdot$	9.75e+1	5.00e+13	15.959	3
$CH_3C(O\cdot)*CH_2CH_2CH_2CH_2* \rightarrow CH_3C(O)CH_2CH_2CH_2CH_2\cdot$	6.82e+6	1.00e+14	9.767	3
$CH_3CH(O\cdot)CH*CH_2CH_2CH_2* \rightarrow HC(O)CH*CH_2CH_2CH_2* + CH_3\cdot$	4.68e+2	5.00e+13	15.031	3
$CH_3CH(O\cdot)CH*CH_2CH_2CH_2* \rightarrow CH_3CHO + CH_2*CH_2CH(\cdot)CH_2*$	8.76e+4	5.00e+13	11.934	3
$CH_2*CH_2CH_2CH(O\cdot)CH_2CH_2* \rightarrow .CH_2CH_2CH_2CH_2CH_2CHO$	4.95e+4	1.00e+14	12.682	2
$CH_3CH_2C(O\cdot)*CH_2CH_2CH_2* \rightarrow CH_2*CH_2C(O)CH_2* + CH_3CH_2\cdot$	9.48e+3	5.00e+13	13.250	3
$CH_3CH_2C(O\cdot)*CH_2CH_2CH_2* \rightarrow CH_3CH_2C(O)CH_2CH_2CH_2\cdot$	2.94e+10	1.00e+14	4.813	3
$.OCH_2CH*CH_2CH_2CH_2CH_2* \rightarrow HCHO + CH_2*CH_2CH_2CH(\cdot)CH_2*$	6.74e+4	5.00e+13	12.089	3
$CH_3CH(O\cdot)C(CH_3)(CH_3)CH_3 \rightarrow CH_3C(CH_3)(CH_3)CHO + CH_3\cdot$	2.78e+2	5.00e+13	15.340	3
$CH_3CH(O\cdot)C(CH_3)(CH_3)CH_3 \rightarrow CH_3CHO + CH_3C(\cdot)(CH_3)CH_3$	8.96e+7	5.00e+13	7.832	3
$CH_3CH_2CH_2C(O\cdot)(CH_3)CH_3 \rightarrow CH_3CH_2CH_2C(O)CH_3 + CH_3\cdot$	3.47e+3	1.00e+14	14.256	3
$CH_3CH_2CH_2C(O\cdot)(CH_3)CH_3 \rightarrow CH_3C(O)CH_3 + CH_3CH_2CH_2\cdot$	2.49e+5	5.00e+13	11.315	3
$CH_3CH(CH_3)C(O\cdot)(CH_3)CH_3 \rightarrow CH_3C(O)CH(CH_3)CH_3 + CH_3\cdot$	5.13e+3	1.00e+14	14.024	3
$CH_3CH(CH_3)C(O\cdot)(CH_3)CH_3 \rightarrow CH_3C(O)CH_3 + CH_3CH(\cdot)CH_3$	1.87e+7	5.00e+13	8.760	3
$CH_3C(O\cdot)(CH_3)C(CH_3)(CH_3)OH \rightarrow CH_3C(O)C(CH_3)(CH_3)OH + CH_3\cdot$	6.66e+3	1.00e+14	13.869	3
$CH_3C(O\cdot)(CH_3)C(CH_3)(CH_3)OH \rightarrow CH_3C(O)CH_3 + CH_3C(\cdot)(CH_3)OH$	9.94e+9	5.00e+13	5.045	3
$CH_3CH(O\cdot)OC(CH_3)(CH_3)CH_3 \rightarrow CH_3C(CH_3)(CH_3)OCHO + CH_3\cdot$	1.98e+5	5.00e+13	11.451	2
$CH_3C(O\cdot)*CH_2CH_2CH_2CH_2CH_2* \rightarrow CH_2*CH_2CH_2C(O)CH_2CH_2* + CH_3\cdot$	9.75e+1	5.00e+13	15.959	3
$CH_3C(O\cdot)*CH_2CH_2CH_2CH_2CH_2* \rightarrow CH_3C(O)CH_2CH_2CH_2CH_2CH_2\cdot$	4.99e+5	1.00e+14	11.315	3
$.OCH_2CH*CH_2CH_2CH_2CH_2CH_2* \rightarrow HCHO + CH_2*CH_2CH_2CH(\cdot)CH_2CH_2*$	6.74e+4	5.00e+13	12.089	3
$CH_3C(O\cdot)(CH_3)C(CH_3)(CH_3)CH_3 \rightarrow CH_3C(O)C(CH_3)(CH_3)CH_3 + CH_3\cdot$	4.50e+3	1.00e+14	14.102	3
$CH_3C(O\cdot)(CH_3)C(CH_3)(CH_3)CH_3 \rightarrow CH_3C(O)CH_3 + CH_3C(\cdot)(CH_3)CH_3$	4.30e+8	5.00e+13	6.903	3

Temperature dependence, if assigned, given by k(T) = A x exp(-Ea/RT), where R=0.0019872. Units of k and A are cm^3 $molec^{-1}$ s^{-1}. Units of Ea 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 or data for radicals estimated to have non-negligible isomerization reactions. A factors are estimated to be 5 x 10^{-13} sec^{-1} × 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 × 10^{-13} sec^{-1} x 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 A-56 (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 A-57. Branching ratios assigned for various reactions.

Reactants [a]	Products	Fraction	Ref [b]
$CH_3OH + OH$	$H_2O + .CH_2OH$	0.85	1
	$H_2O + CH_3O\cdot$	0.15	
$HC(O)OH + OH$	$H_2O + HCO_2\cdot$	1	2
HC#CH + OH	$CH=CHOH$	1	3
	CH_2CHO	0	
$CH_2=CH_2 + O_3P$	CH_2*CH_2O*	0.1	4
	CH_3CHO	0.1	
	$CH_2CHO + H.$	0.29	
	$HCO\cdot + CH_3\cdot$	0.51	
$CH=CHOH + O_2$	$HC(O)OH + HCO\cdot$	0.33	3
	$HC(O)CHO + OH$	0.67	
$CH_3CHO + OH$	$H_2O + CH_3C(O)\cdot$	0.95	1
	$H_2O + .CH_2CHO$	0.05	
$CH_3CH_2OH + OH$	$H_2O + CH_3CH(\cdot)OH$	0.9	1
	$H_2O + CH_3CH_2O\cdot$	0.05	
	$H_2O + .CH_2CH_2OH$	0.05	
$CH_3C(O)OH + OH$	$H_2O + .CH_2C(O)OH$	0.3	1
	$H_2O + CH_3C(O)O\cdot$	0.7	
$HC(O)CH_2OH + OH$	$H_2O + CO(\cdot)CH_2OH$	0.8	1
	$H_2O + HC(O)CH(\cdot)OH$	0.2	
$HC(O)CH_2OH + HV$	$CH_2OH + HCO\cdot$	0.83	
	$CH_3OH + CO$	0.1	
	$CH_2CHO + OH$	0.07	
$HC(O)C(O)O-ONO_2$	$CO_2 + HCO\cdot + NO_3$	1	5
$CH_2=CHCHO + OH$	$H_2O + CH_2=CHC(O)\cdot$	0.68	6
	$HC(O)CH(\cdot)CH_2OH$	0.26	
	$CH_2CH(CHO)OH$	0.06	
$CH_3C(\cdot)=CHOH + O_2$	$HC(O)OH + CO + CH_3\cdot$	0.3	7
	$CH_3C(O)CHO + OH$	0.7	
$CH_3OCH_2OCH_3 + OH$	$H_2O + CH_3OCH_2OCH_2\cdot$	0.67	8
	$H_2O + CH_3OCH(\cdot)OCH_3$	0.33	
$CH*=CHOCH=CH* + OH$	$HOCH*CH(\cdot)CH=CH-O*$	0.24	9
	$HC(O)CH(\cdot)CH=CHOH$	0.76	
$CH*=CHOCH=CH* + NO_3$	$O_2NOCH*CH(\cdot)CH=CH-O*$	1	10
$CH_2=C(CH_3)CHO + O_3$	$HCHO + CH_3C[OO]-CHO \{*O_3Ole\}$	0.1	11
	$CH_3C(O)CHO + CH_2OO \{*O_3Ole\}$	0.9	
$CH_2=CHC(O)CH_3 + OH$	$CH_3C(O)CH(\cdot)CH_2OH$	0.7	12
	$CH_3C(O)CH(CH_2\cdot)OH$	0.3	
$CH_2=CHC(O)CH_3 + O_3$	$HCHO + CH_3C(O)CHOO \{*O_3Ole\}$	0.05	11
	$CH_3C(O)CHO + CH_2OO \{*O_3Ole\}$	0.95	
$CH_3C(\cdot)=C(CH_3)OH + O_2$	$CH_3C(O)OH + CO + CH_3\cdot$	0.26	7
	$CH_3C(O)COCH_3 + OH$	0.74	
$HOCH*CH(\cdot)CH=CH-O* \{*OHadd\}$	$HOCH*CH(\cdot)CH=CH-O*$	0.24	9
	$HC(O)CH(\cdot)CH=CHOH$	0.76	
$CO*C(O)COOCO*$	$CO_2 + CO + CO + CO$	1	13

Table A-57 (continued)

Reactants [a]	Products	Fraction	Ref [b]
$CH_2=CHC(=CH_2)CH_3 + O_3$	$HCHO + CH_2=CHC[OO]\text{-}CH_3$ $\{*O_3Ole\}$	0.2	14
	$HCHO + CH_2=C(CH_3)CHOO$ $\{*O_3Ole\}$	0.2	
	$CH_2=C(CH_3)CHO + CH_2OO$ $\{*O_3Ole\}$	0.39	
	$CH_2=CHC(O)CH_3 + CH_2OO$ $\{*O_3Ole\}$	0.16	
	$CH_2=CHC*(CH_3)CH_2O* + O_2$	0.025	
	$CH_2=C(CH_3)CH*CH_2O* + O_2$	0.025	
$CH_2=CHC(=CH_2)CH_3 + O_3P$	$CH_2=CHC*(CH_3)CH_2O*$	0.5	15
	$CH_2=C(CH_3)CH*CH_2O*$	0.25	
	$CH_2=CHC(O)CH_2\cdot + CH_3\cdot$	0.25	
$CH_2=CHC(=CH_2)CH_3 + NO_3$	$CH_2=CHC(\cdot)(CH_3)CH_2ONO_2$	1	14
$CH_2=CHC(=CH_2)CH_3 + Cl.$	$CH_3C(CH_2\cdot)=CHCH_2Cl$	0.42	16
	$CH_2=C(CH_3)CH(CH_2\cdot)Cl$	0.07	
	$CH_2=CHC(CH_3)(CH_2\cdot)Cl$	0.02	
	$CH_2=CHC(\cdot)(CH_3)CH_2Cl$	0.34	
	$HCl + CH_2=C(CH_2\cdot)CH=CH_2$	0.15	
$CH_2=CHC(=CH_2)CH_3 + OH$	$CH_3C(CH_2\cdot)=CHCH_2OH$	0.386	17
	$CH_2=CHC(\cdot)(CH_3)CH_2OH$	0.557	
	$CH_2=C(CH_3)CH(CH_2\cdot)OH$	0.028	
	$CH_2=CHC(CH_3)(CH_2\cdot)OH$	0.028	
$CH_3C*=CHCH=CH\text{-}O* + OH$	$CH_3C*(OH)CH(\cdot)CH=CH\text{-}O*$	0.3	9
	$CH_3C(\cdot)*CH=CHCH(OH)O*$	0.26	
	$CH_3C(\cdot)(OH)CH=CHCHO$	0.18	
	$CH_3C(O)CH(\cdot)CH=CHOH$	0.26	
$CH_3C*=CHCH=CH\text{-}O* + NO_3$	$CH_3C*(ONO_2)CH(\cdot)CH=CH\text{-}O*$	0.536	18
	$CH_3C(\cdot)*CH=CHCH(ONO_2)O*$	0.464	
$CH_3C*=CHOCH=CH* + OH$	$CH_3C(\cdot)*CH=CHOCH*OH$	0.63	9
	$CH_3C*=CHCH(OH)OCH(\cdot)*$	0.1	
	$CH_3C(=CHOH)CH(\cdot)CHO$	0.18	
	$CH_3C(\cdot)(CHO)CH=CHOH$	0.09	
$CH_3C*=CHOCH=CH* + NO_3$	$CH_3C(\cdot)*CH=CHOCH*ONO_2$	0.863	18
	$CH_3C*=CHCH(ONO_2)OCH(\cdot)*$	0.137	
$CH_2=CHC(CH_3)(CH_3)OH + OH$	$CH_3C(CH_3)(OH)CH(\cdot)CH_2OH$	0.667	19
	$CH_3C(CH_3)(OH)CH(CH_2\cdot)OH$	0.333	
$CH_2=CHC(CH_3)(CH_3)OH + O_3$	$HCHO + CH_3C(CH_3)(CHOO)OH$ $\{*O_3Ole\}$	0.3	20
	$CH_3C(CH_3)(CHO)OH + CH_2OO$ $\{*O_3Ole\}$	0.7	
$CH_3C(CH_3)(CH_3)OCH_3 + OH$	$H_2O + CH_3C(CH_3)(CH_3)OCH_2\cdot$	0.8	21
	$H_2O + CH_3C(CH_3)(CH_2\cdot)OCH_3$	0.2	
$CH_3C*(OH)CH(\cdot)CH=CH\text{-}O*$ {*OHadd}	$CH_3C(\cdot)(OH)CH=CHCHO$	0.375	9
	$CH_3C*(OH)CH(\cdot)CH=CH\text{-}O*$	0.625	
$CH_3C(\cdot)*CH=CHCH(OH)O*$ {*OHadd}	$CH_3C(O)CH(\cdot)CH=CHOH$	0.5	9
	$CH_3C(\cdot)*CH=CHCH(OH)O*$	0.5	
$CH_3C(\cdot)*CH=CHOCH*OH$ {*OHadd}	$CH_3C(=CHOH)CH(\cdot)CHO$	0.222	9
	$CH_3C(\cdot)*CH=CHOCH*OH$	0.778	
$CH_3C*=CHCH(OH)OCH(\cdot)*$ {*OHadd}	$CH_3C(\cdot)(CHO)CH=CHOH$	0.474	9
	$CH_3C*=CHCH(OH)OCH(\cdot)*$	0.526	
$CH_3C*=CHCH=C(CH_3)O* + OH$	$CH_3C(O)CH(\cdot)CH=C(CH_3)OH$	0.28	9
	$CH_3C(\cdot)*CH=CHC(CH_3)(OH)O*$	0.72	
$CH_3C*=CHCH=C(CH_3)O* + NO_3$	$CH_3C(\cdot)*CH=CHC(CH_3)(ONO_2)O*$	1	10

Table A-57 (continued)

Reactants [a]	Products	Fraction	Ref [b]
$CH_3C(\cdot)^*CH{=}CHC(CH_3)(OH)O^*$ {*OHadd}	$CH_3C(O)CH(\cdot)CH{=}C(CH_3)OH$	0.28	9
	$CH_3C(\cdot)^*CH{=}CHC(CH_3)(OH)O^*$	0.72	
$CH_3OC(O)CH_2CH_2CH_2C(O)OCH_3$ + OH	$H_2O + CH_3OC(O)CH_2CH_2CH_2C(O)OCH_2\cdot$	0.39	22
	$H_2O + CH_3OC(O)CH_2CH_2CH(\cdot)C(O)OCH_3$	0.2	
	$H_2O + CH_3OC(O)CH_2CH(\cdot)CH_2C(O)OCH_3$	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 (2000), ignoring H_2 + ketene route. Although Calvert (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_2, where N_2O5 is observed but no PAN compound. However, these products may be formed in the reaction of $HC(O)COC(O)\cdot$ with O_2 without the intermediacy of $HC(O)C(O)COOONO_2\cdot$.

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_2, so this is incorporated in the competing reaction where it is formed.

8 Based on ratio of yields of CH_3OCH_2OCHO relative to $CH_3OC(O)OCH_3$ + CH_3OCHO 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_3 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 $O_2\cdot$ additions that do not form allylic radicals are assumed to be equally probable.

18 This represents the effects of NO_3 addition followed by stabilization. Branching ratios for the two O_2 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 $CH_3OC(O)CH_2CH_2CH_2C(O)OH$ observed by Tuazon et al. (1999).

A5.4. Thermochemical Group Data

Table A-58. 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 A-58 (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 A-58 (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 A-58 (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 A-58 (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 A-58 (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 A-58 (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 A-58 (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 A-58 (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 A-59. 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 A-59 (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(ONO2)=CH..H, CH2=CH-C(CH3)=CH..H
Cd_(Cd)(CO)(CO*)	3.83	7	

Table A-59 (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 $CH_3C(CH=CH_2)(CH=CH_2)OH$ + $CH_3C(CH=CH_2)(CH_3)$-ONO_2 is the same as $CH_3C(CH=CH_2)(CH=CH_2)ONO_2$ + $CH_3C(CH=CH_2)(CH_3)OH$.

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 $CH_2=C(CHO)CHO$ as $CH_2=C(CH_3)CHO$.

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 A-60. 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 A-60 (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 A-60 (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 $CH_3C(..H)(CH_3)Ph$ bond dissociation energy of 84.75, which is estimated based on those for $Ph-CH_2...H$, $CH_2=CH-CH_2..H$ and $CH_2=CH-C(..H)(CH_3)CH_3$.

6 Derived to yield a $CH_3CH(..H)Ph$ bond dissociation energy of 86.92, which is estimated based on those for $Ph-CH_2\cdot.H$, $CH_2=CH-CH_2\cdot.H$ and $CH_2=CH-CH(..H)CH_3\cdot$.

7 Derived to yield a $CH_3C(..H)(OH)Ph$ bond dissociation energy of 84.76, which is estimated based on those for $Ph-CH_2\cdot.H$, $CH_2=CH-CH_2\cdot.H$ and $CH_2=CH-C(..H)(OH)CH_3$.

8 Rough estimate assuming that alpha-ONO_2 substitution in benzyl type radicals does not affect C..H bond dissociation energy. This is highly uncertain since effects on -ONO_2 substitution does not seem to be consistent for other cases.

9 Derived to yield the $Ph-CH_2..H$ bond dissociation energy of 90.44 kcal/mole (reference citation not found).

10 Derived to yield a $HOCH(..H)Ph$ bond dissociation energy of 82.26, which is estimated based on those for $Ph-CH_2..H$, $CH_2=CH-CH_2..H$ and $CH_2=CH-CH(..H)OH$.

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 $CX2=C(O\cdot)CH_3$ are similar to those derived for $(\cdot)CHXC(O)CH_3$, where X = H or $CH_3\cdot$. Uncertainty is at least 0.5 kcal/mole.

16 Assumed same $Ph-O\cdot.H$ bond dissociation energy as estimated for $CH_2=CH-O\cdot.H$.

17 Estimated assuming heats of formation for $CX2=CH(O\cdot)$ are similar to those derived for $(\cdot)CHX-CHO$, where X = H or $CH_3\cdot$ Uncertainty is at least 0.5 kcal/mole.

Table A-61. 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 A-62. Heats of formation (kcal/mole) assigned to specific species.

Stable species [a]	ΔHf	Ref [b]
H_2	0	1
N_2	0	1
H_2O	-57.80	2
HNO	26.10	2
NO	21.76	2
O_2	0	1
$HO_2\cdot$	2.94	2
HOOH	-32.48	2
NO_2	8.12	2
O_3	33.87	2
HOOOH	-21.51	2
NO_3	17.85	2
HNO_3	-32.10	2
NO_2OH	-32.10	2
HOOOOH	-10.61	2
$HO\text{-}ONO_2$	-12.91	2
NO_2ONO_2	3.18	2
CH4	-17.82	2
CO	-26.42	2
HCHO	-25.98	2
CH_3OH	-48.04	2
$HCO\text{-}NH_2$	-46.34	2
$NH_2C(O)NH_2$	-58.75	2
HC(O)OH	-90.49	2
CH_3OOH	-31.60	2
$HOCH_2OH$	-73.90	2
CO_2	-94.05	2
$CH_3\text{-}NO_2$	-17.76	2
HC(O)OOH	-68.19	2
$CH_3\text{-}ONO_2$	-29.21	2
$CH_2{=}CH_2$	12.52	2
CH_3CH_3	-20.04	2
$CH_3CH_2\text{-}NH_2$	-11.35	2
CH_3CHO	-39.70	3
CH_3CH_2OH	-56.12	2
CH_3OCH_3	-44.00	2
HC(O)CHO	-50.67	2
$CH_2{=}C(OH)OH$	-72.30	2
$CH_3C(O)OH$	-103.44	2
CH_3OCHO	-85.42	2
$HC(O)CH_2OH$	-76.00	2
CH_3CH_2OOH	-39.89	2
$HOCH_2CH_2OH$	-93.74	2
HC(O)CH(OH)OH	-118.55	2
$HOCH_2C(O)OH$	-139.34	2
HOC(O)COOH	-174.90	2
$HOCH_2OOCH_2OH$	-136.64	2
$CH_3C(O)O\text{-}ONO_2$	-57.39	2
$CH_2{=}CH\text{-}CH_3$	4.78	2
$CH_3CH_2CH_3$	-25.02	2
$CH_3CH_2CH_2\text{-}NH_2$	-16.92	2
$CH_3\text{-}N(CH_3)CH_3$	-5.64	2
$CH_2{=}CH\text{-}CHO$	-17.76	2

Radical species	ΔHf	Ref
H.	52.10	2
O_3P	59.57	2
OH	8.93	2
$CH_3\cdot$	35.06	2
$.CH_2\text{-}NH_2$	35.61	2
$CH_3\text{-}NH.$	44.00	2
$HCO\cdot$	10.55	2
$.CH_2OH$	-4.06	2
$CH_3O\cdot$	5.02	2
$CO(\cdot)OH$	-46.13	2
$CH_3OO\cdot$	2.15	2
$.CH_2\text{-}NO_2$	35.21	2
$NO_2CH(\cdot)NO_2$	40.39	2
$CH_2{=}CH.$	70.60	2
$CH_3CH_2\cdot$	28.90	2
$CH_3C(O)\cdot$	-2.46	2
$CH_3CH(\cdot)OH$	-12.72	2
$CH_3CH_2O\cdot$	-4.10	3
$CH_3OCH_2\cdot$	0.91	2
$.CH_2C(O)OH$	-60.47	2
$CH_3C(O)O\cdot$	-46.01	2
$CH_3\text{-}OC(O)\cdot$	-41.54	2
$CO(\cdot)CH_2OH$	-36.81	2
$HC(O)OCH_2\cdot$	-37.09	2
$CH_3CH_2OO\cdot$	-6.55	2
$CH_3OOCH_2\cdot$	17.07	2
$CH_3C(O)OO\cdot$	-36.90	2
$CH_2{=}CH\text{-}CH_2\cdot$	39.70	2
$CH_3CH(\cdot)CH_3$	20.70	2
$CH_3CH_2CH_2\cdot$	24.21	2
$CH_3CH_2C(O)\cdot$	-8.70	2
$CH_3C(O)CH_2\cdot$	-8.13	2
$CH_3CH_2OCH_2\cdot$	-7.48	2
$CH_3CH_2OC(O)\cdot$	-46.51	2
$CH_3C(O)OCH_2\cdot$	-50.33	2
$CH_3CH(OO\cdot)CH_3$	-15.60	3

Stable species [a]	ΔHf	Ref [b]
CH_3CH_2CHO	-44.36	2
$CH_3C(O)CH_3$	-51.90	3
$CH_3CH(CH_3)OH$	-65.15	2
$CH_3CH_2CH_2OH$	-60.97	2
$CH_3CH_2OCH_3$	-51.72	2
CH_3CH_2OCHO	-93.88	2
$CH_3C(O)CH_2OH$	-89.15	2
$CH_3OCH_2OCH_3$	-83.29	2
$CH_3C(CHO)(OH)OH$	-131.64	2
$HOCH_2CH(OH)CH_2OH$	-138.12	2
$CH_3CH_2CH_2CH_3$	-30.03	2
$CH_3C(O)OOC(O)CH_3$	-119.50	2

Radical species	ΔHf	Ref

[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)