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Gas-Phase Tropospheric Chemistry of Volatile Organic Compounds: 1. Alkanes and Alkenes

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Literature data (through mid-1996) concerning the gas-phase reactions of alkanes and alkenes (including isoprene and monoterpenes) leading to their first generation products are reviewed and evaluated for tropospheric conditions. The recommendations of the most recent IUPAC evaluation [J. Phys. Chem. Ref. Data, **26**, No. 3 (1997)] are used for the $\leq C_3$ organic compounds, unless more recent data necessitates reevaluation. The most recent review and evaluation of Atkinson [J. Phys. Chem. Ref. Data, Monograph **2**, 1 (1994)] concerning the kinetics of the reactions of OH radicals, NO_3 radicals, and O_3 is also updated for these two classes of volatile organic compounds. *© 1997 American Institute of Physics and American Chemical Society.* [S0047-2689(97)00302-4]

Key words: Alkanes; alkenes, kinetics; reaction mechanisms; reaction products; hydroxyl radical; nitrate radical; ozone.

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1. Introduction

Nonmethane volatile organic chemicals (VOCs) are introduced into the atmosphere from both anthropogenic and biogenic sources,[1–3] with estimated biogenic and anthropogenic nonmethane organic compound emissions of ~1150 and ~100 mil tonne yr^{-1}, respectively.[2,3] These VOC emissions lead to a complex series of chemical transformation and physical removal processes in the atmosphere which result in such effects as ozone formation in urban and rural areas[4] and in the global troposphere,[5] stratospheric ozone depletion,[2] long range transport of chemicals,[6] acid deposition,[7] and global climate change.[2,8] A large amount of experimental data concerning the chemical and physical processes of emitted organic compounds has been obtained from laboratory and ambient air studies over the past two decades, and there is now an understanding, at varying levels of detail, of the atmospheric chemistry of the various classes of VOCs emitted into the troposphere.[2,9–11] Because of the complexity of the physical and chemical processes involved and the often nonlinear response of the parameters of interest to changes in the input(s), the use of computer models incorporating the emissions, atmospheric chemistry, and atmospheric transport processes is generally necessary to elucidate the effects of emissions of anthropogenic and biogenic VOCs on the atmosphere.

The accuracies of chemical mechanisms used in the computer models designed to simulate the troposphere and/or stratosphere are then dependent on the accuracy of the individual rate constants, reaction mechanisms, and product distributions for the multitude of elementary reactions which actually occur in the atmosphere. It is therefore crucial that in addition to ambient air studies and experimental and theoretical studies of the kinetics, mechanisms, and products of the atmospheric reactions of organic compounds, there must be an ongoing, parallel effort to critically review and evaluate these data. These evaluations present the current status of knowledge of atmospheric chemistry for both modelers and experimental and theoretical researchers, and highlight the areas of uncertainty for designing future experimental and/or theoretical studies. The reactions of interest for modeling the chemistry occurring in the stratosphere have been reviewed and evaluated on an ongoing basis by the National Atmospheric and Space Administration (NASA) Panel for Data Evaluation (with the most recent evaluation being Number 11, published in 1994[10]) and by the IUPAC (formerly CODATA) Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry (with the most recent evaluation being Supplement V[11]). While these two data evaluation panels were originally concerned largely with stratospheric chemistry due to the potential for stratospheric ozone depletion by inputs of ClO_x and NO_x into the stratosphere, tropospheric chemistry is now being included to an increasing degree in both evaluations[10,11] through the tropospheric chemistry of the hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) proposed, and used, as alternatives to the chlorofluorocarbons and, especially in the more recent IUPAC evaluations,[11] by the inclusion of the reactions of $\leqslant C_3$ alkanes, alkenes, alkynes, and oxygen-, nitrogen-, and sulfur-containing organic compounds. The gas-phase atmospheric reactions of $\leqslant C_3$ HFCs, HCFCs, and organosulfur compounds are therefore dealt with in detail on an ongoing basis by these evaluations.[10,11]

However, the vast majority of the at least several hundred VOCs emitted into the troposphere are $\geqslant C_4$ species, and there is an obvious need for the review and evaluation of the chemical reactions which occur in the troposphere for these VOCs. The tropospheric chemistry of VOCs (alkanes, alkenes, alkynes, aromatic hydrocarbons, their oxygen- and nitrogen-containing degradation products, carbonyls, alcohols, and ethers) has been reviewed and evaluated by Atkinson in 1990[12] and 1994.[9] In addition to these reviews of tropospheric VOC chemistry,[9,12] there have been critical reviews and evaluations of the kinetics and mechanisms of the reactions of organic compounds with OH radicals,[9,13,14] NO_3 radicals,[9,15] and O_3,[9,16] with the most recent being the monograph of Atkinson[9] which updates earlier reviews.[12–16]

The present article deals with the tropospheric chemistry of alkanes and alkenes leading to first generation products, and updates and extends the Atkinson[9] review to take into account more recent data. Alkanes and alkenes constitute ~60% of the carbon content of nonmethane VOCs in the highly urbanized (and dominated by anthropogenic emissions) Los Angeles air basin,[17] and alkenes are estimated to constitute ~55% of the carbon content of nonmethane VOCs emitted from vegetation worldwide.[3]

Only gas-phase reactions are discussed, because, while highly important under many tropospheric conditions, the reactions occurring in the particle and/or aqueous phase (for example, in fog, cloud, and rain droplets), on surfaces (heterogeneous reactions), and gas-to-particle conversion are beyond the scope of the present article. As in the previous review,[9] the most recent NASA[10] and, especially, IUPAC[11] evaluations are used for the $\leq C_3$ reactions, generally without reevaluation or detailed discussion. In addition, previous articles[9,13–16] dealing with the kinetics and mechanisms of the gas-phase reactions of OH radicals, NO_3 radicals, and O_3 with alkanes and alkenes have been updated, with the data reported since approximately 1993[9] being tabulated, discussed, and evaluated in Secs. 3, 4, and 5. In these sections, discussion is limited to those reactions for which new information has become available since the most recent review article[9] was prepared. Previous data are not included in the tables of rate constants, and hence the previous reviews[9,13–16] must be consulted for rate constant and mechanistic information available and used at the times of their finalization. The literature through mid-1996 has been included in this article.

Rate constants k determined as a function of temperature are generally cited using the Arrhenius expression, $k = A\ e^{-B/T}$, where A is the Arrhenius pre-exponential factor and B is in K. In some cases rate constants have been obtained over extended temperature ranges and the simple Arrhenius expression, as expected, does not hold, with curvature in the Arrhenius plots being observed.[9,14] In these cases, a three parameter equation, $k = CT^n\ e^{-D/T}$ has been used,[9,11,14] generally with $n = 2$ ($k = CT^2\ e^{-D/T}$). The equation, $k = CT^n\ e^{-D/T}$, can be transformed into the Arrhenius expression, $k = A\ e^{-B/T}$, centered at a temperature T, with $A = Ce^nT^n$ and $B = D + nT$.

Reactions which are in the falloff region between second and third order kinetics or between first and second order kinetics are dealt with by using the Troe falloff expression,[18] with

$$k = \left(\frac{k_0[M]}{1 + \dfrac{k_0[M]}{k_\infty}} \right) F^{[1 + (\log_{10} k_0[M]/k)^2]^{-1}},$$

where k_0 is the limiting low pressure rate constant, k_∞ is the limiting high pressure rate constant, [M] is the concentration of the third body gas (generally air in this article), and F is the broadening coefficient. In general, the rate constants k_0 and k_∞ have T^n temperature dependencies. The temperature dependence of F is given by $F = e^{-T/T^*}$ for temperatures appropriate to the troposphere, where T^* is a constant for a given reaction.[11,19] All rate constants are given in cm molecule s units, and pressures are generally given in Torr (1 Torr = 133.3 Pa).

2. Gas-Phase Tropospheric Chemistry of Organic Compounds

2.1. Alkanes

The atmospheric chemistry of alkanes has been reviewed and discussed previously.[1–3] The kinetics and mechanisms of the reactions of alkanes with OH radicals, NO_3 radicals, and O_3 have also been reviewed and evaluated previously,[3–7] and these reviews and evaluations are updated in Secs. 3.1, 4.1, and 5.1, respectively. The gas-phase reactions of the alkanes with O_3 are of negligible importance as an atmospheric loss process, since the available data (Ref. 4 and Sec. 5.1) show that the room temperature rate constants for these reactions are $<10^{-22}$ cm^3 molecule^{-1} s^{-1}. Under atmospheric conditions, the potential loss processes for the alkanes involve gas-phase reactions with OH and NO_3 radicals and, at least under certain conditions,[8] Cl atoms.

2.1.1. OH Radical Reactions

The kinetics and mechanisms of the reactions of the OH radical with alkanes have been reviewed and evaluated by Atkinson,[3,6] and the 1989[6] and 1994[3] evaluations are updated

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TABLE 1. Rate constants k at 298 K and parameters C, D, and n in $k = CT^n \, e^{-D/T}$ for the reactions of OH radicals with alkanes (see Sec. 3.1)

Alkane	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	$10^{18} \times C$ (cm^3 molecule^{-1} s^{-1})	n	D (K)
Methane	0.00618	0.0965	2.58	1082
Ethane	0.254	15.2	2	498
Propane	1.12	15.5	2	61
n-Butane	2.44	16.9	2	−145
2-Methylpropane	2.19	11.6	2	−225
n-Pentane	4.00	24.4	2	−183
2-Methylbutane	3.7			
2,2-Dimethylpropane	0.848	18.0	2	189
n-Hexane	5.45	15.3	2	−414
2-Methylpentane	5.3			
3-Methylpentane	5.4			
2,2-Dimethylbutane[a]	2.34	3.22×10^7	0	781
2,3-Dimethylbutane	5.78	12.4	2	−494
n-Heptane	7.02	15.9	2	−478
2,2-Dimethylpentane	3.4			
2,4-Dimethylpentane	5.0			
2,2,3-Trimethylbutane	4.24	8.46	2	−516
n-Octane	8.71	27.6	2	−378
2,2-Dimethylhexane	4.8			
2,2,4-Trimethylpentane	3.57	20.8	2	−196
2,3,4-Trimethylpentane	7.1			
2,2,3,3-Tetramethylbutane	1.05	19.1	2	144
n-Nonane	10.0	25.1	2	−447
2-Methyloctane	10.1			
4-Methyloctane	9.7			
2,3,5-Trimethylhexane	7.9			
3,3-Diethylpentane	4.9			
n-Decane	11.2	31.3	2	−416
n-Undecane	12.9			
n-Dodecane	13.9			
n-Tridecane	16			
n-Tetradecane	18			
n-Pentadecane	21			
n-Hexadecane	23			
Cyclopropane	0.084			
Cyclobutane	1.5			
Cyclopentane	5.02	25.7	2	−235
Cyclohexane	7.21	28.8	2	−309
Isopropylcyclopropane	2.7			
Cycloheptane	13			
Methylcyclohexane	10.0			
Bicyclo[2.2.1]heptane	5.3			
Quadricyclo[2.2.1.$0^{2,6}0^{3,5}$]heptane	1.8			
Cyclooctane	14			
Bicyclo[2.2.2]octane	14			
Bicyclo[3.3.0]octane	11			
1,1,3-Trimethylcyclohexane	8.7			
cis-Bicyclo[4.3.0]nonane	17			
trans-Bicyclo[4.3.0]nonane	17			
cis-Bicyclo[4.4.0]decane	19			
trans-Bicyclo[4.4.0]decane	20			
Tricyclo[5.2.1.$0^{2,6}$]decane	11			
Tricyclo[3.3.1.$1^{3,7}$]decane	22			
2,6,6-Trimethylbicyclo[3.1.1]heptane	13			
1,7,7-Trimethyltricyclo[2.2.1.$0^{2,6}$]heptane	2.8			

[a]The Arrhenius expression cited is only applicable over the restricted temperature range 245–330 K.

in Sec. 3.1. Rate constants have been determined over significant temperature ranges for a number of alkanes and, as expected from theoretical considerations, the Arrhenius plots exhibit curvature.[3,6] Accordingly, the three parameter expression $k = CT^2 \, e^{-D/T}$ is generally used (see also Sec. 3.1). The 298 K rate constants and the recommended parameters C and D are given in Table 1 (see also Sec. 3.1). Room temperature rate constants for alkanes for which recommendations have not been given (generally due to only single studies being carried out) are also given in Table 1.

These OH radical reactions proceed via H-atom abstraction from the C–H bonds,

$$\mathrm{OH}+\mathrm{RH}\rightarrow \mathrm{H_2O}+\dot{\mathrm{R}},$$

leading to the formation of an alkyl radical, $\dot{\mathrm{R}}$. The rate constants for these OH radical reactions with alkanes can be fit to within a factor of ~2 over the temperature range 250–1000 K from consideration of the CH_3–, –CH_2–, and >CH– groups in the alkane and the neighboring substituent groups.[5,9] Thus

$$k(\mathrm{CH_3{-}X})=k_{\mathrm{prim}}F(\mathrm{X}),$$

$$k(\mathrm{X{-}CH_2{-}Y})=k_{\mathrm{sec}}F(\mathrm{X})F(\mathrm{Y}),$$

and

$$k\left(\mathrm{X{-}CH}\begin{matrix}\diagup \mathrm{Y}\\ \diagdown \mathrm{Z}\end{matrix}\right)=k_{\mathrm{tert}}F(\mathrm{X})F(\mathrm{Y})F(\mathrm{Z}),$$

where k_{prim}, k_{sec}, and k_{tert} are the OH radical rate constants per $-CH_3$, $-CH_2-$, and >CH– group, respectively, for X=Y=Z=$-CH_3$ as the standard substituent group, and $F(X)$, $F(Y)$, and $F(Z)$ are the substituent factors for X, Y, and Z substituent groups. As derived by Kwok and Atkinson[9] from the data base available in 1995 (primarily the evaluations of Atkinson[3,6]), $k_{\mathrm{prim}}=4.49\times10^{-18}\ T^2 e^{-320/T}$ cm^3 molecule^{-1} s^{-1}, $k_{\mathrm{sec}}=4.50\times10^{-18}\ T^2 e^{253/T}$ cm^3 molecule^{-1} s^{-1}, $k_{\mathrm{tert}}=2.12\times10^{-18}\ T^2 e^{696/T}$ cm^3 molecule^{-1} s^{-1}, $F(-CH_3)=1.00$, and $F(-CH_2-)=F(>CH-)=F(>C<)=e^{62/T}$. For cycloalkanes, the effects of ring strain are taken into account by means of ring factors,[9] of 0.020, 0.28, and 0.64 at 298 K for 3-, 4-, and 5-member rings, respectively, and with the ring strain factor for a 6-member strain-free ring being 1.00[9] and those for 7- and 8-member rings being ~1.0 at 298 K.[9] It should be noted that many of the 298 K rate constants for the OH radical reactions with alkanes recommended here (Table 1) are ~4% lower than those used in the optimization of the parameters for the OH radical reaction rate constant estimation method.[9] This estimation technique not only allows the calculation of OH radical reaction rate constants for alkanes for which experimental data do not exist, but also allows the initially formed isomeric alkyl radical distribution to be approximately estimated for a given alkane.

2.1.2. NO_3 Radical Reactions

The NO_3 radical reacts with the alkanes with rate constants at room temperature in the range 10^{-17} to 10^{-16} cm^3 molecule^{-1} s^{-1} (Refs. 3 and 7 and Sec. 4.1). The recommended 298 K rate constants and temperature dependent parameters, taken from Refs. 3 and 7 and Sec. 4.1, are given in Table 2. Table 2 also includes the room temperature rate constants for alkanes for which only a single study has been carried out and for which no recommendations are given. Under atmospheric conditions, the nighttime reactions of the alkanes with the NO_3 radical can be calculated to be typically 2 orders of magnitude less important as an atmospheric loss process than are the daytime OH radical reactions[7] (although the relative importance of the NO_3 radical reactions may vary widely, depending on the tropospheric OH radical and NO_3 radical concentrations[7]).

TABLE 2. Rate constants k at 298 K and temperature dependent parameters, $k=A\ e^{-B/T}$, for the reaction of NO_3 radicals with alkanes (from Sec. 4.1 and Refs. 3 and 7)

Alkane	$10^{12}\times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	$10^{17}\times k$ (cm^3 molecule^{-1} s^{-1})
Methane			<0.1
Ethane			0.14[a]
Propane			1.7[a]
n-Butane	2.76	3279	4.59
2-Methylpropane	3.05	3060	10.6
n-Pentane			8.7[b]
2-Methylbutane	2.99	2927	16.2
n-Hexane			11[b]
2-Methylpentane			18[b]
3-Methylpentane			22[b]
2,3-Dimethylbutane			44[b]
Cyclohexane			14[b]
n-Heptane			15[b]
2,4-Dimethylpentane			15[b]
2,2,3-Trimethylbutane			24[b]
n-Octane			19[b]
2,2,4-Trimethylpentane			9[b]
2,2,3,3-Tetramethylbutane			<5
n-Nonane			23[b]
n-Decane			28[b]

[a] Estimated from group rate constants, see text.

[b] The measured rate constants of Atkinson *et al.*[10,11] and Aschmann and Atkinson[12] at 296±2 K have been extrapolated to 298 K using an estimated temperature dependence of $B=3000$ K.

Similar to the OH radical reactions, these NO_3 radical reactions proceed via H-atom abstraction from the C–H bonds.

$$\mathrm{NO_3}+\mathrm{RH}\rightarrow \mathrm{HONO_2}+\dot{\mathrm{R}}.$$

For the *n*-alkane series, the 298 K rate constants and the distribution of initially formed alkyl radical isomers can be calculated from $-CH_3$ and $-CH_2-$ group rate constants and substituent factors,[12] with $k_{\mathrm{prim}}=7.0\times10^{-19}$ cm^3 molecule^{-1} s^{-1}, $k_{\mathrm{sec}}=1.22\times10^{-17}$ cm^3 molecule^{-1} s^{-1}, $F(-CH_3)=1.00$ and $F(-CH_2-)=1.67$ at 298 K.[12] Unfortunately, the rate constants for the reactions of the NO_3 radical with branched alkanes cannot be reliably calculated using such an approach.[12]

2.1.3. Cl Atom Reactions

Rate constants for the reactions of the Cl atom with a number of alkanes are now available, and Table 3 gives room temperature rate constants and the temperature dependent parameters for these reactions. Rate constants for the reactions of the Cl atom with methane, ethane, propane, *n*-butane, 2-methylpropane, and 2,2-dimethylpropane have been measured using absolute rate techniques,[13–16] and the rate constants given in Table 3 for these alkanes are those recommended by the IUPAC evaluation[13] (methane and ethane) or are based on the absolute rate constants of Lewis *et al.*,[14] Biechert *et al.*,[15] and Kambanis *et al.*[16] (propane,

TABLE 3. Rate constants k at 298 K and temperature dependent parameters, $k=A\ e^{-B/T}$, for the gas-phase reactions of Cl atoms with alkanes[a]

Alkane	$10^{12}\times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	$10^{11}\times k$ (cm^3 molecule^{-1} s^{-1})	Reference
Methane	9.6	1350	0.010	Atkinson *et al.*[13]
Ethane	81	95	5.9	Atkinson *et al.*[13]
Propane	120	−40	13.7	Lewis *et al.*;[14] Biechert *et al.*[15]
n-Butane	21.8	0	21.8	Lewis *et al.*;[14] Biechert *et al.*[15]
2-Methylpropane			14.3	Lewis *et al.*;[14] Biechert *et al.*[15]
n-Pentane			28	Aschmann and Atkinson,[17] Hooshiyar and Niki[18]
2-Methylbutane			22	Aschmann and Atkinson;[17] Hooshiyar and Niki[18]
2,2-Dimethylpropane	11.1	0	11.1	Kambanis *et al.*[16]
n-Hexane			34	Aschmann and Atkinson;[17] Hooshiyar and Niki[18]
2-Methylpentane			29	Aschmann and Atkinson;[17] Hooshiyar and Niki[18]
3-Methylpentane			28	Aschmann and Atkinson[17]
2,3-Dimethylbutane			23	Aschmann and Atkinson;[17] Hooshiyar and Niki[18]
Cyclohexane			35	Aschmann and Atkinson[17]
n-Heptane			39	Aschmann and Atkinson;[17] Hooshiyar and Niki[18]
2-Methylhexane			35	Hooshiyar and Niki[18]
2,4-Dimethylpentane			29	Aschmann and Atkinson[17]
2,2,3-Trimethylbutane			20	Aschmann and Atkinson[17]
Methylcyclohexane			39	Aschmann and Atkinson[17]
n-Octane			46	Aschmann and Atkinson;[17] Hooshiyar and Niki[18]
2,2,4-Trimethylpentane			26	Aschmann and Atkinson;[17] Hooshiyar and Niki[18]
2,2,3,3-Tetramethylbutane			17.5	Aschmann and Atkinson[17]
n-Nonane			48	Aschmann and Atkinson[17]
n-Decane			55	Aschmann and Atkinson[17]
cis-Bicyclo[4,4,0]decane			48	Aschmann and Atkinson[17]

[a] The rate constants measured by Aschmann and Atkinson[17] and Hooshiyar and Niki[18] are placed on an absolute basis by using a rate constant for the reaction of the Cl atom with *n*-butane of 2.18×10^{-10} cm^3 molecule^{-1} s^{-1}.

n-butane, 2-methylpropane, and 2,2-dimethylpropane). For the remaining alkanes listed in Table 3, the rate constants determined by Aschmann and Atkinson[17] and Hooshiyar and Niki[18] from relative rate studies are placed on an absolute basis using the recommended rate constant for the reaction of the Cl atom with *n*-butane of 2.18×10^{-10} cm^3 molecule^{-1} s^{-1} at room temperature (Table 3). Because of the differing rate constants used for the reaction of the Cl atom with *n*-butane, the rate constants for the $>C_4$ alkanes given in Table 3 are 12% higher than those reported by Aschmann and Atkinson[17] and Hooshiyar and Niki.[18]

The rate constants for the reactions of the Cl atom with alkanes at 298 K (and presumably the distribution of initially formed alkyl radicals) can be reliably calculated using an approach exactly analogous to that used for the calculation of OH radical reaction rate constants.[17,18] Using the rate constant for the reaction of the Cl atom with *n*-butane given in Table 3, the group rate constants and substituent factors for the Cl atom reactions are $k_{\text{prim}}=3.5\times10^{-11}$ cm^3 molecule^{-1} s^{-1}, $k_{\text{sec}}=9.3\times10^{-11}$ cm^3 molecule^{-1} s^{-1}, $k_{\text{tert}}=6.8\times10^{-11}$ cm^3 molecule^{-1} s^{-1}, $F(-CH_3)=1.00$ and $F(-CH_2-)=F(>CH-)=F(>C<)=0.79$ at 298 K.[17,18] The rate constants for the $\geq C_3$ alkanes are expected to be essentially independent of temperature over the temperature range encountered in the atmosphere (see Table 3 and Refs. 14 and 16).

2.1.4. Alkyl ($\dot{R}$) Radical Reactions

The available kinetic and mechanistic data show that under tropospheric conditions the alkyl radicals react with O_2 to form an alkyl peroxy radical.

$$\dot{R}+O_2\xrightarrow{M}R\dot{O}_2.$$

The presently available room temperature rate constants for O_2 addition to alkyl radicals are given in Table 4. The methyl and ethyl radical reactions are in the falloff regime at and below atmospheric pressure at room temperature and below, and the IUPAC recommended values of k_0, k_∞, and F for these O_2 reactions are:[13] methyl, $k_0=1.0\times10^{-30}\ (T/300)^{-3.3}$ cm^6 molecule^{-2} s^{-1}, $k_\infty=1.8\times10^{-12}\ (T/300)^{1.1}$ cm^3 molecule^{-1} s^{-1} and $F=0.27$ at 298 K; ethyl, $k_0=5.9\times10^{-29}\ (T/300)^{-3.8}$ cm^6 molecule^{-2} s^{-1}, $k_\infty=7.8\times10^{-12}$ cm^3 molecule^{-1} s^{-1} and $F=0.54$ at 298 K. In addition, Xi *et al.*[21] have measured a rate constant of $k_\infty=2.1\times10^{-12}\ (T/300)^{-2.1}$ cm^3 molecule^{-1} s^{-1} for the reaction of O_2 with the 2,2-dimethyl-1-propyl (neopentyl) radical over the temperature range 266–374 K.

The recent study of Dilger *et al.*[22] of the kinetics of the addition of the C_2H_5 radical to O_2 is in general agreement with the IUPAC recommendation.[13] Dilger *et al.*[22] obtained a value of $k_\infty=(8.7\pm0.8)\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 294 K, with the measured rate constant at 1.5 bar (1125 Torr) of ethene being close to the high pressure limit. The rate con-

TABLE 4. High pressure rate cosntants k_∞ for the reactions of alkyl radicals ($\dot{R}$) with O_2 at room temperature.

$\dot{R}$	$10^{12}\times k_\infty$ (cm^3 $molecule^{-1}$ s^{-1})	T (K)	Reference
Methyl	$1.8^{+1.8}_{-0.9}$	298	Atkinson *et al.*[13]
	0.95^a	298	
Ethyl	$7.8^{+4.6}_{-2.9}$	298	Atkinson *et al.*[13]
	7.0^a	298	
1-Propyl	8^{+5}_{-3}	298	Atkinson *et al.*[13]
2-Propyl	$11^{+11}_{-5.5}$	298	Atkinson *et al.*[13]
1-Butyl	7.5±1.4	300	Lenhardt *et al.*[19]
2-Butyl	16.6±2.2	300	Lenhard *et al.*[19]
2-Methyl-2-propyl	23.4±3.9	300	Lenhardt *et al.*[19]
2-Methyl-1-propyl	2.9±0.7	298±3	Wu and Bayes[20]
2,2-Dimethyl-1-propyl[b]	2.4±0.4	293±1	Xi *et al.*[21]
Cyclopentyl	17±3	293	Wu and Bayes[20]
Cyclohexyl	14±2	298±3	Wu and Bayes[20]

[a] Value at 760 Torr total calculated from the falloff expression (see text).
[b] Note $k=2.1\times10^{-12}$ $(T/300)^{-2.1}$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 266–374 K.[21]

stant at 1.5 bar of ethene was observed to decrease slightly with temperature over the range 222–475 K, with measured rate constants of (in units of 10^{-12} cm^3 $molecule^{-1}$ s^{-1}) 8.5 ±0.5 at 222 K, 9.3±0.6 at 243 K, 6.8±0.4 at 319 K, 6.2 ±0.3 at 387 K, and 5.1±0.3 at 475 K.[22]

The reactions of alkyl radicals with O_2 proceed by initial addition to form an activated complex which is either collisionally stabilized or decomposes back to reactants or to an HO_2 radical plus an alkene.[23]

$$\begin{tikzcd} \dot{R}+O_2 \arrow[r, shift left] & {[\dot{R}O_2]^*} \arrow[l, shift left] \arrow[r] \arrow[d, "M"] & HO_2+\text{alkene} \\ & \dot{R}O_2 & \end{tikzcd}$$

At the high pressure limit, alkyl peroxy radical formation is therefore the sole reaction process. At 760 Torr and 298 K, the formation yield of $C_2H_4+HO_2$ from the reaction of the ethyl radical with O_2 is 0.004.[13]

Hence, for the alkyl radicals studied to date, under tropospheric conditions the reactions with O_2 proceed via addition to form an alkyl peroxy radical, with a room temperature rate constant of $\gtrsim10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. For the smaller alkyl radicals these reactions are in the falloff regime between second and third order kinetics, but are reasonably close to the high pressure rate constant at 760 Torr of air. Under atmospheric conditions, reaction with O_2 is the sole loss process for alkyl radicals, and other reactions need not be considered.

2.1.5. Alkyl Peroxy ($\dot{R}O_2$) Radical Reactions

As discussed above, alkyl peroxy ($\dot{R}O_2$) radicals are formed from the addition of O_2 to alkyl radicals. Under tropospheric conditions, $\dot{R}O_2$ radicals react with NO (by two pathways),

$$\begin{tikzcd} & RONO_2 \\ \dot{R}O_2+NO \arrow[ur, "M"] \arrow[dr] & \\ & \dot{R}O+NO_2 \end{tikzcd}$$

with HO_2 radicals,

$$\dot{R}O_2+HO_2\rightarrow ROOH+O_2$$

with $\dot{R}O_2$ radicals (either self-reaction or reaction with other alkyl peroxy radicals),

$$\dot{R}O_2+\dot{R}O_2\rightarrow\text{products}$$

and with NO_2,

$$\dot{R}O_2+NO_2\xrightarrow{M}ROONO_2.$$

The reaction pathways which occur depend on the NO to HO_2 and/or $\dot{R}O_2$ radical concentration ratios, and in the troposphere the reaction with NO is expected to dominate for NO concentrations $\gtrsim7\times10^8$ molecule cm^{-3}.[24,25] The reaction of $\dot{R}O_2$ radicals with NO_2 to form alkyl peroxynitrates is generally unimportant under lower tropospheric conditions due to the rapid thermal decomposition of the alkyl peroxynitrates back to reactants.[3,13]

2.1.5.a. Reaction with NO. The room temperature rate constants and the temperature dependent parameters determined from absolute rate studies are given in Table 5. While a number of such studies have been carried out for the reaction of the methyl peroxy radical with NO[26–37] (with three temperature dependent studies[30,31,36]), for each of the other alkyl peroxy radical reactions only a few studies (and often only a single study) have been carried out. The most extensive studies are those of Howard and coworkers[36,42,45] carried out as a function of temperature for the methyl peroxy,[36] ethyl peroxy,[42] and 1- and 2-propyl peroxy[42,45] radicals. The 298 K rate constant measured by Villalta *et al.*[36] for the methyl peroxy radical reaction is in excellent agreement with the majority of the previous absolute rate constants (Table 5), and with the most recent NASA[48] and IUPAC[13] evaluations. Accordingly, the recommended rate constants for the reactions of alkyl peroxy radicals with NO are based on the rate constant data of Howard and coworkers.[36,42,45,47] For the methyl peroxy radical reaction, the rate constant data of Villalta *et al.*[36] are recommended, with

$$k(CH_3\dot{O}_2+NO)=2.9\times10^{-12}\ e^{285/T}\ cm^3\ molecule^{-1}\ s^{-1}$$
$$=7.5\times10^{-12}\ cm\ molecule^{-1}\ s^{-1}$$
$$\text{at 298 K.}$$

This recommendation differs somewhat from the IUPAC recommendation[13] of $k(CH_3\dot{O}_2+NO)=4.2\times10^{-12}\ e^{180/T}$ cm^3 $molecule^{-1}$ s^{-1} (7.6×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 298 K). Based on the data of Howard and coworkers[42,45,47] for

TABLE 5. Absolute room temperature rate constants k and temperature dependent parameters, $k=A\ e^{-B/T}$, for the reactions of $R\dot{O}_2$ radicals with NO

$R\dot{O}_2$	$10^{12}\times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	$10^{12}\times k$ (cm^3 molecule^{-1} s^{-1})	At T (K)	Reference
$CH_3\dot{O}_2$			8.0 ± 2.0	295 ± 2	Plumb *et al.*[26]
			3.0 ± 0.2	~298	Adachi and Basco[27]
			6.5 ± 2.0	298	Cox and Tyndall[28]
			7.1 ± 1.4	298	Sander and Watson[29]
	6.3 ± 2.5	-86 ± 112	7.8 ± 1.2	298	Ravishankara *et al.*[30]
	2.1 ± 1	-380 ± 250	7.7 ± 0.9	296	Simonaitis and Heicklen[31]
			8.6 ± 2.0	295	Plumb *et al.*[32]
			7 ± 2	298	Zellner *et al.*[33]
			8.8 ± 1.4	295 ± 2	Sehested *et al.*[34]
			11.2 ± 1.4	298 ± 5	Masaki *et al.*[35]
	2.8 ± 0.5	-285 ± 60	7.5 ± 1.3	298	Villalta *et al.*[36]
			7.5 ± 1.0	298	Helleis *et al.*[37]
$CH_3CH_2\dot{O}_2$			2.66 ± 0.17	~298	Adachi and Basco[38]
			8.9 ± 3.0	295	Plumb *et al.*[39]
			8.5 ± 1.2	295 ± 2	Sehested *et al.*[34]
			8.2 ± 1.6	298	Daële *et al.*[40]
	$3.1^{+1.5}_{-1.0}$	-330 ± 110	10.0 ± 1.5	295	Maricq and Szente[41]
	2.6 ± 0.4	-380 ± 70	9.3 ± 1.6	298	Eberhard and Howard[42]
$CH_3CH_2CH_2\dot{O}_2$	2.9 ± 0.5	-350 ± 60	9.4 ± 1.6	298	Eberhard and Howard[42]
$(CH_3)_2CH\dot{O}_2$			3.50 ± 0.34	~298	Adachi and Basco[43]
			5.0 ± 1.2	290	Peeters *et al.*[44]
	2.7 ± 0.5	-360 ± 60	9.0 ± 1.5	298	Eberhard *et al.*[45]
			9.1 ± 1.5	298	Eberhard and Howard[42]
$(CH_3)_3C\dot{O}_2$			>1	298	Anastasi *et al.*[46]
			4.0 ± 1.1	290	Peeters *et al.*[44]
			7.9 ± 1.3	297 ± 2	Eberhard and Howard[47]
$(CH_3)_3CCH_2\dot{O}_2$			4.7 ± 0.4	295 ± 2	Sehested *et al.*[34]
$CH_3CH(\dot{O}_2)CH_2CH_2CH_3$			8.0 ± 1.4	297 ± 2	Eberhard and Howard[47]
cyclo-$C_5H_9\dot{O}_2$			10.9 ± 1.9	297 ± 2	Eberhard and Howard[47]
$(CH_3)_3CC(CH_3)_2CH_2\dot{O}_2$			1.8 ± 0.2	295 ± 2	Sehested *et al.*[34]
$CH_2{=}CHCH_2\dot{O}_2$			10.5 ± 1.8	297 ± 2	Eberhard and Howard[47]

the $\geqslant C_2$ alkyl peroxy radicals (Table 5), it is recommended that the rate constants for the $\geqslant C_2$ alkyl peroxy radicals are identical, with

$$k(R\dot{O}_2+NO)=2.7\times10^{-12}\ e^{360/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

$$=9.0\times10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K}.$$

These recommendations differ from those given in the most recent NASA[48] and IUPAC[13] evaluations (especially for the ethyl peroxy and propyl peroxy radicals in the IUPAC evaluation[13]).

The reaction of the $CH_3\dot{O}_2$ radical with NO has been shown to proceed primarily by,[13,30,33,48]

$$CH_3\dot{O}_2+NO\rightarrow CH_3\dot{O}+NO_2$$

and Plumb *et al.*[39] have also shown that the reaction of the $C_2H_5\dot{O}_2$ radical with NO leads to the formation of NO_2 with a yield of $\geqslant0.80$ at 295 K and 5 Torr total pressure of helium diluent.

For the larger alkyl peroxy radicals, the reaction pathway forming the alkyl nitrate becomes important.[49–56] At room temperature and atmospheric pressure of air, the product data of Atkinson *et al.*,[51–54] Harris and Kerr,[55] and Aschmann *et al.*[56] show that for the C_2–C_8 secondary alkyl peroxy radicals the rate constant ratio $k_a/(k_a+k_b)$, where k_a and k_b are the rate constants for the reaction pathways (a) and (b), respectively,

$$R\dot{O}_2+NO \longrightarrow \begin{cases} \xrightarrow{M} RONO_2 & \text{(a)} \\ \longrightarrow R\dot{O}+NO_2 & \text{(b)} \end{cases}$$

increases monotonically with the carbon number of the $R\dot{O}_2$ radical. Furthermore, for a given alkyl peroxy radical the rate constant ratio $k_a/(k_a+k_b)$ (and, equivalently, the rate constant ratio k_a/k_b), is pressure and temperature dependent, increasing with increasing pressure and with decreasing temperature.[52,54,55]

The pressure and temperature dependent rate constant ratios k_a/k_b for secondary alkyl peroxy radicals[51–54] are fit by the empirical expression[57]

$$\frac{k_a}{k_b}=\left[\frac{Y_0^{300}[M](T/300)^{-m_0}}{1+\dfrac{Y_0^{300}[M](T/300)^{-m_0}}{Y_\infty^{300}(T/300)^{-m_\infty}}}\right]F^z,$$

TABLE 6. Recommended rate constant parameters k_0, k_∞, and F for the gas-phase reactions of $\mathrm{R\dot{O}_2}$ radicals with NO_2, together with calculated rate constants k at 298 K and 760 Torr total pressure[a]

$\mathrm{R\dot{O}_2}$	k_0 (cm^6 molecule^{-2} s^{-1})	k_∞ (cm^3 molecule^{-1} s^{-1})	F (298 K)	$10^{12}\times k$ (cm^3 molecule^{-1} s^{-1})[b]
$\mathrm{CH_3\dot{O}_2}$	$2.5\times10^{-30}(T/300)^{-5.5}$	7.5×10^{-12}	0.36	3.9
$\mathrm{C_2H_5\dot{O}_2}$	$1.3\times10^{-29}(T/300)^{-6.2}$	8.8×10^{-12}	0.31	6.1

[a]From Atkinson *et al.*[13]
[b]At 298 K and 760 Torr total pressure.

where

$$z=\left(1+\left\{\log_{10}\left[\frac{Y_0^{300}[\mathrm{M}](T/300)^{-m_0}}{Y_\infty^{300}(T/300)^{-m_\infty}}\right]\right\}^2\right)^{-1}$$

and $Y_0^{300}=\alpha\ e^{\beta n}$, n is the number of carbon atoms in the alkyl peroxy radical, and α and β are constants. The evaluation of Carter and Atkinson[57] of the experimental data of Atkinson *et al.*[51–54] leads to $Y_\infty^{300}=0.826$, $\alpha=1.94\times10^{-22}$ cm^3 molecule^{-1}, $\beta=0.97$, $m_0=0$, $m_\infty=8.1$, and $F=0.411$. The experimental data of Harris and Kerr[55] for the heptyl nitrates formed from the OH radical reaction with n-heptane over the temperature range 253–325 K at 730 Torr total pressure of air are in good agreement with predictions from this equation.

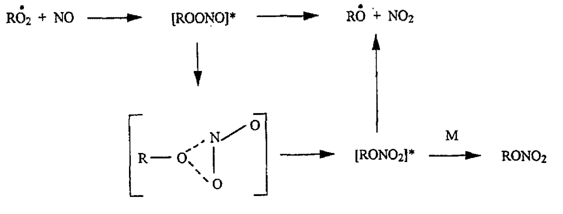
The corresponding rate constant ratios k_a/k_b for primary and tertiary RO_2 radicals appear to be lower, by a factor of ~2.5 for primary alkyl peroxy radicals and by a factor of ~3.3 for tertiary alkyl peroxy radicals, than the rate constant ratios k_a/k_b for the secondary alkyl peroxy radicals.[54,57] Therefore,

$$(k_a/k_b)_{\mathrm{primary}}\approx0.40(k_a/k_b)_{\mathrm{secondary}}$$

and

$$(k_a/k_b)_{\mathrm{primary}}\approx0.3(k_a/k_b)_{\mathrm{secondary}}.$$

The use of the above equations to calculate the rate constant ratios k_a/k_b appears to be solely applicable to alkyl peroxy radicals (see Sec. 2.2). The reactions of alkyl peroxy ($\mathrm{R\dot{O}_2}$) radicals with NO are postulated[52] to occur by,



and the overall rate constants are therefore expected to be independent of total pressure, but with the rate constant ratio k_a/k_b being pressure and temperature dependent, as observed. As expected, no deuterium isotope effect has been observed for these reactions, with the 298 K rate constants for the reactions of the $\mathrm{CH_3\dot{O}_2}$ and $\mathrm{CD_3\dot{O}_2}$ radicals with NO being identical within the experimental uncertainties.[35,37]

2.1.5.b. Reaction with NO_2. The reactions of alkyl peroxy radicals with NO_2 proceed via combination to yield the alkyl peroxynitrates[13]

$$\mathrm{R\dot{O}_2+NO_2\xrightarrow{M}ROONO_2}.$$

The rate constants for the reactions of the $\mathrm{CH_3\dot{O}_2}$ and $\mathrm{C_2H_5\dot{O}_2}$ radicals with NO_2 are in the falloff regime between second and third order kinetics at and below atmospheric pressure at room temperature. The IUPAC recommendations[13] for the values of k_0, k_∞, and F and the rate constants k for these two reactions at 298 K and 760 Torr total pressure of air as calculated from the falloff expressions are given in Table 6. The observations that the reactions of the $\mathrm{CH_3\dot{O}_2}$ and $\mathrm{C_2H_5\dot{O}_2}$ radicals with NO_2 are in the falloff regime between second and third order kinetics at and below atmospheric pressure at room temperature[13] are in agreement with data for the reverse thermal decomposition reactions of the alkyl peroxynitrates CH_3OONO_2 and $C_2H_5OONO_2$.[13]

Absolute rate constants have also been obtained at room temperature for the reactions of the $\mathrm{(CH_3)_2CH\dot{O}_2}$ (Ref. 43) and $\mathrm{(CH_3)_3C\dot{O}_2}$ (Ref. 46) radicals, of $(5.65\pm0.17)\times10^{-12}$ cm^3 molecule^{-1} s^{-1} and $\geq5\times10^{-13}$ cm^3 molecule^{-1} s^{-1}, respectively. However, the rate constant of Adachi and Basco[43] for the $\mathrm{(CH_3)_2CH\dot{O}_2}$ radical reaction is anticipated to be erroneously low,[3] by analogy with the measurement by the same authors of the rate constant for the corresponding reaction of the $\mathrm{C_2H_5\dot{O}_2}$ radical with NO_2,[58] for which a rate constant of $(1.25\pm0.07)\times10^{-12}$ cm^3 molecule^{-1} s^{-1} was obtained independent of pressure over the range 44–676 Torr[58] and which is in significant disagreement with the IUPAC recommendation[13] given in Table 6.

Based upon the data for the $\mathrm{CH_3\dot{O}_2}$ and $\mathrm{C_2H_5\dot{O}_2}$ radical reactions[13] (Table 6), it is recommended that the limiting high pressure rate constants for the $\geq C_3$ alkyl peroxy radicals are identical to those for the $\mathrm{C_2H_5\dot{O}_2}$ radical, with

$$k_\infty(\mathrm{R\dot{O}_2+NO_2})=9\times10^{-12}\mathrm{cm^3\ molecule^{-1}\ s^{-1}},$$

approximately independent of temperature over the range ~250–350 K. This recommendation is consistent with the kinetic data of Zabel *et al.*[59] for the thermal decompositions of a series of alkyl peroxynitrates ($ROONO_2$, where R=CH_3, C_2H_5, C_4H_9, C_6H_{13}, and C_8H_{17}) at 253 K and 600 Torr total pressure of N_2, which show that the thermal decomposition rates for the C_2–C_8 alkyl peroxynitrates are reasonably similar. In particular, the thermal decomposition rates for the

TABLE 7. Rate constants at 298 K, k, and temperature dependent parameters, $k=A\ e^{-B/T}$, for the gas-phase reactions of alkyl peroxy radicals with the HO_2 radical

$R\dot{O}_2$	$10^{13}\times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	$10^{12}\times k$ (cm^3 molecule^{-1} s^{-1})	Reference
$CH_3\dot{O}_2$	3.8	-780 ± 500	$5.2^{+5.2}_{-2.6}$	Atkinson *et al.*[13]
$CH_3CH_2\dot{O}_2$	2.7	-1000 ± 300	$7.7^{+4.5}_{-2.9}$	Atkinson *et al.*[13]
$(CH_3)_3CCH_2\dot{O}_2$	1.43 ± 0.46	-1380 ± 100	15 ± 4	Rowley *et al.*[60]
cyclo-$C_5H_9\dot{O}_2$	2.1 ± 1.3	-1323 ± 185	18 ± 3	Rowley *et al.*[61]
cyclo-$C_6H_{11}\dot{O}_2$	2.6 ± 1.2	-1245 ± 124	17 ± 3	Rowley *et al.*[61]

C_4–C_8 alkyl peroxynitrates at 253 K and 600 Torr total pressure of N_2 were within 30% of the calculated high pressure thermal decomposition rate of $C_2H_5OONO_2$ at the same temperature.[59] The pressures at which these $R\dot{O}_2+NO_2$ reactions exhibit kinetic falloff behavior from the second to third order regime will decrease as the size of the $R\dot{O}_2$ radical increases, and it is expected that at room temperature and 760 Torr total pressure of air the rate constants for the reactions of $\geq C_3$ alkyl peroxy radicals with NO_2 are close to the high pressure limits.

2.1.5.c. Reaction with HO_2 Radicals. To date, rate constants for the reactions of the HO_2 radical with alkyl peroxy radicals have been measured only for the methyl peroxy,[13] ethyl peroxy,[13] 2,2-dimethyl-1-propyl peroxy (neopentyl peroxy),[60] cyclopentyl peroxy,[61] and cyclohexyl peroxy[61] radicals. The 298 K rate constants and the temperature dependent parameters recommended for the $CH_3\dot{O}_2$ and $C_2H_5\dot{O}_2$ radical reactions[13] and the measured values for the other three alkyl peroxy radicals for which data are presently available[60,61] are given in Table 7. The rate constants for the reactions of the $CH_3\dot{O}_2$ and $C_2H_5\dot{O}_2$ radicals with the HO_2 radical recommended by the most recent IUPAC evaluation[13] (Table 7) are recommended and should be used. Based on rate constant data of Rowley *et al.*[60,61] for the neopentyl peroxy,[60] cyclopentyl peroxy,[61] and cyclohexyl peroxy[61] radicals, rate constants for the $\geq C_3$ alkyl peroxy radical reactions with the HO_2 radical of

$$k(HO_2+R\dot{O}_2)=1.9\times10^{-13}\ e^{1300/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$
$$=1.5\times10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K}$$

are recommended, with an estimated uncertainty in the 298 K rate constant of a factor of 2.

The reactions of the HO_2 radical with $CH_3\dot{O}_2$,[62,63] $CD_3\dot{O}_2$,[64] $C_2H_5\dot{O}_2$,[65] neopentyl peroxy,[60] cyclopentyl peroxy,[61] and cyclohexyl peroxy[61] radicals have been shown to proceed by H-atom abstraction to form the hydroperoxide, with a yield of unity within the experimental uncertainties.[60–65]

$$R\dot{O}_2+HO_2\rightarrow ROOH+O_2.$$

2.1.5.d. Reaction with $R\dot{O}_2$ Radicals. Numerous studies of the combination reactions (including the self-reactions) of $R\dot{O}_2$ radicals have been carried out.[66,67] These reactions can proceed by three pathways,

$$2R_1R_2CH\dot{O}_2\rightarrow 2R_1R_2CH\dot{O}+O_2, \quad \text{(a)}$$

$$2R_1R_2CH\dot{O}_2\rightarrow R_1R_2CHOH+R_1C(O)R_2+O_2, \quad \text{(b)}$$

and

$$2R_1R_2CH\dot{O}_2\rightarrow R_1R_2CHOOCHR_1R_2+O_2, \quad \text{(c)}$$

with pathway (b) not being accessible for tertiary $R\dot{O}_2$ radicals. At around room temperature, product studies of the self-reactions of the $CH_3\dot{O}_2$,[68–70] $C_2H_5\dot{O}_2$,[71,72] $(CH_3)_3C\dot{O}_2$,[73] neopentyl peroxy,[74] and cyclohexyl peroxy[75] radicals show no evidence for the occurrence of reaction pathway (c). In the following discussion, pathway (c) is taken to be of negligible importance and only pathways (a) and (b) are assumed to occur.

The IUPAC panel recommendations[13] for the overall rate constants ($k=k_a+k_b$) and the rate constant ratios k_a/k for the self-reactions of the $\leq C_3$ $R\dot{O}_2$ radicals and for the reactions of the $CH_3\dot{O}_2$ radical with $CH_3C(O)\dot{O}_2$ and $CH_3C(O)CH_2\dot{O}_2$ radicals are given in Table 8, together with the available literature data for other $R\dot{O}_2$ radical reactions. For the self-reaction of the *tert*-butyl peroxy radical, the rate constants reported by Anastasi *et al.*,[46] Kirsch *et al.*,[81] and Lightfoot *et al.*[76] at room temperature and above are in good agreement.[76] Because of the wider temperature range studied, the Arrhenius expression of Lightfoot *et al.*[76] is preferred.

Although an Arrhenius expression is given in Table 8 for the self-reaction of neopentyl peroxy radicals,[76] the rate constants measured by Lightfoot *et al.*[76] exhibit non-Arrhenius behavior. (Note that the three parameter expression of $k=3.02\times10^{-19}\ (T/298)^{9.46}\ e^{4260/T}$ cm^3 molecule^{-1} s^{-1} cited by Lightfoot *et al.*[76] does not fit their data, and the expression $k=3.02\times10^{-19}\ (T/298)^{9.46}\ e^{4530/T}$ cm^3 molecule^{-1} s^{-1} appears to be a better fit[3].) The overall rate constant k and branching ratio k_a/k determined by Wallington *et al.*[74] at 297 K for the self-reaction of neopentyl peroxy radicals are in excellent agreement with the more extensive measurements of Lightfoot *et al.*[76]

The Arrhenius expressions for k_a/k are only applicable over the cited temperature ranges, since over extended temperature ranges the calculated values can exceed unity. The more correct temperature dependent format uses the rate constant-ratio k_a/k_b, and Lightfoot *et al.*[76] obtained the rate constant ratio $k_a/k_b=(197\pm67)\ e^{[-(1658\pm98)/T]}$ for the self-reaction of neopentyl peroxy radicals over the temperature range 248–373 K. Similarly, Rowley *et al.*[77] obtained the rate constant ratio $k_a/k_b=1146\ e^{[-(2350\pm320)/T]}$ over the tem-

TABLE 8. Rate constants k at 298 K and temperature dependent parameters, $k=A\ e^{-B/T}$, for the gas-phase combination reactions of $R\dot{O}_2$ radicals

$R\dot{O}_2+R\dot{O}_2$	$10^{12}\times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	$10^{13}\times k$ (298 K) (cm^3 molecule^{-1} s^{-1})	k_a/k	Reference
Self-reactions					
$CH_3\dot{O}_2+CH_3\dot{O}_2$	0.11	-365 ± 200	$3.7^{+1.2}_{-0.9}$	$5.4\ e^{-874/T}$	Atkinson *et al.*[13]
$C_2H_5\dot{O}_2+C_2H_5\dot{O}_2$	0.064	0^{+300}_{-100}	$0.64^{+0.21}_{-0.16}$	0.62 ± 0.10 (298 K)	Atkinson *et al.*[13]
$CH_3CH_2CH_2\dot{O}_2+CH_3CH_2CH_2\dot{O}_2$			3^{+9}_{-2}		Atkinson *et al.*[13]
$(CH_3)_2CH\dot{O}_2+(CH_3)_2CH\dot{O}_2$	1.6	2200 ± 300	$0.010^{+0.010}_{-0.005}$ (300–400 K)	$2.0\ e^{-380/T}$	Atkinson *et al.*[13]
$(CH_3)_3C\dot{O}_2+(CH_3)_3C\dot{O}_2$	10	3894	0.00021		Lightfoot *et al.*[76]
$(CH_3)_3CCH_2\dot{O}_2+(CH_3)_3CCH_2\dot{O}_2$	0.0016	-1961 ± 100	10.4 ± 0.9	0.40 (298 K)	Lightfoot *et al.*[76]
cyclo-$C_5H_9\dot{O}_2$+cyclo-$C_5H_9\dot{O}_2$			<0.67		Rowley *et al.*[77]
cyclo-$C_6H_{11}\dot{O}_2$+cyclo-$C_6H_{11}\dot{O}_2$			0.284 ± 0.016	0.29 ± 0.02 (298 K)	Rowley *et al.*[75]
	0.077	184	0.42		Rowley *et al.*[77]
Cross-reactions					
$CH_3\dot{O}_2+C_2H_5\dot{O}_2$			2.0 ± 0.5	0.48[a] (298 K)	Villenave and Lesclaux[78]
$CH_3\dot{O}_2+(CH_3)_3C\dot{O}_2$	0.37	1420	0.032	$5.9\ e^{-1130/T}$ (313–393 K)	Osborne and Waddington[73]
$CH_3\dot{O}_2+(CH_3)_3CCH_2\dot{O}_2$			15 ± 5	0.36[a] (298 K)	Villenave and Lesclaux[78]
$CH_3\dot{O}_2$+cyclo-$C_6H_{11}\dot{O}_2$			0.90 ± 0.015	0.31[a] (298 K)	Villenave and Lesclaux[78]
$CH_3\dot{O}_2+CH_2{=\!=}CHCH_2\dot{O}_2$	0.28 ± 0.07	-515 ± 75	16	0.47[a] (298 K)	Vellenave and Lesclaux[78]
$CH_3\dot{O}_2+C_6H_5CH_2\dot{O}_2$			<20	0.36[a] (298 K)	Vellenave and Lesclaux[78]
$CH_3\dot{O}_2+CH_3C(O)\dot{O}_2$	5.1	-272	130	0.86 (298 K)	Atkinson *et al.*[13]
			98 ± 16	$0.90^{+0.05}_{-0.19}$ (298 K)	Roehl *et al.*[79]
	0.85	-726 ± 75	97	minor (209–358 K)	Maricq and Szente[80]
			82 ± 6	0.65[a] (298 K)	Vellenave and Lesclaux[78]
$CH_3\dot{O}_2+CH_3C(O)CH_2\dot{O}_2$			38	0.3 (298 K)	Atkinson *et al.*[13]
$C_2H_5O_2+(CH_3)_3CCH_2\dot{O}_2$			5.6 ± 0.8	0.51[a] (298 K)	Villenave and Lesclaux[78]
$C_2H_5O_2$+cyclo-$C_6H_{11}\dot{O}_2$			0.40 ± 0.02	0.46[a] (298 K)	Villenave and Lesclaux[78]
$C_2H_5\dot{O}_2+CH_2{=\!=}CHCH_2\dot{O}_2$			10 ± 3	0.62[a] (298 K)	Villenave and Lesclaux[78]
$C_2H_5\dot{O}_2+CH_3C(O)\dot{O}_2$			100 ± 30	0.82[a] (298 K)	Villenave and Lesclaux[78]
$(CH_3)_3CCH_2\dot{O}_2+(CH_3)_3C\dot{O}_2$			0.3 ± 0.1 (373 K)		Lightfoot *et al.*[76]

[a] Calculated assuming that the value of k_a/k for the $R_1\dot{O}_2+R_2\dot{O}_2$ radical reaction is the arithmetic average of the k_a/k values for the self-reactions of the $R_1\dot{O}_2$ and $R_2\dot{O}_2$ radicals.[78]

perature range 253–373 K for the self-reaction of the cyclohexyl peroxy radical, and Horie and Moortgat[82] measured a rate constant ratio of $k_a/k_b=2.2\times10^6\ e^{-3870/T}$ for the reaction of the methyl peroxy radical with the acetyl peroxy radical over the temperature range 263–333 K from a product analysis study. However, the studies of Horie and Moortgat,[82] Roehl *et al.*,[79] and Maricq and Szente[80] concerning the rate constant ratio k_a/k_b [or $k_a/(k_a+k_b)$] are not in agreement, with Horie and Moortgat[82] and Roehl *et al.*[79] concluding that the reaction channel (a),

$$CH_3C(O)\dot{O}_2+CH_3\dot{O}_2 \left[\begin{array}{ll} \rightarrow CH_3C(O)\dot{O}+CH_3\dot{O}+O_2 & \text{(a)} \\ \rightarrow CH_3C(O)OH+HCHO+O_2\,, & \text{(b)} \end{array}\right.$$

dominates at room temperature (and at temperatures >265 K[82]), while Maricq and Szente[80] observed no evidence for the contribution of pathway (a) over the entire temperature range studied (209–358 K). Note that there is general agreement concerning the overall room temperature rate constant (k_a+k_b) (Table 8).[13,78–80]

For the self-reaction of the cyclopentyl peroxy radical, Rowley *et al.*[77] measured rate constants k_{obs} over the temperature range 243–373 K from the flash photolysis of Cl_2–cyclopentane–O_2–N_2 mixtures, by monitoring the second order decays of the cyclopentyl peroxy radical absorption. However, at a given temperature the measured values of k_{obs} were a function of the O_2/Cl_2 concentration ratio, with the measured value of k_{obs} increasing with the O_2/Cl_2 concentration ratio.[77] This behavior was explained[77] by competitive reactions of the $\dot{C}H_2CH_2CH_2CH_2CHO$ radical, formed from decomposition of the cyclopentyloxy radical produced in reaction pathway (a), with Cl_2 and O_2. Rowley *et al.*[77] obtained a rate constant for the "molecular" channel (b) of

$$\begin{aligned} &k_b(\text{cyclopentyl peroxy})\\ &\quad=(1.3\pm0.4)\times10^{-14}\ e^{(188\pm83)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\\ &\quad=2.2\times10^{-14}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K,}\end{aligned}$$

and an upper limit to the overall rate constant (k_a+k_b) of

$$\begin{aligned} &(k_a+k_b)\\ &\quad\leq(2.9\pm0.8)\times10^{-13}\ e^{[-(555\pm77)/T]}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\\ &\quad\leq6.7\times10^{-14}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K.}\end{aligned}$$

In addition to the data given in Table 8, Heimann and Warneck[83] carried out a product study of the OH radical initiated reaction of 2,3-dimethylbutane and derived rate constant ratios k_a/k at 297 K for the self-reaction of the 2-propyl peroxy radical of 0.39±0.08 and for the self-reaction of the $(CH_3)_2CHCH(CH_3)CH_2\dot{O}_2$ (2,3-dimethyl-1-butyl peroxy) radical of 0.44±0.07. This value of k_a/k for the 2-propyl peroxy radical[83] is somewhat lower than the IUPAC recommendation[13] of 0.56 at 298 K (Table 8). Rate constants for the cross-combination reactions of the 2,3-dimethyl-1-butyl peroxy radical with 2-propyl peroxy and 2,3-dimethyl-2-butyl peroxy radicals were also derived.[83]

For all of the combination reactions of alkyl peroxy radicals for which data are available and for which both reaction pathways (a) and (b) are allowed, the reaction pathway (a) to yield the alkoxy radicals increases in importance as the temperature increases (Table 8 and Refs. 76 and 77), with pathway (a) accounting for ~30–80% of the overall reaction at 298 K. For the self-recombination reaction of $CH_3\dot{O}_2$ radicals, Kan and Calvert[84] and Kurylo *et al.*[85] have shown that, in contrast to the combination reaction of HO_2 radicals,[13] H_2O vapor has no effect on the measured room temperature rate constant.

In the absence of experimental data for a wider variety of $R\dot{O}_2$ radicals, the following self-reaction rate constants are recommended as being reasonably representative for primary, secondary, and tertiary alkyl peroxy radicals at 298 K,

$$\begin{aligned} &k(\text{primary } R\dot{O}_2+\text{primary } R\dot{O}_2)\\ &\quad\sim2.5\times10^{-13}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1},\end{aligned}$$

$$\begin{aligned} &k(\text{secondary } R\dot{O}_2+\text{secondary } R\dot{O}_2)\\ &\quad\sim5\times10^{-15}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1},\end{aligned}$$

and

$$\begin{aligned} &k(\text{tertiary } R\dot{O}_2+\text{tertiary } R\dot{O}_2)\\ &\quad\sim2\times10^{-17}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1},\end{aligned}$$

all with uncertainties at 298 K of at least a factor of 5. For the self-reactions of primary and secondary $R\dot{O}_2$ radicals, the few available data (Table 8) suggest a rate constant ratio of $k_a/k=0.45\pm0.2$ at 298 K. For the self-reactions of tertiary $R\dot{O}_2$ radicals, only reaction pathway (a) can occur.

For the reactions of nonidentical alkyl peroxy radicals,

$$R_1\dot{O}_2+R_2\dot{O}_2\rightarrow\text{products,}$$

the available data (Table 8 and Ref. 78) indicate that the rate constants are very approximately given by the geometric mean equation,[86] with $k_{12}\sim2(k_1k_2)^{0.5}$, where k_{12} is the rate constant for the $R_1\dot{O}_2+R_2\dot{O}_2$ reaction and k_1 and k_2 are the rate constants for the self-reactions of $R_1\dot{O}_2$ and $R_2\dot{O}_2$ radicals, respectively. A much larger data base is clearly required for the reactions of the HO_2 radical with alkyl peroxy $(R\dot{O}_2)$ radicals and for the reactions of $R\dot{O}_2$ radicals with $R\dot{O}_2$ radicals (including for the cross-combination reactions).

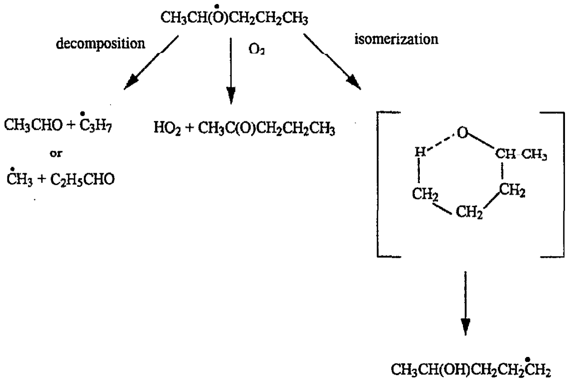
2.1.6. Alkoxy ($R\dot{O}$) Radical Reactions

Under tropospheric conditions, the major alkoxy radical removal processes involve reaction with O_2, unimolecular decomposition, and isomerization.[1–3,87] The alkoxy radical isomerizations proceed by a cyclic transition state and, because of the ring strain involved, 1,4-H shift isomerizations proceeding through a 5-member ring transition state[88] are calculated to be much less important (by a factor of $\sim5\times10^3$ at 298 K[88]) than 1,5-H shift isomerizations proceeding through a 6-member, essentially strain-free, transition state.[1,88] In agreement with these predictions,[1,88] Eberhard *et al.*[89] observed no evidence for 1,4-H shift isomerizations of the 2- and 3-hexoxy radicals and 1,4-H shift isomerization reactions of alkoxy radicals are therefore neglected in the following discussion. For the 2-pentoxy radical, the decomposition and isomerization reactions and the reaction with O_2 are shown in Reaction Scheme 1.

TABLE 9. Recommended 298 K rate constants and temperature dependent expressions, $k=A\ e^{-B/T}$, for the reactions of O_2 with alkoxy ($R\dot{O}$) radicals.[a]

$R\dot{O}$	$10^{14}\times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	$10^{15}\times k$ (298 K) (cm^3 molecule^{-1} s^{-1})
$CH_3\dot{O}$	7.2	1080	1.9
$CH_3CH_2\dot{O}$	6.0	550	9.5
$(CH_3)_2CH\dot{O}$	1.5	200	8

[a] From Atkinson *et al.*[13] The Arrhenius expressions cited are only applicable for temperatures ≤600 K.



Reactions of the alkoxy radicals with NO and NO_2, though of no importance under tropospheric conditions, must be considered for laboratory conditions.[3]

2.1.6.a. Reaction with O_2. Absolute rate constants for the reactions of alkoxy radicals with O_2 have been determined for the $CH_3\dot{O}$,[90–93] $C_2H_5\dot{O}$,[91,94] and $(CH_3)_2CH\dot{O}$[95] radicals, and the IUPAC recommendations[13] for the rate constants for these reactions are given in Table 9. In addition to these absolute rate constants, Zellner and coworkers[96] have reported, using an indirect method, rate constants at 298 K for the reactions of O_2 with propoxy, 1-butoxy, 2-methyl-1-propoxy, pentoxy, hexoxy, heptoxy, and octoxy radicals of $(7.3\text{–}8)\times10^{-15}$ cm^3 molecule^{-1} s^{-1}, very similar to the room temperature rate constants for the ethoxy and 2-propoxy radicals given in Table 9. Based on the recommended[13] rate constants for the reactions of the $C_2H_5\dot{O}$ and $(CH_3)_2CH\dot{O}$ radicals with O_2, it is recommended that for the primary ($RCH_2\dot{O}$) and secondary ($R_1R_2CH\dot{O}$) alkoxy radicals formed from the alkanes,

$$k(RCH_2\dot{O}+O_2)$$
$$=6.0\times10^{-14}\ e^{-550/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\quad (T\leq600\ \text{K})$$
$$=9.5\times10^{-15}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},\qquad\text{(I)}$$

and

$$k(R_1R_2CH\dot{O}+O_2)$$
$$=1.5\times10^{-14}\ e^{-200/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\quad (T\leq600\ \text{K})$$
$$=8\times10^{-15}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K}.\qquad\text{(II)}$$

These recommendations are identical to those of Atkinson.[3] For the reaction of the $C_2H_2\dot{O}$ radical with O_2, Hartmann *et al.*[94] measured the formation yield of the HO_2 radical after conversion to OH radicals and laser-induced fluorescence (LIF) detection of OH radicals, and obtained a formation yield of HO_2 radicals of $0.89^{+0.22}_{-0.12}$, showing that within the experimental uncertainties the reaction proceeds by

$$CH_3CH_2\dot{O}+O_2\rightarrow CH_3CHO+HO_2.$$

Relationships between the rate constants for the reactions of the alkoxy radicals with O_2 (k_{O_2}) and the exothermicities of these reactions (ΔH_{O_2}) have previously been derived[3,88,95] and, based on the three reactions for which recommendations are given (Table 9) and using the heats of formation given in the IUPAC evaluation,[13] a unit weighted least-squares analysis leads to[97]

$$k(R\dot{O}+O_2)$$
$$=k_{O_2}=4.0\times10^{-19}\,n\ e^{-(0.28\Delta H_{O_2})}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\qquad\text{(III)}$$

at 298 K, where n is the number of abstractable H atoms in the alkoxy radical and ΔH_{O_2} is in kcal mol^{-1}. At 760 Torr total pressure of air and 298 K, Eq. (III) leads to

$$k_{O_2}[O_2]=2.1\ n\ e^{-(0.28\Delta H_{O_2})}\ \text{s}^{-1}.\qquad\text{(IV)}$$

Equations (I) and (II) or, if the value of ΔH_{O_2} differs significantly from the values of ΔH_{O_2} for the reactions of the ethoxy or 2-propoxy radicals with O_2, Eqs. (III) or (IV) can be used to estimate the rate constants and reaction rates for the reactions of alkoxy radicals with O_2.

2.1.6.b. Alkoxy Radical Decompositions. The gas-phase decompositions of alkoxy radicals formed from the OH radical initiated reactions of alkanes have been the subject of several previous reviews and discussions.[1–3,87,88,97–102] Rate constants for the decomposition of the ethoxy,[103] 2-propoxy,[104] 2-butoxy,[105] *tert*-butoxy,[106–109] 2-pentoxy,[110] and 2-methyl-2-butoxy[111] radicals have been measured by Batt and coworkers[103–109,111] and Dóbé *et al.*[110] relative to the alkoxy radical combination reactions with NO,

$$R\dot{O}+NO\xrightarrow{M}RONO.$$

Alkoxy radical decomposition rate constants are also available from the studies of Carter *et al.*,[112] Cox *et al.*,[113] and Drew *et al.*[114] for the 2-butoxy radical, Lightfoot *et al.*[76] and Wallington *et al.*[74] for the 2,2-dimethyl-1-propoxy (neopentoxy) radical, and Atkinson *et al.*[115] for the 3-pentoxy radical, relative to the alkoxy radical reactions with O_2[74,76,112,113,115] or relative to other decomposition pathways.[114]

Atkinson[97] used this data base[74,76,103–115] and the approach of Choo and Benson,[101] in which the Arrhenius activation energy of the decomposition reaction is assumed to depend on the specific leaving radical, to derive an expression allowing the decomposition rate constants for alkoxy and β-hydroxyalkoxy radicals to be calculated (see also Sec. 2.2). The literature[103–111] alkoxy radical decomposition rate constants, $k_d = A\ e^{-E/RT}$, were first reevaluated[97] to be relative to the present recommendation for the combination reaction of alkoxy radicals with NO, of k_∞ ($\dot{R}O$+NO) $2.3\times10^{-11}\ e^{150/T}$ cm^3 molecule^{-1} s^{-1} (see below). The pre-exponential factors A were then set at $A = 2\times10^{14}\ d$ s^{-1}, where d is the reaction path degeneracy [the mean of the various values of A after re-evaluation to the common value of $k_\infty(\dot{R}O+NO)$[97]] and the Arrhenius activation energies E adjusted to yield the same rate constants at the midpoint of the temperature ranges employed in the experimental studies. The 298 K decomposition rate constant for the 2-butoxy radical obtained by extrapolation of the rate constants measured relative to the alkoxy radical reaction with NO at 440–470 K[105] is then within a factor of 4 of the rate constants measured relative to the rate constant for the O_2 reaction at room temperature.[112,113] Given the uncertainties in the rate constants for the reference reactions with NO and O_2 and the extrapolation of the decomposition rate constants from 440 to 298 K, this is reasonable agreement and certainly within the likely uncertainties.

Assuming that the Arrhenius activation energy for the alkoxy radical decomposition reaction E is related to the heat of reaction ΔH_d by[3,87,88,99–102] $E = a + b\Delta H_d$, and using an analogous equation to that proposed by Choo and Benson[101] to relate E and a, Atkinson[97] obtained

$$E = [2.4(\mathrm{IP}) - 8.1] + 0.36\Delta H_d, \qquad (\mathrm{V})$$

where IP is the ionization potential (in eV) of the alkyl radical leaving group and E and ΔH_d are in kcal mol^{-1}. This leads to values of a(kcal mol^{-1}) of: methyl, 15.5; primary alkyl, $R\dot{C}H_2$, 11.1 (including ethyl, 11.4 and 1-propyl, 11.3); secondary alkyl, $R_1R_2\dot{C}H$, 9.3 (including 2-propyl, 9.6); and tertiary alkyl, $R_1R_2R_3\dot{C}$, 7.9 (including *tert*-butyl, 8.0).

The Arrhenius activation energies E calculated from Eq. (V) agree with the experimental values of E (as re-evaluated,[97] as discussed above) to within $\sim\pm1$ kcal mol^{-1}. Furthermore, for the 2-butoxy and 3-pentoxy radicals the decomposition rate constants k_d at 298 K calculated from $k_d = 2\times10^{14}\ d\ e^{-E/RT}$ s^{-1}, with E given by Eq. (V), are in excellent agreement (within a factor of 1.5) with the decomposition rate constants calculated relative to the rate constants for their reactions with O_2,[112,113,115] using Eq. (II) to calculate the rate constants k_{O_2}. A decomposition rate constant for the neopentoxy radical is also available relative to the rate constant for its reaction with O_2.[76] However, the rate constant for the decomposition of the neopentoxy radical calculated from the measured rate constant ratio k_d/k_{O_2} depends on whether Eq. (II) or (III) is used to calculate k_{O_2} (because the calculated value of ΔH_{O_2} for the neopentoxy radical differs significantly from that for the corresponding reaction of the ethoxy radical[97]), and the agreement between the values of k_d calculated from Eq. (V) and those calculated relative to the rate constant for reaction with O_2 ranges from excellent to a discrepancy of a factor of $\sim$8 (equivalent to an uncertainty in E of 1.2 kcal mol^{-1}).[97] Within the uncertainties in the heats of decomposition ΔH_d (because of uncertainties in the alkoxy and alkyl radical heats of formation) and the uncertainties in Eq. (V), the agreement between the decomposition rate constants calculated from Eq. (V) and those derived from room temperature measurements of k_d/k_{O_2} is good, typically to within a factor of 5 or 1 kcal mol^{-1} in E).

The alkoxy radical decomposition reactions may be in the falloff region between first order and second order kinetics at room temperature and atmospheric pressure.[88,95,99,100,102,107–109,116] For the two alkoxy radicals for which pressure dependent decomposition rate constants have been observed [2-propoxy[95,116] and 2-methyl-2-propoxy (*tert*-butoxy)[107–109]], the rate constants at room temperature and atmospheric pressure are reasonably close to the limiting high pressure values.[95,107,108] (See also Table II in Baldwin *et al.*,[88] which predicts that the corrections for falloff behavior are small for C_3 and higher alkoxy radicals, being less than a factor of 2 at room temperature and atmospheric pressure.)

2.1.6.c. Alkoxy Radical Isometrizations. Apart from the radical trapping study of Dóbé *et al.*,[110] only recently has direct evidence for the occurrence of alkoxy radical isomerization been reported.[89,115,117–120] Previously, the occurrence of alkoxy radical isomerization reactions in the alkane photooxidations were inferred by the absence of the products expected from the alkoxy radical decomposition and/or reaction with O_2.[112,113,121,122] No absolute rate constants for the isomerization reactions are available, but isomerization rate constants have previously been estimated[1,3,88,121] and experimental data are available concerning the rate constants for the isomerization reactions of the 1-butoxy,[112,113,122] 2-pentoxy,[115] and 2- and 3-hexoxy[89] radicals relative to the reactions of these alkoxy radicals with O_2. The measured rate constant ratios k_{isom}/k_{O_2} are given in Table 10, and those for the 1-butoxy radical[112,113,122] are in good agreement. Rate constants k_{isom} can be obtained from these rate constant ratios k_{isom}/k_{O_2} using the rate constants k_{O_2} recommended above, and the resulting isomerization rate constants are also given in Table 10. The rate constant for isomerization of the 2-pentoxy radical obtained by Dóbé *et al.*[110] relative to the 2-pentoxy radical decomposition rate using a radical trapping method is a factor of $\sim$20 lower than the other values of k_{isom} involving H-atom abstraction from $-CH_3$ groups, and is clearly in error (probably due to difficulties in quantitatively trapping the 4-hydroxy-1-pentyl radicals formed after the isomerization).

The data presented in Table 10 show that alkoxy radical isomerization proceeding by H-atom abstraction from a $-CH_3$ group has a rate constant of $\sim2\times10^5$ s^{-1} at room temperature and, based on the rather uncertain data of Eber-

TABLE 10. Rate constant ratios $k_{\mathrm{isom}}/k_{\mathrm{O_2}}$ and rate constants k_{isom} for the reactions of alkoxy radicals formed from alkanes

$R\dot{O}$	$k_{\mathrm{isom}}/k_{\mathrm{O_2}}$ (molecule cm^{-3})	at T (K)	Reference[a]	k_{isom} (s^{-1})
Abstraction from a $-CH_3$ *group (per* $-CH_3$ *group)*				
1-Butoxy	1.6×10^{19}	303	Carter *et al.*[112]	
	$(1.5\pm0.5)\times10^{19}$	295 ± 2	Cox *et al.*[113]	1.6×10^{5}
	$(1.9\pm0.2)\times10^{19}$	298 ± 2	Niki *et al.*[122]	
2-Pentoxy	3.1×10^{19}	296 ± 2	Atkinson *et al.*[115]	2.5×10^{5}
		301	Dóbé *et al.*[110]	-6×10^{3} [b]
3-Hexoxy	$(2.3-5.4)\times10^{19}$	297 ± 3	Eberhard *et al.*[89]	$(1.8-4.3)\times10^{5}$
Abstraction from a $-CH_2-$ *group (per* $-CH_2-$ *group)*				
2-Hexoxy	$(1.7-5.9)\times10^{20}$	297 ± 3	Eberhard *et al.*[89]	$(1.4-4.7)\times10^{6}$

[a] Using rate constants recommended above for the reaction of the 1-butoxy radical with O_2 of 9.5×10^{-15} cm^3 molecule^{-1} s^{-1} and for the reactions of the 2-pentoxy and 2- and 3-hexoxy radicals with O_2 of 8×10^{-15} cm^3 molecule^{-1} s^{-1}.

[b] The isomerization rate constant is relative to the decomposition rate constant measured in the same study[110] and revised as discussed above and by Atkinson.[97]

hard *et al.*[89] for the 2-hexoxy radical, that alkoxy radical isomerization proceeding by H-atom abstraction from a $-CH_2-$ group has a isomerization rate constant at room temperature of $\sim2\times10^{6}$ s^{-1}.

The rate constant for isomerization via H-atom abstraction from a $-CH_3$ group at 298 K is a factor of 3 higher than the estimate of Atkinson[3] (which was based on the experimental data for the 1-butoxy radical[112,113,122]), and is a factor of ~3 lower than the original estimate by Baldwin *et al.*[88] However, the rate constant for isomerization by H-atom abstraction from a $-CH_2-$ group at 298 K is significantly lower than previous estimates,[1-3,88] and the experimental data (Table 10) showing that H-atom abstraction from a $-CH_2-$ group is a factor of 10 faster than from a $-CH_3$ group differ significantly from the estimate[88] of a factor of 100 for this ratio.

By analogy with H-atom abstraction from $-CH_3$, $-CH_2-$, and $>CH-$ groups by the OH radical,[9] Atkinson[97] postulated that for isomerization from $-CH_3$, $-CH_2-$, and $>CH-$ groups,

$$k_{\mathrm{isom}}(CH_3-X)=k_{\mathrm{prim}}F(X),$$

$$k_{\mathrm{isom}}(X-CH_2-Y)=k_{\mathrm{sec}}F(X)F(Y),$$

and

$$k_{\mathrm{isom}}\left(X-CH\begin{matrix}\diagup Y\\ \diagdown Z\end{matrix}\right)=k_{\mathrm{tert}}F(X)F(Y)F(Z),$$

where X, Y, and Z are the substituent groups around the $-CH_3$, $-CH_2-$, and $>CH-$ groups, and F(X), F(Y), and F(Z) are the substituent factors for these groups. By definition, $F(-CH_3)=1.00$ and $F(X)=e^{F_X/T}$.[97] Tables 11 and 12 give the group rate constants k_{prim}, k_{sec}, and k_{tert} and the substituent factors for $-CH_3$, $-CH_2-$, $>CH-$, $>C<$, and $-OH$ groups derived by Atkinson.[97] As an example, the rate constant for isomerization of the $CH_3CH_2CH_2CH_2\dot{O}$ radical is $k_{\mathrm{isom}}=k_{\mathrm{prim}}F_{\mathrm{isom}}(-CH_2-)=1.6\times10^{5}\times1.27$ s^{-1} $=2.0\times10^{5}$ s^{-1}.

TABLE 11. Arrhenius parameters, $k=A_{\mathrm{isom}}\,e^{-B_{\mathrm{isom}}/T}$, for the isomerization of alkoxy radicals[a]

H-atom abstraction from	A_{isom} (s^{-1})	B_{isom} (K)	k_{isom} (s^{-1}) at 298 K
$-CH_3$ (k_{prim})	2.4×10^{11}	4240	1.6×10^{5}
$-CH_2-$ (k_{sec})	1.6×10^{11}	3430	1.6×10^{6}
$>CH-$ (k_{tert})	8×10^{10}	2745	4×10^{6}

[a] From Atkinson.[97]

As discussed in detail by Atkinson,[97] the calculated rate constants (or rates) for the decomposition, isomerization, and reaction with O_2 can be used to assess the dominant reaction pathways of alkoxy radicals formed during the degradation reactions of alkanes under tropospheric conditions.

For the cyclohexoxy (cyclo-$C_6H_{11}O$) radical the reaction with O_2,

$$\text{cyclo-}C_6H_{11}\dot{O}+O_2\rightarrow\text{cyclohexanone}+HO_2,$$

accounts for ~40% of the overall reaction pathways at 296 ±2 K and atmospheric pressure of air[56,123] (consistent with the product data of Rowley *et al.*[75]). This relative importance of the O_2 reaction suggests that the isomerization reaction is not important for the cyclo-$C_6H_{11}\dot{O}$ radical, and that the competing pathway is the alkoxy radical decomposition reaction.[75] Indeed, the conformation of the cyclohexane ring prohibits isomerization of the cyclohexyloxy radical, and this expectation has been confirmed by the absence of the isomerization product using atmospheric pressure ionization tandem mass spectrometry.[56] The reaction rates of the cyclohexoxy radical at 298 K and 760 Torr total pressure of air are calculated to be 2.2×10^{4} s^{-1} for reaction with O_2 [using Eq. (IV)] and 6.3×10^{4} s^{-1} for decomposition [using Eq. (V)], consistent with the experimental data.[56,123] The alkoxy radical $\dot{O}CH_2(CH_2)_4CHO$ formed subsequent to decomposition of the cyclohexoxy radical appears to undergo mainly isomerization,[56] as predicted.

The δ-hydroxyalkyl radical formed from the isomerization of the initial alkoxy radical then adds O_2 to produce a δ-hydroxyalkyl peroxy radical (see Sec. 2.2 below), which then undergoes a sequence of reactions similar to those of alkyl peroxy radicals, as discussed above. In the presence of

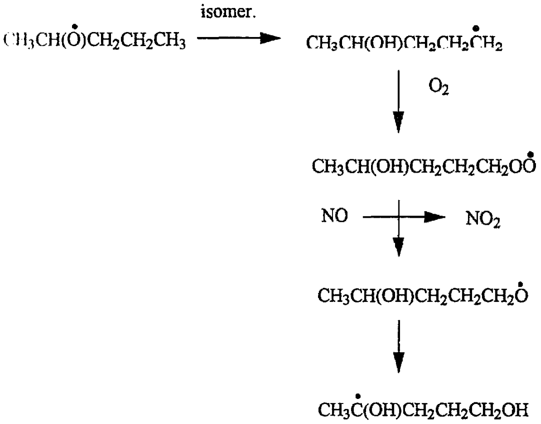
TABLE 12. Group substituent factors F_{isom}(X) for alkoxy radical isomerizations

Substituent group X	F_{isom}(X) at 298 K[a]
$-CH_3$	1.00[b]
$-CH_2-$ $>CH-$ $>C<$	1.27
$-OH$	4.3

[a] From Atkinson.[97] $F_{\mathrm{isom}}(X)=e^{B_X/T}$.

[b] By definition.[97]

NO, the δ-hydroxyalkyl peroxy radical forms the δ-hydroxyalkyl nitrate or the δ-hydroxyalkoxy radical plus NO_2. The formation yields of the δ-hydroxyalkyl nitrates from the δ-hydroxyalkyl peroxy radical reactions with NO are not known, although Eberhard *et al.*[89] have reported the formation of 2-hydroxy-5-hexyl nitrate as a product following the isomerization of the 2-hexoxy radical. The δ-hydroxyalkoxy radicals formed from the δ-hydroxyalkyl peroxy radical plus NO reactions are expected to undergo a second isomerization if that is possible (if an abstractable H atom is available). For example, the expected reactions of the 2-pentoxy radical in the presence of NO, and omitting organic nitrate formation, are shown in Reaction Scheme 2.



The α-hydroxy radicals expected to be formed subsequent to the second isomerization reaction, such as the $CH_3\dot{C}(OH)CH_2CH_2CH_2OH$ radical formed from the 2-pentoxy radical reaction sequence shown in Reaction Scheme 2 above, are expected (see Refs. 2, 3, and 13 and Sec. 2.2) to react solely with O_2 under tropospheric conditions to form the HO_2 radical and a carbonyl. For example the α-hydroxy radical formed in Reaction Scheme 2 reacts with O_2

$$CH_3\dot{C}(OH)CH_2CH_2CH_2OH+O_2$$
$$\rightarrow CH_3C(O)CH_2CH_2CH_2OH+HO_2$$

to form the δ-hydroxycarbonyl 5-hydroxy-2-pentanone. α-Hydroxy radical reactions are discussed in more detail in Sec. 2.2.

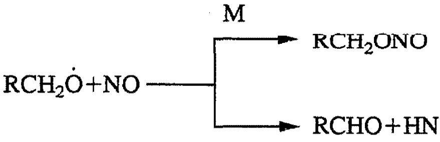
The second isomerization is estimated to be generally significantly more rapid than the first isomerization, and for the 2-pentoxy radical reactions shown in Scheme 2 the first isomerization [of the $CH_3CH(\dot{O})CH_2CH_2CH_3$ radical] is calculated to have a rate constant of $k_{isom}=2\times10^5$ s^{-1} at 298 K, with the second isomerization [of the $CH_3CH(OH)CH_2CH_2CH_2\dot{O}$ radical] being calculated to have a rate constant of $\sim2\times10^7$ s^{-1} at 298 K (Tables 11 and 12), leading to the second isomerization dominating over decomposition or reaction with O_2. The expected δ-hydroxycarbonyls have recently been observed from the OH radical initiated reactions of the *n*-alkanes *n*-butane through *n*-octane and *n*-pentane-d_{12} through *n*-octane-d_{18} by Eberhard *et al.*,[89] Atkinson *et al.*,[115] and Kwok *et al.*[119] using derivatization procedures[89] and direct air sampling atmospheric pressure ionization mass spectrometry.[115,119]

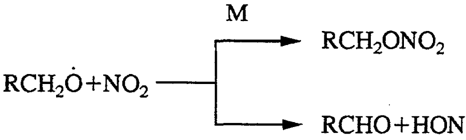
TABLE 13. Recommended rate constant parameters for the gas-phase combination reactions of $R\dot{O}$ radicals with NO (from Atkinson *et al.*[13])

$R\dot{O}$	k_0 (cm^6 $molecule^{-2}$ s^{-1})	k_∞ (cm^3 $molecule^{-1}$ s^{-1})	*F*
$CH_3\dot{O}$	1.6×10^{-29} $(T/300)^{-3.5}$	3.6×10^{-11} $(T/300)^{-0.6}$	0.6
$C_2H_5\dot{O}$		4.4×10^{-11}	
$(CH_3)_2CH\dot{O}$		3.4×10^{-11}	

2.1.6.d. Reactions of $R\dot{O}$ Radicals with NO and NO_2.

Alkoxy radicals can also react with NO and NO_2 under atmospheric conditions. For example,





Absolute rate constants have been measured for the reactions of the $CH_3\dot{O}$, $C_2H_5\dot{O}$, and $(CH_3)_2CH\dot{O}$ radicals with NO and NO_2, and the recommended[13] 298 K limiting high pressure rate constants and temperature dependent parameters are given in Tables 13 and 14, respectively. The rate constants for the reactions of the $CH_3\dot{O}$ radical with NO and NO_2 are in the falloff region between second and third order kinetics,[13] with calculated rate constants at 298 K and 760 Torr total pressure of air of 2.6×10^{-11} cm^3 $molecule^{-1}$ s^{-1} and 1.5×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, respectively. The kinetic data obtained by Balla *et al.*[95] for the reactions of the $(CH_3)_2CH\dot{O}$ radical with NO and NO_2 were at, or close to, the high pressure limit, and show that these reactions have rate constants at room temperature of $(3-4)\times10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, with small negative temperature dependencies.[95]

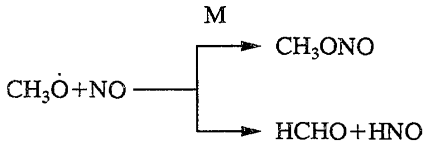
TABLE 14. Recommended rate constant parameters for the combination reactions of $R\dot{O}$ radicals with NO_2 (from Atkinson *et al.*[13])

$R\dot{O}$	k_0 (cm^6 $molecule^{-2}$ s^{-1})	k_∞ (cm^3 $molecule^{-1}$ s^{-1})	*F*
$CH_3\dot{O}$	2.8×10^{-29} $(T/300)^{-4.5}$	2.0×10^{-11}	0.44
$C_2H_5\dot{O}$		2.8×10^{-11}	
$(CH_3)_2CH\dot{O}$		3.5×10^{-11}	

A large amount of relative rate data have been obtained for these NO and NO_2 reactions, as discussed by Batt.[102] These relative rate data show that for the reaction of $R\dot{O}$ radicals with NO, the addition rate constants at ~400 K are $\sim 3 \times 10^{-11}$ cm^3 molecule s^{-1}, with an uncertainty of a factor of ~2–3. While H-atom abstraction from the $R\dot{O}$+NO reactions is observed at low total pressures,[124,125] at total pressures close to the high pressure limit the H-atom abstraction process appears to be minor (<0.05) for the methoxy, ethoxy, and 2-propoxy (and presumably other alkoxy) radicals.[102,126]

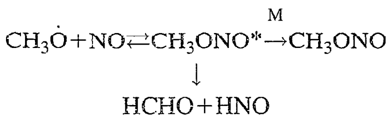
For the $R\dot{O}$ radical reactions with NO_2, the relative rate data cited by Batt[102] suggest that $k(R\dot{O}+NO_2) \sim 3 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at ~400 K and approximately atmospheric pressure (similar to the rate constants for the corresponding NO reactions), and the H-atom abstraction channel is minor, with the most recent relative rate data yielding H-atom abstraction rate constants at ~450 K of $\sim 7 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} for the $CH_3\dot{O}$ radical, $\sim 4 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} for the $C_2H_5\dot{O}$ radical, and $\sim 1 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} for the $(CH_3)_2CH\dot{O}$ radical,[102] with the H-atom abstraction channel accounting for 4±1%, 10±1%, and 2.7±0.6% of the overall reaction over the limited temperature ranges studied (443–474 K for the methoxy radical reaction).[102] Batt and Rattray[126] also report that for the reaction of the $CH_3\dot{O}$ radical with NO_2 at ~400 K, the H-atom abstraction channel accounts for ≤5% of the overall reaction at close to one atmosphere total pressure.

As discussed by Frost and Smith[124] and Smith,[127] these reactions of $R\dot{O}$ radicals with NO and NO_2 can proceed by two parallel, and independent, pathways, as for example,



$$CH_3\dot{O}+NO \xrightarrow{M} CH_3ONO$$
$$CH_3\dot{O}+NO \rightarrow HCHO+HNO$$

or by formation of HCHO+HNO from the energy rich $RONO^*$ intermediate,



$$\begin{tikzcd} CH_3\dot{O}+NO \arrow[r, shift left] & CH_3ONO^* \arrow[l, shift left] \arrow[r, "M"] \arrow[d] & CH_3ONO \\ & HCHO+HNO & \end{tikzcd}$$

It is likely that the second alternative, involving formation of the H-atom abstraction products from the $RONO^*$ and $RONO_2^*$ intermediates, is the operative reaction scheme.[128] Hence at the high pressure limit at around room temperature and below, RONO and $RONO_2$ formation is the sole process expected, and the situation is then analogous to the $\dot{R}+O_2$ reaction system (see above).

The relative rate data[102] are consistent with the absolute rate constants available (Tables 13 and 14), and the following recommendations for all alkoxy ($R\dot{O}$) radicals are made:

$$k_\infty(R\dot{O}+NO) = 2.3 \times 10^{-11}\ e^{150/T}\ cm^3\ molecule^{-1}\ s^{-1}$$
$$= 3.8 \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1} \text{ at } 298\ K$$

with the H-atom abstraction pathway being of minor or negligible importance under tropospheric conditions, and

$$k_\infty(R\dot{O}+NO_2) = 2.3 \times 10^{-11}\ e^{150/T}\ cm^3\ molecule^{-1}\ s^{-1}$$
$$= 3.8 \times 10^{-11}\ cm\ molecule^{-1}\ s^{-1} \text{ at } 298\ K$$

with the H-atom abstraction process being of negligible importance under atmospheric conditions. For the $CH_3\dot{O}$ and $C_2H_5\dot{O}$ radical reactions, the recommended rate constants[13] should be used. Furthermore, the $CH_3\dot{O}$ radical reactions are in the falloff region under atmospheric conditions.[13]

Under ambient tropospheric conditions, these alkoxy radical reactions with NO and NO_2 are generally of negligible importance, but may be important in laboratory experiments. These reactions are, however, of potential importance for tertiary alkoxy radicals, such as the $(CH_3)_3C\dot{O}$ radical, where reaction with O_2 cannot occur and the decomposition reaction is the other competing process. For example, for the *tert*-butoxy radical, $(CH_3)_3C\dot{O}$, the thermal decomposition rate constant is $k_\infty = 790\ s^{-1}$ at 298 K.[97] At 298 K and 760 Torr total pressure of air or N_2, this decomposition rate constant, $k[(CH_3)_3C\dot{O} \rightarrow CH_3C(O)CH_3+\dot{C}H_3]$ is in the falloff region and is a factor of 1.26 lower[108] than the high pressure value, and is hence $\sim 625\ s^{-1}$. At 298 K and 760 Torr total pressure of air the NO and NO_2 reactions with the $(CH_3)_3C\dot{O}$ radical therefore become significant for NO_x concentrations $> 2.5 \times 10^{12}$ molecule cm^{-3} (100 parts-per-billion mixing ratio).

Reaction Scheme 3 shows the reactions of the 2-pentyl radical occurring in the troposphere in the presence of NO (with the $R\dot{O}_2$+NO reactions dominating over the other $R\dot{O}_2$ radical reactions), with the organic nitrates formed not being specifically identified and the alkoxy radical reactions with NO and NO_2 being neglected.

The further reactions of the "first generation" products arising from the above reactions have been discussed previously,[3] and that review and evaluation will be updated in a future publication.

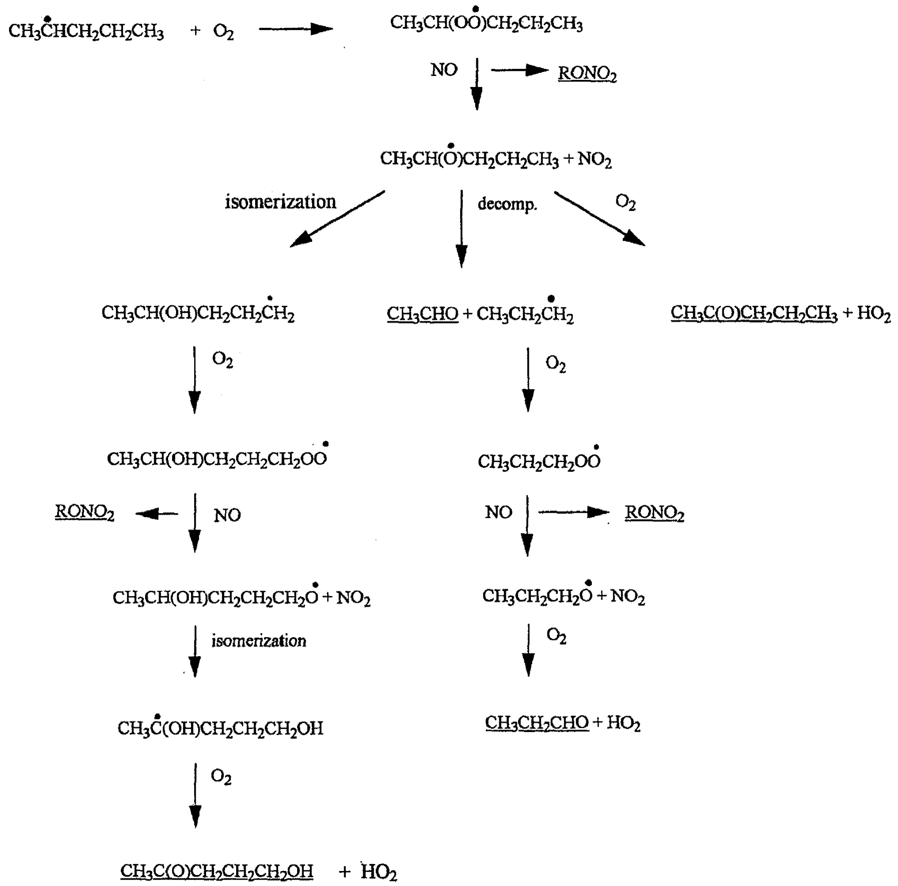


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TABLE 15. Rate constants k at 298 K and 760 Torr total pressure of air and Arrhenius parameters ($k = A\,e^{-B/T}$; $T \sim 250$–425 K) for the reaction of OH radicals with alkenes at 760 Torr total pressure of air[a]

Alkene	$10^{12} \times k$ (298 K) (cm^3 molecule^{-1} s^{-1})	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)
Ethene[b]	8.52	1.96	−438
Propene[c]	26.3	4.85	−504
1-Butene	31.4	6.55	−467
cis-2-Butene	56.4	11.0	−487
trans-2-Butene	64.0	10.1	−550
2-Methylpropene	51.4	9.47	−504
1-Pentene	31.4		
cis-2-Pentene	65		
trans-2-Pentene	67		
3-Methyl-1-butene	31.8	5.32	−533
2-Methyl-1-butene	61		
2-Methyl-2-butene	86.9	19.2	−450
1-Hexene	37		
2-Methyl-1-pentene	63		
2-Methyl-2-pentene	89		
trans-4-Methyl-2-pentene	61		
2,3-Dimethyl-2-butene	110		
3,3-Dimethyl-1-butene	28		
1-Heptene	40		
trans-2-Heptene	68		
2,3-Dimethyl-2-pentene	103		
trans-4,4-Dimethyl-2-pentene	55		
trans-4-Octene	69		
Propadiene	9.82	7.66	−74
1,2-Butadiene	26		
1,3-Butadiene	66.6	14.8	−448
1,2-Pentadiene	35.5		
cis-1,3-Pentadiene	101		
1,4-Pentadiene	53		
3-Methyl-1,2-butadiene	57		
2-Methyl-1,3-butadiene	101	25.4	−410
trans-1,3-Hexadiene	112		
trans-1,4-Hexadiene	91		
1,5-Hexadiene	62		
cis- + *trans*-2,4-Hexadiene	134		
2-Methyl-1,4-pentadiene	79		
2-Methyl-1,3-pentadiene	136		
4-Methyl-1,3-pentadiene	131		
2,3-Dimethyl-1,3-butadiene	122		
2-Methyl-1,5-hexadiene	96		
2,5-Dimethyl-1,5-hexadiene	120		
2,5-Dimethyl-2,4-hexadiene	210		
cis-1,3,5-Hexatriene	110		
trans-1,3,5-Hexatriene	111		
Myrcene	215		
Ocimene (*cis*- and *trans*-)	252		
Cyclopentene	67		
Cyclohexene	67.7		
1,3-Cyclohexadiene	164		
1,4-Cyclohexadiene	99.5		
Cycloheptene	74		
1,3-Cycloheptadiene	139		
1,3,5-Cycloheptatriene	97		
1-Methylcyclohexene	94		
Bicyclo[2.2.1]-2-heptene	49		
Bicyclo[2.2.1]-2,5-heptadiene	120		
Bicyclo[2.2.2]-2-octene	41		
Camphene	53		
2-Carene	80		
3-Carene	88		
Limonene	171		
α-Phellandrene	313		

TABLE 15. Rate constants k at 298 K and 760 Torr total pressure of air and Arrhenius parameters ($k=A\ e^{-B/T}$; $T\sim250-425$ K) for the reaction of OH radicals with alkenes at 760 Torr total pressure of air[a]—Continued

Alkene	$10^{12}\times k$ (298 K) (cm^3 molecule^{-1} s^{-1})	$10^{12}\times A$ (cm^3 molecule^{-1} s^{-1})	B (K)
β-Phellandrene	168		
α-Pinene	53.7	12.1	−444
β-Pinene	78.9	23.8	−357
Sabinene	117		
α-Terpinene	363		
γ-Terpinene	177		
Terpinolene	225		
α-Cedrene	67		
α-Copaene	90		
β-Caryophyllene	197		
α-Humulene	293		
Longifolene	47		

[a] Except for ethene, propene, and propadiene, these are essentially the high pressure rate constants k_∞.

[b] $k_\infty=9.0\times10^{-12}\ (T/298)^{-1.1}$ cm^3 molecule^{-1} s^{-1}.

[c] $k_\infty=2.8\times10^{-11}\ (T/298)^{-1.3}$ cm^3 molecule^{-1} s^{-1}.

2.2. Alkenes

The major tropospheric loss processes of alkenes are by reaction with OH radicals, NO_3 radicals, and O_3.[1,2] Under laboratory conditions, the reactions of alkenes with $O(^3P)$ atoms[3] and, for conjugated dienes, with NO_2 must also be considered.[3,4] The kinetics of the reactions of alkenes with Cl atoms are also dealt with, briefly, for completeness.

2.2.1. OH Radical Reactions

The kinetics and mechanisms of the reactions of the OH radical with alkenes, cycloalkenes, and dienes have been reviewed and evaluated by Atkinson,[2,5] and these reviews are updated in Sec. 3.2. For ethene and the methyl-substituted ethenes (propene, 2-methylpropene, the 2-butenes, 2-methyl-2-butene, and 2,3-dimethyl-2-butene), at atmospheric pressure the OH radical reactions proceed essentially totally by OH radical addition to the carbon–carbon double bond, with H-atom abstraction from the $-CH_3$ substituent groups accounting for <5% of the total reaction at room temperature and atmospheric pressure of air.[5] For 1-butene, the product data of Hoyermann and Sievert[6] and Atkinson *et al.*[7] show that H-atom abstraction accounts for <10% of the overall reaction at room temperature. To date, only for 1,3- and 1,4-cyclohexadiene have H-atom abstraction been shown to occur to any significant extent,[8] with this process accounting for ~9% and ~15% of the overall OH radical reactions with 1,3- and 1,4-cyclohexadiene, respectively, at room temperature.[8] However, for the alkenes with alkyl side chains a small amount of H-atom abstraction must occur with, for example, this pathway being calculated to account for 17% of the overall OH radical reaction for 1-heptene at 298 K.[9]

The rate constants k at 298 K and the temperature dependent parameters (with the temperature dependencies being given in the Arrhenius form of $k=A\ e^{-B/T}$) at 760 Torr total pressure of air and over the temperature range ~250–425 K for the alkenes and cycloalkenes (including monoterpenes and sesquiterpenes) for which data are available are given in Table 15. Although the temperature dependent rate constants are given in the Arrhenius form, $k=A\ e^{-B/T}$, these Arrhenius expressions are only applicable over restricted temperature ranges of ~250–425 K. At temperatures >425 K the hydroxyalkyl radicals formed after OH radical addition to the $>C=C<$ bond(s) undergo thermal decomposition,[5] and at temperatures <250 K the measured rate constants for the reactions of the OH radical with 1-butene and the 2-butenes deviate from Arrhenius behavior.[10] As discussed in Sec. 3.2, the temperature dependent expression reported by Siese *et al.*[11] for the reaction of the OH radical with isoprene (2-methyl-1,3-butadiene) of $k=9.7\times10^{-11}\ (T/298)^{-1.36}$ cm^3 molecule^{-1} s^{-1} over the temperature range 249–438 K gives rate constants which deviate from a linear Arrhenius plot by <6%.

Apart from ethene, propene, and propadiene,[5] the rate constants given in Table 15 can be considered to be at the high pressure limit which, for the $\geq C_4$ alkenes, are essentially attained at total pressures of ~50 Torr total pressure of air.[5] For ethene and propene, the Troe falloff parameters k_0, k_∞, and F derived by Atkinson[2,5] are (M=air): ethene, $k_0=6\times10^{-29}\ (T/298)^{-4}$ cm^6 molecule^{-2} s^{-1}, $k_\infty=9.0\times10^{-12}\ (T/298)^{-1.1}$ cm^3 molecule^{-1} s^{-1} and $F=0.70$ at 298 K; pro-

TABLE 16. Rate constants, k, for the gas-phase reactions of β-hydroxyalkyl radicals with O_2

$\dot{R}$	$10^{12}\times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Reference
$HOCH_2\dot{C}H_2$	3.0±0.4	293±3	Miyoshi *et al.*[14]
$CH_3\dot{C}HCH_2OH$	11.6±2.2	296±4	Miyoshi *et al.*[15]
$CH_3CH(OH)\dot{C}H_2$	3.82±0.60	296±4	Miyoshi *et al.*[15]
$CH_3CH(OH)\dot{C}HCH_3$	28±18	300	Lenhardt *et al.*[16]
$(CH_3)_2C(OH)\dot{C}H_2$	1.8±0.2	296	Langer *et al.*[17]

TABLE 17. Rate constants k for the reactions of β-hydroxyalkyl peroxy radicals with NO and NO_2

$R\dot{O}_2$	$10^{12}\times k$ (cm^3 $molecule^{-1}$ s^{-1}) for reaction with NO	NO_2	T (K)	Reference
$HOCH_2CH_2\dot{O}_2$	9 ± 4		298 ± 2	Becker *et al.*[24]
$(CH_3)_2C(OH)CH_2\dot{O}_2$	4.9 ± 0.9	6.7 ± 0.9^a	296	Langer *et al.*[17]

[a] Total pressure reported to be $\geqslant 75$ Torr of SF_6.

pene, $k_0=3\times10^{-27}$ $(T/298)^{-3}$ cm^6 $molecule^{-2}$ s^{-1}, $k_\infty \approx 2.8\times10^{-11}$ $(T/298)^{-1.3}$ cm^3 $molecule^{-1}$ s^{-1} and $F=0.5$ at 298 K.

As discussed above, OH radical addition to the $>C{=}C<$ bond(s) is the dominant reaction pathway.[5,9] For monoalkenes, dienes, or trienes with nonconjugated $>C{=}C<$ bonds, the OH radical can add to either end of the double bond(s), and Cvetanović[12] reported that for propene addition to the terminal carbon occurs ~65% of the time, as expected on thermochemical grounds.[13]

$$OH+CH_3CH{=}CH_2 \xrightarrow{M} 0.35\ CH_3CH(OH)\dot{C}H_2+0.65\ CH_3\dot{C}HCH_2OH.$$

The resulting β-hydroxyalkyl radicals then react rapidly with O_2, with the measured room temperature rate constants[14–17] being in the range $(1.8\text{–}28)\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} (Table 16). Under atmospheric conditions, the sole reaction of the β-hydroxyalkyl radicals is then with O_2. For example,

$$CH_3\dot{C}HCH_2OH+O_2\xrightarrow{M}CH_3CH(O\dot{O})CH_2OH.$$

For dienes with conjugated double bonds, such as 1,3-butadiene, isoprene (2-methyl-1,3-butadiene), myrcene, ocimene, α- and β-phellandrene, and α-terpinene, OH radical addition to the $>C{=}C{-}C{=}C<$ system is expected to occur at the 1- and/or 4-positions, leading to formation of the thermochemically favored allylic radicals,[3]

$$OH+CH_2{=}CHC(CH_3){=}CH_2\xrightarrow{M}HOCH_2\dot{C}HC(CH_3){=}CH_2$$

and

$$CH_2{=}CH\dot{C}(CH_3)CH_2OH$$

which can isomerize to the δ-hydroxyalkyl radicals,[3,18]

$$CH_2{=}CH\dot{C}(CH_3)CH_2OH\leftrightarrow\dot{C}H_2CH{=}C(CH_3)CH_2OH.$$

By analogy with the allyl ($\dot{C}_3H_5$) radical, for which rate constants for the reaction with O_2 to form the allyl peroxy ($CH_2{=}CHCH_2\dot{O}_2$) radical have been measured, of $\sim4\times10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at 380 K and 50 Torr total pressure of Ar diluent[19] and $(6\pm2)\times10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at 296 ± 2 K and 740–800 Torr of N_2+O_2,[20] the various hydroxy substituted allylic radicals are expected to react solely with O_2 under tropospheric conditions.

$$CH_2{=}CH\dot{C}(CH_3)CH_2OH+O_2\xrightarrow{M}CH_2{=}CHC(O\dot{O})(CH_3)CH_2OH$$

and

$$\dot{C}H_2CH{=}C(CH_3)CH_2OH+O_2\xrightarrow{M}\dot{O}OCH_2CH{=}C(CH_3)CH_2OH.$$

To date, few direct experimental data are available concerning the atmospherically important reactions of β-hydroxyalkyl peroxy radicals,[17,21–27] with no data having been reported to date for δ-hydroxyalkyl peroxy radicals. As for the alkyl peroxy radicals formed from the alkanes (Sec. 2.1) these radicals are expected to react with NO,

TABLE 18. Yields of β-hydroxyalkyl nitrates from the OH radical initiated reactions of alkenes in the presence of NO

Alkene	β-Hydroxyalkyl nitrate	Yield at	T (K) and	P (Torr)	Reference
Propene	$CH_3CH(OH)CH_2ONO_2$	0.0053^a	299	b	Shepson *et al.*[28]
	$CH_3CH(ONO_2)CH_2OH$	0.011^a	299	b	Shepson *et al.*[28]
cis-2-Butene	$CH_3CH(OH)CH(ONO_2)CH_3$	0.037 ± 0.009	c	b	Muthuramu *et al.*[29]
2,3-Dimethyl-2-butene	$(CH_3)_2C(OH)C(ONO_2)(CH_3)_2$	~0.15	~298	~700	Niki *et al.*[30]
Isoprene	Unidentified^d	~0.08–0.13	298 ± 2	740	Tuazon and Atkinson[4]

[a] Yield defined as $([\text{nitrate}]_{\text{formed}}/[\text{propene}]_{\text{reacted}})$.
[b] Atmospheric pressure, not reported.
[c] Room temperature, not reported.
[d] Individual nitrate(s) not identified; probably includes unsaturated δ-hydroxynitrates such as $HOCH_2C(CH_3){=}CHCH_2ONO_2$ and $HOCH_2CH{=}C(CH_3)CH_2ONO_2$.

TABLE 19. Literature rate constants k for the self-reactions of β-hydroxyalkyl peroxy radicals and for their reactions with the HO_2 radical

$R\dot{O}_2$	k (cm^3 $molecule^{-1}$ s^{-1}) for reaction with HO$_2$	Self-reaction	T(K)	Reference
$HOCH_2CH_2\dot{O}_2$	$(1.0^{+1.0}_{-0.5})\times 10^{-11}$	$(2.3^{+2.3}_{-1.2})\times 10^{-12}$	298	Atkinson *et al.*[31]
	$(1.5\pm 0.3)\times 10^{-11}$	2.1×10^{-12a}	~298	Jenkin and Hayman[26]
$(CH_3)_2C(OH)CH_2\dot{O}_2$		$\leqslant(7.8\pm 1.5)\times 10^{-12b}$	296	Langer *et al.*[17]
	$(1.30\pm 0.05)\times 10^{-11c}$	$(3.88\pm 0.16)\times 10^{-12d}$	306	Boyd *et al.*[27]
$CH_3CH(OH)CH(CH_3)\dot{O}_2$	$(1.5\pm 0.4)\times 10^{-11}$	$\leqslant 8.4\times 10^{-13b}$	~298	Jenkin and Hayman[26]
$(CH_3)_2C(OH)C(CH_3)_2\dot{O}_2$	$\sim 2\times 10^{-11}$	5.7×10^{-15e}	~298	Jenkin and Hayman[26]

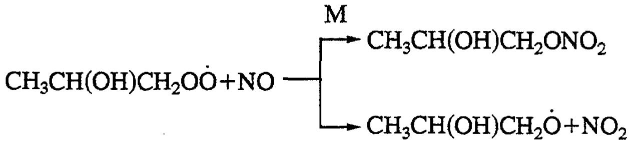
[a] Derived from the observed rate coefficient using the rate constant ratio $k_a/(k_a+k_b)=0.5$ as observed by Barnes *et al.*[25]

[b] Upper limit is the observed rate coefficient. No data exist concerning the rate constant ratio $k_a/(k_a+k_b)$.

[c] Rate constants obtained over the temperature range 306–398 K lead to the Arrhenius expression $k=(5.6\pm 2.0)\times 10^{-14}$ $e^{[(1650\pm 130)/T]}$ cm^3 $molecule^{-1}$ s^{-1} (1.4×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 298 K).[27]

[d] Rate constants obtained over the temperature range 306–398 K lead to the Arrhenius expression $k=(1.4\pm 0.6)\times 10^{-14}$ $e^{[(1740\pm 150)/T]}$ cm^3 $molecule^{-1}$ s^{-1}. (4.8×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 298 K).[27]

[e] Based on $k_a/(k_a+k_b)=1.0$ because of the lack of an α-H-atom.[26]



$$CH_3CH(OH)CH_2O\dot{O}+NO \xrightarrow{M} CH_3CH(OH)CH_2ONO_2$$
$$CH_3CH(OH)CH_2O\dot{O}+NO \rightarrow CH_3CH(OH)CH_2\dot{O}+NO_2$$

NO_2 (to form thermally unstable hydroxyalkyl peroxynitrates),

$$CH_3CH(OH)CH_2O\dot{O}+NO_2 \xrightarrow{M} CH_3CH(OH)CH_2OONO_2$$

HO_2 radicals,

$$CH_3CH(OH)CH_2O\dot{O}+HO_2 \rightarrow CH_3CH(OH)CH_2OOH+O_2$$

and organic peroxy radicals.

$$CH_3CH(OH)CH_2O\dot{O}+R\dot{O}_2 \rightarrow \text{products.}$$

The available data for the reactions of β-hydroxyalkylperoxy radicals with NO and NO_2 are given in Table 17 (kinetic data for the allyl peroxy radical reaction are given in Table 5 in Sec. 2.1). The rate constants reported for the reactions of the $HOCH_2CH_2\dot{O}_2$ and $(CH_3)_2C(OH)CH_2\dot{O}_2$ radicals with NO (with that of Becker *et al.*[24] for the $HOCH_2CH_2\dot{O}_2$ radical being an indirect estimate) are within a factor of 2 of the recommendation given in Sec. 2.1 for the rate constants for the reactions of NO with the $\geqslant C_2$ alkyl peroxy radicals formed from the alkanes, of

$$k(R\dot{O}_2+NO)=2.7\times 10^{-12}\ e^{360/T}\ cm^3\ molecule^{-1}\ s^{-1}$$
$$=9.0\times 10^{-12}\ cm^3\ molecules^{-1}\ s^{-1}\ \text{at } 298\ K,$$

implying that this recommendation for the reaction of alkyl peroxy radicals with NO is also applicable to the corresponding β-hydroxyalkyl peroxy (and δ-hydroxyalkyl peroxy) radical reactions. Similarly, the rate constant of Langer *et al.*[17] for the reaction of the $(CH_3)_2C(OH)CH_2\dot{O}_2$ radical with NO_2 is similar to the recommendation given in Sec. 2.1 for the reactions of NO_2 with the alkyl peroxy radicals formed from the alkanes of

$$k_\infty(R\dot{O}_2+NO_2)=9\times 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1},$$

independent of temperature over the range ~250–350 K. This agreement suggests that this recommendation also applies to the reactions of β-hydroxyalkyl peroxy (and δ-hydroxyalkyl peroxy) radicals with NO_2.

The formation of β-hydroxyalkyl nitrates from the OH radical initiated reactions of alkenes in the presence of NO has been observed for propene,[28] *cis*-2-butene,[29] 2,3-dimethyl-2-butene,[30] and isoprene.[4] The yields of β-hydroxyalkyl nitrates reported in the literature are given in Table 18. The OH radical reaction with propene leads to the formation of the two β-hydroxyalkyl peroxy radicals $CH_3CH(OH)CH_2\dot{O}_2$ and $CH_3CH(O\dot{O})CH_2OH$, with approximate yields of 0.35 and 0.65, respectively,[12] and the data of Shepson *et al.*[28] therefore indicate formation yields of $CH_3CH(OH)CH_2ONO_2$ and $CH_3CH(ONO_2)CH_2OH$ from the corresponding $CH_3CH(OH)CH_2\dot{O}_2$ and $CH_3CH(O\dot{O})CH_2OH$ radicals, respectively, of ~0.015 and ~0.017, respectively, both with uncertainties of ±50%.[28] Based on the limited data available (Table 18) it appears that at room temperature and atmospheric pressure of air, hydroxyalkyl nitrate formation from the reactions of C_n-hydroxyalkyl peroxy radicals with NO is ~50% of the alkyl nitrate formation yields from the reactions of C_n-alkyl peroxy radicals with NO (see Sec. 2.1).

Rate constants for the self-reactions of β-hydroxyalkyl peroxy radicals and for their reaction with the HO_2 radical are given in Table 19, which includes the most recent IUPAC recommendations[31] for the reactions of the $HOCH_2CH_2\dot{O}_2$ radical. The rate constants for the reactions of the β-hydroxyalkyl peroxy radicals with the HO_2 radical for which data are available (Table 19) are in the range $(1-2)\times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K, virtually identical to the recommendation for the reactions of the HO_2 radical with alkyl peroxy radicals given in Sec. 2.1 of

$$k(R\dot{O}_2+HO_2)=1.5\times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}\ \text{at } 298\ K.$$

Furthermore, the temperature dependence of the rate constant for the reaction of the $(CH_3)_2C(OH)CH_2\dot{O}_2$ radical with the HO_2 radical obtained by Boyd *et al.*,[27] of $B=-(1650\pm130)$ K, is similar to the temperature dependence recommended for the reactions of alkyl peroxy radicals with the HO_2 radical, of $B=-1300$ K (Sec. 2.1).

Thus, the recommendation of

$$k(R\dot{O}_2+HO_2)=1.9\times10^{-13}\ e^{1300/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$
$$=1.5\times10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}\ at\ 298\ K}$$

for the reactions of alkyl peroxy radicals with the HO_2 radical (Sec. 2.1) also appears to hold for the reactions of β-hydroxyalkyl (and probably for δ-hydroxyalkyl) peroxy radicals with the HO_2 radical.

The available data for the self-reactions of β-hydroxyalkyl peroxy radicals are given in Table 19. Barnes *et al.*[25] carried out a product study of the self-reaction of the $HOCH_2CH_2\dot{O}_2$ radical at 295±3 K and at various total pressures and O_2 pressures, and determined that the rate constant ratio for the reactions

$$2HOCH_2CH_2\dot{O}_2 \left[\begin{array}{ll}\rightarrow 2HOCH_2CH_2\dot{O}+O_2 & \qquad (a)\\ \rightarrow HOCH_2CH_2OH+HOCH_2CHO+O_2 & \qquad (b)\end{array}\right.$$

is $k_a/k_b=1.02\pm0.23$ $[k_a/(k_a+k_b)=0.50\pm0.06]$, independent of the method of generation of the $HOCH_2CH_2\dot{O}_2$ radicals (photolysis of H_2O_2–ethene–N_2–O_2 or of $HOCH_2CH_2I$–N_2–O_2 mixtures).[25] Using this rate constant ratio, Jenkin and Hayman[26] have derived a rate constant for the self-reaction of the $HOCH_2CH_2\dot{O}_2$ radical, (k_a+k_b), in excellent agreement with the IUPAC recommendation[31] based on the previous measurements of Jenkin and Cox,[21] Anastasi *et al.*,[22] and Murrells *et al.*[23] The room temperature rate constants for the self-reactions of the primary, secondary, and tertiary β-hydroxyalkyl peroxy radicals given in Table 19 are higher, by factors of ~5–300, than the 298 K rate constants for the self-reactions of primary, secondary, and tertiary alkyl peroxy radicals (Sec. 2.1).

For the self-reaction of the $(CH_3)_2C(OH)CH_2\dot{O}_2$ radical, Boyd *et al.*[27] derived a rate constant ratio for the reactions

$$2(CH_3)_2C(OH)CH_2\dot{O}_2 \left[\begin{array}{ll}\rightarrow 2(CH_3)_2C(OH)CH_2\dot{O}+O_2 & \qquad (a)\\ \rightarrow (CH_3)_2C(OH)CH_2OH+(CH_3)_2C(OH)CHO+O_2 & \qquad (b)\end{array}\right.$$

of $k_a/(k_a+k_b)=0.59\pm0.15$ independent of temperature over the range 306–398 K from flash photolysis ultraviolet absorption experiments and $k_a/(k_a+k_b)=0.60\pm0.07$ at 296 K from a product analysis using Fourier transform infrared (FTIR) absorption spectroscopy.[27]

In addition to the products formed from the reactions of the β-hydroxyalkoxy radicals (see below), Barnes *et al.*,[25] Hatakeyama *et al.*,[32] and Tuazon *et al.*[33] have observed the formation of the hydroxycarbonyls,[25,33] dihydroxyalkanes,[25,33] and hydroxyhydroperoxides[25,32,33] expected from the OH radical initiated reactions of alkenes in the absence of NO for the alkenes ethene,[25,32] propene,[33] 2-methylpropene,[33] *cis*-2-butene,[33] *trans*-2-butene,[33] 2-methyl-2-butene,[33] and 2,3-dimethyl-2-butene.[33] For example, for the 2-butenes:

$$CH_3CH(OH)CH(O\dot{O})CH_3+HO_2\rightarrow CH_3CH(OH)CH(OOH)CH_3+O_2$$

$$2CH_3CH(OH)CH(O\dot{O})CH_3 \left[\begin{array}{l}\rightarrow 2CH_3CH(OH)CH(\dot{O})CH_3+O_2\\ \rightarrow CH_3CH(OH)C(O)CH_3+CH_3CH(OH)CH(OH)CH_3+O_2\,.\end{array}\right.$$

Jenkin *et al.*[20] and Boyd *et al.*[34] have studied the kinetics and products of the self-reaction of the allyl peroxy radical ($CH_2{=}CHCH_2\dot{O}_2$). Jenkin *et al.*[20] identified and quantified the products $CH_2{=}CHCHO$ and $CH_2{=}CHCH_2OH$ by FTIR absorption spectroscopy, and additional absorption bands were attributed to the hydroperoxide $CH_2{=}CHCH_2OOH$.[20] Based on the product yields, a rate constant ratio for the reactions

$$2CH_2{=}CHCH_2\dot{O}_2 \rightarrow \begin{cases} 2CH_2{=}CHCH_2\dot{O}+O_2 & \text{(a)} \\ CH_2{=}CHCHO+CH_2{=}CHCH_2OH+O_2 & \text{(b)} \end{cases}$$

of $k_a/k_b=1.56\pm0.46[k_a/(k_a+k_b)=0.61\pm0.07]$ and a rate constant of $(k_a+k_b)=(6.8\pm1.3)\times10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at 296±2 K were obtained.[20] Boyd *et al.*[34] used a flash photolysis ultraviolet absorption technique to obtain a rate constant $(k_a+k_b)=(5.4\pm1.1)\times10^{-14}$ $e^{[(760\pm70)/T]}$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 286–394 K, with $(k_a+k_b)=(7.0\pm0.02)\times10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at 296 K, in excellent agreement with the value reported by Jenkin *et al.*[20] (A rate constant ratio of $k_a/k_b=76$ $e^{-1150/T}$ was used in the data analysis,[34] using the rate constant ratio of Jenkin *et al.*[20] at 296 K and an assumed temperature dependence.) This room temperature rate constant for the self-reaction of the allyl peroxy radical is of a similar magnitude (within a factor of 10) to those for the self-reactions of primary alkyl peroxy radicals (Sec. 2.1 and Table 8, which also lists the reported rate constants for the combination reactions of the allyl peroxy radical with $CH_3\dot{O}_2$ and $C_2H_5\dot{O}_2$ radicals).

Boyd *et al.*[34] also obtained a rate constant for the reaction of the allyl peroxy radical with the HO_2 radical

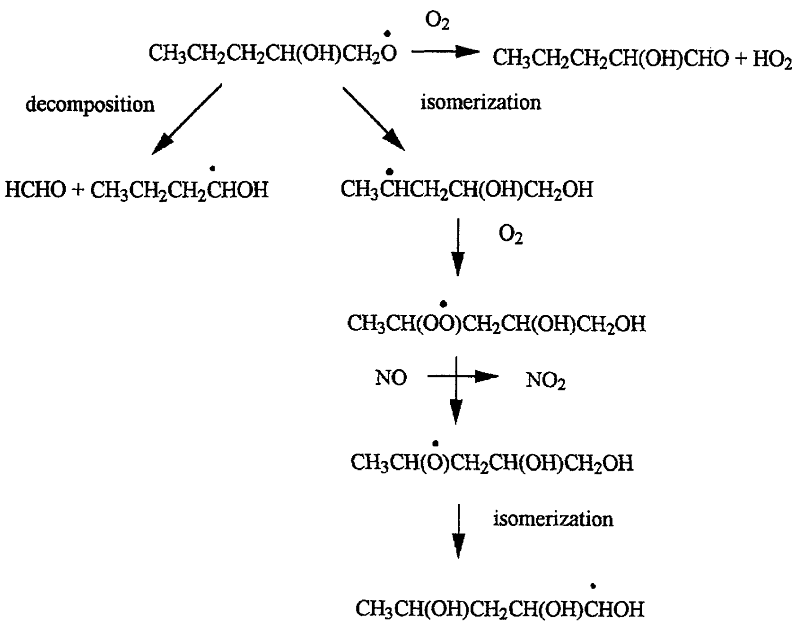
$$CH_2{=}CHCH_2\dot{O}_2+HO_2\rightarrow CH_2{=}CHCH_2OOH+O_2$$

of $(5.6\pm0.4)\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, independent of temperature over the range 393–426 K. The magnitude of this rate constant is similar to the present recommendation for the reactions of RO_2 radicals with the HO_2 radical (5.2×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 393 K and 4.0×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 426 K). However, the observed lack of a temperature dependence of the rate constant in the study of Boyd *et al.*[34] suggests either that the temperature dependence for the $CH_2{=}CHCH_2\dot{O}_2+HO_2$ reaction is $B<-1300$ K or that the experimental uncertainties were such that the expected temperature dependence was not apparent over the restricted temperature range employed.

In the presence of NO, the β- and δ-hydroxyalkyl peroxy radicals are therefore expected to form NO_2 plus the corresponding β- or δ-hydroxyalkoxy radical, with a small amount of β- or δ-hydroxyalkyl nitrate also being formed. For example, the reactions of the $CH_3CH(OH)CH(O\dot{O})CH_3$ radical formed subsequent to OH radical addition to *cis*- or *trans*-2-butene are:

$$CH_3CH(OH)CH(O\dot{O})CH_3+NO \rightarrow \begin{cases} \xrightarrow{M} CH_3CH(OH)CH(ONO_2)CH_3 \\ \rightarrow CH_3CH(OH)CH(\dot{O})CH_3+NO_2\,. \end{cases}$$

The hydroxyalkoxy radicals can then decompose, react with O_2 or isomerize, as discussed in Sec. 2.1 above and by Atkinson.[35] Reaction Scheme 4 shows these reactions for the alkoxy radical formed after internal addition of the OH radical to 1-pentene.



As shown in Reaction Scheme 4 and discussed in Sec. 2.1 and by Atkinson,[35] isomerization of a hydroxyalkoxy radical will generally be followed by a second isomerization (if feasible).

The α-hydroxyalkyl radicals formed from the decomposition and isomerization reactions of the β-hydroxyalkoxy radicals (Reaction Scheme 4) react rapidly with O_2, with rate constants at room temperature of $\sim(0.9-4)\times10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} (Table 20). Under atmospheric conditions, these reactions with O_2 are then the sole loss process for α-hydroxy radicals.

The simplest α-hydroxyalkyl radical, $\dot{C}H_2OH$, reacts with O_2 to form the HO_2 radical and HCHO,[31,36-40]

$$\dot{C}H_2OH + O_2 \rightarrow HCHO + HO_2$$

and product studies have shown that the higher (C_2–C_4) α-hydroxyalkyl radicals also react by overall H-atom abstraction to yield the corresponding carbonyls[41-44]

$$R_1\dot{C}(OH)R_2 + O_2 \rightarrow R_1C(O)R_2 + HO_2.$$

Therefore, the first generation products from the reactions of the β-hydroxyalkoxy radical $CH_3CH_2CH_2CH(OH)CH_2\dot{O}$ are the carbonyls $HCHO + CH_3CH_2CH_2CHO$ from the decomposition reaction, the β-hydroxycarbonyl $CH_3CH_2CH_2CH(OH)CHO$ from the O_2 reaction, and the dihydroxycarbonyl $CH_3CH(OH)CH_2CH(OH)CHO$ from the isomerization reaction.

Grotheer *et al.*[44,45] and Nesbitt *et al.*[46] have studied the temperature dependence of the rate constant for the reaction of the $\dot{C}H_2OH$ radical with O_2. These studies[44-46] show that the rate constant decreases below room temperature[46] and also decreases slightly above room temperature, and then increases more rapidly with increasing temperature, exhibiting a minimum at ~450 K.[44,45,47] A similar slight decrease in the rate constant for the reaction of the $CH_3\dot{C}HOH$ radical with O_2 with increasing temperature over the range 300–474 K was observed by Grotheer *et al.*,[44] with the rate constant then increasing at higher temperatures (474–682 K).[44] The lack of a deuterium isotope effect on the room temperature rate constant for the reactions of the $\dot{C}H_2OH$ and $\dot{C}H_2OD$ radicals with O_2[45,48] and the temperature dependence of the rate constant shows that this reaction proceeds by initial O_2 addition,

$$\dot{C}H_2OH + O_2 \rightarrow [\dot{O}OCH_2OH \rightleftarrows HOOCH_2\dot{O}] \rightarrow HCHO + HO_2$$

with the initially formed $HOCH_2O\dot{O}$ radical isomerizing through a 5-member transition state to the $HOOCH_2\dot{O}$ radical followed by decomposition to products. Similar reaction mechanisms are expected to occur for the $>C_2$ α-hydroxyalkyl radicals.

The experimental data show that for the $HOCH_2CH_2\dot{O}$ radical formed after OH radical addition to ethene, at room temperature and atmospheric pressure decomposition and re-

TABLE 20. Room temperature rate constants k for the reactions of α-hydroxyalkyl radicals with O_2

α-Hydroxy radical	$10^{12}\times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Reference
$\dot{C}H_2OH$	$9.4^{+3.0}_{-2.3}$	298	Atkinson *et al.*[31]
$CH_3\dot{C}HOH$	$19^{+19}_{-9.5}$	298	Atkinson *et al.*[31]
$CH_3CH_2\dot{C}HOH$	26.1±4.1	296±4	Miyoshi *et al.*[15]
$Ch_3\dot{C}(OH)CH_3$	37.1±6.2	296±4	Miyoshi *et al.*[15]

action with O_2 both occur,[25,49] with $k_a/k_b=(5.4\pm1.0)\times10^{-20}$ cm^3 molecule^{-1} at 300 K,[49] where k_a and k_b are the rate constants for the pathways.

$$HOCH_2CH_2\dot{O}+O_2\rightarrow HOCH_2CHO+HO_2 \qquad (a)$$

and

$$HOCH_2CH_2\dot{O}\rightarrow \dot{C}H_2OH+HCHO. \qquad (b)$$

Thus at 298 K and 760 Torr total pressure of air, the reaction with O_2 to yield glycolaldehyde ($HOCH_2CHO$) accounts for 22% of the overall reaction of the $HOCH_2CH_2\dot{O}$ radical, with the remainder proceeding by decomposition. The data of Barnes *et al.*[25] obtained from the photolysis of $HOCH_2CH_2I-N_2-O_2-NO$ mixtures are in good agreement with the rate constant ratio of Niki *et al.*,[49] although the data presented by Barnes *et al.*[25] for photolyses of $HOCH_2CH_2I-N_2-O_2$ mixtures in the absence of NO do not appear to be quantitatively consistent with the expected reactions of $HOCH_2CH_2\dot{O}$ radicals formed from the self-reactions of the $HOCH_2CH_2\dot{O}_2$ radicals.

TABLE 21. Fraction of the overall OH radical initiated reactions of acyclic monoalkenes proceeding by decomposition of the intermediate β-hydroxyalkoxy radicals at room temperature and atmospheric pressure of air

Alkene	Decomposition[a]	Reference
Ethene	0.78	Niki *et al.*[49]
Propene	0.86–0.98[b]	Niki *et al.*[36]
2-Methylpropene	0.78–0.92[b]	Tuazon *et al.*[33]
cis-2-Butene	0.79–0.93[b]	Tuazon *et al.*[33]
trans-2-Butene	1.05	Niki *et al.*[36]
1-Butene	0.94±0.12	Atkinson *et al.*[7]
2-Methyl-2-butene	0.81–0.97[b]	Tuazon *et al.*[33]
1-Pentene	0.73–0.88[b]	Atkinson *et al.*[50]
2,3-Dimethyl-2-butene	0.85±0.05	Niki *et al.*[30]
	0.80–0.85[b]	Tuazon *et al.*[33]
1-Hexene	0.46–0.57[b]	Atkinson *et al.*[50]
1-Heptene	0.30–0.49[b]	Atkinson *et al.*[50]
1-Octene	0.15±0.07	Paulson and Seinfeld[51]
	0.21–0.39[b]	Atkinson *et al.*[50]
2,3-Dimethyl-1-butene	0.74±0.07	Atkinson *et al.*[50]

[a] Not corrected to take into account β-hydroxyalkyl nitrate formation from the $R\dot{O}_2+NO$ reactions (see text and Table 18).

[b] Ranges shown are for the two individual decomposition products (for example, for HCHO and for heptanal from 1-octene), or for independent measurements (for example, by GC-FID and FTIR analyses).

For the methyl substituted ethenes propene, 2-methylpropene, *cis*- and *trans*-2-butene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene, the experimental studies of Niki *et al.*[36] and Tuazon *et al.*[33] at room temperature and atmospheric pressure of air show that decomposition dominates over reaction with O_2 (Table 21), with no evidence for the occurrence of the O_2 reaction.[33] While this is also the case for the β-hydroxyalkoxy radicals formed after OH radical addition to 1-butene,[7] 2,3-dimethyl-1-butene,[50] and 1-pentene through 1-octene,[50,52] the β-hydroxyalkoxy radicals formed after OH radical addition to 1-pentene through 1-octene also undergo isomerization.[52] Thus, for the 1-alkenes 1-butene through 1-octene the formation yields of the products arising from decomposition of the intermediate β-hydroxyalkoxy radicals decreases from 0.94±0.12 for the 1-butene reaction to ~0.3 for the 1-octene reaction (Table 21),[7,50] and Kwok *et al.*[52] have used atmospheric pressure ionization mass spectrometry (API-MS) to observe the dihydroxycarbonyls formed after isomerization of the intermediate β-hydroxyalkoxy radicals (see Reaction Scheme 4). The API-MS analyses showed that the β-hydroxyalkoxy radical isomerization reaction/decomposition reaction product yield ratio increased from the 1-butene reaction to the 1-octene reaction,[52] and, combined with the data of Atkinson *et al.*,[7,50] Kwok *et al.*[52] estimated that β-hydroxyalkoxy radical isomerization accounts for ~4% of the overall 1-butene reaction pathways and for ~65±25% of the overall reaction pathways for the 1-hexene through 1-octene reactions at room temperature and atmospheric pressure of air.

Atkinson[35] has proposed methods for the estimation of rate constants for the decomposition, isomerization and reaction with O_2 of alkoxy and β-hydroxyalkoxy radicals (see also Sec. 2.1). As discussed in Sec. 2.1, rate constants for the reactions of primary and secondary hydroxyalkoxy radicals with O_2 (except for α-hydroxyalkyl radicals which have been discussed above) of

$$k(RCH_2\dot{O}+O_2)=6.0\times10^{-14}\ e^{-550/T}\ cm^3\ molecule^{-1}\ s^{-1}$$
$$(T\lesssim600\ K)$$
$$=9.5\times10^{-15}\ cm^3\ molecule^{-1}\ s^{-1}$$
$$at\ 298\ K$$

and

$$k(R_1R_2CH\dot{O}+O_2)=1.5\times10^{-14}\ e^{-200/T}\ cm^3\ molecule^{-1}\ s^{-1}$$
$$(T\lesssim600\ K)$$
$$=8\times10^{-15}\ cm^3\ molecule^{-1}\ s^{-1}$$
$$at\ 298\ K$$

are recommended, based on the IUPAC recommendations[31] for the ethoxy and 2-propoxy radicals. For hydroxyalkoxy radicals for which the heats of reaction with O_2, ΔH_{O_2}, differ significantly from the values of ΔH_{O_2} for the "primary" ethoxy radical (-32.0 kcal mol^{-1}) or the "secondary" 2-propoxy radical (-35.9 kcal mol^{-1}), Atkinson[35] proposed that

$$k(R\dot{O}+O_2)=k_{O_2}$$
$$=4.0\times10^{-19}\ n\ e^{-(0.28\Delta O_2)}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$
$$\text{at } 298\ \mathrm{K},$$

where n is the number of abstractable α-H-atoms in the alkoxy radical. At 298 K and 760 Torr total pressure of air, this expression leads to $k_{O_2}[O_2] = 2.1\ n\ e^{-(0.28\Delta O_2)}\ s^{-1}$.

As also discussed in Sec. 2.1, for the unimolecular decomposition of hydroxyalkoxy radicals the decomposition rate constants k_d are given by the Arrhenius expression, $k_d = A\ e^{-E/RT}$, where $A=2\times10^{14}\ d\ s^{-1}$, d is the reaction path degeneracy, and $E=a+b\Delta H_d$. Based on the literature data for the decomposition reactions of alkoxy radicals formed after OH radical reaction with alkanes, Atkinson[35] extended the previous approach of Choo and Benson[53] and derived values for a and b, leading to $E=[2.4(\mathrm{I.P.})-8.1]+0.36\Delta H_d$, where ΔH_d is the heat of the decomposition reaction, I.P. is the ionization potential in eV of the leaving radical, and E and ΔH_d are in kcal mol^{-1}. For the following leaving radicals involved in hydroxyalkoxy radical decompositions, the values of a (in kcal mol^{-1}) are: $\dot{C}H_2OH$, 10.0,[35] $R_1\dot{C}HOH$, 8.0,[35] $R_1R_2\dot{C}OH$, 7.5,[35] and $RCH=\dot{C}H$, 11.7.[54] For example, for the reaction,

$$CH_3CH(\dot{O})CH_2OH \rightarrow CH_3CHO+\dot{C}H_2OH,$$

$\Delta H_d=7.6$ kcal mol^{-1},[31,54] $a=10.0$ kcal mol^{-1}, $E=12.74$ kcal mol^{-1}, and $k_d=9.1\times10^4\ s^{-1}$ at 298 K.[35] The application of this estimation method to unsaturated β- and δ-hydroxyalkoxy radicals is discussed below in the context of the OH radical initiated reaction of isoprene.

For alkoxy radical isomerization, Atkinson[35] postulated that for isomerization from $-CH_3$, $-CH_2-$, and $>CH-$ groups,

$$k_{\mathrm{isom}}(CH_3-X)=k_{\mathrm{prism}}F(X),$$

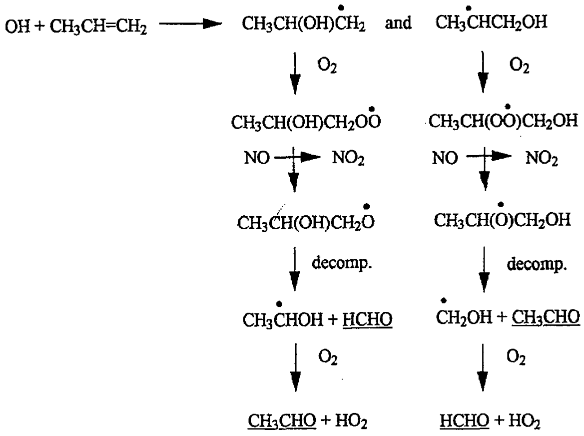
$$k_{\mathrm{isom}}(X-CH_2-Y)=k_{\mathrm{sec}}F(X)F(Y),\quad\text{and}$$

$$k_{\mathrm{isom}}\left(X-CH\begin{smallmatrix}\diagup Y\\ \diagdown Z\end{smallmatrix}\right)=k_{\mathrm{tert}}F(X)F(Y)F(Z),$$

where X, Y, and Z are the substituent groups around the $-CH_3$, $-CH_2-$ and $>CH-$ groups, and $F(X)$, $F(Y)$, and $F(Z)$ are the substituent factors for these groups. By definition, $F(-CH_3)=1.00$ and $F(X)=e^{Ex/T}$.[35] The group rate constants k_{prim}, k_{sec}, and k_{tert} and the substituent factors for $-CH_3$, $-CH_2-$, $>CH-$, $>C<$, and $-OH$ groups[35] are given in Sec. 2.1 in Tables 11 and 12.

The calculated rate constants (or rates) for the decomposition, isomerization, and reaction with O_2 can then be used to assess the dominant reaction pathways under tropospheric conditions.[35]

The OH radical initiated reaction scheme for propene in the presence of NO is therefore as shown below in Reaction Scheme 5 (first generation products are underlined and the minor amount of nitrate formation[28] is neglected for clarity).



The OH radical initiated reactions of other acyclic monoalkenes (including ethene, the methyl substituted ethenes, and 1-butene through 1-octene) in the presence of NO proceed by analogous reaction schemes, with isomerization of the β-hydroxyalkoxy radicals potentially occurring for alkenes containing $>C{=}CCC<$ structures.[35,50,52] It should be noted that H-atom abstraction from $-CH_2-$ and $>CH-$ groups may become significant for alkenes with large alkyl substituent groups (for example, for 1-heptene and 1-octene).

TABLE 22. Calculated reaction rates (s^{-1}) for reaction with O_2, decomposition, and isomerizaton of the hydroxyalkoxy radicals formed after OH radical addition to isoprene at 298 K and 760 Torr of air

Alkoxy radical	$k_{O_2}[O_2]$	k_{decomp}	k_{isom}	Isomerization product
$HOCH_2C(CH_3)(\dot{O})CH=CH_2$	[a]	9.3×10^6	[b]	
$HOCH_2CH(\dot{O})C(CH_3)=CH_2$	$\sim2.0\times10^5$	3.1×10^6	[b]	
$\dot{O}CH_2C(CH_3)(OH)CH=CH_2$	2.8×10^4	6.3×10^8	[c]	$HOCH_2C(CH_3)(OH)CH=\dot{C}H$
$\dot{O}CH_2CH(OH)C(CH_3)=CH_2$	3.6×10^4	2.7×10^8	2.0×10^5	$HOCH_2CH(OH)C(\dot{C}H_2)=CH_2$
			[c]	$HOCH_2CH(OH)C(CH_3)=\dot{C}H$
$HOCH_2C(CH_3)=CHCH_2\dot{O}$	1.0×10^5	~0.3[d]	6.9×10^6	$HO\dot{C}HC(CH_3)=CHCH_2OH$
			2.0×10^5	$HOCH_2C(\dot{C}H_2)=CHCH_2OH$
$HOCH_2CH=C(CH_3)CH_2\dot{O}$	8.5×10^4	~0.2[d]	6.9×10^6	$HO\dot{C}HCH=C(CH_3)CH_2OH$

[a] Reaction not possible (no α-H-atom).
[b] Isomerization via a 6-member transition state not possible.
[c] Isomerization involving abstraction of a vinylic H-atom expected to be negligibly slow.
[d] Based on a value of $a=11.7$ kcal mol^{-1} derived using I.P. $(CH_2=\dot{C}H)=8.25$ eV.[54]

Generally similar reaction schemes are expected to apply to the conjugated dienes such as 1,3-butadiene and isoprene (2-methyl-1,3-butadiene). For example, for isoprene initial OH radical addition can occur at the 1-, 2-, 3-, and 4-positions, leading after O_2 addition to the β-hydroxyalkyl or δ-hydroxyallylic radicals to the six peroxy radicals

$$\mathrm{HOCH_2C(O\dot{O})(CH_3)CH{=}CH_2},$$

$$\mathrm{HOCH_2C(CH_3){=}CHCH_2O\dot{O}},$$

$$\mathrm{\dot{O}OCH_2C(OH)(CH_3)CH{=}CH_2},$$

$$\mathrm{CH_2{=}C(CH_3)CH(OH)CH_2O\dot{O}},$$

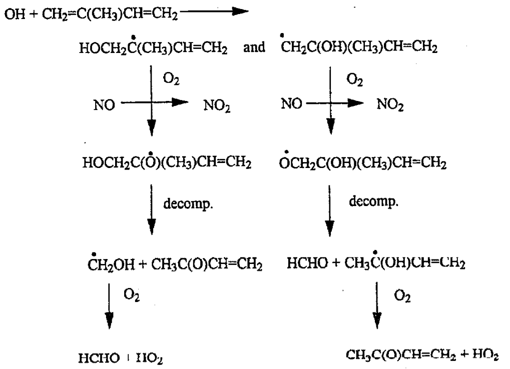
$$\mathrm{CH_2{=}C(CH_3)CH(O\dot{O})CH_2OH}$$

and

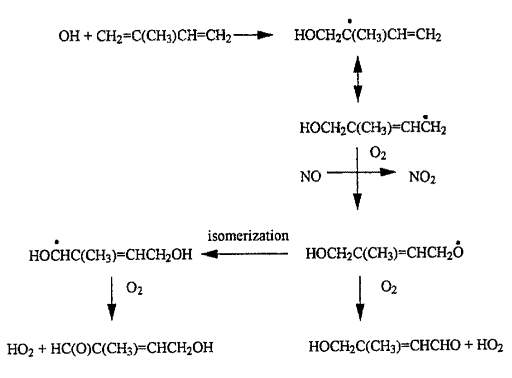
$$\mathrm{\dot{O}OCH_2C(CH_3){=}CHCH_2OH},$$

with the four peroxy radicals arising from terminal OH radical addition at the 1- or 4-positions being expected to dominate. In the presence of NO or after self-reaction via the radical pathway, the corresponding β- and δ-hydroxyalkoxy radicals are $\mathrm{HOCH_2C(\dot{O})(CH_3)CH{=}CH_2}$, $\mathrm{HOCH_2C(CH_3){=}CHCH_2\dot{O}}$, $\mathrm{\dot{O}CH_2C(OH)(CH_3)CH{=}CH_2}$, $\mathrm{CH_2{=}C(CH_3)CH(OH)CH_2\dot{O}}$, $\mathrm{CH_2{=}C(CH_3)CH(\dot{O})CH_2OH}$, and $\mathrm{\dot{O}CH_2C(CH_3){=}CHCH_2OH}$. The calculated reaction rates for the decomposition, isomerization, and reaction with O_2 of these alkoxy radicals are given in Table 22, using the estimation methods given above[35] and with a $>C{=}C<$ substituent group factor for the isomerization reaction of $F(>C{=}C<)\sim1.0$ (by analogy with the OH radical reactions[9]).

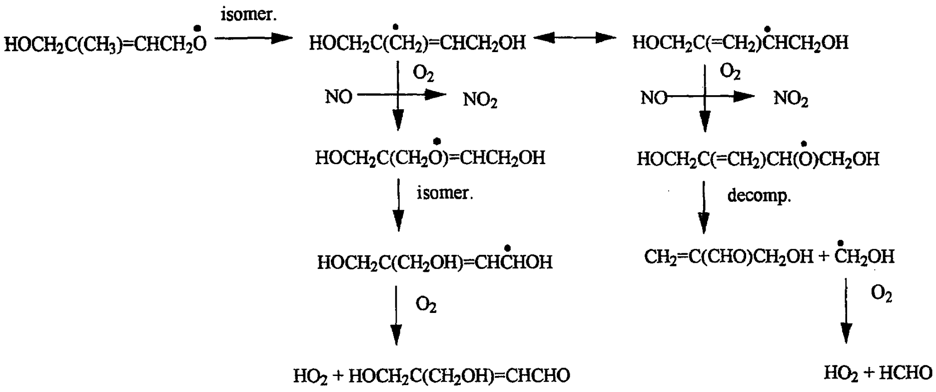
The dominant reaction pathways predicted using these estimation methods are consistent with the products observed[3,4,18,55] and with the recent detailed chemical mechanism of Carter and Atkinson[56] (which included the data from the API-MS study of Kwok *et al.*[18] and the derivatization study of Yu *et al.*[57]). In the presence of NO, and omitting the relatively small amount of nitrate formation from the $\mathrm{R\dot{O}_2}$+NO reactions,[4] the four β-hydroxyalkoxy radicals decompose to form methacrolein plus HCHO or methyl vinyl ketone plus HCHO, depending on which $>C{=}C<$ bond the OH radical initially adds to. For example, for OH radical addition to the $\mathrm{CH_2{=}C(CH_3)}$– moiety, the reactions involving β-hydroxyalkoxy radicals are as shown in Reaction Scheme 6, leading to the formation of methyl vinyl ketone plus HCHO, irrespective of which carbon atom in the $\mathrm{CH_2{=}C(CH_3)}$–moiety the OH radical adds to. By an analogous reaction scheme, OH radical addition to the $\mathrm{CH_2{=}CH}$– moiety leads to the formation of methacrolein plus HCHO.



The reactions of the unsaturated δ-hydroxyalkoxy radicals $\mathrm{HOCH_2C(CH_3){=}CHCH_2\dot{O}}$ and $\mathrm{HOCH_2CH{=}C(CH_3)CH_2\dot{O}}$ are predicted to be mainly by isomerization (Table 22) to form the unsaturated δ-hydroxyaldehydes $\mathrm{HOCH_2C(CH_3){=}CHCHO}$ and $\mathrm{HOCH_2CH{=}C(CH_3)CHO}$, as shown below in Reaction Scheme 7. It should be noted that the calculations of the isomerization rate constants assumed that the orientation of the hydroxyalkoxy radical was such that a 6 member transition state was feasible (and therefore in a *cis*- conformation). As evident from Reaction Scheme 7 and the analogous reaction scheme involving the $\mathrm{HOCH_2CH{=}C(CH_3)CH_2\dot{O}}$ radical, the same two products are formed from these two δ-hydroxyalkoxy radicals if the reaction with O_2 dominates.[18]



Isomerization of the $\mathrm{HOCH_2C(CH_3){=}CHCH_2\dot{O}}$ radical by H-atom abstraction from the $-CH_3$ group can lead to the dihydroxyaldehyde $\mathrm{(HOCH_2)_2C{=}CHCHO}$ and/or hydroxymethacrolein, $\mathrm{CH_2{=}C(CHO)CH_2OH}$,[56] as shown in Reaction Scheme 8.



The API-MS study of Kwok *et al.*[18] gave evidence for the formation of hydroxymethacrolein but not for the dihydroxyaldehyde.

The three recent studies of the products formed from the gas-phase reaction of the OH radical with isoprene[3,4,55] show that in the presence of NO methyl vinyl ketone and methacrolein (together with their expected HCHO coproduct) account for ~55% of the overall reaction pathways. In the Fourier transform infrared absorption spectroscopy study of Tuazon and Atkinson,[4] the reaction of isoprene with the $O(^3P)$ atom[3,58] formed from photolysis of NO_2 was not taken into account. Using the absolute rate constant measured by Paulson *et al.*,[58] this reaction is calculated to contribute ~8% of the overall isoprene reacted in the study of Tuazon and Atkinson,[4] and the product yields of Tuazon and Atkinson[4] and Atkinson *et al.*,[59] corrected to take into account this $O(^3P)$ atom reaction, are then: methyl vinyl ketone, 0.32 ±0.07; methacrolein, 0.22±0.05; HCHO, 0.63±0.10; 3-methylfuran, 0.048±0.006; organic nitrates, ~0.08–0.14; and unidentified carbonyl compounds, ~0.21–0.27. The formaldehyde yield was slightly higher than (though in agreement within the uncertainties with) the sum of the methyl vinyl ketone and methacrolein yields,[4] and this additional HCHO may arise as a coproduct to hydroxymethacrolein formation.[56] Paulson *et al.*[3] determined formation yields of methyl vinyl ketone, methacrolein and 3-methylfuran of 0.355±0.03, 0.25±0.03, and 0.04±0.02, respectively, from a generally similar product study, but using gas chromatography for product analysis. The influence of the $O(^3P)$ atom reaction with isoprene was taken into account by computer modeling, using an estimated rate constant a factor of 1.5–1.6 higher than that recently measured,[58] and the formation yields reported by Paulson *et al.*[3] are therefore expected to be slightly high. Miyoshi *et al.*[55] reported methyl vinyl ketone, methacrolein and HCHO formation yields of 0.32±0.05, 0.22±0.02, and 0.57 ±0.06, respectively, using a rate constant for the $O(^3P)$ atom reaction rate constant similar to that recently measured.[58] These studies are in excellent agreement, and show that methyl vinyl ketone and methacrolein formation account for ~55% of the overall OH radical reaction with isoprene in the presence of NO. The data of Tuazon and Atkinson[4] indicate that organic nitrate formation, presumably from the reactions of RO_2 radicals with NO, accounts for ~8–14% of the overall reaction, and that other carbonyl compounds, probably hydroxycarbonyls, account for ~24% of the reaction. These hydroxycarbonyls have been tentatively identified as $HOCH_2C(CH_3){=}CHCHO$ and $HOCH_2CH{=}C(CH_3)CHO$ from an API-MS study of the OH radical initiated reactions of isoprene and isoprene-d_8 in the presence of NO.[18]

3-Methylfuran also arises from the OH radical initiated reaction of isoprene,[3,59,60] possibly in part after the formation of δ-hydroxyalkoxy radicals.[59,60] Aerosol formation from isoprene photooxidation has been shown to be of negligible importance under atmospheric conditions,[61] and the aerosol composition has been investigated by Palen *et al.*[62]

For unsymmetrical dienes the expected products formed depend on which $>C{=}C<$ bond OH addition occurs. For conjugated dienes, the estimation technique of Ohta[63] allows the fraction of the overall OH radical addition reaction proceeding at each $>C{=}C<$ double bond to be calculated (this information cannot be obtained from the estimation technique of Atkinson[64] or Kwok and Atkinson[9]). Thus for isoprene, rate constants for OH radical addition to the $CH_2{=}CH-$ and $CH_2{=}C<$ bonds of isoprene are calculated[63] to be in the ratio 34/66 at room temperature, consistent with the observation that the methyl vinyl ketone yield is a factor of ~1.5 higher than that of methacrolein.[3,4,55]

The OH radical initiated reaction of 1,3-butadiene in the presence of NO is expected to be analogous to the corresponding isoprene reaction. However, the absence of the methyl substituent group leads to a simpler set of reaction schemes, leading to the formation of acrolein ($CH_2{=}CHCHO$) plus HCHO by decomposition of the intermediate β-hydroxyalkoxy radicals $CH_2{=}CHCH(\dot{O})CH_2OH$ and $CH_2{=}CHCH(OH)CH_2\dot{O}$, and the unsaturated δ-hydroxyaldehyde $HOCH_2CH{=}CHCHO$ from isomerization of the δ-hydroxyalkoxy radical $HOCH_2CH{=}CHCH_2\dot{O}$. Maldotti *et al.*[65] observed the formation of acrolein from irradiated NO_x–1,3-butadiene–air mixtures, with

TABLE 23. Products observed and their molar formation yields from the reactions of the OH radical with cycloalkenes and monoterpenes in the presence of NO at room temperature and atmospheric pressure of air

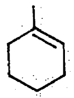
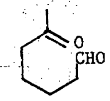
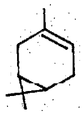
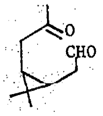
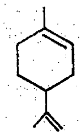
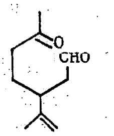
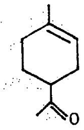
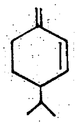
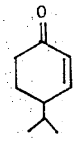
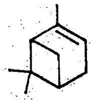
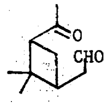
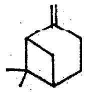
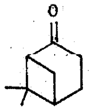
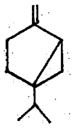
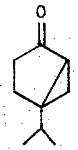
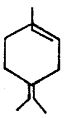
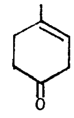
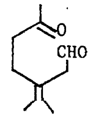
Alkene	Structure	Product	Yield[a]	Reference
1-Methylcyclohexene			0.31 ± 0.08	Atkinson *et al.*[50]
3-Carene			0.34 ± 0.08	Hakola *et al.*[70]
Limonene			0.29 ± 0.06	Hakola *et al.*[70]
			0.20 ± 0.03	Hakola *et al.*[70]
β-Phellandrene			0.29 ± 0.07	Hakola *et al.*[69]
α-Pinene			0.28 ± 0.05	Hakola *et al.*[70]
			0.56 ± 0.04[b]	Hatakeyama *et al.*[68]
β-Pinene			0.27 ± 0.04	Hakola *et al.*[70]
			0.79 ± 0.08[b]	Hatakayama *et al.*[68]
		HCHO	0.54 ± 0.05[b]	Hatakeyama *et al.*[68]
Sabinene			0.17 ± 0.03	Hakola *et al.*[70]

TABLE 23. Products observed and their molar formation yields from the reactions of the OH radical with cycloalkenes and monoterpenes in the presence of NO at room temperature and atmospheric pressure of air – Continued (3)

Alkene	Structure	Product	Yield[a]	Reference
Terpinolene			0.26 ± 0.06	Hakola *et al.*[70]
			0.08 ± 0.02[c]	Arey *et al.*[67]; Hakola *et al.*[70]

[a] Indicated uncertainties are two least-squares standard deviations and include uncertainties in the analytical calibration factors, unless noted otherwise.

[b] Indicated uncertainties are one standard deviation; the 6,6-dimethylbicyclo[3.3.1]heptan-2-one and pinonaldehyde as measured by Fourier transform infrared absorption spectroscopy may have included IR contributions from other as yet unidentified carbonyl-containing compounds.

[c] Product identification tentative.

[acrolein]$_{\text{max}}$/[1,3-butadiene]$_{\text{initial}}$=0.59±0.07. Based on the rate constants for the OH radical reactions with acrolein and 1,3-butadiene,[2,5] this ratio corresponds to a formation yield of acrolein from the OH radical initiated reaction of 1,3-butadiene of 0.98±0.12. However, Ohta[66] measured a yield of acrolein (apparently uncorrected for secondary reaction of acrolein with the OH radical, although this should be minor for this reaction system) of 0.25 in the absence of NO$_x$ and 0.39 in the presence of NO$_x$. Clearly, there is significant disagreement between these two studies.[65,66] Additionally, furan is formed in a minor amount from the OH radical initiated reaction of 1,3-butadiene, with measured yields of 0.039±0.011 (in the presence of NO)[59] and 0.060±0.020 (the indicated error being two standard deviations), independent of the presence or absence of NO.[66]

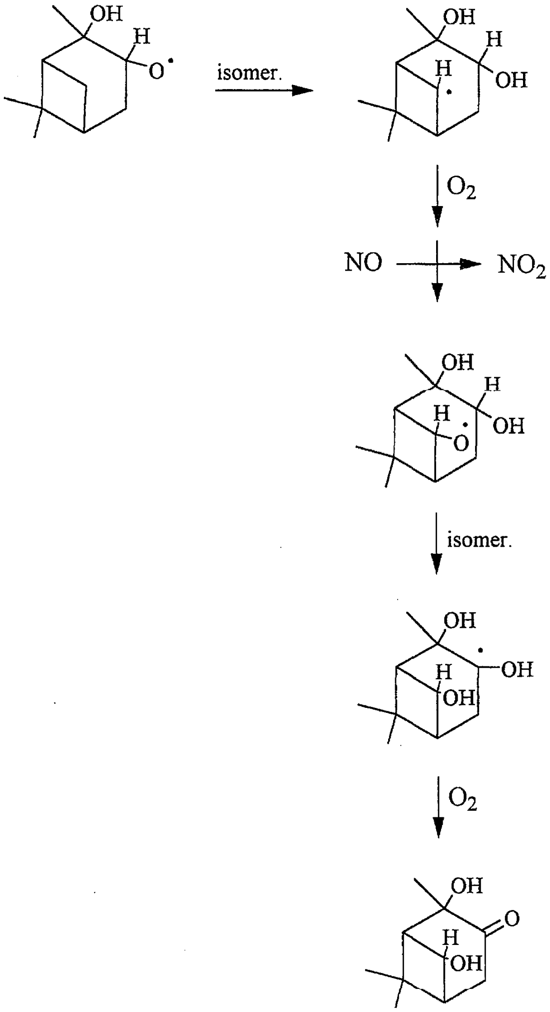
Although not expected to be specifically involved as a significant intermediate alkoxy radical in the OH radical initiated reactions of alkenes, the dominant reaction of the allyloxy radical, $\mathrm{CH_2{=}CHCH_2\dot{O}}$, at 298 K and one atmosphere of air appears to be by reaction with O_2,[20]

$$\mathrm{CH{=}CHCH_2\dot{O}+O_2 \rightarrow CH_2{=}CHCHO+HO_2}$$

consistent with the estimated rates of decomposition (5 s^{-1}) and reaction with O_2 (1.1×10^5 s^{-1}) at 298 K and 760 Torr of air.[35]

To date, few quantitative product studies have been carried out for cycloalkenes[50] or monoterpenes,[67–70] and the reported data are given in Table 23 (the study of Hakola *et al.*[70] is in agreement with, but supersedes, that of Arey *et al.*[67]). In addition to the data given in Table 23, Grosjean *et al.*[71] have identified a number of carbonyl products from the NO–air irradiations of cyclohexene, and Grosjean *et al.*[72] identified the formation of pinonaldehyde, nopinone, and 4-acetyl-1-methylcyclohexene from the NO–air irradiations of α-pinene, β-pinene, and limonene, respectively, although it cannot be ascertained from these NO–air–alkene irradiations whether these carbonyls were formed from the OH radical or O_3 reactions, or both. The yields reported by Hatakeyama *et al.*[68] for specific C_9 and C_{10} carbonyls formed from α- and β-pinene are probably too high because of contributions to the observed infrared absorptions from other, as yet unidentified, carbonyl containing compounds (including dihydroxycarbonyls[73]). Only a relatively small fraction of the overall reaction products have been accounted for to date, and Arey *et al.*[67] and Hakola *et al.*[70] observed no significant products by gas chromatography with flame ionization detection from the OH radical reactions with myrcene[67] or camphene[70] in the presence of NO$_x$.

The products identified and quantified by Arey *et al.*,[67] Hakola *et al.*,[69,70] and Atkinson *et al.*[50] are those expected from decomposition of the intermediate β-hydroxyalkoxy radicals. By analogy with the OH radical reactions with the monoalkenes,[35] the intermediate β-hydroxyalkoxy radicals formed from the cycloalkenes and monoterpenes are expected to react mainly by decomposition or isomerization, if the isomerization pathway is sterically favorable. The formation of hydroxycarbonyls from the reaction of the intermediate β-hydroxyalkoxy radicals with O_2 is expected to be of negligible or minor importance.[35] Product analyses of the OH radical initiated reactions of several monoterpenes in the presence of NO using atmospheric pressure ionization tandem mass spectrometry have shown evidence for the formation of dihydroxycarbonyls,[73] presumably formed after isomerization of the initially formed β-hydroxyalkoxy radical. For example, one of the two β-hydroxyalkoxy radicals formed after OH radical addition to α-pinene in the presence of NO can react as follows:[73]



Hatakeyama *et al.*[68] observed that the pinonaldehyde yield in the absence of NO was significantly lower than in the presence of NO. Aerosol formation from the reactions of the OH radical with α- and β-pinene have been studied by Hatakeyama *et al.*,[68] Pandis *et al.*,[61] and Zhang *et al.*,[74] and the aerosol composition investigated.[62] These references[61,62,68,74] should be consulted for further details.

Obviously, although significant advances have been made in the past three to four years, especially concerning the realization that isomerization of hydroxyalkoxy radicals can be important, further product and mechanistic data are required for the OH radical reactions with the more complex alkenes and for the monoterpenes of biogenic origin.

2.2.2. NO_3 Radical Reactions

The kinetics and mechanisms of the gas-phase reactions of the NO_3 radical with alkenes, cycloalkenes, and dienes were most recently reviewed and evaluated by Atkinson,[2,75] and these reviews and evaluations are updated in Sec. 4.2. The room temperature rate constants and temperature dependent parameters for alkenes, cycloalkenes, and dienes are given in Table 24. These reactions proceed by NO_3 radical addition to the $>C{=}C<$ bond, with H-atom abstraction being insignificant.[75]

The products of the gas-phase reactions of the NO_3 radical with a series of alkenes at room temperature and atmospheric pressure have been studied experimentally and theoretically by Akimoto *et al.*,[76] Hoshino *et al.*,[77] Bandow *et al.*,[78] Shepson *et al.*,[28] Kotzias *et al.*,[79] Dlugokencky and Howard,[80] Barnes *et al.*,[81] Hjorth *et al.*,[82] Wille *et al.*,[83] Skov *et al.*,[84,85] Wängberg *et al.*,[86] Berndt and Böge,[87,88] Olzmann *et al.*,[89] Benter *et al.*,[90] and Berndt *et al.*,[91] and the reaction mechanisms have previously been discussed by Atkinson.[2,75] At low total pressures, the formation of NO_2 plus the oxirane is observed from the NO_3 radical reactions with propene,[88] 1-butene,[88] 2-methylpropene,[83,88] *cis*-2-butene,[83,85,90] *trans*-2-butene,[80,85,88,90] 2-methyl-2-butene,[83,88] 2,3-dimethyl-2-butene,[83,85,87,90] isoprene,[80,85,90] 2,3-dimethyl-1,3-butadiene,[90] cyclohexene,[90] 1,3-cyclohexadiene,[90,91] β-pinene,[80] and α-terpinene,[90] with the oxirane plus NO_2 formation yields tending to unity as the total pressure decreases to zero.[80,83,85,87–90]

In the absence of O_2, the oxirane plus NO_2 yields from the reactions of the NO_3 radical with 2,3-dimethyl-2-butene are essentially unity and independent of total pressure over the range 0.75–750 Torr of He, Ar, or N_2,[83,85,87,90] with reported oxirane or NO_2 yields of 0.90 ± 0.10 at 2.25–7.5 Torr of He[83] or 22.5 Torr of Ar,[90] 0.95 at 20 Torr of Ar,[85] 1.0 ($\pm \sim 0.15$) at 0.75–600 Torr of He or N_2,[87] 0.86 ± 0.05 at 735–740 Torr of Ar,[85] and 0.75 ± 0.10 at 750 Torr of Ar.[90] For the propene, 1-butene, 2-methylpropene, *trans*-2-butene and 2-methyl-2-butene reactions, Berndt and Böge[88] report oxirane yields at 600 Torr of N_2 of 1.00, 1.00, 0.82, 1.00, and 0.95, respectively. Benter *et al.*[90] measured NO_2 yields from the reactions of the NO_3 radical with *trans*-2-butene, cyclohexene, 1,3-cyclohexadiene and α-terpinene over the pressure range 0.75–20 Torr of Ar, and observed no significant decrease in the NO_2 yield from unity as the pressure increased. Over a wide pressure range, Berndt *et al.*[91] observed the oxirane (7-oxa-bicyclo[4.1.0]hept-2-ene) yield from the 1,3-cyclohexadiene reaction to decrease with increasing pressure from ~ 0.9 below ~ 35–40 Torr N_2 to a value of ~ 0.2 at ~ 180 Torr total pressure of N_2 diluent. Skov *et al.*[85,90] measured oxirane yields from the *cis*- and *trans*-2-butene reactions of ~ 0.53 and ~ 0.58, respectively, at 20 Torr of Ar, with identical yields of the two stereoisomers from both the *cis*- and *trans*-2-butene reactions[85,90] (showing that oxirane formation is not a direct process[85,90]), with the lower than unit yields of the oxiranes possibly being due to the presence of NO_2 and the reaction of NO_2 with the nitrooxyalkyl radi-

TABLE 24. Room temperature rate constants k and temperature dependent parameters, $k = A\ e^{-B/T}$, for the gas-phase reactions of the NO_3 radicals with alkenes

Alkene	A (cm^3 molecule^{-1} s^{-1})	B (K)	k (cm^3 molecule^{-1} s^{-1}) at 298 K
Ethene	[a]	[a]	2.05×10^{-16}
Propene	4.59×10^{-13}	1156	9.49×10^{-15}
1-Butene	3.14×10^{-13}	938	1.35×10^{-14}
2-Methylpropene			3.32×10^{-13}
cis-2-Butene			3.50×10^{-13}
trans-2-Butene	[b]	[b]	3.90×10^{-13}
2-Methyl-2-butene			9.37×10^{-12}
2,3-Dimethyl-2-butene			5.72×10^{-11}
1,3-Butadiene			1.0×10^{-13}
2-Methyl-1,3-butadiene	3.03×10^{-12}	446	6.78×10^{-13}
2,3-Dimethyl-1,3-butadiene			2.1×10^{-12}
cis-1,3-Pentadiene			1.4×10^{-12}
trans-1,3-Pentadiene			1.6×10^{-12}
trans, trans-2,4-Hexadiene			1.6×10^{-11}
Myrcene			1.1×10^{-11}
Ocimene			2.2×10^{-11}
Cyclopentene			5.3×10^{-13}
Cyclohexene	1.05×10^{-12}	174	5.9×10^{-13}
1,3-Cyclohexadiene			1.16×10^{-11}
1,4-Cyclohexadiene			6.6×10^{-13}
1-Methylcyclohexene	1.7×10^{-11}	0	1.7×10^{-11}
Cycloheptene			4.8×10^{-13}
1,3-Cycloheptadiene			6.5×10^{-12}
1,3,5-Cycloheptatriene			1.2×10^{-12}
Bicyclo[2.2.1]-2-heptene			2.5×10^{-13}
Bicyclo[2.2.1]-2,5-heptadiene			1.0×10^{-12}
Bicyclo[2.2.2]-2-octene			1.45×10^{-13}
Camphene			6.6×10^{-13}
2-Carene			1.9×10^{-11}
3-Carene			9.1×10^{-12}
Limonene			1.22×10^{-11}
α-Phellandrene			7.3×10^{-11}
β-Phellandrene			8.0×10^{-12}
α-Pinene	1.19×10^{-12}	−490	6.16×10^{-12}
β-Pinene			2.51×10^{-12}
Sabinene			1.0×10^{-11}
α-Terpinene			1.4×10^{-10}
γ-Terpinene			2.9×10^{-11}
Terpinolene			9.7×10^{-11}
α-Cedrene			8.2×10^{-12}
α-Copaene			1.6×10^{-11}
β-Caryophyllene			1.9×10^{-11}
α-Humulene			3.5×10^{-11}
Longifolene			6.8×10^{-13}

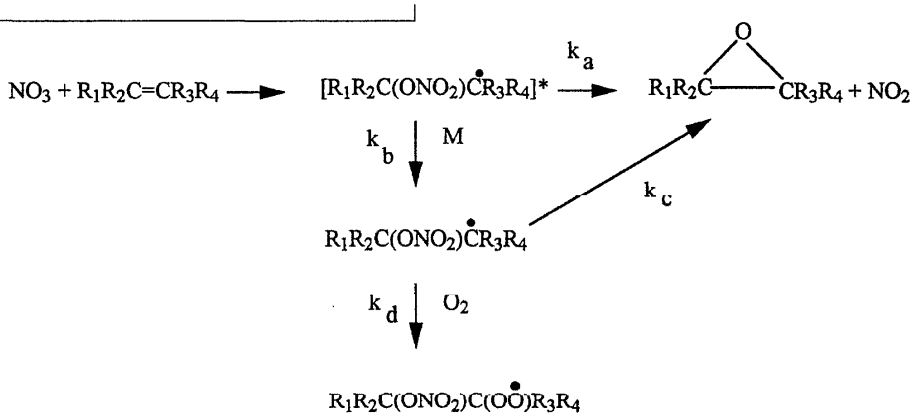
[a] $k = 4.88\times10^{-18}\ T^2\ e^{-2282/T}$ cm^3 molecule^{-1} s^{-1} over the temperature range 290–523 K recommended.[2,73]

[b] $k = 1.22\times10^{-18}\ T^2\ e^{382/T}$ cm^3 molecule^{-1} s^{-1} over the temperature range 204–378 K recommended.[2,75]

cals in competition with decomposition of the nitrooxy radicals to oxirane plus NO_2.[85] For the NO_3 radical reaction with isoprene, the oxirane and NO_2 yields decrease significantly with increasing total pressure, from an approximate unit yield at <1 Torr total pressure[80,90] to 0.16–0.43 at 19–20 Torr of Ar,[85,90] and a similar effect of total pressure of Ar was observed for the 2,3-dimethyl-1,3-butadiene reaction.[90]

In air, Ar–O_2 or N_2–O_2 mixtures, however, the oxirane formation yields from the reactions of the NO_3 radical with alkenes (propene,[88] 1-butene,[88] 2-methylpropene,[88] *cis*-2-butene,[85] *trans*-2-butene,[88] 2-methyl-2-butene,[88] and 2,3-dimethyl-2-butene[85,88,90]) and isoprene[85] are markedly lower (depending on the O_2 concentration[85,88,91]) than in the absence of O_2. For example, the oxirane yields from the NO_3 radical reactions with propene, 1-butene, 2-methylpropene, *trans*-2-butene, and 2-methyl-2-butene at 750 Torr of air measured by Berndt and Böge[88] were 0.28, 0.18, 0.07, 0.12, and 0.09, respectively, although Skov *et al.*[85] report oxirane yields of <1% from the *cis*- and *trans*-2-butene and isoprene reactions in the presence of 740 Torr of air. For the NO_3 radical reaction with 2,3-dimethyl-2-butene, the oxirane yield at 740–750 Torr of air has been measured by Skov *et al.*[85] and Berndt and Böge,[88] with the measured yields of 0.174±0.035[85] and ~0.20[88] being in good agreement.

The product studies of Bandow *et al.*,[78] Shepson *et al.*,[28] Dlugokencky and Howard,[80] Barnes *et al.*,[81] Hjorth *et al.*,[82] Wille *et al.*,[83] Skov *et al.*,[84,85] Wängberg *et al.*,[86] Berndt and Böge,[87,88] Benter *et al.*,[90] and Berndt *et al.*,[91] and the theoretical interpretation by Olzmann *et al.*[89] allow the general features of the reaction mechanisms to be understood. The initial reaction involves addition of the NO_3 radical to the $>C=C<$ bond(s) to form an excited nitrooxyalkyl radical which either decomposes to the oxirane plus NO_2 [reaction (a)] or is collisionally stabilized to a thermalized nitrooxyalkyl radical [reaction (b)]. In addition, the data suggest that the thermalized nitrooxyalkyl radical can also decompose to form the oxirane plus NO_2 [reaction (c)]. Under tropospheric conditions, rapid addition of O_2 will occur to the nitrooxyalkyl radical [reaction (d)], leading to the formation of a nitrooxyalkyl peroxy radical.



Berndt and Böge[87,88] derived rate constant ratios at room temperature of $k_b/k_a=(1.75\pm0.19)\times10^{-19}$ cm^3 molecule^{-1} and $k_d/k_c=(1.30\pm0.34)\times10^{-16}$ cm^3 molecule^{-1} for the reactions of the NO_3-2,3-dimethyl-2-butene adduct,[87] and rate constant ratios k_b/k_a for the NO_3-propene, NO_3-1-butene, NO_3-*trans*-2-butene, NO_3-2-methylpropene, and NO_3-2-methyl-2-butene adducts of (in units of 10^{-19} cm^3 molecule^{-1}) 1.53±0.17, 1.93±0.19, 3.26±0.23, and 4.37±0.17, respectively.[88] Equating k_b with the collision frequency,[87,89,90] the rate constant k_a for the decomposition of the activated $[(CH_3)_2C(ONO_2)\dot{C}(CH_3)_2]^*$ radical to tetramethyloxirane plus NO_2 has been estimated to be in the range $(2.0-4.4)\times10^9$ s^{-1},[87,89,90] while the corresponding decomposition rate constant for the activated NO_3-isoprene adduct is estimated to be 9×10^7 s^{-1}.[90]

While the reactions of the NO_3 radical with monoalkenes will lead to β-nitrooxyalkyl and β-nitrooxyalkyl peroxy radicals, the reactions of the NO_3 radical with 1,3-butadiene and isoprene appear to proceed mainly (if not exclusively) by addition to the terminal carbon, with subsequent O_2 addition leading to β- or δ-nitrooxyalkyl peroxy radicals.

$$\begin{array}{lll} NO_3+CH_2=C(CH_3)CH=CH_2\rightarrow & O_2NOCH_2\dot{C}(CH_3)CH=CH_2 & \leftrightarrow O_2NOCH_2C(CH_3)=CH\dot{C}H_2 \\ & \downarrow O_2 & \downarrow O_2 \\ & O_2NOCH_2C(O\dot{O})(CH_3)CH=CH_2 & O_2NOCH_2C(CH_3)=CHCH_2\dot{O}_2 \end{array}$$

When NO_3 radicals are present, NO concentrations will be extremely low,[31] and the β- or δ-nitrooxyalkyl peroxy radicals formed will then either react with HO_2 and other $R\dot{O}_2$ radicals, or reversibly add NO_2 to yield the thermally unstable nitrooxy-peroxynitrates.[28,78,81,82,84] For example, for the β-nitrooxyalkyl peroxy radical $CH_3CH(O\dot{O})CH_2ONO_2$ formed from propene:

$$CH_3CH(O\dot{O})CH_2ONO_2+NO_2\rightleftarrows CH_3CH(OONO_2)CH_2ONO_2 \qquad \text{(a,-a)}$$

$$CH_3CH(O\dot{O})CH_2ONO_2+HO_2\rightarrow CH_3CH(OOH)CH_2ONO_2+O_2 \qquad \text{(b)}$$

$$CH_3CH(O\dot{O})CH_2ONO_2+R\dot{O}_2 \rightarrow \alpha CH_3CH(OH)CH_2ONO_2+(1-\alpha)\ CH_3C(O)CH_2ONO_2+O_2+R\dot{O}_2 \text{ products} \quad \text{(c1)}$$

$$\rightarrow CH_3CH(\dot{O})CH_2ONO_2+R\dot{O}+O_2 \quad \text{(c2)}$$

Because of the rapid thermal decomposition of peroxy nitrates,[2] the nitrooxy-peroxynitrates act as a temporary reservoir of the nitrooxyalkyl peroxy radicals. If NO is present at sufficiently high concentrations to react with the peroxy radicals (see Sec. 2.1), then the corresponding nitrooxyalkoxy radical will be formed together with NO_2, and dinitrates may be formed from the $R\dot{O}_2$+NO reaction.

$$CH_3CH(O\dot{O})CH_2ONO_2+NO \xrightarrow{M} CH_3CH(ONO_2)CH_2ONO_2 \quad \text{(d1)}$$

$$\rightarrow CH_3CH(\dot{O})CH_2ONO_2+NO_2 \quad \text{(d2)}$$

The nitrooxyalkoxy radicals formed from reactions (c2) and (d2) can then react with O_2, decompose or isomerize, as discussed above and by Atkinson.[2,35] For example, for the $CH_3CH(\dot{O})CH_2ONO_2$ radical formed from propene.

$$\begin{array}{l} CH_3CH(\dot{O})CH_2ONO_2 \rightarrow CH_3CHO+\dot{C}H_2ONO_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad HCHO+NO_2 \end{array} \quad \text{(e)}$$

$$CH_3CH(\dot{O})CH_2ONO_2+O_2 \rightarrow CH_3C(O)CH_2ONO_2+HO_2 \quad \text{(f)}$$

In addition, under laboratory conditions with high NO_2 concentrations, the nitrooxyalkoxy radicals can also react with NO_2

$$CH_3CH(\dot{O})CH_2ONO_2+NO_2 \xrightarrow{M} CH_3CH(ONO_2)CH_2ONO_2 \quad \text{(g)}$$

Based on this reaction scheme, in the absence of NO dinitrates are expected to be formed from reaction (g) and their yields should decrease with decreasing NO_2 concentration. This is consistent with the studies of Shepson *et al.*[28] and Bandow *et al.*[78] for propene and with the more recent data of Barnes *et al.*[81] and Hjorth *et al.*[82] for other acyclic alkenes, but not with the data of Wängberg[86] for the reactions of the NO_3 radical with cyclopentene, cyclohexene and 1-methylcyclohexene in the presence of initial NO_2 concentrations in the range $(1.0-12)\times10^{14}$ molecule cm^{-3}, where the dinitrate yields were found to be invariant of the initial NO_2 concentration. Under atmospheric conditions the formation of dinitrates from reaction (g) is expected to be of no importance. Neglecting isomerization of the alkoxy radicals, the expected major products of the NO_3 radical initiated reactions of the simple alkenes are then oxiranes from the decomposition of the initially formed activated nitrooxyalkyl radical (in generally small yield apart from the 2,3-dimethyl-2-butene reaction) carbonyl compounds [reaction (e)], nitrooxycarbonyls [reactions (c1) and (f)], nitrooxyalcohols [reaction (c1)], and nitrooxyhydroperoxides [reaction (b)].

The products observed by Barnes *et al.*,[81] Hjorth *et al.*,[82] Skov *et al.*,[85] and Berndt and Böge[87,88] from the gas-phase reactions of the NO_3 radical with a series of acyclic monoalkenes at room temperature and one atmosphere of air, and their measured formation yields, are given in Table 25. The products observed are generally consistent with the reactions schemes shown above, although hydroxynitrates expected to be formed from reaction (c1) have only been observed from the 2-butene[82] and 2-methyl-2-butene[88] reactions. There are clearly significant discrepancies concerning the formation yields of the individual products from the various reactions (Table 25), and it is possible that these differences in the product yields may be due, at least in part, to the fact that product yields of Barnes *et al.*[81] and Berndt and Böge[88] were obtained after addition of NO to the reaction system to promote the thermal decomposition of the nitrooxyalkyl-peroxynitrates such as $CH_3CH(OONO_2)CH_2ONO_2$, while the yields reported by Hjorth *et al.*[82] were those after the peroxynitrates had been allowed to thermally decompose, without addition of NO. The addition of NO to the reaction systems leads to the formation of alkoxy radicals in high yield [reaction (d2) above], and OH radicals may also be formed from reaction of the alkoxy radicals with O_2 in the presence of NO.[28,92] Indeed, Shepson *et al.*[28] observed enhanced formation of HCHO and CH_3CHO relative to $CH_3C(O)CH_2ONO_2$ from a reacting propene system after the addition of NO, and similar observations were made by Wängberg[86] for the reactions of the NO_3 radical with cyclopentene, cyclohexene, and 1-methylcyclohexene. The product data of Shepson *et al.*[28] obtained prior to the addition of NO show that similar yields of HCHO and CH_3CHO are formed from propene, with the yield of $CH_3C(O)CH_2ONO_2$ being a factor of ~2 higher. The products identified and measured by Wängberg[86] from the reactions of the NO_3 radical with cyclopentene, cyclohexene, and 1-methylcyclohexene are consistent with the reaction scheme outlined above. The data of Wängberg[86] for these cycloalkene reactions indicate that if reactions (c1) and (c2) both occur [reaction (c1) clearly occurred because of the observed formation of hydroxynitrates as well as nitrooxycarbonyls], then the nitrooxyalkoxy radicals formed from reaction (c2) primarily decompose to form dicarbonyls plus NO_2 [reaction (e)] rather than react with O_2 [reaction (f)].

The reactions of the NO_3 radical with conjugated dienes have been studied by Barnes *et al.*,[81] Skov *et al.*,[84,85] Berndt *et al.*,[91] and Kwok *et al.*[93] Oxirane formation from the isoprene reaction has been shown to be of negligible importance (<1%) at atmospheric pressure of air.[85] At room temperature and atmospheric pressure of air, Barnes *et al.*[81] observed the formation of CO, HCHO, acrolein ($CH_2{=}CHCHO$), and "total nitrates" from the 1,3-butadiene reaction, with yields of 0.04, 0.12, 0.12, and ~0.60, respectively, and observed CO, HCHO, and total nitrates from the isoprene reaction with yields of 0.04, 0.11, and ~0.80, respectively. Skov *et al.*[84] used FTIR absorption spectroscopy to investigate the products of the reactions of the NO_3 radical with 1,3-butadiene, 1,3-butadiene-1,1,4,4-d_4, 1,3-butadiene-d_6, isoprene (2-methyl-1,3-butadiene), 2-methyl-1,3-butadiene-4,4-d_2, and 2,3-dimethyl-1,3-butadiene. The most definitive data were obtained for the 1,3-butadiene and isoprene reactions, and the absorption spectra of the products indicated that terminal addition of the NO_3 radical dominated, with initial addition to the 1- and 4-positions of isoprene being in the ratio 3.5:1.[84] The major products observed[84] from the 1,3-butadiene and isoprene reactions at 295±2 K and 740±5 Torr total pressure of air were $O_2NOCH_2CH{=}CHCHO$ (*cis*- and *trans*-) and $O_2NOCH_2C(O)CH{=}CH_2$ from 1,3-butadiene and $O_2NOCH_2C(CH_3){=}CHCHO$ (major) and $O_2NOCH_2CH{=}C(CH_3)CHO$, $O_2NOCH_2C(O)C(CH_3){=}CH_2$, $O_2NOCH_2CH(OH)C(CH_3){=}CH_2$ and $O_2NOCH_2C(CH_3){=}CHCH_2OH$ from isoprene. Using gas chromatography, Kwok *et al.*[93] showed that at room temperature and atmospheric pressure of air, methacrolein and methyl vinyl ketone were minor products of the NO_3 radical initiated reaction of isoprene (with formation yields of 0.035 ±0.014 each). The formation of C_5-nitrooxycarbonyls (for example, $O_2NOCH_2C(CH_3){=}CHCHO$ and its isomers), C_5-hydroxynitrates (for example, $O_2NOCH_2C(CH_3){=}CHCH_2OH$ and its isomers), nitrooxyhydroperoxides (for example, $O_2NOCH_2C(CH_3){=}CHCH_2OOH$ and its isomers), and C_5-hydroxycarbonyls (for example, $HOCH_2C(CH_3){=}CHCHO$ and its isomers) from the reactions of the NO_3 radical with isoprene and isoprene-d_8 was observed using atmospheric pressure ionization tandem mass spectrometry (API-MS/MS) at room temperature and 740 Torr total pressure of air.[93] The product data of Skov *et al.*[81] and Kwok *et al.*[93] are consistent with the reaction schemes shown above, leading to the formation of nitrooxycarbonyls, hydroxynitrates, and nitrooxyhydroperoxides. The formation of the C_5-hydroxycarbonyl(s)[93] is believed to arise from isomerization of the δ-nitrooxyalkoxy radical $O_2NOCH_2C(CH_3){=}CHCH_2\dot{O}$.[56]

$$O_2NOCH_2C(CH_3){=}CHCH_2\dot{O}$$

$$\rightarrow O_2NO\dot{C}HC(CH_3){=}CHCH_2OH$$

$$NO_2+HC(O)C(CH_3){=}CHCH_2OH$$

The product study of Barnes *et al.*[81] for α- and β-pinene, 3-carene, and limonene led to the formation of aerosols, although for α- and β-pinene IR spectral features indicated the presence of $>C{=}O$ and $-ONO_2$ groups. Aerosol formation could be expected because of the relatively high concentrations of monoterpenes ($\sim 5\times 10^{14}$ molecule cm^{-3}) used.[81]

It is clear that further product studies are required before the reaction mechanisms and product yields of these NO_3 radical reactions with the alkenes are reliably known. Furthermore, and very importantly, it is not clear that the products identified and the measured product formation yields from laboratory studies can be used for troposphere conditions, because in the laboratory NO_3 radical reactions appear to be dominated by nitrooxyalkyl peroxy radical +nitrooxyalkyl peroxy radical reactions, while in the troposphere the dominant reactions of the nitroooxyalkyl peroxy radicals are expected to be with HO_2 radicals, leading to nitrooxyhydroperoxides.

2.2.3. O_3 Reaction

The kinetics and mechanisms of the gas-phase reactions of O_3 with the alkenes, cycloalkenes, and dienes were last reviewed and evaluated by Atkinson,[2] and that review and evaluation is updated in Sec. 5.2. The 298 K rate constants and the temperature dependent parameters for the gas-phase reactions of O_3 with alkenes are given in Table 26. These reactions proceed by initial O_3 addition to the $>C{=}C<$ bond to yield an energy rich ozonide, which rapidly decomposes to a carbonyl and an initially energy rich biradical

TABLE 25. Products and their yields observed from the gas-phase reactions of the NO_3 radical with acyclic monoalkenes at room temperature and atmospheric pressure of air

Alkene	Product	Yield (molar) Barnes *et al.*[81]	Hjorth *et al.*[82] Skov *et al.*[85]	Berndt and Böge[87,88]
Propene	HCHO	0.08	0.10±0.05	
	CH_3CHO	0.12	0.10±0.05	0.60
	Total nitrates	~0.58[a]		
	$CH_3C(O)CH_2ONO_2$			~0.12
	Methyloxirane			0.28
1-Butene	HCHO	0.11		
	CH_3CH_2CHO	0.12		0.65
	Total nitrates	~0.60[a]		
	$CH_3CH_2C(O)CH_2ONO_2$			~0.17
	Ethyloxirane			0.18
2-Methylpropene	HCHO	0.80	0.24±0.08	
	$CH_3C(O)CH_3$	0.85	0.24±0.08	0.88
	Total nitrates	~0.25[a]		
	$(CH_3)_2CHCHO$			~0.05
	2,2-dimethyloxirane			0.07
trans-2-Butene	CH_3CHO	0.70	0.34±0.12[b]	~1.00
	$CH_3C(O)CH(ONO_2)CH_3$	0.55	0.41±0.13[b]	0.38
	$CH_3CH(ONO_2)CH(ONO_2)CH_3$	0.04		
	$CH_3CH(OH)CH(ONO_2)CH_3$		0.15±0.05[b]	
	2,3-dimethyloxirane		≤0.01[b]	0.12
2-Methyl-2-butene	CH_3CHO		0.22±0.06	0.70
	$CH_3C(O)CH_3$		0.22±0.06	0.70
	$CH_3C(O)C(ONO_2)(CH_3)_2$			0.10
	Hydroxynitrate			~0.08
	$(CH_3)_2CHC(O)CH_3$			~0.03
	2,2,3-trimethyloxirane			0.09
2,3-Dimethyl-2-butene	$CH_3C(O)CH_3$		1.04±0.26	1.60
	$(CH_3)_2C(ONO_2)C(ONO_2)(CH_3)_2$		0.05±0.02	
	Tetramethyloxirane		0.174±0.035	0.20

[a] Estimated from the use of IR absorption cross-sections for 14 compounds containing the $-ONO_2$ group.
[b] Yields also apply for *cis*-2-butene.

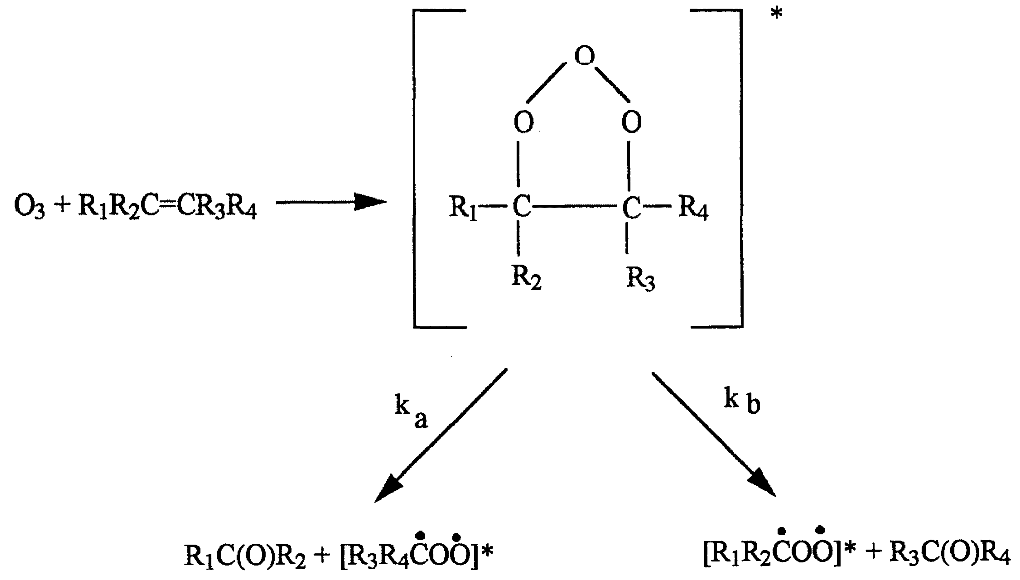


TABLE 26. Rate constants k at 298 K and Arrhenius parameters, $k=A\ e^{-B/T}$, for the gas-phase reactions of O_3 with alkenes, cycloalkenes, and dienes (see also Ref. 2 and Sec. 5.2)

Alkene	$10^{18}\times k$ (298 K) (cm^3 molecule^{-1} s^{-1})	$10^{15}\times A$ (cm^3 molecule^{-1} s^{-1})	B (K)
Ethene	1.59	9.14	2580
Propene	10.1	5.51	1878
1-Butene	9.64	3.36	1744
2-Methylpropene	11.3	2.70	1632
cis-2-Butene	125	3.22	968
trans-2-Butene	190	6.64	1059
1-Pentene	10.0		
2-Methyl-1-butene	16		
2-Methyl-2-butene	403	6.51	829
3-Methyl-1-butene	11		
1-Hexene	11.0		
cis-3-Hexene	150		
trans-3-Hexene	170		
2-Methyl-1-pentene	15		
3-Methyl-1-pentene	4.9		
4-Methyl-1-pentene	9.2		
cis-3-Methyl-2-pentene	450		
trans-3-Methyl-2-pentene	560		
2,3-Dimethyl-1-butene	13		
3,3-Dimethyl-1-butene	5.2		
2,3-Dimethyl-2-butene	1130	3.03	294
2-Ethyl-1-butene	13		
1-Heptene	12		
2,3,3-Trimethyl-1-butene	8.3		
1-Octene	14		
cis-4-Octene	95		
trans-4-Octene	140		
trans-2,5-Dimethyl-3-hexene	41		
trans-2,2-Dimethyl-3-hexene	42		
cis- +*trans*-3,4-Dimethyl-3-hexene	≥380		
2,2,4-Trimethyl-2-pentene	140		
3-Methyl-2-isopropyl-1-butene	3.3		
1-Decene	9.3		
cis-5-Decene	120		
trans-5-Decene	≥130		
3,4-Diethyl-2-hexene	4.2		
1,2-Propadiene	0.19	1.54	2689
1,3-Butadiene	6.3	13.4	2283
2-Methyl-1,3-butadiene	12.8	7.86	1913
trans-1,3-Pentadiene	43		
cis-2, *trans*-4-Hexadiene	310		
trans-2, *trans*-4-Hexadiene	370		
2-Methyl-1,4-pentadiene	13		
2,3-Dimethyl-1,3-butadiene	26.5	6.9	1668
2,4-Dimethyl-1,3-butadiene	80		
2,5-Dimethyl-1,5-hexadiene	14		
cis-, *trans*-1,3,5-Hexatriene	26		
Myrcene	470		
cis-, *trans*-Ocimene	540		
Cyclopentene	570	1.8	350
1-Methyl-1-cyclopentene	670		
Cyclohexene	81.4	2.88	1063
1-Methyl-1-cyclohexene	165		
4-Methyl-1-cyclohexene	82		
1,2-Dimethyl-1-cyclohexene	207		
1,3-Cyclohexadiene	1220		
1,4-Cyclohexadiene	46		
Cycloheptene	245	1.29	494
Bicyclo[2.2.1]-2-heptene	1550		
1,3-Cycloheptadiene	155		
Bicyclo[2.2.1]-2,5-heptadiene	3550		
1,3,5-Cycloheptatriene	54		
cis-Cyclooctene	375		

TABLE 26. Rate constants k at 298 K and Arrhenius parameters, $k=A\ e^{-B/T}$, for the gas-phase reactions of O_3 with alkenes, cycloalkenes, and dienes (see also Ref. 2 and Sec. 5.2)—Continued

Alkene	$10^{18}\times k$ (298 K) (cm^3 molecule^{-1} s^{-1})	$10^{15}\times A$ (cm^3 molecule^{-1} s^{-1})	B (K)
trans-Cyclooctene	29		
Bicyclo[2.2.2]-2-octene	71		
Camphene	0.90		
2-Carene	230		
3-Carene	37		
Limonene	200		
α-Phellandrene	2980		
β-Phellandrene	47		
α-Pinene	86.6	1.01	732
β-Pinene	15		
Sabinene	86		
α-Terpinene	21 100		
γ-Terpinene	140		
Terpinolene	1880		
α-Cedrene	28		
α-Copaene	160		
β-Caryophyllene	11 600		
α-Humulene	11 700		
Longifolene	<0.5		

where [ ]* denotes an energy rich species. The carbonyl compound(s) formed in this decomposition of the ozonide will be denoted as the primary carbonyl(s) in the discussion below. While it was originally assumed that $k_a \sim k_b$ for the alkene reactions,[94] recent product studies have shown that this is not generally the case.[71,95–102] As discussed previously[2] and below, OH radicals are generated from the reactions of O_3 with alkenes, and unless these OH radicals are scavenged the products observed and measured from the reactions of O_3 with alkenes arise from the reactions of both the OH radical and O_3 with the alkenes. Table 27 gives the formation yields of the primary carbonyl compounds measured at room temperature and atmospheric pressure of air in reaction systems where the OH radicals formed from the O_3 reactions with the alkenes were scavenged, for alkenes which can form two primary carbonyls [cycloalkenes containing internal >C═C< bond(s) lead to the formation of carbonyl substituted biradicals].

The formation yields of both of the primary carbonyls have been measured for 33 monoalkenes in the presence of an OH radical scavenger (Table 27),[30,71,95–103] and in most cases the measured sum of the two primary carbonyls is within 20% of unity. Note that the carbonyl yields of Grosjean *et al.*,[103] apart from those for 2-ethyl-1-butene, were obtained at low relative humidities of 3–7% and are in some cases erroneously low because of less than unit collection and derivatization efficiencies at low relative humidities.[96] These data of Grosjean *et al.*[103] are superseded by the more recent studies of Grosjean and Grosjean[96,100] and Grosjean *et al.*[97] carried out at higher relative humidities (55±10%). (Note that the primary carbonyl formation yields are independent of relative humidity, as expected.)

Apart from earlier data reported by Grosjean and Grosjean[96] and Grosjean *et al.*[103] for the O_3 reactions with 2-methyl-1-butene[96] and 2-ethyl-1-butene,[103] the sum of the measured formation yields of the two primary carbonyls is in the range 0.94–1.40 (Table 27). It is likely that observation that the measured sum of the two primary carbonyls formed is often slightly in excess of unity is due to additional formation of one or more of the primary carbonyls from decomposition and/or reactions of the biradicals (see below),[95,97,99] especially for those unsymmetrical alkenes with HCHO as one of the primary carbonyls.[95,97] Obviously, symmetrical alkenes lead to the formation of a single primary carbonyl and the experimental data given in Table 27 shows that, as expected, the yield of this primary carbonyl is unity within the experimental uncertainties.[30,97,99,102] Although additional reaction pathways to the formation of this carbonyl exist (see below), these must be of minor importance.

For unsymmetrical alkenes, two primary carbonyls are formed (Table 27). For many of the 1-alkenes $RCH{=}CH_2$ (other than 1-butene[97]), the two primary carbonyls RCHO and HCHO are formed in essentially equal yields[95,97,101,102] (using the CH_3CHO yield from propene and assuming that the higher yield of HCHO arises from decomposition of the $[CH_3\dot{C}HO\dot{O}]^*$ biradical[97,102]) showing that for these alkenes $k_a \approx k_b$. However, for the O_3 reactions with 3-methyl-1-pentene, 4-methyl-1-pentene, and 3,3-dimethyl-1-butene, there is a preference for formation of the aldehyde RCHO[101] (Table 27). For alkenes of structure $CH_2{=}CR_1R_2$ (2-methylpropene,[97,102] 2-methyl-1-butene,[96,100] 2-ethyl-1-butene,[100,103] 2-methyl-1-pentene,[100] 2,3-dimethyl-1-butene,[95,98] 2,3,3-trimethyl-1-butene,[100] and 3-methyl-2-isopropyl-1-butene[100]) the primary ozonide decomposes preferentially to form the di-substituted biradical (and hence to $HCHO+[R_1R_2\dot{C}O\dot{O}]^*$). For alkenes of structure $R_1CH{=}CR_2R_3$ (2-methyl-2-butene,[97,102] 2,4,4-trimethyl-

TABLE 27. Primary carbonyls formed and their yields from the gas-phase reactions of O_3 with alkenes in the presence of an OH radical scavenger

Alkene	Primary carbonyl	Formation yield[a]	Reference
Ethene	HCHO	1.060±0.071	Grosjean *et al.*[97]
		0.992±0.061	Grosjean and Grosjean[99]
Propene	HCHO	0.780±0.015	Grosjean *et al.*[97]
		0.645±0.048[b]	Tuazon *et al.*[102]
	CH_3CHO	0.520±0.026	Grosjean *et al.*[97]
		0.446±0.092	Tuazon *et al.*[102]
1-Butene	HCHO	0.630±0.031	Grosjean *et al.*[97]
	CH_3CH_2CHO	0.350±0.018	Grosjean *et al.*[97]
cis-2-Butene	CH_3CHO	1.19±0.14	Tuazon *et al.*[102]
		1.08±0.08[b]	Tuazon *et al.*[102]
trans-2-Butene	CH_3CHO	1.14±0.14	Tuazon *et al.*[102]
		1.09±0.09[b]	Tuazon *et al.*[102]
2-Butene (*cis*+*trans*)	CH_3CHO	1.150±0.104	Grosjean *et al.*[97]
2-Methylpropene	HCHO	0.950±0.098	Grosjean *et al.*[97]
		1.01±0.07[b]	Tuazon *et al.*[102]
	$CH_3C(O)CH_3$	0.340±0.031	Grosjean *et al.*[97]
		0.323±0.030	Tuazon *et al.*[102]
		0.294±0.030[b]	Tuazon *et al.*[102]
1-Pentene	HCHO	0.595±0.055	Atkinson *et al.*[95]
		0.505±0.003	Grosjean and Grosjean[98]
	$CH_3CH_2CH_2CHO$	0.541±0.065	Atkinson *et al.*[95]
		0.496±0.016	Grosjean and Grosjean[98]
2-Methyl-1-butene	HCHO	0.63±0.06	Grosjean and Grosjean[96]
		0.657±0.064	Grosjean and Grosjean[100]
	$CH_3C(O)CH_2CH_3$	0.214±0.009	Grosjean and Grosjean[96]
		0.346±0.007	Grosjean and Grosjean[100]
2-Methyl-2-butene	CH_3CHO	0.685±0.019	Grosjean *et al.*[97]
		0.745±0.099	Tuazon *et al.*[102]
	$CH_3C(O)CH_3$	0.302±0.006	Grosjean *et al.*[97]
		0.376±0.032	Tuazon *et al.*[102]
		0.339±0.030[b]	Tuazon *et al.*[102]
3-Methyl-1-butene	HCHO	0.497±0.042	Grosjean and Grosjean[101]
	$(CH_3)_2CHCHO$	0.509±0.033	Grosjean and Grosjean[101]
1-Hexene	HCHO	0.575±0.057	Atkinson *et al.*[95]
		0.501±0.006	Grosjean and Grosjean[98]
	$CH_3CH_2CH_2CH_2CHO$	0.518±0.095	Atkinson *et al.*[95]
		0.536±0.023	Grosjean and Grosjean[98]
cis-3-Hexene	CH_3CH_2CHO	1.022±0.077	Grosjean and Grosjean[99]
trans-3-Hexene	CH_3CH_2CHO	1.011±0.049	Grosjean *et al.*[97]
2-Methyl-1-pentene	HCHO	0.618±0.022	Grosjean and Grosjean[100]
	$CH_3C(O)CH_2CH_2CH_3$	0.323±0.003	Grosjean and Grosjean[100]
3-Methyl-1-pentene	HCHO	0.394±0.012	Grosjean and Grosjean[101]
	$CH_3CH_2CH(CH_3)CHO$	0.631±0.012	Grosjean and Grosjean[101]
4-Methyl-1-pentene	HCHO	0.441±0.012	Grosjean and Grosjean[101]
	$(CH_3)_2CHCH_2CHO$	0.706±0.049	Grosjean and Grosjean[101]
2,3-Dimethyl-2-butene	$CH_3C(O)CH_3$	1.02±0.13[b]	Niki *et al.*[30]
		1.006±0.049	Grosjean *et al.*[97]
		0.977±0.086	Tuazon *et al.*[102]
		1.14±0.19[b]	Tuazon *et al.*[102]
3,3-Dimethyl-1-butene	HCHO	0.316±0.011	Grosjean and Grosjean[101]
	$(CH_3)_3CCHO$	0.670±0.008	Grosjean and Grosjean[101]

TABLE 27. Primary carbonyls formed and their yields from the gas-phase reactions of O_3 with alkenes in the presence of an OH radical scavenger—Continued

Alkene	Primary carbonyl	Formation yield[a]	Reference
2-Ethyl-1-butene	HCHO	0.407±0.070	Grosjean *et al.*[103]
		0.582±0.002	Grosjean and Grosjean[100]
	$CH_3CH_2C(O)CH_2CH_3$	0.178±0.017	Grosjean *et al.*[103]
		0.429±0.004	Grosjean and Grosjean[100]
1-Heptene	HCHO	0.533±0.049	Atkinson *et al.*[95]
		0.511±0.014	Grosjean and Grosjean[98]
	$CH_3(CH_2)_4CHO$	0.582±0.078	Atkinson *et al.*[95]
		0.512±0.049	Grosjean and Grosjean[98]
2,3-Dimethyl-1-butene	HCHO	0.776±0.071	Atkinson *et al.*[95]
		0.663±0.010	Grosjean and Grosjean[98]
	$CH_3C(O)CH(CH_3)_2$	0.391±0.050	Atkinson *et al.*[95]
		0.369±0.012	Grosjean and Grosjean[98]
2,3,3-Trimethyl-1-butene	HCHO	0.639±0.030	Grosjean and Grosjean[100]
	$CH_3C(O)C(CH_3)_3$	0.352±0.022	Grosjean and Grosjean[100]
1-Octene	HCHO	0.519±0.054	Atkinson *et al.*[95]
		0.476±0.029	Grosjean *et al.*[71]
	$CH_3(CH_2)_5CHO$	0.527±0.070	Atkinson *et al.*[95]
		0.473±0.023	Grosjean *et al.*[71]
cis-4-Octene	$CH_3CH_2CH_2CHO$	1.206±0.022	Grosjean and Grosjean[99]
trans-4-Octene	$CH_3CH_2CH_2CHO$	1.145±0.027	Grosjean and Grosjean[99]
trans-2,5-Dimethyl-3-hexene	$(CH_3)_2CHCHO$	1.398±0.085	Grosjean and Grosjean[99]
cis- +*trans*-3,4-Dimethyl-3-hexene	$CH_3C(O)CH_2CH_3$	1.159±0.064	Grosjean and Grosjean[99]
3-Methyl-2-isopropyl-1-butene	HCHO	0.607±0.077	Grosjean and Grosjean[100]
	$(CH_3)_2CHC(O)CH(CH_3)_2$	0.425±0.029	Grosjean and Grosjean[100]
2,4,4-Trimethyl-2-pentene	$CH_3C(O)CH_3$	0.187±0.010	Grosjean and Grosjean[100]
	$(CH_3)_3CCHO$	0.839±0.040	Grosjean and Grosjean[100]
1-Decene	HCHO	0.529±0.014	Grosjean *et al.*[71]
	$CH_3(CH_2)_7CHO$	0.492±0.012	Grosjean *et al.*[71]
cis-5-Decene	$CH_3CH_2CH_2CH_2CHO$	1.208±0.033	Grosjean and Grosjean[99]
trans-5-Decene	$CH_3CH_2CH_2CH_2CHO$	1.093±0.057	Grosjean and Grosjean[99]
3,4-Diethyl-2-hexene	CH_3CHO	0.705±0.041	Grosjean and Grosjean[100]
	$CH_3CH_2C(O)CH(CH_2CH_3)_2$	0.287±0.034	Grosjean and Grosjean[100]
2-Methyl-1,3-butadiene	HCHO	0.90±0.04	Grosjean *et al.*[104]
	$CH_3C(O)CH{=}CH_2$	0.17	Grosjean *et al.*[104]
		0.159±0.013	Aschmann and Atkinson[105]
	$CH_2{-}C(CH_3)CHO$	0.44	Grosjean *et al.*[104]
		0.387±0.030	Aschmann and Atkinson[105]

2-pentene,[100] and 3,4-diethyl-2-hexene[100]) the situation is similar to the alkenes of structure $CH_2{=}CR_1R_2$ in that the di-substituted biradical is formed preferentially. The data presented in Table 27 indicate that the initial products, after decomposition of the initially formed ozonide, are:

$$O_3+R_1R_2C{=}CR_2R_1 \rightarrow R_1C(O)R_2+[R_1R_2\dot{C}O\dot{O}]^*$$

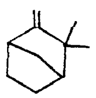
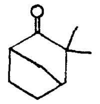
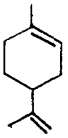
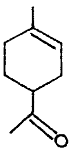
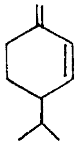
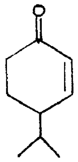
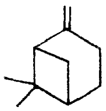
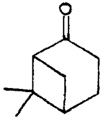
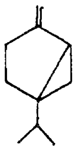
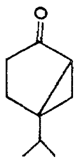
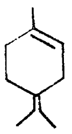
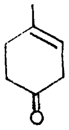
$$O_3+R_1CH{=}CH_2 \rightarrow \sim 0.5(R_1CHO+[\dot{C}H_2O\dot{O}]^*) + \sim 0.5(HCHO+[R\dot{C}HO\dot{O}]^*)$$

$$O_3+R_1R_2C{=}CH_2 \rightarrow \sim 0.35(R_1C(O)R_2+[\dot{C}H_2O\dot{O}]^*) + \sim 0.65(HCHO)+[R_1R_2\dot{C}O\dot{O}]^*)$$

$$O_3+R_1R_2C{=}CHR_3 \rightarrow \sim 0.35(R_1C(O)R_2+[R_3\dot{C}HO\dot{O}]^*) + \sim 0.65(R_3CHO+[R_1R_2\dot{C}O\dot{O}]^*)$$

The cyclic monoterpenes camphene, β-pinene and sabinene are of the structural type $CH_2{=}CR_1R_2$, and the formation

TABLE 27. Primary carbonyls formed and their yields from the gas-phase reactions of O_3 with alkenes in the presence of an OH radical scavenger -- Continued

Alkene	Primary Carbonyl	Formation Yield[a]	Reference
Camphene 	Camphenilone 	0.36 ± 0.06	Hakola *et al.*[70]
Limonene[c] 	4-Acetyl-1-methylcyclohexene 	≤0.04	Hakola *et al.*[70]
β-Phellandrene[d] 	4-Isopropyl-2-cyclohexen-1-one 	0.29 ± 0.06	Hakola *et al.*[69]
β-Pinene 	HCHO	0.42	Grosjean *et al.*[106]
	Nopinone 	0.22 0.23 ± 0.05	Grosjean *et al.*[106] Hakola *et al.*[70]
Sabinene 		0.50 ± 0.09	Hakola *et al.*[70]
Terpinolene[d] 	4-Methyl-3-cyclohexen-1-one 	0.40 ± 0.06	Hakola *et al.*[70]

[a] Measured by chromatographic methods, unless indicated otherwise.

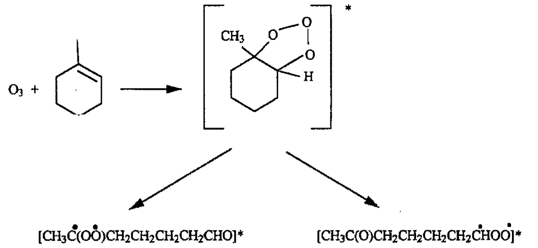
[b] By FT-IR absorption spectroscopy.

[c] O_3 reaction with limonene expected to proceed mainly by O_3 addition to the $>C=C<$ bond in the six-member ring.

[d] O_3 reaction is expected to proceed, at least in part, by addition to the $>C=C<$ bond in the six-member ring.

yields of camphenilone from camphene[70] and of nopinone from β-pinene[70,106] indicate that the di-substituted biradical is formed preferentially (similar to the case for the corresponding acyclic monoalkenes). However, the primary ozonide formed from the reaction of O_3 with sabinene appears to decompose equally to the two sets of primary carbonyl plus biradical.[70]

The reactions of O_3 with cycloalkenes containing internal $>C=C<$ bond(s) lead to the formation of two (or, for symmetrical cycloalkenes, one) carbonyl substituted biradicals. For example, for 1-methylcyclohexene,



and primary carbonyl formation does not occur from decomposition of the initially formed ozonide. The major question then concerns the fate of the initially energy rich biradicals. The energy rich biradicals can be collisionally stabilized or unimolecularly decompose.

$$[R_1R_2\dot{C}O\dot{O}]^* + M \rightarrow R_1R_2\dot{C}O\dot{O} + M$$

$$[R_1R_2\dot{C}O\dot{O}]^* \rightarrow \text{products}$$

The fraction of the initially formed biradical which is collisionally stabilized is pressure dependent.[107,108] For *trans*-2-butene, the fraction of the biradical which is stabilized was observed to increase from essentially zero at zero total pressure of air to a high pressure limit of 0.185, attained at ~600 Torr total pressure of air.[107] For ethene, however, a significant fraction of the initially formed biradical is formed thermally "cold" at low pressures,[108,109] and Hatakeyama *et al.*[108] determined this fraction to be 0.20±0.03 by extrapolation of data obtained over the total pressure range 10–1140 Torr to zero pressure. At room temperature and one atmosphere total pressure, the fractional yields of stabilized biradicals formed from the alkenes studied to date are given in Table 28. The yield of stabilized biradicals from ethene obtained by Hatakeyama *et al.*[107,108] is in excellent agreement with values of 0.38, 0.37, and 0.35 obtained by Su *et al.*[110] Kan *et al.*[111] and Niki *et al.*,[112] respectively, and that for *trans*-2-butene of Hatakeyama *et al.*[107] agrees well with the stabilized biradical yield of 0.18 obtained by Niki *et al.*[113] from *cis*-2-butene.

TABLE 28. Yields of stabilized biradicals from the gas-phase reactions of O_3 with alkenes at room temperature and atmospheric pressure

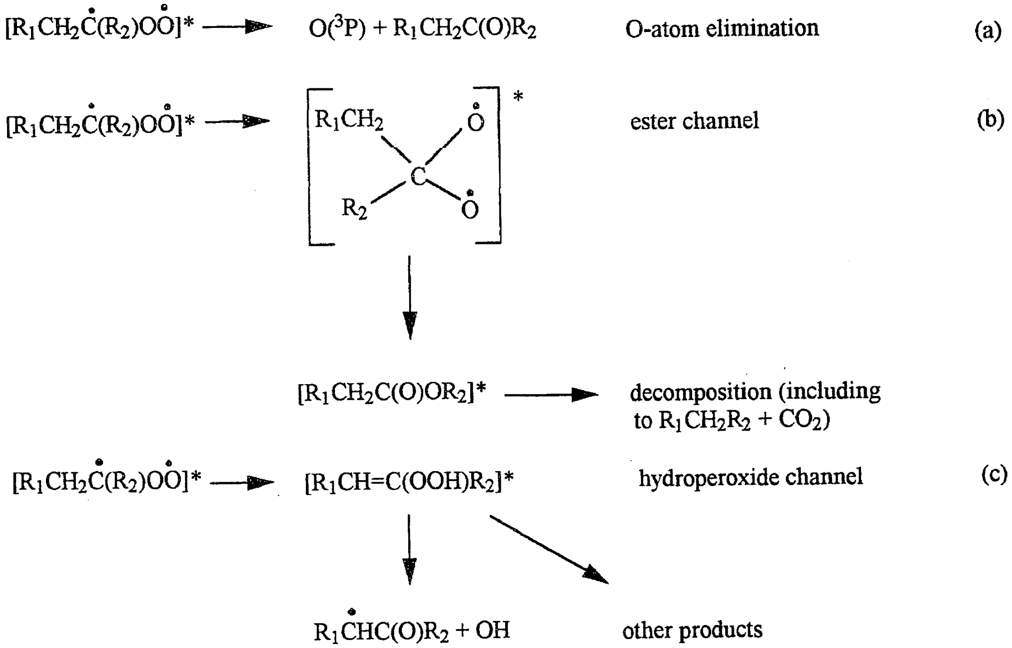
Alkene	Yield	Reference
Ethene	0.38	Su *et al.*[110]
	0.37±0.02[a]	Kan *et al.*[111]
	0.35±0.05	Niki *et al.*[112]
	0.390±0.053	Hatakeyama *et al.*[107,108]
	0.47	Horie and Moortgat[114]
Propene	0.254±0.023	Hatakeyama *et al.*[107]
	0.44	Horie and Moortgat[114]
2-Methylpropene	0.174±0.032	Hatakeyama *et al.*[107]
cis-2-Butene	0.18	Niki *et al.*[113]
trans-2-Butene	0.185±0.028	Hatakeyama *et al.*[107]
	0.42	Horie and Moortgat[114]
2,3-Dimethyl-2-butene	0.30	Niki *et al.*[30]
1-Octene	0.22	Paulson and Seinfeld[51]
Cyclopentene	0.052±0.013	Hatakeyama *et al.*[107]
Cyclohexene	0.032±0.024	Hatakeyama *et al.*[107]
Cycloheptene	0.029±0.015	Hatakeyama *et al.*[107]
1-Methylcyclohexene	0.104±0.065	Hatakeyama *et al.*[107]
Methylenecyclohexane	0.216±0.026	Hatakeyama *et al.*[107]
α-Pinene	0.125±0.040	Hatakeyama *et al.*[107]
β-Pinene	0.249±0.024	Hatakeyama *et al.*[107]

[a]Independent of temperature over the range 283–304 K.

However, the biradical stabilization yields at room temperature and atmospheric pressure determined by Hatakeyama *et al.*[107,108] from the conversion of SO_2 to sulfuric acid aerosol do not agree well with the yields reported by Horie and Moortgat[114] from a product analysis/modeling study. In the absence of further data, it is recommended that the biradical stabilization yield from ethene at 298 K and atmospheric pressure is 0.37, and for the other alkenes that the data of Hatakeyama *et al.*[107] and Niki *et al.*[30,113] be used. Thus, at ~760 Torr total pressure of air and ~298 K the fractions of the $[\dot{C}H_2O\dot{O}]^*$ and $[CH_3\dot{C}HO\dot{O}]^*$ biradicals which are stabilized from the ethene and 2-butene systems are 0.37 and 0.18, respectively. As recommended above, $k_a \approx k_b$ for decomposition of the ozonide formed from the reaction of O_3 with propene and, assuming that the stabilization yields of the $[\dot{C}H_2O\dot{O}]^*$ and $[CH_3\dot{C}HO\dot{O}]^*$ biradicals formed from the O_3 reaction with propene are identical to those formed from ethene and the 2-butenes, a total stabilized biradical yield from propene ($\dot{C}H_2O\dot{O}$ plus $CH_3\dot{C}HO\dot{O}$) of 0.275 is predicted, in good agreement with the measured yield of 0.254±0.023.[107] However, the data of Hatakeyama *et al.*[107] for the stabilized biradical yield from the O_3 reaction with 2-methylpropene, of 0.174 at room temperature and atmospheric pressure, are less consistent with the above data for the stabilization yield of $[\dot{C}H_2O\dot{O}]^*$ (0.37), the stabilization yield of 0.30 for the $[(CH_3)_2\dot{C}O\dot{O}]^*$ biradical in the 2,3-dimethyl-2-butene reaction,[30] and the fractions of the O_3 reaction leading to the two sets of carbonyl plus biradical recommended above. This suggests that the stabilization yields of the various biradicals depend on the alkene precursor, in agreement with the differing $[\dot{C}H_2O\dot{O}]^*$ biradical stabilization yields observed from ethene (0.37) and vinyl chloride (0.25).[115]

Experimental data concerning the decomposition pathways of the energy rich biradicals arise mainly from the low pressure (4–8 Torr) stopped flow mass spectrometric studies of Herron and Huie,[94,116] Martinez *et al.*,[117,118] Martinez,[119] and Martinez and Herron,[120,121] and the atmospheric pressure studies with Fourier infrared absorption spectroscopic and/or gas chromatographic detection of reactants and products of

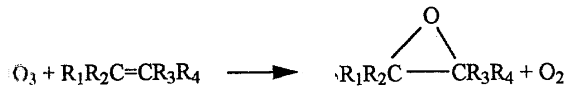
Niki *et al.*,[30,109,113] Su *et al.*,[110] Horie and Moortgat,[114] Horie *et al.*,[122] Paulson *et al.*,[123] Paulson and Seinfeld,[51] Atkinson *et al.*,[95,124–126] Grosjean *et al.*,[71,97,104] Atkinson and Aschmann,[127] Aschmann and Atkinson,[105] Hakola *et al.*,[70] Shu and Atkinson,[128] Grosjean and Grosjean,[98–101] Chew and Atkinson,[129] Tuazon *et al.*,[102] and Alvarado *et al.*[130] Based on these studies (and mainly on those of Niki *et al.*[30] and Martinez and Herron[121]), the energy rich biradicals can undergo decomposition by three pathways.



While the $O(^3P)$-atom elimination channel has been observed for the reaction of O_3 with *trans*-1,2-dichloroethene,[109,131] to date there is no evidence for its occurrence in the reactions of the biradicals formed from the reactions of O_3 with monoalkenes (including cycloalkenes) at atmospheric pressure of air,[30,51,126,130,131] with upper limits to $O(^3P)$ atom formation yields of <0.04 for the propene reaction,[126] <0.02 for each of the 1-butene,[126] *cis*-2-butene,[126] *trans*-2-butene,[126] and 2,3-dimethyl-2-butene[126] reactions, <0.03 for the α-pinene reaction,[130] and <0.04 for the 1,2-dimethylcyclohexene reaction.[130] At low total pressure (4 Torr), Martinez and Herron[120] obtained a fit between experimental and predicted data for the O_3 reaction with 2,3-dimethyl-2-butene when a 20% $O(^3P)$-atom elimination channel was included.

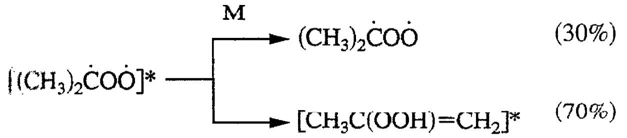
Paulson *et al.*[123] concluded from a product study of the reaction of O_3 with isoprene that $O(^3P)$ atom formation accounted for 45±20% of the overall reaction ($\Delta[O(^3P)]/\Delta[\text{isoprene}]=0.45\pm0.20$) at room temperature and atmospheric pressure, based on the observed formation of 2-ethenyl-2-methyl oxirane and 2-(1-methylethenyl)oxirane. However, a study of the products formed from the reaction of O_3 with isoprene in N_2 and air diluents in the presence of an OH radical scavenger showed that the formation of these two oxiranes was due to a direct reaction channel not involving the intermediate formation of $O(^3P)$ atoms,[125] and an upper limit to the $O(^3P)$ atom formation yield of <0.10 was obtained.[125] The formation of ethenyl oxirane was also observed from the reaction of O_3 with 1,3-butadiene,[126] and again experiments in N_2 and air diluents showed that the oxirane is formed as a direct reaction channel not involving $O(^3P)$ atoms, with an upper limit to the $O(^3P)$ atom formation yield of <0.05.[126]

Oxirane formation has been observed and measured from the O_3 reactions with isoprene,[125] 1,3-butadiene,[126] α-pinene,[130] and 1,2-dimethyl-1-cyclohexene,[130] with formation yields of 0.039 ± 0.008 (sum of both oxirane isomers),[125] 0.023 ± 0.004,[126] 0.018 ± 0.004,[130] and 0.019 ± 0.007,[130] respectively. However, oxirane formation was not observed from propene, 1-butene, *cis*-2-butene, and *trans*-2-butene, with upper limits to the formation yields of <0.006.[126] It therefore appears that the formation of oxiranes by the reaction pathway



occurs to a small extent for at least certain dienes and cycloalkenes.

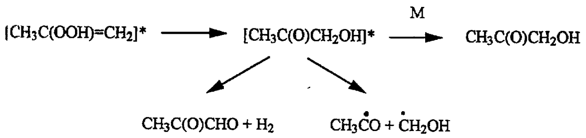
The occurrence of the hydroperoxide channel was postulated from the studies of Niki *et al.*[30] and Martinez and Herron[120] of the products and mechanism of the reaction of O_3 with 2,3-dimethyl-2-butene. For this reaction at room temperature and atmospheric pressure, ~30% of the initially energy rich biradical $[(CH_3)_2\dot{C}O\dot{O}]^*$ was observed to be stabilized,[30] with the remainder isomerizing to the hydroperoxide,[30]



followed by dissociation of the hydroperoxide to an OH radical and the $CH_3C(O)\dot{C}H_2$ radical,[30]

$$[CH_3C(OOH){=}CH_2]^* \rightarrow OH + CH_3C(O)\dot{C}H_2.$$

Martinez and Herron[120] postulated that at ~4 Torr total pressure the hydroperoxide decomposes to an energy rich hydroxyacetone molecule which is either collisionally stabilized or undergoes decomposition.[120]



Gutbrod *et al.*[132] have recently carried out computations supporting the hydroperoxide channel as the source of OH radicals from the $[(CH_3)_2\dot{C}O\dot{O}]^*$ biradical.

The product studies of Niki *et al.*,[30] Paulson *et al.*,[123] Atkinson *et al.*,[95,124] Paulson and Seinfeld,[51] Atkinson and Aschmann,[127] Shu and Atkinson,[128] Chew and Atkinson,[129] and Alvarado *et al.*[130] and the theoretical and experimental study of Gutbrod *et al.*[132] show that the reactions of O_3 with alkenes are a source of OH radicals, and these studies[30,51,95,123,124,127–130,132] have obtained OH radical formation yields from the reactions of O_3 with a wide range of alkenes (Table 29). In the study of Niki *et al.*[30] of the reaction of O_3 with 2,3-dimethyl-2-butene, the yield of the stabilized biradical, of ~0.29, was obtained from the amount of isobutene ozonide formed when HCHO was added to the reactant mixtures and the OH radical formation yield was derived from the measured reaction stoichiometry of Δ[2,3-dimethyl-2-butene]/$\Delta[O_3]=1.7\pm0.1$ in the absence of added OH radical scavengers. More recently, Paulson *et al.*[123] and Paulson and Seinfeld[51] added trace concentrations of 1-methylcyclohexane to O_3–alkene–air reactant mixtures to monitor the OH radical concentrations during the experiments, while Atkinson and co-workers[95,124,127,128,130] have used cyclohexane to scavenge ≥90% of the OH radicals formed from the O_3 reactions and derived the OH radical formation yields from the amounts of cyclohexanone plus cyclohexanol produced. Both of these methods have problems; the tracer method requires that all of the OH radical loss processes be quantitatively known (including the reactions of OH radicals with the products of the O_3 and OH radical reactions with the alkene being studied) and the use of cyclohexane as an OH radical scavenger suffers from the fact that cyclohexanone and cyclohexanol are formed from the OH radical reaction with cyclohexane by complex reaction sequences which may depend on the specific reaction system being studied.[124,127,129]

More recently, Chew and Atkinson[129] have used 2-butanol to scavenge the OH radicals formed from the reactions of O_3 with four alkenes, determining the OH radical formation yields from the amounts of 2-butanone formed. Because the formation yield of 2-butanone from the reaction of the OH radical with 2-butanol proceeds through the intermediary of the α-hydroxyalkyl radical $CH_3\dot{C}(OH)CH_2CH_3$,[2,9,129]

$$\begin{array}{r} OH + CH_3CH(OH)CH_2CH_3 \rightarrow H_2O + CH_3\dot{C}(OH)CH_2CH_3 \\ \downarrow O_2 \\ CH_3C(O)CH_2CH_3 + HO_2 \end{array}$$

the 2-butanone formation yield from the OH radical reaction with 2-butanol is independent of the presence or absence of NO and does not involve peroxy radical reactions. The OH radical formation yields from the reactions of O_3 with 2-methyl-2-butene,[129] 2,3-dimethyl-2-butene,[129] 1,2-dimethyl-1-cyclohexene,[130] α-pinene,[129] and sabinene[129] using 2-butanol as an OH radical scavenger are in good agreement with those measured using cyclohexane as an OH radical scavenger[124,127,130] (Table 29), suggesting that the OH radical formation yields previously measured by Atkinson and co-workers[124,127,128] using cyclohexane as an OH radical scavenger are correct within ~±25%. For the simple acyclic monoalkenes, the OH radical formation yields appear to increase as the yield of di-substituted biradicals increase,[127] with the OH radical formation yields increasing along the series $CH_2{=}CH_2$, $RCH{=}CH_2$, $R_1R_2C{=}CH_2$, $R_1CH{=}CR_2R_3$ and $R_1R_2C{=}CR_3R_4$.[127] This behavior is consistent with the smaller dialkyl substituted biradicals (for example, $[(CH_3)_2\dot{C}O\dot{O}]^*$) leading to the formation of OH radicals by the hydroperoxide channel in high, close to unit, yield.

In addition to the OH radical formation yields given in Table 29, Grosjean and Grosjean[96,98–101] and Grosjean *et al.*[71,97,103,104] have observed the formation of cyclohexanone, a product of the reaction of the OH radical with cyclohexane, from the reactions of O_3 with many of the alkenes listed in Table 29 and with 3-methyl-1-butene,[101] *cis*-3-hexene,[99] *trans*-3-hexene,[97] 2-methyl-1-pentene,[100] 3-methyl-1-pentene,[101] 4-methyl-1-pentene,[101] 2-ethyl-1-butene,[100,103] 3,3-dimethyl-1-butene,[101] 2,3,3-trimethyl-1-butene,[100] 3-methyl-2-isopropyl-1-butene,[100] 2,4,4-trimethyl-

TABLE 29. OH radical formation yields from the gas-phase reactions of O_3 with alkenes at room temperature and atmospheric pressure

Alkene	OH radical formation yield[a]	Reference
Ethene	0.12	Atkinson *et al.*[124]
Propene	0.33	Atkinson and Aschmann[127]
1-Butene	0.41	Atkinson and Aschmann[127]
cis-2-Butene	0.41	Atkinson and Aschmann[127]
trans-2-Butene	0.64	Atkinson and Aschmann[127]
2-Methylpropene	0.84	Atkinson and Aschmann[127]
1-Pentene	0.37	Atkinson *et al.*[95]
2-Methyl-1-butene	0.83	Atkinson and Aschmann[127]
2-Methyl-2-butene	0.89	Atkinson and Aschmann[127]
	0.93 ± 0.14[b]	Chew and Atkinson[129]
1-Hexene	0.32	Atkinson *et al.*[95]
2,3-Dimethyl-1-butene	0.50	Atkinson *et al.*[95]
2,3-Dimethyl-2-butene	0.7 ± 0.1[c]	Niki *et al.*[30]
	1.00	Atkinson and Aschmann[127]
	0.80 ± 0.12[b]	Chew and Atkinson[129]
	$\sim$0.5[d]	Gutbrod *et al.*[132]
1-Heptene	0.27	Atkinson *et al.*[95]
1-Octene	0.45 ± 0.20[e]	Paulson and Seinfeld[51]
	0.18	Atkinson *et al.*[95]
1,3-Butadiene	0.08	Atkinson and Aschmann[127]
Isoprene	0.68 ± 0.15[e]	Paulson *et al.*[123]
	0.27	Atkinson *et al.*[124]
Cyclopentene	0.61	Atkinson *et al.*[95]
Cyclohexene	0.68	Atkinson and Aschmann[127]
1-Methylcyclohexene	0.90	Atkinson *et al.*[95]
1,2-Dimethyl-1-cyclohexene	1.04	Alvarado *et al.*[130]
	1.02 ± 0.16[b]	Alvarado *et al.*[130]
Camphene	$\leq$0.18	Atkinson *et al.*[124]
3-Carene	1.06	Atkinson *et al.*[124]
Limonene	0.86	Atkinson *et al.*[124]
Myrcene	1.15	Atkinson *et al.*[124]
cis- and *trans*-Ocimene	0.63	Atkinson *et al.*[124]
β-Phellandrene	0.14	Atkinson *et al.*[124]
α-Pinene	0.85	Atkinson *et al.*[124]
	0.76 ± 0.11[b]	Chew and Atkinson[129]
β-Pinene	0.35	Atkinson *et al.*[124]
Sabinene	0.26	Atkinson *et al.*[124]
	0.33 ± 0.06[b]	Chew and Atkinson[129]
Terpinolene	1.03	Atkinson *et al.*[124]
α-Cedrene	0.67	Shu and Atkinson[128]
α-Copaene	0.38	Shu and Atkinson[128]
	0.32	Shu and Atkinson[128]
β-Caryophyllene	0.06	Shu and Atkinson[128]
α-Humulene	0.22	Shu and Atkinson[128]

[a] The estimated overall uncertainties for the OH radical formation yields measured by Atkinson *et al.*,[95,124] Atkinson and Aschmann,[127] Shu and Atkinson,[128] and Alvarado *et al.*[130] from the amounts of cyclohexanone plus cyclohexanol formed in the presence of cyclohexane as an OH radical scavenger are a factor of ~1.5. Unless noted otherwise, data are from studies using cyclohexane as an OH radical scavenger.

[b] Using 2-butanol as an OH radical scavenger.

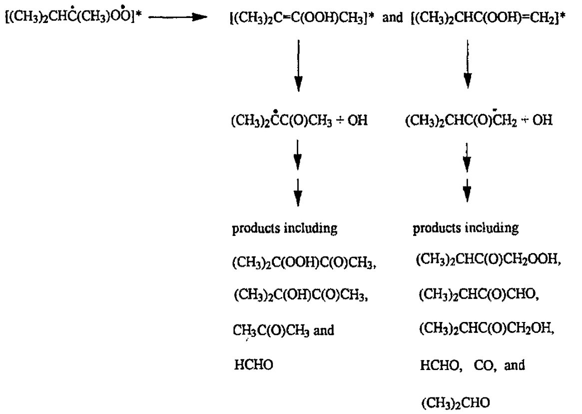
[c] From a comprehensive product study.

[d] No details of experimental techniques given.[132]

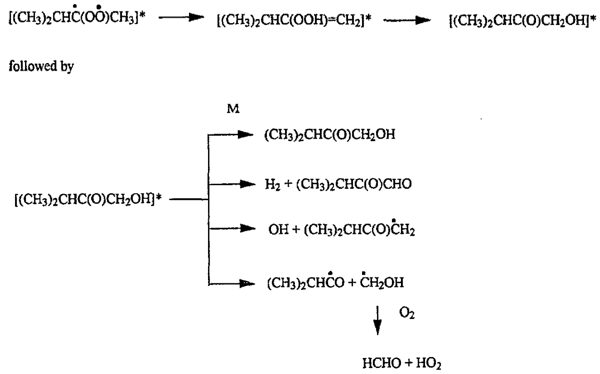
[e] Using 1-methylcyclohexane as a tracer to monitor the OH radical concentration.

2-pentene,[100] *cis*-4-octene,[99] *trans*-4-octene,[99] *trans*-2,5-dimethyl-3-hexene,[99] *cis*+*trans*-3,4-dimethyl-3-hexene,[99] 1-decene,[71] *cis*-5-decene,[99] *trans*-5-decene,[99] and 3,4-diethyl-2-hexene,[100] showing that OH radicals are also formed during the reactions of O_3 with these alkenes.

Decomposition of the energy rich biradicals through the hydroperoxide channel[132] and/or the ester channel leads to the formation of a variety of product species, including carbonyl compounds with less carbons than the primary carbonyls.[30,51,71,95,97–101,103,133] For example, the $[(CH_3)_2CH\dot{C}(CH_3)O\dot{O}]^*$ biradical formed from the reaction of O_3 with 2,3-dimethyl-1-butene can isomerize to form two hydroperoxides which, after decomposition to yield OH radicals, lead to the formation of a number of carbonyls and radicals, as shown in Reaction Scheme 9.

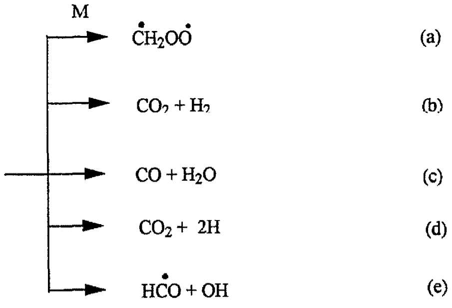


These products arise from peroxy radical+peroxy radical and peroxy radical+HO_2 radical reactions, and the expected formation of $CH_3C(O)CH_3$ is consistent with the experimental observations of Grosjean and Grosjean,[98] while a small amount of HCHO formation from the initially formed biradicals is suggested by the observations that the measured yields of the primary carbonyls, HCHO plus 2-butanone, are 1.17 ± 0.09[95] and 1.03.[98] It should be noted that Grosjean and coworkers[71,97–101,103] postulate that the hydroperoxide may further isomerize to the β-hydroxycarbonyl, followed by decomposition and/or stabilization (as postulated earlier by Martinez and Herron[120] to explain their low pressure data for the O_3 reaction with 2,3-dimethyl-2-butene). For example, for the $[(CH_3)_2CH\dot{C}(CH_3)O\dot{O}]^*$ biradical the reaction sequence would be,



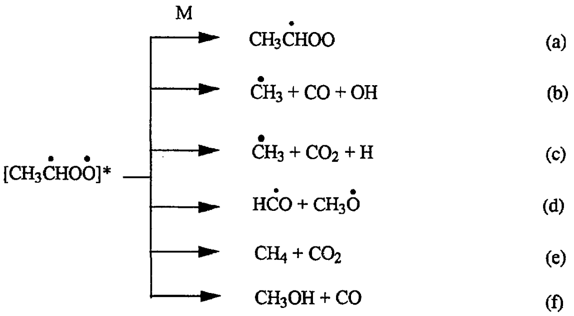
leading to the same products as expected from the subsequent reactions of the $(CH_3)_2CHC(O)\dot{C}H_2$ radical formed after decomposition of the hydroperoxide (Reaction Scheme 9). These two views of the biradical reactions by the hydroperoxide channel therefore appear to be equivalent, although the formation of OH radicals directly from decomposition of the hydroperoxide (Reaction Scheme 9) appears more likely than through the intermediary of the energy rich β-hydroxycarbonyl (see also Gutbrod *et al.*[132]).

Even for the reactions of O_3 with ethene, propene, and the 2-butenes, the fates of the initially formed biradicals are not completely understood.[2,122] For the reaction of O_3 with ethene, the reactions of the $[CH_2O\dot{O}]^*$ biradical are postulated to include the following reaction channels.



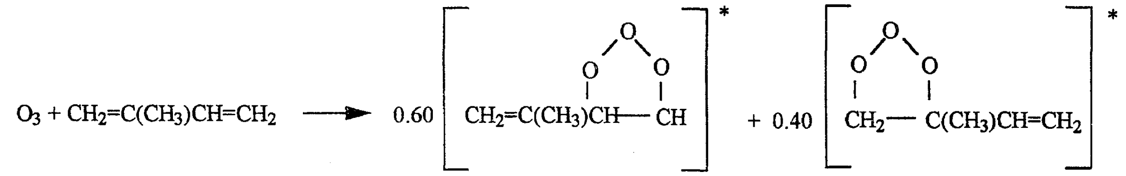
The studies of Herron and Huie[116] (supposedly adjusted to be applicable to atmospheric pressure[31,134]), Su *et al.*[110] and Horie and Moortgat[114] lead to fractions of the pathways (a) through (d) of: channel (a), 0.37; channel (b), ~0.13;[31,114] channel (c), 0.31–0.58;[31,110,114] and channel (d), 0.06–0.10.[31,114] However, Atkinson *et al.*[124] have observed OH radicals to be formed with an ~0.12 yield, presumably via channel (e), and the IUPAC evaluation[31] suggests that the fractions of the reactions of the $[\dot{C}H_2O\dot{O}]^*$ biradical proceeding by the various channels at room temperature and atmospheric pressure are: channel (a), 0.37; channel (b), ~0.13; channel (c), ~0.38; and channel (e), ~0.12. Significant discrepancies between the various studies are apparent, even for the reactions of the simplest biradical, $[\dot{C}H_2O\dot{O}]^*$.

For the $[CH_3\dot{C}HO\dot{O}]^*$ biradical formed from the reactions of O_3 with propene and the 2-butenes, the following reactions are postulated

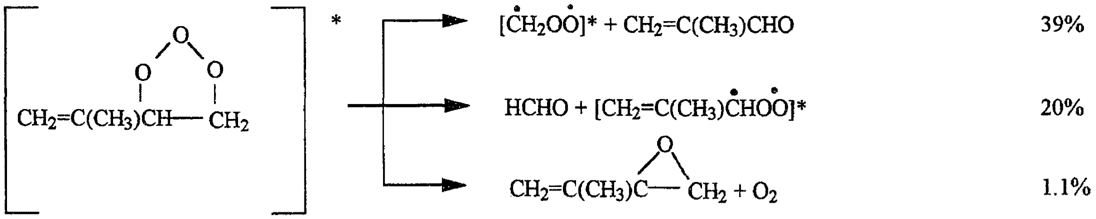


Previous evaluations[47] and studies[107,113,114,122] of the reaction of O_3 with propene[47,107,114] and the 2-butenes[47,107,113,114,122] have concluded that channels (a)–(f) account for: channel (a), 0.15–0.42; channel (b), 0.14–0.30; channel (c), 0.17–0.32; channel (d), 0–0.07; channel (e) 0.14–0.17; and channel (f), 0–0.07, with the experimental data of Horie and Moortgat[114] and Horie *et al.*[122] leading to fractions of the reaction proceeding by channels (a) through (f) of 0.40–0.42, 0.14–0.24, 0.17–0.21, 0, 0.12–0.17, and 0.06–0.07, respectively. These various studies lead to differing product distributions from the O_3 reaction with propene. As one example, the OH radical formation yields vary from 0.10[114] to 0.15,[47] while Atkinson and Aschmann[127] have derived an OH radical formation yield of 0.33 (uncertain by a factor of ~1.5) from monitoring the formation of cyclohexanane plus cyclohexanol formed from the OH radical reaction with cyclohexane in a reacting O_3–propene–cyclohexane–air mixture (Table 29). The most recent IUPAC evaluation[31] suggests that the fractions of the reactions of the $[CH_3\dot{C}HO\dot{O}]^*$ biradical proceeding by the various channels at room temperature and atmospheric pressure are: channel (a), 0.15; channel (b), ~0.54; channels (c) plus (d), ~0.17; and channel (e), ~0.14.

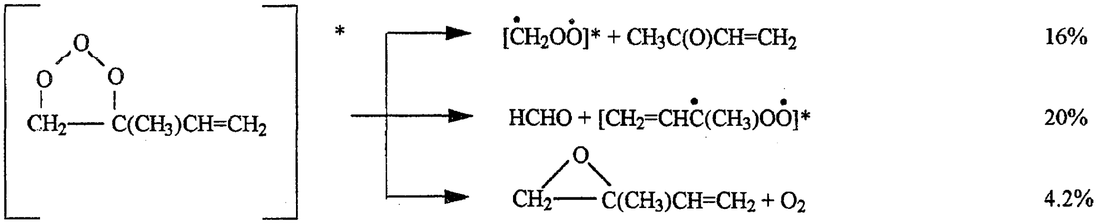
The products of the reaction of O_3 with isoprene in the presence of an OH radical scavenger have been studied by Grosjean *et al.*,[104] Atkinson *et al.*,[124,125] and Aschmann and Atkinson,[105] and Aschmann and Atkinson[105] proposed the following reaction mechanism:



followed by



and



The $[\dot{C}H_2O\dot{O}]^*$ biradical is assumed to react as discussed and shown above, and the $[CH_2{=}CH\dot{C}(CH_3)O\dot{O}]^*$ biradical is assumed[105] to form OH radicals by the hydroperoxide channel,

$$[CH_2{=}CH\dot{C}(CH_3)O\dot{O}]^* \rightarrow [CH_2{=}CHC(OOH){=}CH_2]^*$$

$$\rightarrow OH + CH_2{=}CHC(O)\dot{C}H_2$$

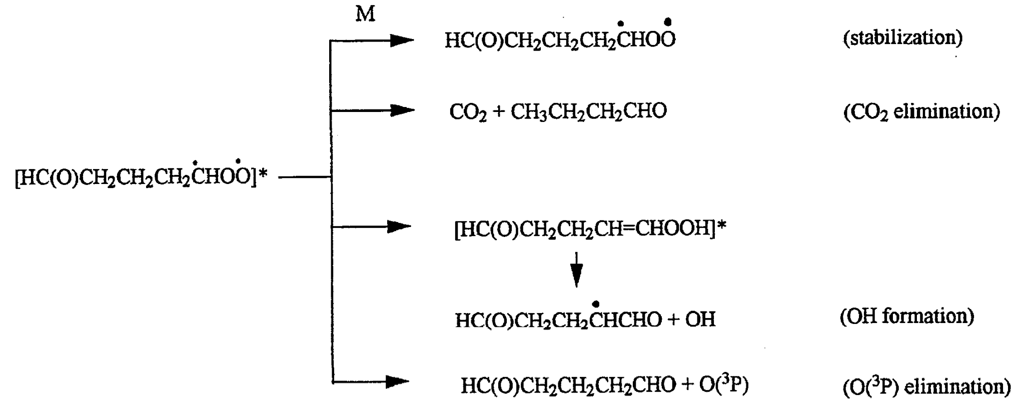
with the $CH_2{=}CHC(O)\dot{C}H_2$ radical reacting to lead to the formation of HCHO. The $[CH_2{=}C(CH_3)\dot{C}HO\dot{O}]^*$ biradical was assumed[105] not to lead to the formation of OH radicals or HCHO; the formation of propene (as observed by Paulson *et al.*[123] in 7±3% yield and by Aschmann and Atkinson[135] in ~4.3% yield) may arise from decomposition of the $[CH_2{=}C(CH_3)\dot{C}HO\dot{O}]^*$ biradical.[56]

$$[CH_2{=}C(CH_3)\dot{C}HO\dot{O}]^* \rightarrow CH_3CH{=}CH_2 + CO_2$$

A detailed chemical mechanism which includes the reaction of O_3 with isoprene, based on the above mentioned studies,[104,105,123–125,135] has been formulated and tested by Carter and Atkinson,[56] and that article should be consulted for further details of that mechanism.

The products of the gas-phase reactions of O_3 with cycloalkenes (including cyclic monoterpenes) have been studied by Schuetzle and Rasmussen,[136] Hull,[137] Niki *et al.*,[109] Hatakeyama *et al.*,[138–140] Yokouchi and Ambe,[141] Izumi *et al.*,[142] Jay and Stieglitz,[143] Hatakeyama and Akimoto,[144] Grosjean *et al.*,[71,106] Hakola *et al.*,[69,70] Atkinson *et al.*,[95] Grosjean and Grosjean,[98] and Alvarado *et al.*[130] However, only in the studies of Grosjean *et al.*,[71,106] Hakola *et al.*,[69,70] Atkinson *et al.*,[95] Grosjean and Grosjean,[98] and Alvarado *et al.*[130] were the OH radicals formed from the reactions of O_3 with the cycloalkenes scavenged and hence only these studies[69–71,95,98,106,130] are free from consumption of the cycloalkenes by OH radicals and the formation of OH radical reaction products. The products observed, and their measured formation yields, from these studies[69–71,95,98,106,130] are given in Table 30 (the data for camphene, β-pinene, limonene, β-phellandrene, sabinene, and terpinolene are also given, at least in part, in Table 27).

No significant formation of products was observed by Hakola *et al.*[70] by gas chromatography-flame ionization detection (GC-FID) and gas chromatography-mass spectrometric (GC-MS) analyses from the O_3 reactions with 3-carene or limonene. For the cycloalkenes containing only internal $>C{=}C<$ bond(s), the initially formed energy rich ozonide decomposes to two biradicals (or, for symmetrical cycloalkenes such as cyclopentene, cyclohexene and 1,2-dimethyl-1-cyclohexene, to one biradical), and no primary carbonyls are formed from the decomposition(s) of the ozonide. Hence the reaction products are formed from the reactions of the biradical(s). As discussed above, these biradicals can then undergo collisional stabilization and reactions involving decomposition and isomerization. For example, the potential reactions of the biradical formed from cyclopentene are:



$$[HC(O)CH_2CH_2CH_2\dot{C}HO\dot{O}]^* \xrightarrow{M} HC(O)CH_2CH_2CH_2\dot{C}HO\dot{O} \quad \text{(stabilization)}$$

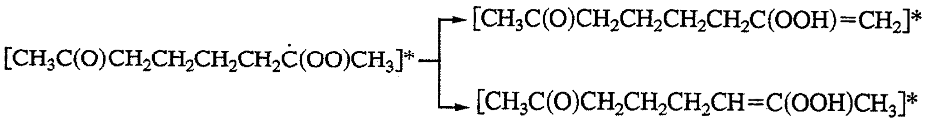
$$\rightarrow CO_2 + CH_3CH_2CH_2CHO \quad \text{(CO}_2\text{ elimination)}$$

$$\rightarrow [HC(O)CH_2CH_2CH{=}CHOOH]^* \rightarrow HC(O)CH_2CH_2\dot{C}HCHO + OH \quad \text{(OH formation)}$$

$$\rightarrow HC(O)CH_2CH_2CH_2CHO + O(^3P) \quad \text{(O(}^3\text{P) elimination)}$$

In addition to the formation of the biradical(s), the direct formation of an oxirane from the reactions of O_3 with 1,2-dimethyl-1-cyclohexene and *α*-pinene has been observed in ~2% yield for each reaction.[130] Table 31 shows the fractions of the overall reactions of the biradical(s) proceeding by the various possible pathways, derived from the reported product yields.[70,71,95,98,130] The CO_2 elimination pathway, presumably via the ester channel, is significant for the cyclopentene and cyclohexene reactions; but less so for the 1-methyl-1-cyclohexene reaction and not observed for the reactions of the other three cycloalkenes listed in Table 31. This CO_2 elimination pathway therefore appears to occur only for biradicals of structure $[R\dot{C}HO\dot{O}]^*$. For the O_3 reaction with 1-methyl-1-cyclohexene, the $[CH_3C(O)(CH_2)_4\dot{C}HO\dot{O}]^*$ biradical leading to 2-hexanone[98] is expected to be formed in lower yield than the dialkyl-substituted $[CH_3\dot{C}(O\dot{O})(CH_2)_4CHO]^*$ biradical.

The observed formation of 5-oxohexanal ($CH_3C(O)CH_2CH_2CH_2CHO$) from the reaction of O_3 with 1,2-dimethyl-1-cyclohexene[130] almost certainly occurs from the subsequent reactions of the $CH_3C(O)CH_2CH_2CH_2CH_2C(O)\dot{C}H_2$ and $CH_3C(O)CH_2CH_2CH_2\dot{C}HC(O)CH_3$ radicals formed together with the OH radical in the hydroperoxide channel:



$$[CH_3C(O)CH_2CH_2CH_2CH_2\dot{C}(OO)CH_3]^* \rightarrow [CH_3C(O)CH_2CH_2CH_2CH_2C(OOH){=}CH_2]^*$$

$$[CH_3C(O)CH_2CH_2CH_2CH_2\dot{C}(OO)CH_3]^* \rightarrow [CH_3C(O)CH_2CH_2CH_2CH{=}C(OOH)CH_3]^*$$

followed by

$$[CH_3C(O)CH_2CH_2CH_2CH_2C(OOH){=}CH_2]^* \rightarrow OH + CH_3C(O)CH_2CH_2CH_2CH_2C(O)\dot{C}H_2$$

and

$$[CH_3C(O)CH_2CH_2CH_2CH{=}C(OOH)CH_3]^* \rightarrow OH + CH_3C(O)CH_2CH_2CH_2\dot{C}HC(O)CH_3.$$

Additional expected dicarbonyls and hydroxycarbonyls formed from these radicals in the absence of NO_x have been observed by atmospheric pressure ionization mass spectrometry.[130]

As noted above, $O(^3P)$ atom formation from the reactions of O_3 with *α*-pinene and 1,2-dimethyl-1-cyclohexene have not been observed, with the measured upper limits to the $O(^3P)$ atom formation yields being given in Table 31.[130] Interestingly however, the formation of 6-oxoheptanal from 1-methyl-1-cyclohexene, of 2,7-octanedione from 1,2-dimethyl-1-cyclohexene, and of pinonaldehyde (3-acetyl-2,2-dimethylcyclobutaneacetaldehyde) from *α*-pinene have been observed[70,130] (Table 31). These products are not formed by the $O(^3P)$ atom elimination channel, and to date

TABLE 30. Carbonyl products observed, and their formation yields, from the gas-phase reactions of O_3 with cycloalkenes at room temperature and atmospheric pressure of air in the presence of an OH radical scavenger

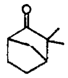
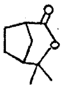
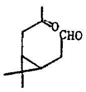
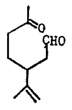
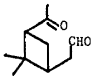
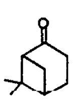
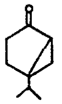
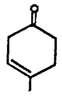
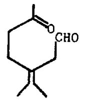
Cycloalkene	Product	Yield	Reference
Cyclopentene	butanal	0.195 ± 0.027 0.120 ± 0.001	Atkinson *et al.*[95] Grosjean and Grosjean[98]
	glyoxal	0.150 ± 0.010	Grosjean and Grosjean[98]
	$HC(O)(CH_2)_3C(O)OH$	a	Grosjean and Grosjean[98]
Cyclohexene	pentanal	0.156 ± 0.004	Grosjean *et al.*[71]
1-Methyl-1-cyclohexene	6-oxoheptanal	0.100 ± 0.024	Atkinson *et al.*[95]
	2-hexanone	0.040 ± 0.010	Grosjean and Grosjean[98]
	$CH_3C(O)(CH_2)_4C(O)OH$	a	Grosjean and Grosjean[98]
1,2-Dimethyl-1-cyclohexene	2,7-octanedione	0.069 ± 0.013	Alvarado *et al.*[130]
	5-oxohexanal	0.194 ± 0.046	Alvarado *et al.*[130]
Camphene		0.36 ± 0.06	Hakola *et al.*[70]
		~0.2	Hakola *et al.*[70]
3-Carene		≤0.08	Hakola *et al.*[70]
Limonene		≤0.04	Hakola *et al.*[70]
β-Phellandrene		0.29 ± 0.06	Hakola *et al.*[69]
α-Pinene		0.19 ± 0.04 0.143 ± 0.024	Hakola *et al.*[70] Alvarado *et al.*[130]
β-Pinene	HCHO	0.42	Grosjean *et al.*[106]
		0.22 0.23 ± 0.05	Grosjean *et al.*[106] Hakola *et al.*[70]
Sabinene		0.50 ± 0.09	Hakola *et al.*[70]

TABLE 30. Carbonyl products observed, and their formation yields, from the gas-phase reactions of O_3 with cycloalkenes at room temperature and atmospheric pressure of air in the presence of an OH radical scavenger -- Continued (2)

Cycloalkene	Product	Yield	Reference
Terpinolene		0.40 ± 0.06	Hakola *et al.*[70]
		≤0.02	Hakola *et al.*[70]

[a] No product yields reported.

the formation pathways leading to these products have not been elucidated, although it is possible that they arise from reactions of the stabilized biradical(s) since the biradical stabilization yields and the C_n-dicarbonyl yields for the 1-methyl-1-cyclohexene and α-pinene reactions are similar (Table 31) [for the 1,2-dimethyl-1-cyclohexene reaction, the concentrations of the cyclohexane OH radical scavenger were varied by a factor of 3 such that 93% to 98% of the OH radicals formed were calculated to be scavenged by cyclohexane, with no effect on the 2,7-octanedione formation yield[130]]. The product formation pathway yield data shown in Table 31 suggest that, while a large fraction of the carbon is not accounted for (primarily associated with OH radical formation through the hydroperoxide channel), the majority of the reaction pathways of the biradicals are accounted for. For example, the sum of the oxirane formation, biradical stabilization, CO_2 elimination, and OH radical formation pathways account for 82% of the cyclopentene reaction, 87% of the cyclohexene reaction, 104% of the 1-methyl-1-cyclohexene reaction, 104±16% of the 1,2-dimethyl-1-cyclohexene reaction (with no biradical stabilization yield being available), 106% of the 3-carene reaction (with no biradical stabilization yield being available), and 90±12% of the α-pinene reaction, with the sum of the yields for the cyclopentene, cyclohexene, 1-methyl-1-cyclohexene and 3-carene reactions being subject to significant uncertainties (Table 31).

The formation of aerosols has been investigated from the photooxidations of 1-octene,[145,146] isoprene,[61,62] cyclopentene,[139] cyclohexene,[138,142] cycloheptene,[139] 1-methylcyclohexene,[144] methylenecyclohexane,[144] α-pinene,[74,140,141] β-pinene,[61,62,74,140,141] and limonene,[141] and these references should be consulted for further details. The recent study of Zhang *et al.*[74] of the photooxidations of α- and β-pinene at initial concentrations of $(0.9-14)\times10^{12}$ molecule cm^{-3} (37 to 582 parts-per-billion mixing ratios) showed that the aerosol carbon yields varied from 0–5.3% for α-pinene, depending on the initial alkene/NO_x concentration ratio.[74]

The stabilized biradicals are known to react with aldehydes, SO_2, CO, H_2O, and NO_2,[147] and it is expected that they will also react with NO.[148,149] Based upon the available data for the reactions of the $\dot{C}H_2O\dot{O}$ biradical with these reactants, with rate constants relative to the reaction of the $\dot{C}H_2O\dot{O}$ biradical with SO_2 of: HCHO, ~0.25;[110] CO, 0.0175;[110] H_2O, $(2,3\pm1)\times10^{-4}$ (Ref. 150) and

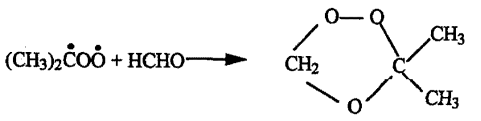
TABLE 31. Fractions of the overall biradical reactions proceeding by the various pathways, as derived from the product formation yields at room temperature and atmospheric pressure of air

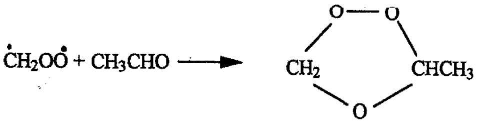
Cycloalkene	Stabilization[a]	CO_2 ellimination[b]	OH formation[c]	$O(^3P)$ elimination[d]	C_n-dicarbonyl formation[e]
Cyclopentene	0.052±0.013	0.16	$0.61^{+0.31}_{-0.21}$		
Cyclohexene	0.032±0.024	0.16	$0.68^{+0.34}_{-0.23}$		
1-Methyl-1-cyclohexene	0.104±0.065	0.04	$0.90^{+0.45}_{-0.30}$		0.10±0.03
1,2-Dimethyl-1-cyclohexene			1.02±0.16	<0.04	0.07±0.02
3-Carene			$1.06^{+0.53}_{-0.36}$		⩽0.08
α-Pinene	0.125±0.040		0.76±0.11	<0.03	0.17±0.05

[a] From Hatakeyama *et al.*[107]
[b] From Atkinson *et al.*,[95] Grosjean and Grosjean,[98] and Grosjean *et al.*[71]
[c] From Atkinson *et al.*,[95] Atkinson and Aschmann,[127] Chew and Atkinson,[129] and Alvarado *et al.*[130]
[d] From Alvarado *et al.*[130]
[e] From Hakola *et al.*,[70] Atkinson *et al.*,[95] and Alvarado *et al.*[130]

$(8.3\pm3.6)\times10^{-4}$;[151] and NO_2, 0.014,[152] it appears that the reaction of stabilized biradicals with water vapor will be their dominant loss process under atmospheric conditions. The rate constant ratios for the reactions of the $\dot{C}H_2O\dot{O}$ biradical with water vapor and SO_2 derived by Suto *et al.*[150] and Becker *et al.*[151] are in reasonable agreement. Furthermore, the corresponding rate constant ratio for the reactions of the $(CH_3)_2\dot{C}O\dot{O}$ biradical with water vapor and SO_2 of $(4.1\pm2.2)\times10^{-4}$ measured by Becker *et al.*[151] is similar to the values for the $\dot{C}H_2O\dot{O}$ biradical.[150,151]

The reaction of the $\dot{C}H_2O\dot{O}$ biradical with acetaldehyde and the reactions of the more complex biradicals such as $CH_3\dot{C}HO\dot{O}$ and $(CH_3)_2\dot{C}O\dot{O}$ with aldehydes lead to the formation of secondary ozonides.[30,109,113]



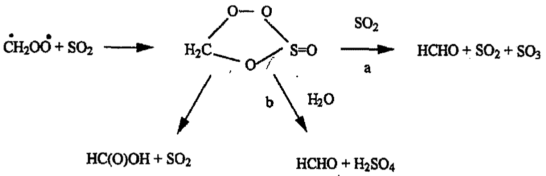


However, the formation of ethene ozonide is not observed during the reaction of O_3 with ethene,[109–112] and the reaction of the $\dot{C}H_2O\dot{O}$ biradical with HCHO was previously[109–112,114] proposed to lead to the formation of $HOCH_2OCHO$. The recent study of Neeb *et al.*[153] indicates that the reaction of the $\dot{C}H_2O\dot{O}$ biradical with HCHO does not form $HOCH_2OCHO$, and Neeb *et al.*[153] have shown that the $\dot{C}H_2O\dot{O}$ biradical reacts with formic acid, HC(O)OH, to form hydroperoxymethylformate,

$$\dot{C}H_2O\dot{O}+HC(O)OH\rightarrow HOOCH_2OCHO$$

which decomposes to formic acid anhydride, HC(O)OCHO, plus H_2O, and that $HOOCH_2OCHO$ was previously[109–112,114] incorrectly identified as $HOCH_2OCHO$.

The reaction of the $\dot{C}H_2O\dot{O}$ biradical with SO_2 is proposed to proceed through an intermediate which can decompose or react with SO_2 and water vapor,[147,154]

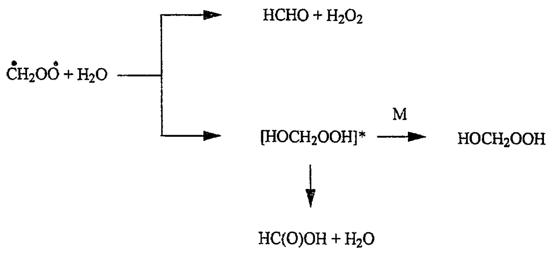


and a rate constant ratio of $k_b/k_a=6.0\times10^{-3}$ was estimated.[154] Under tropospheric conditions, the reaction of the adduct with water vapor will then dominate, leading to the formation of sulfuric acid and HCHO.[147]

In addition to the formation of carboxylic acids from the reactions of stabilized biradicals with H_2O,

$$R\dot{C}HO\dot{O}+H_2O\rightarrow RC(O)OH+H_2O,$$

the studies of Gäb *et al.*,[155] Becker *et al.*,[151,156] Simonaitis *et al.*,[157] Hewitt and Kok,[158] Hatakeyama *et al.*,[159] and Horie *et al.*[160] have reported the formation of H_2O_2,[151,156–159] and organic hydroperoxides[155,157–160] from the reactions of O_3 with alkenes. There are significant quantitative discrepancies between the studies of Becker *et al.*,[151,156] Simonaitis *et al.*,[157] Hatakeyama *et al.*[159] and Horie *et al.*,[160] and these may be related to the analytical methods used,[154,159] with Becker *et al.*,[151,156] and Horie *et al.*[160] using infrared absorption spectroscopy to measure H_2O_2[151,156,160] and hydroxymethyl hydroperoxide[160] while Simonaitis *et al.*[157] and Hatakeyama *et al.*[159] used wet chemical methods for hydroperoxide measurements. The data of Becker *et al.*[151,156] and Horie *et al.*[160] show that for the alkenes studied the molar formation yields of H_2O_2 in the presence of $(3-5)\times10^{17}$ molecule cm^{-3} of water vapor are in the range 0.001–0.018. A possible reaction sequence is,[154,159,160]



with the reaction channel leading to H_2O_2 being a minor pathway.

2.2.4. Cl Atom Reactions

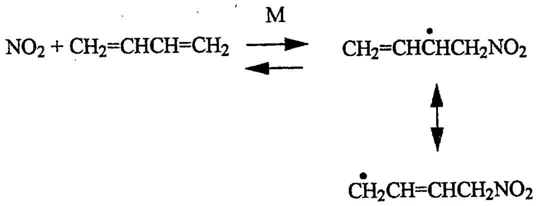
Cl atoms react rapidly with alkenes, and the literature rate constants at room temperature and atmospheric pressure of air are given in Table 32. Although the rate constants for these Cl atom reactions are close to gas kinetic, the ratios of the rate constants for the reactions of alkenes with the Cl atom relative to the rate constants for reaction with the OH radical, k_{Cl}/k_{OH}, are ~10, a factor of ~10 lower than the corresponding values of k_{Cl}/k_{OH} ~100 for the $\geqslant C_3$ alkanes (Table 3, Sec. 2.1). Hence the Cl atom reactions with the alkenes are expected to be generally of minor or negligible importance as a tropospheric loss process for the alkenes.

The reactions of the Cl atom with ethene and propene proceed by Cl atom addition to the >C=C< bond and by H-atom abstraction from the C–H bonds.[165,166] At 298 K and 760 Torr total pressure of air, the Cl atom addition pathway totally dominates for ethene[165] and accounts for ~90% of the Cl atom reaction with propene.[166] Both reactions are in the falloff regime between second and third order kinetics at 298 K and $\leqslant$760 Torr total pressure of air. The parameters in the Troe falloff expression derived by Kaiser and Wallington[165,166] at 298 K are: for ethene,[165] $k_0=1.42\times10^{-29}$ cm^6 molecule^{-2} s^{-1}, $k_\infty=3.2\times10^{-10}$ cm^3 molecule^{-1} s^{-1}, $F=0.6$ (or, giving an equivalently good fit to the experimental data, $k_0=1.64\times10^{-29}$ cm^6 molecule^{-2} s^{-1}, $k_\infty=5.7\times10^{-10}$ cm^3 molecule^{-1} s^{-1}, and $F=0.4$) and for propene,[166] $k_0=4.0\times10^{-28}$ cm^6 molecule^{-2} s^{-1}, $k_\infty=2.7\times10^{-10}$ cm^3 molecule^{-1} s^{-1}, $F=0.6$, and $k_{abs}=2.3\times10^{-11}$ cm^3 molecule^{-1} s^{-1}. H-atom abstraction from the vinyl C–H bonds is of negligible importance at room temperature and below,[165] and for propene H-atom abstraction occurs from the C–H bonds of the methyl substituent group.[166]

2.2.5. NO_2 Reactions

NO_2 reacts with conjugated dienes with rate constants at room temperature of $>10^{-20}$ cm^3 molecule^{-1} s^{-1}.[92,168] These reactions are of negligible importance as a tropospheric loss process for alkenes and dienes, but may be of some importance in environmental chamber experiments carried out at high NO_2 concentrations.[3,4]

The only monoalkenes and nonconjugated dienes which have been shown to react with NO_2 at room temperature at an observable rate are 2,3-dimethyl-2-butene,[92,169] β-caryophyllene,[170] and α-humulene,[170] with the room temperature rate constants for other nonconjugated alkenes being $<10^{-20}$ cm^3 molecule^{-1} s^{-1}.[92,168] The room temperature rate constants for the gas-phase reactions of NO_2 with 2,3-dimethyl-2-butene, β-caryophyllene, and α-humulene and selected dienes are given in Table 33. As shown by Atkinson *et al.*[92] and Niki *et al.*,[169] the reaction sequences are as follows, taking 1,3-butadiene as an example



with the initial reaction being reversible, at least for 2,3-dimethyl-2-butene[169] and β-caryophyllene.[170] In the case of the reaction of NO_2 with β-caryophyllene, the nitroalkyl radical decomposes, at least in part, to a sesquiterpene isomeric with β-caryophyllene and with very similar IR and MS spectra.[170]

The initially formed nitroalkyl radical then adds O_2

$$CH_2{=}CH\dot{C}HCH_2NO_2 + O_2 \xrightarrow{M} CH_2{=}CHCH(O\dot{O})CH_2NO_2$$

$$\dot{C}H_2CH{=}CH_2NO_2 + O_2 \xrightarrow{M} \dot{O}OCH_2CH{=}CH_2NO_2$$

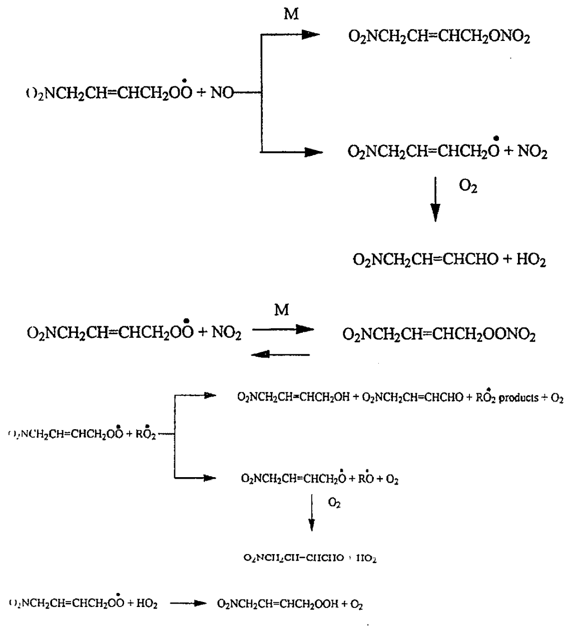
to form a nitroalkyl peroxy radical, which can then react with NO, NO_2, organic peroxy radicals and/or HO_2 radicals (as discussed above for hydroxyalkyl peroxy and nitrooxalkyl peroxy radicals). For example, for the $O_2NCH_2CH{=}CHCH_2O\dot{O}$ radical, the reactions are:

32. Rate constants k for the gas-phase reactions of the Cl atom with at 298±2 K and 740–760 Torr total pressure of air

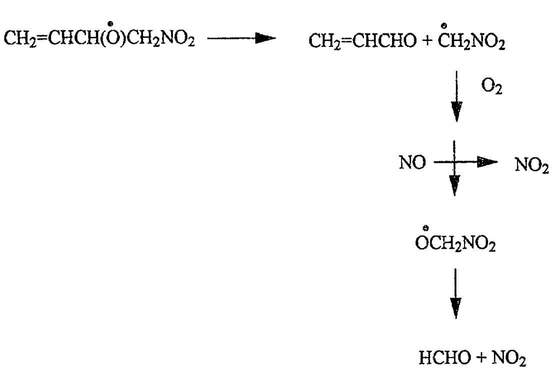
Alkene	$10^{11}\times k$ (cm^3 $molecule^{-1}$ s^{-1})^a	Reference
ne	10.7	Atkinson and Aschmann;[161,162]
		Wallington *et al.*;[163,164]
		Kaiser and Wallington[165]
pene	28	Atkinson and Aschmann;[161]
		Wallington *et al.*;[163]
		Kaiser and Wallington[166]
Propadiene	42	Wallington *et al.*[163]
Butadiene	49^b	Bierbach *et al.*[167]
thyl-1,3-butadiene (prene)	48^b	Bierbach *et al.*[167]

[a] constants relative to rate constants for the reactions of the Cl atom with ethane and/or n-butane of 5.9×10^{-11} cm^3 $molecule^{-1}$ s^{-1} and 10^{-10} cm^3 $molecule^{-1}$ s^{-1}, respectively, (Table 3 in Sec. 2.1), unless noted otherwise.

[b] Relative to a rate constant for the reaction of the Cl atom with propene of 10^{-10} cm^3 $molecule^{-1}$ s^{-1}.



As noted, the dominant reaction of the $O_2NCH_2CH=CHCH_2\dot{O}$ alkoxy radical is expected to be with O_2 leading to the formation of the HO_2 radical, and hence, in the presence of NO, to the OH radical, consistent with the observations of OH radical formation from the dark reactions of isoprene and 1,3-cyclohexadiene with NO_2 in the presence of NO.[4,92] The dominant reaction of the $CH_2=CHCH(\dot{O})CH_2NO_2$ alkoxy radical is expected to be by decomposition



to lead in the presence of NO to acrolein, HCHO and NO_2, but with no HO_2 (or OH) radical formation. The dark reaction of NO_2 with isoprene leads to the formation of methacrolein, methyl vinyl ketone and HCHO,[3,4] and OH radicals are also formed in the presence of NO.[4] These observations suggest that in the presence of NO the intermediate alkoxy radicals include $O_2NCH_2C(\dot{O})(CH_3)CH=CH_2$ and $O_2NCH_2C(CH_3)=CHCH_2\dot{O}$.

2.2.6. O(^{3}P) Atom Reactions

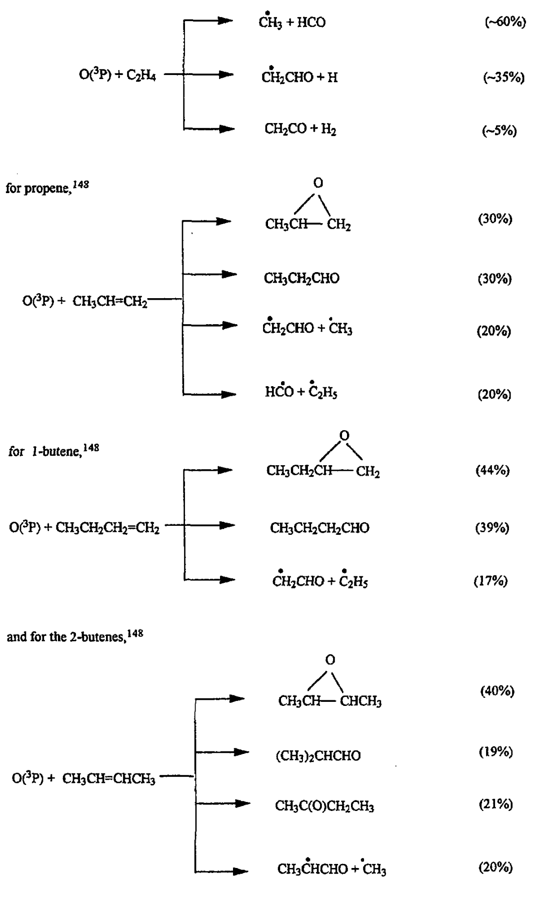
The O(^{3}P) atom reactions with the alkenes are of little importance under atmospheric conditions, but can become significant in laboratory irradiations of NO_x–alkene–air mixtures (see, for example, Paulson *et al.*[4] and Paulson and Seinfeld[51]). The kinetics, reaction mechanisms and products formed under atmospheric conditions have been previously reviewed by Cvetanović and Singleton,[174] Atkinson and Lloyd,[148] and Cvetanović.[175] The rate constants have been reviewed and evaluated by Cvetanović,[175] with more recent kinetic studies being reported by Mahmud *et al.*,[176] Klemm *et al.*,[177] Mahmud and Fontijn,[178] Ko *et al.*,[179] Knyazev *et al.*,[180] Adusei and Fontijn,[181,182] Biehl *et al.*,[183] Paulson *et al.*,[58] and Luo *et al.*[184] For ethene, propene, 1-butene, *cis*-2-butene, *trans*-2-butene, 2-methylpropene, 2-methyl-2-butene, 2,3-methyl-2-butene, and 1,3-butadiene, the room temperature rate constants from these more recent studies are in generally excellent agreement (within ~±10%) with the recommendations of Cvetanović.[175] Table 34 gives the 298 K rate constants for alkenes, generally taken from the review of Cvetanović[175] apart from the rate constants for isoprene and a number of monoterpenes which are based on the recent studies of Paulson *et al.*[58] and Luo *et al.*[184] and for the rate constant for 2-methyl-2-butene which is based on the absolute rate constant studies of Atkinson and Pitts[185] and Biehl *et al.*[183]

The initial reaction involves addition of the O(^{3}P) atom to the >C=C< bond, followed by collisional stabilization to a carbonyl or oxirane, or decomposition. As generally recommended by Atkinson and Lloyd,[148] at atmospheric pressure and 298 K the products are, for ethene,[148,180,186]

TABLE 33. Room temperature rate constants k for the gas-phase reactions of NO_2 with selected alkenes and dienes at atmospheric pressure of air

Alkene	$10^{20} \times k$ (cm^3 $molecule^{-1}$ s^{-1})[a]
2,3-Dimethyl-2-butene	1.0
1,3-Butadiene	3.0
2-Methyl-1,3-butadiene (isoprene)	15
Myrcene	26
Ocimene (*cis*- and *trans*-)	89
α-Phellandrene	1300
β-Phellandrene	~70
α-Terpinene	650
β-Caryophyllene	50
α-Humulene	16

[a] From Glasson and Tuesday,[171] Atkinson *et al.*,[92,172] Gu *et al.*,[60] Ohta *et al.*,[168] Niki *et al.*,[169] Shorees *et al.*,[173] Paulson *et al.*,[3] and Shu and Atkinson.[170] Uncertainties are a factor of ~1.5, except for β-phellandrene and α-humulene, for which the uncertainties are a factor of ~2.



although other fragmentation pathways cannot be excluded for the 2-butenes. It should be noted that the formation of 2-methylpropanal in the 2-butene reactions, involving migration of a methyl group from the energy rich oxirane, needs to be verified in air diluent.[187]

TABLE 34. Rate constants k at 298 K for the gas-phase reactions of the $O(^3P)$ atom with alkenes.

Alkene	$10^{12} \times k$ (cm^3 $molecule^{-1}$ s^{-1})[a]
Ethene	0.73
Propene	4.00
1-Butene	4.15
2-Methylpropene	16.9
cis-2-Butene	17.6
trans-2-Butene	21.8
1-Pentene	4.65
cis-2-Pentene	17
3-Methyl-1-butene	4.15
2-Methyl-2-butene	51[b]
1-Hexene	4.65
2,3-Dimethyl-2-butene	76.4
1,2-Propadiene	12.3
1,3-Butadiene	19.8
2-Methyl-1,3-butadiene	35[c]
Cyclopentene	21
Cyclohexene	20
1-Methyl-1-cyclohexene	90
1,3-Cyclohexadiene	91
2-Carene	34[d,e]
3-Carene	32[e,f]
Camphene	25[d,e]
Limonene	72[d,e]
α-Pinene	32[e,f]
β-Pinene	27[d,e]
γ-Terpinene	86[d,e]
Terpinolene	102[d,e]

[a] Rate constant are those recommended by Cvetanović,[175] unless noted otherwise.

[b] Average of 298 K rate constants of Atkinson and Pitts[185] and Biehl *et al.*[183]

[c] From Paulson *et al.*[58]

[d] From Luo *et al.*[184]

[e] The measured rate constant ratios of Luo *et al.*[184] at 302–307 K have been placed on an absolute basis using the 298 K rate constant for the reaction of $O(^3P)$ atoms with 2-methyl-2-butene, assuming that the temperature dependence of the rate constants for the reactions of the $O(^3P)$ atom with 2-methyl-2-butene and the monoterpenes are similar. The rate constants so derived for the reactions of the $O(^3P)$ atom with 2-methylpropene, *cis*-2-butene, *trans*-2-butene, 3-methyl-1-butene, and 2,3-dimethyl-2-butene are in excellent agreement with the values recommended above.

[f] Average of rate constants of Paulson *et al.*[58] and Luo *et al.*[184]

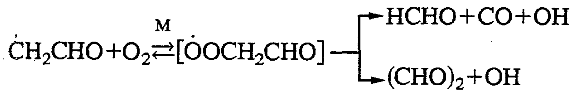
Paulson *et al.*[3] observed the formation of 2-ethenyl-2-methyl-oxirane, 2-(1-methylethenyl) oxirane and 2-methyl-2-butanal from the reaction of the $O(^3P)$ atom with isoprene at room temperature and atmospheric pressure of air, with formation yields of 0.63±0.08, 0.22±0.03, and 0.017 ±0.008, respectively, together with two unidentified products which were calculated to account for 11±4% of the overall reaction products. These observed products and the relative importance of addition *versus* decomposition products are consistent with the data and the trend observed for propene and the butenes (see above). The products of the reaction of the $O(^3P)$ atom with α-pinene have been studied by Alvarado *et al.*[130] at 298±2 K and 740 Torr total pressure of N_2 diluent. α-Pinene oxide and two unidentified isomeric carbonyls were observed, with formation yields of 0.766 ±0.059 for α-pinene oxide and 0.184±0.015 and 0.057 ±0.007 for the two isomeric carbonyls.[130] The overall formation yield of these three isomeric $C_{10}H_{16}O$ products was

1.01±0.08,[130] showing no evidence for the formation of decomposition products.

The atmospheric reactions of the carbonyl compounds and epoxides have been previously reviewed by Atkinson.[2] The $\dot{C}H_2CHO$ (vinoxy) radical reacts with O_2,[188,189] NO,[188] and NO_2.[190] Under atmospheric conditions, the only important reaction is with O_2. The rate constant for the O_2 reaction is in the falloff region between second and third order kinetics at ~100–300 Torr of He, N_2, or SF_6 at room temperature.[188,189] The limiting high pressure rate constant for this reaction is[188,189]

$$k_\infty(\dot{C}H_2CHO+O_2)=2.5\times10^{-13}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}\ at\ 298\ K},$$

with little or no temperature dependence over the range 292–476 K[188] (see also Lorenz *et al.*[189]). The magnitude of the rate constant and the pressure dependence shows that the reaction of the vinoxy radical with O_2 proceeds by initial addition to form the $\dot{O}OCH_2CHO$ radical (or its isomer). While the products of this reaction have not been directly monitored, there is evidence from the OH radical initiated reaction of acetylene[191,192] that OH radicals are produced. Hence, based on the studies of Gutman and Nelson[188] and Schmidt *et al.*,[191,192] the reaction possibly proceeds by:



$$\dot{C}H_2CHO+O_2\overset{M}{\rightleftarrows}[\dot{O}OCH_2CHO]\longrightarrow\begin{cases}\rightarrow HCHO+CO+OH\\ \rightarrow (CHO)_2+OH\end{cases}$$

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3. Kinetics and Mechanisms of the Gas-Phase Reactions of the OH Radical with Alkanes and Alkenes

Recent kinetic and mechanistic data for the gas-phase reactions of the OH radical with alkanes and alkenes are presented and discussed in this section.

3.1. Alkanes

The rate constants reported since the previous review of Atkinson[1] are given in Table 35.

3.1.1. Methane

Absolute rate constants for the reaction of the OH radical with methane have recently been determined by Lancar *et al.*,[2] Sharkey and Smith,[3] Dunlop and Tully,[4] Saunders *et al.*,[5] and Mellouki *et al.*[6] (Table 35). The absolute rate constants of Bott and Cohen,[19] Vaghjiani and Ravishankara,[20] Finlayson-Pitts *et al.*,[21] Dunlop and Tully,[4] and Mellouki *et al.*[6] are plotted in Arrhenius form in Fig. 1 and are seen to be in generally excellent agreement. As also discussed by Atkinson[1] (based on the data of Vaghjiani and Ravishankara[20] and Finlayson-Pitts *et al.*[21]), these recent rate constants are somewhat lower than those measured in earlier studies over the temperature range ~290–420 K. Dunlop and Tully[4] best-fit their data[4] and those of Vaghjiani and Ravishankara,[20] covering the combined temperature range 223–800 K, and obtained the three parameter expression $k(\text{methane})=9.65\times10^{-20}\ T^{2.58}\ e^{-1082/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$. This expression is also plotted in Fig. 1, and the agreement between this expression and the rate constants of Bott and Cohen,[19] Vaghjiani and Ravishankara,[20] Finlayson-Pitts *et al.*,[21] Dunlop and Tully,[4] and Mellouki *et al.*[6] is excellent. Accordingly, it is recommended that

$$k(\text{methane})=$$
$$9.65\times10^{-20}\ T^{2.58}\ e^{-1082/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 223–1234 K, and

$$k(\text{methane})=$$
$$6.18\times10^{-15}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at}\ 298\ \text{K},$$

with an estimated overall uncertainty at 298 K of ±15%. This recommendation is significantly different than the previous recommendation[1] of $k(\text{methane})=7.44\times10^{-18}\ T^2\ e^{-1361/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$ over the temperature range 223–1512 K, especially at ~400–500 K where the present recommendation yields rate constants ~17% lower than the previous recommendation.[1]

3.1.2. Ethane

Absolute rate constants have been determined by Sharkey and Smith,[3] El Maimouni *et al.*,[9] Talukdar *et al.*,[10] Koffend and Cohen,[11] and Donahue *et al.*,[12] and relative rate constants have been measured by Finlayson-Pitts *et al.*[8] (Table 35). The rate constants of Finlayson-Pitts *et al.*,[8] El Maimouni *et al.*,[9] Talukdar *et al.*,[10] and Donahue *et al.*[12] are in excellent agreement with the previous recommendation of Atkinson,[1] and the absolute rate constants of Howard and Evenson,[22] Leu,[23] Margitan and Watson,[24] Tully *et al.*,[25,26] Smith *et al.*,[27] Devolder *et al.*,[28] Baulch *et al.*,[29] Stachnik *et al.*,[30] Bourmada *et al.*,[31] Wallington *et al.*,[32] Zabarnick *et al.*,[33] Abbatt *et al.*,[34] Bott and Cohen,[35] Talukdar *et al.*,[10] and Koffend and Cohen[11] are plotted in Arrhenius form in Fig. 2.

The agreement between the studies of Howard and Evenson,[22] Leu,[23] Margitan and Watson,[24] Tully *et al.*,[25,26] Smith *et al.*,[27] Devolder *et al.*,[28] Baulch *et al.*,[29], Stachnik *et al.*,[30] Bourmada *et al.*,[31] Wallington *et al.*,[32] Zabarnick *et al.*,[33] Abbatt *et al.*,[34] Bott and Cohen,[35] Talukdar *et al.*,[10] Koffend and Cohen,[11] and Donahue *et al.*[12] is generally excellent. Using the expression $k=CT^2\ e^{-D/T}$, a unit weighted least-squares analysis of these data[10–12,22–35] leads to the recommendation of

$$k(\text{ethane})=$$

$$1.52\times10^{-17}\ T^2\ e^{-(498\pm24)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 226–1225 K, where the indicated error is two least-squares standard deviations, and

$$k(\text{ethane})=$$

$$2.54\times10^{-13}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty at 298 K of ±15%. This recommendation agrees, to within 2% over the entire temperature range 226–1225 K, with the previous recommendation of Atkinson[1] of $k=1.51\times10^{-17}\ T^2\ e^{-492/T}$ $\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$ (which was for the more restricted temperature range 226–800 K).

3.1.3. Propane

Absolute rate constants have been determined by Mellouki *et al.*,[6] and Talukdar *et al.*[10] and relative rate constants have been measured by Finlayson-Pitts *et al.*[8] and DeMore *et al.*[13] (Table 35). These data[6,8,10,13] are in generally good agreement with the previous recommendation of Atkinson.[1] The absolute rate constants of Greiner,[36] Bott and Cohen,[37] Smith *et al.*,[38] Baulch *et al.*,[29] Droege and Tully,[39] Abbatt *et al.*,[34] Mac Leod *et al.*,[40] Mellouki *et al.*,[6] and Talukdar *et al.*[10] and the relative rate constants of Baker *et al.*[41,42] and Atkinson *et al.*[43] (revised to be consistent with the present recommendation for the rate constant for the reaction of the OH radical with n-butane) are plotted in Arrhenius form in Fig. 3. The agreement is good and, using the expression $k=CT^2\ e^{-D/T}$, a unit weighted least-squares analysis of these data[6,10,29,34,36–43] leads to the recommendation of

$$k(\text{propane})=$$

$$1.55\times10^{-17}\ T^2\ e^{-(61\pm28)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 233–1220 K, where the indicated error is two least-squares standard deviations, and

$$k(\text{propane})=$$

$$1.12\times10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty at 298 K of ±15%. This recommendation agrees to within 4% over the entire temperature range 233–1220 K with the previous recommendation of Atkinson[1] of $k(\text{propane})=1.50\times10^{-17}\ T^2\ e^{-44/T}$ $\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$ (which covered the more restricted temperature range 293–1220 K), and significantly extends the temperature range of the recommendation to lower temperatures characteristic of the upper troposphere.

3.1.4. *n*-Butane

The absolute rate constants of Talukdar *et al.*[10] are given in Table 35, and are plotted in Arrhenius form in Fig. 4 together with the absolute rate constants of Greiner,[36] Stuhl,[44] Perry *et al.*,[45] Paraskevopoulos and Nip,[46] Droege and Tully,[47] and Abbatt *et al.*[34] and the relative rate constant of Baker *et al.*[41,42] The agreement is generally reasonable, and, using the expression $k=CT^2\ e^{-D/T}$, a unit weighted least-squares analysis of these data[10,34,36,41,42,44–47] leads to the recommendation of

$$k(n\text{-butane})=$$

$$1.69\times10^{-17}\ T^2\ e^{(145\pm46)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 231–753 K, where the indicated error is two least-squares standard deviations, and

$$k(n\text{-butane})=$$

$$2.44\times10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty at 298 K of ±20%. This recommendation is slightly different from the previous recommendation of Atkinson[1] of $k(n\text{-butane})=1.51\times10^{-17}$ $T^2\ e^{190/T}$ $\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$ over the more restricted temperature range 294–753 K. In particular, the present recommendation at 298 K is 4% lower than the previous recommendation,[1] and this affects the rate constants calculated from a number of relative rate studies.

3.1.5. 2-Methylpropane

The absolute rate constants of Talukdar *et al.*[10] are given in Table 35 and are plotted, together with the absolute rate constants of Greiner,[36] Tully *et al.*,[48] and Bott and Cohen[19] and the relative rate constants of Baker *et al.*[41,42] and Atkinson *et al.*[49] (revised to be consistent with the present recommendation for n-butane), in Arrhenius form in Fig. 5. The agreement is seen to be reasonable, although some of the rate constants of Greiner[36] at 297–338 K are ~20% higher than the rate constants from other studies.[10,48,49] Using the

TABLE 35. Rate constants k and temperature dependent parameters, C, n, and D in $k=CT^n\ e^{-D/T}$ for the gas-phase reactions of the OH radical with alkanes

Alkane	$10^{12}\times C$ (cm^3 molecule^{-1} s^{-1})	n	D (K)	$10^{12}\times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
Methane				0.0262±0.0027	378	DF-EPR	Lancar *et al.*[2]	378–422
				0.0427±0.0018	422			
				<0.0003	178	LP-LIF	Sharkey and Smith[3]	178–298
				0.00165±0.0002	216			
				0.0076±0.0003	298			
				0.00562±0.00043	293	LP-LIF	Dunlop and Tully[4]	293–800
				0.0371±0.0022	409			
				0.0422±0.0023	420			
				0.101±0.004	498			
				0.152±0.010	547			
				0.237±0.014	602			
				0.367±0.022	654			
				0.474±0.026	704			
				0.576±0.032	745			
	9.65×10^{-8}	2.58	1082	0.756±0.042	800			
				0.0054±0.0002	292	LP-LIF	Saunders *et al.*[5]	
				0.00132±0.00005	233	LP-LIF	Mellouki *et al.*[6]	233–343
				0.00208±0.00030	243			
				0.00215±0.00030	252			
				0.00370±0.00020	273			
				0.00642±0.00060	295			
				0.00634±0.00056	298			
				0.0105±0.0006	323			
	2.56±0.53		1765±146	0.0168±0.0015	343			
Methane-d$_1$ [CH$_3$D]	1.06×10^{-7}	2.58	1157	0.00528	298	RR [relative to k(methane) $=9.65\times10^{-20}$ $T^{2.58}$ $e^{-1082/T}$][a]	DeMore[7]	298–358
	1.58×10^{-7}	2.58	1266	0.00546	298	RR [relative to k(methane) $=9.65\times10^{-20}$ $T^{2.58}$ e^{-1082T}][a]	DeMore[7]	293–361
Methane-d$_4$ [CD$_4$]				0.00083±0.00008	293	LP-LIF	Dunlop and Tully[4]	293–800
				0.00215±0.00018	333			
				0.00422±0.00032	365			
				0.00910±0.00058	409			
				0.0191±0.0011	459			
				0.0306±0.0022	498			
				0.0530±0.0032	547			
				0.0900±0.0056	602			
				0.150±0.010	654			
				0.197±0.012	704			
				0.302±0.018	753			
	8.70×10^{-10}	3.23	1334	0.385±0.024	800			
Ethane				0.013±0.002	138	LP-LIF	Sharkey and Smith[3]	138–298
				0.025±0.003	178			
				0.0785±0.004	216			
				0.295±0.014	298			
				0.283±0.007	298	RR [relative to k(propane) $=1.55\times10^{-17}$ T^2 $e^{-61/T}$][a]	Finlayson-Pitts *et al.*[8]	298–373
				0.278±0.013	298			
				0.370±0.014	323			
				0.474±0.013	348			
				0.582±0.010	373			
				0.243	297±3	DF-RF	El Maimouni *et al.*[9]	
				0.0882±0.0024	231	LP-LIF	Talukdar *et al.*[10]	231–377
				0.1269±0.0069	252			
				0.1303±0.0015	253			
				0.1778±0.0043	273			
				0.2461±0.0032	299			
				0.3380±0.0037	327			
				0.4589±0.0050	355			
	10.3±0.65		1108±40	0.5641±0.0082	377			
	1.53×10^{-5}	2	512±7					

TABLE 35. Rate constants k and temperature dependent parameters, C, n, and D in $k=CT^n\ e^{-D/T}$ for the gas-phase reactions of the OH radical with alkanes—Continued

Alkane	$10^{12}\times C$ (cm^3 molecule^{-1} s^{-1})	n	D (K)	$10^{12}\times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
				8.37	970	SH-RA	Koffend and Cohen[11]	
				0.255±0.03	300	DF-LIF	Donahue *et al.*[12]	
Propane				1.10±0.06	298	RR [relative to k(n-butane) $=2.44\times10^{-12}$]^a	Finlayson-Pitts *et al.*[8]	
				1.11±0.06	298			
				0.981±0.057	298	RR [relative to k(2-methylpropane)$=2.19\times10^{-12}$]^a	Finlayson-Pitts *et al.*[8]	
				1.14±0.04	298			
				1.09±0.06	298			
				0.965±0.097	298±2	RR [relative to k(ethane) $=2.54\times10^{-13}$]^a	DeMore[13]	
				0.61±0.04	233	LP-LIF	Mellouki *et al.*[6]	233–363
				0.75±0.04	253			
				0.92±0.04	273			
				1.05±0.04	295			
				1.25±0.04	318			
				1.51±0.02	343			
	9.81±0.11		650±30	1.65±0.07	363			
				0.623±0.016	233	LP-LIF	Talukdar *et al.*[10]	233–376
				0.741±0.019	252			
				0.862±0.023	272			
				1.123±0.040	299			
				1.342±0.064	325			
				1.574±0.052	351			
	10.1±0.8		657±46	1.816±0.067	376			
	1.58×10^{-5}	2	74±25					
n-Butane				1.560±0.015	231	LP-LIF	Talukdar *et al.*[10]	231–378
				1.788±0.018	252			
				2.097±0.024	273			
				2.459±0.018	299			
				2.828±0.060	328			
				3.196±0.032	352			
	2.04×10^{-5}	2	−85±8	3.647±0.022	378			
	11.8		470±40 (231–298 K)					
2-Methylpropane				1.55±0.18	213	LP-LIF	Talukdar *et al.*[10]	213–372
				1.58±0.09	224			
				1.69±0.06	234			
				1.67±0.06	243			
				1.745±0.06	253			
				1.82±0.11	272			
				2.13±0.10	296			
				2.19±0.04	297			
				1.96±0.09	298			
				2.29±0.07	323			
				2.40±0.10	343			
				2.54±0.03	357			
	9.32×10^{-6}	2	−274±16	2.73±0.06	372			
	5.72		293±40 (213–298 K)					
n-Pentane				3.99±0.05	302	RR [relative to k(2-methyl-propane) $=2.23\times10^{-12}$]^a	Donaghy *et al.*[14]	
				2.64±0.06	224	LP-LIF	Talukdar *et al.*[10]	224–372
				2.67±0.14	233			
				2.75±0.10	233			
				2.85±0.10	233			
				3.11±0.09	253			
				3.54±0.11	272			

TABLE 35. Rate constants k and temperature dependent parameters, C, n, and D in $k=CT^n$ $e^{-D/T}$ for the gas-phase reactions of the OH radical with alkanes—Continued

Alkane	$10^{12}\times C$ (cm^3 molecule^{-1} s^{-1})	n	D (K)	$10^{12}\times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
				4.02±0.20	296			
				4.01±0.11	297			
				4.04±0.10	297			
				4.50±0.12	309			
				4.83±0.08	323			
				5.06±0.12	340			
				5.54±0.26	358			
	3.13×10^{-5}	2	−116±24	5.81±0.16	372			
	15.0		392±40 (224–297 K)					
n-Hexane				5.64±0.21	301±2	RR [relative to k(n-pentane) $=4.06\times10^{-12}$]^a	McLoughlin *et al.*[15]	
				21.8	962	SH-RA	Koffend and Cohen[11]	
n-Heptane				33.4	1186	SH-RA	Koffend and Cohen[11]	
				7.49±0.32	295±2	RR [relative to k(n-octane) $=8.65\times10^{-12}$]^a	Ferrari *et al.*[16]	
n-Octane				44.2	1078	SH-RA	Koffend and Cohen[11]	
n-Nonane				45.5	1097	SH-RA	Koffend and Cohen[11]	
				10.4±0.3	295±2	RR [relative to k(n-octane) $=8.65\times10^{-12}$]^a	Ferrari *et al.*[16]	
n-Decane				56.4	1109	SH-RA	Koffend and Cohen[11]	
Cyclohexane				7.25	297±2	RR [relative to k(n-hexane) $=5.44\times10^{-12}$]^a	Sommerlade *et al.*[17]	
				6.7±0.9	298	DF-LIF	Saunders *et al.*[18]	
				7.6±0.8	300	DF-LIF	Donahue *et al.*[12]	

[a] From present recommendations.

expression $k=CT^2$ $e^{-D/T}$, a unit weighted least-squares analysis of the rate constants of Greiner,[36] Baker *et al.*,[41,42] Atkinson *et al.*,[49] Tully *et al.*,[48] Bott and Cohen,[19] and Talukdar *et al.*[10] leads to the recommendation of

$$k(\text{2-methylpropane})=$$

$$1.16\times10^{-17}\ T^2\ e^{(225\pm31)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 213–1146 K, where the indicated error is two least-squares standard deviations, and

$$k(\text{2-methylpropane})=$$

$$2.19\times10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty at 298 K of ±20%. At temperatures <700 K this recommendation leads to slightly lower rate constants than does the previous recommendation of Atkinson[1] of k(2-methylpropane)$=1.11\times10^{-17}$ T^2 $e^{256/T}$ cm^3 molecule^{-1} s^{-1} for the more restricted temperature range 293–1146 K (by ~10% at 213 K).

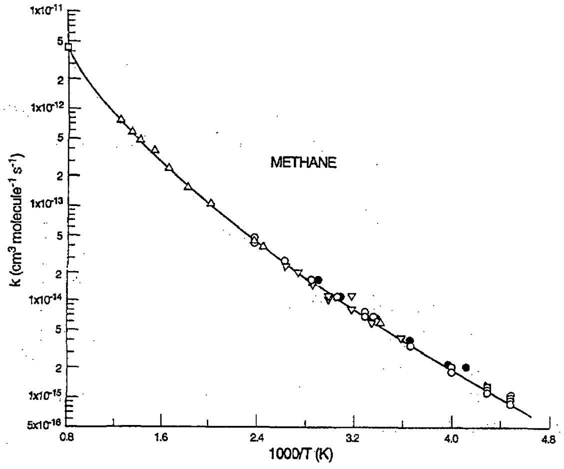

FIG. 1. Arrhenius plot of selected rate constants for the reaction of the OH radical with methane. (□) Bott and Cohen (Ref. 19); (○) Vaghjiani and Ravishankara (Ref. 20); (∇) Finlayson-Pitts *et al.*, (Ref. 21); (△) Dunlop and Tully (Ref. 4); (●) Mellouki *et al.* (Ref. 6); (—) recommendation (see text).

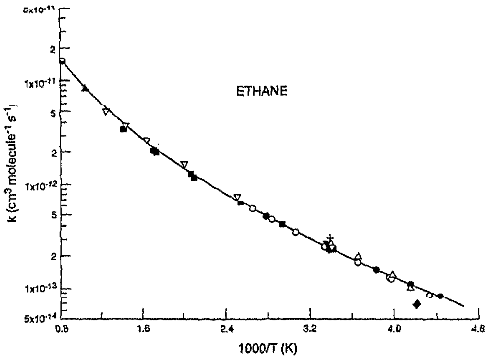

FIG. 2. Arrhenius plot of selected rate constants for the reaction of the OH radical with ethane. (+) Howard and Evenson (Ref. 22); (▼) Leu (Ref. 23); (◆) Margitan and Watson (Ref. 24); (▽) Tully *et al.* (Ref. 25); (△) Smith *et al.* (Ref. 27); (◇) Devolder *et al.* (Ref. 28); Baulch *et al.* (Ref. 29); Bourmada *et al.* (Ref. 31); Zabarnick *et al.* (Ref. 33); (■) Tully *et al.* (Ref. 26); (□) Stachnik *et al.* (Ref. 30); (●) Wallington *et al.* (Ref. 32); (x) Abbatt *et al.* (Ref. 34); (○) Bott and Cohen (Ref. 35); (○) Talukdar *et al.* (Ref. 10); (▲) Koffend and Cohen (Ref. 11); (—) recommendation (see text).

3.1.6. *n*-Pentane

The relative rate constant of Donaghy *et al.*[14] and the absolute rate constants of Talukdar *et al.*[10] are given in Table 35. The absolute rate constants of Abbatt *et al.*[34] and Talukdar *et al.*[10] and the relative rate constants of Baldwin and Walker,[42] Atkinson *et al.*[43] (revised), and Behnke *et al.*[50] (revised) are plotted in Arrhenius form in Fig. 6.

The agreement between these studies is good and a unit weighted least-squares analysis of these data,[10,34,42,43,50] using the expression $k=CT^2\ e^{-D/T}$, leads to the recommendation of

$$k(n\text{-pentane})=$$

$$2.44\times10^{-17}\ T^2\ e^{(183\pm41)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 224–753 K, where the indicated error is two least-squares standard deviations, and

$$k(n\text{-pentane})=$$

$$4.00\times10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty at 298 K of ±20%. This recommendation agrees to within 10% over the entire temperature range 224–753 K with the previous recommendation of Atkinson[1] of $k(n\text{-pentane})=2.10\times10^{-17}\ T^2\ e^{223/T}$ cm^3 molecule^{-1} s^{-1} (which covered the more restricted temperature range of 243–753 K).

3.1.7. *n*-Hexane

The relative rate constant of McLoughlin *et al.*[15] and the absolute rate constant of Koffend and Cohen[11] are given in Table 35. Using the expression $k=CT^2\ e^{-D/T}$, a unit weighted least-squares analysis of the room temperature relative rate constants of Atkinson *et al.*,[51,52] Atkinson and Aschmann,[53] and Behnke *et al.*[50,54] (revised[50,51,54] when necessary) and the absolute 962 K rate constant of Koffend and Cohen[11] leads to the recommendation of

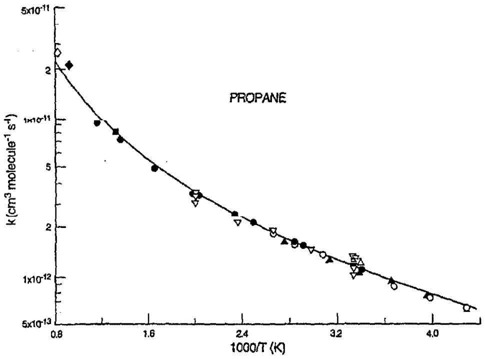

FIG. 3. Arrhenius plot of selected rate constants for the reaction of the OH radical with propane. (■) Baker *et al.* (Refs. 41 and 42); (▽) Greiner (Ref. 36); (▼) Atkinson *et al.* (Ref. 43); (◇) Bott and Cohen (Ref. 37); (◆) Smith *et al.* (Ref. 38); (△) Baulch *et al.* (Ref. 29); (●) Droege and Tully (Ref. 39); (□) Abbatt *et al.* (Ref. 34) and Mac Leod *et al.* (Ref. 40); (▲) Mellouki *et al.* (Ref. 6); (○) Talukdar *et al.* (Ref. 10); (—) recommendation (see text).

$$k(n\text{-hexane})=$$

$$1.53\times10^{-17}\ T^2\ e^{(414\pm22)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 295–962 K, where the indicated error is two least-squares standard deviations, and

$$k(n\text{-hexane})=$$

$$5.45\times10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty at 298 K of ±25%. The rate constant of Koffend and Cohen[11] is the first reported absolute rate constant for this reaction and the first rate constant measured outside of a narrow temperature range around room temperature (295–312 K).

3.1.8. 2,3-Dimethylbutane

No new data for this reaction have been reported. Consistent with the review of Atkinson,[1] the recommendation for the rate constant for this reaction uses the absolute rate constants of Greiner[36] and Bott and Cohen[55] and the relative rate constants of Atkinson *et al.*[51] and Harris and Kerr[56] (revised to be consistent with the present recommendations). However, the rate constants measured by Harris and Kerr[56] relative to *n*-butane and *n*-pentane were used in the present evaluation, whereas only the rate constants measured relative to *n*-butane[56] were used previously.[1,57] The expression $k=CT^2\ e^{-D/T}$ was used, and a least-squares analysis of these data[36,51,55,56] leads to the recommendation of

$$k(2,3\text{-dimethylbutane})=$$

$$1.24\times10^{-17}\ T^2\ e^{(494\pm63)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

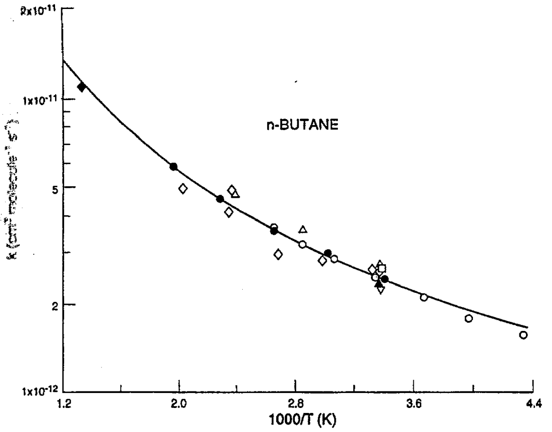

FIG. 4. Arrhenius plot of selected rate constants for the reaction of the OH radical with *n*-butane. (◆) Baker *et al.* (Refs. 41 and 42); (◇) Greiner (Ref. 36); (▲) Stuhl (Ref. 44); (△) Perry *et al.* (Ref. 45); (□) Paraskevopoulos and Nip (Ref. 46); (●) Droege and Tully (Ref. 47); (▽) Abbatt *et al.* (Ref. 34); (○) Talukdar *et al.* (Ref. 10); (—) recommendation (see text).

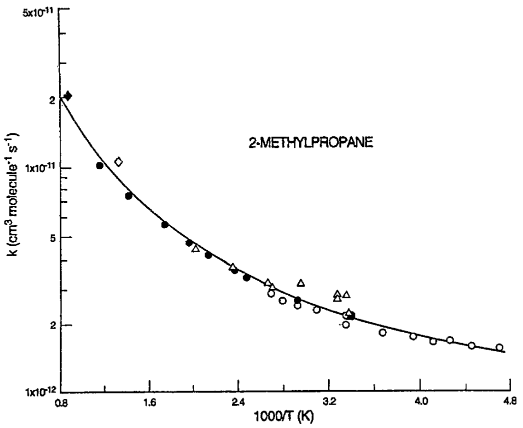

FIG. 5. Arrhenius plot of selected rate constants for the reaction of the OH radical with 2-methylpropane. (◇) Baker *et al.* (Refs. 41 and 42); (△) Greiner (Ref. 36); (▲) Atkinson *et al.* (Ref. 49); (●) Tully *et al.* (Ref. 48); (◆) Bott and Cohen (Ref. 19); (○) Talukdar *et al.* (Ref. 10); (—) recommendation (see text).

over the temperature range 247–1220 K, where the indicated error is two least-squares standard deviations, and

$$k(\text{2,3-dimethylbutane}) = 5.78\times10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty at 298 K of ±25%. The present recommendation leads to rate constants over the temperature range 247–1220 K which are within 5% of those predicted from the previous recommendation of Atkinson,[1] of $k(\text{2,3-dimethylbutane}) = 1.21\times10^{-17}\ T^2\ e^{512/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$ over the same temperature range.

3.1.9. *n*-Heptane

The absolute rate constant of Koffend and Cohen[11] at 1186 K and the relative rate constant of Ferrari *et al.*[16] are given in Table 35. The rate constant of Koffend and Cohen[11] is the first absolute rate constant measured for *n*-heptane, and the first at temperatures other than room temperature. Using the expression $k = CT^2\ e^{-D/T}$, a unit weighted least-squares analysis of the relative rate constants of Atkinson *et al.*[43] and Behnke *et al.*[50,54] (revised when needed to be consistent with the present recommendations) and the absolute rate constant of Koffend and Cohen[11] leads to the recommendation of

$$k(n\text{-heptane}) = 1.59\times10^{-17}\ T^2\ e^{(478\pm31)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 299–1146 K, where the indicated error is two least-squares standard deviations, and

$$k(n\text{-heptane}) = 7.02\times10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty at 298 K of ±25%.

3.1.10. *n*-Octane

The absolute rate constant of Koffend and Cohen[11] at 1078 K is given in Table 35. The absolute rate constants of Greiner[36] and Koffend and Cohen[11] and the relative rate constants of Atkinson *et al.*[43] and Behnke *et al.*[50] (revised to be consistent with the present recommendations) are plotted in Arrhenius form in Fig. 7. Using the expression $k = CT^2\ e^{-D/T}$, a unit weighted least-squares analysis of these data[11,36,43,50] leads to the recommendation of

$$k(n\text{-octane}) = 2.76\times10^{-17}\ T^2\ e^{(378\pm62)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 296–1078 K, where the indicated error is two least-squares standard deviations, and

$$k(n\text{-octane}) = 8.71\times10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty at 298 K of ±20%. This recommendation supersedes that of Atkinson[1] of $k(n\text{-octane}) = 3.15\times10^{-11}\ e^{-384/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$ over the more restricted temperature range 296–497 K.

3.1.11. 2,3,4-Trimethylpentane

No new data have been reported for this reaction. However, the temperature dependent recommendation for the *n*-hexane rate constant derived here allows the relative rate constants of Harris and Kerr[56] over the temperature range 243–313 K to be placed on a reliable absolute basis. A least-squares analysis of these data[56] leads to the Arrhenius expression

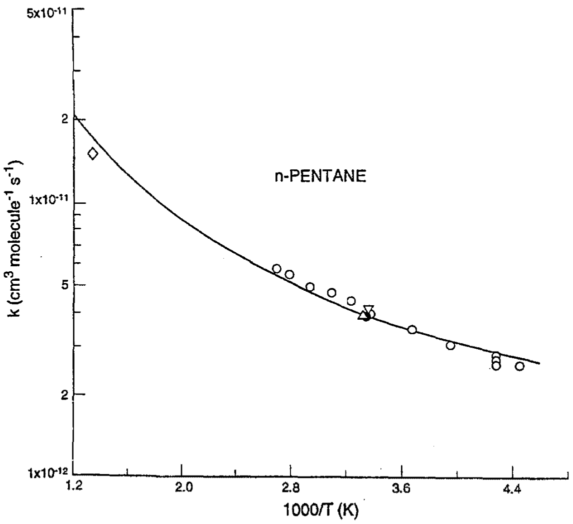

FIG. 6. Arrhenius plot of selected rate constants for the reaction of the OH radical with *n*-pentane. (◇) Baldwin and Walker (Ref. 42); (●) Atkinson *et al.* (Ref. 43); (△) Behnke *et al.* (Ref. 50); (▽) Abbott *et al.* (Ref. 34); (○) Talukdar *et al.* (Ref. 10); (—) recommendation (see text).

k(2,3,4-trimethylpentane) =

$$1.88\times10^{-12}\,e^{(397\pm139)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 243–313 K, where the indicated error is two least-squares standard deviations, and

k(2,3,4-trimethylpentane) =

$$7.1\times10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty at 298 K of ±30%. This recommended Arrhenius expression should not be used outside of the temperature range 243–313 K.

3.1.12. *n*-Nonane and *n*-Decane

The absolute rate constants of Koffend and Cohen[11] at ~1100 K for both *n*-nonane and *n*-decane and the relative rate constant of Ferrari *et al.*[16] at 295±2 K for *n*-nonane are given in Table 35. The rate constants of Koffend and Cohen[11] are the first absolute rate constants for these two alkanes and the first at elevated temperatures. Using the expression $k=CT^2\ e^{-D/T}$, least-squares analyses of the absolute rate constants of Koffend and Cohen[11] and the relative rate constants of Atkinson *et al.*,[43] Behnke *et al.*,[54] Nolting *et al.*,[58] and (for the *n*-nonane reaction only) Behnke *et al.*[50] lead to the recommendations of

k(n-nonane) =

$$2.51\times10^{-17}T^2\ e^{(447\pm33)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 299–1097 K, and

k(n-decane) =

$$3.13\times10^{-17}\,T^2\ e^{(416\pm76)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 299–1109 K, where the indicated errors are two least-squares standard deviations, and

k(n-nonane) =

$$1.00\times10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K}$$

and

k(n-decane) =

$$1.12\times10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

with estimated overall uncertainties at 298 K of ±25% in each case.

3.1.13. Cyclohexane

The absolute and relative rate constants of Saunders *et al.*,[18] Donahue *et al.*,[12] and Sommerlade *et al.*[17] are given in Table 35. As discussed by Atkinson,[57] there is a significant degree of scatter in the measured rate constants for this reaction. The absolute rate constants of Droege and Tully[59] and Donahue *et al.*[12] and the relative rate constants of Atkinson *et al.*,[51,60] Tuazon *et al.*,[61] and Atkinson and Aschmann[62] (revised when needed to be consistent with the present recommendations) have been used to evaluate the rate constant for this reaction. Using the expression $k=CT^2\ e^{-D/T}$, a unit weighted least-squares analysis of these data[12,51,59–62] leads to the recommendation of

k(cyclohexane) =

$$2.88\times10^{-17}\,T^2\ e^{(309\pm35)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 292–491 K, where the indicated error is two least-squares standard deviations, and

k(cyclohexane) =

$$7.21\times10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty at 298 K of ±20%. This recommendation leads to rate constants within 4% of the previous recommendation[1,57] of $k(\text{cyclohexane})=2.66\times10^{-17}\ T^2\ e^{344/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$ over the temperature range 292–497 K.

3.1.14. Other Alkanes

For the reactions of the OH radical with 2-methylbutane, 2,2-dimethylpropane, 2- and 3-methylpentane, 2,2-dimethylbutane, 2,2,3-trimethylbutane, 2,2,4-trimethylpentane, 2,2,3,3-tetramethylbutane, *n*-undecane, *n*-dodecane, and *n*-tridecane, the same data bases as used in the Atkinson 1989[57] and 1994[1] evaluations have been used, with the rate constants from relative rate studies being reevaluated to be consistent with the present recommendations. The results of these reanalyses are given in Table 1 in Sec. 2.1. For alkanes for which generally only single studies have been carried out

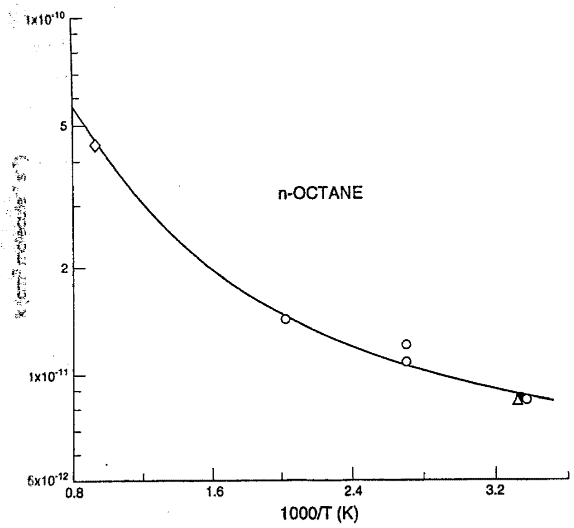

FIG. 7. Arrhenius plot of selected rate constants for the reaction of the OH radical with *n*-octane, (○) Greiner (Ref. 36); (●) Atkinson *et al.* (Ref. 43); (△) Behnke *et al.* (Ref. 50); (◇) Koffend and Cohen (Ref. 11); (—) recommendation (see text).

and no prior recommendations made,[1,57] rate constants from relative rate studies have also been recalculated to be consistent with the present recommendations.

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3.2. Alkenes

The rate constants for the gas-phase reactions of the OH radical with alkenes at, or close to, the high pressure limit reported since the review and evaluation of Atkinson[1] are given in Table 36.

3.2.1. 1-Butene, *cis*-2-Butene and *trans*-2-Butene

The absolute rate constants of Sims *et al.*,[2] obtained over the temperature range 23–295 K, are given in Table 36. The rate constants obtained by Sims *et al.*[2] are, apart from the values at 295 K, for temperatures below those encountered in earth's atmosphere. The 295 K rate constants measured by Sims *et al.*[2] are within 9% of the rate constants at 295 K recommended by Atkinson.[1,6] However, the rate constant measured by Sims *et al.*[2] at 170 K are 25–34% lower than the rate constants calculated from the Arrhenius expression recommended by Atkinson.[1,6] Clearly, Arrhenius expression for the addition reactions of OH radicals to alkenes are only valid over the restricted temperature ranges of ~250–425 K (see also below for isoprene), and Sims *et al.*[2] fit their measured rate constants by the expression k(1-butene)$=5.2\times10^{-10}$ $e^{-0.0094/T}$ cm^3 $molecule^{-1}$ s^{-1}, k(*cis*-2-butene)$=4.7\times10^{-10}$ $e^{-0.0069/T}$ cm^3 $molecule^{-1}$ s^{-1}, and k(*trans*-2-butene)$=5.4\times10^{-10}$ $e^{-0.007/T}$ cm^3 molecule s^{-1} for the temperature range 23–295 K.

The previous recommendations[1,6] (given in Table 15 of Sec. 2.1) are unchanged, but should be recognized to be only

TABLE 36. Rate constants k and temperature dependent parameters $k=A\ (T/298)^n$, at, or close to, the high pressure limit for the gas-phase reactions of the OH radical with alkenes

Alkene	$10^{12}\times A$ (cm^3 $molecule^{-1}$ s^{-1})	n	$10^{12}\times k$ (cm^3 $molecule^{-1}$ s^{-1})	at T (K)	Technique	Reference	Temperature Range (K)
1-Butene			427±56	23	LP-LIF	Sims *et al.*[2]	23–295
			315±40	44			
			273±16	75			
			77.1±10.6	170			
			34.9±1.1	295			
			33.0±1.2	295			
cis-2-Butene			389±23	23	LP-LIF	Sims *et al.*[2]	23–295
			328±33	44			
			302±14	75			
			130±13	170			
			61.8±5.7	295			
trans-2-Butene			425±32	23	LP-LIF	Sims *et al.*[2]	23–295
			403±44	44			
			317±24	75			
			169±8.3	170			
			68.3±2.2	295			
2,3-Dimethyl-2-butene			104±7	296±2	RR [relative to k(isoprene) $=1.01\times10^{-10}$][a]	Shu and Atkinson[3]	
			108±8	296±2	RR [relative to k(isoprene) $=1.01\times10^{-10}$][a]	Atkinson *et al.*[4]	
2-Methyl-1,3-butadiene (isoprene)	97	−1.36	97	298	FP-RF	Siese *et al.*[5]	249–438
α-Cedrene			66.9±1.9	296±2	RR [relative to k(2,3-dimethyl-2-butene) $=1.10\times10^{-10}$][a]	Shu and Atkinson[3]	
α-Copaene			89.9±4.9	296±2	RR [relative to k(2,3-dimethyl-2-butene) $=1.10\times10^{-10}$][a]	Shu and Atkinson[3]	
β-Caryophyllene			197±25	296±2	RR [relative to k(2,3-dimethyl-2-butene) $=1.10\times10^{-10}$][a]	Shu and Atkinson[3]	
α-Humulene			293±30	296±2	RR [relative to k(2,3-dimethyl-2-butene) $=1.10\times10^{-10}$][a]	Shu and Atkinson[3]	
Longifolene			47.2±1.7	296±2	RR [relative to k(*trans*-2-butene) $=6.48\times10^{-11}$][a]	Shu and Atkinson[3]	

[a] From present and previous[1,6] recommendations.

applicable for the temperature range ~250–425 K; at lower temperatures the rate constants diverge from the simple Arrhenius expression (and are lower than predicted from the Arrhenius expression).

3.2.2. 2.3-Dimethyl-2-butene

The relative rate constants of Shu and Atkinson[3] and Atkinson *et al.*[4] (Table 36) are in excellent agreement with the previous recommendation[1,6] of k(2,3-dimethyl-2-butene) $=1.10\times10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K, which is therefore unchanged.

3.2.3. 2-Methyl-1,3-butadiene (Isoprene)

Absolute rate constants have been determined by Siese *et al.*[5] over the temperature range 249–438 K (Table 36). The individual rate constants are not tabulated, but shown graphically.[5] The temperature dependent expression reported by Siese *et al.*[5] of $k(\text{isoprene})=9.7\times10^{-11}\ (T/298)^{-1.36}$ cm^3 molecule^{-1} s^{-1} agrees with the recommended Arrhenius expression of Atkinson[1,6] of $k(\text{isoprene})=2.54\times10^{-11}\ e^{410/T}$ cm^3 molecule^{-1} s^{-1} to within 10% over the temperature range 250–425 K. As noted above, the Arrhenius expression is only applicable over restricted temperature ranges; however, the previous recommendation of Atkinson[1,6] is appropriate for the temperature range 250–425 K.

3.2.4. Other alkenes

The rate constants for the sesquiterpenes α-cedrene, α-copaene, β-caryophyllene, α-humulene, and longifolene[3] (Table 36) are the first reported.

[1] R. Atkinson, J. Phys. Chem. Ref. Data Monograph **2**, 1 (1994).
[2] I. R. Sims, I. W. M. Smith, P. Bocherel, A. Defrance, D. Travers, and B. R. Rowe, J. Chem. Soc. Faraday Trans. **90**, 1473 (1994).
[3] Y. Shu and R. Atkinson, J. Geophys. Res. **100**, 7275 (1995).
[4] R. Atkinson, J. Arey, S. M. Aschmann, S. B. Corchnoy, and Y. Shu, Int. J. Chem. Kinet. **27**, 941 (1995).
[5] M. Siese, R. Koch, C. Fittschen, and C. Zetzsch, "Cycling of OH in the Reaction Systems Toluene/O_2/NO and Acetylene/O_2 and the Addition of OH to Isoprene," in Transport and Transformation of Pollutants in the Troposphere, Proceedings of EUROTRAC Symposium '94, edited by P. M. Borrell, P. Borrell, T. Cvitaš, and W. Seiler, Garnisch-Partenkirchen, Germany (SPB Academic Publishing, 1994), pp. 115–119.
[6] R. Atkinson, J. Phys. Chem. Ref. Data Monograph **1** (1989).

4. Kinetics and Mechanisms of the Gas-Phase Reactions of the NO_3 Radical with Alkanes and Alkenes

4.1. Alkanes

The kinetic data reported since the last review and evaluation of Atkinson[1] are given in Table 37.

4.1.1. 2-Methylbutane

The relative rate constant of Aschmann and Atkinson[2] (Table 37) is in excellent agreement with the absolute room temperature rate constant of Bagley *et al.*[5] The rate constants of Bagley *et al.*[5] and Aschmann and Atkinson[2] are plotted in Arrhenius form in Fig. 8, and a least-squares analysis of these data[2,5] yields the recommended Arrhenius expression of

$$k(\text{2-methylbutane})=$$
$$2.99\times10^{-12}\ e^{-(2927\pm173)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 296–523 K, where the indicated error is two least-squares standard deviations, and

$$k(\text{2-methylbutane})=$$
$$1.62\times10^{-16}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty at 298 K of ±35%.

4.1.2. *n*-Nonane

The relative rate constant of Aschmann and Atkinson[2] at 296±2 K (Table 37) is 20% lower than (but in agreement within the combined uncertainties with) the previous relative rate constant of Atkinson *et al.*[6] An average of these rate constants[2,6] results in $k(n\text{-nonane})=2.17\times10^{-16}$ cm^3 molecule^{-1} s^{-1} at 296±2 K, with an estimated overall uncertainty of ±40%.

[1] R. Atkinson, J. Phys. Chem. Ref. Data, Monograph **2**, 1 (1994).
[2] S. M. Aschmann and R. Atkinson Atmos. Env. **29**, 2311 (1995).
[3] S. Langer, E. Ljungström, and I. Wängberg, J. Chem. Soc. Faraday Trans. **89**, 425 (1993).
[4] R. Atkinson, J. Phys. Chem. Ref. Data **20**, 459 (1991).
[5] J. A. Bagley, C. Canosa-Mas, M. R. Little, A. D. Parr, S. J. Smith, S. J. Waygood, and R. P. Wayne, J. Chem. Soc. Faraday Trans. **86**, 2109 (1990).
[6] R. Atkinson, C. N. Plum, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **88**, 2361 (1984).

4.2. Alkenes

The rate constants reported since the previous review and evaluation of Atkinson[1] are given in Table 38.

4.2.1. 1-Butene

The absolute rate constants of Rudich *et al.*[2] are given in Table 38 and are plotted, together with the absolute rate constants of Canosa-Mas *et al.*[8] and the relative rate constants of Atkinson *et al.*[9,10] and Barnes *et al.*[11] in Arrhenius form in Fig. 9. The rate constants of Rudich *et al.*[2] are uniformly higher than those of Canosa-Mas *et al.*[8] by ~30%. A unit weighted least-squares analysis of the rate constant data of Atkinson *et al.*,[9,10] Barnes *et al.*,[11] Canosa-Mas *et al.*,[8] and Rudich *et al.*[2] leads to the recommended Arrhenius expression of

$$k(\text{1-butene})=$$
$$3.14\times10^{-13}\ e^{-(938\pm106)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 232–437 K, where the indicated error is two least-squares standard deviations, and

TABLE 37. Rate constants k for the gas-phase reactions of the NO_3 radical with alkanes

Alkane	$10^{16}\times k$ (cm^3 $molecule^{-1}$ s^{-1})	at T (K)	Technique	Reference
2-Methylbutane	1.56 ± 0.16	296 ± 2	RR [relative to k(2,3-dimethylbutane) $=4.08\times10^{-16}$][a]	Aschmann and Atkinson[2]
n-Hexane	$\leq(2.8\pm0.3)$	296 ± 2	DF-A	Langer *et al.*[3]
2-Methylpentane	1.71 ± 0.18	296 ± 2	RR [relative to k(2,3-dimethylbutane) $=4.08\times10^{-16}$][a]	Aschmann and Atkinson[2]
3-Methylpentane	2.04 ± 0.21	296 ± 2	RR [relative to k(2,3-dimethylbutane) $=4.08\times10^{-16}$][a]	Aschmann and Atkinson[2]
2,4-Dimethylpentane	1.44 ± 0.45	296 ± 2	RR [relative to k(2,3-dimethylbutane) $=4.08\times10^{-16}$][a]	Aschmann and Atkinson[2]
2,2,3-Trimethylbutane	2.23 ± 0.33	296 ± 2	RR [relative to k(2,3-dimethylbutane) $=4.08\times10^{-16}$][a]	Aschmann and Atkinson[2]
2,2,4-Trimethylpentane	0.75 ± 0.32	296 ± 2	RR [relative to k(2,3-dimethylbutane) $=4.08\times10^{-16}$][a]	Aschmann and Atkinson[2]
2,2,3,3-Tetramethylbutane	<0.49	296 ± 2	RR [relative to k(2,3-dimethylbutane) $=4.08\times10^{-16}$][a]	Aschmann and Atkinson[2]
n-Nonane	1.92 ± 0.53	296 ± 2	RR [relative to k(2,3-dimethylbutane) $=4.08\times10^{-16}$][a]	Aschmann and Atkinson[2]
n-Decane	2.59 ± 0.61	296 ± 2	RR [relative to k(2,3-dimethylbutane) $=4.08\times10^{-16}$][a]	Aschmann and Atkinson[2]

[a]From previous recommendations.[1,4]

k(1-butene)=

$$1.35\times10^{-14}\ cm^3\ molecule^{-1}\ s^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty at 298 K of ±30%. This recommendation leads to higher rate constants at temperatures above 220 K than the previous recommendation of Atkinson[1] of k(1-butene)$=2.04\times10^{-13}\ e^{-843/T}$ cm^3 $molecule^{-1}$ s^{-1}.

4.2.2. *trans*-2-Butene

The absolute rate constants of Rudich *et al.*[2] at 267 and 298 K (Table 38) are in excellent agreement (within 4%) with the previous recommendation of Atkinson,[1,7] which is therefore unchanged (Table 24 in Sec. 2.2).

4.2.3. Cyclopentene

The absolute room temperature rate constant of Ljungström *et al.*[3] is given in Table 38. This rate constant[3] is 27% higher than the relative rate constant of Atkinson *et al.*,[12] and an average of these two rate constants[3,12] leads to the recommendation of

k(cyclopentene)=

$$5.3\times10^{-13}\ cm^3\ molecule^{-1}\ s^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty of ±30%.

4.2.4. Cyclohexene

The absolute rate constants of Ljungström *et al.*,[3] measured over the temperature range 267–349 K, are given in Table 38 and show little temperature dependence over the range studied. The room temperature rate constant of Ljungström *et al.*[3] is 19% higher than that of Atkinson *et al.*[13] An average of the room temperature rate constants of Atkinson *et al.*[13] and Ljungström *et al.*,[3] combined with a temperature dependence calculated from a unit weighted least-squares analysis of the data of Ljungström *et al.*,[3] leads to the recommendation of

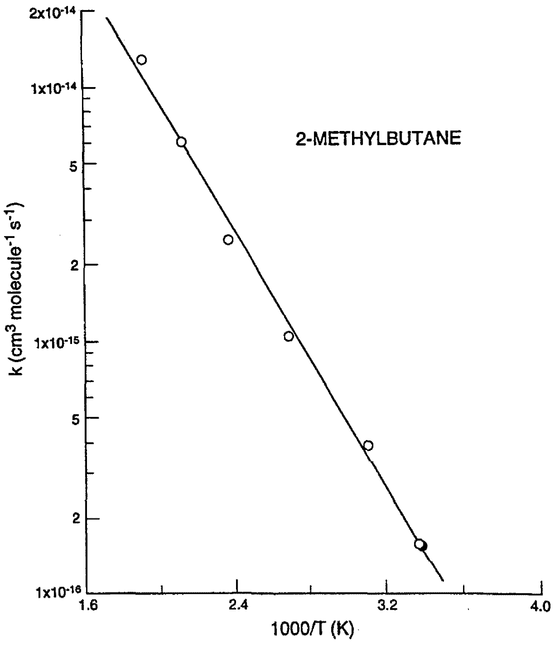

FIG. 8. Arrhenius plot of selected rate constants for the reaction of the NO_3 radical with 2-methylbutane. (○) Bagley *et al.* (Ref. 5); (●) Aschmann and Atkinson (Ref. 2); (—) recommendation (see text).

k(cyclohexene)=

$$1.05\times10^{-12}\ e^{-174/T}\ cm^3\ molecule^{-1}\ s^{-1}$$

over the temperature range 267–349 K, and

k(cyclohexene)=

$$5.9\times10^{-13}\ cm^3\ molecule^{-1}\ s^{-1}\ at\ 298\ K,$$

with an estimated overall uncertainty at 298 K of ±30%.

4.2.5. 1,3-Butadiene, 2-Methyl-1,3-Butadiene, and 2,3-Dimethyl-1,3-butadiene

The absolute rate constants of Ellermann *et al.*[4] (which were also included in the review of Atkinson[1]) are given in Table 38, and are higher than the recommendation of Atkinson[1,7] by factors of 1.8, 1.6, and 1.3, respectively. The recommendations of Atkinson[1,7] are unchanged.[1]

4.2.6. 1,3-Cyclohexadiene

The absolute and relative rate constants of Ellermann *et al.*[4] and Berndt *et al.*[5] are given in Table 38. These rate constants[4,5] are in excellent agreement with the previous recommendation of k(1,3-cyclohexadiene)$=1.16\times10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K,[1,7] which is therefore unchanged.

4.2.7. α-Phellandrene and α-Terpinene

The relative rate constants of Berndt *et al.*[5] (Table 38) for α-phellandrene and α-terpinene are 30% and 45% lower, respectively, than the rate constants of Atkinson *et al.*[14] Averaging these rate constants[5,14] leads to rate constants at 298 K of

k(α-phellandrene)=

$$7.3\times10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$$

with an estimated overall uncertainty of ±40%, and

k(α-terpinene)=

$$1.4\times10^{-10}\ cm^3\ molecule^{-1}\ s^{-1}$$

with an estimated overall uncertainty of a factor of 2.

[1] R. Atkinson, J. Phys. Chem. Ref. Data Monograph **2**, 1 (1994).
[2] Y. Rudich, R. K. Talukdar, R. W. Fox, and A. R. Ravishankara, J. Phys. Chem. **100**, 5374 (1996).
[3] E. Lungström, I. Wängberg, and S. Langer, J. Chem. Soc. Faraday Trans. **89**, 2977 (1993).
[4] T. Ellermann, O. J. Nielsen, and H. Skov, Chem. Phys. Lett. **200**, 224 (1992).
[5] T. Berndt, O. Böge, I. Kind, and W. Rolle, Ber. Bunsenges. Phys. Chem. **100**, 462 (1996).
[6] Y. Shu and R. Atkinson, J. Geophys. Res. **100**, 7275 (1995).
[7] R. Atkinson, J. Phys. Chem. Ref. Data **20**, 459 (1991).
[8] C. E. Canosa-Mas, P. S. Monks, and R. P. Wayne, J. Chem. Soc. Faraday Trans. **88**, 11 (1992).
[9] R. Atkinson, C. N. Plum, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **88**, 1210 (1984).
[10] R. Atkinson, S. M. Aschmann, and J. N. Pitts, Jr., J. Phys. Chem. **92**, 3454 (1988).
[11] I. Barnes, V. Bastian, K. H. Becker, and Z. Tong, J. Phys. Chem. **94**, 2413 (1990).
[12] R. Atkinson, S. M. Aschmann, W. D. Long, and A. M. Winer, Int. J. Chem. Kinet. **17**, 957 (1985).
[13] R. Atkinson, S. M. Aschmann, A. M. Winer, and J. N. Pitts, Jr., Env. Sci. Technol. **18**, 370 (1984).
[14] R. Atkinson, S. M. Aschmann, A. M. Winer, and J. N. Pitts, Jr., Env. Sci. Technol. **19**, 159 (1985).

5. Kinetics and Mechanisms of the Gas-Phase Reactions of O_3 with Alkanes and Alkenes

5.1. Alkanes

The kinetic data reported since the previous review and evaluation of Atkinson[1] are given in Table 39.

5.1.1. Cyclohexane

The upper limits to the rate constants determined by Grosjean and Grosjean[4,5,7,8] and Grosjean *et al.*[2,3,6,9] at around room temperature (Table 39) are consistent with previous kinetic data for the reactions of O_3 with alkanes[10] and with the recommended upper limits to the rate constants for these reactions.[1,10]

[1] R. Atkinson, J. Phys. Chem. Ref. Data Monograph **2**, 1 (1994).
[2] D. Grosjean, E. Grosjean, and E. L. Williams II, Int. J. Chem. Kinet. **25**, 783 (1993).
[3] D. Grosjean, E. Grosjean, and E. L. Williams II, Env. Sci. Technol. **27**, 2478 (1993).
[4] E. Grosjean and D. Grosjean, Int. J. Chem. Kinet. **26**, 1185 (1994).
[5] D. Grosjean and E. Grosjean, J. Geophys. Res. **100**, 22 815 (1995).

TABLE 38. Rate constants k and temperature dependent parameters, $k=A\ e^{-B/T}$, for the gas-phase reactions of the NO_3 radical with alkenes

Alkene	$10^{12}\times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	k (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
1-Butene			$(5.7\pm0.6)\times10^{-15}$	232	DF-LIF	Rudich *et al.*[2]	232–401
			$(6.9\pm0.7)\times10^{-15}$	249			
			$(9\pm0.9)\times10^{-15}$	263			
			$(1.15\pm0.09)\times10^{-14}$	279			
			$(1.30\pm0.10)\times10^{-14}$	296			
			$(1.38\pm0.10)\times10^{-14}$	296			
			$(1.35\pm0.10)\times10^{-14}$	296			
			$(1.34\pm0.10)\times10^{-14}$	296			
			$(1.34\pm0.10)\times10^{-14}$	296			
			$(1.71\pm0.14)\times10^{-14}$	314			
			$(2.25\pm0.19)\times10^{-14}$	333			
			$(1.88\pm0.19)\times10^{-14}$	334			
			$(1.92\pm0.19)\times10^{-14}$	334			
			$(2.48\pm0.25)\times10^{-14}$	352			
			$(3.03\pm0.31)\times10^{-14}$	374			
			$(3.16\pm0.33)\times10^{-14}$	377			
			$(3.18\pm0.35)\times10^{-14}$	396			
	0.52	1067 ± 31	$(3.82\pm0.42)\times10^{-14}$	401			
trans-2-Butene			$(3.55\pm0.33)\times10^{-13}$	267	DF-LIR	Rudich *et al.*[2]	267–298
			$(4.06\pm0.36)\times10^{-13}$	298			
Cyclopentene			$(5.9\pm1.1)\times10^{-13}$	294	DF-A	Ljungström *et al.*[3]	
Cyclohexene			$(6.8\pm1.3)\times10^{-13}$	267	DF-A	Ljungström *et al.*[3]	267–349
			$(6.3\pm1.3)\times10^{-13}$	294			
			$(7.4\pm1.6)\times10^{-13}$	323			
		120 ± 482	$(7.7\pm1.4)\times10^{-13}$	349			
1-Methylcyclohexene			$(1.7\pm0.6)\times10^{-11}$	265	DF-A	Ljungström *et al.*[3]	265–371
			$(1.5\pm0.5)\times10^{-11}$	293			
			$(2.0\pm0.8)\times10^{-11}$	324			
			$(1.9\pm0.8)\times10^{-11}$	350			
		0 ± 602	$(1.4\pm0.5)\times10^{-11}$	371			
1,3-Butadiene			$(1.8\pm0.4)\times10^{-13}$	295 ± 2	PR-A	Ellermann *et al.*[4]	
2-Methyl-1,3-butadiene			$(1.07\pm0.20)\times10^{-12}$	295 ± 2	PR-A	Ellermann *et al.*[4]	
2,3-Dimethyl-1,3-butadiene			$(2.7\pm0.2)\times10^{-12}$	295 ± 2	PR-A	Ellermann *et al.*[4]	
cis-1,3-Pentadiene			$(1.4\pm0.1)\times10^{-12}$	295 ± 2	PR-A	Ellermann *et al.*[4]	
trans-1,3-Pentadiene			$(1.6\pm0.1)\times10^{-12}$	295 ± 2	PR-A	Ellermann *et al.*[4]	
1,3-Cycohexadiene			$(1.2\pm0.2)\times10^{-11}$	295 ± 2	PR-A	Ellermann *et al.*[4]	
			$(1.08\pm0.3)\times10^{-11}$	298	RR [relative to k(2-methyl-2-butene) $=9.37\times10^{-12}$][a]	Berndt *et al.*[5]	
trans, *trans*-2,4-Hexadiene			$(1.6\pm0.3)\times0^{-11}$	295 ± 2	PR-A	Ellermann *et al.*[4]	
α-Phellandrene			$(5.98\pm0.21)\times10^{-11}$	298	RR [relative to k(2,3-dimethyl-2-butene) $=5.72\times10^{-11}$][a]	Berndt *et al.*[5]	
α-Terpinene			$(1.03\pm0.06)\times10^{-10}$	298	RR [relative to k(2,3-dimethyl-2-butene) $=5.72\times10^{-11}$][a]	Berndt *et al.*[5]	
α-Cedrene			$(8.16\pm0.73)\times10^{-12}$	296 ± 2	RR [relative to k(2-methyl-2-butene) $=9.37\times10^{-12}$][a]	Shu and Atkinson[6]	
α-Copaene			$(1.61\pm0.08)\times10^{-11}$	296 ± 2	RR [relative to k(2-methyl-2-butene) $=9.37\times10^{-12}$][a]	Shu and Atkinson[6]	
β-Caryophyllene			$(1.92\pm0.35)\times10^{-11}$	296 ± 2	RR [relative to k(2-methyl-2-butene) $=9.37\times10^{-12}$][a]	Shu and Atkinson[6]	
α-Humulene			$(3.53\pm0.27)\times10^{-11}$	296 ± 2	RR [relative to k(2-methyl-2-butene) $=9.37\times10^{-12}$][a]	Shu and Atkinson[6]	
Longifolene			$(6.77\pm0.47)\times10^{-13}$	296 ± 2	RR [relative to k(*trans*-2-butene) $=3.89\times10^{-13}$][a]	Shu and Atkinson[6]	

[a] From previous[1,7] and present recommendations.

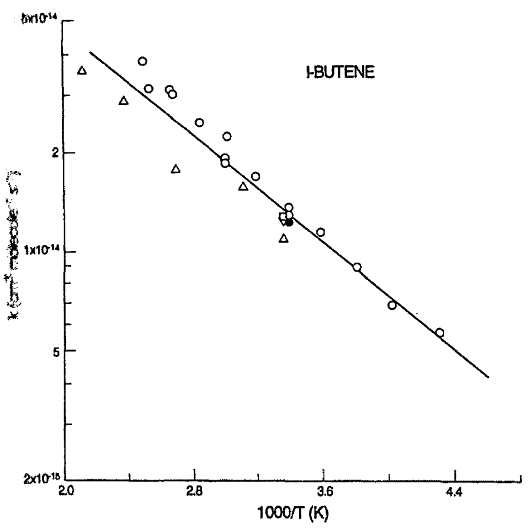

Fig. 9. Arrhenius plot of selected rate constants for the reaction of the NO_3 radical with 1-butene. (▽) Atkinson *et al.* (Ref. 9); (●) Atkinson *et al.* (Ref. 10); (□) Barnes *et al.* (Ref. 11); (△) Canosa-Mas *et al.* (Ref. 8); (○) Rudich *et al.* (Ref. 2); (—) recommendation (see text).

5.2. Alkenes

The kinetic data reported since the previous review and evaluation of Atkinson[1] are given in Table 40.

5.2.1. *cis*-2-Butene

The 298 K absolute rate constant and Arrhenius parameters reported by Treacy and Sidebottom[2] (the individual rate constants were not listed) are given in Table 40. Rate constants calculated from the Arrhenius expression of Treacy and Sidebottom[2] are in good agreement (within 7% over the temperature range 240–324 K) with those from the previous recommendation[1] of $k(cis\text{-2-butene})=3.22\times10^{-15}\ e^{-968/T}$ $cm^3\ molecule^{-1}\ s^{-1}$ over the temperature range 225–364 K, which is therefore unchanged.

TABLE 39. Rate constants k for the gas-phase reactions of O_3 with alkanes

Alkane	k ($cm^3\ molecule^{-1}\ s^{-1}$)	at T (K)	Technique	Reference
Cyclohexane	$<1.2\times10^{-22}$	290±5	S-UV	Grosjean *et al.*;[2,3] Grosjean and Grosjean[4,5]
	$\leq1.3\times10^{-21}$	295±1	S-UV	Grosjean *et al.*[6]
	$<3\ \times10^{-22}$	290±1	S-UV	Grosjean and Grosjean[7]
	$<2.0\times10^{-22}$	288±2	S-UV	Grosjean *et al.*[8]
	$\leq1.7\times10^{-22}$	291±5	S-UV	Grosjean and Grosjean[9]

5.2.2. 2-Methyl-2-butene

The 298 K absolute rate constant and Arrhenius parameters reported by Treacy and Sidebottom[2] (the individual rate constants were not listed) and the room temperature relative rate constant of Kwok *et al.*[4] are given in Table 40. Rate constants calculated from the Arrhenius expression of Treacy and Sidebottom[2] agree with those from the previous recommendation[1] of $k(\text{2-methyl-2-butene})=6.51\times10^{-15}$ $e^{-798/T}\ cm^3\ molecule^{-1}\ s^{-1}$ over the temperature range 227–363 K, to within 19% over the temperature range 240–324 K, while the rate constant of Kwok *et al.*[4] is in excellent agreement (within 3%) with the previous recommendation.[1] The previous recommendation[1] is therefore unchanged.

5.2.3. 1-Pentene and 1-Hexene

The rate constants of Grosjean and Grosjean[3] (Table 40) are in good agreement with the previous recommendations[1] of $k(\text{1-pentene})=1.00\times10^{-17}\ cm^3\ molecule^{-1}\ s^{-1}$ at 298 K and $k(\text{1-hexene})=1.10\times10^{-17}\ cm^3\ molecule^{-1}\ s^{-1}$ at 298 K, which are therefore unchanged.

5.2.4. Other Acyclic Monoalkenes

The rate constants of Grosjean and Grosjean[3,5,6] and Grosjean *et al.*[7] (Table 40) are preferred over previous room temperature measurements[14] for these alkenes. However, for 2-ethyl-1-butene, the studies of Grosjean *et al.*[7] and Grosjean and Grosjean[3] differ by a factor of 1.7, well outside of the cited combined uncertainties. The rate constants for these alkenes,[3,5–7] measured at ~285–295 K, have been extrapolated to 298 K using values of B in $k=A\ e^{-B/T}$ of 1600 K for 2-methyl-1-butene, 2-methyl-1-pentene, 2,3,3-trimethyl-1-butene, and 3-methyl-2-isopropyl-1-butene; 1000 K for *cis*- and *trans*-3-hexene, *cis*- and *trans*-4-octene, the dimethyl-3-hexenes, 2,2,4-trimethyl-2-pentene, *cis*- and *trans*-5-decene, and 3,4-diethyl-2-hexene; and 1800 K for 3-methyl-1-butene, 3-methyl-1-pentene, 2,3-dimethyl-1-butene, 3,3-dimethyl-1-butene, 2-ethyl-1-butene, 1-heptene, 1-octene and 1-decene, and the resulting 298 K rate constants are given in Table 26 in Sec. 2.2.

5.2.5. 2-Methyl-1,3-butadiene (isoprene)

The rate constants of Grosjean *et al.*[8] at 293±2 K and Grosjean and Grosjean[5] at 290.7±2.1 K (Table 40) are 22% lower and 4% higher, respectively, than the rate constants calculated from the recommendation of Atkinson,[1] of $k(\text{isoprene})=7.86\times10^{-15}\ e^{-1913/T}\ cm^3\ molecule^{-1}\ s^{-1}$ over the temperature range 240–324 K. The agreement with the most recent measurement of Grosjean and Grosjean[5] is excellent, and the previous recommendation[1] is therefore unchanged.

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TABLE 40. Rate constants k and temperature dependent parameters, $k=A\ e^{-B/T}$, for the gas-phase reactions of O_3 with alkenes

Alkene	A (cm^3 molecule^{-1} s^{-1})	B (K)	k (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
cis-2-Butene	$(3.06\pm0.15)\times10^{-15}$	940 ± 42	$(1.31\pm0.05)\times10^{-16}$	298 ± 4	S-CL	Treacy and Sidebottom[2]	240–324
1-Pentene			$(9.6\pm1.6)\times10^{-18}$	286 ± 1	S-UV	Grosjean and Grosjean[3]	
2-Methyl-1-butene			$(1.33\pm0.14)\times10^{-17}$	288 ± 1	S-UV	Grosjean and Grosjean[3]	
2-Methyl-2-butene	$(5.21\pm0.50)\times10^{-15}$	734 ± 136	$(4.50\pm0.15)\times10^{-16}$	298 ± 4	S-CL	Treacy and Sidebottom[2]	240–324
			$(3.91\pm0.14)\times10^{-16}$	297 ± 2	RR [relative to k(*cis*-2-butene) $=1.24\times10^{-16}$][a]	Kwok *et al.*[4]	
3-Methyl-1-butene			$(9.50\pm1.23)\times10^{-18}$	292.8 ± 1.6	S-UV	Grosjean and Grosjean[5]	
1-Hexene			$(9.7\pm1.4)\times10^{-18}$	287 ± 1	S-UV	Grosjean and Grosjean[3]	
cis-3-Hexene			$(1.44\pm0.17)\times10^{-16}$	294.7 ± 1.9	S-UV	Grosjean and Grosjean[6]	
trans-3-Hexene			$(1.57\pm0.25)\times10^{-16}$	289.7 ± 2.8	S-UV	Grosjean and Grosjean[6]	
2-Methyl-1-pentene			$(1.25\pm0.11)\times10^{-17}$	287 ± 1	S-UV	Grosjean and Grosjean[3]	
			$(1.31\pm0.18)\times10^{-17}$	288.8 ± 3.9	S-UV	Grosjean and Grosjean[5]	
3-Methyl-1-pentene			$(3.84\pm0.57)\times10^{-18}$	286 ± 2	S-UV	Grosjean and Grosjean[3]	
4-Methyl-1-pentene			$(7.31\pm0.67)\times10^{-18}$	287 ± 1	S-UV	Grosjean and Grosjean[3]	
2,3-Dimethyl-1-butene			$(1.00\pm0.03)\times10^{-17}$	285 ± 1	S-UV	Grosjean and Grosjean[3]	
3,3-Dimethyl-1-butene			$(3.93\pm0.93)\times10^{-18}$	285 ± 1	S-UV	Grosjean and Grosjean[3]	
2-Ethyl-1-butene			$(8.1\pm0.3)\times10^{-18}$	293 ± 1	S-UV	Grosjean *et al.*[7]	
			$(1.37\pm0.09)\times10^{-17}$	287 ± 1	S-UV	Grosjean and Grosjean[3]	
1-Heptene			$(9.4\pm0.4)\times10^{-18}$	287 ± 2	S-UV	Grosjean and Grosjean[3]	
2,3,3-Trimethyl-1-butene			$(7.75\pm1.08)\times10^{-18}$	294.2 ± 2.7	S-UV	Grosjean and Grosjean[5]	
1-Octene			$(1.25\pm0.04)\times10^{-17}$	293 ± 1	S-UV	Grosjean and Grosjean[3]	
cis-4-Octene			$(8.98\pm0.97)\times10^{-17}$	293.3 ± 1.3	S-UV	Grosjean and Grosjean[6]	
trans-4-Octene			$(1.31\pm0.15)\times10^{-16}$	290.1 ± 0.2	S-UV	Grosjean and Grosjean[6]	
trans-2,5-Dimethyl-3-hexene			$(3.83\pm0.50)\times10^{-17}$	291.1 ± 1.9	S-UV	Grosjean and Grosjean[6]	
trans-2,2-Dimethyl-3-hexene			$(4.03\pm0.67)\times10^{-17}$	295.2 ± 1.0	S-UV	Grosjean and Grosjean[6]	
cis- + *trans*-3,4-Dimethyl-3-hexene			$\geqslant3.70\times10^{-16}$	295.8 ± 0.5	S-UV	Grosjean and Grosjean[5]	
2,4,4-Trimethyl-2-pentene			$(1.39\pm0.17)\times10^{-16}$	296.6 ± 1.8	S-UV	Grosjean and Grosjean[5]	
3-Methyl-2-isopropyl-1-butene			$(3.02\pm0.52)\times10^{-18}$	293.6 ± 1.2	S-UV	Grosjean and Grosjean[5]	
1-Decene			$(8.0\pm1.4)\times10^{-18}$	291 ± 2	S-UV	Grosjean and Grosjean[3]	
cis-5-Decene			$(1.14\pm0.13)\times10^{-16}$	292.7 ± 2.3	S-UV	Grosjean and Grosjean[6]	
trans-5-Decene			$\geqslant1.30\times10^{-16}$	294.8 ± 0.3	S-UV	Grosjean and Grosjean[6]	
3,4-Diethyl-2-hexene			$(3.98\pm0.43)\times10^{-18}$	293.2 ± 1.4	S-UV	Grosjean and Grosjean[5]	
2-Methyl-1,3-butadiene			$(8.95\pm0.25)\times10^{-18}$	293 ± 2	S-UV	Grosjean *et al.*[8]	
			$(1.13\pm0.32)\times10^{-17}$	290.7 ± 2.1	S-UV	Grosjean and Grosjean[5]	
Cyclopentene	$(1.6\pm0.3)\times10^{-15}$	349 ± 44	$(4.91\pm0.40)\times10^{-16}$	298 ± 4	S-CL	Treacy and Sidebottom[2]	240–324
1-Methyl-1-cyclopentene			$(6.73\pm0.99)\times10^{-16}$	298 ± 4	S-CL	Treacy and Sidebottom[2]	
Cyclohexene	$(2.60\pm0.40)\times10^{-15}$	1063 ± 267	$(8.5\pm0.8)\times10^{-17}$	298 ± 4	S-CL	Treacy and Sidebottom[2]	240–324
			$(8.46\pm0.10)\times10^{-17}$	291 ± 1	S-UV	Grosjean and Grosjean[3]	
1,3-Cyclohexadiene			$(1.22\pm0.05)\times10^{-15}$	296 ± 2	RR [relative to k(2,3-dimethyl-2-butene) $=1.12\times10^{-15}$][a]	Greene and Atkinson[9]	
Cycloheptene	$(1.28\pm0.40)\times10^{-15}$	494 ± 106	$(2.37\pm0.21)\times10^{-16}$	298 ± 4	S-CL	Treacy and Sidebottom[2]	240–324
			$(2.26\pm0.04)\times10^{-16}$	296 ± 2	RR [relative to k(*cis*-2-butene) $=1.22\times10^{-16}$][a]	Greene and Atkinson[9]	
1,3-Cycloheptadiene			$(1.54\pm0.03)\times10^{-16}$	296 ± 2	RR [relative to k(*cis*-2-butene) $=1.22\times10^{-16}$][a]	Greene and Atkinson[9]	
1-Methyl-1-cyclohexene	$(5.25\pm0.50)\times10^{-15}$	1040 ± 137	$(1.66\pm0.12)\times10^{-16}$	298 ± 4	S-CL	Treacy and Sidebottom[2]	240–324
4-Methyl-1-cyclohexene	$(2.16\pm0.40)\times10^{-15}$	952 ± 45	$(8.2\pm0.3)\times10^{-17}$	298 ± 4	S-CL	Treacy and Sidebottom[2]	240–324
Bicyclo[2,2,1]-2-heptene			$(1.55\pm0.05)\times10^{-15}$	296 ± 2	RR [relative to k(2,3-dimethyl-2-butene) $=1.12\times10^{-15}$][a]	Greene and Atkinson[9]	
Bicyclo[2,2,1]-2,5-heptadiene			$(3.55\pm0.07)\times10^{-15}$	296 ± 2	RR [relative to k(2,3-dimethyl-2-butene) $=1.12\times10^{-15}$][a]	Greene and Atkinson[9]	
cis-Cyclooctene	$(7.8\pm0.3)\times10^{-16}$	217 ± 51	$(3.74\pm0.11)\times10^{-16}$	298 ± 4	S-CL	Treacy and Sidebottom[2]	240–324
cis-Cyclodecene	$(1.08\pm0.57)\times10^{-15}$	1081 ± 171	$(2.9\pm0.2)\times10^{-17}$	298 ± 4	S-CL	Treacy and Sidebottom[2]	240–324
1,2-Dimethyl-1-cyclohexene			$(2.07\pm0.04)\times10^{-16}$	296 ± 2	RR [relative to k(2-methyl-2-butene) $=3.96\times10^{-16}$][a]	Alvarado *et al.*[10]	

TABLE 40. .Rate constants k and temperature dependent parameters, $k=A\ e^{-B/T}$, for the gas-phase reactions of O_3 with alkenes—Continued

Alkene	A (cm^3 molecule^{-1} s^{-1})	B (K)	k (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K) 4-Vinylcyclohexene
4-Vinylcyclohexene			2.7×10^{-16}	296.7	S-CL	Zhang *et al.*[11]	
Bicyclo[2,2,2]-2-octene			$(7.09\pm0.10)\times10^{-17}$	296±2	RR [relative to k(*cis*-2-butene)= 1.22×10^{-16}]^a	Greene and Atkinson[9]	
Limonene			3.5×10^{-16}	297.3	S-CL	Zhang *et al.*[11]	
			$(2.01\pm0.07)\times10^{-16}$	296±2	RR [relative to k(*cis*-2-butene) $=1.22\times10^{-16}$]^a	Shu and Atkinson[12]	
α-Phellandrene			$(2.98\pm0.09)\times10^{-15}$	296±2	RR [relative to k(2,3-dimethyl-2-butene) $=1.12\times10^{-15}$]^a	Shu and Atkinson[12]	
β-Pinene			$(1.22\pm0.13)\times10^{-17}$	295±1	S-UV	Grosjean *et al.*[13]	
α-Terpinene			$(2.69\pm0.90)\times10^{-14}$	296±2	RR [relative to k(2,3-dimethyl-2-butene) $=1.12\times10^{-15}$]^a	Shu and Atkinson[12]	
			$(2.11\pm0.07)\times10^{-14}$	296±2	RR [relative to k(β-caryophyllene) $=1.16\times10^{-16}$]^a	Shu and Atkinson[12]	
Terpinolene			$(1.88\pm0.08)\times10^{-15}$	296±2	RR [relative to k(2,3-dimethyl-2-butene) $=1.12\times10^{-13}$]^a	Shu and Atkinson[12]	
α-Cedrene			$(2.87\pm0.86)\times10^{-17}$	296±2	RR [relative to k(2-methyl-2-butene) $=3.96\times10^{-16}$]^a	Shu and Atkinson[12]	
			$(2.78\pm0.14)\times10^{-17}$	296±2	RR [relative to k(*cis*-2-butene) $=1.22\times10^{-16}$]^a	Shu and Atkinson[12]	
α-Copaene			$(1.58\pm0.07)\times10^{-16}$	296±2	RR [relative to k(2-methyl-2-butene) $=3.96\times10^{-16}$]^a	Shu and Atkinson[12]	
β-Caryophyllene			$(8.70\pm1.30)\times10^{-15}$	296±2	RR [relative to k(2-methyl-2-butene) $=3.96\times10^{-16}$]^a	Shu and Atkinson[12]	
			$(1.12\pm0.07)\times10^{-14}$	296±2	RR [relative to k(2,3-dimethyl-2-butene) $=1.12\times10^{-15}$]^a	Shu and Atkinson[12]	
			$(1.20\pm0.04)\times10^{-14}$	296±2	RR [relative to k(terpinolene) $=1.88\times10^{-15}$]^a	Shu and Atkinson[12]	
α-Humulene			$(1.15\pm0.18)\times10^{-14}$	296±2	RR [relative to k(2,3-dimethyl-2-butene) $=1.12\times10^{-15}$]^a	Shu and Atkinson[12]	
			$(1.19\pm0.10)\times10^{-14}$	296±2	RR [relative to k(α-terpinene) $=2.11\times10^{-14}$]^a	Shu and Atkinson[12]	
Longifolene			$<7\times10^{-18}$	296±2	RR [relative to k(*cis*-2-butene) $=1.22\times10^{-16}$]^a	Shu and Atkinson[12]	
			$<5\times10^{-19}$	296±2	RR [relative to k(propene) $=9.68\times10^{-18}$]^a	Shu and Atkinson[12]	

[a] From previous[1,14] and present recommendations.

5.2.6. Cyclopentene

The absolute rate constant at 298 K and the Arrhenius parameters of Treacy and Sidebottom[2] are given in Table 40. The room temperature rate constant of Treacy and Sidebottom[2] is 22% lower than the previous recommendation of Atkinson,[1] and an average of the room temperature rate constants of Nolting *et al.*,[15] Greene and Atkinson,[16] and Treacy and Sidebottom[2] is recommended, of

$$k(\text{cyclopentene})=$$

$$5.7\times10^{-16}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty of ±35%. This recommendation supersedes the previous recommendation[1] of k(cyclopentene)$=6.3\times10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

5.2.7. Cyclohexene

The rate constants of Treacy and Sidebottom[2] and Grosjean and Grosjean[3] are given in Table 40. These rate constants[2,3] are in reasonable agreement with the previous recommendation of $k(\text{cyclohexene})=7.2\times10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.[1] Using the value of $B=-1063$ K^2 to extrapolate the measured rate constants to 298 K, a unit weighted average of the room temperature rate constants of Nolting *et al.*,[15] Greene and Atkinson,[16] Treacy and Sidebottom,[2] and Grosjean and Grosjean[3] leads to the recommendation of

$$k(\text{cyclohexene})=8.1\times10^{-17}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty of ±25%.

5.2.8. Cycloheptene

The rate constants of Treacy and Sidebottom[2] and Greene and Atkinson[9] are given in Table 40. The room temperature rate constants of Nolting *et al.*,[15] Treacy and Sidebottom,[2] and Greene and Atkinson[9] are in good agreement, and a unit weighted average leads to the recommendation of

$$k(\text{cycloheptene})=2.45\times10^{-17}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty of ±25%. This recommendation supersedes the previous recommendation[1] of $k(\text{cycloheptene})=2.9\times10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

5.2.9. Limonene

The rate constant of Shu and Atkinson[12] for limonene (Table 40) is in excellent agreement with the previous measurement of Atkinson *et al.*[17] of $k(\text{limonene})=2.04\times10^{-16}$ cm^3 molecule^{-1} s^{-1} at 296±2 K.[1,17] Based on these two studies[12,17] it is recommended that

$$k(\text{limonene})=2.03\times10^{-16}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty of ±25%.

5.2.10. β-Pinene

The rate constant of Grosjean *et al.*[13] for β-pinene (Table 40) is in reasonable agreement with the previous recommendation of Atkinson[1] of $k(\beta\text{-pinene})=1.5\times10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K, which is therefore unchanged.

5.2.11. Other cycloalkenes (including monoterpenes)

The rate constants of Greene and Atkinson[9] (Table 40) supercede the previous data of Atkinson *et al.*[18,19] For α-phellandrene, α-terpinene and terpinolene, the rate constants of Shu and Atkinson[12] (Table 40) supercede the previous data of Atkinson *et al.*,[19] as discussed by Shu and Atkinson.[12]

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