Chem. Rev. **2003,** *103,* 4605–4638

Atmospheric Degradation of Volatile Organic Compounds

Roger Atkinson*,† and Janet Arey

Air Pollution Research Center and Department of Environmental Sciences, University of California, Riverside, California 92521

Received February 11, 2003

Contents

1. Introduction

Volatile organic compounds (VOCs) are emitted into the atmosphere from anthropogenic and biogenic sources,[1−5] and may also be formed in situ in the atmosphere as products of the atmospheric transformations of other VOCs. On a worldwide basis, emission of VOCs from biogenic sources (mainly vegetation) dominates, with estimated emissions being 1150 Tg (C) per year from vegetation[2] and ~100 Tg (C) per year from anthropogenic sources.[1] Although on a worldwide basis VOCs from biogenic sources dominate over those from anthropogenic sources by a factor of ~10, in urban areas anthropogenic VOCs often dominate.

The major classes of emitted VOCs are alkanes, alkenes, aromatic hydrocarbons, and oxygenated compounds, with vegetative emissions typically being composed of alkenes (isoprene, monoterpenes, and sesquiterpenes) and oxygenated VOCs (including 2-methyl-3-buten-2-ol, acetone, methanol, *cis*-3-hexen-1-ol, *cis*-3-hexenyl acetate, and camphor)[2,3,6] and anthropogenic emissions resulting from vehicle emissions (comprising mainly gasoline constituents, including, in the U.S., the ethanol and methyl *tert*-butyl ether oxygenates added to the fuel) and emissions from, for example, landfills, refineries, petrochemical sources, solvent usage, and industrial facilities. In urban air in cities such as Los Angeles, CA and Boston, MA, the nonmethane VOCs are typically made up of the following: alkanes, 40−45%; alkenes, 10%; aromatic hydrocarbons, 20%; and oxygenates, 10−15%; plus unidentified VOCs.[7,8] As noted, the alkane and aromatic hydrocarbon fractions of these urban air nonmethane VOCs often have a composition generally similar to that of gasoline.

In the atmosphere, VOCs from both anthropogenic and biogenic sources undergo a number of physical and chemical processes leading to their removal from the atmosphere or transformation in the atmosphere.[9] Physical removal of VOCs to the earth's surface may occur by dry deposition and wet deposition. These processes have been discussed in detail elsewhere[10,11] and are not dealt with here. The chemical processes leading to the atmospheric degradation of VOCs are the subject of this article.

2. Tropospheric VOC Transformation Processes

2.1. Initial Reactions and Lifetimes

In the troposphere, VOCs are transformed by the chemical processes of photolysis (at wavelengths >290 nm because shorter wavelengths are absorbed by O_2 and O_3 in the stratosphere), reaction with the hydroxyl (OH) radical (typically during daylight hours), reaction with the nitrate (NO_3) radical during

---

* To whom correspondence should be addressed. Phone: (909) 787-4191. Fax: (909) 787-5004. E-mail: ratkins@mail.ucr.edu.
† Also Department of Chemistry.

10.1021/cr0206420 CCC: $44.00

Roger Atkinson was born in the U.K. and received a Ph.D. in Physical Chemistry from the University of Cambridge in 1969. He is presently a Research Chemist at the Air Pollution Research Center and Distinguished Professor in the Department of Environmental Sciences and the Department of Chemistry at the University of California at Riverside.

Janet Arey received a B. S. in Chemistry from the Massachusetts Institute of Technology in 1971 and a Ph.D. in Environmental Health Sciences from the University of Michigan in 1980. She is presently a Research Chemist at the Air Pollution Research Center and Professor in the Department of Environmental Sciences at the University of California at Riverside.

evening and nighttime hours, reaction with O_3, and in coastal and marine areas reaction with Cl atoms during daylight hours.[9] The sources of OH radicals, NO_3 radicals, Cl atoms, and O_3 in the troposphere are discussed elsewhere[9,12] and hence are not dealt with here.

Rate constants for the gas-phase reactions of alkanes, alkenes, aromatic hydrocarbons, aliphatic and aromatic aldehydes, ketones, alcohols, hydroperoxides, selected ethers, and alkyl nitrates are listed in Table 1 (OH radical reactions), Table 2 (O_3 reactions), and Table 3 (NO_3 radical reactions). All of the alkanes, alkenes, aromatic hydrocarbons, aldehydes (RCHO, where R = alkyl or aryl), ketones (RC(O)R′, where R and R′ are alkyl), alcohols (ROH, where R = alkyl), hydroperoxides, and alkyl nitrates for which apparently reliable data are available are included in Tables 1−3. Also included in these tables are rate data for the unsaturated carbonyls methyl vinyl ketone, methacrolein, and 3-isopropenyl-6-oxo-heptanal, and the dicarbonyls glyoxal, methylglyoxal, pinonaldehyde, and caronaldehyde.

The rate constants and temperature-dependent parameters listed in Tables 1−3 are, wherever possible, taken from reviews and evaluations.[8,13−16,29,30] Temperature-dependent rate expressions are given as the Arrhenius expression, $k = Ae^{-B/T}$, or (especially for the reactions of OH radicals with alkanes) as the three-parameter expression $k = AT^{n}e^{-B/T}$, with n often being set at 2.[13,29,30] For VOCs not included in these reviews and evaluations[8,13−16,29,30] or for which new data now exist that supersede previous recommendations, data are listed in Tables 1−3 from selected, apparently reliable, studies. Data obtained from relative rate studies have been reevaluated, when necessary, to be consistent with recent recommendations for the reference compound(s) used. It needs to be pointed out that the rate data for those VOCs in Tables 1−3 not referenced to the recent reviews and evaluations of Atkinson,[13] Calvert et al.,[8,15] and IUPAC[16] have not undergone recent critical evaluation. Thus, for the VOCs reviewed and evaluated by Atkinson[29,30] (and even for certain VOCs included in Calvert et al.[8,15]), rate constants obtained from relative rate studies may require reevaluation.

Rate constants for the reactions of a VOC with OH radicals, NO_3 radicals, Cl atoms, and O_3 can be combined with measured, computed, or estimated tropospheric concentrations of OH radicals, NO_3 radicals, Cl atoms, and O_3 to provide lifetimes of the VOC with respect to each of these potential transformation processes. Such calculated lifetimes depend on the temperature (or, equivalently, altitude) assumed, and on the concentrations of OH radicals, NO_3 radicals, Cl atoms, and O_3 used. Additionally, absorption cross-sections and photolysis quantum yields (both as a function of wavelength) can be combined with the actinic flux (again as a function of wavelength) to obtain the photolysis rate of the VOC (if it absorbs at wavelengths >290 nm and has a nonzero quantum yield for chemical change). Table 4 gives calculated lower tropospheric (298 K) lifetimes of selected VOCs from anthropogenic and biogenic sources with respect to reaction with OH radicals, NO_3 radicals, and O_3. Additionally, as noted above, certain VOCs (formaldehyde and acetone among those listed in Table 1) undergo photolysis.

It should be recognized that Cl atom reactions may also be an important VOC transformation process in certain locales such as in the Arctic troposphere during springtime, and possibly in some coastal regions.[60] However, on a global basis Cl atom reactions are believed to be of minor importance as a VOC loss process[61−63] and, therefore, are not included in this article. For those interested, the kinetics and initial reaction mechanisms of the reactions of Cl atoms with $\leq C_4$ VOCs are evaluated on an ongoing basis by the NASA[64] and IUPAC[16] evaluations, and rate constants for reactions of Cl atoms with alkanes and alkenes (as of 1997) are listed in Atkinson.[14]

Because the temperature in the troposphere varies from ~200 K (upper troposphere) to ~300 K (lower troposphere), it is desirable to have kinetic data over this temperature range. Furthermore, as noted below for alkenes and, especially, aromatic hydrocarbons, useful mechanistic information can be obtained for the OH radical reactions from kinetic studies conducted at elevated temperatures (>600 K in the case

Table 1. Room-Temperature Rate Constants, Temperature-Dependent Parameters, and Temperature Ranges over Which These Rate Expressions Are Applicable for the Gas-Phase Reactions of OH Radicals with Alkanes, Alkenes, Aromatic Hydrocarbons, Aldehydes, Ketones, Alcohols, Hydroperoxides, Selected Ethers, and Alkyl Nitrates

organic	10^{12} x k (298 K) (cm^3 molecule^{-1} s^{-1})	A (cm^3 molecule^{-1} s^{-1})	n	B (K)	temperature range (K)	ref
		Alkanes				
methane	0.00640	1.85×10^{-20}	2.82	987	195−1234	13
methane-d_1	0.00528	3.19×10^{-18}	2	1322	249−422	13
methane-d_2	0.00340	2.18×10^{-12}		1926	270−354	13
methane-d_3	0.00195	1.46×10^{-12}		1972	270−354	13
methane-d_4	0.000916	5.70×10^{-18}	2	1882	244−800	13
ethane	0.248	1.49×10^{-17}	2	499	180−1225	13
propane	1.09	1.65×10^{-17}	2	87	190−1220	13
n-butane	2.36	1.81×10^{-17}	2	−114	231−753	13
2-methylpropane	2.12	1.17×10^{-17}	2	−213	213−1146	13
n-pentane	3.80	2.52×10^{-17}	2	−158	224−753	13
2-methylbutane	3.6					13
2,2,-dimethylpropane	0.825	1.86×10^{-17}	2	207	287−901	13
n-hexane	5.20	2.54×10^{-14}	1	112	292−962	13
2-methylpentane	5.2					13
3-methylpentane	5.2					13
2,2-dimethylbutane	2.23	3.37×10^{-11}		809	245−328	13
2,3-dimethylbutane	5.78	1.66×10^{-17}	2	−407	247−1220	13
n-heptane	6.76	1.95×10^{-17}	2	−406	299−1086[a]	13
2,4-dimethylpentane	4.77					13
2,2,3-trimethylbutane	3.81	9.20×10^{-18}	2	−459	243−753	13
n-octane	8.11	2.72×10^{-17}	2	−361	299−1078	13
2,2,4-trimethylpentane	3.34	2.35×10^{-17}	2	−140	297−1186	13
2,3,4-trimethylpentane	6.6				243−313[b]	13
2,2,3,3-tetramethylbutane	0.972	1.99×10^{-17}	2	178	290−1180	13
n-nonane	9.70	2.53×10^{-17}	2	−436	295−1097[a]	13
3,3-diethylpentane	4.8					13
n-decane	11.0	3.17×10^{-17}	2	−406	296−1109[a]	13
3,4-diethylhexane	6.92					13
n-undecane	12.3					13
n-dodecane	13.2					13
n-tridecane	15.1					13
n-tetradecane	17.9 (312 K)					13
n-pentadecane	20.7 (312 K)					13
n-hexadecane	23.2 (312 K)					13
cyclopropane	0.0815[c]	4.21×10^{-18}	2	454	200−459	13
isopropylcyclopropane	2.61					13
cyclobutane	2.03	2.10×10^{-17}	2	−25	272−366	13
cyclopentane	4.97	2.73×10^{-17}	2	−214	273−1194	13
cyclohexane	6.97	3.26×10^{-17}	2	−262	292−497	13
methylcyclohexane	9.64					13
n-butylcyclohexane	14.7					13
cycloheptane	12.4	3.99×10^{-17}	2	−373	298−388	13
cyclooctane	13.3	5.91×10^{-17}	2	−276	298−387	13
bicyclo[2.2.1]heptane	5.12					13
bicyclo[2.2.2]octane	13.7					13
bicyclo[3.3.0]octane	10.3					13
cis-bicyclo[4.3.0]nonane	16.0					13
trans-bicyclo[4.3.0]-nonane	16.5					13
cis-bicyclo[4.4.0]decane	18.6					13
trans-bicyclo[4.4.0]-decane	19.0					13
tricyclo[5.2.1.0^{2,6}]decane	10.6					13
tricyclo[3.3.1.1^{3,7}]decane	21.5					13
trans-pinane	12.4					13
tricyclene	2.66					13
quadricyclane	1.70					13
		Alkenes				
ethene	8.52	1.96×10^{-12}		−438	291−425	14,15
propene	26.3	4.85×10^{-12}		−504	293−467[d]	14,15
1-butene	31.4	6.55×10^{-12}		−467	295−424[e]	14,15
cis-2-butene	56.4	1.10×10^{-11}		−487	295−425[f]	14,15
trans-2-butene	64.0	1.01×10^{-11}		−550	295−425[f]	14,15
2-methylpropene	51.4	9.47×10^{-12}		−504	295−425	14,15
1-pentene	31.4					14,15
cis-2-pentene	65					14,15
trans-2-pentene	67					14,15
2-methyl-1-butene	61					14,15
3-methyl-1-butene	31.8	5.32×10^{-12}		−533	295−423	14,15
2-methyl-2-butene	86.9	1.92×10^{-11}		−450	295−426	14,15

Table 1. (Continued)

organic	10^{12} x *k* (298 K) (cm^3 molecule^{-1} s^{-1})	*A* (cm^3 molecule^{-1} s^{-1})	*n*	*B* (K)	temperature range (K)	ref
Alkenes (Continued)						
1-hexene	37					14,15
2-methyl-1-pentene	63					14,15
2-methyl-2-pentene	89					14,15
trans-4-methyl-2- pentene	61					14,15
3,3-dimethyl-1-butene	28					14,15
2,3-dimethyl-2-butene	110					14,15
1-heptene	40					14,15
trans-2-heptene	68					14,15
2,3-dimethyl-2-pentene	103					14,15
trans-4,4-dimethyl-2-pentene	55					14,15
trans-4-octene	69					14,15
propadiene	9.82	7.66×10^{-12}		−74	295−478	14,15
1,2-butadiene	26					14,15
1,3-butadiene	66.6	1.48×10^{-11}		−448	295−483	14,15
1,2-pentadiene	35.5					14,15
cis−1,3-pentadiene	101					14,15
1,4-pentadiene	53					14,15
2-methyl-1,3-butadiene (isoprene)	100	2.7×10^{-11}		−390	249−422	16
3-methyl-1,2-butadiene	57					14,15
trans-1,3-hexadiene	112					14,15
trans-1,4-hexadiene	91					14,15
1,5-hexadiene	62					14,15
cis- and *trans*-2,4-hexadiene	134					14,15
2-methyl-1,4-pentadiene	79					14,15
2-methyl-1,3-pentadiene	136					14,15
4-methyl-1,3-pentadiene	131					14,15
2,3-dimethyl-1,3-butadiene	122					14,15
2-methyl-1,5-hexadiene	96					14,15
2,5-dimethyl-1,5-hexadiene	120					14,15
2,5-dimethyl-2,4-hexadiene	210					14,15
cis-1,3,5-hexatriene	110					14,15
trans-1,3,5-hexatriene	111					14,15
myrcene	215					14,15
ocimene (*cis*- and *trans*-)	252					14,15
cyclopentene	67					14,15
cyclohexene	67.7					14,15
1,3-cyclohexadiene	164					14,15
1,4-cyclohexadiene	99.5					14,15
cycloheptene	74					14,15
1,3-cycloheptadiene	139					14,15
1,3,5-cycloheptatriene	97					14,15
1-methyl-1-cyclohexene	94					14,15
bicyclo[2.2.1]-2-heptene	49					14,15
bicyclo[2.2.1]-2,5-heptadiene	120					14,15
bicyclo[2.2.2]-2-octene	41					14,15
camphene	53					14,15
2-carene	80					14,15
3-carene	88					14,15
limonene	164	4.28×10^{-11}		−401	294−363	17,18
α-phellandrene	313					14,15
β-phellandrene	168					14,15
α-pinene	52.3	1.21×10^{-11}		−436	294−364	17,18
β-pinene	74.3	1.55×10^{-11}		−467	294−364	17,18
sabinene	117					14,15
α-terpinene	363					14,15
γ-terpinene	177					14,15
terpinolene	225					14,15
α-cedrene	67					14,15
α-copaene	90					14,15
β-caryophyllene	197					14,15
α-humulene	293					14,15
longifolene	47					14,15
Aromatic Hydrocarbons						
benzene	1.22	2.33×10^{-12}		193	239−342	8
toluene	5.63	1.18×10^{-12}		−338	213−383	8
ethylbenzene	7.0					8
o-xylene	13.6					8
m-xylene	23.1	2.31×10^{-11}		0	250−315	8
p-xylene	14.3	1.43×10^{-11}		0	296−335	8
n-propylbenzene	5.8					8
isopropylbenzene	6.3					8

Table 1. (Continued)

organic	10^{12} x k (298 K) (cm^3 molecule^{-1} s^{-1})	A (cm^3 molecule^{-1} s^{-1})	n	B (K)	temperature range (K)	ref
Aromatic Hydrocarbons (Continued)						
o-ethyltoluene	11.9					8
m-ethyltoluene	18.6					8
p-ethyltoluene	11.8					8
1,2,3-trimethylbenzene	32.7					8
1,2,4-trimethylbenzene	32.5					8
1,3,5-trimethylbenzene	56.7					8
tert-butylbenzene	4.5					8
4-isopropyltoluene	14.5					8
hexamethylbenzene	113					19
indan	19					8
indene	78					8
tetralin	34					8
styrene	58					8
α-methylstyrene	51					8
β-methylstyrene	57					8
β,*β*-dimethylstyrene	32					8
naphthalene	23.0	1.56×10^{-11}		−117	294−366	8
biphenyl	7.1					8
Aldehydes						
formaldehyde	9.37	1.20×10^{-14}	1	−287	228−1205	16
acetaldehyde	15	4.4×10^{-12}		−365	202−348	16
propanal	20	5.1×10^{-12}		−405	240−372	16
butanal	24	6.0×10^{-12}		−410	258−422	16
2-methylpropanal	26	7.3×10^{-12}		−390	243−423	20,21
pentanal	28	9.9×10^{-11}		−310	243−410	20−23
2-methylbutanal	33					23
3-methylbutanal	27					20,23
2,2-dimethylpropanal	28	4.3×10^{-11}		−560	243−425	20,21,23
hexanal	30					22,23
2-methylpentanal	33					23
3-methylpentanal	29					23
4-methylpentanal	26					23
3,3-dimethylbutanal	21					23
2-ethylbutanal	40					23
heptanal	30					24
benzaldehyde	12					25
o-tolualdehyde	18					25
m-tolualdehyde	17					25
p-tolualdehyde	13					25
Dicarbonyls and Unsaturated Carbonyls						
glyoxal	11					16
methylglyoxal	15					16
methyl vinyl ketone	20	2.6×10^{-12}		−610	232−378	16
methacrolein	29	8.0×10^{-12}		−380	234−373	16
pinonaldehyde	44					26,27
caronaldehyde	48					26
3-isopropenyl-6-oxo-heptanal	110					28
Ketones						
acetone	0.17	g		g	202−395	16
2-butanone	1.22	2.53×10^{-18}	2	−503	240−440	16
2-pentanone	4.4					29−31
3-pentanone	2.0					29,30
3-methyl-2-butanone	2.9	1.58×10^{-12}		−193	253−372	32
2-hexanone	9.1					29,30
3-hexanone	6.9					29,30
3-methyl-2-pentanone	6.9					33
4-methyl-2-pentanone	13	7.9×10^{-13}		−834	253−372	29,30,32
3,3-dimethyl-2-butanone	1.2					29
2-heptanone	11					31
5-methyl-2-hexanone	10	1.33×10^{-12}		−649	263−372	32
2,4-dimethyl-3-pentanone	5.0					29
2-octanone	11					29
2-nonanone	12					29
2,6-dimethyl-4-heptanone	26					29
2-decanone	13					29
cyclobutanone	0.87					29
cyclopentanone	2.9					29
cyclohexanone	6.4					29
camphenilone	4.8					30
nopinone	15					28,30
sabinaketone	4.9					26
camphor	4.3					34

Table 1. (Continued)

organic	10^{12} x k (298 K) (cm^3 molecule^{-1} s^{-1})	A (cm^3 molecule^{-1} s^{-1})	n	B (K)	temperature range (K)	ref
Alcohols						
methanol	0.94	6.0×10^{-18}	2	−170	235−1205	16,35
ethanol	3.2	6.1×10^{-18}	2	−530	227−599	16,35
1-propanol	5.8	4.6×10^{-12}		−70	263−372	16
2-propanol	5.1	4.03×10^{-18}	2	−792	253−587	16
1-butanol	8.5	5.3×10^{-12}		−140	263−372	16
2-butanol	8.7					16
2-methyl-1-propanol	9.3					36
2-methyl-2-propanol	1.06	4.07×10^{-18}	2	−321	240−440	37,38
1-pentanol	11					30
2-pentanol	12					29,36,39
3-pentanol	13					29
3-methyl-1-butyl alcohol	13					36,40
3-methyl-2-butanol	12					29
2,2-dimethyl-1-propanol	5.5	h	h	h	293−764	30
1-hexanol	15					41
2-hexanol	12					29
1-heptanol	14					29,30
1-octanol	14					30
cyclopentanol	11					29
cyclohexanol	19					42
Hydroperoxides						
methyl hydroperoxide	5.5	2.9×10^{-12}		−190	223−423	16
tert-butyl hydroperoxide	3.0					30
Ethers						
dimethyl ether	2.8	1.14×10^{-17}	2	−303	230−650	16
diethyl ether	13.1	8.91×10^{-18}	2	−837	230−442	30,43
methyl *tert*-butyl ether	2.94	6.54×10^{-18}	2	−483	230−440	30,43
ethyl *tert*-butyl ether	8.7	6.70×10^{-18}	2	−800	234−372	43
tert-amyl methyl ether	6.1	7.56×10^{-18}	2	−656	231−372	43
Alkyl Nitrates						
methyl nitrate	0.023	4.0×10^{-13}		845	221−298	16
ethyl nitrate	0.18	6.7×10^{-13}		395	233−298	16
1-propyl nitrate	0.58					16
2-propyl nitrate	0.29	6.2×10^{-13}		230	233−300	16
1-butyl nitrate	1.6					16
2-butyl nitrate	0.86					16
2-methyl-1-propyl nitrate	1.5					30
1-pentyl nitrate	3.0					30
2-pentyl nitrate	1.7					29,30
3-pentyl nitrate	1.0					29,30
2-methyl-1-butyl nitrate	2.3					30
3-methyl-1-butyl nitrate	2.3					30
3-methyl-2-butyl nitrate	1.7					29,30
2,2-dimethyl-1-propyl nitrate	0.79					29,30
2-hexyl nitrate	3.0					29,30
3-hexyl nitrate	2.5					29,30
2-methyl-2-pentyl nitrate	1.6					29,30
3-methyl-2-pentyl nitrate	2.8					29,30
cyclohexyl nitrate	3.1					29,30
3-heptyl nitrate	3.4					29,30
3-octyl nitrate	3.6					29,30

[a] Data only available at room temperature and at ~1100 K (i.e., no rate data have been measured between room temperature and ~1100 K). [b] Although rate constants are available over this temperature range, no temperature-dependent rate expression is recommended.[13] [c] Because of significantly different temperature dependencies in the studies conducted, the recommended rate expression leads to a 298 K rate constant which is 10% higher than room-temperature measurements.[13] [d] Rate constant also available at 103 ± 9 K.[44] [e] Rate constants are also available at 23, 44, 75, and 170 K[45] and at 103 ± 9 K.[44] [f] Rate constants are also available at 23, 44, 75, and 170 K.[45] [g] $k = 8.8 \times 10^{-12}\, e^{-1320/T} + 1.7 \times 10^{-14}\, e^{420/T}$ cm^3 molecule^{-1} s^{-1}. [h] See ref 30 and references therein.

of alkenes and >450 K in the case of aromatic hydrocarbons).[29,30]

2.2. Reaction Mechanisms

Whereas the reaction mechanism occurring in the troposphere after initial reaction of a VOC with OH radicals, NO_3 radicals, Cl atoms, and O_3, or after photodissociation, depends on the specific VOC, in most cases the reaction mechanism involves formation (at least in part) of an alkyl or substituted alkyl radical (for example, hydroxyalkyl, nitrooxyalkyl [containing an $-ONO_2$ group], or oxoalkyl [containing

Table 2. Room-Temperature Rate Constants, Temperature-Dependent Parameters, and Temperature Ranges over Which These Data Have Been Measured for the Gas-Phase Reactions of O_3 with Alkanes, Alkenes, Aromatic Hydrocarbons, Aldehydes, Ketones, Alcohols, and Selected Unsaturated Carbonyls

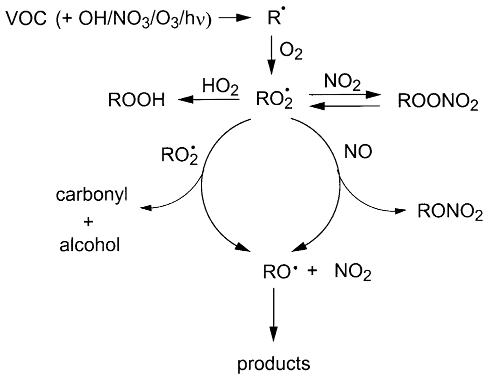
organic	10^{17} x *k* (298 K) (cm^3 $molecule^{-1}$ s^{-1})	*A* (cm^3 $molecule^{-1}$ s^{-1})	*B* (K)	temperature range (K)	ref
		Alkanes			
all alkanes	$<1 \times 10^{-6}$				14,30,46
		Alkenes			
ethene	0.159	9.14×10^{-15}	2580	178−362	14−16
propene	1.01	5.51×10^{-15}	1878	235−362	14−16
1-butene	0.964	3.36×10^{-15}	1774	225−363	14,15
cis-2-butene	12.5	3.22×10^{-15}	968	225−364	14,15
trans-2-butene	19.0	6.64×10^{-15}	1059	225−364	14,15
2-methylpropene	1.13	2.70×10^{-15}	1632	225−363	14,15
1-pentene	1.06	2.13×10^{-15}	1580	240−324	15
cis-2-pentene	13	3.7×10^{-15}	1002	278−353	47
trans-2-pentene	16	7.1×10^{-15}	1132	278−353	47
2-methyl-1-butene	1.4	4.9×10^{-15}	1741	278−353	47
3-methyl-1-butene	0.95 (293 K)				15
2-methyl-2-butene	40.3	6.51×10^{-15}	829	227−363	14,15
1-hexene	1.13	1.62×10^{-15}	1480	240−324	15
cis-2-hexene	11	3.2×10^{-15}	1017	278−353	47
trans-2-hexene	15	7.6×10^{-15}	1163	278−353	47
cis-3-hexene	14 (295 K)				15
trans-3-hexene	16 (290 K)				15
2-methyl-1-pentene	1.6				15
3-methyl-1-pentene	0.38 (286 K)				15
4-methyl-1-pentene	1.0				15
cis-3-methyl-2-pentene	45				14,15
trans-3-methyl-2-pentene	56 (299 K)				14,15
2,3-dimethyl-1-butene	1.00 (285 K)				15
3,3-dimethyl-1-butene	0.39 (285 K)				15
2,3-dimethyl-2-butene	113	3.03×10^{-15}	294	227−363	14,15
2-ethyl-1-butene	1.3				14,15
1-heptene	1.2	4.2×10^{-15}	1756	278−353	47
2,3,3-trimethyl-1-butene	0.775 (294 K)				15
1-octene	1.4				14,15
cis-4-octene	9.0 (293 K)				15
trans-4-octene	13 (290 K)				15
trans-2,5-dimethyl-3-hexene	3.8 (291 K)				15
trans-2,2-dimethyl-3-hexene	4.0 (295 K)				15
cis- and *trans*-3,4-dimethyl-3-hexene	>37 (296 K)				15
2,4,4-trimethyl-2-pentene	14 (297 K)				14,15
3-methyl-2-isopropyl-1-butene	0.30 (294 K)				15
1-decene	0.93				14,15
cis-5-decene	11 (293 K)				15
trans-5-decene	>13 (295 K)				14,15
3,4-diethyl-2-hexene	0.40 (293 K)				15
propadiene	0.0185	1.54×10^{-15}	2690	226−325	15
1,3-butadiene	0.63	1.34×10^{-14}	2283	231−324	14,15
1,3-pentadiene	4.3	2.1×10^{-15}	1158	240−324	15
1,4-pentadiene	1.45				15
2-methyl-1,3-butadiene (isoprene)	1.27	1.03×10^{-14}	1995	242−353	16
cis-2,trans−4-hexadiene	31 (294 K)				14,15
trans-2,trans−4-hexadiene	37 (294 K)				14,15
2-methyl-1,4-pentadiene	1.3				15
2-methyl-1,3-pentadiene	8.0				15
2,3-dimethyl-1,3-butadiene	2.6	6.9×10^{-15}	1668	240−324	14,15
2,4-dimethyl-1,3-butadiene	8.0				14
2,5-dimethyl-1,5-hexadiene	1.4				14,15
cis- and *trans*-1,3,5-hexatriene	2.6 (294 K)				14,15
myrcene	47 (296 K)				14,15
cis-ocimene[a]	54 (296 K)				14,15
cyclopentene	57	1.8×10^{-15}	350	240−324	14,15
1-methyl-1-cyclopentene	67				14,15
cyclohexene	8.1	2.87×10^{-15}	1063	240−324	15
1,3-cyclohexadiene	120				15
1,4-cyclohexadiene	4.6				14,15
cycloheptene	25	1.3×10^{-15}	494	240−324	15
1,3-cycloheptadiene	15				15
1,3,5-cycloheptatriene	5.4 (294 K)				14,15
1-methyl-1-cyclohexene	16	5.25×10^{-15}	1040	240−324	15
4-methyl-1-cyclohexene	8.9	2.16×10^{-15}	952	240−324	15
methylenecyclohexane	1.1 (293 K)				48
1,2-dimethyl-1-cyclohexene	20.7 (296 K)				14
vinylcyclohexane	0.75 (292 K)				48

Table 2. (Continued)

organic	10^{17} x k (298 K) (cm^3 molecule^{-1} s^{-1})	A (cm^3 molecule^{-1} s^{-1})	B (K)	temperature range (K)	ref
		Alkenes (Continued)			
bicyclo[2.2.1]-2-heptene	160				15
bicyclo[2.2.1]-2,5-heptadiene	360				15
bicyclo[2.2.2]-2-octene	7.1				15
cis-cyclooctene	38	7.8×10^{-16}	217	240−324	15
cis-cyclodecene	2.9	1.08×10^{-15}	1081	240−324	15
camphene	0.090 (296 K)				14,15
2-carene	23				14,15
3-carene	3.7				14,15
limonene	21	2.95×10^{-15}	783	296−363	14,15,49
α-phellandrene	300				15
β-phellandrene	4.7				14,15
α-pinene	8.4	5.0×10^{-16}	530	276−363	14,15,49
β-pinene	1.5	1.2×10^{-15}	1300	296−363	14,15,49
sabinene	8.3				15
α-terpinene	2100				15
γ-terpinene	14				14,15
terpinolene	190				15
α-cedrene	2.8				14,15
α-copaene	16 (296 K)				14,15
β-caryophyllene	1160 (296 K)				14,15
α-humulene	1170 (296 K)				14,15
longifolene	<0.05 (296 K)				14,15
		Aromatic Hydrocarbons			
benzene and alkylbenzenes	$<1 \times 10^{-3}$				8,30
indene	17				8
styrene	1.7				8
naphthalene	<0.02				8
biphenyl	<0.02				8
		Saturated Aldehydes, Ketones, and Alcohols			
all	$<1 \times 10^{-3}$				30,46
		Unsaturated Carbonyls			
methyl vinyl ketone	0.52	8.5×10^{-16}	1520	240−324	16
methacrolein	0.12	1.4×10^{-15}	2100	240−324	16
3-isopropenyl-6-oxo-heptanal	0.83				28

[a] Rate constant for trans isomer 10 ± 10% lower.

Scheme 1



a carbonyl, C═O, group] radicals). In general, these alkyl or substituted alkyl radicals react in the troposphere as shown in Scheme 1, with the key intermediates then being organic peroxy ($RO_2^•$) and alkoxy ($RO^•$) radicals. More detailed discussions of the specific reactions involved are given for each of the classes of VOCs discussed herein.

In the following sections, the current status of knowledge, as well as areas of uncertainty and needed future research, is discussed for the kinetics and products of the OH radical-, NO_3 radical-, and O_3-initiated reactions of alkanes, alkenes, and aromatic hydrocarbons and for selected classes of oxygenated VOCs (aldehydes, ketones, alcohols, and selected ethers) and for alkyl nitrates. No discussion is given here of the atmospheric chemistry of halogen- or sulfur-containing VOCs, which are dealt with on an ongoing basis by the NASA[64] and IUPAC[16] evaluations, and no discussion is given here of secondary organic aerosol formation.

3. Atmospheric Chemistry of Alkanes

In the troposphere, alkanes react with OH radicals and, to a much lesser extent, with NO_3 radicals (Table 4).[9,14] Alkanes do not absorb in the actinic region (i.e., at wavelengths >290 nm) and no reaction with O_3 has been observed (Tables 2 and 4).[9,14,46]

3.1. Kinetic Data for the Initial OH Radical and NO_3 Radical Reactions

Room-temperature rate constants, temperature-dependent rate parameters, and temperature ranges over which the rate expressions are applicable are given in Table 1 for the OH radical reactions and Table 3 for the NO_3 radical reactions. The rate data in Table 1 for the OH radical reactions of alkanes are from the recent review and evaluation of Atkinson.[13] Apart from the entries for methane, ethane, propane, and *n*-butane, which are from the IUPAC evaluation,[16] the data in Table 3 for the NO_3 radical

Table 3. Room-Temperature Rate Constants, Temperature-Dependent Parameters, and Temperature Ranges over Which These Data Have Been Measured for the Gas-Phase Reactions of NO_3 Radicals with Alkanes, Alkenes, Aromatic Hydrocarbons, Aldehydes, Ketones, and Alcohols

organic	*k* (298 K) (cm^3 molecule^{-1} s^{-1})	*A* (cm^3 molecule^{-1} s^{-1})	*n*	*B* (K)	temperature range (K)	ref
Alkanes						
methane	$<1 \times 10^{-18}$					14,16
ethane	$<1 \times 10^{-17}$					16
propane	$<7 \times 10^{-17}$					16
n-butane	4.59×10^{-17}	2.76×10^{-12}		3279	298−423	14,16
2-methylpropane	1.06×10^{-16}	3.05×10^{-12}		3060	296−423	14
n-pentane	8.7×10^{-17}					14
2-methylbutane	1.62×10^{-16}	2.99×10^{-12}		2927	296−523	14
n-hexane	1.1×10^{-16}					14
2-methylpentane	1.8×10^{-16}					14
3-methylpentane	2.2×10^{-16}					14
2,3-dimethylbutane	4.4×10^{-16}					14
n-heptane	1.5×10^{-16}					14
2,4-dimethylpentane	1.5×10^{-16}					14
2,2,3-trimethylbutane	2.4×10^{-16}					14
n-octane	1.9×10^{-16}					14
2,2,4-trimethylpentane	9×10^{-17}					14
2,2,3,3-tetramethylbutane	$<5 \times 10^{-17}$					14
n-nonane	2.3×10^{-16}					14
n-decane	2.8×10^{-16}					14
cyclohexane	1.4×10^{-16}					14
Alkenes						
ethene	2.05×10^{-16}	4.88×10^{-18}	2	2282	295−523	14−16
propene	9.49×10^{-15}	4.59×10^{-13}		1156	296−423	14−16
1-butene	1.35×10^{-14}	3.14×10^{-13}		938	232−437	14,15
cis-2-butene	3.52×10^{-13}					15
trans-2-butene	3.90×10^{-13}	1.22×10^{-18}	2	−382	204−378	14,15
2-methylpropene	3.44×10^{-13}					15
1-pentene	1.5×10^{-14}					50
2-methyl-2-butene	9.37×10^{-12}					14,15
1-hexene	1.8×10^{-14}					50
2,3-dimethyl-2-butene	5.72×10^{-11}					14,15
2-ethyl-1-butene	4.52×10^{-13}					51
1-heptene	2.0×10^{-14}					50
1,3-butadiene	1.0×10^{-13}					14,15
2-methyl-1,3-butadiene (isoprene)	7.0×10^{-13}	3.15×10^{-12}		450	251−381	16
2,3-dimethyl-1,3-butadiene	1.4×10^{-12}					51
cis-1,3-pentadiene	1.4×10^{-12}					14,15
trans-1,3-pentadiene	1.6×10^{-12}					14,15
trans-2, *trans*-4-hexadiene	1.6×10^{-11}					14,15
myrcene	1.1×10^{-11}					14,15
ocimene (*cis*- and *trans*-)	2.2×10^{-11}					14,15
cyclopentene	4.2×10^{-13}					51,52
cyclohexene	5.1×10^{-13}			~ 0	267−349	51,53,54
1,3-cyclohexadiene	1.15×10^{-11}					15
1,4-cyclohexadiene	6.6×10^{-13}					14,15
cycloheptene	5.1×10^{-13}					51,52
1,3-cycloheptadiene	6.5×10^{-12}					14,15
1,3,5-cycloheptatriene	1.2×10^{-12}					14,15
1-methyl-1-cyclohexene	1.0×10^{-11}			~ 0	265−371	51,54
methylenecyclopropane	1.49×10^{-14}					51
methylenecyclobutane	4.21×10^{-13}					51
methylenecyclopentane	1.52×10^{-12}					51
methylenecyclohexane	5.38×10^{-13}					51
methylenecycloheptane	1.01×10^{-12}					51
3-methylene-cyclohexene	5.72×10^{-12}					51
1,2-dimethyl-1-cyclohexene	5.15×10^{-11}					51
2,3-dimethyl-1-cyclohexene	1.54×10^{-11}					51
bicyclo[2.2.1]-2-heptene	2.5×10^{-13}					14,15
bicyclo[2.2.1]-2,5-heptadiene	1.0×10^{-12}					14,15
bicyclo[2.2.2]-2-octene	1.45×10^{-13}					14,15
camphene	6.6×10^{-13}					14,15
2-carene	1.9×10^{-11}					14,15
3-carene	9.1×10^{-12}					14,15
limonene	1.22×10^{-11}					14,15
α-phellandrene	7.3×10^{-11}					14,15
β-phellandrene	8.0×10^{-12}					14,15
α-pinene	6.16×10^{-12}	1.19×10^{-12}		−490	261−384	14,15
β-pinene	2.51×10^{-12}					14,15
sabinene	1.0×10^{-11}					14,15
α-terpinene	1.4×10^{-10}					14,15

Table 3. (Continued)

organic	*k* (298 K) (cm^3 molecule^{-1} s^{-1})	*A* (cm^3 molecule^{-1} s^{-1})	*n*	*B* (K)	temperature range (K)	ref
Alkenes (Continued)						
γ-terpinene	2.9×10^{-11}					14,15
terpinolene	9.7×10^{-11}					14,15
α-cedrene	8.2×10^{-12}					14,15
α-copaene	1.6×10^{-11}					14,15
β-caryophyllene	1.9×10^{-11}					14,15
α-humulene	3.9×10^{-11}					14,15
longifolene	6.8×10^{-13}					14,15
isolongifolene	3.9×10^{-12}					55
alloisolongifolene	1.4×10^{-12}					55
α-neoclovene	8.2×10^{-12}					55
Aromatic Hydrocarbons						
benzene	$<3 \times 10^{-17}$					15
toluene	7.0×10^{-17}					15
ethylbenzene	$<6 \times 10^{-16}$					15
o-xylene	4.1×10^{-16}					15
m-xylene	2.6×10^{-16}					15
p-xylene	5.0×10^{-16}					15
4-ethyltoluene	8.6×10^{-16}					15
1,2,3-trimethylbenzene	1.9×10^{-15}					15
1,2,4-trimethylbenzene	1.8×10^{-15}					15
1,3,5-trimethylbenzene	8.8×10^{-16}					15
4-isopropyltoluene	1.0×10^{-15}					15
indan	7.3×10^{-15}					15
tetralin	8.5×10^{-15}					15
indene	4.1×10^{-12}					15
styrene	1.5×10^{-12}					15
Aldehydes						
formaldehyde	5.6×10^{-16}					16
acetaldehyde	2.7×10^{-15}	1.4×10^{-12}		1860	264−374	16
propanal	6.5×10^{-15}					16
butanal	1.1×10^{-14}	1.7×10^{-12}		1500	267−322	16
2-methylpropanal	1.1×10^{-14}	3.6×10^{-12}		1724	267−332	23,56,57
pentanal	1.5×10^{-14}					22,23,56
2-methylbutanal	2.7×10^{-14}					23
3-methylbutanal	1.9×10^{-14}					23
2,2-dimethylpropanal	2.4×10^{-14}					23,56
hexanal	1.6×10^{-14}					22,23,56,58
2-methylpentanal	2.7×10^{-14}					23
3-methylpentanal	2.4×10^{-14}					23
4-methylpentanal	1.7×10^{-14}					23
2-ethylbutanal	4.5×10^{-14}					23
3,3-dimethylbutanal	1.8×10^{-14}					23,58
heptanal	1.9×10^{-14}					58
octanal	1.7×10^{-14}					58
nonanal	2.0×10^{-14}					58
decanal	2.2×10^{-14}					58
benzaldehyde	2.4×10^{-15}					15
Dicarbonyls and Unsaturated Carbonyls						
methyl vinyl ketone	$<6 \times 10^{-16}$					16
methacrolein	3.4×10^{-15}					16
pinonaldehyde	2.0×10^{-14}					26
caronaldehyde	2.5×10^{-14}					26
3-isopropenyl-6-oxo-heptanal	2.6×10^{-13}					28
Ketones						
acetone	$<3 \times 10^{-17}$					16
nopinone	$<2 \times 10^{-15}$					28
sabinaketone	$<6 \times 10^{-16}$					26
camphor	$<3 \times 10^{-16}$					34
Alcohols						
methanol	1.3×10^{-16}	9.4×10^{-13}		2650	258−367	16
ethanol	$<2 \times 10^{-15}$					16
2-propanol	1.4×10^{-15}					16
2-butanol	2.1×10^{-15}					16

reactions of alkanes have not been critically evaluated.[14] Clearly, the kinetic database for the OH radical reactions is significantly larger than that for the NO_3 radical reactions, with no rate constants having been measured to date for the NO_3 radical reactions below 296 K (Table 3).

As may be anticipated, the kinetic database for the OH radical reactions (the dominant tropospheric transformation process for alkanes) varies significantly from alkane to alkane. The smaller $\leq C_5$ alkanes (methane, ethane, propane, *n*-butane, 2-methylpropane, and *n*-pentane) have been studied

Table 4. Calculated Lower Tropospheric Lifetimes (at 298 K) for Selected VOCs[a]

VOC	OH	NO_3	O_3
propane	11 d	>1.8 yr	>4500 yr
2,2,4-trimethylpentane	3.5 d	1.4 yr	>4500 yr
n-octane	1.4 d	240 d	>4500 yr
ethene	1.4 d	225 d	10 d
propene	5.3 h	4.9 d	1.6 d
isoprene	1.4 h	48 min	1.3 d
α-pinene	2.7 h	5.4 min	4.7 hr
benzene	9.5 d	>4 yr	>4.5 yr
toluene	2.1 d	1.8 yr	>4.5 yr
1,2,4-trimethylbenzene	4.3 h	26 d	>4.5 yr
o-cresol	3.4 h	2.4 min	55 d
formaldehyde[b]	1.2 d	83 d	>4.5 yr
acetone[b]	68 d	>4 yr	
ethanol	3.6 d	>23 d	
methyl *tert*-butyl ether	3.9 d	64 d	

[a] The 298 K rate constants are taken from Tables 1−3, except for those for *o*-cresol which are from Calvert et al.[8] and that for reaction of NO_3 radicals with methyl *tert*-butyl ether which is from Langer and Ljungström.[59] Lifetime calculated using the following: for OH radical reactions, a 12-h daytime average of 2.0×10^6 molecule cm^{-3}; for NO_3 radical reactions, a 12-h nighttime average of 5×10^8 molecule cm^{-3}; and for O_3, a 24-h average of 7×10^{11} molecule cm^{-3}. [b] Also undergo photolysis, with estimated lifetimes due to photolysis of ~4 h for formaldehyde with overhead sun, and ~60 d for acetone.[9]

numerous times using absolute or both absolute and relative rate methods, and rate constants are available over wide temperature ranges (see Table 1), including down to temperatures representative of the upper troposphere/lower stratosphere in a few cases. In contrast, rate constants for the larger $\geq C_6$ alkanes and for cycloalkanes have generally been studied only at room temperature and above, and often using mainly, or only, relative rate methods. This difference in the quantity and quality of rate data for the reactions of the OH radical with the smaller alkanes versus the larger alkanes is illustrated by the Arrhenius plots shown in Figure 1 for the reactions of OH radicals with propane, where only the more recent data[13] are shown, and 2,2,4-trimethylpentane, where all of the available data[13] are shown. Particularly obvious is that the propane reaction has been studied down to 190 K, whereas the 2,2,4-trimethylpentane reaction has not been studied below room temperature, and the numerous rate constant measurements for propane compared to only three studies for 2,2,4-trimethylpentane.[13] Also illustrated by Figure 1 is that for alkanes there is generally excellent agreement between relative rate measurements and absolute rate measurements.[13]

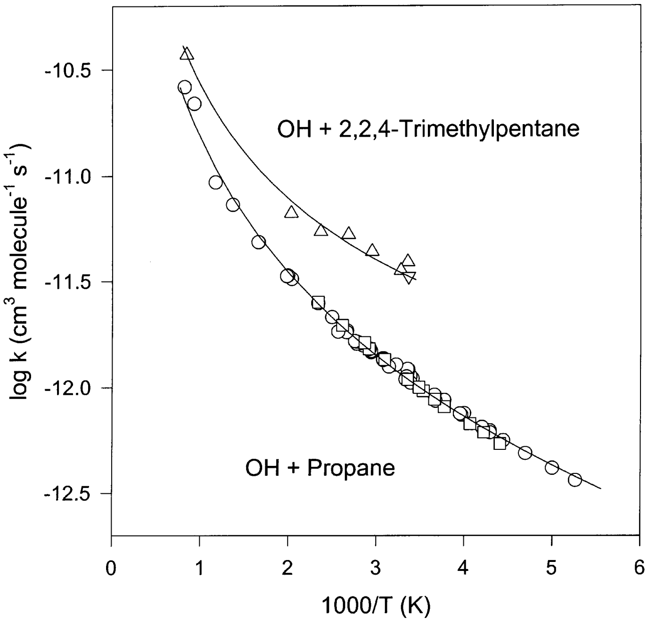


Figure 1. Arrhenius plot of rate constants for the reactions of OH radicals with propane and 2,2,4-trimethylpentane. The rate data used are those used by Atkinson[13] for evaluation of the rate constants for these reactions; (Δ, ○) absolute rate data; (□, ∇) relative rate data.

3.2. Reaction Mechanism

For alkanes the initial reaction with OH and NO_3 radicals proceeds by initial H-atom abstraction, and the subsequent reactions in the troposphere are shown in Scheme 1. As indicated schematically, under tropospheric conditions alkyl ($R^\bullet$) radicals react only with O_2 to form the corresponding alkyl peroxy ($RO_2^\bullet$) radical.[14−16,64]

$$R^\bullet + O_2 (+ M) \rightarrow RO_2^\bullet (+ M) \qquad (1)$$

3.2.1. Reactions of Organic Peroxy ($RO_2^\bullet$) Radicals

In the troposphere, organic peroxy radicals react with NO, NO_2, HO_2 radicals, organic peroxy radicals, and NO_3 radicals, as shown, for example, for $RCH_2O_2^\bullet$.

$$RCH_2O_2^\bullet + NO \rightarrow RCH_2O^\bullet + NO_2 \qquad (2a)$$

$$RCH_2O_2^\bullet + NO (+ M) \rightarrow RCH_2ONO_2 (+ M) \qquad (2b)$$

$$RCH_2O_2^\bullet + NO_2 (+ M) \rightarrow RCH_2OONO_2 (+ M) \qquad (3)$$

$$RCH_2O_2^\bullet + HO_2 \rightarrow RCH_2OOH + O_2 \qquad (4a)$$

$$RCH_2O_2^\bullet + HO_2 \rightarrow RCHO + H_2O + O_2 \qquad (4b)$$

$$RCH_2O_2^\bullet + RCH_2O_2^\bullet \rightarrow RCH_2O^\bullet + RCH_2O^\bullet + O_2 \qquad (5a)$$

$$RCH_2O_2^\bullet + RCH_2O_2^\bullet \rightarrow RCHO + RCH_2OH + O_2 \qquad (5b)$$

$$RCH_2O_2^\bullet + NO_3 \rightarrow RCH_2O^\bullet + NO_2 + O_2 \qquad (6)$$

These reactions, or subsets of these reactions, have been reviewed and evaluated previously,[65−69] and the reactions of the $\leq C_3$ alkyl peroxy radicals are included in the ongoing NASA[64] and IUPAC[16] evaluations (the IUPAC evaluation[16] also includes selected C_4 alkyl peroxy radicals).

Rate constants for the reactions of a number of alkyl peroxy radicals with NO have been measured using absolute rate methods,[14,16,70−72] and room-temperature rate constants and temperature-dependent parameters are listed in Table 5. For the $\geq C_2$ alkyl peroxy radicals formed from alkanes the rate constants are essentially identical, with $k_2 = 2.7 \times$

Table 5. Room-Temperature Rate Constants and Temperature-Dependent Parameters for the Gas-Phase Reactions of Alkyl Peroxy ($RO_2^•$) Radicals with NO

$RO_2^•$ radical	$10^{12} \times k$ (298 K) (cm^3 $molecule^{-1}$ s^{-1})	$10^{12} \times A$ (cm^3 $molecule^{-1}$ s^{-1})	B (K)	temperature range (K)	ref
methyl peroxy	7.7	2.95	−285	199−429	16
ethyl peroxy	9.2	2.6	−380	207−403	16
1-propyl peroxy	9.4	2.9	−350	201−402	16
2-propyl peroxy	9.0	2.7	−360	201−401	16
tert-butyl peroxy	7.9				70
2-pentyl peroxy	8.0				70
2,2-dimethyl-1-propyl peroxy	4.7				71
2,2,3,3-tetramethyl-1-butyl peroxy	1.8				71
cyclopentyl peroxy	10.9				70
cyclohexyl peroxy	6.7				72

Table 6. Room-Temperature Rate Constants and Temperature-Dependent Parameters for the Gas-Phase Reactions of Alkyl Peroxy ($RO_2^•$) Radicals with HO_2 Radicals

$RO_2^•$ radical	$10^{12} \times k$ (298 K) (cm^3 $molecule^{-1}$ s^{-1})	$10^{13} \times A$ (cm^3 $molecule^{-1}$ s^{-1})	B (K)	temperature range (K)	ref
methyl peroxy	5.2	3.8	−780	228−573	16
ethyl peroxy	7.7	3.8	−900	210−480	16
2,2-dimethyl-1-propyl peroxy	15	1.43	−1380	248−365	88
cyclopentyl peroxy	17	2.6	−1240	214−364	89,90
cyclohexyl peroxy	17	2.6	−1245	249−364	89

10^{-12} $e^{360/T}$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range ∼200−400 K and $k_2 = 9.0 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.[14] Less data are available for the branching ratios k_{2b}/k_2,[72−85] especially at other than room temperature and atmospheric pressure.[75,77−79,82,83] For the reactions of secondary alkyl peroxy radicals, $RCH(OO^•)R'$, with NO, the alkyl nitrate yields at room temperature and atmospheric pressure of air increase with increasing carbon number[74,75,79,84] (see also the discussion of products below). On the basis of the small amount of data available, the alkyl nitrate yields from the reactions of NO with primary, $RCH_2O_2^•$, and tertiary, $RR'R''CO_2^•$, alkyl peroxy radicals appear to be lower than that for a secondary alkyl peroxy radical of the same carbon number.[76,77] For the alkyl nitrates formed from the OH radical-initiated reactions of *n*-pentane,[75] *n*-heptane,[75,78] 2,2-dimethyl-2-propane,[77] 2-methylbutane,[77] and 3-methylpentane,[77] the yields increase with decreasing temperature[75,77−79] and with increasing pressure.[75,77,79]

The reactions of $RO_2^•$ radicals with NO_2 form peroxynitrates ($ROONO_2$, R = alkyl) which decompose rapidly, with lifetimes of typically 0.1−1 s at 298 K and atmospheric pressure.[16,86,87] However, the decomposition lifetimes are significantly longer at temperatures representative of elevated altitudes, being ∼2 days at 215 K for cyclohexyl peroxynitrate.[87] Reactions of $RO_2^•$ radicals with HO_2 and organic peroxy radicals have been measured for a rather small number of the simpler alkyl peroxy radicals, and Table 6 gives the room-temperature rate constants and temperature-dependent parameters for reactions of HO_2 radicals with alkyl peroxy radicals formed from alkanes. As shown in Table 6, measured rate constants for the $RO_2^• + HO_2$ reactions exhibit a negative temperature dependence, with an approximate (to a factor of ∼2) rate constant for the larger, $\geq C_3$, $RO_2^•$ radicals of $k_4 = 1.9 \times 10^{-13}$ $e^{1300/T}$ cm^3 $molecule^{-1}$ s^{-1}, with $k_4 = 1.5 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.[14] Rate constants for the self- and cross-reactions of the simpler organic peroxy radicals have been recently reviewed by Tyndall et al.[69] and are evaluated on an ongoing basis by the NASA[64] and IUPAC[16] data evaluations. Kinetic and product data for the reactions of alkyl peroxy radicals with the NO_3 radical are available only for the $CH_3O_2^•$ and $C_2H_5O_2^•$ radicals.[16]

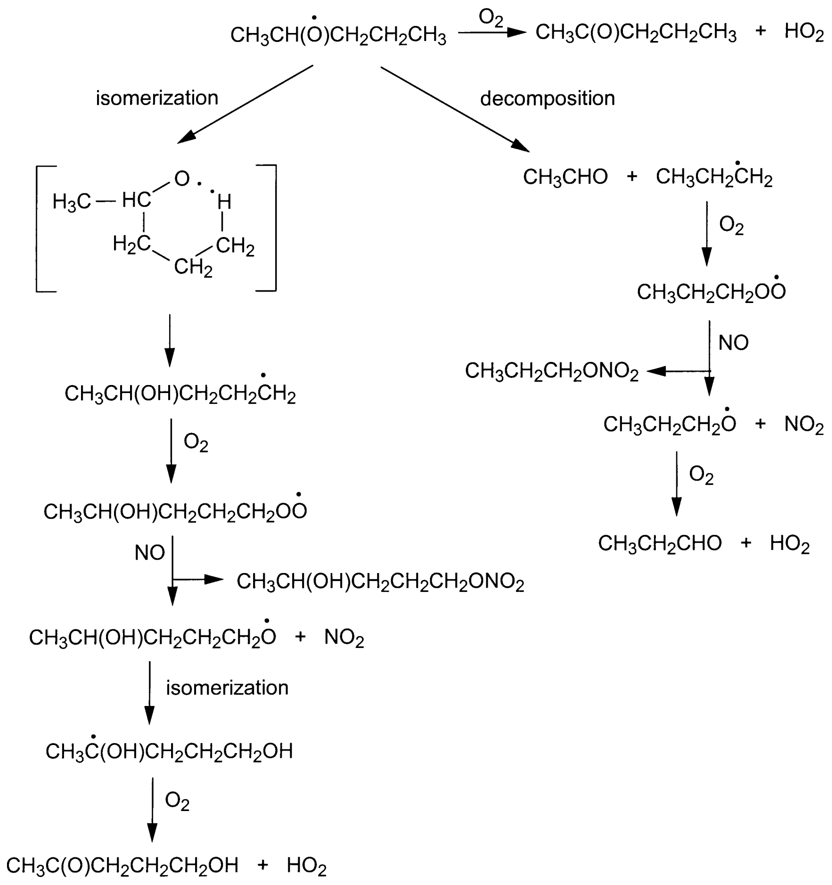
Clearly, given the large number of alkyl peroxy radicals present in the atmosphere, the present database concerning their reactions is sparse. The reactions of alkyl peroxy radicals (and organic peroxy radicals in general) lead through reactions (2−6) to the formation, at least in part, of the corresponding alkoxy radical. As evident from Figure 1, at NO concentrations such that $RO_2^•$ radicals react dominantly with NO, then the key intermediate(s) in the oxidation of organic compounds are the alkoxy radicals. Reactions of $RO_2^•$ radicals with NO dominate over other $RO_2^•$ radical reactions for NO mixing ratios >10−30 parts-per-trillion (ppt; corresponding to NO concentrations of $>(2-7) \times 10^8$ molecule cm^{-3} at ground level).[91]

3.2.2. Reactions of Alkoxy ($RO^•$) Radicals

Under tropospheric conditions, alkoxy radicals react by one or more of four pathways.[9] The majority of alkoxy radicals can potentially undergo reaction with O_2, unimolecular decomposition, and unimolecular isomerization,[92] as shown in Scheme 2 for the 2-pentoxy radical formed from *n*-pentane. In addition to the three reaction pathways shown in Scheme 2, alkoxy radicals of structure $RC(O)OCH(O^•)R'$ formed from esters can undergo isomerization proceeding through a five-membered transition state,[93,94] as shown in Scheme 3.

The database from absolute rate methods concerning the reactions of alkoxy radicals is sparse. For the reactions with O_2, rate constants are available from absolute rate studies only for methoxy, ethoxy, 1- and 2-propoxy, 1- and 2-butoxy, and 3-pentoxy radicals

Scheme 2



Scheme 3

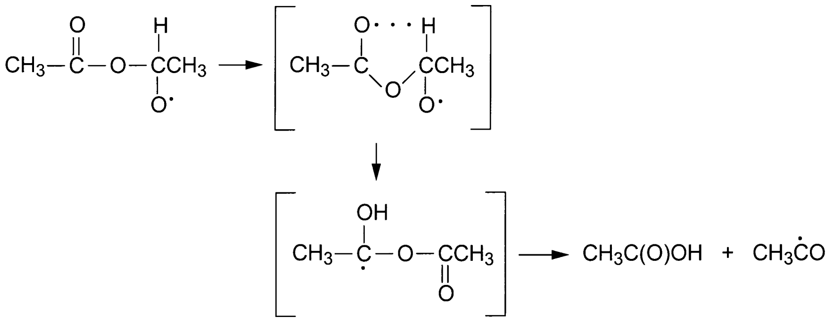


Table 7. Absolute Rate Data for the Reactions of O_2 with Alkoxy (RO•) Radicals

RO• radical	$10^{15} \times k$ (298 K) (cm^3 molecule^{-1} s^{-1})	$10^{14} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	temperature range (K)	ref
methoxy	1.9	7.2	1080	298–610	16
ethoxy	8.1	2.4	325	295–354	95,96
1-propoxy	11	2.4	235	223–381	96,97
2-propoxy	7.1	1.5	225	218–384	96–98
1-butoxy	14 ± 7			293	99
2-butoxy	6.5 ± 2			293	100
	12 ± 4	0.133	−659 ± 83	223–311	101
	7.7	0.12	−553 ± 193	221–266	102
3-pentoxy	7.2 ± 3.5			293	103
	12 ± 6	0.41	−319	220–285	102

(Table 7). The studies of Zellner and co-workers[97,99,100,103] are somewhat indirect in that the alkoxy radical reaction rate constants were obtained from fitting to an assumed mechanism the OH radical and NO_2 time–concentration profiles observed after pulsed formation of the parent alkyl radical. For the 2-butoxy and 3-pentoxy radical reactions, there are up to factor of 2 discrepancies in the room-temperature rate constants obtained from the studies of Hein et al.[100,103] and Deng et al.[101,102] For the 2-butoxy and 3-pentoxy radicals, Deng et al.[101,102] obtained negative temperature dependencies, in contrast to the small positive temperature dependencies for the ethoxy,[95,96] 1-propoxy,[96,97] and 2-propoxy[96–98] radical reactions,

Table 8. Rate Constants from Absolute Studies for Alkoxy (RO$^\bullet$) Radical Decomposition and Isomerization

RO$^\bullet$ radical	k (s^{-1}) at 298 K	E/R (K)	temperature range (K)	ref
ethoxy	5 (k_∞)	8456	391−471	104
2-propoxy	8.2×10^2 (k_∞)	7662	330−408	105
1-butoxy	$(3.5 \pm 2) \times 10^{4\,a}$		293 (37.5 Torr)	99
2-butoxy	$(3.5 \pm 2) \times 10^3$		293 (37.5 Torr)	100
1-pentoxy	$\geq 1.0 \times 10^{5\,a}$		293 (37.5 Torr)	99
3-pentoxy	$(5.0 \pm 2.5) \times 10^3$		293 (37.5 Torr)	103
tert-butoxy	1.4×10^3 (k_∞)	6856	303−393	106
	2.5×10^3 (k_∞)	7277	323−383	107

[a] Attributed to isomerization.[99]

Table 9. Comparison of Measured Rate Constant Ratios from Product Studies Conducted at Atmospheric Pressure with Ratios Calculated from Individual Rate Constants

RO$^\bullet$ radical	rate constant ratio at T (K) and P (Torr)	from	ref
Decomposition	$k_{\text{decomp}}/k_{\text{O2}}$ (molecule cm^{-3})		
2-butoxy	3.1×10^{18} (303 K, 740 Torr)	products	110
	$(2.60 \pm 0.35) \times 10^{18}$ (296 K, 760 Torr)	products	111
	$(2.3 \pm 0.5) \times 10^{18}$ (298 K, 750 Torr)	products	112
	5.4×10^{17} (293 K, 37.5 Torr)	rate data	100
3-pentoxy	3.3×10^{18} (296 K, 740 Torr)	products	80
	6.9×10^{17} (293 K, 37.5 Torr)	rate data	103
Isomerization	$k_{\text{isomer}}/k_{\text{O2}}$ (molecule cm^{-3})		
1-butoxy	1.6×10^{19} (303 K, 740 Torr)	products	110
	$(1.5 \pm 0.5) \times 10^{19}$ (296 K, 760 Torr)	products	111
	$(1.9 \pm 0.2) \times 10^{19}$ (298 K, 700 Torr)	products	113
	2.5×10^{18} (293 K, 37.5 Torr)	rate data	99

despite the general similarity in the room-temperature rate constants (Table 7).

As shown in Table 8, absolute rate constants for the decomposition and isomerization of alkoxy radicals are available only for the decomposition of ethoxy, 2-propoxy, 2-butoxy, *tert*-butoxy, and 3-pentoxy radicals, and for the isomerization of 1-butoxy and 1-pentoxy radicals. Note that the experimental study of Hein et al.[99] did not provide direct evidence for isomerization versus decomposition. The studies of Hein et al.[99,100,103] were conducted at 37.5 Torr total pressure, and theoretical calculations[108,109] indicate that the measured rate constants at 37.5 Torr total pressure for the decomposition and isomerization reactions are in the falloff region under these conditions, being lower than those at 760 Torr of air by factors of ~5.[109] Under atmospheric conditions, decompositions of the ethoxy and 2-propoxy radicals are of no importance, because the O_2 reaction dominates.

The bulk of the present database concerning alkoxy radical reactions arises from product studies, from which rate constant ratios of $k_{\text{decomp}}/k_{\text{O2}}$ or $k_{\text{isomer}}/k_{\text{O2}}$ are derived.[92] Table 9 compares ratios of $k_{\text{decomp}}/k_{\text{O2}}$ or $k_{\text{isomer}}/k_{\text{O2}}$ derived from product studies carried out at room temperature and atmospheric pressure of air with ratios calculated from absolute rate data for the individual reactions carried out at 37.5 Torr total pressure. Because the rate constants measured at 293 K and 37.5 Torr total pressure[99,100,103] for the decomposition and isomerization reactions are in the falloff region,[109] there are significant differences between the two "sets" of data. Clearly, accurate knowledge of the relative importance of the various alkoxy radical reaction pathways is needed to correctly predict the products formed from VOC photooxidations (see, for example, Scheme 2). In addition to forming different reaction products, by breaking the carbon skeleton in the decomposition reaction while maintaining it in isomerization and reaction with O_2 (but generally forming multifunctional hydroxycarbonyl products from the isomerization pathway), the three alkoxy radical pathways lead to differing amounts of NO converted to NO_2 and hence differing amounts of O_3 formed.

An additional degree of complexity for alkoxy radical decompositions (and potentially isomerizations) arises from observations that a fraction of certain alkoxy radicals (for example, $CF_3CHFO^\bullet$ [114] and $HOCH_2CH_2O^\bullet$ [115]) formed from the $RO_2^\bullet$ + NO reaction, which is exothermic by ~10−11 kcal mol^{-1},[16] are chemically activated and undergo "prompt" decomposition.[114,115] In contrast, alkoxy radicals formed from the self- or cross-reactions of $RO_2^\bullet$ radicals, which is slightly endothermic for simple $RO_2^\bullet + RO_2^\bullet \rightarrow RO^\bullet + RO^\bullet + O_2$ reactions,[16] are thermalized. As an example of this chemical activation, ~25% of the $HOCH_2CH_2O^\bullet$ radicals formed from the OH radical-initiated reaction of ethene in the presence of NO undergo "prompt" decomposition, independent of temperature.[115] This "prompt" decomposition of alkoxy radicals formed from the exothermic $RO_2^\bullet$ + NO reaction appears to be important for alkoxy radicals with a barrier to decomposition of approximately 9 kcal mol^{-1} or less,[82] and for alkoxy radicals with higher barriers to decomposition (such as the cyclohexoxy radical[82] with a barrier to decomposition of 11.5 ± 2.2 kcal mol^{-1}) prompt decomposition is unimportant. For the 2-butoxy radical, with a measured barrier to decomposition of 11.3 kcal mol^{-1},[112] Libuda et al.[112] observed ~8% of the 2-butoxy radicals formed from the $RO_2^\bullet$ + NO reaction to undergo "prompt" decomposition over the temperature range 280−313 K. "Prompt" decomposition would have also occurred in the Carter et al.[110] and Cox et al.[111]

Table 10. Measured Formation Yields (%) of Carbonyls (from Alkoxy Radical Decompositions and Reactions with O_2), Alkyl Nitrates, 1,4-Hydroxycarbonyls, and Hydroxyalkyl Nitrates from the OH Radical-Initiated Reactions of C_4-C_8 *n*-Alkanes at Room Temperature and Atmospheric Pressure of Air

product class	*n*-butane[a]	*n*-pentane[b]	*n*-hexane[c]	*n*-heptane[c]	*n*-octane[c]
carbonyls[d]	83	47	10[e]	≤1[e]	≤1[e]
alkyl nitrates	7.7	10.5	14.1	17.8	22.6
hydroxycarbonyls		36	53	46	27
hydroxyalkyl nitrates		2.6	4.6	4.7	5.4
total	91	96^{+40}_{-20}	82^{+55}_{-30}	69^{+50}_{-25}	55^{+30}_{-15}

[a] From Cox et al.[111] (carbonyl products) and Atkinson et al.[74] (alkyl nitrates). [b] From Atkinson et al.[80] and Arey et al.[84] [c] From Arey et al.[84] [d] Carbonyls are formed from the alkoxy radical reactions with O_2 and from alkoxy radical decompositions (see text and Scheme 2). Yields refer to product carbon. [e] From Kwok et al.[120]

studies and this could be the reason for the slightly higher rate constant ratios of $k_{decomp.}/k_{O2}$ obtained in these studies[110,111] compared to that of Libuda et al.[112] in which the "prompt" decomposition was taken into account (see Table 9). It is also possible that a similar "prompt" isomerization of chemically activated alkoxy radicals may occur for alkoxy radicals formed from the $RO_2^• + NO$ reaction.[116,117]

For thermalized alkoxy radicals, the rates of decomposition and isomerization are significantly temperature dependent, and hence the dominant atmospheric reaction pathway (decomposition, isomerization, and reaction with O_2) can change with increasing altitude, as observed for the cyclohexoxy radical.[82] For example, at 298 K and atmospheric pressure of air the reaction rates of the 2-pentoxy radical are estimated[92,109] to be the following: reaction with O_2, 4.1×10^4 s^{-1}; decomposition, $(1.0-1.7) \times 10^4$ s^{-1}; and isomerization, $(2-5) \times 10^5$ s^{-1}. At 220 K and 100 Torr total pressure, the rates are estimated[92] (see also Somnitz and Zellner[109]) to be the following: reaction with O_2, 5.6×10^3 s^{-1}; decomposition, 4 s^{-1}; and isomerization, 1.4×10^3 s^{-1}. This results in a predicted changeover from mainly isomerization in the lower troposphere to mainly reaction with O_2 in the upper troposphere. However, the occurrence of a significant fraction of a given alkoxy radical undergoing "prompt" decomposition (or isomerization) could significantly change this picture.

As noted above, for some of the simpler alkyl, alkyl peroxy, and alkoxy radicals the reactions involved in Scheme 1 have been studied directly (see the IUPAC[16] and NASA[64] evaluations and Tables 5−8). However, the majority of the data concerning the first-generation products arise from end-product analyses carried out at room temperature and atmospheric pressure of air.[14,72−82,84,85,110−113,118−122] As shown in Schemes 1 and 2, the first-generation products from the OH radical-initiated reactions of alkanes in the presence of NO are alkyl nitrates ($RONO_2$) formed from the $RO_2^• + NO$ reaction, where R = alkyl, (reaction 2b); carbonyls (aldehydes or ketones) formed from the $RO^• + O_2$ reaction and $RO^•$ decomposition; and hydroxyalkyl nitrates and hydroxycarbonyls formed after $RO^•$ isomerization (see Scheme 2). Note that even if the 1,4-hydroxyalkoxy radical formed after the first isomerization (Scheme 2) cannot undergo a second isomerization, it is likely that hydroxycarbonyl products containing the same or fewer carbon atoms as the alkane reactant will still be formed.

Until 1995 there was no direct evidence for the occurrence of alkoxy radical isomerization at room temperature and below; rather the occurrence of this reaction was inferred from the lack of a product carbon balance.[110,111,113] During the past decade, hydroxycarbonyls have been observed from (a) the OH radical-initiated reaction of *n*-hexane and the photolysis of 2-hexyl nitrite by derivatizing the carbonyl group using 2,4-dinitrophenyl hydrazine and analyzing the 2,4-dinitrophenylhydrazone by GC−MS;[119] (b) from the OH radical-initiated reactions of *n*-pentane through *n*-octane using in situ atmospheric pressure ionization mass spectrometry (APIMS), as the protonated molecular ion $[M + H]^+$ and the fragment ion $[M + H - H_2O]^+$, and as the NO_2^- adduct;[80,84,85,120,121] and (c) from the OH radical-initiated reactions of *n*-pentane through *n*-octane using solid-phase microextraction (SPME) fibers coated with *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride for on-fiber derivatization of the carbonyl group to form an oxime which can be readily analyzed by gas chromatography.[122] Reisen et al.[122] have observed, using SPME with on-fiber derivatization and GC−MS analyses, the formation of each of the 1,4-hydroxycarbonyls expected after initial H-atom abstraction from the various CH_3 and CH_2 groups in the *n*-pentane through *n*-octane reactions, carried out in the presence of NO such that $RO_2^•$ radicals reacted with NO.

Table 10 shows product yields obtained from the reactions of OH radicals with C_4-C_8 *n*-alkanes in the presence of NO. Clearly, the yield of carbonyl compounds formed from reactions of the alkoxy radicals with O_2 and decomposition decreases markedly with increasing carbon number in the *n*-alkane series, and for the $\geq C_7$ *n*-alkanes alkoxy radical isomerization totally dominates over decomposition and reaction with O_2, at least at room temperature and atmospheric pressure of air.[84,85,120] Although the measurements of the yields of hydroxycarbonyls arising after alkoxy radical isomerization have large associated uncertainties (a factor of ∼2),[84,85] hydroxycarbonyl formation is clearly important for the larger *n*-alkanes. In fact, for *n*-heptane, *n*-octane, and *n*-decane, the only products observed were the alkyl nitrates formed from the reaction of NO with the initially formed alkyl peroxy radicals, together with hydroxyalkyl nitrates and hydroxycarbonyls formed from alkoxy radical isomerization.[84,85] The <100% product yields for the larger *n*-alkanes shown in Table 10 could be due to a number of things, includ-

Table 11. Room-Temperature Rate Constants for the Reactions of 5-Hydroxy-2-pentanone and 4,5-Dihydro-2-methylfuran

	room-temperature rate constant (cm^3 molecule^{-1} s^{-1})	
reaction with	5-hydroxy-2-pentanone[a]	4,5-dihydro-2-methylfuran[b]
OH radicals	$(1.6 \pm 0.4) \times 10^{-11}$	$(2.18 \pm 0.11) \times 10^{-10}$
NO_3 radicals		$(1.68 \pm 0.12) \times 10^{-10}$
O_3		$(3.49 \pm 0.24) \times 10^{-15}$

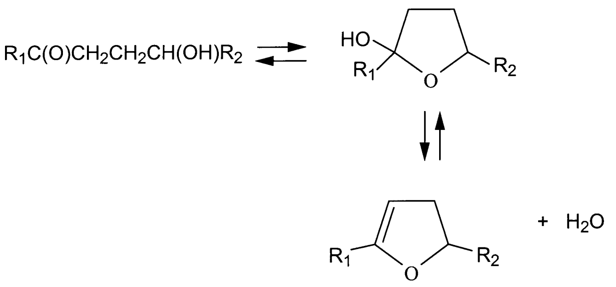
[a] From Aschmann et al.[125] [b] From Martin et al.[124]

ing losses of products to the chamber walls (being more important for the larger and less volatile species), an incorrect assumption that the APIMS response factor for 5-hydroxy-2-pentanone is applicable to the larger 1,4-hydroxycarbonyls, and cyclization of 1,4-hydroxycarbonyls with loss of water (see below) becoming more important for the larger 1,4-hydroxycarbonyls. Clearly, more quantitative, and isomer-specific, product data are needed.

For branched alkanes, at room-temperature, decomposition of the intermediate alkoxy radicals can compete with isomerization[85,121] (and in some cases isomerization is not feasible due to a lack of an H-atom attached to the 4-position carbon atom, relative to the carbon atom to which the alkoxy O is attached). Carbonyl compounds with fewer carbons than the alkane are then observed, a good example being 3,4-diethylhexane where the coproducts acetaldehyde, propanal, and 3-pentanone account for ~40% of the product carbon.[85]

There is therefore a general, semiquantitative understanding of the reactions of alkanes in the troposphere, and especially for the OH radical-initiated reactions in the presence of NO. However, products studies of only relatively few alkanes have been carried out,[72−82,84,85,110−112,118−122] and then mainly for the *n*-alkanes and the two cycloalkanes cyclopentane and cyclohexane. Note that Cl atoms, rather than OH radicals, were used by Orlando et al.[82] to produce cyclopentyl and cyclohexyl radicals in their study of cyclopentane and cyclohexane degradation products. Apart from product studies of the Cl-initiated reactions of cyclopentane (230−300 K) and cyclohexane (273−296 K) in the presence of NO[82] and measurements of the yields of alkyl nitrates from the OH radical-initiated reactions of five alkanes,[75,77,78] all alkane product studies have been carried out at room temperature. As noted above, in some cases the dominant alkoxy radical reaction pathway(s) will change as the temperature and O_2 concentration decrease (i.e., as altitude increases), from (for example) decomposition and/or isomerization at ground level to reaction with O_2 in the upper troposphere, thereby leading to a different product distribution. An example of this shown by the cyclohexoxy radical, with decomposition and reaction with O_2 being competitive at room temperature,[72,73,81,82] but with the O_2 reaction dominating at temperatures <270 K.[82] As discussed above and evident from Table 10, the alkyl nitrate yields from the *n*-alkane photooxidations increase with carbon number.[74,84,85] Furthermore, for a given alkane (or alkyl peroxy radical), the alkyl nitrate yield decreases with increasing temperature[75,77−79] and with decreasing pressure.[75,77,79]

Scheme 4



Because the pressure effects have been observed in only two studies by the same research group,[75,77] further studies of the effects of temperature and pressure on the alkyl nitrate yields from the reactions of alkyl peroxy radicals with NO (i.e., measurements of the rate constant ratio k_{2b}/k_2 or k_{2b}/k_{2a}) are needed. Furthermore, even though the reaction mechanisms are understood in a general sense, isomer-specific product identification and quantification remains a future research need (and challenge).

3.2.3. Subsequent Reactions of 1,4-Hydroxycarbonyls

As evident from Table 10, 1,4-hydroxycarbonyls are an important class of products formed from many alkanes. 1,4-Hydroxycarbonyls can cyclize to form the hemiacetal (Scheme 4). In dry N_2 or air, 5-hydroxy-2-pentanone has been shown[123,124] to cyclize and lose water to form 4,5-dihydro-2-methylfuran. The measured first-order rate constants for the disappearance of 5-hydroxy-2-pentanone at room temperature were 2.2×10^{-4} s^{-1} in a 480-L glass chamber[123] and 2.5×10^{-4} s^{-1} in a 5800-L Teflon-coated chamber,[124] suggesting that this may be a homogeneous process (Scheme 4). However, whereas 5-hydroxy-2-pentanone is converted to 4,5-dihydro-2-methylfuran in dry air, in air at 5% relative humidity (2.5×10^{16} molecule cm^{-3}) at 298 K 4,5-dihydro-2-methylfuran was observed to decay at a rate of 8.0×10^{-5} s^{-1} to form 5-hydroxy-2-pentanone,[124] and 5-hydroxy-2-pentanone showed no evidence of converting to 4,5-dihydro-2-methylfuran at 5% relative humidity and room temperature.[125]

Rate constants for the reactions of OH radicals with 5-hydroxy-2-pentanone[125] and of OH radicals, NO_3 radicals, and O_3 with 4,5-dihydro-2-methylfuran[124] have been measured at 296−298 K, and are listed in Table 11. Using in situ APIMS analyses and SPME with on-fiber derivatization and GC−MS analyses, $CH_3C(O)CH_2CH_2CHO$ and $CH_3C(O)CH_2CHO$ have been observed from the reaction of OH radicals with 5-hydroxy-2-pentanone in the presence of NO.[125] The major product observed from the reactions of 4,5-dihydro-2-methylfuran with OH radicals (in the presence of NO), NO_3 radicals, and O_3 is $CH_3C(O)OCH_2CH_2CHO$,[124] with formation yields of 74 ± 19, 5.4−12, and 23%, respectively.[124] As shown in Table 11, 4,5-dihydro-2-methylfuran is an order of magnitude more reactive than 5-hydroxy-2-pentanone toward OH radicals, and also reacts very rapidly with NO_3 radicals and O_3. Hence, if 5-hydroxy-2-pentanone is converted to 4,5-dihydro-2-methylfuran to any significant extent in the atmosphere, this will have a marked effect on the effective lifetime of 5-hydroxy-2-pentanone, including continued reaction during nighttime. Clearly, further investigation of the atmospheric behavior of 1,4-hydroxycarbonyls and their unsaturated five-membered ring interconversion species is needed.

4. Atmospheric Chemistry of Alkenes

Alkenes react with OH radicals, NO_3 radicals, and O_3 (and with Cl atoms),[14,15] and room-temperature rate constants, temperature-dependent parameters, and temperature ranges over which the rate expressions are applicable are given in Tables 1, 2, and 3 for the OH radical, O_3, and NO_3 radical reactions, respectively. The rate data given in Table 1 for the OH radical reactions are those at the high-pressure limit or, for ethene and propene, at conditions applicable to atmospheric pressure.[14,15,29,30] As shown in Table 4 for selected anthropogenic and biogenic alkenes, all three of these reactions are important loss processes in the lower troposphere. The relative importance of the OH radical, NO_3 radical reaction, and O_3 reaction as an alkene loss process varies from alkene to alkene and, for a given alkene, with decreasing temperature (or increasing altitude). The relative importance of the O_3 reactions will decrease with increasing altitude because the O_3 reactions have rate constants which decrease with decreasing temperature (Table 2),[14,15] while the OH radical reactions have rate constants which increase slightly with decreasing temperature (Table 1).[14,15] The OH radical, NO_3 radical, and O_3 reactions proceed mainly (OH and NO_3 radical) or totally (O_3) by initial addition to the C=C bond(s).[9,14,15]

4.1. Rate Constants for the Initial Reactions of Alkenes with OH and NO_3 Radicals and O_3

Rate constants have been measured, using both absolute and relative rate methods, for the reactions of OH radicals, O_3, and NO_3 radicals with a large number of alkenes (Tables 1−3). These rate constants have been reviewed and evaluated (through approximately 1997) by Atkinson[14] and Calvert et al.,[15] and on an ongoing basis for ethene and propene also by the NASA[64] and IUPAC[16] evaluations (the IUPAC evaluation[16] now also includes isoprene).

Despite the large number of alkenes for which rate data are available, including many monoterpenes and several sesquiterpenes of biogenic origin, only for a few alkenes are temperature-dependent rate constants for the OH radical and NO_3 radical reactions available at temperatures relevant to the middle or upper troposphere (Tables 1 and 3). For example, to date, rate constants for reaction with OH radicals are available below room temperature only for propene (with a rate constant at 103 ± 9 K[44] and otherwise at ≥293 K), 1-butene (with rate constants at 23, 44, 75, 103 ± 9, and 170 K,[44,45] and otherwise at ≥295 K), *cis*- and *trans*-2-butene (with rate constants at 23, 44, 75, and 170 K,[45] and otherwise at ≥295 K), and isoprene [2-methyl-1,3-butadiene] (with rate constants available over the temperature range 249−422 K) [see Table 1]. Similarly, for the NO_3 radical reactions, rate constants are available only below room temperature for 1-butene, *trans*-2-butene, isoprene, cyclohexene, 1-methyl-1-cyclohexene, and α-pinene (Table 3). In contrast, rate constants for the reactions of O_3 have been measured down to ~240 K for a number of simple alkenes, dienes, and monoterpenes (Table 2).

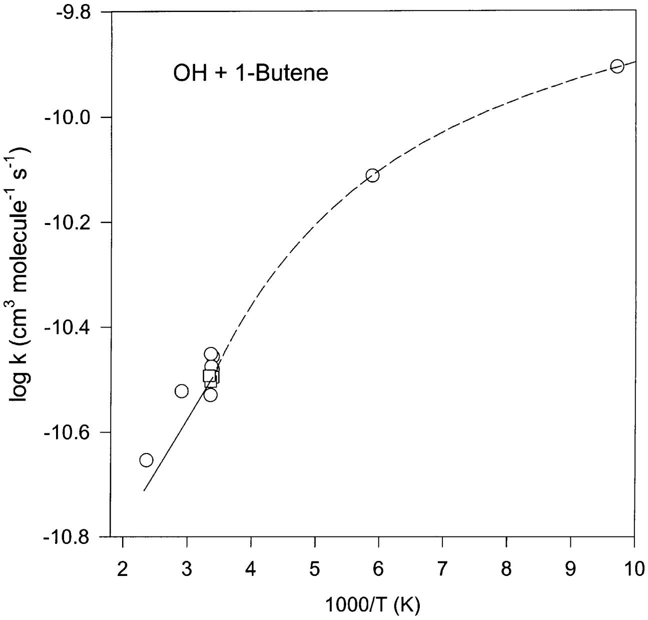


Figure 2. Arrhenius plot of rate constants for the reaction of OH radicals with 1-butene (below 500 K). The rate constants plotted are those used in the Calvert et al.[15] evaluation, together with the 109 and 170 K rate constants of Vakhtin et al.[44] and Sims et al.,[45] respectively. The solid line is the recommendation of Calvert et al.,[15] and the dashed line is given by $k = 2.56 \times 10^{-10}\ e^{-2.10T/298}$ cm^3 molecule^{-1} s^{-1} and is for illustrative purposes only; (○) absolute rate data; (□) relative rate data.

As an example of the database available for the OH radical reactions with alkenes, Figure 2 shows an Arrhenius plot of rate constants for the reactions of OH radicals with 1-butene over the temperature range 100−500 K, and Figure 3 shows Arrhenius plots for propene and isoprene for temperatures of <500 K. Above ~650 K the OH-alkene adducts rapidly thermally decompose, and only rate constants for the abstraction process are then observed.[29,30]

4.2. Mechanism of the OH Radical Reaction

For the OH radical reactions, the major reaction pathway involves initial addition of the OH radical to the carbon atoms of the C=C bond(s),[14,15,29] forming a 1,2-hydroxyalkyl radical which then reacts with O_2 (analogously to alkyl radicals, see Scheme 1) to form the corresponding 1,2-hydroxyalkyl peroxy radical.[14] At room temperature and below, H-atom abstraction

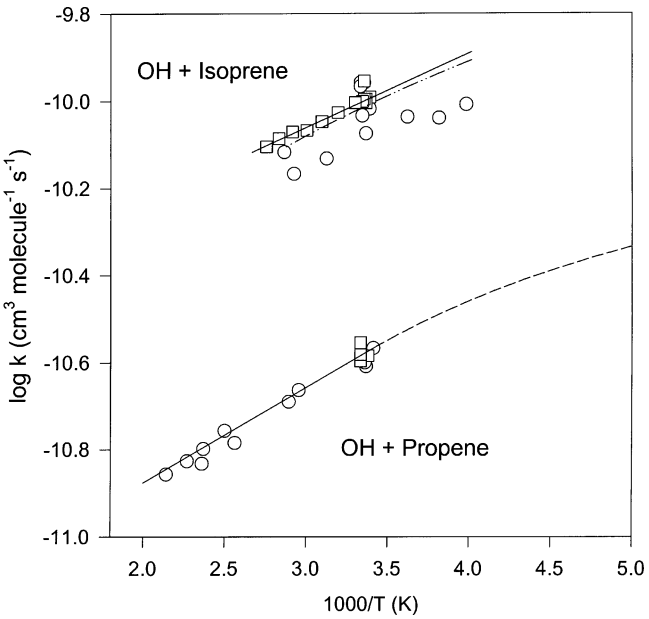


Figure 3. Arrhenius plots of rate constants for the reaction of OH radicals with propene and isoprene (below 500 K). The rate constants plotted are those used in the Calvert et al.[15] evaluation for propene and the IUPAC[16] evaluation for isoprene, and the dash–dot–dot (– • •) line is the expression of Siese et al. (cited in refs 14–16). The solid lines are the recommendation of Calvert et al.[15] and IUPAC,[16] and the dashed line for propene is given by $k = 1.47 \times 10^{-10}\ e^{-1.72T/298}$ cm^3 molecule^{-1} s^{-1} to fit the 103 K rate constant of Vakhtin et al.[44] and is for illustrative purposes only; (○) absolute rate data; (□) relative rate data.

Table 12. Room-Temperature Rate Constants for the Reactions of 1,2-Hydroxyalkyl Peroxy and 1,4-Hydroxyalkyl Peroxy Radicals with NO and with HO_2 Radicals

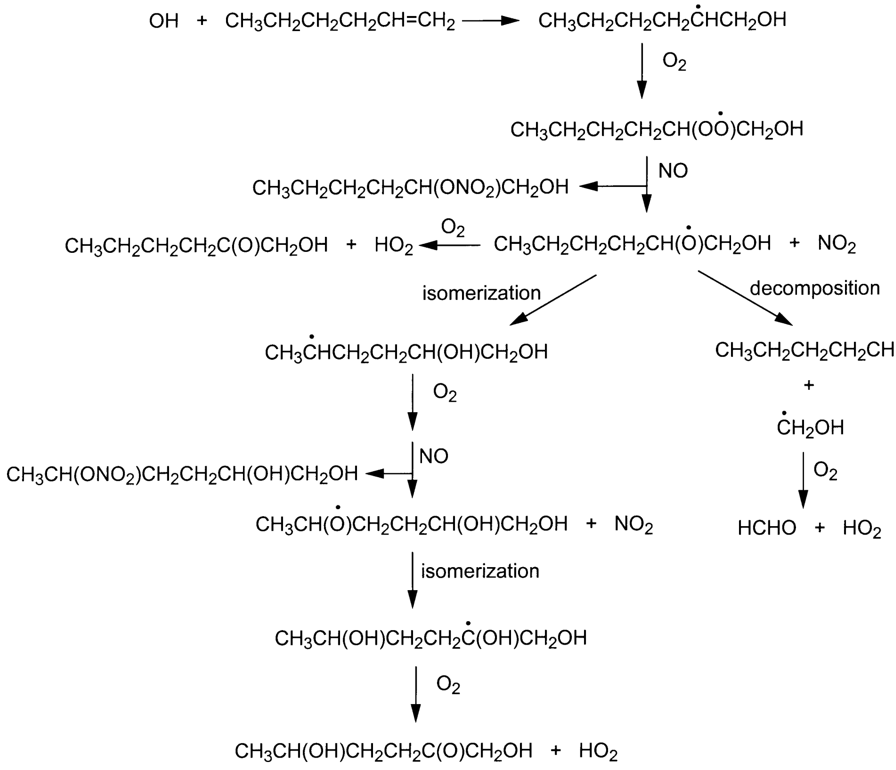
	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})		
$RO_2^\bullet$ radical	reaction with NO	reaction with HO_2	ref
$HOCH_2CH_2O_2^\bullet$	9	10	16
$(CH_3)_2C(OH)CH_2O_2^\bullet$	4.9 ± 0.9		129
		14[a]	130
$CH_3CH(OH)CH(CH_3)O_2^\bullet$		15	131
$(CH_3)_2C(OH)C(CH_3)_2O_2^\bullet$		~20	131
$HOC_5H_8O_2^{\bullet b}$	~9		132
	11 ± 8		133
	25 ± 5		134

[a] Rate constants obtained over the temperature range 306–398 K, with $k = 5.6 \times 10^{-14}\ e^{1650/T}$ cm^3 molecule^{-1} s^{-1}. Cited rate constant is that calculated from the Arrhenius expression at 298 K. [b] "Lumped" hydroxy-peroxy radicals formed after OH radical addition to isoprene, and includes 1,2- and 1,4-hydroxy-peroxy radicals (see text).

from the methyl-substituted ethenes, 1-butene and 3-methyl-1-butene, is minor, being <5–10% at room temperature,[14,15,29] but it accounts for 12–15% and 9% of the 1,4-cyclohexadiene[29,33] and 1,3-cyclohexadiene[29] reactions, respectively, at 298 K. The reactions after OH radical addition are as shown schematically in Scheme 1 and, in the presence of NO, lead to formation of 1,2-hydroxyalkyl nitrates[126–128] and 1,2-hydroxyalkoxy radicals (see Scheme 5 for the reaction of 1-hexene proceeding by OH radical addition at the terminal carbon).

Analogous to alkyl peroxy radical reactions (2) through (6), the 1,2-hydroxyalkyl peroxy radicals formed after reaction of 1,2-hydroxyalkyl radicals with O_2 can react with NO, NO_2, HO_2 radicals, organic peroxy radicals, and NO_3 radicals.[9,14,15] Rate constants for the reactions of 1,2-hydroxyalkyl peroxy radicals with NO and with HO_2 radicals, most measured only at room temperature, are given in Table 12. Although the available database is very

Scheme 5



small, the room-temperature rate constants for the reactions of 1,2-hydroxyalkyl peroxy radicals with NO and HO_2 radicals are similar, within a factor of ~2 or less, to those for the analogous reactions of alkyl peroxy radicals (Tables 5 and 6). This suggests that the rate constants recommended[14] for reactions of alkyl peroxy radicals with NO ($k = 2.7 \times 10^{-12}\ e^{360/T}$ $cm^3\ molecule^{-1}\ s^{-1}$ over the temperature range ~200−400 K, with $k = 9.0 \times 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}$ at 298 K) and with HO_2 radicals ($k = 1.9 \times 10^{-13}\ e^{1300/T}\ cm^3\ molecule^{-1}\ s^{-1}$, with $k = 1.5 \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$ at 298 K) may be applicable for reactions of 1,2-hydroxyalkyl peroxy radicals if experimental data do not exist. Rate constants have also been measured for the self- and cross-reactions of a number of 1,2-hydroxyalkyl peroxy radicals.[16,130,131,135,136]

As for the reactions of alkoxy radicals described in the alkanes section above, the 1,2-hydroxyalkoxy radicals formed from reactions analogous to reactions 2a, 5a, and 6 can react with O_2, decompose, or isomerize, as shown in Scheme 5. The decomposition reaction leads to formation of an α-hydroxyalkyl radical ($^{\bullet}CH_2OH$ in Scheme 5),

$$CH_3CH_2CH_2CH_2CH(O^{\bullet})CH_2OH \rightarrow CH_3CH_2CH_2CH_2CHO + {}^{\bullet}CH_2OH \quad (7)$$

which appears to react rapidly and solely with O_2 to form the carbonyl plus HO_2.

$$^{\bullet}CH_2OH + O_2 \rightarrow HCHO + HO_2 \quad (8)$$

Reaction 8, and presumably also the analogous reactions of other α-hydroxy radicals with O_2, is not a simple H-atom abstraction reaction, but rather is an addition−elimination reaction with no significant deuterium isotope effect.[16]

At room temperature, decomposition of 1,2-hydroxyalkoxy radicals appears to dominate over reaction with O_2,[14,137,138] except for the $HOCH_2CH_2O^{\bullet}$ radical where these reactions are competitive.[14] For larger 1,2-hydroxyalkoxy radicals isomerization may compete with decomposition (see Scheme 5).[14,139,140] Orlando et al.[115] and Vereecken et al.[141] have investigated the products formed from the OH radical-initiated reactions of ethene[115] and propene,[141] and shown that (a) $HOCH_2CH_2O^{\bullet}$ radicals formed from the $HOCH_2CH_2OO^{\bullet}$ + NO reaction are chemically activated and ~25% of these undergo "prompt" decomposition, irrespective of pressure and temperature,[115] and (b) the 1,2-hydroxypropoxy radicals formed from propene decompose rather than react with O_2 at temperatures down to 220 K, even for the small fraction (~25%) that are thermalized.[141]

Therefore, the products expected from these reactions are 1,2-hydroxyalkyl nitrates,[14,126] carbonyls (aldehydes and ketones) from the decomposition reaction, and dihydroxynitrates and dihydroxycarbonyls formed after the isomerization reaction (see Scheme 5). These products are observed.[14,15] However, apart from ethene and the methyl-substituted ethenes,[14] a complete accounting of the products has not been obtained, mainly because of the difficulties in identifying and quantifying multi-functional products such as hydroxynitrates, dihydroxynitrates, and dihydroxycarbonyls.

For conjugated dienes such as 1,3-butadiene and isoprene with C=C−C=C bond systems, OH radical addition at the 1- or 4-positions forms an allylic 1-hydroxy-2-alkyl radical which is in resonance with the 1-hydroxy-4-alkyl radical.[14] For example, addition of the OH radical at the 1-position of isoprene

$$OH + CH_2{=}C(CH_3)CH{=}CH_2 \rightarrow HOCH_2C^{\bullet}(CH_3)CH{=}CH_2 \leftrightarrow HOCH_2C(CH_3){=}CHC^{\bullet}H_2 \quad (9)$$

is followed by addition of O_2 to form the corresponding peroxy radicals. Rate constants have been derived for the reactions of hydroxyperoxy radicals formed after OH radical addition to isoprene (i.e., a mixture of 1,2- and 1,4-hydroxyperoxy radicals) with NO and these[132−134] are listed in Table 12. Again, these room-temperature rate constants are similar to those for the reactions of alkyl peroxy radicals with NO (see above and Table 5). In the presence of NO, these hydroxyalkyl peroxy radicals react with NO to form hydroxynitrates or hydroxyalkoxy radicals plus NO_2.

For the isoprene reaction, at room temperature the 1,2-hydroxyalkoxy radicals (for example, $HOCH_2C(O^{\bullet})(CH_3)CH{=}CH_2$ and $HOCH_2CH(O^{\bullet})C(CH_3){=}CH_2$) dominantly decompose to form methacrolein + HCHO and methyl vinyl ketone + HCHO.[14,137,138] In contrast, the 1,4-hydroxyalkoxy radicals (for example, $HOCH_2C(CH_3){=}CHCH_2O^{\bullet}$ and $HOCH_2CH{=}C(CH_3)CH_2O^{\bullet}$) isomerize, and possibly react with O_2, to form the hydroxycarbonyls $HOCH_2C(CH_3){=}CHCHO$ and $HOCH_2CH{=}C(CH_3)CHO$.[117,142] At room temperature and atmospheric pressure of air, the products observed from the OH radical-initiated reaction of isoprene in the presence of NO are C_5-hydroxynitrates, methyl vinyl ketone + HCHO; methacrolein + HCHO, C_5-hydroxycarbonyls and (at least at longer reaction times) 3-methylfuran[14,128,142] (Scheme 6). The observed formation of 3-methylfuran from the OH radical-initiated reaction of isoprene[143] may arise by cyclization of the unsaturated 1,4-hydroxyaldehyes $HOCH_2C(CH_3){=}CHCHO$ and $HOCH_2CH{=}C(CH_3)CHO$ with loss of water,[128] analogous to the cyclization of 1,4-hydroxycarbonyls and loss of water shown in Scheme 4.

Table 13 gives the products observed from a selected number of studies of the OH radical-initiated reactions of 1-hexene, isoprene, and α-pinene in the presence of NO. Note, for example, the observation by APIMS of multifunctional products, such as dihydroxycarbonyls and dihydroxynitrates, in the study of Aschmann et al.[140] of α-pinene and 1-hexene.

4.3. NO_3 Radical Reaction

The reactions of NO_3 radicals with alkenes proceed largely by initial addition of the NO_3 radical to the carbon atoms of the C=C bond(s), and are generally analogous to the corresponding OH radical reactions.[14] At low pressure, the initially formed, chemically activated nitrooxyalkyl radical can decompose

Scheme 6

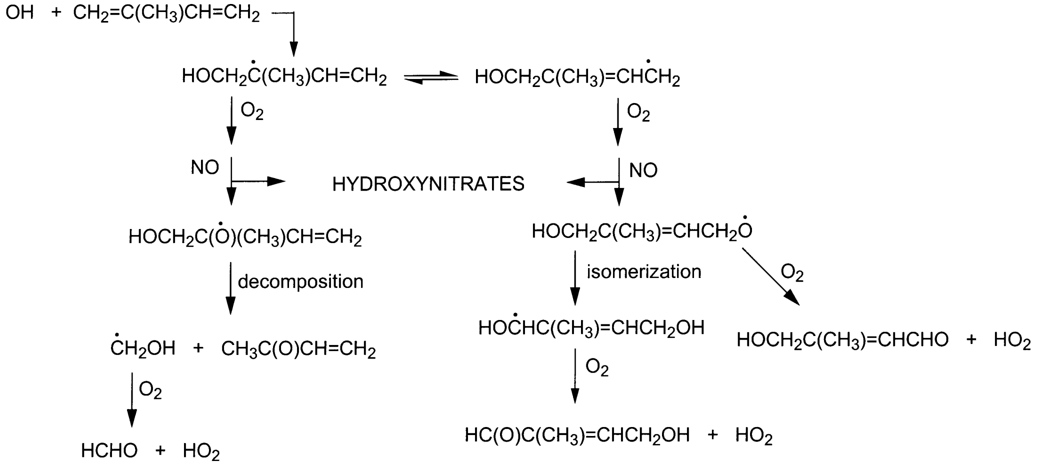


Table 13. Products Observed from the OH Radical-Initiated Reactions (in the Presence of NO) of 1-Hexene, Isoprene, and α-Pinene

alkene	product	molar yield (%)	ref
1-hexene	C_6-hydroxynitrates	5.5 ± 1.0	127
	pentanal (+ HCHO)[a]	46 ± 7	14
	C_6-dihydroxycarbonyls	~40	140
	C_6-dihydroxynitrates	observed	140
isoprene	C_5-hydroxynitrates	4.4 ± 0.8	126
		12	128
	methyl vinyl ketone (+ HCHO)[a]	33 ± 3	14
		44	128
	methacrolein (+ HCHO)[a]	23 ± 3	14
		28	128
	3-methylfuran	4.8 ± 0.6	143
	C_5-hydroxycarbonyls	observed	142
α-pinene	C_{10}-hydroxynitrates	18 ± 9	144
	pinonaldehyde	28 ± 5	140
	C_{10}-dihydroxycarbonyls	~19	140
	MW 200 species[b]	~11	140
	acetone (+ coproduct)[a]	11.0 ± 2.7	145
		5 ± 2	146

[a] Cited yields are for pentanal, methyl vinyl ketone, methacrolein, or acetone. Coproduct shown in parentheses. [b] Attributed to products such as C_{10}-hydroxy-tricarbonyl(s) and/or C_{10}-trihydroxycarbonyl(s).[140]

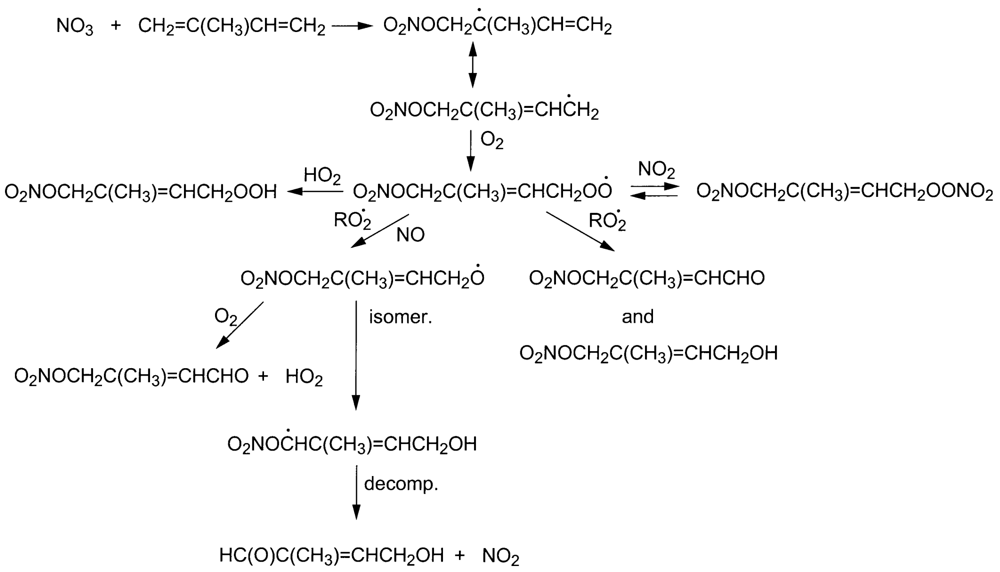
to an oxirane plus NO_2 in competition with collisional stabilization.[14] Thermalized nitrooxyalkyl radicals can also decompose to the oxirane plus NO_2, or react with O_2,[147,148] with the reaction with O_2 to form a nitrooxyalkyl peroxy radical dominating at atmospheric pressure of air.[148] Note that for 2,3-dimethyl-2-butene, an oxirane yield at atmospheric pressure of air of 17–20% has been measured.[147,148] For the reactions of NO_3 radicals with *cis*- and *trans*-2-butene and isoprene at atmospheric pressure of air, Skov et al.[147] observed no formation of the oxiranes (≤ 1%), while Berndt and Böge[149] reported oxirane yields at atmospheric pressure of air of 28% from propene, 18% from 1-butene, 12% from *trans*-2-butene, 9% from 2-methyl-2-butene, and 7% from 2-methylpropene. Clearly, a significant disagreement exists for the oxirane yield at atmospheric pressure of air from the *trans*-2-butene reaction,[147,149] and additional measurements of the oxirane yields from a number of alkenes at atmospheric pressure of air are needed.

Under atmospheric conditions, the nitrooxyalkyl peroxy radicals react with NO, NO_2, HO_2 radicals, organic peroxy radicals, and NO_3 radicals, by reactions analogous to reactions 2–6. Note that because of the rapid reactions of NO with O_3 and with NO_3 radicals,[16] in the atmosphere NO_3 radicals and NO are not simultaneously present at significant concentrations. The reaction with NO_2 forms a thermally labile nitrooxyperoxynitrate [$>C(OONO_2)C(ONO_2)<$].[14] Potential reactions occurring after initial NO_3 radical addition at the 1-position in isoprene are shown in Scheme 7 (where the chemically activated nitrooxyalkyl radical and its decomposition are omitted). The products shown in Scheme 7 have been observed by Skov et al.[150] and Kwok et al.[151] Product studies of the reactions of NO_3 radicals with alkenes conducted to date show, consistent with Scheme 7, the formation of large yields of organic nitrates (see, for example, Atkinson[14]). Note that in some laboratory studies NO was added after the initial reaction to promote the decomposition of the nitrooxyperoxynitrates [$>C(ONO_2)C(OONO_2)<$ species].[14] Hence in those studies the products observed were from reaction of nitrooxyalkoxy radicals, which may be different from the products formed from reactions of nitrooxyalkyl peroxy radicals with HO_2 and $RO_2^{\bullet}$ radicals (see Scheme 7).

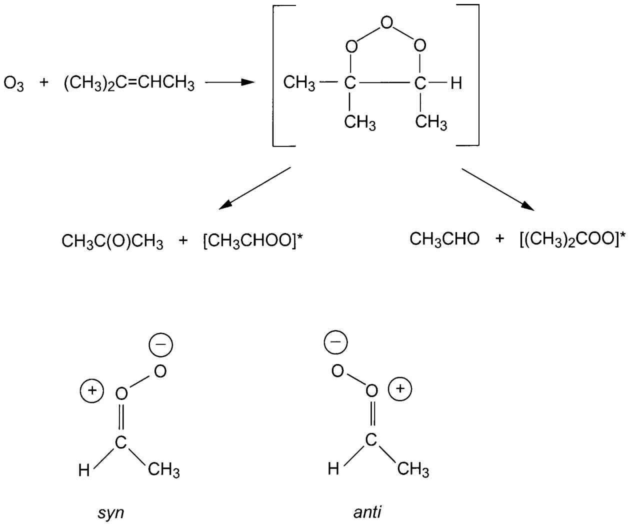
4.4. Reaction with O_3

The reactions of O_3 with alkenes proceed by initial O_3 addition to the C=C bond, to form a primary ozonide which rapidly decomposes via two pathways to a carbonyl plus a "Criegee intermediate", as shown in Scheme 8 for 2-methyl-2-butene. Note that for cyclic alkenes with an internal double bond (such as α-pinene and 2- and 3-carene), a carbonyl-substituted Criegee intermediate is formed from each of the two possible primary ozonide decompositions. Theoretical calculations[152,153] indicate that the Criegee intermediate is a carbonyl oxide which, for monoalkyl-substituted intermediates, can exist in the *syn*- or *anti*-configuration (Scheme 8). The initially energy-rich Criegee intermediates react by a number of routes,[14,15,153–157] including (a) collisional stabilization to a thermalized Criegee intermediate, (b) rearrangement to a "hot" ester followed by decomposition, including to CO_2 + RH for Criegee intermediates of structure [RCHOO]*, and (c) for dialkyl-substituted and *syn*- monoalkyl substituted Criegee intermedi-

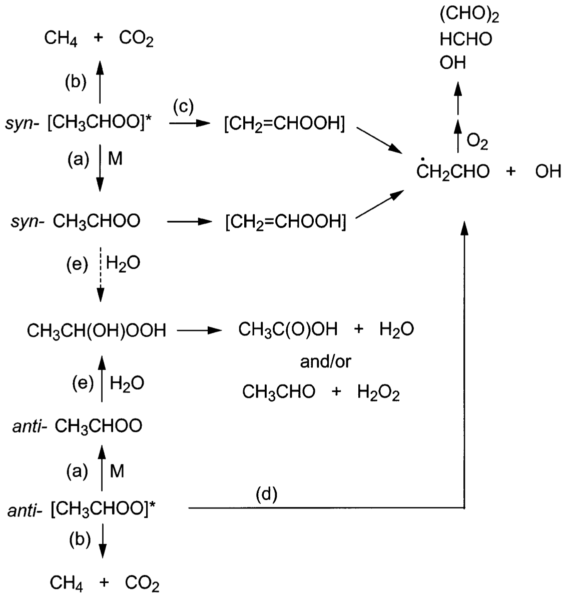
Scheme 7



Scheme 8



Scheme 9

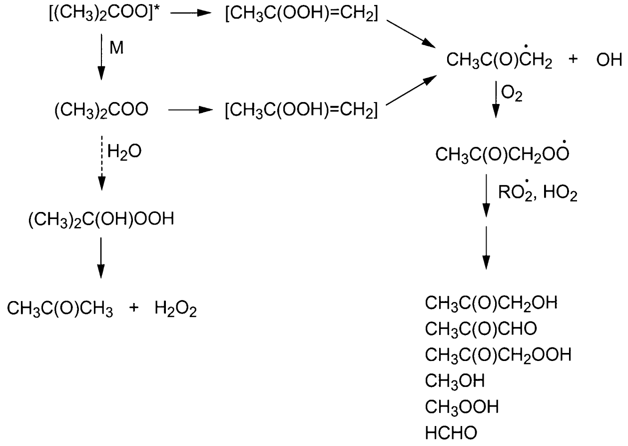


ates, isomerization to a “hot” hydroperoxide followed by decomposition to an OH radical plus a substituted alkyl radical. Using the *syn*- and *anti*- $[CH_3CHOO]^*$ intermediates formed from the 2-methyl-2-butene reaction (Scheme 8) as an example, these pathways are shown in Scheme 9, and labeled (a), (b), and (c) for the *syn*-$[CH_3CHOO]^*$ intermediate and (a) and (b) for the *anti*-$[CH_3CHOO]^*$ intermediate. Note that OH radical formation can also occur, with relatively low efficiency, from *anti*-monosubstituted Criegee intermediates through the “ester” channel[153] (labeled (d) in Scheme 9). OH radical formation also occurs to a minor extent from the $[CH_2OO]^*$ intermediate.[14] Additionally, for isoprene and α-pinene the formation of epoxides, presumably via a direct reaction, has been observed in low, ∼2−5%, yield.[14,158]

The formation of OH radicals from the reactions of O_3 with alkenes at atmospheric pressure is well established.[156,159−161] Kroll et al.[155,156,162] have reported that OH radicals are formed via both “prompt” and “slow” processes at atmospheric pressure, with the “slow” process involving participation of the thermalized dialkyl-substituted or *syn*- monoalkyl-substituted Criegee intermediates.[153−156] Under typical atmospheric conditions, thermalized Criegee intermediates also react with water vapor to form α-hydroxyhydroperoxides (labeled pathway (e) in Scheme 9), which may be stable in the gas phase or decompose to a carbonyl plus H_2O_2 or to a carboxylic acid plus H_2O.[158,163−166]

Laboratory studies conducted at atmospheric pressure of air have shown that the OH radical formation yields from the reactions of O_3 with 2-methyl-2-butene[167] and a series of monoterpenes[168,169] are not affected by the presence of water vapor at up to 36−74% relative humidity at 295−296 K. Furthermore, Johnson et al.[167] have shown that addition of SO_2, 2-butanone, or acetic acid, which are known to react with thermalized Criegee intermediates, has no effect on the OH radical yield from the reaction of O_3 with 2-methyl-2-butene. Therefore, the mechanism of the reaction of O_3 with alkenes may be interpreted as leading to the formation of *syn*- and *anti*- Criegee intermediates (with dialkyl-substituted intermedi-

Scheme 10



ates having one alkyl group in the *syn*- configuration), with the *syn*- intermediates leading to OH radical formation and the *anti*- intermediates being mainly collisionally thermalized and reacting with water vapor (OH radicals can also be formed to some extent from the *anti*- intermediates through the "ester" channel[153]).[153–157,167,169] The organic peroxy radical coproducts to the OH radical will add O_2 and the resulting organic peroxy radicals will then react as do other organic peroxy radicals.[9,14] Schemes 9 and 10 show possible reactions for the Criegee intermediates formed from the reaction of O_3 with 2-methyl-2-butene, including possible ultimate products formed from the organic radical coproduct to the OH radical. Scheme 11 shows a possible mechanism for the O_3 reaction with α-pinene, indicating that OH radical (plus organic radical coproduct) formation (80 ± 10%)[169] together with pinonaldehyde (16 ± 3%)[166] and α-pinene oxide (2%)[158] formation account for 98 ± 11% of the reaction pathways.

Unless OH radicals are scavenged in laboratory product studies, the O_3−alkene reaction involves both OH radicals and O_3, and the products observed and quantified are not applicable solely to the O_3 reaction. Although in most cases the products identified in the presence and absence of an OH radical scavenger are the same, the yields can be somewhat different[170,171] and the formation of products attributed to the OH radical reaction has been observed for a series of methyl-substituted ethenes in the absence of an OH radical scavenger.[172] For most alkenes containing tri- and tetra-alkyl substituted C=C bonds, the measured OH radical formation yields are close to unity.[14,169] The reactions of O_3 with alkenes (both anthropogenic and biogenic) may then be an additional source of OH radicals in the troposphere, including during nighttime.[173]

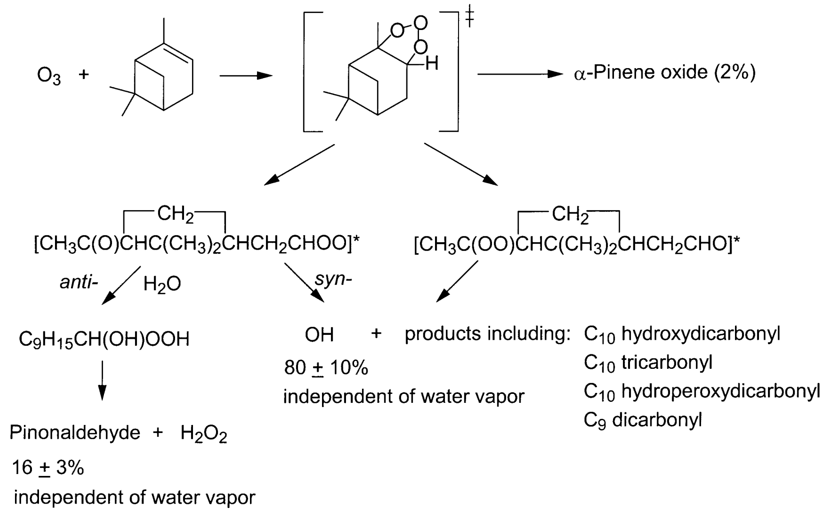
5. Aromatic Hydrocarbons

In the atmosphere, benzene and alkyl-substituted benzenes react with OH radicals and, to a very much lesser extent, with NO_3 radicals (Table 4).[8,9] Rate constants, or upper limits to the rate constants in the case of the O_3 reactions with benzene and alkylbenzenes, and temperature-dependent parameters for the reactions of OH radicals, O_3, and NO_3 radicals with aromatic hydrocarbons are listed in Tables 1−3, respectively. For monocyclic aromatic hydrocarbons, the NO_3 radical reactions proceed by H-atom abstraction from the C−H bonds of the alkyl substituent groups.[8,174] Because of the minor role the NO_3 reactions play in the atmospheric removal of benzene and alkyl-substituted benzenes, these NO_3 radical reactions are not discussed further here.

5.1. Kinetics of the OH Radical Reactions

As shown in Table 1, rate constants have been measured for the gas-phase reactions of OH radicals with a number of aromatic hydrocarbons, with temperature-dependent data being available below room temperature for benzene, toluene, and *m*-xylene (Table 1). Figure 4 shows Arrhenius plots of the OH radical reaction rate constants for benzene and toluene, the two most studied aromatic hydrocarbons. Because the OH−aromatic adducts undergo thermal dissociation back to reactants (OH + aromatic), with a rate constant for the OH−benzene adduct decomposition of $9.4 \times 10^{12}\ e^{-8540/T}\ s^{-1}$ (and similarly for the other OH−aromatic adducts),[29,30] the lifetime of an OH−aromatic adduct is ~0.3 s at 298 K and decreases rapidly with increasing temperature (to ~4

Scheme 11



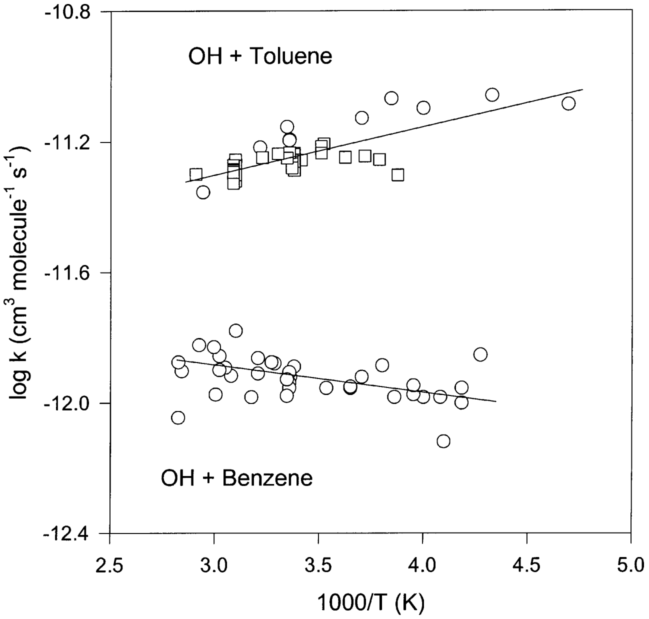
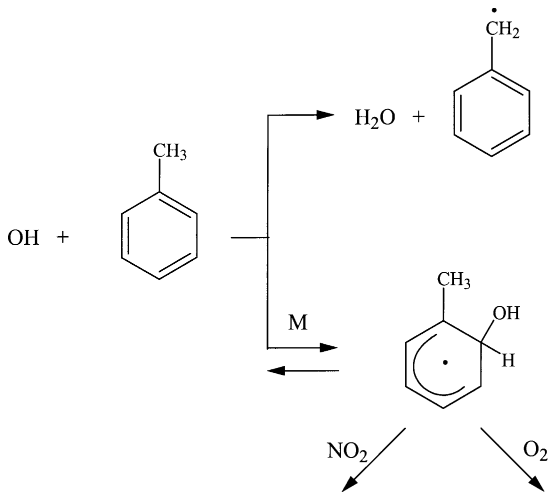


Figure 4. Arrhenius plots of rate constants for the reaction of OH radicals with benzene and toluene (below 400 K). The rate constants plotted are those used in the Calvert et al.[8] evaluations, and the solid lines are the recommendations of Calvert et al;[8] (○) absolute rate data; (□) relative rate data.

ms at 350 K, ~0.2 ms at 400 K, and ~20 μs at 450 K). Therefore, absolute rate methods monitoring the decay of OH radicals on millisecond time-scales will not observe the reversible OH radical addition process above ~450 K, but only the H-atom abstraction pathway.[29] Extrapolation of kinetic data obtained using pulsed generation of OH radicals with time-resolved monitoring of OH radicals over temperature ranges >450 K and <325 K allow rate constants for both the H-atom abstraction pathway and the OH radical addition pathway to be determined (and hence the fraction of the overall OH radical reaction proceeding by H-atom abstraction).[29,30]

As evident from temperature-dependent kinetic studies,[29,30] the OH radical reactions proceed by two pathways; H-atom abstraction from the C−H bonds of the alkyl substituent groups, and addition of the OH radical to the aromatic ring, as shown in Scheme 12 for toluene. At room temperature and atmospheric pressure, the OH radical addition pathway dominates, and H-atom abstraction accounts for <10% of the overall pathway for toluene, xylenes, and trimethylbenzenes.[8,29,30] The hydroxy−alkylcyclohexadienyl radicals (or OH−aromatic adducts) react with O_2 and NO_2. For the OH−benzene, OH−toluene, and OH−*p*-xylene adducts, the room-temperature rate constants for reaction with O_2 are in the range (2−8) × 10^{-16} cm^3 molecule^{-1} s^{-1}.[175−178] These rate constants for the O_2 reaction are those for an irreversible reaction with the OH−aromatic adduct and/or the OH−aromatic−O_2 species (see Bohn and Zetzsch[177] and Bohn[178]). Bohn and Zetzsch[177] and Bohn[178] have shown that the OH−benzene and OH−toluene adducts reversibly add O_2 to form OH−benzene−O_2 and OH−toluene−O_2 peroxy radicals, with O_2 addition rate constants and equilibrium constants of (2 ± 1) × 10^{-15} cm^3 molecule^{-1} s^{-1} and (2.7 ± 0.4) × 10^{-19} cm^3 molecule^{-1}, respectively, for the OH−benzene adduct at 297 ± 2 K,[177] and (3 ± 2) × 10^{-15} cm^3 molecule^{-1} s^{-1} and (3.25 ± 0.33) × 10^{-19} cm^3 molecule^{-1}, respectively, for the OH−toluene adduct at 299 ± 2 K.[178] This means that for benzene and toluene at 298 K and atmospheric pressure of air, the equilibrium concentrations of the OH−aromatic adducts and the OH−aromatic−O_2 peroxy radicals are comparable.

Scheme 12



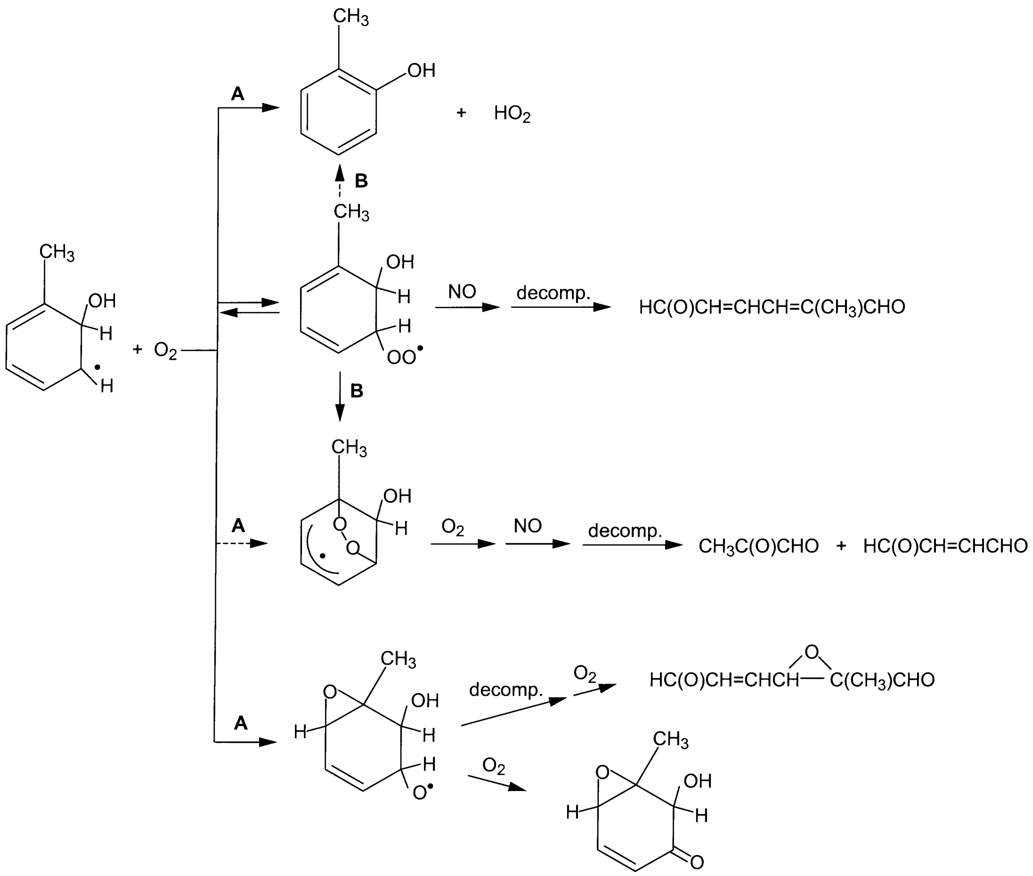
As noted above, an irreversible reaction of the OH−aromatic adducts with O_2 with an "effective" rate constant of (2−8) × 10^{-16} cm^3 molecule^{-1} s^{-1} is observed.[175−178] This irreversible removal of the OH−aromatic adduct in the presence of O_2 can be due to an irreversible reaction of the OH−aromatic adduct with O_2, with rate constants for the OH−benzene and OH−toluene adducts of (2.1 ± 0.2) × 10^{-16} cm^3 molecule^{-1} s^{-1} and (6.0 ± 0.5) × 10^{-16} cm^3 molecule^{-1}, respectively, or to a first-order removal reaction of the OH−benzene−O_2 and OH−toluene−O_2 species with rates of 760 ± 80 s^{-1} and 1850 ± 150 s^{-1}, respectively, or any combination of these two extremes.[177,178]

For the OH−benzene, OH−toluene, and OH−*p*-xylene adducts, the room-temperature rate constants for reaction with NO_2 are ~3 × 10^{-11} cm^3 molecule^{-1} s^{-1}.[175,176] The magnitude of the rate constants for the reactions of OH−aromatic adducts with O_2 (the irreversible process) and with NO_2 indicate that the OH−aromatic adducts will react almost exclusively with O_2 in the troposphere, but that reaction with NO_2 can become important in laboratory studies conducted at high NO_x concentrations [the O_2 and NO_2 reactions are of equal importance at atmospheric pressure of air at an NO_2 concentration of (3−13) × 10^{13} molecule cm^{-3} (a mixing ratio of ~1−5 parts-per-million, ppm)].

No reaction of the OH−benzene−O_2 or OH−toluene−O_2 species with O_2 has been observed.[177,178] For the OH−benzene−O_2 radical, a rate constant for reaction with NO of (1.1−1.7) × 10^{-11} cm^3 molecule^{-1} s^{-1} has been obtained,[177,179] with 23 ± 12% of this reaction being chain terminating and presumably forming organic nitrates.[177]

A possible (but undoubtedly incomplete) reaction scheme for reaction of the OH−toluene adduct with

Scheme 13



O_2 is shown in Scheme 13, noting that initial addition of the OH radical can also occur at the 3- and 4-positions, leading to different, but analogous, products (see Klotz et al.[179] for an analogous reaction scheme for the OH + benzene system). This reaction scheme is based on selected, and relatively recent, product and mechanistic data for the OH radical-initiated reactions of benzene, toluene, the xylenes, and the trimethylbenzenes.[175−187] Reaction pathways that have been shown to be (or are expected to be) unlikely are denoted by dashed arrows. The pathways labeled **A** in Scheme 13 are potential pathways corresponding to an irreversible reaction of the OH−aromatic adduct with O_2 (with maximum rate constants of $\sim 2 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} and $\sim 6 \times 10^{-16}$ cm^3 molecule^{-1} for the benzene and toluene reactions, respectively[175−178]), and those labeled **B** are potential reactions corresponding to a first-order reaction of the OH−aromatic−O_2 species (with maximum rate constants of ~760 and ~1850 s^{-1} for the benzene and toluene systems, respectively[177,178]). Volkamer et al.[187] concluded, from the essential independence of the phenol yield from benzene at low NO_x concentrations as a function of temperature over the range 287−307 K, that phenol is formed from a direct reaction of the OH−benzene adduct with O_2, and not through the intermediary of the OH−benzene−O_2 peroxy radical. On the basis of the reaction scheme shown (and that shown in Klotz et al.[179] for the benzene reaction), di-unsaturated 1,6-dicarbonyls are formed from reaction of OH−aromatic−O_2 peroxy radicals with NO, and their formation yield (and products formed in competing reaction pathways) depends on the NO concentration. This has recently been observed in the benzene reaction.[179]

No detailed reaction mechanism can presently be proposed for the corresponding reactions of OH−aromatic adducts with NO_2. Product studies indicate that some of the same products as observed from reaction of OH−aromatic adducts with O_2 reaction are formed from the reactions of the OH−aromatic adducts with NO_2, including phenol from reaction of the OH−benzene adduct with NO_2 and biacetyl (2,3-butanedione) from reaction of the OH−*o*-xylene adduct with NO_2.[179,180]

The products observed from the OH radical-initiated reactions of benzene and methyl-benzenes are as follows: aromatic aldehydes and benzyl nitrates formed after initial H-atom abstraction;[182,184,185,188−190] phenolic compounds;[179−185,187−189] one or more sets of 1,2-dicarbonyl + unsaturated 1,4-dicarbonyl;[8,30,180−182,184−186,190] di-unsaturated 1,6-dicarbonyls;[179,181,191] unsaturated epoxy-1,6-dicarbonyls,[181,191] and epoxycyclohexenones[181,191] (Scheme 13). Because the measured product formation yields can vary with the NO_2 (and NO) concentration,[179,180,185] product data for atmospheric purposes can only be obtained from product studies carried out at low NO_x concentrations (parts-per-billion, ppb, mixing ratios),[182−184,186,187] or from studies in which the NO_2 was varied sufficiently to allow reliable extrapolation to the low NO_2 concentrations representative of atmospheric conditions.[180,185] Note that the formation yields of the products formed after the H-atom abstraction pathway are independent of NO_2 concentration, at least up to NO_2 mixing ratios of several ppm.[185,188,189]

Table 14. Measured Molar Product Yields from the Reaction of *p*-Xylene with the OH Radical Carried Out at Atmospheric Pressure of Air, Expected to be Applicable to Atmospheric Conditions

product	yield (%)	ref
p-methylbenzyl nitrate	0.82 ± 0.16	189
p-tolualdehyde	7.01 ± 1.03	189
	10.3 ± 1.6	184
	7.06 ± 0.42	185
2,5-dimethylphenol	13 ± 1.8	184
	13.8 ± 1.6	185
glyoxal	39.4 ± 11	184
	35.4 ± 9.3[a]	186
methylglyoxal	21.7 ± 7.6	184
3-hexene-2,5-dione	22.1 ± 4	184
	32.3[b]	185
$HC(O)C(CH_3){=}CHCHO$	7.1	184

[a] Reevaluated relative to a yield for *p*-tolualdehyde of 7.0%. [b] At low NO_2 concentrations.

For benzene, the studies of Volkamer et al.[186,187] show the formation of phenol and glyoxal in $53.1 \pm 6.6\%$ and $35.2 \pm 9.6\%$ molar yields, respectively. These two products are much more reactive toward reaction with the OH radical than is benzene, by factors of >10, and glyoxal also photolyzes.[8] From its concentration−time behavior, glyoxal was concluded to be a primary product, and the lack of secondary formation of glyoxal allowed an upper limit of ≤8% to be placed on the formation yield of the di-unsaturated 1,6-dicarbonyl $HC(O)CH{=}CHCH{=}CHCHO$ at low NO_x concentrations.[186] The yield of $HC(O)CH{=}CHCH{=}CHCHO$ increased at high (part-per-million mixing ratio) NO levels.[179] More extensive product data are available for toluene[180,182,183,186,188] and the xylene isomers.[181,184−186,189] For toluene, the products identified and quantified are: benzaldehyde, 6%;[182,183,188] benzyl nitrate, 0.8%;[188] *o*-cresol, 12%;[180,182,183] *m*-cresol, 2.6%;[182,183] *p*-cresol, 3%;[182,183] glyoxal (and C_5-unsaturated 1,4-dicarbonyl coproducts), ∼30%;[182,186] and methylglyoxal (plus $HC(O)CH{=}CHCHO$ coproduct), 17%,[182] thereby accounting for ∼70% of the reaction products. Table 14 shows the products observed and their formation yields from the *p*-xylene reaction, for which we presently have the most information concerning 1,2-dicarbonyl and unsaturated 1,4-dicarbonyl coproduct formation. Again, the time−concentration profiles of glyoxal[186] and 3-hexene-2,5-dione[185] observed in recent studies show that these dicarbonyls are primary products and that they are not formed to any significant extent from other first-generation products.[185,186]

It therefore appears that the products formed from the H-atom abstraction pathway (typically a few percent) plus phenolic compounds and 1,2-dicarbonyls (plus their coproducts which in most cases have not been quantified, although observed by GC−MS after derivatization[190] and by in situ atmospheric pressure ionization mass spectrometry[181]) account for approximately 70% of the products and reaction pathways. On the basis of studies with product analyses by GC−MS after derivatization[190,191] and by in situ atmospheric pressure ionization mass spectrometry,[181] the remaining products, at least for the xylene reactions, appear to include di-unsaturated 1,6-dicarbonyls, unsaturated epoxy-1,6-dicarbonyls, and epoxycyclohexenones, as shown in Scheme 13 for the toluene reaction. Clearly, much more work is required to identify (in an isomer-specific manner) and quantify such products, and ascertain their formation pathways and yields under atmospheric conditions, as well as any dependence of their yields on NO and NO_2 concentrations.

5.2. Reactions of Phenols

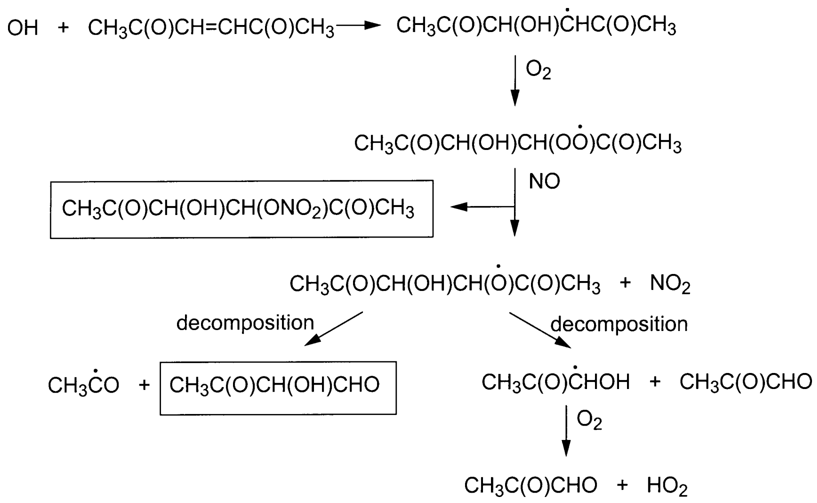
As noted above and in Table 14, phenolic compounds are formed from the atmospheric reactions of aromatic hydrocarbons. In the atmosphere, phenol and the cresol isomers have been shown to react with OH radicals, NO_3 radicals, and O_3,[8,30] and estimated lifetimes of *o*-cresol are listed in Table 4. The reactions with NO_3 radicals are fast,[8,30,174] sufficiently so that daytime reaction with NO_3 radicals may be important.[174] Products of the OH radical- and NO_3 radical-initiated reactions of phenol and the cresols have been studied.[192,193] The products observed from the OH radical-initiated reactions (in the presence of NO) are nitrophenols[192,193] and dihydroxybenzenes,[193] with, for example, *o*-cresol forming 6-methyl-2-nitrophenol in 5−7% yield,[192,193] 3-methyl-1,2-dihydroxybenzene in 73% yield,[193] and methyl-1,4-benzoquinone in 7% yield.[193] The nitrophenols appear to arise after H-atom abstraction from the −OH substituent group,[192,193] through reaction of the phenoxy or methylphenoxy radical with NO_2. Dihydroxybenzenes and 1,4-benzoquinones are postulated to arise after initial OH radical addition to the aromatic ring.[193] Although the nitrophenols are relatively unreactive toward OH radicals[29] and NO_3 radicals,[192] the dihydroxybenzenes are very reactive toward OH radicals, with measured rate constants at room temperature of $(1-2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} for methyl-1,2-hydroxybenzenes.[194] Rate constants at 300 ± 5 K for the reactions of 1,4-benzoquinone and methyl-1,4-benzoquinone with OH radicals have been measured to be 4.6×10^{-12} cm^3 molecule^{-1} s^{-1} and 2.35×10^{-11} cm^3 molecule^{-1} s^{-1}, respectively.[194]

5.3. Reactions of Unsaturated 1,4-Dicarbonyls and Di-Unsaturated 1,6-Dicarbonyls

Under atmospheric conditions, unsaturated 1,4-dicarbonyls are products of the OH radical-initiated reactions of aromatic hydrocarbons (see for example, Scheme 13).[182,184,185,190] On the basis of the data of Klotz et al.[179] for the benzene reaction, where *trans*-,*trans*-2,4-hexadienal has been identified and quantified, di-unsaturated 1,6-dicarbonyls appear to be formed only at high NO concentrations (>0.1 ppm) [see also Scheme 13]. Under conditions representative of the ambient atmosphere, Volkamer et al.[186] derived a ≤8% yield of $HC(O)CH{=}CHCH{=}CHCHO$ from benzene. However, Yu et al.[190] and Kwok et al.[181] reported evidence for the formation of these compounds from the photooxidations of toluene,[190] xylenes[181,190] and trimethylbenzenes[190] at NO_x mixing ratios of ≤1 ppm.

These unsaturated dicarbonyls are more reactive than their precursor aromatic hydrocarbon(s),[8] and their identification and quantification has proven

Scheme 14



difficult. These dicarbonyls react with OH radicals, NO_3 radicals, and O_3, and also photolyze,[8] and the recent review of Calvert et al.[8] should be consulted for details. The products of the atmospheric reactions of unsaturated 1,4-dicarbonyls have been studied by Tuazon et al.,[195] Bierbach et al.,[196] Liu et al.,[197] Bethel et al.,[198] and Tuazon and Atkinson,[199] with the Liu et al.[197] study involving concurrent reactions with OH radicals and O_3, as well as photolysis. Of these unsaturated 1,4-dicarbonyls, 3-hexene-2,5-dione is the most studied,[195−199] with products of the OH radical reaction having been investigated by Tuazon et al.,[195] Bierbach et al.,[196] Bethel et al.,[198] and Tuazon and Atkinson.[199] However, although Bierbach et al.[196] (using in situ FTIR spectroscopy) reported the formation of methylglyoxal in 30−32% yield (as carbon) from *trans*-3-hexene-2,5-dione, Tuazon et al.[195] and Tuazon and Atkinson[199] did not observe methylglyoxal, with a measured upper limit to its molar yield of <10% (and more likely <1%).[199] The discrepancy between the methylglyoxal yields reported by Bierbach et al.[196] and Tuazon and Atkinson[199] is attributed[199] to a mis-identification of the absorption bands in the portion of the FTIR spectrum used in the Bierbach et al.[196] study.

Using in situ atmospheric pressure ionization mass spectrometry, Bethel et al.[198] observed product ion peaks from 3-hexene-2,5-dione attributed to $CH_3C(O)CH(OH)CHO$ (or its enol-form $CH_3C(OH){=}C(OH)CHO$) and $CH_3C(O)CH(OH)CH(ONO_2)C(O)CH_3$. The reactions involved are shown in Scheme 14 (products observed by Bethel et al.[198] are shown in boxes). Photooxidation of $CH_2C(O)CH(OH)CHO$, by photolysis and/or reaction with OH radicals, is expected to lead to formation of methylglyoxal as a second-generation product,[199] and this may explain, at least in part, the observations of Bierbach et al.[196]

6. Atmospheric Reactions of Oxygenated VOCs

As indicated in the Introduction, oxygenated VOCs may react with OH radicals, NO_3 radicals, and O_3, and may also photolyze. OH radical reactions proceed by H-atom abstraction from C−H and, to a much lesser extent, from O−H bonds, by addition to the carbon atoms of any C=C bonds, and by addition to aromatic rings.[9,200] NO_3 radical reactions are generally important only if the oxygenated VOC contains C=C bonds, or is phenolic (with reaction apparently proceeding by an overall H-atom abstraction from the −OH group; see above).[174] H-atom abstraction from C−H bonds by NO_3 radicals is generally slow and minor compared to the corresponding OH radical reaction.[174] O_3 reactions are only important as tropospheric loss processes for oxygenated VOCs containing C=C bonds.[46]

The database concerning rate constants for the reactions of oxygenated VOCs with OH and NO_3 radicals and O_3 is growing rapidly, and for the OH radical reactions (generally the dominant tropospheric loss process for oxygenated VOCs not containing C=C bonds) are available down to 250 K or below for a number of aldehydes, ketones, alcohols, and ethers, and for methyl hydroperoxide (Table 1). In general, after the initial reaction with OH radicals, NO_3 radicals, or O_3, the subsequent reactions are analogous to those described above for the alkanes (i.e., after H-atom abstraction from C−H bonds), alkenes (i.e., after initial addition of OH, NO_3, or O_3 to C=C bonds) and aromatic hydrocarbons (i.e., after initial addition of OH radicals to aromatic rings). Previous reviews[8,9,13−15,29,30,46,174,201] and the ongoing NASA[64] and IUPAC[16] evaluations provide kinetic and product data for a number of oxygenated VOCs, and these should be consulted for details. One reaction not observed in the alkane, alkene, and aromatic hydrocarbons reaction systems involves the rearrangement (or isomerization) of alkoxy radicals of structure $RC(O)OCH(O^\bullet)R'$ to form $RC(O)OH + R'C^\bullet O$ (Scheme 3).[93,94]

As noted in Section 4.1., rate constants for the OH radical reactions with alkenes, which proceed by OH radical addition, generally exhibit negative temperature dependencies below ~600 K[29,30] (Table 1). Many of the reactions of OH radicals with oxygenated VOCs not containing C=C bonds (i.e., containing only saturated C−H bonds) also exhibit negative temperature dependencies, especially at temperatures below room temperature, despite the reactions proceeding by H-atom abstraction. Examples are shown as Arrhenius plots in Figure 5 for 2-propanol[202,203] and

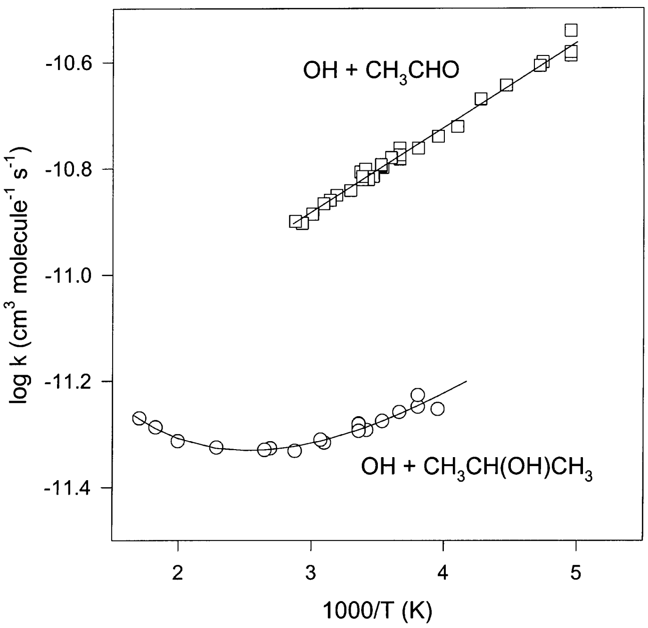


Figure 5. Arrhenius plots of rate constants for the reactions of OH radicals with acetaldehyde (absolute rate data of Sivakumuran and Crowley[204]) and 2-propanol (absolute rate data of Dunlop and Tully[202] and Yujing and Mellouki[203]).

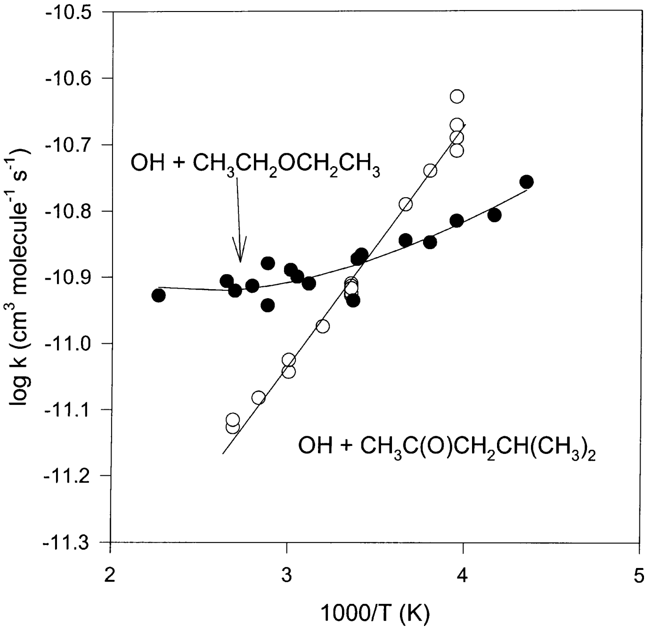


Figure 6. Arrhenius plots of rate constants for the reactions of OH radicals with diethyl ether (absolute rate data of Tully and Droege[205] and Mellouki et al.[43]) and 4-methyl-2-pentanone (absolute rate data of Le Calvé et al.[32]).

acetaldehyde[204] and in Figure 6 for 4-methyl-2-pentanone[32] and diethyl ether,[43,205] noting that rate data from only selected absolute studies are plotted. Clearly, curved Arrhenius plots are observed (as is also the case for alkanes; see Figure 1) and at elevated temperatures the rate constants are observed to increase, or are expected to increase, with increasing temperature (for example, although not shown in Figure 5, at temperatures above 600 K the rate constant for reaction of OH radicals with acetaldehyde increases rapidly with increasing temperature[206]). Measurements of the OH radical reaction rate constants for deuterated 2-propanol,[202] acetaldehyde,[206] and diethyl ether[207] (and other ethers[208]) show that for these compounds, despite their negative temperature dependencies in certain temperature regimes, the rate-determining step in the OH radical reaction involves H-atom abstraction, probably through hydrogen-bonded intermediates.[209]

Although there are numerous atmospherically relevant classes of oxygenated VOCs, many of which are formed in situ in the troposphere from other VOCs, we deal here only with aliphatic and aromatic aldehydes, RCHO, aliphatic ketones, RC(O)R′, aliphatic alcohols, ROH, and aliphatic ethers, ROR′; where R and R′ are alkyl or (for the aromatic aldehydes) aryl groups.

6.1. Aldehydes

In the troposphere, aldehydes undergo photolysis and react with OH radicals and NO_3 radicals (Table 1);[9,16.64] no reaction with O_3 has been observed.[46] Formaldehyde reacts mainly by photolysis, whereas the higher aldehydes appear to react dominantly with OH radicals.[9,16,64,210] Absorption cross-sections and photodissociation quantum yields applicable to atmospheric conditions are available for formaldehyde (including as a function of temperature)[16,64] and acetaldehyde.[16,64] Absorption cross-sections and photodissociation quantum yields have been measured for propanal,[16] *n*-butanal,[16] 2-methylpropanal,[211] *n*-pentanal,[210,212] 3-methylbutanal,[213] 2,2-dimethylpropanal,[213] *n*-hexanal,[214] *n*-heptanal,[215] and benzaldehyde,[216] noting that for certain of these the measured photodissociation quantum yields may not be applicable to atmospheric conditions (for example, if experiments were not carried out in the presence of atmospheric concentrations of O_2, which may affect the photodissociation quantum yields).[16,211−213,216]

As shown in Table 1, rate constants have been measured for the reactions of OH radicals with 16 aliphatic and 4 aromatic aldehydes, and for the keto-aldehydes pinonaldehyde, caronaldehyde, and 3-isopropenyl-6-oxo-heptanal formed from the monoterpenes α-pinene, 3-carene, and limonene, respectively. As also evident from Table 1, rate constants have been measured down to ~250 K or below for most of the $\leq C_5$ aldehydes. For the remaining 9 aliphatic aldehydes, all four aromatic aldehydes, and the keto-aldehydes formed from monoterpenes, rate constants are available only at room temperature, and in several cases only from a single study (Table 1). In all cases where temperature-dependent data are available, the rate constants increase with decreasing temperature below room temperature (Table 1), with an increase in rate constant at higher temperatures (>500−600 K) being observed for formaldehyde[30] and acetaldehyde[206] (the only two aldehydes studied at temperatures high enough for this to be observed). Despite the negative temperature dependencies observed below room temperature (see Figure 5 for acetaldehyde), the reactions of OH radicals with formaldehyde,[16] acetaldehyde,[16,217−219] and propanal[219] have been shown to proceed essentially exclusively by H-atom abstraction from the CHO group.

$$\text{OH} + \text{RCHO} \rightarrow \text{H}_2\text{O} + \text{RC}^{\bullet}\text{O} \tag{10}$$

Although the rate constants for the higher aldehydes indicate that H-atom abstraction from the CHO group accounts for a large fraction of the overall reaction,[200] H-atom abstraction from the various other C−H bonds is also expected.[200] Tuazon et al.[33] investigated the importance of H-atom abstraction from the 2-position CH group in 2,3-dimethylpentanal [$CH_3CH_2CH(CH_3)CH(CH_3)CHO$], and found this to account for 5.4 ± 1.0% of the overall reaction at 298 K, in good agreement with the empirical estimation method of Kwok and Atkinson[200] (note that H-atom abstraction from the 3-position CH group in 2,3-dimethylpentanal is predicted to be more important, at 27% of the overall reaction,[200] but the only unique product formed after H-atom abstraction from groups other than the CHO group was 3-methyl-2-pentanone formed after H-atom abstraction from the 2-position CH group[33]).

The NO_3 radical reactions also proceed by H-atom abstraction from the CHO group,[220] and rate constants have been measured for 16 aliphatic aldehydes and benzaldehyde, and for the keto-aldehydes pinonaldehyde, caronaldehyde, and 3-isopropenyl-6-oxoheptanal formed from the monoterpenes α-pinene, 3-carene, and limonene, respectively (Table 3). Rate constants have been measured below room temperature only for acetaldehyde, butanal, and 2-methylpropanal.

Acyl ($RC^{\bullet}O$) radicals react with O_2 to form acyl peroxy radicals,

$$\text{RC}^{\bullet}\text{O} + \text{O}_2\ (+\ \text{M}) \rightarrow \text{RC(O)OO}^{\bullet}\ (+\ \text{M}) \tag{11}$$

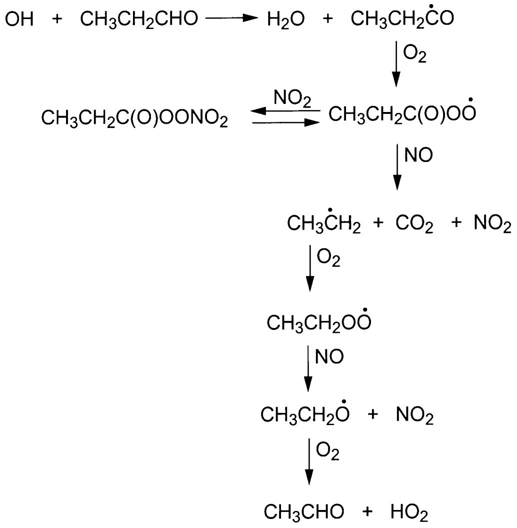
which react with NO, NO_2, HO_2 radicals, organic peroxy and acyl peroxy radicals, and NO_3 radicals.[9,16,64,69] Reaction with NO_2 forms peroxyacyl nitrates $RC(O)OONO_2$,

$$\text{RC(O)OO}^{\bullet} + \text{NO}_2\ (+\ \text{M}) \rightarrow \text{RC(O)OONO}_2\ (+\ \text{M}) \tag{12}$$

with peroxyacetyl nitrate (PAN), $CH_3C(O)OONO_2$, being the simplest member of the homologous series. The reactions of $CH_3C(O)OO^{\bullet}$ and $CH_3CH_2C(O)OO^{\bullet}$ radicals are discussed by Tyndall et al.[69] and by the IUPAC[16] and NASA[64] evaluations, and therefore are not dealt with here. In the presence of sufficient NO that peroxy radicals react dominantly with NO, then the reaction of a C_n-aldehyde with OH radicals leads in part to the formation of the C_{n-1}-aldehyde, as shown in Scheme 15, through the intermediary of an acyl peroxy radical and its corresponding peroxyacyl nitrate.

Rate constants for the reactions of OH and NO_3 radicals and O_3 with the important biogenic α,β-unsaturated aldehyde methacrolein [$CH_2{=}C(CH_3)CHO$] are listed in Tables 1−3, and the products and mechanism of its OH radical-initiated reaction have been studied by Tuazon and Atkinson[221] and Orlando and Tyndall,[222] which are in good agreement.[16,221,222]

Scheme 15



Product studies of the homologous compounds acrolein and crotonaldehyde have also been carried out,[223,224] and these references[16,221−224] should be consulted for details.

6.2. Ketones

In the troposphere, aliphatic ketones undergo photolysis and react with OH radicals and, to a much lesser extent, NO_3 radicals (Table 4);[9,16,30,64] no reactions with O_3 have been observed (Table 2).[46] Acetone is transformed approximately equally by photolysis and reaction with OH radicals,[9] and the same may be the case for 2-butanone.[225] Absorption cross-sections are available for acetone,[16] 2-butanone,[16,226−228] 2- and 3-pentanone,[226] 4-methyl-2-pentanone,[228] 5-methyl-2-hexanone,[228] and 2,4-dimethyl-3-pentanone,[228] including as a function of temperature for acetone and 2-butanone.[227]

As shown in Table 1, rate constants for the reactions of OH radicals are available for 24 ketones, including for nopinone, camphenilone, and sabinaketone formed from the monoterpenes β-pinene, camphene, and sabinene, respectively, and for camphor. Rate constants have been measured below room temperature for the OH radical reactions with acetone, 2-butanone, 3-pentanone, 3-methyl-2-butanone, 4-methyl-2-pentanone, and 5-methyl-2-hexanone (Table 1). As evident from Table 1, negative temperature dependencies are observed for most of the ketones for which temperature-dependent studies have been carried out, and curved Arrhenius plots are observed for acetone (see Figure 7),[16,209,229] 2-butanone,[32] and possibly for 3-methyl-2-butanone, 4-methyl-2-pentanone, and 5-methyl-2-hexanone.[32] In the case of the reaction of OH radicals with acetone, the rate constant decreases with decreasing temperature down to 240−250 K, below which temperature the rate constant becomes independent of temperature (down to 202 K) or may increase slightly (see Figure 7).[209,229] Despite this observed temperature dependence of the rate constant, the reaction of OH radicals with acetone proceeds by H-atom abstraction[209,218] and this is expected to be the case for other ketones. The subsequent reactions of the substi-

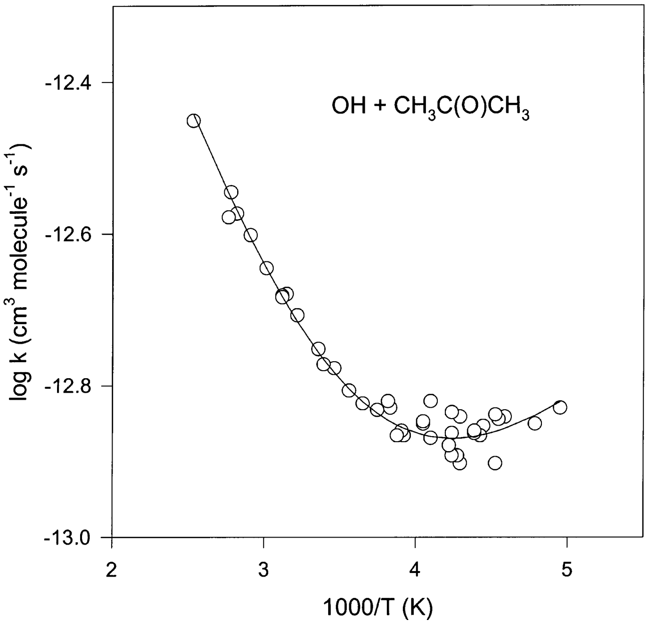


Figure 7. Arrhenius plot of the absolute rate constants of Wollenhaupt et al.[229] for the reaction of OH radicals with acetone.

tuted alkyl radicals (for example, $CH_3C(O)CH_2C^{\bullet}H_2$, $CH_3C(O)C^{\bullet}HCH_3$, and ${}^{\bullet}CH_2C(O)CH_2CH_3$ from 2-butanone) are analogous to reactions of alkyl radicals, noting that alkoxy radicals of structure $RC(O)C(O^{\bullet})<$ dominantly decompose.[230]

The only ketone for which a rate constant (or upper limit thereof) for NO_3 radical reaction has been measured is acetone;[16] the reaction is very slow ($<3 \times 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K)[16] and reactions of aliphatic ketones with NO_3 radicals are probably of no atmospheric consequence.

Rate constants for the reactions of OH and NO_3 radicals and O_3 with the important biogenic α,β-unsaturated ketone methyl vinyl ketone [$CH_3C(O)CH{=}CH_2$] are listed in Tables 1−3. The products and mechanism of its OH radical-initiated reaction have been studied by Tuazon and Atkinson,[231] and this reference[231] should be consulted for details.

6.3. Aliphatic Alcohols

As shown in Tables 1 and 3, aliphatic alcohols react with OH radicals and NO_3 radicals, with the OH radical reaction being estimated to dominate in the troposphere. No reactions with O_3 are expected.[46] As shown in Table 1, rate constants have been measured for the reaction of OH radicals with 20 alcohols, with data being available below room temperature for methanol, ethanol, 1- and 2-propanol, 1-butanol, and 2-methyl-2-propanol [*tert*-butyl alcohol] (Table 1). The reactions proceed by H-atom abstraction from the various C−H and, to a lesser extent at room temperature and below, from the O−H bond.[200] Product studies have been carried out for methanol,[16,30] ethanol,[16,30] 1-propanol,[232] 1-butanol,[233] 2-butanol,[16,39,169] *tert*-butyl alcohol,[234] 1-pentanol,[123] 2-pentanol,[39] and cyclohexanol.[42] Except for tertiary alcohols such as *tert*-butyl alcohol,[234] a significant fraction of the overall OH radical reaction proceeds by H-atom abstraction from the C−H bonds of CHOH or CH_2-OH groups. For example, for 2-butanol,

$$OH + CH_3CH(OH)CH_2CH_3 \rightarrow H_2O + CH_3C^{\bullet}(OH)CH_2CH_3 \quad (13)$$

$$CH_3C^{\bullet}(OH)CH_2CH_3 + O_2 \rightarrow CH_3C(O)CH_2CH_3 + HO_2 \quad (14)$$

with a 2-butanone formation yield of 69 ± 6% at room temperature.[169] For the reactions of OH radicals with 1-propanol, 1-butanol, 1-pentanol, 2-pentanol, and cyclohexanol at room temperature, the reported yields of the carbonyl products arising after H-atom abstraction from the CHOH or CH_2OH groups are as follows: propanal from 1-propanol, 71.9 ± 5.8%;[232] *n*-butanal from 1-butanol, 51.8 ± 7.1%;[233] *n*-pentanal from 1-pentanol, 40.5 ± 8.2%;[123] 2-pentanone from 2-pentanol, 41 ± 4%;[39] and cyclohexanone from cyclohexanol, 55 ± 6%.[42] Note that this reaction pathway and the products formed are independent of the presence or absence of NO because the α-hydroxy radical reacts rapidly with O_2 as shown in reaction 14. H-atom abstraction from C−H bonds on the carbon atom(s) adjacent to the carbon atom to which the OH group is attached is also important, and leads (in the presence of NO) to the formation of 1,2-hydroxyalkoxy radicals, which are expected to dominantly decompose or isomerize (see discussion of OH + alkene reaction mechanisms in Section 4.2.).[92,233] Abstraction from other C−H bonds leads to reactions analogous to those discussed above for the alkanes, and the original product studies[39,42,123,169,232−234] should be consulted for details.

Rate constants, or upper limits thereof, have been measured for the reactions of NO_3 radicals with methanol,[16] ethanol,[16] 1- and 2-propanol,[16] 1-butanol,[235] 2-butanol,[16] and 2-heptanol[235] (see also Table 3). These reactions are slow and it appears that absolute rate studies conducted to date have encountered problems due to secondary reactions, leading to erroneously high measured rate constants.[16] The reactions appear to proceed almost totally by H-atom abstraction from the C−H bonds of the CHOH or CH_2OH groups,[16,235] leading to the formation of, for example, 2-butanone from 2-butanol.[235]

6.4. Ethers

In the troposphere, aliphatic ethers react with OH radicals and, to a lesser extent, with NO_3 radicals.[9,16] No reaction with O_3 is expected[46] and no photolysis occurs. Rate constants have been measured for the reactions of OH radicals with 15 ethers,[16,29,30,38,43,205,236−241] and Table 1 lists the room-temperature rate constants and temperature-dependent parameters for dimethyl ether, diethyl ether, methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), and *tert*-amyl methyl ether (TAME). Rate constants have been measured at temperatures down to ~230 K for several of these ethers, including those listed in Table 1. These reactions proceed by H-atom abstraction,[29,30,207,208] with the C−H bonds on the carbon atom adjacent to the ether O− atom being markedly activated[200] (and with activation of C−H bonds occurring for H atoms located on carbon atoms several away from the ether O-atom). The intermediate alkoxy radicals $ROC(O^{\bullet})R'R''$ (R and $R' =$ alkyl and $R'' =$ H or alkyl) typically decompose to form an ester.[242]

$$ROC(O^{\bullet})R'R'' \rightarrow ROC(O)R'' + {}^{\bullet}R' \qquad (15)$$

Rate constants have been measured for the reactions of NO_3 radicals with 8 ethers,[59,174,235,237,243] with rate constants having been measured for di-isopropyl ether, ethyl *tert*-butyl ether, and *tert*-amyl methyl ether $[CH_3OC(CH_3)_2CH_2CH_3]$ down to 257 K.[243] The room-temperature rate constants reactions are in the range of 10^{-15} cm^3 molecule^{-1} s^{-1}, although there are significant discrepancies in the measured room-temperature rate constants for di-isopropyl ether and ethyl *tert*-butyl ether[59,235,243] and further work is needed to provide reliable rate data. However, the NO_3 radical reactions appear to be of minor atmospheric importance for aliphatic ethers (Table 4).

6.5. Alkyl Nitrates

As noted above in Sections 3.2.1. and 4.2., organic nitrates (including alkyl nitrates) are formed in the atmosphere from one channel of the reactions of organic peroxy radicals with NO. In the atmosphere, alkyl nitrates undergo photolysis

$$RONO_2 + h\nu \rightarrow RO^{\bullet} + NO_2 \qquad (16)$$

with unit quantum yield, and reaction with OH radicals.[16] Photolysis and reaction with OH radicals are evaluated by the NASA[64] and/or the IUPAC[16] panels for methyl nitrate, ethyl nitrate, 1- and 2-propyl nitrate, and 1- and 2-butyl nitrate. In addition to these $\leq C_4$ alkyl nitrates, absorption cross-sections have been measured for 2-methyl-1-propyl nitrate,[244] 1-pentyl nitrate,[244,245] 2-pentyl nitrate,[246] 3-pentyl nitrate,[246] cyclopentyl nitrate,[246] 2-methyl-2-propyl nitrate (*tert*-butyl nitrate),[246] 3-methyl-1-butyl nitrate,[247] and a number of bifunctional organic nitrates.[246,248,249] Consistent with the $\leq C_4$ alkyl nitrates under tropospheric conditions,[16] Zhu and Kellis[245] determined that the photodissociation quantum yield for photolysis of 1-pentyl nitrate at 308 nm to form $RO^{\bullet} + NO_2$ is 1.0 ± 0.1.

Table 1 lists room-temperature rate constants and, for methyl nitrate, ethyl nitrate, and 2-propyl nitrate, temperature-dependent rate expressions applicable to tropospheric conditions for the reactions of OH radicals with alkyl nitrates. Because the ONO_2 group deactivates the C−H bonds on both the carbon to which the ONO_2 group is attached and the adjacent carbon, the products of the OH radical-initiated reaction are expected to be bifunctional organic nitrates such as carbonyl-nitrates and (for the larger alkyl nitrates) hydroxycarbonyl-nitrates, together with dinitrates and hydroxydinitrates. However, no product studies have been conducted to date.

7. Conclusions and Future Research Needs

There is now a large body of kinetic, product, and mechanistic data concerning the atmospheric chemistry of VOCs, and we now have a qualitative, and in some cases semiquantitative or even quantitative, understanding of the chemistry occurring. However, many details remain to be elucidated, especially at temperatures below room temperature (i.e., at temperatures representative of the middle and upper troposphere). For example, there is now a large database concerning the kinetics of the reactions of OH radical, NO_3 radical, and O_3 with VOCs, but relatively few VOCs have been studied below room temperature. Product data have been obtained for a number of VOC atmospheric reactions, mainly in the presence of NO such that organic peroxy radicals dominantly react with NO, with the key intermediates then being (Scheme 1) alkoxy radicals. Empirical estimation methods have been used to predict products and their yields from alkoxy radicals, and comparisons of these predictions with experimental data show approximate agreement in a number of cases.

7.1. Needed Research

7.1.1. Experimental Studies

Rate constants for the reactions of VOCs with OH radicals and, where applicable, NO_3 radicals and O_3 need to be measured for those VOCs for which such data are not presently available (see Tables 1−3). Additionally, kinetic and product data for the reactions of organic peroxy ($RO_2^{\bullet}$) radicals with NO and with HO_2 and $RO_2^{\bullet}$ radicals need to be obtained for a wide variety of $RO_2^{\bullet}$ radicals, and organic nitrate yields from the $RO_2^{\bullet} + NO$ reactions need to be obtained for a wide variety of $RO_2^{\bullet}$ radicals. It is important that all of these studies be conducted under conditions that are representative of the entire troposphere, covering temperatures from ∼210−300 K and pressures from one atmosphere to as low as ∼100 Torr.

Rate constants for the reactions of alkoxy radicals (i.e., decomposition, isomerization, and reaction with O_2) need to be determined for a wide variety of alkoxy radicals (including substituted alkoxy radicals such as 1,2- and 1,4-hydroxyalkoxy and 1,2-nitrooxyalkoxy radicals), preferably using absolute rate techniques. However, it remains to be seen whether such data will be sufficiently accurate, or extensive enough, to supersede rate constant ratios for decomposition vs isomerization vs reaction with O_2 obtained for alkoxy radicals from experimental product studies conducted at atmospheric conditions of temperature and pressure.

Product data for the atmospherically important reactions of VOCs need to be obtained over temperature and pressure ranges representative of tropospheric conditions. This will require advances in analytical techniques to identify and quantify compounds for which standards may not be available and which cannot presently be accurately quantified. Analytical methods should, wherever possible, minimize the potential for sample losses and/or sample reaction (for example, cyclization, isomerization, or decomposition) during any sample collection procedure.

7.1.2. Theoretical Studies and Critical Reviews and Evaluations

Given the very large number of VOCs emitted into the atmosphere or produced in situ in the atmosphere from other VOCs, there is a continuing need to develop and test reliable methods for the prediction of reaction rates and reaction pathways. This is particularly important for alkoxy radical reactions, because these are often the key intermediate species in VOC degradations. Although the NASA[64] and IUPAC[16] evaluations are invaluable, there is a need for an ongoing comprehensive review and evaluation effort dealing with the kinetics and mechanisms of the OH radical, NO_3 radical, and O_3 reactions with atmospherically relevant VOCs, and for their absorption cross-sections and photodissociation quantum yields. Even though this is a major task (and becoming more so as time goes on and the database expands), it is a necessary undertaking for input to both modelers and experimentalists. Such reviews and evaluations should be readily available to the scientific community, preferably through the worldwide web.

Future research into the atmospheric chemistry of VOCs should use a multi-pronged, interactive approach involving (1) experimental kinetic and product studies (including development of new and improved analytical methods), (2) theoretical calculations, (3) an ongoing effort to review and evaluate the kinetic, product, and mechanistic database, and (4) comparison of observations in the real atmosphere with predictions made from experimental laboratory data, either directly (for example, from observations in the atmosphere of VOC reaction products identified in laboratory experiments) or through the use of detailed chemical computer models. The past 5−8 years have seen a real advance in our knowledge of the detailed chemistry of VOCs occurring in the atmosphere, and there is no reason to anticipate that this will not continue.

8. Acknowledgments

We gratefully thank the U.S. Department of Energy for support of this research through Contract DE-FG03-01ER63095. Although this research has been funded by a Federal Agency, the results and content of this publication do not necessarily reflect the views and opinions of the Agency or the U.S. Government.

9. Note Added in Proof

Since this article was prepared, a number of relevant publications have appeared in the literature. Boyd et al.[250] have measured room temperature rate constants for the gas-phase reactions of the HO_2 radical with a series of $RO_2^{\bullet}$ radicals (those formed after H-atom abstraction by OH radicals from methane, ethane, 2,2-dimethylpropane, cyclohexane, *n*-decane, and *n*-tetradecane, and those formed after OH radical reaction (mainly addition) with ethene, 2,3-dimethyl-2-butene, isoprene, cyclohexene, α-pinene, γ-terpinene, and limonene). The rate constants for these reactions of $RO_2^{\bullet}$ radicals formed from *n*-decane, *n*-tetraedecane, 2,3-dimethyl-2-butene, isoprene, cyclohexene, α-pinene, γ-terpinene, and limonene are in the range $(1.50-2.24) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, similar to those listed in Tables 6 and 12 for the $\geq$C4 $RO_2^{\bullet}$ radicals. Park et al.[251] have calculated pressure- and temperature-dependent decomposition rates for the 1,2- and 1,4-hydroxyalkoxy radicals formed after OH radical addition to isoprene. Their results indicate that the 1,2-hydroxyalkoxy radicals undergo rapid decomposition at room temperature and atmospheric pressure and that decomposition of the 1,4-hydroxyalkoxy radicals $HOCH_2C(CH_3){=}CHCH_2O^{\bullet}$ and $HOCH_2CH{=}C(CH_3)CH_2O^{\bullet}$ is very slow, consistent with the results of product studies conducted at atmospheric pressure of air. Gierczak et al.[252] have measured absolute rate constants for the reactions of OH radicals with acetone (199−383 K) and acetone-d_6 (211−383 K), of OD radicals with acetone (at 223 and 296 K) and acetone-d_6 (213−324 K), and of ^{18}OH radicals with acetone (240−296 K), where the temperature ranges covered are given in parentheses. The results of this study were summarized in ref 209. Talukdar et al.[253] have investigated the products of the reaction of OH radicals with acetone and concluded that the reaction proceeds through a hydrogen-bonded complex that yields almost exclusively $H_2O + CH_3C(O)C^{\bullet}H_2$, with a measured yield of $CH_3C(O)C^{\bullet}H_2$ radicals of 96 ± 11%, independent of temperature over the range 242−353 K.

10. References

(1) Scientific Assessment of Ozone Depletion: World Meterolological Organization Global Ozone Research and Monitoring Project; Report No. 37; Geneva, Switzerland, 1994; February 1995.
(2) Guenther, A.; Hewitt, C. N.; Erickson, D.; Fall, R.; Geron, C.; Graedel, T.; Harley, P.; Klinger, L.; Lerdau, M.; McKay, W. A.; Pierce, T.; Scholes, B.; Steinbrecher, R.; Tallamraju, R.; Taylor, J.; Zimmermann, P. *J. Geophys. Res.* **1995**, *100*, 8873.
(3) Guenther, A.; Geron, C.; Pierce, T.; Lamb, B.; Harley, P.; Fall, R. *Atmos. Environ.* **2000**, *34*, 2205.
(4) Sawyer, R. F.; Harley, R. A.; Cadle, S. H.; Norbeck, J. M.; Slott, R.; Bravo, H. A. *Atmos. Environ.* **2000**, *34*, 2161.
(5) Placet, M.; Mann, C. O.; Gilbert, R. O.; Niefer, M. J. *Atmos. Environ.* **2000**, *34*, 2183.
(6) Fall, R. Biogenic Emissions of Volatile Organic Compounds from Higher Plants. In *Reactive Hydroxcarbons in the Atmosphere*; Hewitt, C. N., Ed.; Academic Press: San Diego, CA, 1999; pp 43−96.
(7) Lurmann, F. W.; Main, H. H. *Analysis of the Ambient VOC Data Collected in the Southern California Air Quality Study*; Final Report to California Air Resources Contract A832-130; Sacramento, CA, February 1992.
(8) Calvert, J. G.; Atkinson, R.; Becker, K. H.; Kamens, R. M.; Seinfeld, J. H.; Wallington, T. J.; Yarwood, G. *The Mechanisms of Atmospheric Oxidation of Aromatic Hydrocarbons*; Oxford University Press: New York, 2002.
(9) Atkinson, R. *Atmos. Environ.* **2000**, *34*, 2063.
(10) Bidleman, T. F. *Environ. Sci. Technol.* **1988**, *22*, 361.
(11) Wesely, M. L.; Hicks, B. B. *Atmos. Environ.* **2000**, *34*, 2261.
(12) Finlayson-Pitts, B. J.; Pitts, J. N., Jr. *Chemistry of the Upper and Lower Atmosphere*; Academic Press: San Diego, CA, 2000.
(13) Atkinson, R. *Atmos. Chem. Phys. Discuss.* **2003**, *3*, 4183. http://www.copernicus.org/EGU/acp/acpd/3/4183/acpd-3-4183_p.pdf.
(14) Atkinson, R. *J. Phys. Chem. Ref. Data* **1997**, *26*, 215.
(15) Calvert, J. G.; Atkinson, R.; Kerr, J. A.; Madronich, S.; Moortgat, G. K.; Wallington, T. J.; Yarwood, G. *The Mechanisms of Atmospheric Oxidation of the Alkenes*; Oxford University Press: New York, 2000.
(16) IUPAC; http://www.iupac-kinetic.ch.cam.ac.uk/.
(17) Atkinson, R.; Aschmann, S. M.; Pitts, J. N., Jr. *Int. J. Chem. Kinet.* **1986**, *18*, 287.
(18) Gill, K. J.; Hites, R. A. *J. Phys. Chem. A* **2002**, *106*, 2538.
(19) Berndt, T.; Böge, *Int. J. Chem. Kinet.* **2001**, *33*, 124.

(20) Semmes, D. H.; Ravishankara, A. R.; Gump-Perkins, C. A.; Wine, P. H. *Int. J. Chem. Kinet.* **1985**, *17*, 303.
(21) Thévenet, R.; Mellouki, A.; Le Bras, G. *Int. J. Chem. Kinet.* **2000**, *32*, 676.
(22) Papagni, C.; Arey, J.; Atkinson, R. *Int. J. Chem. Kinet.* **2000**, *32*, 79.
(23) D'Anna, B.; Andresen, Ø.; Gefen, Z.; Nielsen, C. J. *Phys. Chem. Chem. Phys.* **2001**, *3*, 3057.
(24) Albaladejo, J.; Ballesteros, B.; Jiménez, E.; Martín, P.; Martínez, E. *Atmos. Environ.* **2002**, *36*, 3231.
(25) Thiault, G.; Mellouki, A.; Le Bras, G. *Phys. Chem. Chem. Phys.* **2002**, *4*, 2194.
(26) Alvarado, A.; Arey, J.; Atkinson, R. *J. Atmos. Chem.* **1998**, *31*, 281.
(27) Nozière, B.; Spittler, M.; Ruppert, L.; Barnes, I.; Becker, K. H.; Pons, M.; Wirtz, K. *Int. J. Chem. Kinet.* **1999**, *31*, 291.
(28) Calogirou, A.; Jensen, N. R.; Nielsen, C. J.; Kotzias, D.; Hjorth, J. *Environ. Sci. Technol.* **1999**, *33*, 453.
(29) Atkinson, R. *J. Phys. Chem. Ref. Data* **1989**, *Monograph 1*, 1.
(30) Atkinson, R. *J. Phys. Chem. Ref. Data* **1994**, *Monograph 2*, 1.
(31) Atkinson, R.; Tuazon, E. C.; Aschmann, S. M. *Environ. Sci. Technol.* **2000**, *34*, 623.
(32) Le Calvé, S.; Hitier, D.; Le Bras, G.; Mellouki, A. *J. Phys. Chem. A* **1998**, *102*, 4579.
(33) Tuazon, E. C.; Aschmann, S. M.; Nguyen, M. V.; Atkinson, R. *Int. J. Chem. Kinet.* **2003**, *35*, 415.
(34) Reissell, A.; Arey, J.; Atkinson, R. *Int. J. Chem. Kinet.* **2001**, *33*, 56.
(35) Jiménez, E.; Gilles, M. K.; Ravishankara, A. R. *J. Photochem. Photobiol. A: Chem.* **2003**, *157*, 237.
(36) Wu, H.; Mu, Y.; Zhang, X.; Jiang, G. *Int. J. Chem. Kinet.* **2003**, *35*, 81.
(37) Wallington, T. J.; Dagaut, P.; Liu, R.; Kurylo, M. J. *Environ. Sci. Technol.* **1988**, *22*, 842.
(38) Teton, S.; Mellouki, A.; Le Bras, G.; Sidebottom, H. *Int. J. Chem. Kinet.* **1996**, *28*, 291.
(39) Baxley, J. S.; Wells, J. R. *Int. J. Chem. Kinet.* **1998**, *30*, 745.
(40) Saunders, S. M.; Baulch, D. L.; Cooke, K. M.; Pilling, M. J.; Smurthwaite, P. I. *Int. J. Chem. Kinet.* **1994**, *26*, 113.
(41) Aschmann, S. M.; Atkinson, R. *Int. J. Chem. Kinet.* **1998**, *30*, 533.
(42) Bradley, W. R.; Wyatt, S. E.; Wells, J. R.; Henley, M. V.; Graziano, G. M. *Int. J. Chem. Kinet.* **2001**, *33*, 108.
(43) Mellouki, A.; Teton, S.; Le Bras, G. *Int. J. Chem. Kinet.* **1995**, *27*, 791.
(44) Vakhtin, A. B.; Lee, S.; Heard, D. E.; Smith, I. W. M.; Leone, S. R. *J. Phys. Chem. A* **2001**, *105*, 7889.
(45) Sims, I. R.; Smith, I. W. M.; Bocherel, P.; Defrance, A.; Travers, D.; Rowe, B. R. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1473.
(46) Atkinson, R.; Carter, W. P. L. *Chem. Rev.* **1984**, *84*, 437.
(47) Avzianova, E. V.; Ariya, P. A. *Int. J. Chem. Kinet.* **2002**, *34*, 678.
(48) Grosjean, E.; Grosjean, D. *Int. J. Chem. Kinet.* **1997**, *29*, 855.
(49) Khamaganov, V. G.; Hites, R. A. *J. Phys. Chem. A* **2001**, *105*, 815.
(50) Canosa-Mas, C. E.; King, M. D.; McDonnell, L.; Wayne, R. P. *Phys. Chem. Chem. Phys.* **1999**, *1*, 2681.
(51) Kind, I.; Berndt, T.; Bøge, O. *Chem. Phys. Lett.* **1998**, *288*, 111.
(52) Atkinson, R.; Aschmann, S. M.; Long, W. D.; Winer, A. M. *Int. J. Chem. Kinet.* **1985**, *17*, 957.
(53) Atkinson, R.; Aschmann, S. M.; Winer, A. M.; Pitts, J. N., Jr. *Environ. Sci. Technol.* **1984**, *18*, 370.
(54) Ljungström, E.; Wängberg, I.; Langer, S. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 2977.
(55) Canosa-Mas, C. E.; King, M. D.; Scarr, P. J.; Thompson, K. C.; Wayne, R. P. *Phys. Chem. Chem. Phys.* **1999**, *1*, 2929.
(56) D'Anna, B.; Nielsen, C. J. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 3479.
(57) Ullerstam, M.; Langer, S.; Ljungström, E. *Int. J. Chem. Kinet.* **2000**, *32*, 294.
(58) Noda, J.; Holm, C.; Nyman, G.; Langer, S.; Ljungström, E. *Int. J. Chem. Kinet.* **2003**, *35*, 120.
(59) Langer, S.; Ljungström, E. *Int. J. Chem. Kinet.* **1994**, *26*, 367.
(60) Jobson, B. T.; Niki, H.; Yokouchi, Y.; Bottenheim, J.; Hopper, F.; Leaitch, R. *J. Geophys. Res.* **1994**, *99*, 25355.
(61) Singh, H. B.; Thakur, A. N.; Chen, Y. E.; Kanakidou, M. *Geophys. Res. Lett.* **1996**, *23*, 1529.
(62) Rudolph, J.; Koppermann, R.; Plass-Dülmer, Ch. *Atmos. Environ.* **1996**, *30*, 1887.
(63) Rudolph, J.; Ramacher, R.; Plass-Dülmer, Ch.; Müller, K.-P.; Koppermann, R. *Tellus B* **1997**, *49*, 592.
(64) NASA Panel for Data Evaluation; http://jpldataeval.jpl.nasa.gov/index.html.
(65) Lightfoot, P. D.; Cox, R. A.; Crowley, J. N.; Destriau, M.; Hayman, G. D.; Jenkin, M. E.; Moortgat, G. K.; Zabel, F. *Atmos. Environ.* **1992**, *26A*, 1805.
(66) Wallington, T. J.; Dagaut, P.; Kurylo, M. J. *Chem. Rev.* **1992**, *92*, 667.
(67) Lesclaux, R. Combination of Peroxyl Radicals in the Gas Phase. In *Peroxyl Radicals*; Alfassi, Z. B., Ed.; Wiley: New York, 1997; pp 81−112.
(68) Wallington, T. J.; Nielsen O. J. Peroxy Radicals and the Atmosphere. In *Peroxyl Radicals*; Alfassi, Z. B., Ed.; Wiley: New York, 1997; pp 113−172.
(69) Tyndall, G. S.; Cox, R. A.; Granier, C.; Lesclaux, R.; Moortgat, G. K.; Pilling, M. J.; Ravishankara, A. R.; Wallington, T. J. *J. Geophys. Res.* **2001**, *106*, 12157.
(70) Eberhard, J.; Howard, C. J. *J. Phys. Chem. A* **1997**, *101*, 3360.
(71) Sehested, J.; Nielsen, O. J.; Wallington, T. J. *Chem. Phys. Lett.* **1993**, *213*, 457.
(72) Platz, J.; Sehested, J.; Nielsen, O. J.; Wallington, T. J. *J. Phys. Chem. A* **1999**, *103*, 2688.
(73) Takagi, H.; Washida, N.; Bandow, H.; Akimoto, H.; Okuda, M. *J. Phys. Chem.* **1981**, *85*, 2701.
(74) Atkinson, R.; Aschmann, S. M.; Carter, W. P. L.; Winer, A. M.; Pitts, J. N., Jr. *J. Phys. Chem.* **1982**, *86*, 4563.
(75) Atkinson, R.; Carter, W. P. L.; Winer, A. M. *J. Phys. Chem.* **1983**, *87*, 2012.
(76) Atkinson, R.; Aschmann, S. M.; Carter, W. P. L.; Winer, A. M.; Pitts, J. N., Jr. *Int. J. Chem. Kinet.* **1984**, *16*, 1085.
(77) Atkinson, R.; Aschmann, S. M.; Winer, A. M. *J. Atmos. Chem.* **1987**, *5*, 91.
(78) Harris, S. J.; Kerr, J. A. *Int. J. Chem. Kinet.* **1989**, *21*, 207.
(79) Carter, W. P. L.; Atkinson, R. *J. Atmos. Chem.* **1989**, *8*, 165.
(80) Atkinson, R.; Kwok, E. S. C.; Arey, J.; Aschmann, S. M. *Faraday Discuss.* **1995**, *100*, 23.
(81) Aschmann, S. M.; Chew, A. A.; Arey, J.; Atkinson, R. *J. Phys. Chem. A* **1997**, *101*, 8042.
(82) Orlando, J. J.; Iraci, L. T.; Tyndall, G. S. *J. Phys. Chem. A* **2000**, *104*, 5072.
(83) Ranschaert, D. L.; Schneider, N. J.; Elrod, M. J. *J. Phys. Chem. A* **2000**, *104*, 5758.
(84) Arey, J.; Aschmann, S. M.; Kwok, E. S. C.; Atkinson, R. *J. Phys. Chem. A* **2001**, *105*, 1020.
(85) Aschmann, S. M.; Arey, J.; Atkinson, R. *J. Phys. Chem. A* **2001**, *105*, 7598.
(86) Zabel, F. *Z. Phys. Chem.* **1995**, *188*, 119.
(87) Kirchner, F.; Mayer-Figge, A.; Zabel, F.; Becker, K. H. *Int. J. Chem. Kinet.* **1999**, *31*, 127.
(88) Rowley, D. M.; Lesclaux, R.; Lightfoot, P. D.; Hughes, K.; Hurley, M. D.; Rudy, S.; Wallington, T. J. *J. Phys. Chem.* **1992**, *96*, 7043.
(89) Rowley, D. M.; Lesclaux, R.; Lightfoot, P. D.; Nozière, B.; Wallington, T. J.; Hurley, M. D. *J. Phys. Chem.* **1992**, *96*, 4889.
(90) Crawford, M. A.; Szente, J. J.; Maricq, M. M.; Francisco, J. S. *J. Phys. Chem. A* **1997**, *101*, 5337.
(91) Logan, J. A. *J. Geophys. Res.* **1985**, *90*, 10463.
(92) Atkinson, R. *Int. J. Chem. Kinet.* **1999**, *29*, 99.
(93) Tuazon, E. C.; Aschmann, S. M.; Atkinson, R.; Carter, W. P. L. *J. Phys. Chem. A* **1998**, *102*, 2316.
(94) Christensen, L. K.; Ball, J. C.; Wallington, T. J. *J. Phys. Chem. A* **2000**, *104*, 345.
(95) Gutman, D.; Sanders, N.; Butler, J. E. *J. Phys. Chem.* **1982**, *86*, 66.
(96) Fittschen, C.; Frenzel, A.; Imrik, K.; Devolder, P. *Int. J. Chem. Kinet.* **1999**, *31*, 860.
(97) Mund, Ch.; Fockenberg, Ch.; Zellner, R. *Ber. Bunsen-Ges. Phys. Chem.* **1998**, *102*, 709. Mund, Ch.; Fockenberg, Ch.; Zellner, R. *Phys. Chem. Chem. Phys.* **1999**, *1*, 2037.
(98) Balla, R. J.; Nelson, H. H.; McDonald, J. R. *Chem. Phys.* **1985**, *99*, 323.
(99) Hein, H.; Hoffmann, A.; Zellner, R. *Phys. Chem. Chem. Phys.* **1999**, *1*, 3743.
(100) Hein, H.; Hoffmann, A.; Zellner, R. *Ber. Bunsen-Ges. Phys. Chem.* **1998**, *102*, 1840.
(101) Deng, W.; Wang, C.; Katz, D. R.; Gawinski, G. R.; Davis, A. J.; Dibble, T. S. *Chem. Phys. Lett.* **2000**, *330*, 541.
(102) Deng, W.; Davis, A. J.; Zhang, L.; Katz, D. R.; Dibble, T. S. *J. Phys. Chem. A* **2001**, *105*, 8985.
(103) Hein, H.; Somnitz, H.; Hoffmann, A.; Zellner, R. *Z. Phys. Chem.* **2000**, *214*, 449.
(104) Caralp, F.; Devolder, P.; Fittschen, Ch.; Gomez, N.; Hippler, H.; Méreau, R.; Rayez, M. T.; Strieble, F.; Viskolcz, B. *Phys. Chem. Chem. Phys.* **1999**, *1*, 2935.
(105) Devolder, P.; Fittschen, Ch.; Frenzel, A.; Hippler, H.; Poskrebyshev, G.; Strieble, F.; Viskolcz, B. *Phys. Chem. Chem. Phys.* **1999**, *1*, 675.
(106) Blitz, M.; Pilling, M. J.; Robertson, S. H.; Seakins, P. W. *Phys. Chem. Chem. Phys.* **1999**, *1*, 73.
(107) Fittschen, Ch.; Hippler, H.; Viskolcz, B. *Phys. Chem. Chem. Phys.* **2000**, *2*, 1677.
(108) Somnitz, H.; Zellner, R. *Phys. Chem. Chem. Phys.* **2000**, *2*, 1899.
(109) Somnitz, H.; Zellner, R. *Phys. Chem. Chem. Phys.* **2000**, *2*, 1907.
(110) Carter, W. P. L.; Lloyd, A. C.; Sprung, J. L.; Pitts, J. N., Jr. *Int. J. Chem. Kinet.* **1979**, *11*, 45.
(111) Cox, R. A.; Patrick, K. F.; Chant, S. A. *Environ. Sci. Technol.* **1981**, *15*, 587.

(112) Libuda, H. G.; Shestakov, O.; Theloke, J.; Zabel, F. *Phys. Chem. Chem. Phys.* **2002**, *4*, 2579.
(113) Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P. *J. Phys. Chem.* **1981**, *85*, 2698.
(114) Wallington, T. J.; Hurley, M. D.; Fracheboud, J. M.; Orlando, J. J.; Tyndall, G. S.; Sehested, J.; Møgelberg, T. E.; Nielsen, O. J. *J. Phys. Chem.* **1996**, *100*, 18116.
(115) Orlando, J. J.; Tyndall, G. S.; Bilde, M.; Ferronato, C.; Wallington, T. J.; Vereecken, L.; Peeters, J. *J. Phys. Chem. A* **1998**, *102*, 8116.
(116) Lendvay, G.; Viskolcz, B. *J. Phys. Chem. A* **1998**, *102*, 10777.
(117) Dibble, T. S. *J. Phys. Chem. A* **2002**, *106*, 6643.
(118) Cox, R. A.; Derwent, R. G.; Williams, M. R. *Environ. Sci. Technol.* **1980**, *14*, 57.
(119) Eberhard, J.; Müller, C.; Stocker, D. W.; Kerr, J. A. *Environ. Sci. Technol.* **1995**, *29*, 232.
(120) Kwok, E. S. C.; Arey, J.; Atkinson, R. *J. Phys. Chem.* **1996**, *100*, 214.
(121) Aschmann, S. M.; Arey, J.; Atkinson, R. *Environ. Sci. Technol.* **2002**, *36*, 625.
(122) Reisen, F.; Aschmann, S. M.; Atkinson, R.; Arey, J. *Environ. Sci. Technol.* **2003**, to be submitted for publication.
(123) Cavalli, F.; Barnes, I.; Becker, K. H. *Environ. Sci. Technol.* **2000**, *34*, 4111. Barnes, I., personal communication, 2002.
(124) Martin, P.; Tuazon, E. C.; Aschmann, S. M.; Arey, J.; Atkinson, R. *J. Phys. Chem. A* **2002**, *106*, 11492.
(125) Aschmann, S. M.; Arey, J.; Atkinson, R. *J. Atmos. Chem.* **2003**, *45*, 289.
(126) Chen, X.; Hulbert, D.; Shepson, P. B. *J. Geophys. Res.* **1998**, *103*, 25563.
(127) O'Brien, J. M.; Czuba, E.; Hastie, D. R.; Francisco, J. S.; Shepson, P. B. *J. Phys. Chem. A* **1998**, *102*, 8903.
(128) Spengnether, M.; Demerjian, K. L.; Donahue, N. M.; Anderson, J. G. *J. Geophys. Res.* **2002**, *107* (D15), ACH 8−1.
(129) Langer, S.; Ljungström, E.; Sehested, J.; Nielsen, O. J. *Chem. Phys. Lett.* **1994**, *226*, 165.
(130) Boyd, A. A.; Lesclaux, R.; Jenkin, M. E.; Wallington, T. J. *J. Phys. Chem.* **1996**, *100*, 6594.
(131) Jenkin, M. E.; Hayman, G. D. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 1911.
(132) Stevens, P.; L'Esperance, D.; Chuong, B.; Martin, G. *Int. J. Chem. Kinet.* **1999**, *31*, 637.
(133) Chuong, B.; Stevens, P. S. *J. Geophys. Res.* **2002**, *107* (D13), ACH 2−1.
(134) Reitz, J. E.; McGivern, W. S.; Church, W. C.; Wilson, M. D.; North, S. W. *Int. J. Chem. Kinet.* **2002**, *34*, 255.
(135) Boyd, A. A.; Lesclaux, R. *Int. J. Chem. Kinet.* **1997**, *29*, 323.
(136) Boyd, A. A.; Villenave, E.; Lesclaux, R. *Atmos. Environ.* **2003**, *37*, 2751.
(137) Dibble, T. S. *J. Phys. Chem. A* **1999**, *103*, 8559.
(138) Lei, W.; Zhang, R. *J. Phys. Chem. A* **2001**, *105*, 3808.
(139) Kwok, E. S. C.; Atkinson, R.; Arey, J. *Environ. Sci. Technol.* **1996**, *30*, 1048.
(140) Aschmann, S. M.; Atkinson, R.; Arey, J. *J. Geophys. Res.* **2002**, *107* (D14), ACH 6−1.
(141) Vereecken, L.; Peeters, J.; Orlando, J. J.; Tyndall, G. S.; Ferronato, C. *J. Phys. Chem. A* **1999**, *103*, 4693.
(142) Kwok, E. S. C.; Atkinson, R.; Arey, J. *Environ. Sci. Technol.* **1995**, *29*, 2467.
(143) Atkinson, R.; Aschmann, S. M.; Tuazon, E. C.; Arey, J.; Zielinska, B. *Int. J. Chem. Kinet.* **1989**, *21*, 593.
(144) Nozière, B.; Barnes, I.; Becker, K.-H. *J. Geophys. Res.* **1999**, *104*, 23645.
(145) Reissell, A.; Harry, C.; Aschmann, S. M.; Atkinson, R.; Arey, J. *J. Geophys. Res.* **1999**, *104*, 13869.
(146) Orlando, J. J.; Nozière, B.; Tyndall, G. S.; Orzechowska, G.; Paulson, S. E.; Rudich, Y. *J. Geophys. Res.* **2000**, *105*, 11561.
(147) Skov, H.; Benter, Th.; Schindler, R. N.; Hjorth, J.; Restelli, G. *Atmos. Environ.* **1994**, *28*, 1583.
(148) Berndt, T.; Böge, O. *Ber. Bunsen-Ges. Phys. Chem.* **1994**, *98*, 869.
(149) Berndt, T.; Böge, O. *J. Atmos. Chem.* **1995**, *21*, 275.
(150) Skov, H.; Hjorth, J.; Lohse, C.; Jensen, J. R.; Restelli, G. *Atmos. Environ.* **1992**, *26A*, 2771.
(151) Kwok, E. S. C.; Aschmann, S. M.; Atkinson, R.; Arey, J. *Int. J. Chem. Kinet.* **1996**, *28*, 925.
(152) Gutbrod, R.; Schindler, R. N.; Kraka, E.; Cremer, D. *Chem. Phys. Lett.* **1996**, *252*, 221.
(153) Kroll, J. H.; Donahue, N. M.; Cee, V. J.; Demerjian, K. L.; Anderson, J. G. *J. Am. Chem. Soc.* **2002**, *124*, 8518.
(154) Fenske, J. D.; Hasson, A. S.; Ho, A. W.; Paulson, S. E. *J. Phys. Chem. A* **2000**, *104*, 9921.
(155) Kroll, J. H.; Clarke, J. S.; Donahue, N. M.; Anderson, J. G.; Demerjian, K. L. *J. Phys. Chem. A* **2001**, *105*, 1554.
(156) Kroll, J. H.; Sahay, S. R.; Anderson, J. G.; Demerjian, K. L.; Donahue, N. M. *J. Phys. Chem. A* **2001**, *105*, 4446.
(157) Zhang, D.; Zhang, R. *J. Am. Chem. Soc.* **2002**, *124*, 2692.
(158) Alvarado, A.; Tuazon, E. C.; Aschmann, S. M.; Atkinson, R.; Arey, J. *J. Geophys. Res.* **1998**, *103*, 25541.
(159) Paulson, S. E.; Sen, A. D.; Liu, P.; Fenske, J. D.; Fox, M. J. *Geophys. Res. Lett.* **1997**, *24*, 3193.
(160) Pfeiffer, T.; Forberich, O.; Comes, F. J. *Chem. Phys. Lett.* **1998**, *298*, 351.
(161) Siese, M.; Becker, K. H.; Brockmann, K. J.; Geiger, H.; Hofzumahaus, A.; Holland, F.; Mihelcic, D.; Wirtz, K. *Environ. Sci. Technol.* **2001**, *35*, 4660.
(162) Kroll, J. H.; Hanisco, T. F.; Donahue, N. M.; Demerjian, K. L.; Anderson, J. G. *Geophys. Res. Lett.* **2001**, *28*, 3863.
(163) Becker, K. H.; Bechara, J.; Brockmann, K. J. *Atmos. Environ.* **1993**, *27A*, 57.
(164) Sauer, F.; Schäfer, C.; Neeb, P.; Horie, O.; Moortgat, G. K. *Atmos. Environ.* **1999**, *33*, 229.
(165) Winterhalter, R.; Neeb, P.; Grossmann, D.; Kolloff, A.; Horie, O.; Moortgat, G. *J. Atmos. Chem.* **2000**, *35*, 165.
(166) Baker, J.; Aschmann, S. M.; Arey, J.; Atkinson, R. *Int. J. Chem. Kinet.* **2002**, *34*, 73.
(167) Johnson, D.; Lewin, A. G.; Marston, G. *J. Phys. Chem. A* **2001**, *105*, 2933.
(168) Atkinson, R.; Aschmann, S. M.; Arey, J.; Shorees, B. *J. Geophys. Res.* **1992**, *97*, 6065.
(169) Aschmann, S. M.; Arey, J.; Atkinson, R. *Atmos. Environ.* **2002**, *36*, 4347.
(170) Hakola, H.; Arey, J.; Aschmann, S. M.; Atkinson, R. *J. Atmos. Chem.* **1994**, *18*, 75.
(171) Aschmann, S. M.; Atkinson, R. *Environ. Sci. Technol.* **1994**, *28*, 1539.
(172) Tuazon, E. C.; Aschmann, S. M.; Arey, J.; Atkinson, R. *Environ. Sci. Technol.* **1998**, *32*, 2106.
(173) Paulson, S. E.; Orlando, J. J. *Geophys. Res. Lett.* **1996**, *23*, 3727.
(174) Atkinson, R. *J. Phys. Chem. Ref. Data* **1991**, *20*, 459.
(175) Knispel, R.; Koch, R.; Siese, M.; Zetzsch, C. *Ber. Bunsen-Ges. Phys. Chem.* **1990**, *94*, 1375.
(176) Koch, R.; Knispel, R.; Siese, M.; Zetzsch, C. Absolute Rate Constants and Products of Secondary Steps in the Atmospheric Degradation of Aromatics. In *Proceedings of the 6th European Symposium on the Physico-Chemical Behavior of Atmospheric Pollutants*; Angeletti, G., Restelli, G., Eds.; European Commission: Brussels, Belgium, 1994; pp 143−149.
(177) Bohn, B.; Zetzsch, C. *Phys. Chem. Chem. Phys.* **1999**, *1*, 5097.
(178) Bohn, B. *J. Phys. Chem. A* **2001**, *105*, 6092.
(179) Klotz, B.; Volkamer, R.; Hurley, M. D.; Anderson, M. P. S.; Nielsen, O. J.; Barnes, I.; Imamura, T.; Wirtz, K.; Becker, K.-H.; Platt, U.; Wallington, T. J.; Washida, N. *Phys. Chem. Chem. Phys.* **2002**, *4*, 4399.
(180) Atkinson, R.; Aschmann, S. M. *Int. J. Chem. Kinet.* **1994**, *26*, 929.
(181) Kwok, E. S. C.; Aschmann, S. M.; Atkinson, R.; Arey, J. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 2847.
(182) Smith, D. F.; McIver, C. D.; Kleindienst, T. E. *J. Atmos. Chem.* **1998**, *30*, 209.
(183) Klotz, B.; Sørensen, S.; Barnes, I.; Becker, K. H.; Etzkorn, T.; Volkamer, R.; Platt, U.; Wirtz, K.; Martín-Reviejo, M. *J. Phys. Chem. A* **1998**, *102*, 10289.
(184) Smith, D. F.; Kleindienst, T. E.; McIver, C. D. *J. Atmos. Chem.* **1999**, *34*, 339.
(185) Bethel, H. L.; Atkinson, R.; Arey, J. *J. Phys. Chem. A* **2000**, *104*, 8922.
(186) Volkamer, R.; Platt, U.; Wirtz, K. *J. Phys. Chem. A* **2001**, *105*, 7865.
(187) Volkamer, R.; Klotz, B.; Barnes, I.; Imamura, T.; Wirtz, K.; Washida, N.; Becker, K. H.; Platt, U. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1598.
(188) Atkinson, R.; Aschmann, S. M.; Arey, J.; Carter, W. P. L. *Int. J. Chem. Kinet.* **1989**, *21*, 801.
(189) Atkinson, R.; Aschmann, S. M.; Arey, J. *Int. J. Chem. Kinet.* **1991**, *23*, 77.
(190) Yu, J.; Jeffries, H. E.; Sexton, K. G. *Atmos. Environ.* **1997**, *31*, 2261.
(191) Yu, J.; Jeffries, H. E. *Atmos. Environ.* **1997**, *31*, 2281.
(192) Atkinson, R.; Aschmann, S. M.; Arey, J. *Environ. Sci. Technol.* **1992**, *26*, 1397.
(193) Olariu, R. I.; Klotz, B.; Barnes, I.; Becker, K. H.; Mocanu, R. *Atmos. Environ.* **2002**, *36*, 3685.
(194) Olariu, R. I.; Barnes, I.; Becker, K. H.; Klotz, B. *Int. J. Chem. Kinet.* **2000**, *32*, 696.
(195) Tuazon, E. C.; Atkinson, R.; Carter, W. P. L. *Environ. Sci. Technol.* **1985**, *19*, 265.
(196) Bierbach, A.; Barnes, I.; Becker, K. H.; Wiesen, E. *Environ. Sci. Technol.* **1994**, *28*, 715.
(197) Liu, X.; Jeffries, H. E.; Sexton, K. G. *Environ. Sci. Technol.* **1999**, *33*, 4212.
(198) Bethel, H. L.; Arey, J.; Atkinson, R. *Environ. Sci. Technol.* **2001**, *35*, 4477.
(199) Tuazon, E. C.; Atkinson, R. *Environ. Sci. Technol.* **2003**, *37* (15), 3339.
(200) Kwok, E. S. C.; Atkinson, R. *Atmos. Environ.* **1995**, *29*, 1685.
(201) Atkinson, R.; Arey, J. *Atmos. Environ.* **2003**, *37*, *Suppl. 2*, 197.
(202) Dunlop, J. R.; Tully, F. P. *J. Phys. Chem.* **1993**, *97*, 6457.

(203) Yujing, M.; Mellouki, A. *Chem. Phys. Lett.* **2001**, *333*, 63.
(204) Sivakumuran, V.; Crowley, J. N. *Phys. Chem. Chem. Phys.* **2003**, *5*, 106.
(205) Tully, F. P.; Droege, A. T. *Int. J. Chem. Kinet.* **1987**, *19*, 251.
(206) Taylor, P. H.; Rahman, M. S.; Arif, M.; Dellinger, B. *26th Symposium (International) on Combustion*; The Combustion Institute: Pittsburgh, PA, 1996; pp 497−504.
(207) Tully, F. P., cited in ref 29.
(208) Harry, C.; Arey, J.; Atkinson, R. *Int. J. Chem. Kinet.* **1999**, *31*, 425.
(209) Smith, I. W. M.; Ravishankara, A. R. *J. Phys. Chem. A* **2002**, *106*, 4798.
(210) Tadic, J.; Juranic, I.; Moortgat, G. K. *J. Photochem. Photobiol. A: Chem.* **2001**, *143*, 169.
(211) Chen, Y.; Zhu, L.; Francisco, J. S. *J. Phys. Chem. A* **2002**, *106*, 7755.
(212) Cronin, T. J.; Zhu, L. *J. Phys. Chem. A* **1998**, *102*, 10274.
(213) Zhu, L.; Cronin, T.; Narang, A. *J. Phys. Chem. A* **1999**, *103*, 7248.
(214) Tadic, J.; Juranic, I.; Moortgat, G. K. *Molecules* **2001**, *6*, 287.
(215) Tadic, J. M.; Juranic, I. O.; Moortgat, G. K. *J. Chem. Soc., Perkin Trans. 2* **2002**, 135.
(216) Zhu, L.; Cronin, T. J. *Chem. Phys. Lett.* **2000**, *317*, 227.
(217) Cameron, M.; Sivakumaran, V.; Dillon, T. J.; Crowley, J. N. *Phys. Chem. Chem. Phys.* **2002**, *4*, 3628.
(218) Tyndall, G. S.; Orlando, J. J.: Wallington, T. J.; Hurley, M. D.; Goto, M.; Kawasaki, M. *Phys. Chem. Chem. Phys.* **2002**, *4*, 2189.
(219) Vandenberk, S.; Peeters, J. *J. Photobiol. Photochem. A: Chem.* **2003**, *157*, 269.
(220) D'Anna, B.; Langer, S.; Ljungström, E.; Nielsen, C. J.; Ullerstam, M. *Phys. Chem. Chem. Phys.* **2001**, *3*, 1631.
(221) Tuazon, E. C.; Atkinson, R. *Int. J. Chem. Kinet.* **1990**, *22*, 591.
(222) Orlando, J. J.; Tyndall, G. S. *Geophys. Res. Lett.* **1999**, *26*, 2191.
(223) Magneron, I.; Thévenet, R.; Mellouki, A.; Le Bras, G.; Moortgat, G. K.; Wirtz, K. *J. Phys. Chem. A* **2002**, *106*, 2526.
(224) Orlando, J. J.; Tyndall, G. S. *J. Phys. Chem. A* **2002**, *106*, 12252.
(225) Raber, W. H.; Moortgat, G. K. Photooxidation of Selected Carbonyls in Air: Methyl Ethyl Ketone, Methyl Vinyl Ketone, Methacrolein and Methylglyoxal. In *Progress and Problems in Atmospheric Chemistry*, Barker, J., Ed. World Scientific Publishing, Co.: Singapore, 1996; pp. 318−373.
(226) Martinez, R. D.; Buitrago, A. A.; Howell, N. W.; Hearn, C. H.; Joens, J. A. *Atmos. Environ.* **1992**, *26A*, 785.
(227) Hynes, A. J.; Kenyon, E. A.; Pounds, A. J.; Wine, P. H. *Spectrochim. Acta* **1992**, *48A*, 1235.
(228) Yujing, M.; Mellouki, A. *J. Photochem. Photobiol. A: Chem.* **2000**, *134*, 31.
(229) Wollenhaupt, M.; Carl, S. A.; Horowitz, A.; Crowley, J. N. *J. Phys. Chem. A*, **2000**, *104*, 2695.
(230) Orlando, J. J.; Tyndall, G. S.; Vereecken, L.; Peeters, J. *J. Phys. Chem. A* **2000**, *104*, 11578.
(231) Tuazon, E. C.; Atkinson, R. *Int. J. Chem. Kinet.* **1989**, *21*, 1141.
(232) Azad, K.; Andino, J. M. *Int. J. Chem. Kinet.* **1999**, 31, 810.
(233) Cavalli, F.; Geiger, H.; Barnes, I.; Becker, K. H. *Environ. Sci. Technol.* **2002**, *36*, 1263.
(234) Japar, S. M.; Wallington, T. J.; Richert, J. F. O.; Ball, J. C. *Int. J. Chem. Kinet.* **1990**, *22*, 1257.
(235) Chew, A. A.; Atkinson, R.; Aschmann, S. M. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 1083.
(236) Smith, D. F.; McIver, C. D.; Kleindienst, T. E. *Int. J. Chem. Kinet.* **1995**, *27*, 453.
(237) Langer, S.; Ljungström, E.; Wängberg, I.; Wallington, T. J.; Hurley, M. D.; Nielsen, O. J. *Int. J. Chem. Kinet.* **1996**, *28*, 299.
(238) Starkey, D. P.; Holbrook, K. A.; Oldershaw, G. A.; Walker, R. W. *Int. J. Chem. Kinet.* **1997**, *29*, 231.
(239) Stemmler, K.; Mengon, W.; Kerr, J. A. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 2865.
(240) Arif, M.; Dellinger, B.; Taylor, P. H. *J. Phys. Chem. A* **1997**, *101*, 2436.
(241) Bonard, A.; Daële, V.; Delfau, J.-L.; Vovelle, C. *J. Phys. Chem. A* **2002**, *106*, 4384.
(242) Aschmann, S. M.; Atkinson, R. *Int. J. Chem. Kinet.* **1999**, *31*, 501.
(243) Langer, S.; Ljungström, E. *J. Phys. Chem.* **1994**, *98*, 5906.
(244) Clemitshaw, K. C.; Williams, J.; Rattigan, O. V.; Shallcross, D. E.; Law, K. S.; Cox, R. A. *J. Photochem. Photobiol. A: Chem.* **1997**, *102*, 117.
(245) Zhu, L.; Kellis, D. *Chem. Phys. Lett.* **1997**, *278*, 41.
(246) Roberts, J. M.; Fajer, R. W. *Environ. Sci. Technol.* **1989**, *23*, 945.
(247) Turberg, M. P.; Giolando, D. M.; Tilt, C.; Soper, T.; Mason, S.; Davies, M.; Klingensmith, P.; Takacs, G. A. *J. Photochem. Photobiol. A: Chem.* **1990**, *51*, 281.
(248) Barnes, I.; Becker, K. H.; Zhu, T. *J. Atmos. Chem.* **1993**, *17*, 353.
(249) Wängberg, I.; Barnes, I.; Becker, K. H. *Chem. Phys. Lett.* **1996**, *261*, 138.
(250) Boyd, A. A.; Flaud, P.-M.; Daugey, N.; Lesclaux, R. *J. Phys. Chem. A* **2003**, *107*, 818.
(251) Park, J.; Stephens, J. C.; Zhang, R.; North, S. W. *J. Phys. Chem. A* **2003**, *107*, 6408.
(252) Gierczak, T.; Gilles, M. K.; Bauerle, S.; Ravishankara, A. R. *J. Phys. Chem. A* **2003**, *107*, 5014.
(253) Talukdar, R. K.; Gierczak, T.; McCabe, D. C.; Ravishankara, A. R. *J. Phys. Chem. A* **2003**, *107*, 5021.

CR0206420