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**Gas-phase Tropospheric Chemistry  
of Organic Compounds**

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**AIP**

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## Foreword

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Jean W. Gallagher, Editor  
*Journal of Physical and Chemical Reference Data*

# Gas-Phase Tropospheric Chemistry of Organic Compounds

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The gas-phase reactions of selected classes of organic compounds (alkanes, alkenes (including isoprene and monoterpenes), alkynes, aromatic hydrocarbons and oxygen-containing organic compounds and their degradation products) under tropospheric conditions are reviewed and evaluated. The recommendations of the most recent IUPAC evaluation [J. Phys. Chem. Ref. Data **21**, 1125 (1992)] are used for the  $\leq C_3$  organic compounds, unless more recent data necessitates reevaluation. In addition to the review of the gas-phase tropospheric chemistry of these classes of organic compounds, the previous reviews and evaluations of Atkinson [J. Phys. Chem. Ref. Data, Monograph 1 (1989)] for OH radical reactions, Atkinson [J. Phys. Chem. Ref. Data **20**, 459 (1991)] for NO<sub>3</sub> radical reactions and Atkinson and Carter [Chem. Rev. **84**, 437 (1984)] for O<sub>3</sub> reactions with organic compounds are updated.

**Keywords:** atmospheric chemistry; hydroxyl radical; nitrate radical; organic compounds; ozone; reaction kinetics; reaction mechanisms.

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## 1. Introduction

Organic chemicals are introduced into the atmosphere in large quantities from a variety of anthropogenic and biogenic sources,<sup>1-4</sup> with estimated biogenic and anthropogenic non-methane organic compound emissions of ~1000 million ton yr<sup>-1</sup> and ~100 million ton yr<sup>-1</sup>, respectively.<sup>4</sup> These emissions of organic compounds lead to a complex series of chemical and physical transformation and removal processes in the atmosphere which result in such effects as ozone formation in urban<sup>5,6</sup> and rural<sup>7,8</sup> areas and in the global troposphere,<sup>9</sup> stratospheric ozone depletion,<sup>4</sup> long range transport of chemicals,<sup>10</sup> acid deposition,<sup>11</sup> and global climate change.<sup>12</sup> A large amount of experimental data concerning the chemical and physical processes of emitted organic compounds has been obtained from laboratory and ambient air studies over the past two decades, and there is now an understanding, at varying levels of detail, of the atmospheric chemistry of the various classes of organic compounds emitted into the troposphere.<sup>13-19</sup> Because of the complexity of the physical and chemical processes involved and the often non-linear response of the parameters of interest to changes in the input(s), the use of computer models incorporating the emissions, atmospheric chemistry and atmospheric transport processes is generally necessary to elucidate the effects of emissions of chemicals of anthropogenic and biogenic origin on the atmosphere.

Chemical mechanisms of varying levels of detail have been formulated and used as components of these computer modeling studies. For the more complex non-methane organic compounds, the chemical mechanisms are often compared with experimental data obtained from environmental chambers during their development (see, for example, references 20-24) and hence under the concentration conditions of these experimental data the predictions of the chemical mechanisms are constrained to be in reasonable agreement with experimental data. However, these environmental chamber data are of somewhat limited utility due to the difficulties of working at the low reactant concentrations characteristic of the ambient atmosphere and of monitoring product species which are present in low concentrations and/or readily deposit at the chamber walls. The accuracies of chemical mechanisms used in the computer models designed to simulate the troposphere and/or stratosphere are then dependent on the accuracy of the individual rate constants, reaction mechanisms and product distributions for the multitude of elementary reactions which actually occur in the atmosphere.

It is evident that, together with experimental laboratory, ambient air and theoretical studies of the kinetics, mechanisms and products of the atmospheric reactions of organic compounds, there must also be an ongoing parallel effort to critically review and evaluate these data. These evaluation efforts serve to present the current status of knowledge of atmospheric chemistry, in part for modelers, and to point out the areas of uncertainty for

designing future experimental and/or theoretical studies. The reactions of interest for modeling the chemistry occurring in the stratosphere have been reviewed and evaluated for several years by the National Atmospheric and Space Administration (NASA) Panel for Data Evaluation [with the most recent evaluation being Number 10, published in 1992<sup>18</sup>] and by the IUPAC (formerly CODATA) Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry (with the most recent evaluation being Supplement IV<sup>19</sup>). While these two data evaluation panels were originally concerned largely with stratospheric chemistry, due to the potential for stratospheric ozone depletion by inputs of ClO<sub>x</sub> and NO<sub>x</sub> into the stratosphere, tropospheric chemistry is now being included to an increasing degree in both evaluations through the tropospheric chemistry of the hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) proposed as alternatives to the chlorofluorocarbons and, especially in the more recent IUPAC evaluations,<sup>19,25</sup> by the inclusion of the reactions of  $\leq C_3$  alkanes, alkenes, alkynes, aldehydes, ketones, alcohols, carboxylic acids and organosulfur species. The gas-phase atmospheric reactions of the HFCs and HCFCs have been dealt with in detail recently,<sup>14,18,19</sup> and the atmospheric chemistry of reduced organosulfur compounds has been reviewed by Tyndall and Ravishankara.<sup>17</sup>

However, the troposphere contains at least several hundred organic compounds, with the vast majority of them being  $\geq C_4$  species, and there is an obvious need for the review and evaluation of the chemical reactions which occur in the troposphere for these chemicals. To date, several critical reviews and evaluations of the kinetics and mechanisms of the gas-phase reactions of organic compounds with OH radicals,<sup>26-28</sup> NO<sub>3</sub> radicals<sup>15,16</sup> and O<sub>3</sub><sup>29</sup> have been carried out, with the most recent of these being those of Atkinson and Carter<sup>29</sup> for O<sub>3</sub> reactions and Atkinson<sup>16,28</sup> for OH and NO<sub>3</sub> radical reactions. In addition to these reviews of specific (and important) reaction pathways, the tropospheric chemistry of selected organic compounds has been reviewed by Atkinson and Lloyd,<sup>30</sup> Atkinson<sup>13</sup> and Roberts.<sup>31</sup> The review of Atkinson and Lloyd<sup>30</sup> focused on the tropospheric reactions of eight hydrocarbons (*n*-butane, 2,3-dimethylbutane, ethene, propene, 1-butene, *trans*-2-butene, toluene and *m*-xylene) and their degradation products, while that of Atkinson<sup>13</sup> dealt in a more global sense with the tropospheric chemistry of the alkanes, alkenes, alkynes, oxygenates (including those formed during the atmospheric degradations of the hydrocarbon species), nitrogen-containing organics, and aromatic hydrocarbons.

The present article serves to update and extend the Atkinson<sup>13</sup> review to take into account more recent data. In the previous article,<sup>13</sup> the reactions of alkyl, alkyl peroxy and alkoxy radicals, and their substituted analogs, were dealt with as single entities, regardless of the chemical structure of the alkyl radical, alkyl peroxy radical, or alkoxy radical. A somewhat different approach than used by Atkinson<sup>13</sup> is employed here, since recent data for organic radicals indicate that there are significant differ-

ences between the reaction pathways occurring in the troposphere, depending on the structures of the radicals.

The reactions of organic compounds under tropospheric conditions are dealt with in Sec. 2:

- 2.1. Alkanes
- 2.2. Alkenes
- 2.3. Alkynes
- 2.4. Aromatic hydrocarbons and aromatic compounds formed during the tropospheric photooxidations of the aromatic hydrocarbons.
- 2.5. Oxygen-containing organic compounds, including those formed as photooxidation products of the alkanes, alkenes, alkynes and aromatic hydrocarbons.
- 2.6. Nitrogen-containing organic compounds formed as photooxidation products of the alkanes and alkenes.

Only gas-phase reactions are discussed, since while highly important under many tropospheric conditions, the reactions occurring in the particle and/or aqueous phase (for example, in fog, cloud and rain droplets), on surfaces (heterogeneous reactions) and gas-to-particle conversion (see, for example, Refs. 32–38) are beyond the scope of the present article. As in the previous review,<sup>15</sup> the most recent NASA<sup>18</sup> and, especially, IUPAC<sup>19</sup> evaluations are used for the  $\leq C_3$  reactions, generally without reevaluation or detailed discussion. The present article is in essence an extension of the IUPAC evaluation<sup>19</sup> to more complex organic compounds characteristic of the lower troposphere and, in particular, polluted air masses. Thus the present article and the most recent IUPAC evaluation<sup>19</sup> are complementary and both are necessary for an in-depth coverage of the chemistry of organic compounds in the troposphere. In addition, the previous articles<sup>16,28,29</sup> dealing with the kinetics and mechanisms of the gas-phase reactions of OH and NO<sub>3</sub> radicals and O<sub>3</sub> with organic compounds have been updated, with the data reported since these reviews<sup>16,28,29</sup> being tabulated, discussed and evaluated in Secs. 3, 4 and 5. In these sections, discussion is limited to those organic compounds for which new information has become available since these previous review articles<sup>16,28,29</sup> were prepared. Previous data are not included in the tables of rate constants, and hence the previous reviews<sup>16,28,29</sup> must be consulted for rate constant and mechanistic information available and used at the times of their finalization. The literature through mid-1992 has been included in this article. (See Addendum, Sec. 6 for data through early/mid-1993.)

Rate constants  $k$  determined as a function of temperature are generally cited using the Arrhenius expression,  $k = Ae^{-B/T}$ , where  $A$  is the Arrhenius pre-exponential factor and  $B$  is in K. In some cases rate constants have been obtained over extended temperature ranges and the simple Arrhenius expression, as expected, does not hold, with curvature in the Arrhenius plots being observed.<sup>28</sup> In these cases, a three-parameter equation,  $k = CT^n e^{-D/T}$  has been used,<sup>28</sup> generally with  $n = 2$  ( $k = CT^2 e^{-D/T}$ ).

The equation,  $k = CT^n e^{-D/T}$ , can be transformed into the Arrhenius expression,  $k = Ae^{-B/T}$ , centered at a temperature  $T$ , with  $A = Ce^{nT}$  and  $B = D + nT$ .

Reactions which are in the fall-off region between second- and third-order kinetics or between first- and second-order kinetics are dealt with by using the Trost fall-off expression,<sup>39</sup> with

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

where  $k_0$  is the limiting low-pressure rate constant,  $k_\infty$  is the limiting high-pressure rate constant,  $M$  is the concentration of the third-body gas (generally air in this article) and  $F$  is the broadening coefficient. In general, the rate constants  $k_0$  and  $k_\infty$  have  $T^n$  temperature dependencies. The temperature dependence of  $F$  is given by  $F = e^{-T/T^*}$  for temperatures appropriate to the troposphere, where  $T^*$  is a constant for a given reaction.<sup>19,40</sup> All rate constants are given in cm molecule s units, and pressure are given in Torr (1 Torr = 133.3 Pa).

## References

- <sup>1</sup>J. A. Logan, M. J. Prather, S. C. Wofsy, and M. B. McElroy, *J. Geophys. Res.* **86**, 7210 (1981).
- <sup>2</sup>T. E. Graedel, D. T. Hawkins, and L. D. Claxton, "Atmospheric Chemical Compounds: Sources, Occurrence, and Bioassay," Academic Press, Orlando, FL (1986).
- <sup>3</sup>B. Lamb, A. Guenther, D. Gay, and H. Westberg, *Atmos. Environ.* **21**, 1695 (1987).
- <sup>4</sup>"Scientific Assessment of Ozone Depletion: 1991," World Meteorological Organization Global Ozone Research and Monitoring Project – Report No. 25, Geneva, Switzerland (1992).
- <sup>5</sup>W. L. Chameides, R. W. Lindsay, J. Richardson, and C. S. Kiang, *Science* **241**, 1473 (1988).
- <sup>6</sup>J. H. Seinfeld, *Science* **243**, 745 (1989).
- <sup>7</sup>M. Trainer, E. J. Williams, D. D. Parrish, M. P. Buhr, E. J. Allwine, H. Westberg, F. C. Fehsenfeld, and S. C. Liu, *Nature* **329**, 705 (1987).
- <sup>8</sup>S. Sillman, J. A. Logan, and S. C. Wofsy, *J. Geophys. Res.* **95**, 1837 (1990).
- <sup>9</sup>J. A. Logan, *J. Geophys. Res.* **90**, 10463 (1985).
- <sup>10</sup>T. Bidleman, E. L. Atlas, R. Atkinson, B. Bonsang, K. Burns, W. C. Keene, A. H. Knap, J. Miller, J. Rudolph, and S. Tanabe, "The Long-Range Transport of Organic Compounds" in "The Long-Range Atmospheric Transport of Natural and Contaminant Substances," A. H. Knap, Ed., NATO ASI Series C: Mathematical and Physical Sciences, Vol. 297, Kluwer Academic Publishers, Dordrecht, The Netherlands, pp. 259–301 (1990).
- <sup>11</sup>S. E. Schwartz, *Science* **243**, 753 (1989).
- <sup>12</sup>"Climate Change," The Intergovernmental Panel on Climate Change Assessment, J. T. Houghton, G. J. Jenkins, and J. J. Ephraums, Eds., Cambridge Univ. Press, Cambridge (1990).
- <sup>13</sup>R. Atkinson, *Atmos. Environ.* **24A**, 1 (1990).
- <sup>14</sup>"Scientific Assessment of Stratospheric Ozone: 1989," Volume II, Appendix: AFEAS Report. World Meteorological Organization Global Ozone Research and Monitoring Project – Report No. 20, Geneva, Switzerland (1990).
- <sup>15</sup>R. P. Wayne, I. Barnes, P. Biggs, J. P. Burrows, C. E. Canosa-Mas, J. Hjorth, G. Le Bras, G. K. Moortgat, D. Perner, G. Poulet, G. Restelli, and H. Sidebottom, *Atmos. Environ.* **25A**, 1 (1991).

- <sup>16</sup>R. Atkinson, *J. Phys. Chem. Ref. Data*, **20**, 459 (1991).
- <sup>17</sup>G. S. Tyndall and A. R. Ravishankara, *Int. J. Chem. Kinet.* **23**, 483 (1991).
- <sup>18</sup>W. B. DeMore, S. P. Sander, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, A. R. Ravishankara, C. E. Kolb, and M. J. Molina, "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling." NASA Panel for Data Evaluation, Evaluation No. 10, Jet Propulsion Laboratory Publication 92-20, August 15 (1992).
- <sup>19</sup>R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, and J. Troe, *J. Phys. Chem. Ref. Data* **21**, 1125 (1992).
- <sup>20</sup>R. Atkinson, A. C. Lloyd, and L. Wings, *Atmos. Environ.* **16**, 1341 (1982).
- <sup>21</sup>F. W. Lurmann, A. C. Lloyd, and R. Atkinson, *J. Geophys. Res.* **91**, 10905 (1986).
- <sup>22</sup>M. W. Gery, G. Z. Whitten, J. P. Killus, and M. C. Dodge, *J. Geophys. Res.* **94**, 12925 (1989).
- <sup>23</sup>W. R. Stockwell, P. Middleton, J. S. Chang, and X. Tang, *J. Geophys. Res.* **95**, 16343 (1990).
- <sup>24</sup>W. P. L. Carter and F. W. Lurmann, *Atmos. Environ.* **25A**, 2771 (1991).
- <sup>25</sup>R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, and J. Troe, *J. Phys. Chem. Ref. Data* **18**, 881 (1989).
- <sup>26</sup>D. L. Baulch, M. Bowers, D. G. Malcolm, and R. T. Tuckerman, *J. Phys. Chem. Ref. Data* **15**, 465 (1986).
- <sup>27</sup>R. Atkinson, *Chem. Rev.* **86**, 69 (1986).
- <sup>28</sup>R. Atkinson, *J. Phys. Chem. Ref. Data Monograph* **1**, 1 (1989).
- <sup>29</sup>R. Atkinson and W. P. L. Carter, *Chem. Rev.* **84**, 437 (1984).
- <sup>30</sup>R. Atkinson and A. C. Lloyd, *J. Phys. Chem. Ref. Data* **13**, 315 (1984).
- <sup>31</sup>J. M. Roberts, *Atmos. Environ.* **24A**, 243 (1990).
- <sup>32</sup>W. L. Chameides, *J. Geophys. Res.* **89**, 4739 (1984).
- <sup>33</sup>D. J. Jacob, *J. Geophys. Res.* **91**, 9807 (1986).
- <sup>34</sup>D. J. Jacob, E. W. Gottlieb, and M. J. Prather, *J. Geophys. Res.* **94**, 12975 (1989).
- <sup>35</sup>S. N. Pandis and J. H. Seinfeld, *J. Geophys. Res.* **94**, 1105 (1989).
- <sup>36</sup>J. Lelieveld and P. J. Crutzen, *Nature* **343**, 227 (1990).
- <sup>37</sup>S. N. Pandis, S. E. Paulson, J. H. Seinfeld, and R. C. Flagan, *Atmos. Environ.* **25A**, 997 (1991).
- <sup>38</sup>J. Lelieveld and P. J. Crutzen, *J. Atmos. Chem.* **12**, 229 (1991).
- <sup>39</sup>J. Troe, *J. Phys. Chem.* **83**, 114 (1979).
- <sup>40</sup>D. L. Baulch, R. A. Cox, P. J. Crutzen, R. F. Hampson, Jr., J. A. Kerr, J. Troe, and R. T. Watson, *J. Phys. Chem. Ref. Data* **11**, 327 (1982).

## 2. Gas-Phase Tropospheric Chemistry of Organic Compounds

### 2.1. Alkanes

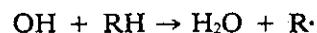
The atmospheric chemistry of the alkanes has been reviewed and discussed previously,<sup>1,2</sup> and the kinetics and mechanisms of the reactions with OH and NO<sub>3</sub> radicals and with O<sub>3</sub> have been reviewed and evaluated<sup>3-5</sup> and these reviews and evaluations are updated in Secs. 3, 4, and 5, respectively. The gas-phase reactions of the alkanes with O<sub>3</sub> are of negligible importance as an atmospheric loss process, since the available data<sup>5</sup> show that the room temperature rate constants for these reactions are <10<sup>-23</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Under atmospheric conditions, the potential loss processes for the alkanes involve gas-phase reactions with OH and NO<sub>3</sub> radicals.

#### OH Radical Reactions

The kinetics and mechanisms of the reactions of the OH radical with alkanes have been reviewed and evalu-

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

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



to generate an alkyl radical and, as discussed previously,<sup>3,6</sup> the rate constants for these OH radical reactions with alkanes can be fit to within a factor of ~2 over the temperature range 250–1000 K from consideration of the CH<sub>3</sub>-, -CH<sub>2</sub>- and >CH- groups in the alkane, and the neighboring substituent groups. Thus

$$k(\text{CH}_3\text{-X}) = k_{\text{prim}} F(\text{X})$$

$$k(\text{X-CH}_2\text{-Y}) = k_{\text{sec}} F(\text{X}) F(\text{Y})$$

and

$$k(\text{X-CH} \begin{matrix} \swarrow \text{Y} \\ \searrow \text{Z} \end{matrix}) = k_{\text{tert}} F(\text{X}) F(\text{Y}) F(\text{Z})$$

where  $k_{\text{prim}}$ ,  $k_{\text{sec}}$  and  $k_{\text{tert}}$  are the OH radical rate constants per -CH<sub>3</sub>-, -CH<sub>2</sub>- and >CH- group, respectively, for X = Y = Z = -CH<sub>3</sub> as the standard substituent group, and *F*(X), *F*(Y) and *F*(Z) are the substituent factors for X, Y and Z substituent groups. As derived by Atkinson,<sup>6</sup>

$$k_{\text{prim}} = 4.47 \times 10^{-18} T^2 e^{-303/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$k_{\text{sec}} = 4.32 \times 10^{-18} T^2 e^{233/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$k_{\text{tert}} = 1.89 \times 10^{-18} T^2 e^{711/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$F(-\text{CH}_3) = 1.00$ , and  $F(-\text{CH}_2-) = F(>\text{CH-}) = F(>\text{C}<) = e^{76/T}$ . For cycloalkanes, the effects of ring strain are taken into account by means of ring factors.<sup>6-8</sup> This estimation technique not only allows the calculation of OH radical reaction rate constants for alkanes for which experimental data do not exist, but also allows the initially formed isomeric alkyl radical distribution to be calculated for a given alkane.<sup>2</sup>

#### NO<sub>3</sub> Radical Reactions

The NO<sub>3</sub> radical reacts with the alkanes with rate constants at room temperature in the 10<sup>-17</sup> to 10<sup>-16</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> range (Ref. 4 and Sec. 4.1). The recommended 298 K rate constants and temperature

TABLE 1. Rate constants  $k$  at 298 K and parameters  $C$  and  $D$  in  $k = CT^2e^{-D/T}$  for the reaction of OH radicals with alkanes (from Ref. 3 and Sec. 3.1)

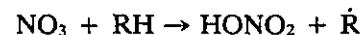
Alkane	$10^{12} \times k$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$10^{18} \times C$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$D$ (K)
Methane	0.00686	7.44	1361
Ethane	0.257	15.1	492
Propane	1.15	15.0	44
<i>n</i> -Butane	2.54	15.1	-190
2-Methylpropane	2.33	11.1	-256
<i>n</i> -Pentane	3.94	21.0	-223
2-Methylbutane	3.9		
2,2-Dimethylpropane	0.849	17.9	187
<i>n</i> -Hexane	5.61		
2-Methylpentane	5.6		
3-Methylpentane	5.7		
2,2-Dimethylbutane	2.32	a	a
2,3-Dimethylbutane	5.99	12.1	-512
<i>n</i> -Heptane	7.15		
2,2-Dimethylpentane	3.4		
2,4-Dimethylpentane	5.2		
2,2,3-Trimethylbutane	4.23	9.04	-495
<i>n</i> -Octane	8.68	b	b
2,2-Dimethylhexane	4.8		
2,2,4-Trimethylpentane	3.59	20.6	-201
2,3,4-Trimethylpentane	7.0		
2,2,3,3-Tetramethylbutane	1.06	19.0	139
<i>n</i> -Nonane	10.2		
2-Methyloctane	10.1		
4-Methyloctane	9.7		
2,3,5-Trimethylhexane	7.9		
<i>n</i> -Decane	11.6		
<i>n</i> -Undecane	13.2		
<i>n</i> -Dodecane	14.2		
<i>n</i> -Tridecane	16		
<i>n</i> -Tetradecane	19		
<i>n</i> -Pentadecane	22		
<i>n</i> -Hexadecane	25		
Cyclopropane	0.084		
Cyclobutane	1.5		
Cyclopentane	5.08	25.5	-241
Cyclohexane	7.49	26.6	-344
Cycloheptane	12.5		
Methylcyclohexane	10.4		
<i>cis</i> - and <i>trans</i> -Bicyclo[4.4.0]decane	20		

<sup>a</sup>Arrhenius expression of  $k = 2.84 \times 10^{-11} e^{-747/T}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> recommended (245–330 K).

<sup>b</sup>Arrhenius expression of  $k = 3.15 \times 10^{-11} e^{-384/T}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> recommended (300–500 K).

dependent parameters, taken from Ref. 4 and Sec. 4.1, are given in Table 2, which also includes the room temperature rate constants for alkanes for which only a single study has been carried out and for which no recommendations are given. Under atmospheric conditions, the nighttime reactions of the alkanes with the NO<sub>3</sub> radical can be calculated to be typically two orders of magnitude less important as an atmospheric loss process than are the daytime OH radical reactions (although the relative importance of the NO<sub>3</sub> radical reactions may vary widely, depending on the OH and NO<sub>3</sub> radical concentrations<sup>4</sup>).

Similar to the OH radical reactions, these NO<sub>3</sub> radical reactions proceed via H-atom abstraction from the C-H bonds



For alkanes for which no experimental data presently exist, the overall 298 K rate constants and the distribution of initially formed alkyl radical isomers can be calculated by the use of -CH<sub>3</sub>, -CH<sub>2</sub>- and >CH- group rate constants and substituent factors, as discussed above for the corresponding OH radical reactions. Atkinson<sup>4</sup> derived group rate constants (in cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> units) at 298 K of  $k_{\text{prim}} = 7.0 \times 10^{-19}$ ,  $k_{\text{sec}} = 1.5 \times 10^{-17}$ , and  $k_{\text{tert}} = 8.2 \times 10^{-17}$ , and substituent factors at 298 K of  $F(-\text{CH}_3) = 1.00$  and  $F(-\text{CH}_2-) = F(>\text{CH}-) = F(>\text{C}<) = 1.5$ , and these can be used to calculate the room tem-

TABLE 2. Rate constants  $k$  at 298 K and temperature dependent parameters,  $k = Ae^{-B/T}$ , for the reaction of  $\text{NO}_3$  radicals with alkanes (from Ref. 4 and Sec. 4.1)

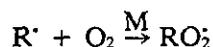
Alkane	$10^{12} \times A$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	$B$ (K)	$10^{17} \times k$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )
Methane			<0.1
Ethane			0.14 <sup>a</sup>
Propane			1.7 <sup>a</sup>
<i>n</i> -Butane	2.76	3279	4.59
2-Methylpropane	3.05	3060	10.6
<i>n</i> -Pentane			8.1
2-Methylbutane			16
<i>n</i> -Hexane			10.5
2,3-Dimethylbutane			43
Cyclohexane			13.5
<i>n</i> -Heptane			14.5
<i>n</i> -Octane			18.2
<i>n</i> -Nonane			24.1

<sup>a</sup>Estimated from group rate constants, see text.

perature rate constants for the  $\text{NO}_3$  radical reactions with the alkanes and the distribution of alkyl radicals formed.

#### Reactions of Alkyl ( $R$ ) Radicals

The available kinetic and mechanistic data show that under tropospheric conditions the alkyl radicals react with  $\text{O}_2$  to form an alkyl peroxy radical.

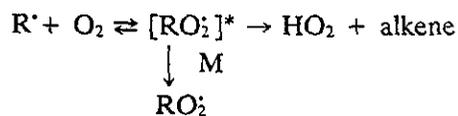


The room temperature kinetic data presently available for  $\text{O}_2$  addition to alkyl radicals are given in Table 3. For methyl and ethyl radicals at room temperature, these reactions are in the fall-off region at and below atmospheric pressure, and the IUPAC recommended values of  $k_0$ ,  $k_\infty$  and  $F$  for these  $\text{O}_2$  reactions are:<sup>9</sup> methyl,  $k_0 = 1.0 \times 10^{-30} (T/300)^{-3.3} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  (200–300 K),  $k_\infty = 2.2 \times 10^{-12} (T/300) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (200–300 K) and  $F = 0.27$  at 298 K; ethyl,  $k_0 = 5.9 \times 10^{-29} (T/300)^{-3.8} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  (200–300 K),  $k_\infty = 7.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (200–300 K) and  $F = 0.54$  at 298 K. In addition, Xi *et al.*<sup>12</sup> have determined a rate constant of  $k_\infty = 2.1 \times 10^{-12} (T/300)^{-2.1} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the reaction of  $\text{O}_2$  with the 2,2-dimethyl-1-propyl (neopentyl) radical over the temperature range 266–374 K.

At elevated temperatures, these reactions of alkyl radicals with  $\text{O}_2$  have been assumed to also occur by an H-atom abstraction pathway, for example



However, this is now recognized not to be a parallel reaction route, but to occur from the activated  $\text{RO}_2^*$  radical<sup>13</sup>

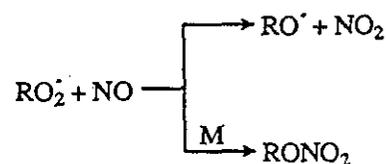


At the high pressure limit, peroxy radical formation is therefore the sole reaction process. At 760 Torr and 298 K, the formation yield of  $\text{C}_2\text{H}_4 + \text{HO}_2$  from the reaction of the ethyl radical with  $\text{O}_2$  is  $\sim 0.05\%$ .<sup>9</sup>

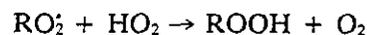
Hence, for the alkyl radicals studied to date, under atmospheric conditions the reactions with  $\text{O}_2$  proceed via addition to form a peroxy radical, with a room temperature rate constant of  $\geq 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at atmospheric pressure. For the smaller alkyl radicals these reactions are in the fall-off regime between second- and third-order kinetics, but are reasonably close to the high-pressure rate constant at 760 Torr of air. Under atmospheric conditions, these reactions with  $\text{O}_2$  are the sole loss process of these alkyl radicals, and other reactions need not be considered.

#### Alkyl Peroxy ( $\text{RO}_2$ ) Radicals

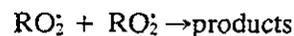
As discussed above, these radicals are formed from the addition of  $\text{O}_2$  to the alkyl radicals. Under tropospheric conditions,  $\text{RO}_2$  radicals react with  $\text{NO}$  (by two pathways),



with  $\text{HO}_2$  radicals,



with  $\text{RO}_2$  radicals (either self-reaction or reaction with other alkyl peroxy radicals),

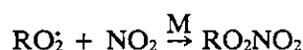


and with  $\text{NO}_2$ .

TABLE 3. High-pressure rate constants  $k_{\infty}$  for the addition reactions of alkyl radicals ( $\dot{R}$ ) with  $O_2$  at around room temperature

$\dot{R}$	$10^{12} \times k_{\infty}$ ( $cm^3 \text{ molecule}^{-1} s^{-1}$ )	$T$ (K)	Reference
Methyl	$2.2^{+2.2}_{-1.1}$	298	Atkinson <i>et al.</i> <sup>9</sup>
	$1.0^a$	298	
Ethyl	$7.8^{+4.6}_{-2.5}$	298	Atkinson <i>et al.</i> <sup>9</sup>
	$7.0^a$	298	
1-Propyl	$8^{+5}_{-3}$	298	Atkinson <i>et al.</i> <sup>9</sup>
2-Propyl	$11^{+11}_{-5}$	298	Atkinson <i>et al.</i> <sup>9</sup>
1-Butyl	$7.5 \pm 1.4$	300	Lenhardt <i>et al.</i> <sup>10</sup>
2-Butyl	$16.6 \pm 2.2$	300	Lenhardt <i>et al.</i> <sup>10</sup>
2-Methyl-2-propyl	$23.4 \pm 3.9$	300	Lenhardt <i>et al.</i> <sup>10</sup>
2-Methyl-1-propyl	$2.9 \pm 0.7$	$298 \pm 3$	Wu and Bayes <sup>11</sup>
2,2-Dimethyl-1-propyl	$2.4 \pm 0.4$	$293 \pm 1$	Xi <i>et al.</i> <sup>12</sup>
Cyclopentyl	$17 \pm 3$	293	Wu and Bayes <sup>11</sup>
Cyclohexyl	$14 \pm 2$	$298 \pm 3$	Wu and Bayes <sup>11</sup>

<sup>a</sup>Value at 760 Torr total pressure calculated from the fall-off expression.



The reaction pathways which occur depend on the NO to  $HO_2$  and/or  $RO_2$  radical concentration ratios, and in the troposphere the reaction with NO is expected to dominate for NO concentrations  $\geq 7 \times 10^8 \text{ molecule cm}^{-3}$ .<sup>14,15</sup> The reaction of  $RO_2$  radicals with  $NO_2$  to form alkyl peroxy nitrates is generally unimportant under lower tropospheric conditions due to the rapid thermal decomposition of the alkyl peroxy nitrates back to reactants (see Sec. 2.6).

#### Reaction with NO

The recommended NASA<sup>16</sup> and IUPAC<sup>9</sup> room temperature rate constants for the reactions of alkyl peroxy radicals with NO and the absolute literature data of Peeters *et al.*<sup>17</sup> and Anastasi *et al.*<sup>18</sup> for the  $(CH_3)_2CHO_2$ <sup>17</sup> and  $(CH_3)_3CO_2$ <sup>17,18</sup> radicals are given in Table 4. Both the NASA<sup>16</sup> and IUPAC<sup>9</sup> evaluations recommend a rate constant for the reaction of  $CH_3O_2$  radicals with NO of  $k(CH_3O_2 + NO) = 4.2 \times 10^{-12} e^{(180 \pm 180)/T} \text{ cm}^3 \text{ molecule}^{-1} s^{-1}$ , with  $k(CH_3O_2 + NO) = 7.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} s^{-1}$  at 298 K. The NASA and IUPAC recommended rate constants for the reaction of the  $C_2H_5O_2$  radical with NO<sup>9,16</sup> are both based on the measurement of Plumb *et al.*<sup>19</sup> Although no experimental temperature-dependent data are available, the NASA evaluation<sup>16</sup> recommends a temperature independent rate constant for the reaction of the  $C_2H_5O_2$  radical with NO. Furthermore, the IUPAC<sup>9</sup> recommendations for the reactions of the  $CH_3CH_2CH_2O_2$  and  $(CH_3)_2CHO_2$  radicals with NO assume that the overall rate constants for these reactions are identical to that for the corresponding  $C_2H_5O_2$  radical reaction. Recently, however, Peeters *et al.*<sup>17</sup> have measured significantly lower rate constants for the reactions of the  $(CH_3)_2CHO_2$  and  $(CH_3)_3CO_2$  radicals with NO at 290 K of  $(5.0 \pm 1.2) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} s^{-1}$  and  $(4.0 \pm 1.1) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} s^{-1}$ , respectively. Unfor-

tunately, no measurements for the  $CH_3O_2$  or  $C_2H_5O_2$  radical reactions were carried out by Peeters *et al.*<sup>17</sup> for comparison with the previous literature data.

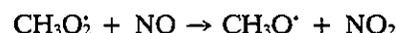
Hence, it is recommended that the rate constant for the reaction of the  $CH_3O_2$  radical with NO is given by

$$k(CH_3O_2 + NO) = 4.2 \times 10^{-12} e^{180/T} \text{ cm}^3 \text{ molecule}^{-1} s^{-1} \\ = 7.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} s^{-1} \text{ at } 298 \text{ K}$$

and that the overall rate constants for the higher ( $\geq C_2$ ) alkyl peroxy radicals with NO are identical, with

$$k(RO_2 + NO) = 4.9 \times 10^{-12} e^{180/T} \text{ cm}^3 \text{ molecule}^{-1} s^{-1} \\ = 8.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} s^{-1} \text{ at } 298 \text{ K.}$$

The reaction of  $CH_3O_2$  with NO has been shown to proceed primarily by<sup>9,16,20,21</sup>



and Plumb *et al.*<sup>19</sup> have shown from direct measurements that the reaction of  $C_2H_5O_2$  radicals with NO forms  $NO_2$  with a yield of  $\geq 0.80$ .

However, for the larger alkyl peroxy radicals, Darnall *et al.*,<sup>22</sup> Takagi *et al.*,<sup>23</sup> Atkinson *et al.*<sup>24-27</sup> and Harris and Kerr<sup>28</sup> have shown that the reaction pathway to form the alkyl nitrate becomes important. At room temperature and atmospheric pressure, the product data of Atkinson *et al.*<sup>24-27</sup> and Harris and Kerr<sup>28</sup> show that for the secondary alkyl peroxy radicals the rate constant ratio  $k_a/(k_a + k_b)$ , where  $k_a$  and  $k_b$  are the rate constants for the reaction pathways (a) and (b), respectively,

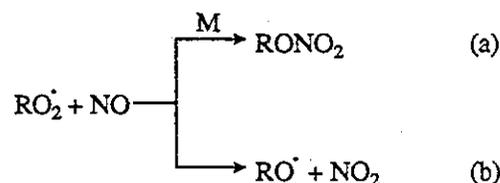


TABLE 4. Absolute room temperature rate constants for the reactions of RO<sub>2</sub> radicals with NO

RO <sub>2</sub>	10 <sup>12</sup> × <i>k</i> (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	<i>T</i> (K)	Reference
CH <sub>3</sub> O <sub>2</sub>	7.6	298	DeMore <i>et al.</i> , <sup>16</sup> Atkinson <i>et al.</i> <sup>9</sup>
C <sub>2</sub> H <sub>5</sub> O <sub>2</sub>	8.9	298	DeMore <i>et al.</i> , <sup>16</sup> Atkinson <i>et al.</i> <sup>9</sup>
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> O <sub>2</sub>	8.9 <sup>a</sup>	298	Atkinson <i>et al.</i> <sup>9</sup>
(CH <sub>3</sub> ) <sub>2</sub> CHO <sub>2</sub>	8.9 <sup>a</sup>	298	Atkinson <i>et al.</i> <sup>9</sup>
	5.0 ± 1.2	290	Peeters <i>et al.</i> <sup>17</sup>
(CH <sub>3</sub> ) <sub>3</sub> CO <sub>2</sub>	> 1	298	Anastasi <i>et al.</i> <sup>18</sup>
	4.0 ± 1.1	290	Peeters <i>et al.</i> <sup>17</sup>

<sup>a</sup>At 760 Torr total pressure (see text).

increases monotonically with the carbon number of the RO<sub>2</sub> radical. Furthermore, for a given alkyl peroxy radical the rate constant ratio  $k_a/(k_a + k_b)$  is pressure- and temperature-dependent, increasing with increasing pressure and with decreasing temperature.<sup>25,27,28</sup>

The pressure and temperature-dependent rate constant ratios  $k_a/k_b$  for secondary alkyl peroxy radicals<sup>24-27</sup> are fit by the fall-off expression<sup>29</sup>

$$\frac{k_a}{k_b} = \left( \frac{Y_o^{300} [M] (T/300)^{-m_o}}{1 + \frac{Y_o^{300} [M] (T/300)^{-m_o}}{Y_\infty^{300} (T/300)^{-m_\infty}}} \right)^{Fz} \quad (\text{II})$$

where

$$z = \left\{ 1 + \left[ \log \left( \frac{Y_o^{300} [M] (T/300)^{-m_o}}{Y_\infty^{300} (T/300)^{-m_\infty}} \right) \right]^2 \right\}^{-1}$$

and  $Y_o^{300} = \alpha e^{\beta n}$ ,  $n$  is the number of carbon atoms in the alkyl peroxy radical, and  $\alpha$  and  $\beta$  are constants. The most recent evaluation<sup>29</sup> of the experimental data of Atkinson *et al.*<sup>24-27</sup> leads to  $Y_o^{300} = 0.826$ ,  $\alpha = 1.94 \times 10^{-22}$  cm<sup>3</sup> molecule<sup>-1</sup>,  $\beta = 0.97$ ,  $m_o = 0$ ,  $m_\infty = 8.1$  and  $F = 0.411$ . The experimental data of Harris and Kerr<sup>28</sup> for the heptyl nitrates formed from the OH radical reaction with  $n$ -heptane at 730 Torr total pressure over the temperature range 253–325 K are in good agreement with predictions from this equation.

Although the rate constant ratios  $k_a/k_b$  at room temperature and atmospheric pressure for secondary RO<sub>2</sub> radicals depend primarily on the number of carbon atoms in the RO<sub>2</sub> molecule, the corresponding rate constant ratios for primary and tertiary RO<sub>2</sub> radicals are significantly lower, by a factor of ~2.5 for primary and a factor of ~3.3 for tertiary alkyl peroxy radicals.<sup>27,29</sup> Accordingly,

$$(k_a/k_b)_{\text{primary}} \approx 0.40 (k_a/k_b)_{\text{secondary}}$$

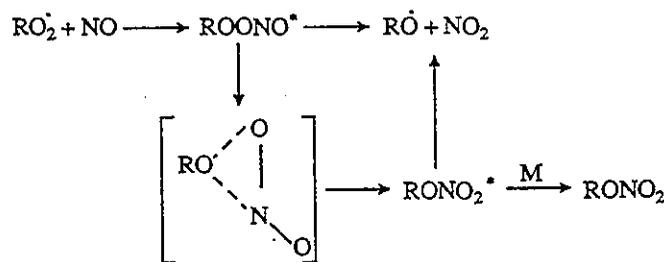
and

$$(k_a/k_b)_{\text{tertiary}} \approx 0.3 (k_a/k_b)_{\text{secondary}}$$

It should be noted that the use of the above equations to calculate rate constant ratios  $k_a/k_b$  is solely applicable to

alkyl peroxy radicals. Thus, although no definitive data exist, computer modeling data suggest<sup>1</sup> that the rate constant ratios for  $\delta$ -hydroxyalkyl peroxy radicals (for example, the RCH(OH)CH<sub>2</sub>CH<sub>2</sub>CH(OO)R<sub>1</sub> radical) are much lower than those for the corresponding alkyl peroxy radicals.

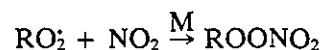
These reactions of RO<sub>2</sub> radicals with NO are postulated<sup>25</sup> to occur by



and it is therefore expected that the overall rate constant is independent of total pressure, but that the rate constant ratio  $k_a/k_b$  is pressure (and temperature) dependent, as observed.

#### Reaction with NO<sub>2</sub>

The reactions of alkyl peroxy radicals with NO<sub>2</sub> all proceed via combination to yield the corresponding peroxy nitrates<sup>9</sup>



The IUPAC recommendations<sup>9</sup> for the values of  $k_o$ ,  $k_\infty$ ,  $F$  and the rate constant,  $k$ , at 298 K and 760 Torr total pressure of air for the reactions of NO<sub>2</sub> with CH<sub>3</sub>O<sub>2</sub> and C<sub>2</sub>H<sub>5</sub>O<sub>2</sub> radicals are given in Table 5. The rate constant at 298 K and 760 Torr total pressure of air calculated from the IUPAC recommendation for the reaction of the CH<sub>3</sub>O<sub>2</sub> radical with NO<sub>2</sub> (Table 5) is in excellent agreement with that of  $(4.4 \pm 0.4) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> measured by Bridier *et al.*<sup>30</sup> at  $298 \pm 1$  K and 760 Torr total pressure of air. These reactions are in the fall-off

TABLE 5. Recommended<sup>a</sup> rate constant parameters  $k_0$ ,  $k_\infty$  and  $F$  for the gas-phase reactions of  $\text{RO}_2$  radicals with  $\text{NO}_2$ , together with calculated rate constants at 298 K and 760 Torr total pressure

$\text{RO}_2$	$k_0$ ( $\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ )	$k_\infty$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	$F(298 \text{ K})$	$10^{12} \times k$ (298 K, 760 Torr)
$\text{CH}_3\text{O}_2$	$2.5 \times 10^{-30}(T/300)^{-5.5}$	$7.5 \times 10^{-12}$	0.4	4.1
$\text{C}_2\text{H}_5\text{O}_2$	$1.3 \times 10^{-29}(T/300)^{-6.2}$	$8.8 \times 10^{-12}$	0.31	6.1

<sup>a</sup>From Atkinson *et al.*<sup>9</sup>

regime between second- and third-order kinetics at and below atmospheric pressure at room temperature, and this is in agreement with the thermal decomposition data for the corresponding peroxy nitrates  $\text{CH}_3\text{OONO}_2$  and  $\text{C}_2\text{H}_5\text{OONO}_2$ .<sup>9</sup>

Absolute rate constants have also been obtained at room temperature for the reactions of  $\text{NO}_2$  with  $(\text{CH}_3)_2\text{CHO}_2$ <sup>31</sup> and  $(\text{CH}_3)_3\text{CO}_2$ <sup>18</sup> radicals, of  $(5.65 \pm 0.17) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $\geq 5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively. The rate constant of Adachi and Basco<sup>31</sup> for the  $(\text{CH}_3)_2\text{CHO}_2$  radicals is anticipated to be erroneously low, by analogy with the rate constant of Adachi and Basco<sup>32</sup> for reaction of the  $\text{C}_2\text{H}_5\text{O}_2$  radical with  $\text{NO}_2$ , for which they measured a rate constant of  $(1.25 \pm 0.07) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at room temperature, independent of total pressure over the range 44–676 Torr.<sup>32</sup>

Based upon the data for the  $\text{CH}_3\text{O}_2$  and  $\text{C}_2\text{H}_5\text{O}_2$  radicals, it is recommended that the limiting high-pressure rate constants for the  $\geq \text{C}_2$  alkyl peroxy radicals are identical to that for the  $\text{C}_2\text{H}_5\text{O}_2$  radical,

$$k(\text{RO}_2 + \text{NO}_2) = 9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

approximately independent of temperature over the range ~250–350 K. This recommendation is consistent with the kinetic data of Zabel *et al.*<sup>33</sup> for the thermal decompositions of a series of alkyl peroxy nitrates ( $\text{ROONO}_2$ , where  $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_4\text{H}_9, \text{C}_6\text{H}_{13}$  and  $\text{C}_8\text{H}_{17}$ ) at 253 K and 600 Torr total pressure of  $\text{N}_2$ , which showed that the thermal decomposition rates for the  $\text{C}_2$ – $\text{C}_8$  alkyl peroxy nitrates were reasonably similar. In particular, the thermal decomposition rates for the  $\text{C}_4$ – $\text{C}_8$  alkyl peroxy nitrates were within  $\pm 30\%$  of the calculated high pressure thermal decomposition rate of  $\text{C}_2\text{H}_5\text{OONO}_2$ .<sup>33</sup> The pressures at which these  $\text{RO}_2 + \text{NO}_2$  reactions will exhibit kinetic fall-off behavior from the second- to third-order regime will decrease as the size of the  $\text{RO}_2$  radical increases, and it is expected that at room temperature and 760 Torr total pressure the  $\geq \text{C}_3$  alkyl peroxy radical reactions are close to the limiting high-pressure region. The thermal decomposition reactions of the alkyl peroxy nitrates are discussed in Sec. 2.6.

#### Reaction with $\text{HO}_2$ Radicals

Relatively few data exist for the reactions of  $\text{HO}_2$  radicals with alkyl peroxy radicals. Absolute rate con-

stants have been determined only for the  $\text{CH}_3\text{O}_2$ ,  $\text{C}_2\text{H}_5\text{O}_2$ , cyclopentylperoxy and cyclohexylperoxy radicals. The Arrhenius expressions recommended by the IUPAC panel for the  $\text{CH}_3\text{O}_2$  and  $\text{C}_2\text{H}_5\text{O}_2$  reactions are<sup>9</sup>:  $k(\text{CH}_3\text{O}_2 + \text{HO}_2) = 3.8 \times 10^{-13} e^{780/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  ( $5.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K); and  $k(\text{C}_2\text{H}_5\text{O}_2 + \text{HO}_2) = 6.5 \times 10^{-13} e^{650/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  ( $5.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K). For the reactions of the cyclopentylperoxy and cyclohexylperoxy radicals with the  $\text{HO}_2$  radical, Rowley *et al.*<sup>34</sup> have measured rate constants over the temperature range 249–364 K of  $(2.1 \pm 1.3) \times 10^{-13} e^{(1323 \pm 185)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $(2.6 \pm 1.2) \times 10^{-13} e^{(1245 \pm 124)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively. At 298 K, the rate constants for these two reactions are both  $(1.7\text{--}1.8) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .<sup>34</sup>

Based upon the recommendations<sup>9</sup> for the  $\text{CH}_3\text{O}_2$  and  $\text{C}_2\text{H}_5\text{O}_2$  reactions and the rate constants for the cyclopentylperoxy and cyclohexylperoxy radicals,<sup>34</sup> a rate constant at 298 K for the reactions of  $\text{HO}_2$  radicals with  $\text{RO}_2$  radicals of

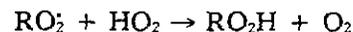
$$k(\text{HO}_2 + \text{RO}_2) = 1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

is indicated, with a likely overall uncertainty of a factor of 2. The temperature dependencies of the reactions studied to date are negative. A mean value of  $B = -1000 \text{ K}$  is chosen in the expression  $k = A e^{-B/T}$  to yield the recommendation of

$$k(\text{HO}_2 + \text{RO}_2) = 3.5 \times 10^{-13} e^{1000/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

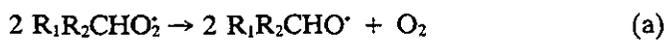
The IUPAC recommendations<sup>9</sup> should be used for the reactions of the  $\text{CH}_3\text{O}_2$  and  $\text{C}_2\text{H}_5\text{O}_2$  radicals with  $\text{HO}_2$ . The reaction of the  $\text{HOCH}_2\text{CH}_2\text{OO}^\cdot$  radical with the  $\text{HO}_2$  radical also has a rate constant of  $\sim 1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at room temperature (see Sec. 2.2).

The reactions of the  $\text{CH}_3\text{O}_2$ ,  $\text{C}_2\text{H}_5\text{O}_2$ , cyclopentylperoxy and cyclohexylperoxy radicals with the  $\text{HO}_2$  radical have been shown to proceed by H-atom abstraction to form the hydroperoxide<sup>34–37</sup>



#### Reaction with $\text{RO}_2$ Radicals

Numerous studies of the self-reactions of  $\text{RO}_2$  radicals have been carried out.<sup>38,39</sup> These reactions can proceed by the three pathways



with pathway (b) not being accessible for tertiary  $RO_2$  radicals. At around room temperature, product studies of the self-reactions of  $CH_3\dot{O}_2$ ,<sup>40-42</sup>  $C_2H_5\dot{O}_2$ ,<sup>43,44</sup> and  $(CH_3)_3C\dot{O}_2$  radicals<sup>45</sup> show no evidence for the occurrence of reaction pathway (c). In the following discussion, pathway (c) is taken to be of negligible importance and only pathways (a) and (b) are assumed to occur.

The IUPAC panel recommendations<sup>9</sup> for the overall rate constants ( $k = k_a + k_b$ ) and the rate constant ratio  $k_a/k_b$  for the  $\leq C_3$   $RO_2$  radicals are given in Table 6, together with the literature data for the  $\geq C_4$   $RO_2$  radicals. For the self-reaction of the *tert*-butyl peroxy radical, the rate constants reported by Anastasi *et al.*,<sup>18</sup> Kirsch *et al.*,<sup>48</sup> and Lightfoot *et al.*,<sup>46</sup> at room temperature and above are in good agreement.<sup>46</sup> Because of the wider temperature range studied, the Arrhenius expression of Lightfoot *et al.*<sup>46</sup> is preferred. Although an Arrhenius expression is given in Table 6 for the self-reaction of neopentyl peroxy radicals,<sup>46</sup> the rate constants measured by Lightfoot *et al.*<sup>46</sup> exhibit non-Arrhenius behavior (note that the three parameter expression of  $k = 3.02 \times 10^{-19} (T/298)^{9.46} e^{4260/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  cited by Lightfoot *et al.*<sup>46</sup> does not fit their data, and the expression  $k = 3.02$

$\times 10^{-19} (T/298)^{9.46} e^{4530/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  appears to be a better fit). The overall rate constant  $k$  and branching ratio  $k_a/k_b$  determined by Wallington *et al.*<sup>49</sup> at 297 K for the self-reaction of neopentyl peroxy radicals are in excellent agreement with the more extensive measurements of Lightfoot *et al.*<sup>46</sup>

The Arrhenius expressions for  $k_a/k_b$  are only applicable over the cited temperature ranges, since over extended temperature ranges the calculated values exceed unity. The more correct temperature-dependent format uses the ratio  $k_a/k_b$  (see, for example, Carter and Atkinson<sup>29</sup> for alkyl nitrate formation from the  $RO_2 + NO$  reactions), and Lightfoot *et al.*<sup>46</sup> have derived the rate constant ratio  $k_a/k_b = 197 e^{-(1658 \pm 98)/T}$  for the self-reaction of neopentyl peroxy radicals over the temperature range 248–373 K.

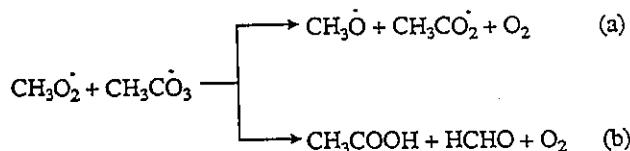
For all of the alkyl peroxy radicals for which data are available and for which both reaction pathways (a) and (b) are allowed, the reaction pathway (a) to yield the alkoxy radicals increases in importance as the temperature increases (Table 6 and Lightfoot *et al.*<sup>46</sup>), with this pathway accounting for 30–60% of the overall reaction at 298 K. For the self-recombination reaction of  $CH_3\dot{O}_2$  radicals, Kan and Calvert<sup>50</sup> and Kurylo *et al.*<sup>51</sup> have shown that, in contrast to the combination reaction of  $HO_2$  radicals,<sup>9</sup>  $H_2O$  vapor has no effect on the measured room temperature rate constant.

In addition to these  $RO_2$  self-combination reaction studies, rate constants have been obtained for the reac-

TABLE 6. Rate constants,  $k$ , at 298 K and temperature-dependent parameters,  $k = Ae^{-B/T}$ , for the gas-phase combination reactions of  $RO_2$  radicals

$RO_2 + RO_2$	$10^{12} \times A$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	$B$ (K)	$10^{13} \times k$ (298 K) ( $\text{cm}^{-3} \text{ molecule}^{-1} \text{ s}^{-1}$ )	$k_a/k_b$	Reference
$CH_3\dot{O}_2 + CH_3\dot{O}_2$	0.11	$-365 \pm 200$	$3.7 \pm 0.7$	$5.4 e^{-870/T}$	Atkinson <i>et al.</i> <sup>9</sup>
$C_2H_5\dot{O}_2 + C_2H_5\dot{O}_2$	0.098	$110 \pm 100$	$0.68 \pm 0.17$	$0.62 \pm 0.10$ (298 K)	Atkinson <i>et al.</i> <sup>9</sup>
$CH_3CH_2CH_2\dot{O}_2 + CH_3CH_2CH_2\dot{O}_2$			$3 \pm 2$		Atkinson <i>et al.</i> <sup>9</sup>
$(CH_3)_3CCH_2\dot{O}_2 + (CH_3)_3CCH_2\dot{O}_2$	0.0016	$-1961 \pm 100$	$10.4 \pm 0.9$	0.40 (298 K)	Lightfoot <i>et al.</i> <sup>46</sup>
$(CH_3)_2CH\dot{O}_2 + (CH_3)_2CH\dot{O}_2$	1.6	$2200 \pm 300$	$0.010 \pm 0.008$	$2.0 e^{-380/T}$ (300–400 K)	Atkinson <i>et al.</i> <sup>9</sup>
cyclo- $C_6H_{11}\dot{O}_2 +$ cyclo- $C_6H_{11}\dot{O}_2$	0.074	274	$0.284 \pm 0.016$	$0.29 \pm 0.02$ (298 K)	Rowley <i>et al.</i> <sup>47</sup>
$(CH_3)_3C\dot{O}_2 + (CH_3)_3C\dot{O}_2$	10	3894	0.00021		Lightfoot <i>et al.</i> <sup>46</sup>
$CH_3\dot{O}_2 + (CH_3)_3C\dot{O}_2$	0.37	1420	0.032	$5.9 e^{-1130/T}$ (313–393 K)	Osborne and Waddington <sup>45</sup>
$(CH_3)_3CCH_2\dot{O}_2 + (CH_3)_3C\dot{O}_2$			$0.3 \pm 0.1$ (373 K)		Lightfoot <i>et al.</i> <sup>46</sup>
$CH_3\dot{O}_2 + CH_3C\dot{O}_3$			110	0.5 (298 K)	Atkinson <i>et al.</i> <sup>9</sup>

tions of the  $\text{CH}_3\text{O}_2^\cdot$  radical with  $(\text{CH}_3)_3\text{CO}_2^{\cdot 45,52}$  and  $\text{CH}_3\text{C}(\text{O})\text{O}_2^\cdot$  radicals<sup>53,54</sup> and for the reaction of the  $(\text{CH}_3)_3\text{CO}_2^\cdot$  radical with the  $(\text{CH}_3)_3\text{CCH}_2\text{O}_2^\cdot$  radical.<sup>46</sup> The rate data obtained or recommended<sup>9</sup> are given in Table 6, with those of Osborne and Waddington<sup>45</sup> being used for the temperature-dependent expressions  $k$  and  $k_a/k$  given in Table 6 for the  $\text{CH}_3\text{O}_2^\cdot + (\text{CH}_3)_3\text{CO}_2^\cdot$  reaction. For the reaction of the  $\text{CH}_3\text{O}_2^\cdot$  radical with  $\text{CH}_3\text{CO}_3^\cdot$  radicals, the two pathways



are of approximately equal importance at 298 K.<sup>9</sup>

In the absence of further experimental data for a wider variety of  $\text{RO}_2^\cdot$  radicals, the following rate constants are recommended as being reasonably representative for primary, secondary and tertiary alkyl peroxy radicals at 298 K:

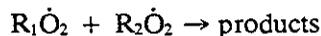
$$k(\text{primary RO}_2^\cdot + \text{primary RO}_2^\cdot) \\ \sim 2.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k(\text{secondary RO}_2^\cdot + \text{secondary RO}_2^\cdot) \\ \sim 5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k(\text{tertiary RO}_2^\cdot + \text{tertiary RO}_2^\cdot) \\ \sim 2 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

all with uncertainties at 298 K of at least a factor of 5. For the self-reactions of primary and secondary  $\text{RO}_2^\cdot$  radicals, the rate constant ratio  $k_a/k \sim 0.45 \pm 0.2$  at 298 K. For the self-reactions of tertiary  $\text{RO}_2^\cdot$  radicals, only reaction pathway (a) can occur.

For the reactions of non-identical alkyl peroxy radicals,



the sparse data set indicates that the rate constants are approximately given by the geometric mean equation,<sup>55</sup> with  $k_{12} \sim 2(k_1k_2)^{0.5}$ , where  $k_{12}$  is the rate constant for the  $\text{R}_1\text{O}_2^\cdot + \text{R}_2\text{O}_2^\cdot$  reaction and  $k_1$  and  $k_2$  are the rate constants for the self-reactions of  $\text{R}_1\text{O}_2^\cdot$  and  $\text{R}_2\text{O}_2^\cdot$  radicals, respectively. Clearly, a much wider data base is required concerning the reactions of the  $\text{HO}_2$  radical with alkyl

peroxy ( $\text{RO}_2^\cdot$ ) radicals and, to a lesser extent, for cross-combination reactions of  $\text{RO}_2^\cdot$  radicals.

### Alkoxy ( $\text{RO}^\cdot$ ) Radical Reactions

Under atmospheric conditions the major alkoxy radical removal processes involve reaction with  $\text{O}_2$ , unimolecular decomposition and unimolecular isomerization (see, for example, Carter and Atkinson<sup>1</sup> and Atkinson and Carter<sup>56</sup>). For the case of the 2-pentoxy radical, these reactions are shown in Reaction Scheme (1) below where the isomerization reaction proceeds by a (generally) 6-member ring transition state. In addition, reactions with  $\text{NO}$  and  $\text{NO}_2$ , though minor under most conditions, must be considered.

**Reaction with  $\text{O}_2$ .** Absolute rate constants for the reactions of alkoxy radicals with  $\text{O}_2$  have been determined for  $\text{CH}_3\dot{\text{O}}$ ,<sup>57-60</sup>  $\text{C}_2\text{H}_5\dot{\text{O}}$ <sup>58,61</sup> and  $(\text{CH}_3)_2\text{CH}\dot{\text{O}}$ <sup>62</sup> radicals, and the IUPAC recommendations<sup>9</sup> for the rate constants for these reactions are given in Table 7.

Based on the recommended rate constants for the reactions of  $\text{C}_2\text{H}_5\dot{\text{O}}$  and  $(\text{CH}_3)_2\text{CH}\dot{\text{O}}$  radicals with  $\text{O}_2$ , it is recommended that for the primary ( $\text{RCH}_2\dot{\text{O}}$ ) and secondary ( $\text{R}_1\text{R}_2\text{CH}\dot{\text{O}}$ ) alkoxy radicals formed from the alkanes

$$k(\text{RCH}_2\dot{\text{O}} + \text{O}_2) = 6.0 \times 10^{-14} e^{-550/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \\ = 9.5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K},$$

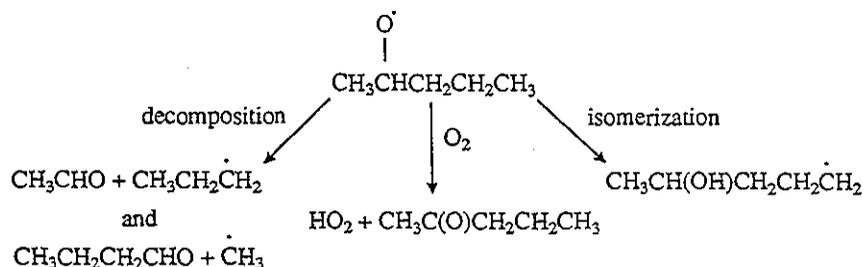
and

$$k(\text{R}_1\text{R}_2\text{CH}\dot{\text{O}} + \text{O}_2) = 1.5 \times 10^{-14} e^{-200/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \\ = 8 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}.$$

Baldwin *et al.*<sup>63</sup> and Balla *et al.*<sup>62</sup> have derived relationships between the rate constants for the reactions of the alkoxy radicals with  $\text{O}_2$  and the exothermicities of these reactions, and such a relationship has also been suggested by Atkinson and Carter.<sup>56</sup> Based on the three reactions for which recommendations are given (Table 7), a unit-weighted least-squares analysis leads to ( $\Delta H_{\text{O}_2}$  in kcal mol<sup>-1</sup>)

$$k(\text{RO}^\cdot + \text{O}_2) = \\ 1.3 \times 10^{-19} n e^{-(0.32\Delta H_{\text{O}_2})} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad \text{(I)}$$

at 298 K, where  $n$  is the number of abstractable H atoms in the alkoxy radical. While this equation differs from those of Baldwin *et al.*<sup>63</sup> ( $k(\text{RO}^\cdot + \text{O}_2) = 6.1 \times 10^{-22} n$



Reaction Scheme (1)

TABLE 7. Recommended 298 K rate constants and temperature dependent expressions,  $k = Ae^{-B/T}$ , for the reactions of  $O_2$  with alkoxy ( $RO\cdot$ ) radicals<sup>a</sup>

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

<sup>a</sup>From Atkinson *et al.*<sup>9</sup>

$e^{-(0.49\Delta H_{O_2})} cm^3 \text{ molecule}^{-1} s^{-1}$  or  $3.3 \times 10^{-21} n e^{-(0.42\Delta H_{O_2})} cm^3 \text{ molecule}^{-1} s^{-1}$  at 298 K) and Balla *et al.*<sup>62</sup> ( $k(RO\cdot + O_2) = 1.0 \times 10^{-22} n e^{-0.51\Delta H_{O_2}} cm^3 \text{ molecule}^{-1} s^{-1}$  at 298 K), these expressions give reasonably similar rate constants for values of  $\Delta H_{O_2} \sim -32 \text{ kcal mol}^{-1}$  (corresponding to the  $C_2H_5O\cdot$  radical). At 760 Torr total pressure of air and 298 K, Eq. (I) leads to

$$k_{O_2}[O_2] = 0.67 n e^{-(0.32\Delta H_{O_2})} s^{-1} \quad (II)$$

The above recommendations for primary and secondary alkoxy radicals are slightly different than those recommended by Atkinson.<sup>2</sup> The rate constants for the reactions of  $O_2$  with substituted alkoxy radicals formed from, for example, the alkenes after initial OH radical reaction (for example, the  $HOCH_2CH_2\dot{O}$  radical) are discussed in the respective sections below.

**Alkoxy Radical Decompositions.** The gas-phase decomposition reactions of alkoxy radicals formed from the OH radical-initiated reactions of alkanes have been the subject of several previous reviews and discussions.<sup>1,2,56,63-68</sup> These previous articles have derived relationships between the measured Arrhenius activation energies for the alkoxy radical decompositions ( $E_d$ ) and the heats of the decomposition reaction ( $\Delta H_d$ ), with the Arrhenius pre-exponential factors for these decomposition reactions all being of a similar magnitude. Most of these relationships have assumed, or shown, that a single relationship between  $E_d$  and  $\Delta H_d$  exists, with

$$E_d = a + b\Delta H_d$$

irrespective of the structure of the alkoxy radical or the leaving alkyl group.<sup>1,2,63,65,66</sup> Choo and Benson,<sup>67</sup> however, presented data indicating that the parameter "a" in the above relationship depends on the leaving alkyl group, with this parameter decreasing monotonically along the alkyl leaving-group series  $\dot{C}H_3$ ,  $\dot{C}_2H_5$ ,  $(CH_3)_2\dot{C}H$  and  $(CH_3)_3\dot{C}$ .

Many of the rate constant data for the alkoxy radical decomposition reactions have been determined relative to the alkoxy radical combination reaction with  $NO$ <sup>65,66,68</sup>



and changes in the  $RO\cdot + NO$  rate constants and, especially, in the heats of the alkoxy radical reactions ( $\Delta H_d$ )

over the past decade makes a reanalysis necessary. Using recent data for the alkyl radical heats of formation,<sup>9,69-72</sup> the recommended Arrhenius parameters for selected alkoxy radical decompositions [those of  $CH_3\dot{O}$ ,  $C_2H_5\dot{O}$ ,  $(CH_3)_2CH\dot{O}$ ,  $CH_3CH_2CH(O)CH_3$ ,  $(CH_3)_3\dot{C}O$  and  $CH_3CH_2C(CH_3)_2\dot{O}$  radicals]<sup>68,73,74</sup> and the present recommendation for the temperature-dependent rate constants for the  $RO\cdot + NO$  reactions of  $k_\infty(RO\cdot + NO) = 2.3 \times 10^{-11} e^{150/T} cm^3 \text{ molecule}^{-1} s^{-1}$  (see below), then

$$E_d = 11.2 + 0.79\Delta H_d,$$

with the energies in  $kcal \text{ mol}^{-1}$ , and

$$A_d = (2 \times 10^{14} d) s^{-1}$$

where d is the reaction path degeneracy for the alkoxy radical decomposition reactions.

This relationship, however, is derived from only a few alkoxy radical decomposition reactions, and the recent data of Lightfoot *et al.*<sup>46</sup> for the decomposition and reaction with  $O_2$  of the 2,2-dimethyl-1-propoxy [ $(CH_3)_3CCH_2\dot{O}$ ] radical shows that the above relationship between  $E_d$  and  $\Delta H_d$  does not hold for this particular alkoxy radical. Specifically, Lightfoot *et al.*<sup>46</sup> obtained a rate constant ratio of  $k_d/k_{O_2} = (2.0 \pm 0.2) \times 10^{20} \text{ molecule cm}^{-3}$  at 298 K, consistent with the lower limit derived by Wallington *et al.*<sup>49</sup> With a value of  $k_{O_2} = 4.7 \times 10^{-15} cm^3 \text{ molecule}^{-1} s^{-1}$  calculated from Eq. (I) with  $\Delta H_{O_2} = -30.6 \text{ kcal mol}^{-1}$  (as obtained from group additivity calculations), this leads to  $k_d = 9.4 \times 10^5 s^{-1}$  at 298 K, in close agreement with the value derived by Lightfoot *et al.*<sup>46</sup> Since  $\Delta H_d = 9.8 \text{ kcal mol}^{-1}$  from group additivity calculations (which can be compared with the heat of reaction of  $8.2 (\pm 2.1) \text{ kcal mol}^{-1}$  calculated by Lightfoot *et al.*<sup>46</sup>), the expressions given above would predict that  $k_d \sim 2 s^{-1}$ , some six orders of magnitude in error.

It is therefore clear that the alkoxy radicals formed from the OH radical reactions with the alkenes and ethers<sup>56</sup> are not the only alkoxy radicals for which the rates of the various reaction processes cannot be accurately predicted.

The empirical method of assessing the relative importance of decomposition versus  $O_2$  reaction for alkoxy radicals proposed by Atkinson and Carter<sup>56</sup> is thus extended further and an attempt is made to place it on a numerical basis. Figure 1 shows a plot of the values of  $\Delta H_d$  and  $\Delta H_{O_2}$

for the alkoxy radicals dealt with by Atkinson and Carter,<sup>56</sup> plus the  $(\text{CH}_3)_3\text{CCH}_2\dot{\text{O}}$  radical formed from neopentane, with the dominant reaction pathways at 298 K and atmospheric pressure of air being denoted by (O) for decomposition, (●) for  $\text{O}_2$  reaction, and ( $\Delta$ ) for those cases where both decomposition and  $\text{O}_2$  reaction are observed to occur at 298 K and 760 Torr total pressure of air. The line drawn separates dominant decomposition from dominant  $\text{O}_2$  reaction, and is defined by the data for the  $\text{HOCH}_2\text{CH}_2\dot{\text{O}}$  and  $\text{CH}_3\text{CH}_2\text{CH}(\dot{\text{O}})\text{CH}_3$  radicals, with allowance being made for the fact that the decomposition/ $\text{O}_2$  reaction ratios for these alkoxy radicals differ from unity at 298 K and 760 Torr total pressure of air. Within the uncertainties of the heats of reaction for the  $(\text{CH}_3)_3\text{CCH}_2\dot{\text{O}}$  radical, the position of this radical on the plot is consistent with decomposition and  $\text{O}_2$  reaction being competitive.

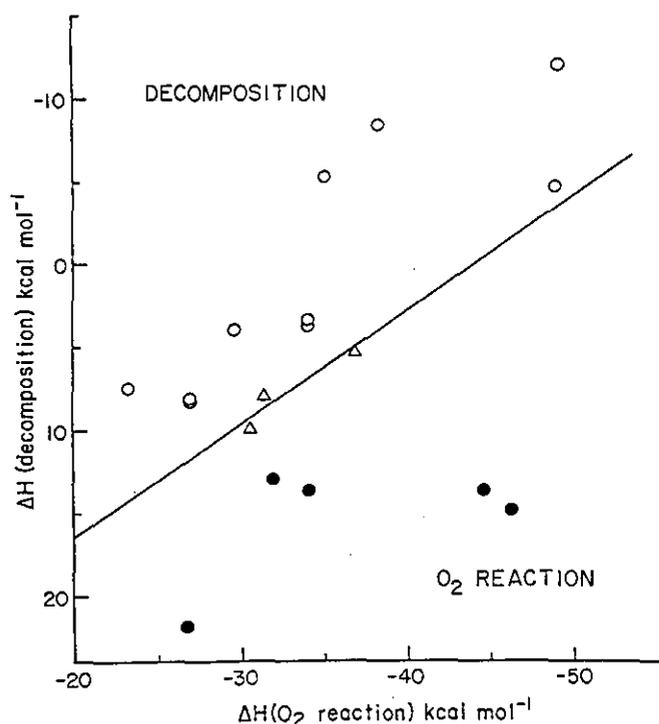


FIG. 1. Plot of the values of  $\Delta H(\text{decomposition})$  against  $\Delta H(\text{O}_2 \text{ reaction})$  for a series of alkoxy radicals. (O) Alkoxy radicals reacting dominantly by decomposition at 298 K and atmospheric pressure of air; (●) alkoxy radicals reacting dominantly by reaction with  $\text{O}_2$  at 298 K and atmospheric pressure of air; ( $\Delta$ ) alkoxy radicals reacting by both decomposition and  $\text{O}_2$  reaction at 298 K and atmospheric pressure of air; (—) line separating dominant decomposition from  $\text{O}_2$  reaction.

The boundary line is given by

$$\Delta H_d^{\text{line}} = 30.3 + 0.69\Delta H_{\text{O}_2}$$

with the energies being in  $\text{kcal mol}^{-1}$ . By definition, on this line  $k_d^{\text{line}} = k_{\text{O}_2}[\text{O}_2]$ . For most alkoxy radicals, the values of  $\Delta H_d$  and  $\Delta H_{\text{O}_2}$  are such that the alkoxy radical does

not fall on this boundary line. By making the approximate (and probably incorrect) assumption that,

$$k_d/k_d^{\text{line}} = e^{-[0.79(\Delta H_d - 30.3 - 0.69\Delta H_{\text{O}_2}) \times 10^3/RT]}$$

then

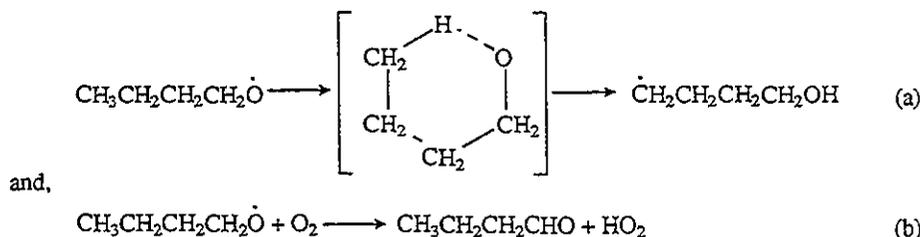
$$k_d = \{2.4 \times 10^{17} \text{ nd } e^{(0.60\Delta H_{\text{O}_2} - 1.33\Delta H_d)}\} \text{ s}^{-1} \text{ at 298 K, (III)}$$

where the energies are again in  $\text{kcal mol}^{-1}$ .

These two expressions for  $k_{\text{O}_2}[\text{O}_2]$  and  $k_d$  at 298 K and atmospheric pressure of air (Eqs. (II) and (III), respectively) appear to give semi-quantitatively correct data for the alkoxy radicals, and allow the alkoxy radical decompositions and reactions with  $\text{O}_2$  to be (semi)-quantitatively compared with the alkoxy radical isomerizations (see below). With regards to the situation at temperatures other than 298 K, as an approximation it is reasonable to use a temperature independent rate constant for the  $\text{O}_2$  reaction (but of course the correct  $\text{O}_2$  concentration must be taken into account) [a temperature dependence of 1000 K corresponds to a variation of the rate constant by a factor of 2.3 over the temperature range 250–300 K]. The value of  $k_d$  at 298 K can be combined with a pre-exponential factor of  $A_d = (2 \times 10^{14} \text{ d}) \text{ s}^{-1}$  to derive approximate values of  $k_d$  at other temperatures. Clearly, this postulated, and empirical, method for assessing the relative importance of the various alkoxy radical reactions under atmospheric conditions needs to be tested against a wider data base.

The alkoxy radical decomposition reactions may be in the fall-off region between first-order and second-order kinetics at room temperature and atmospheric pressure.<sup>63,65,74–77</sup> For the two alkoxy radicals for which pressure dependent decomposition rate constants have been observed [2-propoxy<sup>77</sup> and 2-methyl-2-propoxy (*t*-butoxy)<sup>74–76</sup>], the rate constants at room temperature and atmospheric pressure are reasonably close to the limiting high pressure values<sup>75–77</sup> [see also Table II in Baldwin *et al.*,<sup>63</sup> which predicts that the corrections for fall-off behavior are small for  $\text{C}_3$  and higher alkoxy radicals, being less than a factor of 2 at room temperature and atmospheric pressure].

*Alkoxy Radical Isomerizations.* No direct experimental data are available, but isomerization rate constants have been estimated initially by Carter *et al.*<sup>78</sup> and subsequently, and in more detail, by Baldwin *et al.*<sup>63</sup> The major relevant experimental data available concern measurements of the rate constant ratio for the reactions shown in Reaction Scheme (2), obtained from product yields determined in *n*-butane- $\text{NO}_x$ -air,<sup>79</sup> HONO-*n*-butane-air<sup>80</sup> and *n*-butyl nitrite-air<sup>81</sup> photolyses. Rate constant ratios of  $k_a/k_b$  of  $1.65 \times 10^{19} \text{ molecule cm}^{-3}$  at 303 K,<sup>79</sup>  $1.5 \times 10^{19} \text{ molecule cm}^{-3}$  at 295 K<sup>80</sup> and  $1.9 \times 10^{19} \text{ molecule cm}^{-3}$  at  $298 \pm 2 \text{ K}$ <sup>81</sup> were derived from these studies. These rate constant ratios are in good agreement, with an average value of  $k_a/k_b = 1.7 \times 10^{19} \text{ molecule cm}^{-3}$  at  $\sim 299 \text{ K}$ . Using the rate constant estimated as described above for reaction (b),  $k_{\text{O}_2}$ , this leads to a rate constant of



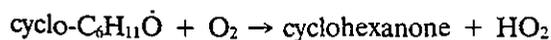
Reaction Scheme (2)

$k_a = 6.7 \times 10^4 \text{ s}^{-1}$  at 299 K, a factor of  $\sim 8$  lower than the estimate of Baldwin *et al.*<sup>63</sup> Considering the large uncertainties in the estimation technique, this estimate is probably in fairly good agreement with the experimental data. However, the data of Dóbé *et al.*<sup>82</sup> for the isomerization of the 2-pentoxo radical lead to an isomerization rate of  $\sim 4 \times 10^3 \text{ s}^{-1}$  at 298 K, significantly lower than the thermochemical estimates. The reasons for this discrepancy are not presently known, but may be due to the difficulties in quantitatively monitoring the end products of this isomerization reaction.<sup>82</sup>

Analogous to the procedure carried out by Carter and Atkinson,<sup>1</sup> the estimated Arrhenius parameters of Baldwin *et al.*<sup>63</sup> have been modified to yield values of  $k_a$  which are a factor of 8 lower at 298 K, and the resulting Arrhenius parameters are given in Table 8 for 1,5-H shift isomerizations of alkoxy radicals (the isomerizations expected to be of importance under atmospheric conditions). These estimates, however, must still be considered to be highly uncertain, and further studies of these isomerization rate constants are needed.

The rate constants for alkoxy radical isomerization given in Table 8 can be combined with the estimated alkoxy radical decomposition rates [Eq. (III)] and rates of reaction with  $\text{O}_2$  [Eq. (II)] to assess the relative importances of these three reaction pathways at 298 K and 760 Torr total pressure of air. Table 9 gives calculated rates of removal due to decomposition, unimolecular isomerization and reaction with  $\text{O}_2$  at 298 K and 760 Torr total pressure of air for a series of alkoxy radicals formed from alkanes, haloalkanes, alkenes, haloalkenes and ethers, together with the available literature data. In all cases, the most important removal pathway is correctly predicted. However, this empirical estimation method appears to grossly overestimate the decomposition rates for exothermic decompositions, and it may be more appropriate to set an upper limit to an alkoxy radical decomposition rate of  $\sim 2 \times 10^7 \text{ s}^{-1}$  at 298 K. It is obvious that more theoretical and experimental work is necessary before we have any scientifically valid and quantitative understanding of the atmospherically important reactions of alkoxy radicals.

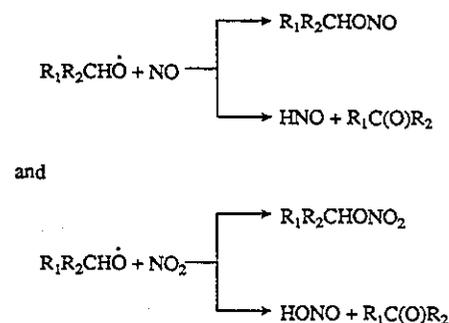
For the cyclohexyloxy (cyclo- $\text{C}_6\text{H}_{11}\dot{\text{O}}$ ) radical, the reaction with  $\text{O}_2$



accounts for  $42 \pm 5\%$  of the overall reaction pathways at  $296 \pm 2 \text{ K}$  and atmospheric pressure of air<sup>83</sup> (consistent

with the product data of Rowley *et al.*<sup>47</sup>). This relative importance of the  $\text{O}_2$  reaction suggests that the isomerization reaction is not important for the cyclo- $\text{C}_6\text{H}_{11}\dot{\text{O}}$  radical, and that the competing pathway is the alkoxy radical decomposition reaction.<sup>47</sup>

*Reactions of  $\dot{\text{R}}\text{O}$  Radicals with  $\text{NO}$  and  $\text{NO}_2$ .* Alkoxy radicals can also react with  $\text{NO}$  and  $\text{NO}_2$  under atmospheric conditions



Absolute rate constants have been measured for the reactions of  $\text{CH}_3\dot{\text{O}}$ ,  $\text{C}_2\text{H}_5\dot{\text{O}}$  and  $(\text{CH}_3)_2\text{CH}\dot{\text{O}}$  radicals with  $\text{NO}$  and  $\text{NO}_2$ , and the recommended 298 K limiting high-pressure rate constants and temperature-dependent parameters are given in Tables 10 and 11, respectively. The rate constants for the reactions of the  $\text{CH}_3\dot{\text{O}}$  radical with  $\text{NO}$  and  $\text{NO}_2$  are in the fall-off region between second- and third-order kinetics,<sup>9</sup> with calculated rate constants at 298 K and 760 Torr total pressure of air of  $2.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively.

The kinetic data obtained by Balla *et al.*<sup>62</sup> for the reactions of the  $(\text{CH}_3)_2\text{CH}\dot{\text{O}}$  radical with  $\text{NO}$  and  $\text{NO}_2$  were at, or close to, the high pressure limit, and show that these reactions have rate constants at room temperature of  $(3-4) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , with small negative temperature dependencies.<sup>62</sup>

A large amount of relative rate data have been obtained for these  $\text{NO}$  and  $\text{NO}_2$  reactions, as discussed by Batt.<sup>68</sup> These relative rate data show that for the reaction of  $\dot{\text{R}}\text{O}$  radicals with  $\text{NO}$ , the addition rate constants at  $\sim 400 \text{ K}$  are  $\sim 3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , with an uncertainty of a factor of  $\sim 2-3$ . While H-atom abstraction from the  $\dot{\text{R}}\text{O} + \text{NO}$  reactions is observed at low total pressures,<sup>84,85</sup> at total pressures close to the high pressure limit the H-atom abstraction process appears to be minor ( $< 0.05$ ).<sup>68</sup>

For the  $\dot{\text{R}}\text{O}$  reactions with  $\text{NO}_2$ , the relative rate data cited by Batt<sup>68</sup> suggest that  $k(\dot{\text{R}}\text{O} + \text{NO}_2) \sim 3 \times 10^{-11}$

TABLE 8. Estimated Arrhenius parameters,  $k = Ae^{-E_a/RT}$ , and room temperature rate constants for 1,5-H shift isomerizations of alkoxy radicals

Type of H Abstracted	$E$ (Abstraction) <sup>a</sup> (kcal mol <sup>-1</sup> )	$E_a$ (Isom) <sup>b</sup> (kcal mol <sup>-1</sup> )	$A^c$ (s <sup>-1</sup> )	$k$ (298 K) (s <sup>-1</sup> )
-CH <sub>3</sub>	7.8	8.3	$8.2 \times 10^{10}$	$6.7 \times 10^4$
-CH <sub>2</sub> -	4.7	5.2	$5.5 \times 10^{10}$	$8.4 \times 10^6$
>CH-	4.7	5.2	$2.7 \times 10^{10}$	$4.1 \times 10^6$
-CH <sub>2</sub> OH	6.6	7.1	$5.5 \times 10^{10}$	$3.4 \times 10^5$
-CH(OH)-	3.5 <sup>d</sup>	4.0	$2.7 \times 10^{10}$	$3.1 \times 10^7$

<sup>a</sup> $E$  (abstraction) = activation energy for abstraction by  $\text{RO}\dot{\text{O}}$  in bimolecular systems (i.e., no ring strain). Estimates of Baldwin *et al.*,<sup>63</sup> increased by 0.6 kcal mol<sup>-1</sup>, have been used.

<sup>b</sup> $E_a$  (Isom) =  $E$  (abstraction) + 0.5 kcal mol<sup>-1</sup> ring strain.

<sup>c</sup>Estimates of Baldwin *et al.*,<sup>63</sup> decreased by a factor of 2.9 (see text), used.

<sup>d</sup>Baldwin *et al.*,<sup>63</sup> did not give an estimate for this abstraction. It is assumed that replacing -H with -OH decreases  $E$  (abstraction) by 1.2 kcal mol<sup>-1</sup>, based on their estimates for abstraction from -CH<sub>3</sub> and -CH<sub>2</sub>- groups.

TABLE 9. Calculated rates (s<sup>-1</sup>) of competing alkoxy radical reactions at 298 K and 760 Torr total pressure of air. Dominant reaction is in italics, and literature data are given in parentheses

Radical	Decomposition	Reaction with O <sub>2</sub>	Isomerization
CH <sub>3</sub> CH( $\dot{\text{O}}$ )C(O)CH <sub>3</sub> <sup>a</sup>	$2.2 \times 10^{11}$	$5.1 \times 10^4$	
CHCl <sub>2</sub> $\dot{\text{O}}$ <sup>a</sup>	$3.8 \times 10^{12}$	$1.5 \times 10^5$	
CH <sub>3</sub> OC(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> $\dot{\text{O}}$	$2.0 \times 10^7$	$2.4 \times 10^3$	$\geq 7 \times 10^4$
CH <sub>3</sub> CH( $\dot{\text{O}}$ )CH(OH)CH <sub>3</sub>	$2.4 \times 10^7$	$9.0 \times 10^3$	
CH <sub>3</sub> CH <sub>2</sub> CH(OH)CH <sub>2</sub> $\dot{\text{O}}$	$9.3 \times 10^5$	$7.6 \times 10^3$	$6.7 \times 10^4$
CH <sub>3</sub> CH(OH)CH <sub>2</sub> $\dot{\text{O}}$	$8.1 \times 10^5$	$7.6 \times 10^3$	
HOCH <sub>2</sub> CHCl $\dot{\text{O}}$ <sup>a</sup>	$3.3 \times 10^{11}$	$4.8 \times 10^6$	
CH <sub>3</sub> CH <sub>2</sub> CH( $\dot{\text{O}}$ )CH <sub>2</sub> OH	$3.9 \times 10^6$	$3.7 \times 10^4$	
CH <sub>3</sub> CH( $\dot{\text{O}}$ )CH <sub>2</sub> OH	$2.6 \times 10^6$	$3.7 \times 10^4$	
HOCH <sub>2</sub> CH <sub>2</sub> $\dot{\text{O}}$	$8.6 \times 10^4$	$3.1 \times 10^4$	
(CH <sub>3</sub> ) <sub>3</sub> CCH <sub>2</sub> $\dot{\text{O}}$	$9.8 \times 10^3$	$2.4 \times 10^4$	
CH <sub>3</sub> CH( $\dot{\text{O}}$ )CH <sub>2</sub> CH <sub>3</sub>	$5.4 \times 10^4$	$8.7 \times 10^4$	
	( $4.3 \times 10^3$ ) <sup>b</sup>		
CH <sub>3</sub> CH( $\dot{\text{O}}$ )CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	$4.9 \times 10^3$	$4.6 \times 10^4$	$6.7 \times 10^4$
	( $9.0 \times 10^3$ ) <sup>c</sup>		
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> $\dot{\text{O}}$	$1.6 \times 10^2$	$2.2 \times 10^4$	$6.7 \times 10^4$
CH <sub>3</sub> CH <sub>2</sub> OCH( $\dot{\text{O}}$ )CH <sub>3</sub> <sup>a</sup>	$2.0 \times 10^7$	$4.5 \times 10^6$	$6.7 \times 10^4$
(CH <sub>3</sub> ) <sub>3</sub> COCH( $\dot{\text{O}}$ )CH <sub>3</sub> <sup>a</sup>	$2.0 \times 10^7$	$4.5 \times 10^6$	$2.0 \times 10^5$
CH <sub>3</sub> CH <sub>2</sub> $\dot{\text{O}}$	$7.8 \times 10^1$	$3.8 \times 10^4$	
	( $1.7 \times 10^{-1}$ ) <sup>b</sup>	( $4.9 \times 10^4$ ) <sup>d</sup>	
CH <sub>2</sub> Cl $\dot{\text{O}}$	8.7	$7.3 \times 10^4$	
CH <sub>3</sub> $\dot{\text{O}}$	$5.3 \times 10^{-2}$	$1.0 \times 10^4$	
		( $9.8 \times 10^3$ ) <sup>d</sup>	
(CH <sub>3</sub> ) <sub>3</sub> COCH <sub>2</sub> $\dot{\text{O}}$	$1.1 \times 10^{-3}$	$3.8 \times 10^6$	$2.0 \times 10^5$
CH <sub>3</sub> OCH <sub>2</sub> $\dot{\text{O}}$	$1.5 \times 10^{-2}$	$2.2 \times 10^6$	

<sup>a</sup>Decomposition reaction is exothermic; see text.

<sup>b</sup>Data from Batt,<sup>68</sup> revised using  $k(\text{RO}\dot{\text{O}} + \text{NO}) = 2.3 \times 10^{-11} e^{150/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (see text).

<sup>c</sup>From Dóbé *et al.*,<sup>82</sup> revised using  $k(\text{RO}\dot{\text{O}} + \text{NO}) = 2.3 \times 10^{-11} e^{150/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

<sup>d</sup>From present recommendations.

TABLE 10. Rate constant parameters for the gas-phase combination reactions of  $\text{RO}\dot{\text{O}}$  radicals with NO (from Atkinson *et al.*)<sup>9</sup>

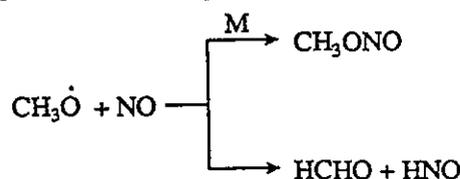
RO	$k_0$ (cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> )	$k_\infty$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$F$	Temperature Range (K)
CH <sub>3</sub> $\dot{\text{O}}$	$1.6 \times 10^{-29} (T/300)^{-3.5}$	$3.6 \times 10^{-11} (T/300)^{-0.6}$	0.6	200-400
C <sub>2</sub> H <sub>5</sub> $\dot{\text{O}}$		$4.4 \times 10^{-11}$		200-300
(CH <sub>3</sub> ) <sub>2</sub> CH $\dot{\text{O}}$		$3.4 \times 10^{-11}$		200-300

TABLE 11. Recommended rate constant parameters for the combination reactions of R $\dot{O}$  radicals with NO<sub>2</sub> (from Atkinson *et al.*<sup>9</sup>)

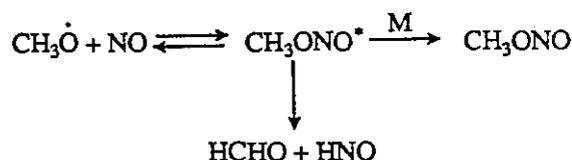
R $\dot{O}$	$k_o$ (cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> )	$k_\infty$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$F$	Temperature Range (K)
CH <sub>3</sub> $\dot{O}$	$2.8 \times 10^{-29} (T/300)^{-4.5}$	$2.0 \times 10^{-11}$	0.44	200-400
C <sub>2</sub> H <sub>5</sub> $\dot{O}$		$2.8 \times 10^{-11}$		200-300
(CH <sub>3</sub> ) <sub>2</sub> CH $\dot{O}$		$3.5 \times 10^{-11}$		200-300

cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at -400 K (similar to the rate constants for the corresponding NO reactions), and that the H-atom abstraction channel is minor, with the most recent relative rate data yielding H-atom abstraction rate constants at ~400 K of  $\sim 6 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for CH<sub>3</sub> $\dot{O}$ ,  $\sim 4 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for C<sub>2</sub>H<sub>5</sub> $\dot{O}$ , and  $\sim 1 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for the (CH<sub>3</sub>)<sub>2</sub>CH $\dot{O}$  radical.<sup>68</sup>

As discussed by Frost and Smith<sup>84</sup> and Smith,<sup>86</sup> these reactions of R $\dot{O}$  radicals with NO and NO<sub>2</sub> can proceed by two parallel, and independent, pathways, for example,



or by formation of HCHO + HNO from the energy-rich RONO\* intermediate:



It is likely that the second alternative, involving formation of the H-atom abstraction products from the RONO\* intermediate, is the operative reaction scheme. Hence at the high-pressure limit, RONO formation is the sole process expected, and the situation would then be analogous to the R' + O<sub>2</sub> reaction system (see above).

The relative rate data<sup>68</sup> are consistent with the absolute rate constants available (Tables 10 and 11), and the following recommendations for all alkoxy (R $\dot{O}$ ) radicals are made:

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

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

$$k_\infty(\text{RO}\cdot + \text{NO}_2) = 2.3 \times 10^{-11} e^{150/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \\ = 3.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with the H-atom abstraction process being of negligible importance under atmospheric conditions. For the CH<sub>3</sub> $\dot{O}$  and C<sub>2</sub>H<sub>5</sub> $\dot{O}$  radical reactions, the recommended rate con-

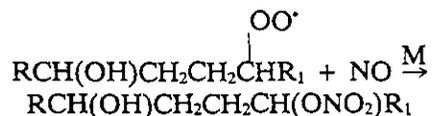
stants<sup>9</sup> should be used. Furthermore, the CH<sub>3</sub> $\dot{O}$  radical reactions are in the fall-off region under atmospheric conditions.<sup>9</sup>

Under ambient tropospheric conditions, these alkoxy radical reactions with NO and NO<sub>2</sub> are generally of negligible importance, but may be important in laboratory environmental chamber experiments. These reactions are, however, of potential importance for tertiary alkoxy radicals, such as the (CH<sub>3</sub>)<sub>3</sub>C $\dot{O}$  radical, where O<sub>2</sub> reaction cannot occur and the decomposition reaction is the other competing process. For example, for the *tert*-butoxy radical, (CH<sub>3</sub>)<sub>3</sub>C $\dot{O}$ , the thermal decomposition rate constant is<sup>74</sup>  $k_\infty = 1.1 \times 10^{14} e^{-7519/T} \text{ s}^{-1}$  ( $k_\infty = 1.21 \times 10^3 \text{ s}^{-1}$  at 298 K). At 298 K and 760 Torr total pressure of air or N<sub>2</sub>, the rate constant  $k[(\text{CH}_3)_3\text{C}\dot{\text{O}} \rightarrow \text{CH}_3\text{C}(\text{O})\text{CH}_3 + \dot{\text{C}}\text{H}_3]$  is in the fall-off region and is a factor of 1.26 lower<sup>76</sup> ( $\sim 960 \text{ s}^{-1}$ ). Hence, at 298 K and 760 Torr total pressure of air the NO and NO<sub>2</sub> reactions with the (CH<sub>3</sub>)<sub>3</sub>C $\dot{O}$  radical become significant for NO<sub>x</sub> concentrations  $\geq 2.5 \times 10^{12}$  molecule cm<sup>-3</sup> (100 parts-per-billion mixing ratio).

The reactions of the alkyl radicals formed from the OH (and NO<sub>3</sub>) radical reactions with the alkanes in the presence of NO are then as shown below [Reaction Scheme (3)] for the (CH<sub>3</sub>)<sub>3</sub>C $\dot{\text{C}}\text{H}_2$  radical formed from 2,2-dimethylpropane (the "stable" products are underlined, the alkyl nitrates (RONO<sub>2</sub>) are not specifically identified, and the R $\dot{O}$  + NO and R $\dot{O}$  + NO<sub>2</sub> combination reactions are neglected) [where RONO<sub>2</sub> is the corresponding alkyl nitrate formed from the alkyl peroxy radicals]. In the absence of NO, the alkyl peroxy radicals react with HO<sub>2</sub> and R $\dot{O}_2$  radicals.

As discussed above, alkoxy radical isomerization can also occur for the longer chain (>C<sub>3</sub>) alkanes in addition to decomposition and reaction with O<sub>2</sub>. For example, Reaction Scheme (4) shows the reactions for the 1-butoxy radical formed from *n*-butane. It is expected by analogy with the reactions of alkyl radicals (Table 2) and  $\beta$ -hydroxyalkyl radicals<sup>10,87,88</sup> (Sec. 2.2) that the  $\delta$ -hydroxyalkyl radicals will react rapidly and solely with O<sub>2</sub> to form the  $\delta$ -hydroxyalkyl peroxy radicals. However, this reaction sequence has not been experimentally confirmed under tropospheric conditions, and the fractions of the reactions of the  $\delta$ -hydroxyalkyl peroxy radicals with NO which yield the corresponding  $\delta$ -hydroxyalkyl nitrates have not been experimentally determined.<sup>1</sup> The limited data available concerning alkyl nitrate formation from these hydroxy-substituted alkyl peroxy radicals (from computer model fits to environmental chamber data) suggest that

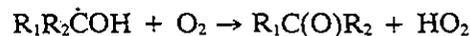
this alkyl nitrate formation is minimal, and Carter and Atkinson<sup>1</sup> recommend that alkyl nitrate formation from the reaction



is essentially zero.

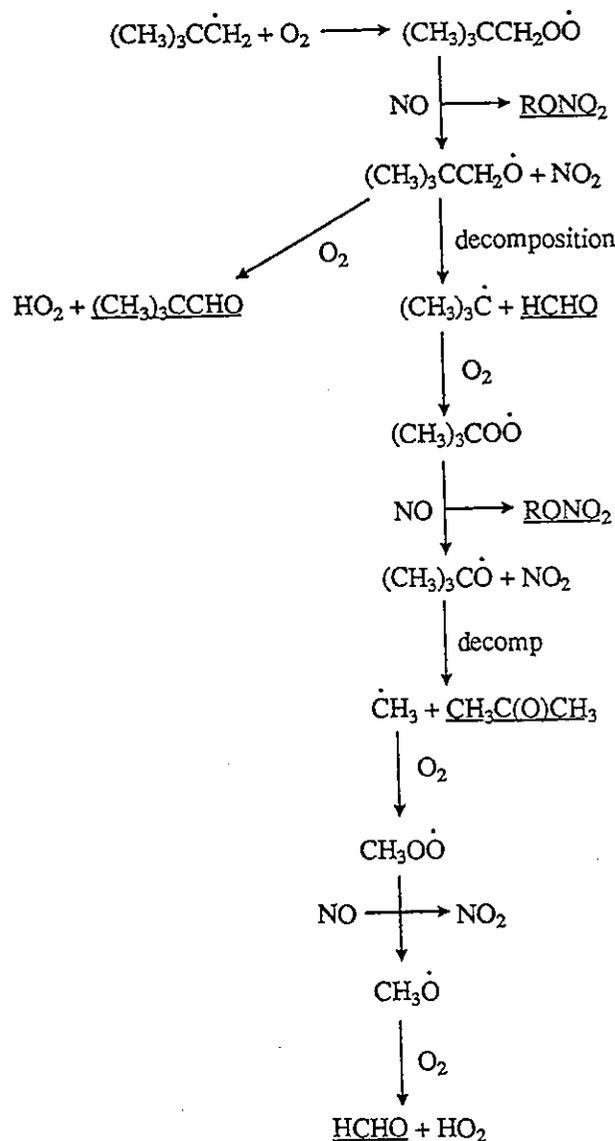
The  $\alpha$ -hydroxy radicals expected to be formed subsequent to the initial isomerization reaction, such as the  $\text{HOCH}_2\text{CH}_2\text{CH}_2\dot{\text{C}}\text{HOH}$  radical formed from the 1-butoxy

radical isomerization, are expected (see Refs 1, 2 and 9 and Sec. 2.2) to react with solely  $\text{O}_2$  under tropospheric conditions to form the  $\text{HO}_2$  radical and the carbonyl.

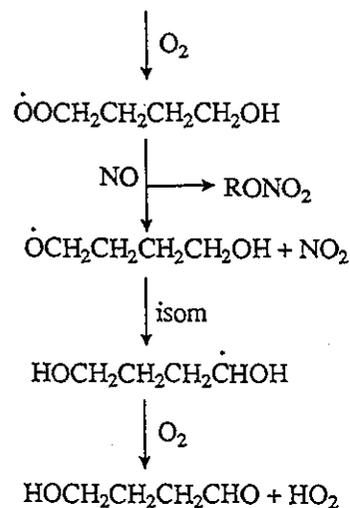


These  $\alpha$ -hydroxy radical reactions are discussed in Sec. 2.2.

The further reactions of the "first-generation" products arising from the above reactions are discussed in Secs. 2.5 (carbonyls, hydroperoxides and alcohols) and 2.6 (alkyl peroxy nitrates, alkyl nitrates and nitrites) below.



Reaction Scheme (3)



Reaction Scheme (4)

## References

- <sup>1</sup>W. P. L. Carter and R. Atkinson, *J. Atmos. Chem.* **3**, 377 (1985).
- <sup>2</sup>R. Atkinson, *Atmos. Environ.* **24A**, 1 (1990).
- <sup>3</sup>R. Atkinson, *J. Phys. Chem. Ref. Data Monograph* **1**, 1 (1989).
- <sup>4</sup>R. Atkinson, *J. Phys. Chem. Ref. Data* **20**, 459 (1991).
- <sup>5</sup>R. Atkinson and W. P. L. Carter, *Chem. Rev.* **84**, 437 (1984).
- <sup>6</sup>R. Atkinson, *Int. J. Chem. Kinet.* **19**, 799 (1987).
- <sup>7</sup>R. Atkinson and S. M. Aschmann, *Int. J. Chem. Kinet.* **20**, 339 (1988).
- <sup>8</sup>R. Atkinson and S. M. Aschmann, *Int. J. Chem. Kinet.* **24**, 983 (1992).
- <sup>9</sup>R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, and J. Troe, *J. Phys. Chem. Ref. Data* **21**, 1125 (1992).
- <sup>10</sup>T. M. Lenhardt, C. E. McDade, and K. D. Bayes, *J. Chem. Phys.* **72**, 304 (1980).
- <sup>11</sup>D. Wu and K. D. Bayes, *Int. J. Chem. Kinet.* **18**, 547 (1986).
- <sup>12</sup>Z. Xi, W. -J. Han, and K. D. Bayes, *J. Phys. Chem.* **92**, 3450 (1988).
- <sup>13</sup>A. F. Wagner, I. R. Slagle, D. Sarzynski, and D. Gutman, *J. Phys. Chem.* **94**, 1853 (1990).
- <sup>14</sup>J. A. Logan, M. J. Prather, S. C. Wofsy, and M. B. McElroy, *J. Geophys. Res.* **86**, 7210 (1981).
- <sup>15</sup>J. A. Logan, *J. Geophys. Res.* **88**, 10785 (1983).
- <sup>16</sup>W. B. DeMore, S. P. Sander, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, A. R. Ravishankara, C. E. Kolb, and M. J. Molina, "Chemical Kinetics and Photochemical Data for use in Stratospheric Modeling," NASA Panel for Data Evaluation, Evaluation No. 10, Jet Propulsion Laboratory, CA, Publication 92-20, August 15, 1992.
- <sup>17</sup>J. Peeters, J. Vertommen, and I. Langhans, *Ber. Bunsenges. Phys. Chem.* **96**, 431 (1992).
- <sup>18</sup>C. Anastasi, I. W. M. Smith, and D. A. Parkes, *J. Chem. Soc., Faraday Trans. 1*, **74**, 1693 (1978).
- <sup>19</sup>I. C. Plumb, K. R. Ryan, J. R. Steven, and M. F. R. Mulcahy, *Int. J. Chem. Kinet.* **14**, 183 (1982).
- <sup>20</sup>A. R. Ravishankara, F. L. Eisele, N. M. Kreutter, and P. H. Wine, *J. Chem. Phys.* **74**, 2267 (1981).
- <sup>21</sup>R. Zellner, B. Fritz, and K. Lorenz, *J. Atmos. Chem.* **4**, 241 (1986).
- <sup>22</sup>K. R. Darnall, W. P. L. Carter, A. M. Winer, A. C. Lloyd, and J. N. Pitts, Jr., *J. Phys. Chem.* **80**, 1948 (1976).
- <sup>23</sup>H. Takagi, N. Washida, H. Bandow, H. Akimoto, and M. Okuda, *J. Phys. Chem.* **85**, 2701 (1981).
- <sup>24</sup>R. Atkinson, S. M. Aschmann, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., *J. Phys. Chem.* **86**, 4563 (1982).
- <sup>25</sup>R. Atkinson, W. P. L. Carter, and A. M. Winer, *J. Phys. Chem.* **87**, 2012 (1983).
- <sup>26</sup>R. Atkinson, S. M. Aschmann, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., *Int. J. Chem. Kinet.* **16**, 1085 (1984).
- <sup>27</sup>R. Atkinson, S. M. Aschmann, and A. M. Winer, *J. Atmos. Chem.* **5**, 91 (1987).
- <sup>28</sup>S. J. Harris and J. A. Kerr, *Int. J. Chem. Kinet.* **21**, 207 (1989).
- <sup>29</sup>W. P. L. Carter and R. Atkinson, *J. Atmos. Chem.* **8**, 165 (1989).
- <sup>30</sup>I. Bridier, R. Lesclaux, and B. Veyret, *Chem. Phys. Lett.* **191**, 259 (1992).
- <sup>31</sup>H. Adachi and N. Basco, *Int. J. Chem. Kinet.* **14**, 1243 (1982).
- <sup>32</sup>H. Adachi and N. Basco, *Chem. Phys. Lett.* **67**, 324 (1979).
- <sup>33</sup>F. Zabel, A. Reimer, K. H. Becker, and E. H. Fink, *J. Phys. Chem.* **93**, 5500 (1989).
- <sup>34</sup>D. M. Rowley, R. Lesclaux, P. D. Lightfoot, B. Nozière, T. J. Wallington, and M. D. Hurley, *J. Phys. Chem.* **96**, 4889 (1992).
- <sup>35</sup>T. J. Wallington and S. M. Japar, *Chem. Phys. Lett.* **166**, 495 (1990).
- <sup>36</sup>T. J. Wallington and S. M. Japar, *Chem. Phys. Lett.* **167**, 513 (1990).
- <sup>37</sup>T. J. Wallington, *J. Chem. Soc. Faraday Trans. 87*, 2379 (1991).
- <sup>38</sup>T. J. Wallington, P. Dagaut, and M. J. Kurylo, *Chem. Rev.* **92**, 667 (1992).
- <sup>39</sup>P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, *Atmos. Environ.* **26A**, 1805 (1992).
- <sup>40</sup>C. S. Kan, J. G. Calvert, and J. H. Shaw, *J. Phys. Chem.* **84**, 3411 (1980).
- <sup>41</sup>H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, *J. Phys. Chem.* **85**, 877 (1981).
- <sup>42</sup>O. Horie, J. N. Crowley, and G. K. Moortgat, *J. Phys. Chem.* **94**, 8198 (1990).
- <sup>43</sup>H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, *J. Phys. Chem.* **86**, 3825 (1982).
- <sup>44</sup>T. J. Wallington, C. A. Gierczak, J. C. Ball, and S. M. Japar, *Int. J. Chem. Kinet.* **21**, 1077 (1989).
- <sup>45</sup>D. A. Osborne and D. J. Waddington, *J. Chem. Soc. Perkin Trans. 2*, 1861 (1984).
- <sup>46</sup>P. D. Lightfoot, P. Roussel, B. Veyret, and R. Lesclaux, *J. Chem. Soc. Faraday Trans. 86*, 2927 (1990).
- <sup>47</sup>D. M. Rowley, P. D. Lightfoot, R. Lesclaux, and T. J. Wallington, *J. Chem. Soc. Faraday Trans. 87*, 3221 (1991).
- <sup>48</sup>L. J. Kirsch, D. A. Parkes, D. J. Waddington, and A. Woolley, *J. Chem. Soc. Faraday Trans. 1*, **74**, 2293 (1978).
- <sup>49</sup>T. J. Wallington, J. M. Andino, A. R. Potts, and O. J. Nielsen, *Int. J. Chem. Kinet.* **24**, 649 (1992).
- <sup>50</sup>C. S. Kan and J. G. Calvert, *Chem. Phys. Lett.* **63**, 111 (1979).
- <sup>51</sup>M. J. Kurylo, P. Dagaut, T. J. Wallington, and D. M. Neuman, *Chem. Phys. Lett.* **139**, 513 (1987).
- <sup>52</sup>D. A. Parkes, 15th International Symposium on Combustion, 1974; The Combustion Institute, Pittsburgh, PA, 1975; pp. 795-805.
- <sup>53</sup>M. C. Addison, J. P. Burrows, R. A. Cox, and R. Patrick, *Chem. Phys. Lett.* **73**, 283 (1980).
- <sup>54</sup>G. K. Moortgat, B. Veyret, and R. Lesclaux, *J. Phys. Chem.* **93**, 2362 (1989).
- <sup>55</sup>L. J. Garland and K. D. Bayes, *J. Phys. Chem.* **94**, 4941 (1990).
- <sup>56</sup>R. Atkinson and W. P. L. Carter, *J. Atmos. Chem.* **13**, 195 (1991).
- <sup>57</sup>N. Sanders, J. E. Butler, L. R. Pasternack, and J. R. McDonald, *Chem. Phys.* **48**, 203 (1980).
- <sup>58</sup>D. Gutman, N. Sanders, and J. E. Butler, *J. Phys. Chem.* **86**, 66 (1982).
- <sup>59</sup>K. Lorenz, D. Rhäsa, R. Zellner, and B. Fritz, *Ber. Bunsenges. Phys. Chem.* **89**, 341 (1985).
- <sup>60</sup>P. J. Wantuck, R. C. Oldenborg, S. L. Baughcum, and K. R. Winn, *J. Phys. Chem.* **91**, 4653 (1987).
- <sup>61</sup>D. Hartmann, J. Karthäuser, J. P. Sawerysyn, and R. Zellner, *Ber. Bunsenges. Phys. Chem.* **94**, 639 (1990).
- <sup>62</sup>R. J. Balla, H. H. Nelson, and J. R. McDonald, *Chem. Phys.* **99**, 323 (1985).
- <sup>63</sup>A. C. Baldwin, J. R. Barker, D. M. Golden, and D. G. Hendry, *J. Phys. Chem.* **81**, 2483 (1977).
- <sup>64</sup>D. M. Golden, "Organic Free Radicals" in "Chemical Kinetic Data Needs for Modeling the Lower Troposphere," NBS Special Publication 557, August 1979, pp. 51-61.
- <sup>65</sup>L. Batt, Proc. 1st European Symposium on the Physico-Chemical Behaviour of Atmospheric Pollutants, Comm. of European Communities, 1980, pp. 167-184.
- <sup>66</sup>L. Batt, *Int. J. Chem. Kinet.* **11**, 977 (1979).
- <sup>67</sup>K. Y. Choo and S. W. Benson, *Int. J. Chem. Kinet.* **13**, 833 (1981).
- <sup>68</sup>L. Batt, *Int. Rev. Phys. Chem.* **6**, 53 (1987).
- <sup>69</sup>J. A. Seetula, J. J. Russell, and D. Gutman, *J. Am. Chem. Soc.* **112**, 1347 (1990).
- <sup>70</sup>P. D. Richards, R. J. Ryther, and E. Weitz, *J. Phys. Chem.* **94**, 3663 (1990).
- <sup>71</sup>P. W. Seakins and M. J. Pilling, *J. Phys. Chem.* **95**, 9874 (1991).
- <sup>72</sup>J. M. Nicovich, C. A. van Dijk, K. D. Kreutter, and P. H. Wine, *J. Phys. Chem.* **95**, 9890 (1991).
- <sup>73</sup>R. M. Drew, J. A. Kerr, and J. Olive, *Int. J. Chem. Kinet.* **17**, 167 (1985).
- <sup>74</sup>L. Batt, M. W. M. Hisham, and M. MacKay, *Int. J. Chem. Kinet.* **21**, 535 (1989).
- <sup>75</sup>L. Batt and G. N. Robinson, *Int. J. Chem. Kinet.* **14**, 1053 (1982).
- <sup>76</sup>L. Batt and G. N. Robinson, *Int. J. Chem. Kinet.* **19**, 391 (1987).
- <sup>77</sup>N. Y. Al Akeel and D. J. Waddington, *J. Chem. Soc. Perkin Trans. 2*, 1575 (1984).
- <sup>78</sup>W. P. L. Carter, K. R. Darnall, A. C. Lloyd, A. M. Winer, and J. N. Pitts, Jr., *Chem. Phys. Lett.* **42**, 22 (1976); W. P. L. Carter, unpublished data (1976).
- <sup>79</sup>W. P. L. Carter, A. C. Lloyd, J. L. Sprung, and J. N. Pitts, Jr., *Int. J. Chem. Kinet.* **11**, 45 (1979).

- <sup>80</sup>R. A. Cox, K. F. Patrick, and S. A. Chant, *Environ. Sci. Technol.* **15**, 587 (1981).
- <sup>81</sup>H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, *J. Phys. Chem.* **85**, 2698 (1981).
- <sup>82</sup>S. Dóbbé, T. Bérces, and F. Márta, *Int. J. Chem. Kinet.* **18**, 329 (1986).
- <sup>83</sup>R. Atkinson, S. M. Aschmann, J. Arey, and B. Shorees, *J. Geophys. Res.* **97**, 6065 (1992).
- <sup>84</sup>M. J. Frost and I. W. M. Smith, *J. Chem. Soc. Faraday Trans.* **86**, 1757 (1990).
- <sup>85</sup>J. A. McCaulley, A. M. Moyle, M. F. Golde, S. M. Anderson, and F. Kaufman, *J. Chem. Soc. Faraday Trans.* **86**, 4001 (1990).
- <sup>86</sup>I. W. M. Smith, *J. Chem. Soc. Faraday Trans.* **87**, 2271 (1991).
- <sup>87</sup>A. Miyoshi, H. Matsui, and N. Washida, *Chem. Phys. Lett.* **160**, 291 (1989).
- <sup>88</sup>A. Miyoshi, H. Matsui, and N. Washida, *J. Phys. Chem.* **94**, 3016 (1990).

## 2.2. Alkenes

As discussed previously,<sup>1,2</sup> the major tropospheric loss processes of the alkenes are by reaction with OH and NO<sub>3</sub> radicals and O<sub>3</sub>. The conjugated dienes also react with NO<sub>2</sub>, and this reaction can be important in environmental chamber experiments carried out at NO<sub>2</sub> concentrations significantly higher than ambient (see, for example, Refs. 3 and 4), as can the reactions of alkenes with O(<sup>3</sup>P) atoms.<sup>4</sup>

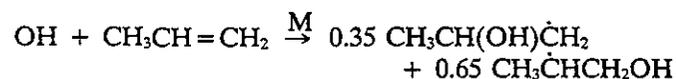
### OH Radical Reactions

The kinetics and mechanisms of the reactions of the OH radical with the alkenes, cycloalkenes and dienes have been reviewed and evaluated by Atkinson,<sup>5</sup> and that review and evaluation is updated in Sec. 3.3. For ethene and the methyl-substituted ethenes (propene, 2-methylpropene, the 2-butenes, 2-methyl-2-butene and 2,3-dimethyl-2-butene), the OH radical reactions proceed essentially totally by OH radical addition to the carbon-carbon double bond at atmospheric pressure, with H-atom abstraction from the -CH<sub>3</sub> substituent groups accounting for <5% of the total reaction at room temperature.<sup>5</sup> For 1-butene, the product data of Hoyermann and Sievert<sup>6</sup> and Atkinson *et al.*<sup>7</sup> show that H-atom abstraction accounts for <10% of the overall reaction at room temperature. To date, only for 1,3- and 1,4-cyclohexadiene has H-atom abstraction been shown to occur to any significant extent,<sup>8</sup> with this process accounting for ~9% and ~15% of the overall OH radical reactions with 1,3- and 1,4-cyclohexadiene, respectively, at room temperature. However, for the alkenes with alkyl side chains a small amount of H-atom abstraction must occur with, for example, this pathway being calculated to account for 10–15% of the overall OH radical reaction for 1-heptene at 298 K.<sup>9</sup>

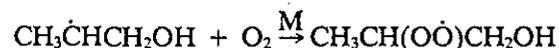
The rate constants, *k*, at 298 K and the temperature-dependent parameters (with  $k = Ae^{-B/T}$ ) at 760 Torr total pressure of air and for temperatures ≤425 K for a number of monoalkenes, dienes, cycloalkenes and monoterpenes are given in Table 12. For all but ethene and propene (and propadiene<sup>5</sup>), these rate constants can be considered to be the high-pressure limits which, for

the ≥C<sub>4</sub> alkenes, are essentially attained at total pressures of ≥50 Torr of air.<sup>5</sup> For ethene and propene, the Troe fall-off parameters *k<sub>0</sub>*, *k<sub>∞</sub>* and *F* derived by Atkinson<sup>5</sup> and in Sec. 3.3 are (*M* = air): ethene, *k<sub>0</sub>* = 6 × 10<sup>-29</sup> (T/298)<sup>-4</sup> cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup>, *k<sub>∞</sub>* = 9.0 × 10<sup>-12</sup> (T/298)<sup>-1.1</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and *F* = 0.70 at 298 K; propene, *k<sub>0</sub>* = 3 × 10<sup>-27</sup> (T/298)<sup>-3</sup> cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup>, *k<sub>∞</sub>* = 2.8 × 10<sup>-11</sup> (T/298)<sup>-1.3</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and *F* = 0.5 at 298 K.

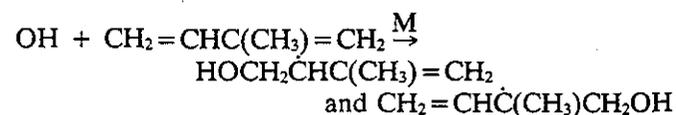
As discussed above, OH radical addition to the >C=C< bond(s) is the dominant reaction pathway. For monoalkenes, dienes or trienes with non-conjugated >C=C< bonds, the OH radical can add to either end of the double bond(s), and Cvetanovic<sup>10</sup> reported that for propene addition to the terminal carbon occurs ~65% of the time, as expected on thermochemical grounds<sup>11</sup>



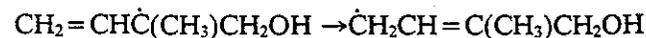
The resulting β-hydroxyalkyl radicals then react rapidly with O<sub>2</sub>, with the measured room temperature rate constants being in the range (3–30) × 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (Table 13). Under atmospheric conditions, the sole reaction of the β-hydroxyalkyl radicals is then with O<sub>2</sub>. For example,



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



These initially formed β-hydroxy allylic radicals may isomerize to δ-hydroxy allylic radicals.<sup>4</sup>



By analogy with the allyl (C<sub>3</sub>H<sub>5</sub>) radical, for which Morgan *et al.*<sup>15</sup> have measured a rate constant for combination with O<sub>2</sub> of ~4 × 10<sup>-13</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 380 K and a total pressure of 50 Torr of Ar diluent, these various hydroxy-substituted allyl-type radicals are expected to react solely with O<sub>2</sub> under tropospheric conditions

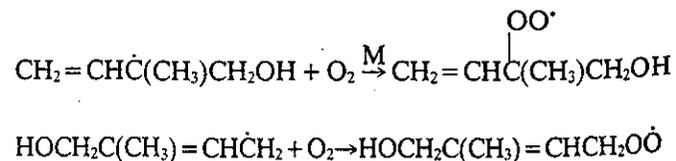


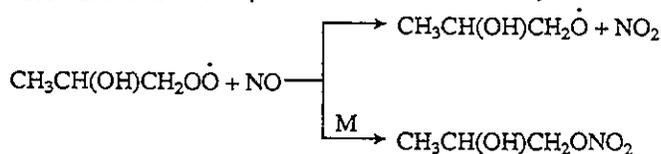
TABLE 12. Rate constants  $k$  at 298 K and 760 Torr total pressure of air and Arrhenius parameters ( $k = Ae^{-B/T}$ ;  $T \leq 425$  K) for the reaction of OH radicals with alkenes at 760 Torr total pressure of air\* [from Ref. 5 and Sec. 3.3.]

Alkene	$10^{12} \times k(298 \text{ K})$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	$10^{12} \times A$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	$B$ (K)
Ethene <sup>b</sup>	8.52	1.96	-438
Propene <sup>c</sup>	26.3	4.85	-504
1-Butene	31.4	6.55	-467
<i>cis</i> -2-Butene	56.4	11.0	-487
<i>trans</i> -2-Butene	64.0	10.1	-550
2-Methylpropene	51.4	9.47	-504
1-Pentene	31.4	5.86 <sup>d</sup>	-500 <sup>d</sup>
<i>cis</i> -2-Pentene	65		
<i>trans</i> -2-Pentene	67		
3-Methyl-1-butene	31.8	5.32	-533
2-Methyl-1-butene	61		
2-Methyl-2-butene	86.9	19.2	-450
1-Hexene	37		
2-Methyl-1-pentene	63		
2-Methyl-2-pentene	89		
<i>trans</i> -4-Methyl-2-pentene	61		
2,3-Dimethyl-2-butene	110		
3,3-Dimethyl-1-butene	28		
1-Heptene	40		
<i>trans</i> -2-Heptene	68		
2,3-Dimethyl-2-pentene	98		
<i>trans</i> -4,4-Dimethyl-2-pentene	55		
<i>trans</i> -4-Octene	69		
1,3-Butadiene	66.6	14.8	-448
2-Methyl-1,3-butadiene	101	25.4	-410
Myrcene	215		
Ocimene ( <i>cis</i> - and <i>trans</i> -)	252		
Cyclopentene	67		
Cyclohexene	67.7		
Cycloheptene	74		
1-Methylcyclohexene	94		
Camphene	53		
2-Carene	80		
3-Carene	88		
Limonene	171		
$\alpha$ -Phellandrene	313		
$\beta$ -Phellandrene	168		
$\alpha$ -Pinene	53.7	12.1	-444
$\beta$ -Pinene	78.9	23.8	-357
Sabinene	117		
$\alpha$ -Terpinene	363		
$\gamma$ -Terpinene	177		
Terpinolene	225		

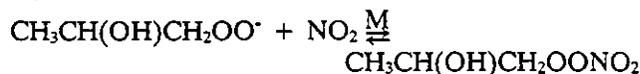
\*Except for ethene and propene, these are essentially the high-pressure rate constants  $k_{\infty}$ .<sup>b</sup> $k_{\infty} = 9.0 \times 10^{-12} (T/298)^{-1.1} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .<sup>c</sup> $k_{\infty} = 2.8 \times 10^{-11} (T/298)^{-1.3} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .<sup>d</sup>Estimated<sup>5</sup>TABLE 13. Rate constants for the gas-phase reactions of  $\beta$ -hydroxyalkyl radicals with  $\text{O}_2$ 

R <sup>•</sup>	$10^{12} \times k$ ( $\text{cm}^3$ $\text{molecule}^{-1} \text{ s}^{-1}$ )	at $T$ (K)	Reference
$\text{HOCH}_2\dot{\text{C}}\text{H}_2$	$3.0 \pm 0.4$	$293 \pm 3$	Miyoshi <i>et al.</i> <sup>12</sup>
$\text{CH}_3\dot{\text{C}}\text{HCH}_2\text{OH}$	$11.6 \pm 2.2$	$296 \pm 4$	Miyoshi <i>et al.</i> <sup>13</sup>
$\text{CH}_3\text{CH}(\text{OH})\dot{\text{C}}\text{H}_2$	$3.82 \pm 0.60$	$296 \pm 4$	Miyoshi <i>et al.</i> <sup>13</sup>
$\text{CH}_3\text{CH}(\text{OH})\dot{\text{C}}\text{HCH}_3$	$28 \pm 18$	300	Lenhardt <i>et al.</i> <sup>14</sup>

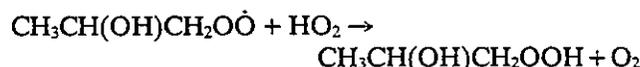
To date, few direct experimental data are available concerning the atmospherically important reactions of these  $\beta$ (or  $\delta$ -)hydroxyalkyl peroxy radicals. As for the alkyl peroxy radicals formed from the alkanes (Sec. 2.1.) these radicals are expected to react with NO,



$\text{NO}_2$  (to form thermally unstable peroxy nitrates),



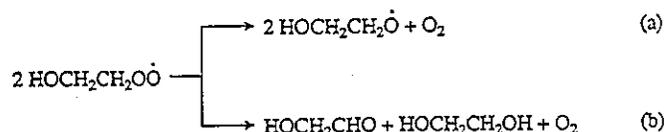
$\text{HO}_2$  radicals,



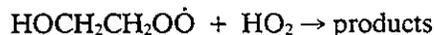
and organic peroxy radicals



In fact, to date the only kinetic data concern the self-reaction of the  $\text{HOCH}_2\text{CH}_2\text{OO}\cdot$  radical<sup>16-18</sup> and its reactions with  $\text{HO}_2$  radicals<sup>16-18</sup> and  $\text{NO}$ .<sup>19,20</sup> Based on the data of Jenkin and Cox,<sup>16</sup> Anastasi *et al.*<sup>17</sup> and Murrells *et al.*,<sup>18</sup> the IUPAC panel recommended<sup>21</sup> for the reactions

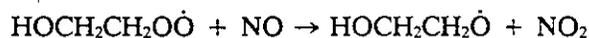


that  $(k_a + k_b) = 2.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k_a/(k_a + k_b) = 0.36 \pm 0.1$  at 298 K, and that the rate constant for the reaction of  $\text{HO}_2$  radicals with the  $\text{HOCH}_2\text{CH}_2\text{OO}\cdot$  radical



is  $k(\text{HO}_2 + \text{HOCH}_2\text{CH}_2\text{OO}\cdot) = 1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.<sup>21</sup> The  $\text{HOCH}_2\text{CH}_2\text{OO}\cdot$  radical self-reaction rate constant is a factor of  $\sim 10$  higher than that recommended for primary alkylperoxy radicals formed from the alkanes (Sec. 2.1. above). The rate constant for the reaction of the  $\text{HOCH}_2\text{CH}_2\text{OO}\cdot$  radical with the  $\text{HO}_2$  radical is identical to that recommended for alkylperoxy radicals in Sec. 2.1.

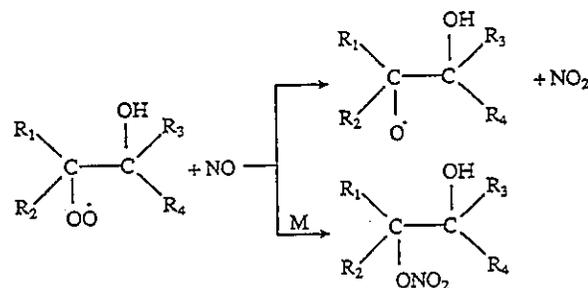
No data are available for the reactions of the  $\beta$ -hydroxyalkylperoxy radicals with  $\text{NO}_2$ , but an indirect estimate for the rate constant for the reaction of the  $\text{HOCH}_2\text{CH}_2\text{OO}\cdot$  radical (formed after OH radical addition to ethene) with NO



of  $(9.0 \pm 4.0) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at  $298 \pm 2 \text{ K}$  has been derived by Becker *et al.*<sup>20</sup> (which supersedes the

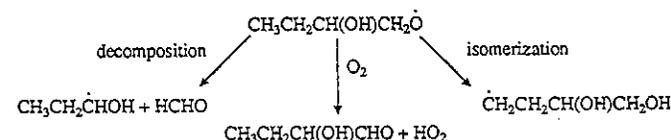
earlier study of Schmidt *et al.*<sup>19</sup>). This rate constant for reaction of NO with a  $\beta$ -hydroxyalkyl peroxy radical is essentially identical to the recommendation for the rate constants for the reactions of NO with the  $\geq \text{C}_2$  alkyl peroxy radicals formed from the alkanes (Sec. 2.1.), implying that these alkylperoxy radical rate constants are also applicable to the  $\beta$ -hydroxyalkyl peroxy radicals.

In the presence of NO, the  $\beta$ -hydroxyalkyl peroxy radicals are therefore expected to form  $\text{NO}_2$  plus the corresponding  $\beta$ -hydroxyalkoxy radical, with a small amount of  $\beta$ -hydroxyalkyl nitrate also being formed.<sup>22</sup>



At atmospheric pressure and room temperature, Shepson *et al.*<sup>22</sup> determined formation yields of  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{ONO}_2$  and  $\text{CH}_3\text{CH}(\text{ONO}_2)\text{CH}_2\text{OH}$  from propene of  $\sim 0.016 \pm 0.008$  for each nitrate.

The  $\beta$ -hydroxyalkoxy radicals can then decompose, react with  $\text{O}_2$  or isomerize, as discussed in Sec. 2.1. above. Thus, for the alkoxy radical formed after internal addition of the OH radical to 1-butene:



The experimental data for the simple alkenes (ethene, propene, 1-butene, and the 2-butenes) show that at room temperature and atmospheric pressure, decomposition dominates over reaction with  $\text{O}_2$ .<sup>7,23,24</sup> Indeed, the available data show that for the  $\beta$ -hydroxyalkoxy radicals formed from the  $\geq \text{C}_3$  alkenes, the reaction with  $\text{O}_2$  is negligible and only the products arising from decomposition of the  $\beta$ -hydroxyalkoxy radicals are observed at room temperature and atmospheric pressure.<sup>7,23</sup> For ethene, Niki *et al.*<sup>24</sup> showed that both reaction with  $\text{O}_2$  and decomposition of the  $\text{HOCH}_2\text{CH}_2\text{O}\cdot$  radical occurs

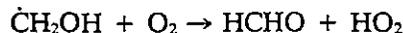


with  $k_b/k_a = (5.4 \pm 1.0) \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1}$  at 298 K and 700 Torr total pressure of air.<sup>24</sup> For the  $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{O}\cdot$  radical formed from 1-butene, the experimental data of Atkinson *et al.*<sup>7</sup> show that isomerization is not important, in accord with the estimates arising from the discussion in Sec. 2.1.

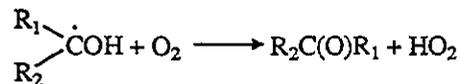
Hence, apart from ethene, for which reaction of the  $\text{HOCH}_2\text{CH}_2\text{O}\cdot$  radical with  $\text{O}_2$  and decomposition are competitive at 298 K and atmospheric pressure, the

$\beta$ -hydroxyalkoxy radicals formed subsequent to OH radical reactions with the simpler monoalkenes (propene and the butenes) undergo decomposition, and the estimation method proposed in Sec. 2.1. allows the relative importance of reaction with  $O_2$ , decomposition and isomerization to be assessed.

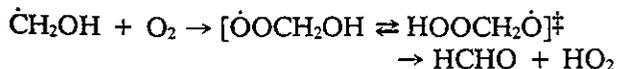
The  $\alpha$ -hydroxy radicals formed from the decomposition reactions of the  $\beta$ -hydroxyalkoxy radicals react rapidly with  $O_2$ , with rate constants at room temperature of  $\sim(0.9-4) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Table 14). Under atmospheric conditions, these reactions with  $O_2$  will then be the sole loss process for the  $\alpha$ -hydroxy radicals. The simplest  $\alpha$ -hydroxy radical,  $\dot{C}H_2OH$ , reacts with  $O_2$  to form the  $HO_2$  radical and  $HCHO$ ,<sup>25-28</sup>



and product studies have shown that the higher ( $C_2-C_4$ )  $\alpha$ -hydroxy radicals also react via H-atom abstraction to yield the corresponding carbonyls<sup>29-32</sup>



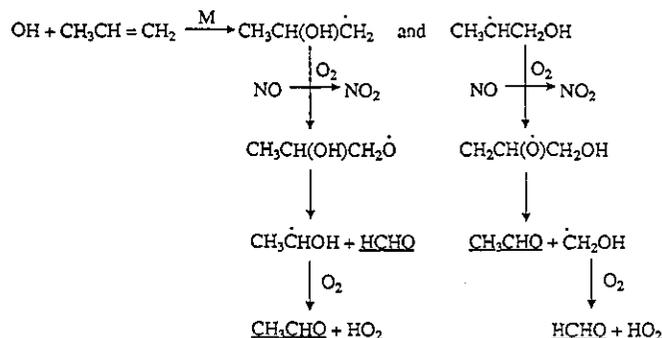
Grotheer *et al.*<sup>32,33</sup> and Nesbitt *et al.*<sup>34</sup> have studied the temperature dependence of the rate constant for the reaction of the  $\dot{C}H_2OH$  radical with  $O_2$ . These studies<sup>32-34</sup> show that the rate constant decreases below room temperature<sup>34</sup> and also decreases slightly above room temperature, and then increases more rapidly with increasing temperature, exhibiting a minimum at  $\sim 450 \text{ K}$ <sup>32,33</sup> (see also Ref. 2). A similar slight decrease in the rate constant for the  $CH_3\dot{C}HOH + O_2$  reaction with increasing temperature over the range 300-474 K was observed by Grotheer *et al.*,<sup>32</sup> with the rate constant then increasing at higher temperatures (474-682 K).<sup>32</sup> The lack of a deuterium isotope effect on the room temperature rate constant for the reactions of the  $\dot{C}H_2OH$  and  $\dot{C}H_2OD$  radicals with  $O_2$ <sup>33,35</sup> and the temperature dependence of the rate constant shows that this reaction proceeds by initial  $O_2$  addition,



with the initially formed energy-rich  $HOCH_2O\dot{O}$  radical isomerizing via a five-membered transition state to the

$HOOCH_2\dot{O}$  radical with subsequent decomposition. Similar reaction mechanisms are expected to occur for the  $\geq C_2$   $\alpha$ -hydroxy radicals.

For propene, the OH radical-initiated reaction scheme, in the presence of  $NO$ , is then ("stable" products are underlined and the minor amount of nitrate formation<sup>22</sup> is neglected for clarity)



and similarly for ethene and the butenes (1-butene, *cis*- and *trans*-2-butene and 2-methylpropene).

However, such reaction schemes involving dominant  $\beta$ -hydroxyalkoxy radical decomposition may not apply to the higher alkenes such as the  $\geq C_3$  1-alkenes. Thus, Paulson and Seinfeld<sup>36</sup> have obtained a yield of heptanal ( $CH_3(CH_2)_5CHO$ ) from the OH radical reaction with 1-octene in the presence of  $NO_x$  of  $15 \pm 5\%$ , much lower than the  $\sim 80-85\%$  expected if the  $\beta$ -hydroxyalkoxy radicals undergo only decomposition (the remaining 15-20% of the overall reaction is predicted to proceed by initial H-atom abstraction from the  $-CH_2-$  groups,<sup>9</sup> leading to the formation of products other than heptanal). This observation suggests that other reaction channels are operative for the more complex  $\beta$ -hydroxyalkoxy radicals, possibly including isomerization as predicted from the discussion in Sec. 2.1. Indeed, for the OH radical reaction with 1-pentene the estimation method proposed in Sec. 2.1. predicts that the  $CH_3CH_2CH_2CH(OH)CH_2\dot{O}$  radical will undergo mainly isomerization, while the  $CH_3CH_2CH_2CH(O\cdot)CH_2OH$  radical (that formed preferentially from the initial OH radical addition) will undergo decomposition. For the  $\geq C_6$  1-alkenes, both of the  $\beta$ -hydroxyalkoxy radicals formed are predicted to react mainly by isomerization, reasonably consistent with the data for 1-octene.<sup>36</sup>

TABLE 14. Room temperature rate constants  $k$  for the reactions of  $\alpha$ -hydroxy radicals with  $O_2$

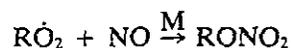
$\alpha$ -Hydroxy radical	$10^{12} \times k$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	at $T$ (K)	Reference
$\dot{C}H_2OH$	9.4	298	Atkinson <i>et al.</i> <sup>21</sup>
$CH_3\dot{C}HOH$	19	298	Atkinson <i>et al.</i> <sup>21</sup>
$CH_3CH_2\dot{C}HOH$	$26.1 \pm 4.1$	$296 \pm 4$	Miyoshi <i>et al.</i> <sup>13</sup>
$CH_3\dot{C}(OH)CH_3$	$37.1 \pm 6.2$	$296 \pm 4$	Miyoshi <i>et al.</i> <sup>13</sup>

Similar reaction schemes are expected to apply to the conjugated dienes. For example, for isoprene (2-methyl-1,3-butadiene) the simple reaction sequence, with no isomerization of the initially formed  $\beta$ -hydroxy allylic radicals and with decomposition of the  $\beta$ -hydroxyperoxy radicals, is expected to lead<sup>37</sup> to the formation of methyl vinyl ketone plus HCHO (OH radical addition to the  $\text{CH}_2=\text{C}(\text{CH}_3)-$  bond) and methacrolein plus HCHO (OH radical addition to the  $\text{CH}_2=\text{CH}-$  bond). For example, Reaction Scheme (5) shows the reaction sequence for terminal OH radical addition (the "stable" first-generation products are underlined), with organic nitrate formation from the  $\text{RO}_2 + \text{NO}$  reaction being omitted for clarity. As shown above for the propene reaction, the same ultimate products are formed from internal OH radical addition with subsequent decomposition of the  $\beta$ -hydroxyalkoxy radicals. However, for unsymmetrical dienes the expected products formed depend on which  $>\text{C}=\text{C}<$  bond OH addition occurs. For conjugated dienes, the estimation technique of Ohta<sup>38</sup> allows the fraction of the overall OH radical addition reaction proceeding at each  $>\text{C}=\text{C}<$  double bond to be calculated (this information cannot be obtained from the estimation technique of Atkinson<sup>9,39</sup>). Thus for isoprene, rate constants for OH radical addition to the  $\text{CH}_2=\text{CH}-$  and  $\text{CH}_2=\text{C}<$  bonds of isoprene are calculated<sup>38</sup> to be in the ratio 34/66 at room temperature.

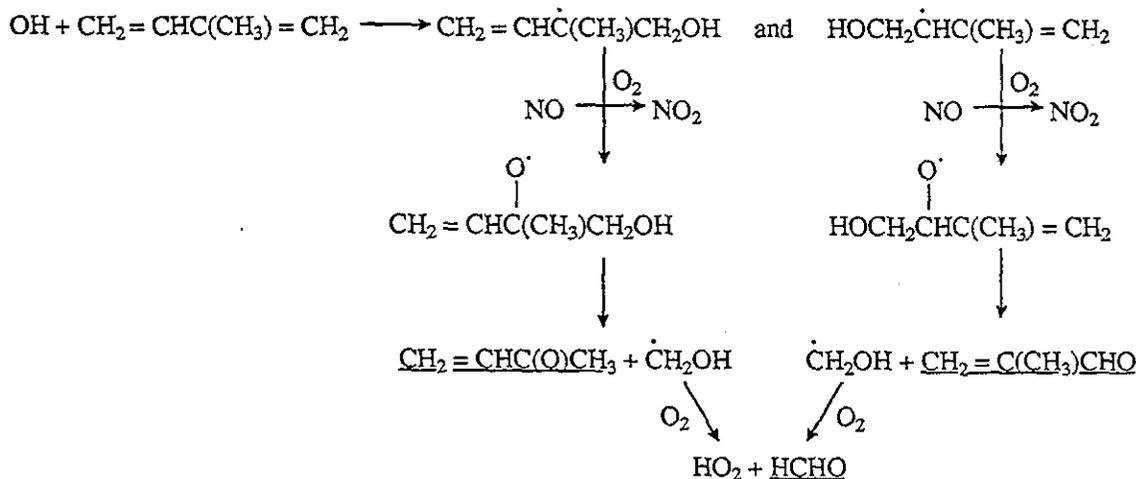
For the OH radical-initiated reaction of 1,3-butadiene at  $298 \pm 2$  K, Maldotti *et al.*<sup>40</sup> observed the formation of acrolein (the expected product, together with HCHO, based on the above reaction scheme) from irradiated  $\text{NO}_x$ -1,3-butadiene-air mixtures, with  $[\text{acrolein}]_{\text{max}}/[\text{1,3-butadiene}]_{\text{initial}} = 0.59 \pm 0.07$ . Based on the rate constants for the OH radical reactions with acrolein and 1,3-butadiene,<sup>5</sup> this ratio corresponds to a formation yield of acrolein from the OH radical-initiated reaction of 1,3-butadiene of  $0.98 \pm 0.12$ . Additionally, furan is formed in minor amount from the OH radical-initiated reaction of

1,3-butadiene, with a yield of  $0.039 \pm 0.011$ .<sup>41</sup>

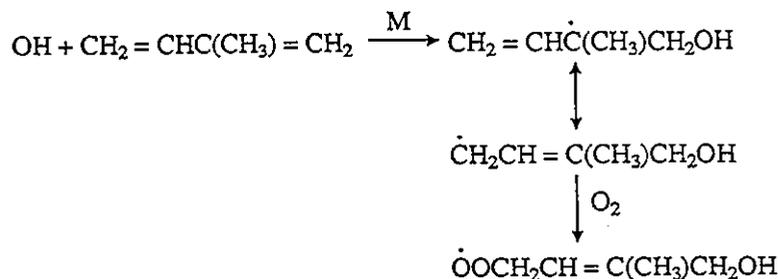
However, two recent studies of the products formed from the gas-phase reaction of the OH radical with isoprene<sup>3,4</sup> show that methyl vinyl ketone and methacrolein (together with their expected HCHO co-product) do not account for the entire reaction pathways. In the Fourier transform infrared absorption spectroscopy study of Tuazon and Atkinson,<sup>3</sup> the reaction of isoprene with the  $\text{O}(^3\text{P})$  atom formed from photolysis of  $\text{NO}_2$  was not taken into account. This reaction is calculated to contribute  $\sim 10$ – $15\%$  of the overall isoprene reacted, and the product yields of Tuazon and Atkinson<sup>3</sup> and Atkinson *et al.*,<sup>41</sup> corrected to take into account this  $\text{O}(^3\text{P})$  atom reaction, are then: methyl vinyl ketone, 33%; methacrolein, 24%; 3-methylfuran, 5%; organic nitrates,  $\sim 13\%$ ; and unidentified carbonyl compounds,  $\sim 25\%$ . The formaldehyde yield was consistent with being a co-product formed together with methyl vinyl ketone and methacrolein.<sup>3</sup> Paulson *et al.*<sup>4</sup> determined yields of methyl vinyl ketone, methacrolein and 3-methylfuran of 35.5%, 25% and 4%, respectively, from a generally similar product study, but using gas chromatography for product analysis. These two studies are in excellent agreement, and show that methyl vinyl ketone and methacrolein formation account for  $\sim 60\%$  of the overall OH radical reaction with isoprene in the presence of  $\text{NO}_x$ . The data of Tuazon and Atkinson<sup>3</sup> indicate that organic nitrate formation, presumably from the reactions,



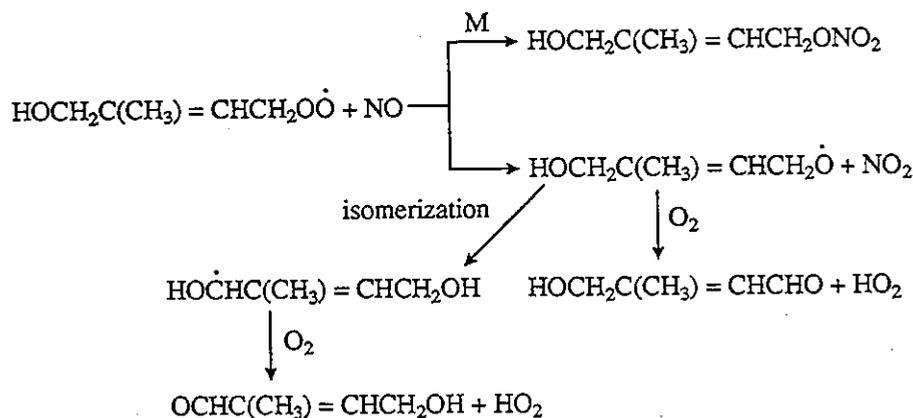
accounts for  $\sim 13\%$  of the overall reaction, and that other carbonyl compounds, including possibly hydroxycarbonyls, account for  $\sim 25\%$  of the reaction. These other, as yet unidentified, carbonyls and/or hydroxycarbonyls may arise from reactions of the  $\delta$ -hydroxyalkoxy radicals formed through the reaction sequence:



Reaction Scheme (5)



followed by



Reaction Scheme (5)

and similarly for terminal OH radical addition to the other  $>\text{C}=\text{C}<$  bond. 3-Methylfuran also arises from the OH radical-initiated reaction of isoprene, possibly in part after the formation of  $\delta$ -hydroxyalkoxy radicals.<sup>41,42</sup> Aerosol formation from isoprene photooxidation has been shown to be of negligible importance under atmospheric conditions,<sup>43</sup> and the aerosol composition has been investigated by Palen *et al.*<sup>44</sup>

To date, few quantitative product studies have been carried out for the monoterpenes,<sup>45-48</sup> and the reported data are given in Table 15 (the study of Hakola *et al.*<sup>48</sup> supersedes that of Arey *et al.*<sup>45</sup>). The yields reported by Hatakeyama *et al.*<sup>46</sup> for specific  $\text{C}_9$  and  $\text{C}_{10}$  carbonyls formed from  $\alpha$ - and  $\beta$ -pinene may be high because of contributions to the observed infrared absorptions from other, as yet unidentified, carbonyl-containing compounds. It appears clear that only a relatively small fraction of the overall reaction products have been accounted for, and Arey *et al.*<sup>45</sup> and Hakola *et al.*<sup>48</sup> observed no significant products by gas chromatography with flame ionization detection from the OH radical reactions with myrcene<sup>45</sup> or camphene<sup>48</sup> in the presence of  $\text{NO}_x$ .

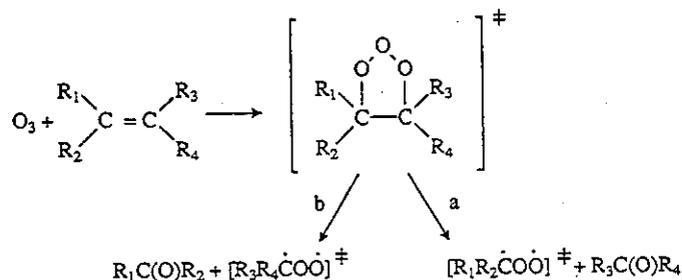
Hatakeyama *et al.*<sup>46</sup> observed that the pinonaldehyde yield in the absence of NO was significantly lower than in the presence of NO. Aerosol formation from the reactions of the OH radical with  $\alpha$ - and  $\beta$ -pinene has been studied by Hatakeyama *et al.*<sup>46</sup> and Pandis *et al.*,<sup>43</sup> and the aerosol composition investigated.<sup>44</sup> These references<sup>43,44,46</sup> should be consulted for further details.

Clearly, further product and mechanistic data are required for the OH radical reactions with the more complex alkenes, especially for the monoterpenes (including

conjugated dienes) of biogenic importance.

### $\text{O}_3$ Reaction

The kinetics and mechanisms of the gas-phase reactions of  $\text{O}_3$  with the alkenes, cycloalkenes and dienes were last reviewed and evaluated by Atkinson and Carter<sup>49</sup> and that review and evaluation is updated in Sec. 5.2. The kinetic data for alkenes of atmospheric importance (taken from Ref. 49 and Sec. 5.2.) are given in Table 16. These reactions proceed by initial  $\text{O}_3$  addition to the  $>\text{C}=\text{C}<$  bond to yield an energy-rich ozonide, which rapidly decomposes to a carbonyl and an initially energy-rich biradical.



where  $[\ ]^\ddagger$  denotes an energy-rich species. It has generally been assumed that  $k_a \sim k_b$  for the alkene systems.<sup>50</sup> However, Horie and Moortgat<sup>51</sup> concluded from a product study that this is not the case for the propene reaction, for which they obtained 62% formation of  $(\text{HCHO} + [\text{CH}_3\dot{\text{C}}\text{HO}]^\ddagger)$  and 38% formation of

- <sup>10</sup>J. Heicklen, J. Desai, A. Bahta, C. Harper, and R. Simonaitis, *J. Photochem.* **34**, 117 (1986).
- <sup>11</sup>S. Förgeteg, S. Dóbe, and T. Bérces, *React. Kinet. Catal. Lett.* **9**, 331 (1978).
- <sup>12</sup>S. Förgeteg, T. Bérces, and S. Dóbe *Int. J. Chem. Kinet.* **11**, 219 (1979).
- <sup>13</sup>J. Desai, J. Heicklen, A. Bahta, and R. Simonaitis, *J. Photochem.* **34**, 137 (1986).
- <sup>14</sup>E. P. Gardner, R. D. Wijayarathne, and J. G. Calvert, *J. Phys. Chem.* **88**, 5069 (1984).
- <sup>15</sup>H. Meyrahn, J. Pauly, W. Schneider, and P. Warneck, *J. Atmos. Chem.* **4**, 277 (1986).
- <sup>16</sup>R. A. Cox, M. C. Addison, J. P. Burrows, and R. Patrick, 14th Informal Conf. Photochem., Newport Beach, CA, March 30-April 3, 1980.
- <sup>17</sup>A. Horowitz, *J. Phys. Chem.* **95**, 10816 (1991).
- <sup>18</sup>C. N. Plum, E. Sanhueza, R. Atkinson, W. P. L. Carter, and J. N. Pitts, Jr., *Environ. Sci. Technol.* **17**, 479 (1983).
- <sup>19</sup>R. Atkinson, *J. Phys. Chem. Ref. Data Monograph* **1**, 1 (1989).
- <sup>20</sup>H. Niki, P. D. Maker, C. M. Savage, and M. D. Hurley, *J. Phys. Chem.* **91**, 2174 (1987).
- <sup>21</sup>C. E. McDade, T. M. Lenhardt, and K. D. Bayes, *J. Photochem.* **20**, 1 (1982).
- <sup>22</sup>H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, *Int. J. Chem. Kinet.* **17**, 547 (1985).
- <sup>23</sup>M. Green, G. Yarwood, and H. Niki, *Int. J. Chem. Kinet.* **22**, 689 (1990).
- <sup>24</sup>R. Atkinson, *Int. J. Chem. Kinet.* **19**, 799 (1987).
- <sup>25</sup>R. Atkinson and W. P. L. Carter, *Chem. Rev.* **84**, 437 (1984).
- <sup>26</sup>R. Atkinson, *J. Phys. Chem. Ref. Data* **20**, 459 (1991).
- <sup>27</sup>R. P. Wayne, I. Barnes, P. Biggs, J. P. Burrows, C. E. Canosa-Mas, J. Hjorth, G. Le Bras, G. K. Moortgat, D. Perner, G. Poulet, G. Restelli, and H. Sidebottom, *Atmos. Environ.* **25A**, 1 (1991).
- <sup>28</sup>J. Hjorth, J. Notholt, and G. Restelli, *Int. J. Chem. Kinet.* **24**, 51 (1992).
- <sup>29</sup>W. R. Stockwell and J. G. Calvert, *J. Geophys. Res.* **88**, 6673 (1983).
- <sup>30</sup>C. A. Cantrell, W. R. Stockwell, L. G. Anderson, K. L. Busarow, D. Perner, A. Schmeltekopf, J. G. Calvert, and H. S. Johnston, *J. Phys. Chem.* **89**, 139 (1985).
- <sup>31</sup>C. A. Cantrell, J. A. Davidson, K. L. Busarow, and J. G. Calvert, *J. Geophys. Res.* **91**, 5347 (1986).
- <sup>32</sup>G. K. Moortgat and R. D. McQuigg, *Proc. 3rd European Symposium on the Physico-Chemical Behaviour of Atmospheric Pollutants*, D. Riedel Pub. Co., Dordrecht, The Netherlands, 1984, pp. 194-204.
- <sup>33</sup>G. K. Moortgat, J. P. Burrows, W. Schneider, G. S. Tyndall, and R. A. Cox, *Proc. 4th European Symposium on the Physico-Chemical Behaviour of Atmospheric Pollutants*, D. Riedel Pub. Co., Dordrecht, The Netherlands, 1987, pp. 271-281.
- <sup>34</sup>W. P. Hess and F. P. Tully, *Chem. Phys. Lett.* **152**, 183 (1988).
- <sup>35</sup>U. Meier, H. H. Grotheer, G. Riekert, and Th. Just, *Chem. Phys. Lett.* **115**, 221 (1985).
- <sup>36</sup>S. M. Japar, T. J. Wallington, J. F. O. Richert, and J. C. Ball, *Int. J. Chem. Kinet.* **22**, 1257 (1990).
- <sup>37</sup>E. C. Tuazon, unpublished data, cited in R. Atkinson and W. P. L. Carter, *J. Atmos. Chem.* **13**, 195 (1991).
- <sup>38</sup>D. F. Smith, T. E. Kleindienst, E. E. Hudgens, C. D. McIver, and J. J. Bufalini, *Int. J. Chem. Kinet.* **23**, 907 (1991).
- <sup>39</sup>E. C. Tuazon, W. P. L. Carter, S. M. Aschmann, and R. Atkinson, *Int. J. Chem. Kinet.* **23**, 1003 (1991).
- <sup>40</sup>D. F. Smith, T. E. Kleindienst, E. E. Hudgens, C. D. McIver, and J. J. Bufalini, *Int. J. Chem. Kinet.* **24**, 199 (1992).
- <sup>41</sup>T. J. Wallington and S. M. Japar, *Environ. Sci. Technol.* **25**, 410 (1991).
- <sup>42</sup>P. H. Wine, R. J. Aсталos, and R. L. Mauldin, III, *J. Phys. Chem.* **89**, 2620 (1985).
- <sup>43</sup>D. L. Singleton, G. Paraskevopoulos, R. S. Irwin, G. S. Jolly, and D. J. McKenney, *J. Am. Chem. Soc.* **110**, 7786 (1988).
- <sup>44</sup>D. L. Singleton, G. Paraskevopoulos, and R. S. Irwin, *J. Am. Chem. Soc.* **111**, 5248 (1989).
- <sup>45</sup>H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, *J. Phys. Chem.* **87**, 2190 (1983).
- <sup>46</sup>G. L. Vaghjiani and A. R. Ravishankara, *J. Phys. Chem.* **93**, 1948 (1989).
- <sup>47</sup>E. P. Gardner, P. D. Sperry, and J. G. Calvert, *J. Phys. Chem.* **91**, 1922 (1987).
- <sup>48</sup>E. C. Tuazon and R. Atkinson, *Int. J. Chem. Kinet.* **22**, 591 (1990).
- <sup>49</sup>S. B. Bertman and J. M. Roberts, *Geophys. Res. Lett.* **18**, 1461 (1991).
- <sup>50</sup>J. M. Roberts and S. B. Bertman, *Int. J. Chem. Kinet.* **24**, 297 (1992).
- <sup>51</sup>I. R. Slagle, J. -Y. Park, M. C. Heaven, and D. Gutman, *J. Am. Chem. Soc.* **106**, 4356 (1984).
- <sup>52</sup>H. Krueger and E. Weitz, *J. Chem. Phys.* **88**, 1608 (1988).
- <sup>53</sup>A. Fahr and A. H. Laufer, *J. Phys. Chem.* **92**, 7229 (1988).
- <sup>54</sup>E. C. Tuazon and R. Atkinson, *Int. J. Chem. Kinet.* **21**, 1141 (1989).
- <sup>55</sup>S. W. Benson, *Thermochemical Kinetics*, 2nd ed. (Wiley, New York, NY, 1976).
- <sup>56</sup>R. Atkinson and A. C. Lloyd, *J. Phys. Chem. Ref. Data* **13**, 315 (1984).
- <sup>57</sup>H. Takagi, N. Washida, H. Akimoto, and M. Okuda, *Spectros. Lett.* **15**, 145 (1982).
- <sup>58</sup>K. H. Becker and Th. Klein, *Proc. 4th European Symp. on the Physico-Chemical Behaviour of Atmospheric Pollutants*, D. Riedel Publishing Co., Dordrecht, The Netherlands, 1987, pp. 320-326.
- <sup>59</sup>E. C. Tuazon, R. Atkinson, and W. P. L. Carter, *Environ. Sci. Technol.* **19**, 265 (1985).

## 2.6. Nitrogen-Containing Organic Compounds

The nitrogen-containing organic compounds considered in this section are the alkyl nitrates expected to be formed in the atmosphere from the alkanes and alkenes (see Secs. 2.1 and 2.2), alkyl nitrites, and peroxyacyl and peroxyalkyl nitrates. The reactions of acetyl peroxy (RC(O)OO<sup>•</sup>) radicals under atmospheric conditions are also discussed in the portion of this section dealing with the chemistry of peroxyacyl nitrates.

### Alkyl Nitrates

Based upon laboratory studies concerning the formation of alkyl nitrates from the NO<sub>x</sub>-air photooxidations of the alkanes (Sec. 2.1 and references 1-3), the major alkyl nitrates expected to be formed in the atmosphere are 2-propyl nitrate, 2-butyl nitrate, 2- and 3-pentyl nitrate, and 2- and 3-hexyl nitrate. Although no experimental data are available concerning the kinetics of the NO<sub>3</sub> radical or O<sub>3</sub> reactions, these are expected to be slow and of no significance as atmospheric loss processes. The major loss processes are then reaction with the OH radical and photolysis. The room temperature OH radical reaction rate constants are given in Table 35 (no temperature dependent data are available).

These reactions proceed by H-atom abstraction from the C-H bonds, and in the absence of product data the estimation technique of Atkinson<sup>6</sup> (as revised by Atkinson and Aschmann<sup>7</sup> to yield the substituent factors at 298 K of  $F(-\text{CH}_2\text{ONO}_2) = F(>\text{CHONO}_2) = F(\Rightarrow\text{CONO}_2) = 0.30$  and  $F(-\text{ONO}_2) = 0.18$ ) can be used to calculate the distribution of the nitratoalkyl radicals formed from the OH radical reactions of the  $\geq\text{C}_4$  alkyl nitrates (see Reaction Scheme (14), for example, at room temperature). The expected subsequent reactions of these radicals are as discussed in Sec. 2.1. For example, in the presence of NO, the reactions expected to occur are as shown in Reaction Scheme (15). At the present time, product data are not available for these reactions,

TABLE 35. Room temperature rate constants  $k$  for the gas-phase reactions of the OH radical with alkyl nitrates and peroxyacetyl nitrate at atmospheric pressure [from Ref. 4 and Sec. 3.8]

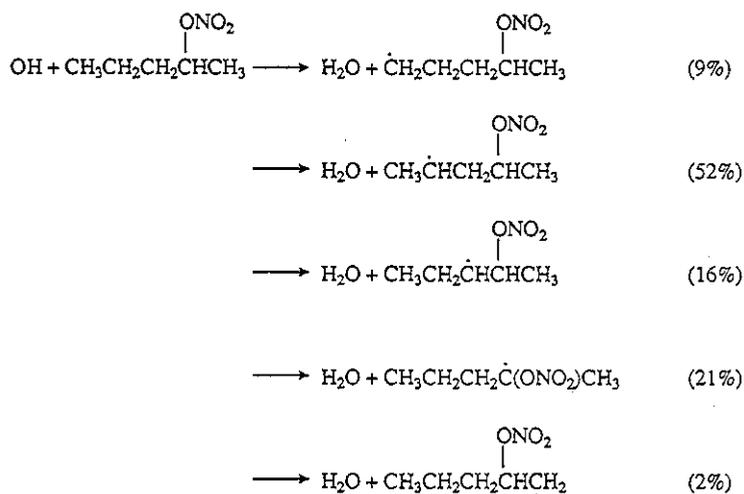
Organic	$10^{12} \times k$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )
Methyl nitrate	0.35
Ethyl nitrate	0.49
1-Propyl nitrate	0.73
2-Propyl nitrate	0.49
1-Butyl nitrate	1.71
2-Butyl nitrate	0.92
2-Pentyl nitrate	1.85
3-Pentyl nitrate	1.12
2-Methyl-3-butyl nitrate	1.82
2,2-Dimethyl-1-propyl nitrate	0.85
2-Hexyl nitrate	3.17
3-Hexyl nitrate	2.70
Cyclohexyl nitrate	3.30
2-Methyl-2-pentyl nitrate	1.72
3-Methyl-2-pentyl nitrate	3.02
3-Heptyl nitrate	3.69
3-Octyl nitrate	3.88
Peroxyacetyl nitrate	0.11 <sup>a</sup>

<sup>a</sup> $k = 9.5 \times 10^{-13} e^{-650/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  recommended over the temperature range 270–300 K.<sup>5</sup>

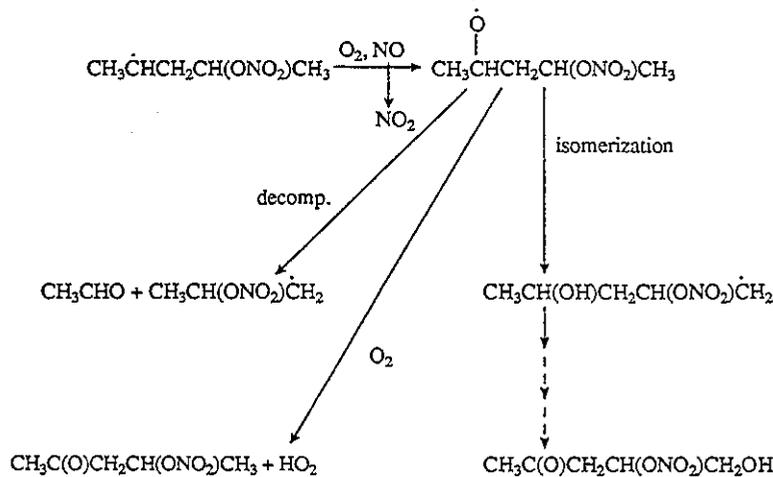
and the estimation method proposed in Sec. 2.1 for the assessment of the relative importance of the various alkoxy radical reaction pathways should be used.

The absorption cross-sections of methyl nitrate, ethyl nitrate and 1- and 2-propyl nitrate have been reviewed and evaluated by the IUPAC panel,<sup>5</sup> and the IUPAC recommended values<sup>5</sup> are based on the measurements of Roberts and Fajer<sup>8</sup> and Turberg *et al.*<sup>9</sup> The IUPAC evaluation<sup>5</sup> should be consulted for the absorption cross-sections for these alkyl nitrates. In addition, Roberts and Fajer<sup>8</sup> measured absorption cross-sections for 1- and 2-butyl nitrate, 2-methyl-2-propyl nitrate (*tert*-butyl nitrate), 2- and 3-pentyl nitrate, cyclopentyl nitrate,  $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{ONO}_2$  and  $\text{HOCH}_2\text{CH}_2\text{ONO}_2$ , while Turberg *et al.*<sup>9</sup> also measured the absorption cross-sections for 1-butyl nitrate and 3-methyl-1-butyl nitrate.

Based on the direct measurements of the photolysis rates under ambient atmospheric conditions conducted by Luke and Dickerson<sup>10</sup> and Luke *et al.*<sup>11</sup> for ethyl nitrate,<sup>10,11</sup> 1-propyl nitrate<sup>11</sup> and 1- and 2-butyl nitrate,<sup>11</sup> the lifetimes of these alkyl nitrates in the lower troposphere due to photolysis are in the range ~15–30 days. Moreover, these measured photolysis rates under ambient atmospheric conditions are in agreement, within the experimental errors, with those calculated assuming a

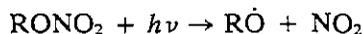


#### Reaction Scheme (14)

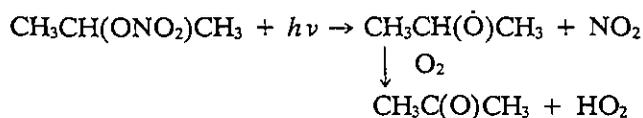


#### Reaction Scheme (15)

photodissociation quantum yield of unity<sup>10,11</sup> (see also Becker and Wirtz<sup>12</sup>). Photolysis leads to cleavage of the O-NO<sub>2</sub> bond,

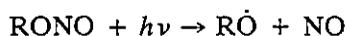


followed by the reactions of the alkoxy radical (Sec. 2.1). For example, Becker and Wirtz<sup>12</sup> have observed the formation of acetone from the photolysis of 2-propyl nitrate:



#### Alkyl Nitrites

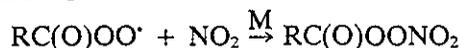
Under atmospheric conditions, the simple alkyl nitrites rapidly photolyze,<sup>13</sup> with lifetimes measured in minutes.



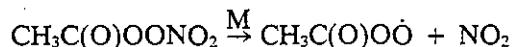
Their reactions with the OH radical (reference 4 and Sec. 3.8) are of negligible importance as an atmospheric loss process.<sup>14</sup> Because of their rapid photolysis, the formation of alkyl nitrites from the R $\dot{\text{O}}$  + NO combination reactions can be essentially neglected under atmospheric conditions. However, the formation of alkyl nitrites from the R $\dot{\text{O}}$  + NO reactions can be important in the photooxidations, under laboratory conditions, of RONO-NO-organic-air mixtures.

#### Peroxyacyl Nitrates and Peroxy Nitrites

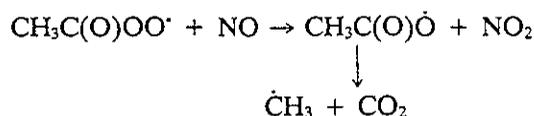
Peroxyacetyl nitrate (PAN; CH<sub>3</sub>C(O)OONO<sub>2</sub>) and the higher members of this class of compounds are formed from the atmospheric degradations of many organics (see Sec. 2.5) by the combination reaction of acyl peroxy radicals with NO<sub>2</sub>.



The reaction of OH radicals with PAN (the only peroxyacyl nitrate studied to date) is slow at tropospheric temperatures (Table 35) and this OH radical reaction is expected to be a significant atmospheric loss process for PAN only at the low temperatures encountered in the upper troposphere. The absorption cross-sections for PAN are given in the IUPAC evaluation.<sup>5</sup> The major, and usually totally dominant, loss process for PAN in the lower troposphere is by its thermal decomposition



Thus, PAN is in equilibrium with NO<sub>2</sub> and the CH<sub>3</sub>C(O)OO radical. In the presence of NO, the reaction

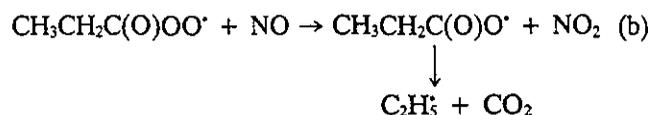


leads to removal of PAN.

The thermal decomposition rate constant for PAN is temperature and pressure dependent,<sup>5</sup> being in the fall-off region at room temperature at and below atmospheric pressure. Using the Troe fall-off expression, the IUPAC evaluation panel recommended for the temperature range 280–330 K that:<sup>5</sup>  $k_0 = 4.9 \times 10^{-3} e^{-12100/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $k_\infty = 4.0 \times 10^{16} e^{-13600/T} \text{ s}^{-1}$  and  $F = 0.3$  at 298 K. Thus,  $k_\infty(\text{PAN}) = 6.1 \times 10^{-4} \text{ s}^{-1}$  at 298 K, and at 298 K and 760 Torr total pressure of air  $k(\text{PAN}) = 5.2 \times 10^{-4} \text{ s}^{-1}$ , in good agreement with the atmospheric pressure data of Schurath and Wipprecht<sup>15</sup> ( $k = 3.2 \times 10^{16} e^{-13592/T} \text{ s}^{-1} = 5.0 \times 10^{-4} \text{ s}^{-1}$  at 298 K), Roberts and Bertman<sup>16</sup> ( $k = 2.5 \times 10^{17} e^{-14343/T} \text{ s}^{-1} = 3.1 \times 10^{-4} \text{ s}^{-1}$  at 298 K) and Roumelis and Glavas<sup>17</sup> ( $k = 3.1 \times 10^{-4} \text{ s}^{-1}$  at 296.7 K).

The decomposition rates of the higher peroxyacyl nitrates are expected to be similar to that for PAN, with the decomposition rate constants being closer to the high pressure limit at a given pressure than for PAN.

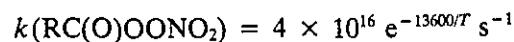
For the formation and decomposition of peroxypropionyl nitrate (PPN),



Kerr and Stocker<sup>18</sup> obtained a rate constant ratio of  $k_b/k_a = 1.9$  at ~730 Torr total pressure of air and  $302 \pm 3$  K, essentially identical to the rate constant ratio for the analogous reactions of the CH<sub>3</sub>C(O)OO radical.<sup>5</sup> At atmospheric pressure, Schurath and Wipprecht<sup>15</sup> and Mineshos and Glavas<sup>19</sup> determined thermal decomposition rate constants for peroxypropionyl nitrate (PPN; C<sub>2</sub>H<sub>5</sub>C(O)OONO<sub>2</sub>) of  $k(\text{PPN}) = 1.6 \times 10^{17} e^{-14073/T} \text{ s}^{-1}$ <sup>15</sup> and  $2 \times 10^{15} e^{-12800/T} \text{ s}^{-1}$ <sup>19</sup> ( $5.0 \times 10^{-4} \text{ s}^{-1}$ <sup>15</sup> and  $4.4 \times 10^{-4} \text{ s}^{-1}$ <sup>19</sup> at 298 K and atmospheric pressure).

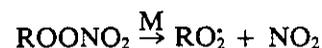
Roberts and Bertman<sup>16</sup> have studied the thermal decomposition of CH<sub>2</sub>=C(CH<sub>3</sub>)C(O)OONO<sub>2</sub> (MPAN) [formed from the OH radical-initiated reaction of methacrolein (Sec. 2.5)] and determined a thermal decomposition rate constant at atmospheric pressure of  $k(\text{MPAN}) = 1.6 \times 10^{16} e^{-13488/T} \text{ s}^{-1}$  ( $3.5 \times 10^{-4} \text{ s}^{-1}$  at 298 K).

These data indicate that for the thermal decompositions of the peroxyacyl nitrates,



to within a factor of ~1.5 at 298 K.

For the peroxyalkyl nitrates, ROONO<sub>2</sub>, the only significant lower troposphere loss process is again thermal decomposition,



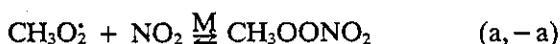
with the thermal decomposition rate constants for CH<sub>3</sub>OONO<sub>2</sub> and C<sub>2</sub>H<sub>5</sub>OONO<sub>2</sub> being in the fall-off

regime at pressures of one atmosphere and below.<sup>5,20</sup> Using the Troe fall-off expression, the IUPAC evaluation panel recommended<sup>5</sup> for the temperature range 250–300 K that: for  $\text{CH}_3\text{OONO}_2$ ,  $k_0 = 9 \times 10^{-5} e^{-9690/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $k_\infty = 1.1 \times 10^{16} e^{-10560/T} \text{ s}^{-1}$ , and  $F = 0.4$  at 298 K; and for  $\text{C}_2\text{H}_5\text{OONO}_2$ ,  $k_0 = 4.8 \times 10^{-4} e^{-9285/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $k_\infty = 8.8 \times 10^{15} e^{-10440/T} \text{ s}^{-1}$ , and  $F = 0.31$ . At 760 Torr total pressure of air and 298 K,  $k(\text{CH}_3\text{OONO}_2) = 1.8 \text{ s}^{-1}$  and  $k(\text{C}_2\text{H}_5\text{OONO}_2) = 4.0 \text{ s}^{-1}$ , which can be compared to the limiting high-pressure values of  $k_\infty(\text{CH}_3\text{OONO}_2) = 4.5 \text{ s}^{-1}$  and  $k_\infty(\text{C}_2\text{H}_5\text{OONO}_2) = 5.4 \text{ s}^{-1}$  at 298 K. The decomposition rates for the higher  $\text{ROONO}_2$  species are expected to be similar to that for  $\text{CH}_3\text{OONO}_2$ , except that they will be closer to the high pressure first-order limit.

Indeed, Zabel *et al.*<sup>20</sup> have shown that the thermal decomposition rate constants for the  $\text{C}_4\text{H}_9\text{OONO}_2$ ,  $\text{C}_6\text{H}_{13}\text{OONO}_2$  and  $\text{C}_8\text{H}_{17}\text{OONO}_2$  species at 600 Torr total pressure and 253 K are within 30% of the high-pressure limiting value for  $\text{C}_2\text{H}_5\text{OONO}_2$ .<sup>20</sup> Hence it is recommended that:

$$k_\infty(\text{ROONO}_2) = 9 \times 10^{15} e^{-10450/T} \text{ s}^{-1}.$$

Bridier *et al.*<sup>21</sup> have experimentally measured the equilibrium constant  $K = k_2/k_{-2}$  for the reactions



over the temperature range 333–373 K, with  $K = 2.73 \times 10^{-28} e^{10910/T} \text{ cm}^3 \text{ molecule}^{-1}$ , in good agreement with the equilibrium constant calculated from the forward and reverse rate constants  $k_\infty$  recommended by the IUPAC evaluation<sup>5</sup> of  $6.8 \times 10^{-28} e^{10560/T} \text{ cm}^3 \text{ molecule}^{-1}$  over the temperature range 333–373 K. Absorption cross-sections have been measured for  $\text{CH}_3\text{OONO}_2$ <sup>21–24</sup> and those of Cox and Tyndall,<sup>22</sup> Sander and Watson<sup>23</sup> and Morel *et al.*<sup>24</sup> were considered in the IUPAC evaluation.<sup>5</sup> The absorption cross-sections reported by Bridier *et al.*<sup>21</sup> for the wavelength range 200–280 nm are in general agreement with the IUPAC recommendation,<sup>5</sup> except for wavelengths 220–230 nm and 280 nm.

## References

- W. P. L. Carter and R. Atkinson, *J. Atmos. Chem.* **3**, 377 (1985).
- W. P. L. Carter and R. Atkinson, *J. Atmos. Chem.* **8**, 165 (1989).
- R. Atkinson, *Atmos. Chem.* **24A**, 1 (1990).
- R. Atkinson, *J. Phys. Chem. Ref. Data Monograph* **1**, 1 (1989).
- R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, and J. Troe, *J. Phys. Chem. Ref. Data* **21**, 1125 (1992).
- R. Atkinson, *Int. J. Chem. Kinet.* **19**, 799 (1987).
- R. Atkinson and S. M. Aschmann, *Int. J. Chem. Kinet.* **21**, 1123 (1989).
- J. M. Roberts and R. W. Fajer, *Environ. Sci. Technol.* **23**, 945 (1989).
- M. P. Turberg, D. M. Giolando, C. Tilt, T. Soper, S. Mason, M. Davies, P. Klingensmith, and G. A. Takacs, *J. Photochem. Photobiol., A: Chemistry* **51**, 281 (1990).
- W. T. Luke and R. R. Dickerson, *Geophys. Res. Lett.* **15**, 1181 (1988).
- W. T. Luke, R. R. Dickerson, and L. J. Nunnermacker, *J. Geophys. Res.* **94**, 14905 (1989).
- K. H. Becker and K. Wirtz, *J. Atmos. Chem.* **9**, 419 (1989).
- W. D. Taylor, T. D. Allston, M. J. Moscato, G. B. Fazekas, R.

Kozlowski, and G. A. Takacs, *Int. J. Chem. Kinet.* **12**, 231 (1980).

- O. J. Nielsen, H. W. Sidebottom, M. Donlon, and J. Treacy, *Int. J. Chem. Kinet.* **23**, 1095 (1991).
- U. Schurath and V. Wipprecht, *Proc. 1st European Symp. on the Physico-Chemical Behaviour of Atmospheric Pollutants*, pp. 157–166, *Commiss. European Commun.* (1980).
- J. M. Roberts and S. B. Bertman, *Int. J. Chem. Kinet.* **24**, 297 (1992).
- N. Roumelis and S. Glavas, *Monatshefte für Chemie*, **123**, 63 (1992).
- J. A. Kerr and D. W. Stocker, *J. Photochem.* **28**, 475 (1985).
- G. Mineshos and S. Glavas, *React. Kinet. Catal. Lett.* **45**, 305 (1991).
- F. Zabel, A. Reimer, K. H. Becker, and E. H. Fink, *J. Phys. Chem.* **93**, 5500 (1989).
- I. Bridier, R. Lesclaux, and B. Veyret, *Chem. Phys. Lett.* **191**, 259 (1992).
- R. A. Cox and G. S. Tyndall, *Chem. Phys. Lett.* **65**, 357 (1979).
- S. P. Sander and R. T. Watson, *J. Phys. Chem.* **84**, 1664 (1980).
- O. Morel, R. Simonaitis, and J. Hecklen, *Chem. Phys. Lett.* **73**, 38 (1980).

## 3. Kinetics and Mechanisms of the Gas-Phase Reactions of the OH Radical with Organic Compounds

Recent kinetic and mechanistic data for the gas-phase reactions of the OH radical with organic compounds are presented and discussed in this section. Recommended rate constant expressions are given using either the Arrhenius expression,  $k = A e^{-B/T}$ , or, if curvature in the Arrhenius plot is evident, the three parameter equation  $k = C T^n e^{-D/T}$ , where at a given temperature  $T$  the three parameter equation can be transformed into the Arrhenius expression with  $A = C e^n T^n$  and  $B = D + nT$ .

### 3.1. Alkanes

The rate constants reported since the previous review of Atkinson<sup>1</sup> are given in Table 36. In addition to these rate constants, Cantrell *et al.*<sup>17</sup> have determined the rate constant for the OH radical reactions with methane-<sup>12</sup>C relative to that for methane-<sup>13</sup>C over the temperature range 273–353 K, and obtained  $k(^{12}\text{CH}_4)/k(^{13}\text{CH}_4) = 1.0054 \pm 0.0009$  independent of temperature over this range.

*Methane and Methane-<sup>13</sup>C.* Absolute rate constants for the reactions of the OH radical with methane have been determined by Bott and Cohen<sup>2</sup> at  $1234 \pm 15 \text{ K}$ , and by Vaghjiani and Ravishankara<sup>3</sup> and Finlayson-Pitts *et al.*<sup>4</sup> over the temperature ranges 223–420 K and 278–378 K, respectively (Table 36). While the high-temperature rate constant of Bott and Cohen<sup>2</sup> is in good agreement (within 15%) with the recommendation<sup>1</sup> of

$$k(\text{methane}) = 6.95 \times 10^{-18} T^2 e^{-1282/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

the absolute rate constants determined by Vaghjiani and Ravishankara<sup>3</sup> and Finlayson-Pitts *et al.*<sup>4</sup> over the temperature ranges 223–420 K and 278–378 K, respectively, are ~20% lower than most of the previously reported absolute rate constants. In particular, the rate constants of Vaghjiani and Ravishankara<sup>3</sup> and Finlayson-

$k(\text{CH}_3\text{SSCH}_3) = 2.27 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K,

with an estimated overall uncertainty at 298 K of  $\pm 25\%$ . This recommendation supersedes that of Atkinson<sup>1</sup> of

$k(\text{CH}_3\text{SSCH}_3) = 5.83 \times 10^{-11} e^{383/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

over the same temperature range of 249–367 K, with a 298 K rate constant of  $2.11 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

## References

- <sup>1</sup>R. Atkinson, J. Phys. Chem. Ref. Data Monograph 1, 1 (1989).
- <sup>2</sup>O. J. Nielsen, H. W. Sidebottom, L. Nelson, J. J. Treacy, and D. J. O'Farrell, Int. J. Chem. Kinet. 21, 1101 (1989).
- <sup>3</sup>J. P. D. Abbatt, F. F. Fenter, and J. G. Anderson, J. Phys. Chem. 96, 1780 (1992).
- <sup>4</sup>O. J. Nielsen, H. W. Sidebottom, L. Nelson, O. Rattigan, J. J. Treacy, and D. J. O'Farrell, Int. J. Chem. Kinet. 22, 603 (1990).
- <sup>5</sup>S. M. Japar, T. J. Wallington, J. M. Andino, and J. C. Ball, Environ. Sci. Technol. 24, 313 (1990).
- <sup>6</sup>S. M. Japar, T. J. Wallington, J. M. Andino, and J. C. Ball, Environ. Sci. Technol. 24, 894 (1990).
- <sup>7</sup>G. S. Tyndall and A. R. Ravishankara, J. Phys. Chem. 93, 4707 (1989).
- <sup>8</sup>P. H. Wine, R. J. Thompson, and D. H. Semmes, Int. J. Chem. Kinet. 16, 1623 (1984).
- <sup>9</sup>A. J. Hynes and P. H. Wine, J. Phys. Chem. 91, 3672 (1987).
- <sup>10</sup>P. H. Wine, N. M. Kreutter, C. A. Gump, and A. R. Ravishankara, J. Phys. Chem. 85, 2660 (1981).
- <sup>11</sup>A. J. Hynes, P. H. Wine, and D. H. Semmes, J. Phys. Chem. 90, 4148 (1986).
- <sup>12</sup>Y.-C. Hsu, D.-S. Chen, and Y.-P. Lee, Int. J. Chem. Kinet. 19, 1073 (1987).
- <sup>13</sup>I. Barnes, V. Bastian, and K. H. Becker, Int. J. Chem. Kinet. 20, 415 (1988).
- <sup>14</sup>D. Martin, J. L. Jourdain, and G. Le Bras, Int. J. Chem. Kinet. 17, 1247 (1985).
- <sup>15</sup>I. Barnes, V. Bastian, and K. H. Becker, 9th International Symposium on Gas Kinetics, University of Bordeaux, Bordeaux, France, July 20–25, 1986.
- <sup>16</sup>R. A. Cox and D. Sheppard, Nature 284, 330 (1980).
- <sup>17</sup>I. Barnes, V. Bastian, and K. H. Becker, Proc. 4th European Symposium on the Physico-Chemical Behaviour of Atmospheric Pollutants, D. Riedel Pub. Co., Dordrecht, The Netherlands, 1987, pp. 327–337.

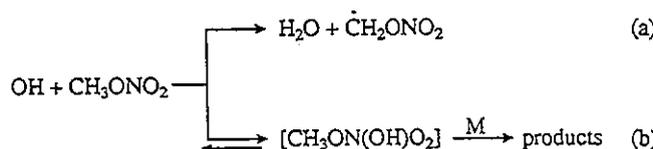
### 3.8. Nitrogen-Containing Organic Compounds

The rate constants reported since the review and evaluation of Atkinson<sup>1</sup> are given in Tables 43 (OH radical reactions) and 44 (OD radical reactions). For several nitrogen-containing compounds, the rate constants given in Table 43 are the first reported.

#### 3.8.1 Nitrates

**Methyl nitrate.** The absolute and relative rate constants of Nielsen *et al.*<sup>2</sup> are given in Table 43. These rate constants were obtained at one atmosphere total pressure of air or argon. The room temperature absolute and relative rate constants of Nielsen *et al.*<sup>2</sup> are in agreement with the relative rate constant of Kerr and Stocker,<sup>12</sup> also obtained at one atmosphere total pressure, but are a factor of  $\sim 10$

higher than the rate constant obtained at a total pressure of 2–3 Torr by Gaffney *et al.*<sup>13</sup> These observations indicate that at room temperature the rate constant for the reaction of the OH radical with methyl nitrate is pressure dependent, and that the reaction proceeds by an H-atom abstraction pathway (a) and an addition pathway (b),



where the products of the addition pathway may include  $\text{CH}_3\dot{\text{O}} + \text{HONO}_2$ .<sup>2</sup> This situation is similar to the OH radical reactions with the alkyl nitrites and nitroalkane (see below). Comparison of the low pressure<sup>13</sup> and atmospheric pressure<sup>2,12</sup> rate constants at room temperature further indicates that at atmospheric pressure and room temperature the OH radical reaction with methyl nitrate proceeds mainly ( $\sim 90\%$ ) by the addition pathway (b). This conclusion is consistent with the observation of a marked negative temperature dependence of the rate constant at atmospheric pressure (Table 43 and Ref. 2).

At the present time the total pressure at which the high-pressure limiting rate constant is attained is not known. A unit-weighted average of the atmospheric pressure absolute rate constant of Nielsen *et al.*<sup>2</sup> and the atmospheric pressure relative rate constants of Kerr and Stocker<sup>12</sup> and Nielsen *et al.*<sup>2</sup> leads to the recommendation of

$$k(\text{methyl nitrate}) = 3.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K and 760 Torr total pressure of air, with an estimated overall uncertainty of a factor of 1.5. In the absence of kinetic and mechanistic data for this reaction as a function of temperature and pressure, no recommendations are made concerning the temperature or pressure dependence of the rate constant.

**Ethyl nitrate.** The absolute and relative rate constants of Nielsen *et al.*<sup>2</sup> are given in Table 43. At room temperature, these rate constants, obtained at one atmosphere total pressure of argon or air, are in agreement with the atmospheric pressure relative rate constant of Kerr and Stocker.<sup>12</sup> Accordingly, a unit-weighted average of the absolute rate constant of Nielsen *et al.*<sup>2</sup> and the relative rate constants of Kerr and Stocker<sup>12</sup> and Nielsen *et al.*<sup>2</sup> leads to the recommendation of

$$k(\text{ethyl nitrate}) = 4.9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K and 760 Torr total pressure of air, with an estimated overall uncertainty of a factor of 1.5. Analogous to the OH radical reaction with methyl nitrate, the room temperature rate constant for the reaction of the OH radical with ethyl nitrate is expected to be pressure dependent, and the negative temperature dependence

determined by Nielsen *et al.*<sup>2</sup> at atmospheric pressure of argon diluent is consistent with the reaction proceeding mainly by OH radical addition at 298 K and 760 Torr total pressure of air, as also concluded by Nielsen *et al.*<sup>2</sup>

**1-Propyl nitrate.** The absolute and relative rate constants of Nielsen *et al.*<sup>2</sup> are given in Table 43. The room temperature rate constants of Nielsen *et al.*,<sup>2</sup> obtained at one atmosphere total pressure of argon or air, are in agreement with the atmospheric pressure relative rate measurements of Kerr and Stocker<sup>12</sup> and Atkinson and Aschmann.<sup>14</sup> A unit-weighted average of the absolute rate constant of Nielsen *et al.*<sup>2</sup> and the relative rate constants of Kerr and Stocker,<sup>12</sup> Atkinson and Aschmann<sup>14</sup> and Nielsen *et al.*<sup>2</sup> leads to the recommendation of

$$k(1\text{-propyl nitrate}) = 7.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K and 760 Torr total pressure of air, with an estimated overall uncertainty of a factor of 1.5. Consistent with the observed lack of a temperature dependence for the rate constant at one atmosphere total pressure of argon diluent,<sup>2</sup> the reaction of the OH radical with 1-propyl nitrate is expected to proceed by both H-atom abstraction and initial OH radical addition, with the two pathways possibly being of approximately comparable importance at 298 K and one atmosphere total pressure of air.<sup>2</sup>

**2-Propyl nitrate.** The room temperature relative rate constant of Becker and Wirtz<sup>3</sup> is given in Table 43. This rate constant<sup>3</sup> is in agreement, within the experimental errors, with the relative rate constant of Atkinson and Aschmann<sup>14</sup> (which supersedes the previous measurement of Atkinson *et al.*<sup>15</sup>). A unit-weighted average of the rate constants of Atkinson and Aschmann<sup>14</sup> and Becker and Wirtz<sup>3</sup> leads to the recommendation of

$$k(2\text{-propyl nitrate}) = 4.9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K and 760 Torr total pressure of air, with an estimated overall uncertainty of a factor of 2. The OH radical reaction with 2-propyl nitrate at room temperature and atmospheric pressure is again expected to proceed by H-atom abstraction and initial OH radical addition.

**1-Butyl nitrate.** The room temperature absolute and relative rate constants of Nielsen *et al.*<sup>2</sup> are given in Table 43. These rate constants, obtained at a total pressure of one atmosphere of argon or air, are in good agreement with the previous relative rate constant of Atkinson and Aschmann<sup>14</sup> (which supersedes the earlier measurement of Atkinson *et al.*<sup>15</sup>). Accordingly, a unit-weighted average of the absolute rate constant of Nielsen *et al.*<sup>2</sup> and the relative rate constants of Atkinson and Aschmann<sup>14</sup> and Nielsen *et al.*<sup>2</sup> leads to the recommendation of

$$k(1\text{-butyl nitrate}) = 1.71 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K and 760 Torr total pressure of air, with an estimated overall uncertainty of  $\pm 35\%$ . Based on the correlation of Nielsen *et al.*<sup>2</sup> of the Cl atom and OH radical

reaction rate constants with a series of alkyl nitrates, it is expected that the OH radical reaction with 1-butyl nitrate proceeds mainly by H-atom abstraction at 298 K and atmospheric pressure.

**2-Methyl-3-butyl nitrate.** The relative rate constant of Becker and Wirtz<sup>3</sup> obtained at room temperature and atmospheric pressure is given in Table 43. This rate constant<sup>3</sup> is in good agreement with that of Atkinson *et al.*,<sup>16</sup> and a unit-weighted average of these rate constants<sup>3,16</sup> leads to the recommendation of

$$k(2\text{-methyl-3-butyl nitrate}) = 1.82 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K and atmospheric pressure of air, with an estimated overall uncertainty of  $\pm 35\%$ . It is expected that this OH radical reaction proceeds mainly by H-atom abstraction under atmospheric conditions.

**Other alkyl nitrates.** Only single studies have been conducted for the alkyl nitrates other than those discussed above and 2-butyl nitrate (for which the study of Atkinson and Aschmann<sup>14</sup> supersedes that of Atkinson *et al.*<sup>15</sup>). While no firm recommendations are made, the rate constants of Atkinson *et al.*,<sup>15,16</sup> (other than for 2-butyl nitrate for which the rate constant of Atkinson and Aschmann<sup>14</sup> should be used), Becker and Wirtz<sup>3</sup> and Nielsen *et al.*<sup>2</sup> should be used.

### 3.8.2. Alkyl nitrites

**Methyl nitrite.** The absolute and relative rate constants of Nielsen *et al.*<sup>5</sup> are given in Table 43. The room temperature rate constants of Nielsen *et al.*,<sup>5</sup> obtained at one atmosphere total pressure of argon or air, are consistent with the previous relative rate constants of Tuazon *et al.*,<sup>17</sup> but are lower by a factor of  $\sim 4$  than the rate constants of Campbell and Goodman,<sup>18</sup> Audley *et al.*<sup>19</sup> and Baulch *et al.*<sup>20</sup> Consistent with the previous discussion by Atkinson,<sup>1</sup> a unit-weighted average of the absolute and relative rate constants of Tuazon *et al.*<sup>17</sup> and Nielsen *et al.*<sup>5</sup> leads to the recommendation of

$$k(\text{methyl nitrite}) = 2.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K and 760 Torr total pressure of air, with an estimated overall uncertainty of a factor of 3. It is likely that at room temperature and atmospheric pressure the OH radical reaction with methyl nitrite proceeds by both H-atom abstraction and initial OH radical addition.<sup>5</sup>

**Other alkyl nitrites.** Rate constants for the C<sub>2</sub> through C<sub>5</sub> n-alkyl nitrites have been determined by Nielsen *et al.*<sup>5</sup> (Table 43) at room temperature and atmospheric pressure. These rate constants for ethyl nitrite, 1-propyl nitrite and 1-butyl nitrite<sup>5</sup> are significantly lower (by factors of  $\sim 2$ ) than the previous rate constants of Audley *et al.*<sup>19</sup> and Baulch *et al.*<sup>20</sup> Consistent with the above recommendation for methyl nitrite, the rate constants of Nielsen *et al.*<sup>5</sup> are preferred.

TABLE 43. Rate constants  $k$  and temperature-dependent parameters at, or close to, the high-pressure limit for the gas-phase reactions of the OH radical with nitrogen-containing organics

Organic	$10^{12} \times A$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$B$ (K)	$10^{12} \times k$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	at $T$ (K)	Technique	Reference	Temperature range covered (K)
Methyl nitrate		-1057	0.32 ± 0.05	298 ± 2	PR-RA	Nielsen <i>et al.</i> <sup>2</sup>	298-393
			0.22 ± 0.06	323			
			0.15 ± 0.03	358			
			0.14 ± 0.03	393			
			0.339 ± 0.070	298 ± 2	RR [relative to $k(2\text{-methyl-} \text{propane}) = 2.33 \times 10^{-12}$ ] <sup>a</sup>	Nielsen <i>et al.</i> <sup>2</sup>	
Ethyl nitrate		-705	0.53 ± 0.06	298 ± 2	PR-RA	Nielsen <i>et al.</i> <sup>2</sup>	298-373
			0.37 ± 0.05	338			
			0.33 ± 0.05	373			
			0.458 ± 0.030	298 ± 2			
1-Propyl nitrate		~0	0.82 ± 0.08	298 ± 2	PR-RA	Nielsen <i>et al.</i> <sup>2</sup>	298-368
			0.72 ± 0.15	338			
			0.76 ± 0.05	368			
			0.767 ± 0.080	298 ± 2			
2-Propyl nitrate			0.575 ± 0.225	295 ± 2	RR [relative to $k(n\text{-butane}) = 2.50 \times 10^{-12}$ ] <sup>a</sup>	Becker and Wirtz <sup>3</sup>	
1-Butyl nitrate			1.74 ± 0.19	298 ± 2	PR-RA	Nielsen <i>et al.</i> <sup>2</sup>	
			1.61 ± 0.08	298 ± 2	RR [relative to $k(2\text{-methyl-} \text{propane}) = 2.33 \times 10^{-12}$ ] <sup>a</sup>	Nielsen <i>et al.</i> <sup>2</sup>	
2-Methyl-1-propyl nitrate			1.63 ± 0.20	295 ± 2	RR [relative to $k(n\text{-butane}) = 2.50 \times 10^{-12}$ ] <sup>a</sup>	Becker and Wirtz <sup>3</sup>	
1-Pentyl nitrate			3.32 ± 0.30	298 ± 2	PR-RA	Nielsen <i>et al.</i> <sup>2</sup>	
			2.95 ± 0.09	298 ± 2	RR [relative to $k(2\text{-methyl-} \text{propane}) = 2.33 \times 10^{-12}$ ] <sup>a</sup>	Nielsen <i>et al.</i> <sup>2</sup>	
2-Methyl-3-butyl nitrate			1.93 ± 0.15	295 ± 2	RR [relative to $k(n\text{-butane}) = 2.50 \times 10^{-12}$ ] <sup>a</sup>	Becker and Wirtz <sup>3</sup>	
2-Methyl-1-butyl nitrate			2.48 ± 0.15	295 ± 2	RR [relative to $k(n\text{-butane}) = 2.50 \times 10^{-12}$ ] <sup>a</sup>	Becker and Wirtz <sup>3</sup>	

Organic	$10^{12} \times A$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	<i>B</i> (K)	$10^{12} \times k$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	at <i>T</i> (K)	Technique	Reference	Temperature range covered (K)
3-Methyl-1-butyl nitrate			2.53 ± 0.35	295 ± 2	RR [relative to <i>k</i> ( <i>n</i> -butane) = 2.50 × 10 <sup>-12</sup> ]	Becker and Wirtz <sup>3</sup>	
CH <sub>3</sub> C(O)CH <sub>2</sub> ONO <sub>2</sub>			<0.44	298 ± 2	RR [relative to <i>k</i> ( <i>n</i> -butane) = 2.54 × 10 <sup>-12</sup> ]	Zhu <i>et al.</i> <sup>4</sup>	
CH <sub>3</sub> CH <sub>2</sub> C(O)CH <sub>2</sub> ONO <sub>2</sub>			0.907 ± 0.153	298 ± 2	RR [relative to <i>k</i> ( <i>n</i> -butane) = 2.54 × 10 <sup>-12</sup> ]	Zhu <i>et al.</i> <sup>4</sup>	
CH <sub>3</sub> CH(ONO <sub>2</sub> )C(O)CH <sub>3</sub>			1.27 ± 0.15	298 ± 2	RR [relative to <i>k</i> ( <i>n</i> -butane) = 2.54 × 10 <sup>-12</sup> ]	Zhu <i>et al.</i> <sup>4</sup>	
CH <sub>3</sub> CH(ONO <sub>2</sub> )CH <sub>2</sub> ONO <sub>2</sub>			<0.32	298 ± 2	RR [relative to <i>k</i> (propane) = 1.15 × 10 <sup>-12</sup> ]	Zhu <i>et al.</i> <sup>4</sup>	
CH <sub>3</sub> CH <sub>2</sub> CH(ONO <sub>2</sub> )CH <sub>2</sub> ONO <sub>2</sub>			1.70 ± 0.33	298 ± 2	RR [relative to <i>k</i> (propane) = 1.15 × 10 <sup>-12</sup> ]	Zhu <i>et al.</i> <sup>4</sup>	
CH <sub>3</sub> CH(ONO <sub>2</sub> )CH(ONO <sub>2</sub> )CH <sub>3</sub>			1.07 ± 0.26	298 ± 2	RR [relative to <i>k</i> (propane) = 1.15 × 10 <sup>-12</sup> ]	Zhu <i>et al.</i> <sup>4</sup>	
O <sub>2</sub> NOCH <sub>2</sub> CH=CHCH <sub>2</sub> ONO <sub>2</sub>			15.1 ± 1.6	298 ± 2	RR [relative to <i>k</i> (ethene) = 8.52 × 10 <sup>-12</sup> ]	Zhu <i>et al.</i> <sup>4</sup>	
O <sub>2</sub> NOCH <sub>2</sub> CH(ONO <sub>2</sub> )CH=CH <sub>2</sub>			10.1 ± 0.6	298 ± 2	RR [relative to <i>k</i> (ethene) = 8.52 × 10 <sup>-12</sup> ]	Zhu <i>et al.</i> <sup>4</sup>	
Methyl nitrite			0.26 ± 0.05	298 ± 2	PR-RA	Nielsen <i>et al.</i> <sup>5</sup>	298–393
			0.42 ± 0.03	323			
			0.74 ± 0.10	353			
			1.05 ± 0.10	393			
	100 ± 30 <sup>30</sup>	1764 ± 300	0.30 ± 0.10	298 ± 2	RR [relative to <i>k</i> (2-methylpropane) = 2.33 × 10 <sup>-12</sup> ]	Nielsen <i>et al.</i> <sup>5</sup>	
Ethyl nitrite			0.70 ± 0.11	298 ± 2	PR-RA	Nielsen <i>et al.</i> <sup>5</sup>	
			0.70 ± 0.15	298 ± 2	RR [relative to <i>k</i> (2-methylpropane) = 2.33 × 10 <sup>-12</sup> ]	Nielsen <i>et al.</i> <sup>5</sup>	
1-Propyl nitrite			1.20 ± 0.05	298 ± 2	PR-RA	Nielsen <i>et al.</i> <sup>5</sup>	
			1.10 ± 0.15	298 ± 2	RR [relative to <i>k</i> (2-methylpropane) = 2.33 × 10 <sup>-12</sup> ]	Nielsen <i>et al.</i> <sup>5</sup>	

TABLE 43. Rate constants  $k$  and temperature-dependent parameters at, or close to, the high-pressure limit for the gas-phase reactions of the OH radical with nitrogen-containing organics — Continued

Organic	$10^{12} \times A$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$B$ (K)	$10^{12} \times k$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	at $T$ (K)	Technique	Reference	Temperature range covered (K)
1-Butyl nitrite			2.72 ± 0.60	298 ± 2	PR-RA	Nielsen <i>et al.</i> <sup>5</sup>	
			2.26 ± 0.08	298 ± 2	RR [relative to $k(2\text{-methyl-propane}) = 2.33 \times 10^{-12}$ ] <sup>a</sup>	Nielsen <i>et al.</i> <sup>5</sup>	
1-Pentyl nitrite			4.25 ± 0.80	298 ± 2	PR-RA	Nielsen <i>et al.</i> <sup>5</sup>	
			3.72 ± 0.50	298 ± 2	RR [relative to $k(2\text{-methyl-propane}) = 2.33 \times 10^{-12}$ ] <sup>a</sup>	Nielsen <i>et al.</i> <sup>5</sup>	
Nitromethane			0.16 ± 0.05	295 ± 3	PR-RA	Nielsen <i>et al.</i> <sup>6</sup>	
			0.107 ± 0.010	295 ± 3	RR [relative to $k(2,2\text{-dimethylpropane})$ $= 8.26 \times 10^{-13}$ ] <sup>a</sup>	Nielsen <i>et al.</i> <sup>6</sup>	
			0.0158 ± 0.0009	298	FP-RF	Liu <i>et al.</i> <sup>7</sup>	298–400
			0.0321 ± 0.0057	400			
Nitromethane- $d_3$			0.10 ± 0.02	295 ± 3	PR-RA	Nielsen <i>et al.</i> <sup>6</sup>	
			0.087 ± 0.010	295 ± 3	RR [relative to $k(2,2\text{-dimethylpropane})$ $= 8.26 \times 10^{-13}$ ] <sup>a</sup>	Nielsen <i>et al.</i> <sup>6</sup>	
			0.0090 ± 0.0004	298	FP-RF	Liu <i>et al.</i> <sup>7</sup>	298–400
0.0119 ± 0.0003	400						
Nitroethane			0.15 ± 0.05	295 ± 3	PR-RA	Nielsen <i>et al.</i> <sup>6</sup>	
			0.145 ± 0.010	295 ± 3	RR [relative to $k(2,2\text{-dimethylpropane})$ $= 8.26 \times 10^{-13}$ ] <sup>a</sup>	Nielsen <i>et al.</i> <sup>6</sup>	
			0.0438 ± 0.003	253	FP-RF	Liu <i>et al.</i> <sup>7</sup>	253–400
			0.0722 ± 0.0082	298			
			0.100 ± 0.004	330			
			0.112 ± 0.009	350			
1.9 ± 0.5	960 ± 90	0.175 ± 0.007	400				
1-Nitropropane			0.34 ± 0.08	295 ± 3	PR-RA	Nielsen <i>et al.</i> <sup>6</sup>	
			0.533 ± 0.078	295 ± 3	RR [relative to $k(2,2\text{-dimethylpropane})$ $= 8.26 \times 10^{-13}$ ] <sup>a</sup>	Nielsen <i>et al.</i> <sup>6</sup>	

TABLE 43. Rate constants  $k$  and temperature-dependent parameters at, or close to, the high-pressure limit for the gas-phase reactions of the OH radical with nitrogen-containing organics — Continued

Organic	$10^{12} \times A$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$B$ (K)	$10^{12} \times k$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	at $T$ (K)	Technique	Reference	Temperature range covered (K)
	$3.7 \pm 0.2$	$690 \pm 17$	$0.207 \pm 0.016$	240	FP-RF	Liu <i>et al.</i> <sup>7</sup>	240–400
			$0.364 \pm 0.018$	298			
			$0.448 \pm 0.032$	330			
			$0.514 \pm 0.031$	350			
			$0.663 \pm 0.055$	400			
2-Nitropropane	$2.1 \pm 0.7$	$630 \pm 106$	$0.145 \pm 0.014$	240	FP-RF	Liu <i>et al.</i> <sup>7</sup>	240–400
			$0.259 \pm 0.011$	298			
			$0.314 \pm 0.020$	330			
			$0.322 \pm 0.015$	350			
			$0.439 \pm 0.018$	400			
1-Nitrobutane			$1.55 \pm 0.09$	$295 \pm 3$	PR-RA	Nielsen <i>et al.</i> <sup>6</sup>	
			$1.68 \pm 0.11$	$295 \pm 3$	RR [relative to $k(2,2\text{-dimethylpropane}) = 8.26 \times 10^{-13}$ ] <sup>a</sup>	Nielsen <i>et al.</i> <sup>6</sup>	
	$6.1 \pm 0.9$	$660 \pm 49$	$0.404 \pm 0.032$	240	FP-RF	Liu <i>et al.</i> <sup>7</sup>	240–400
			$0.658 \pm 0.042$	298			
			$0.790 \pm 0.074$	330			
			$0.930 \pm 0.054$	350			
			$1.20 \pm 0.06$	400			
1-Nitropentane			$3.30 \pm 0.05$	$295 \pm 3$	PR-RA	Nielsen <i>et al.</i> <sup>6</sup>	
			$3.17 \pm 0.15$	$295 \pm 3$	RR [relative to $k(2,2\text{-dimethylpropane}) = 8.26 \times 10^{-13}$ ] <sup>a</sup>	Nielsen <i>et al.</i> <sup>6</sup>	
	$10.9 \pm 1.7$	$710 \pm 47$	$0.574 \pm 0.033$	240	FP-RF	Liu <i>et al.</i> <sup>7</sup>	240–440
			$1.00 \pm 0.06$	298			
			$1.33 \pm 0.07$	330			
			$1.48 \pm 0.09$	350			
			$1.81 \pm 0.13$	400			
Nitroethene [CH <sub>2</sub> =CHNO <sub>2</sub> ]			$1.2 \pm 0.2$	$298 \pm 2$	PR-RA	Nielsen <i>et al.</i> <sup>8</sup>	
3-Nitropropene [CH <sub>2</sub> =CHCH <sub>2</sub> NO <sub>2</sub> ]			$12.2 \pm 2.1$	$298 \pm 2$	PR-RA	Nielsen <i>et al.</i> <sup>8</sup>	
1-Nitrocyclohexene			$43.7 \pm 4.3$	$298 \pm 2$	RR [relative to $k(\text{cis-2-butene}) = 5.64 \times 10^{-11}$ ] <sup>a</sup>	Nielsen <i>et al.</i> <sup>8</sup>	

TABLE 43. Rate constants  $k$  and temperature-dependent parameters at, or close to, the high-pressure limit for the gas-phase reactions of the OH radical with nitrogen-containing organics — Continued

Organic	$10^{12} \times A$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$B$ (K)	$10^{12} \times k$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	at $T$ (K)	Technique	Reference	Temperature range covered (K)
CH <sub>3</sub> CN			0.0138 ± 0.0008	256.5	LP-LIF	Hynes and Wine <sup>9</sup>	256–388
			0.0146 ± 0.0009	256.5			
			0.0199 ± 0.0013	273			
			0.0184 ± 0.0018	274.5			
			0.0188 ± 0.0024	274.5			
			0.0230 ± 0.0013	278			
			0.0248 ± 0.0038	298			
			0.0330 ± 0.0055	318			
			0.0315 ± 0.0013	318			
			0.0368 ± 0.0050	336			
			0.0361 ± 0.0091	338.5			
			0.0540 ± 0.007	345.5			
			0.0471 ± 0.0024	352.5			
			0.0507 ± 0.0019	366.5			
			0.0571 ± 0.0052	370.5			
0.0611 ± 0.0069	377						
0.0594 ± 0.0020	388						
CD <sub>3</sub> CN	1.1 ± 0.3	1130 ± 90	0.00941 ± 0.00041 <sup>b</sup>	256	LP-LIF	Hynes and Wine <sup>9</sup>	256–379
			0.0126 ± 0.0013 <sup>b</sup>	275			
			0.0216 ± 0.0011 <sup>b</sup>	298			
			0.0259 ± 0.0023 <sup>b</sup>	335			
			0.0364 ± 0.0051 <sup>b</sup>	358.5			
2-Vinylpyridine			56.7 ± 3.7	298 ± 2	RR [relative to $k(2\text{-methyl-1,3-butadiene})$ $= 1.01 \times 10^{-10}$ ] <sup>a</sup>	Tuazon <i>et al.</i> <sup>10</sup>	
(CH <sub>3</sub> ) <sub>2</sub> NC(O)SCH <sub>3</sub>			13.3 ± 0.6	298 ± 2	RR [relative to $k(\text{cyclohexane})$ $= 7.49 \times 10^{-12}$ ] <sup>a</sup>	Kwok <i>et al.</i> <sup>11</sup>	
(CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> NC(O)SCH <sub>2</sub> CH <sub>3</sub>			31.0 ± 2.9	298 ± 2	RR [relative to $k(\text{propene})$ $= 2.63 \times 10^{-11}$ ] <sup>a</sup>	Kwok <i>et al.</i> <sup>11</sup>	
			34.0 ± 3.8	298 ± 2	RR [relative to $k(2\text{-methyl-1,3-butadiene})$ $= 1.01 \times 10^{-10}$ ] <sup>a</sup>	Kwok <i>et al.</i> <sup>11</sup>	
CH <sub>3</sub> CH <sub>2</sub> ( <i>c</i> -C <sub>6</sub> H <sub>11</sub> )NC(O)SCH <sub>2</sub> CH <sub>3</sub>			35.4 ± 5.7	298 ± 2	RR [relative to $k(2\text{-methyl-1,3-butadiene})$ $= 1.01 \times 10^{-10}$ ] <sup>a</sup>	Kwok <i>et al.</i> <sup>11</sup>	

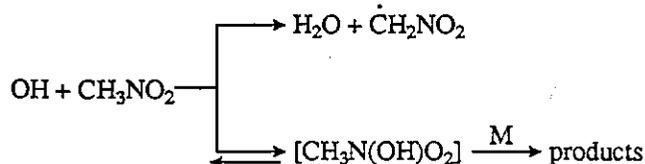
<sup>a</sup>From present and previous<sup>1</sup> recommendations.<sup>b</sup>At total pressures of N<sub>2</sub> ≥ 550 Torr.

## 3.8.3. Nitroalkanes

The absolute and relative rate constants determined by Nielsen *et al.*<sup>6</sup> at one atmosphere of argon or air and the absolute rate constants of Liu *et al.*,<sup>7</sup> obtained at total pressures of argon diluent of 25–50 Torr, are given in Table 43 (the absolute rate constants of Nielsen *et al.*<sup>6</sup> were included in the review of Atkinson,<sup>1</sup> but are included here for completeness). The data from this study of Nielsen *et al.*<sup>6</sup> supersede those reported earlier.<sup>21</sup>

The rate constants of Liu *et al.*<sup>7</sup> for CH<sub>3</sub>NO<sub>2</sub> are in reasonable agreement with the absolute rate constants of Zabarnick *et al.*,<sup>22</sup> and those of Liu *et al.*<sup>7</sup> for the nitroalkanes studied are generally significantly lower than the atmospheric pressure rate constants of Nielsen *et al.*<sup>6</sup> (Table 43). While these observations suggest an effect of total pressure on the rate constant, neither Zabarnick *et al.*<sup>22</sup> or Liu *et al.*<sup>7</sup> observed an effect of the pressure of the argon diluent on the measured rate constants over total pressure ranges of 100–300 Torr<sup>22</sup> and 25–50 Torr.<sup>7</sup>

Only for the reaction of the OH radical with 1-nitrobutane have studies been conducted at atmospheric pressure by more than one research group, and the rate constants of Atkinson and Aschmann<sup>14</sup> and Nielsen *et al.*<sup>6</sup> are in reasonable agreement. While definitive experimental evidence still remains to be obtained, the experimental data suggest that the rate constants for the reactions of the OH radical with the <C<sub>4</sub> nitroalkanes studied to date are pressure dependent at around room temperature, and that these reactions proceed by both H-atom abstraction and initial OH radical addition



Based on unit-weighted averages of the absolute and relative rate constants of Nielsen *et al.*<sup>6</sup> for nitromethane, nitromethane-*d*<sub>3</sub>, nitroethane, 1-nitropropane and 1-nitropentane, and of the rate constants of Atkinson and Aschmann<sup>14</sup> and Nielsen *et al.*<sup>6</sup> for 1-nitrobutane, the following recommendations are made for 298 K and 760 Torr total pressure of air:

$$k(\text{nitromethane}) = 1.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$k(\text{nitromethane-}d_3) = 9 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$k(\text{nitroethane}) = 1.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$k(1\text{-nitropropane}) = 4.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

all with estimated overall uncertainties of a factor of 2,

$$k(1\text{-nitrobutane}) = 1.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

and

$$k(1\text{-nitropentane}) = 3.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

both with estimated overall uncertainties of  $\pm 35\%$ .

## 3.8.4. Nitriles

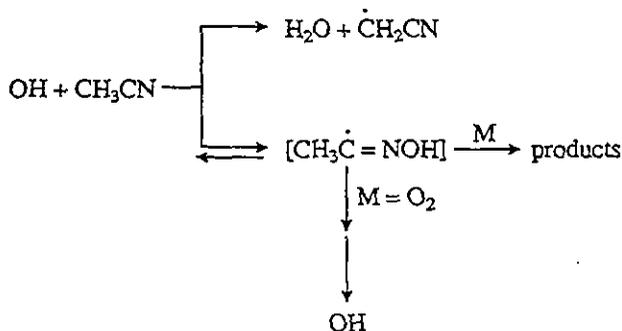
*Acetonitrile* (CH<sub>3</sub>CN). The absolute rate constants of Hynes and Wine<sup>9</sup> for the reactions of the OH radical with CH<sub>3</sub>CN and CD<sub>3</sub>CN are given in Table 43, and the rate constants for the reactions of the OD radical with CH<sub>3</sub>CN and CD<sub>3</sub>CN<sup>9</sup> are given in Table 44.

At 298 K, rate constants for the reaction of the OH radical with CH<sub>3</sub>CN were obtained over the total pressure range 46–700 Torr of N<sub>2</sub> and at 580–630 Torr total pressure of He. The measured rate constants were independent of total pressure within the experimental uncertainties, although a tendency for the rate constant to decrease for total pressures of N<sub>2</sub> of <100–200 Torr was observed.<sup>9</sup> In contrast, the rate constant for the reaction of the OH radical with CD<sub>3</sub>CN increased with increasing pressure at 298 K, from  $\sim 1.3 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at  $\sim 50$  Torr total pressure of N<sub>2</sub> to  $2.16 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 680 Torr total pressure of N<sub>2</sub>.<sup>9</sup> The 298 K rate constants for the reactions of the OD radical with CH<sub>3</sub>CN and CD<sub>3</sub>CN were observed to be independent of total pressure of N<sub>2</sub> diluent over the pressure range 50–700 Torr.<sup>9</sup> In the presence of O<sub>2</sub>, OH radical regeneration was observed<sup>9</sup> from both of the OH radical reactions with CH<sub>3</sub>CN and CD<sub>3</sub>CN, and similarly OD radical regeneration was observed from the reactions of the OD radical with both CH<sub>3</sub>CN and CD<sub>3</sub>CN.<sup>9</sup>

These data show that these reactions are complex,<sup>9</sup> with bimolecular and termolecular channels. The essential lack of deuterium isotope effects for the reactions of the OH radical with CH<sub>3</sub>CN and CD<sub>3</sub>CN also indicates that an addition reaction is important. It is possible that the reactions proceed by, for example,

TABLE 44. Rate constants *k* at, or close to, the high-pressure limit for the gas-phase reactions of the OD radical with nitrogen-containing organics

Organic	$10^{12} \times k(\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$	at <i>T</i> (K)	Technique	Reference
CH <sub>3</sub> CN	$0.0318 \pm 0.0040$	298	LP-LIF	Hynes and Wine <sup>9</sup>
CD <sub>3</sub> CN	$0.0225 \pm 0.0028$	298	LP-LIF	Hynes and Wine <sup>9</sup>



The rate constants of Hynes and Wine<sup>9</sup> for the reaction of the OH radical with CH<sub>3</sub>CN are plotted, together with those of Fritz *et al.*,<sup>23</sup> Zetzsch,<sup>24</sup> Kurylo and Knable<sup>25</sup> and Poulet *et al.*,<sup>26</sup> in Arrhenius form in Fig. 43 (the 100–300 Torr total pressure rate constant of Zetzsch<sup>24</sup> is plotted, since Zetzsch<sup>24</sup> also observed the rate constant to be pressure dependent, especially at total pressures (of argon) below 100 Torr). The agreement between these studies is reasonable.

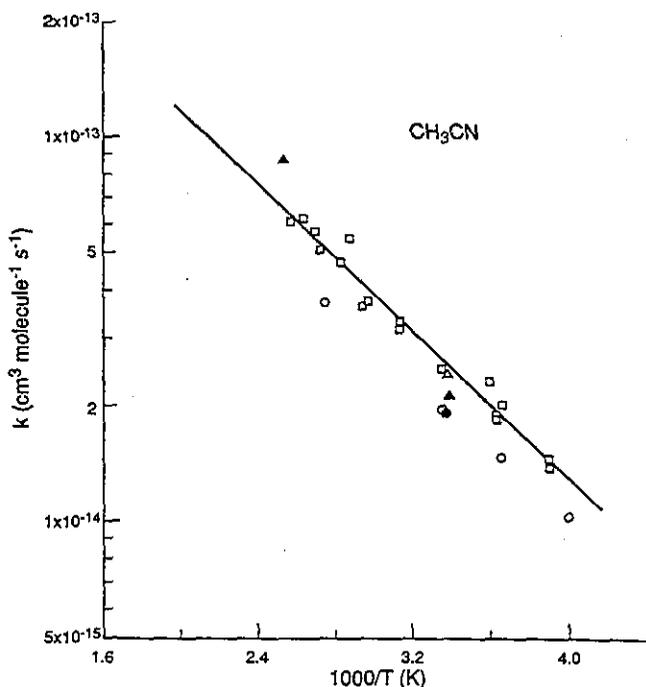


FIG. 43. Arrhenius plot of selected rate constants for the reaction of the OH radical with CH<sub>3</sub>CN. ( $\Delta$ ) Fritz *et al.*,<sup>23</sup> ( $\bullet$ ) Zetzsch<sup>24</sup> (for total pressures 100–300 Torr of argon); ( $\circ$ ) Kurylo and Knable;<sup>25</sup> ( $\blacktriangle$ ) Poulet *et al.*,<sup>26</sup> ( $\square$ ) Hynes and Wine;<sup>9</sup> (—) recommendation (see text).

Because of the much more extensive study of Hynes and Wine,<sup>9</sup> the data from that study are preferred, and a

unit-weighted least-squares analysis of the rate constants of Hynes and Wine<sup>9</sup> leads to the recommendation of

$$k(\text{CH}_3\text{CN}) = (1.08^{+0.33}_{-0.29}) \times 10^{-12} e^{-(1107 \pm 95)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 256–388 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{CH}_3\text{CN}) = 2.63 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

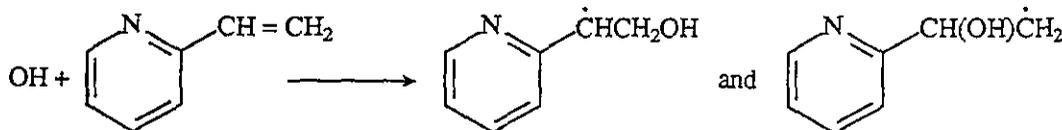
with an estimated overall uncertainty at 298 K of  $\pm 40\%$ . This recommended expression should not be used outside of the stated temperature range (256–388 K) or at total pressures  $\leq 100$  Torr.

### 3.8.5. Miscellaneous

*2-Vinylpyridine*. The rate constant of Tuazon *et al.*<sup>10</sup> is given in Table 43. The magnitude of the rate constant, when compared to that for pyridine,<sup>1</sup> and the product data of Tuazon *et al.*<sup>10</sup> show that the reaction proceeds by initial OH radical addition to the  $-\text{CH}=\text{CH}_2$  substituent group as shown below [Reaction Scheme (16)] with subsequent reactions of these initially formed radicals leading to the formation of 2-pyridinecarboxaldehyde with a yield of  $0.78 \pm 0.14$ .<sup>10</sup>

## References

- R. Atkinson, *J. Phys. Chem. Ref. Data Monograph* 1, 1 (1989).
- O. J. Nielsen, H. W. Sidebottom, M. Donlon, and J. Treacy, *Chem. Phys. Lett.* 178, 163 (1991).
- K. H. Becker and K. Wirtz, *J. Atmos. Chem.* 9, 419 (1989).
- T. Zhu, I. Barnes, and K. H. Becker, *J. Atmos. Chem.* 13, 301 (1991).
- O. J. Nielsen, H. W. Sidebottom, M. Donlon, and J. Treacy, *Int. J. Chem. Kinet.* 23, 1095 (1991).
- O. J. Nielsen, H. W. Sidebottom, D. J. O'Farrell, M. Donlon, and J. Treacy, *Chem. Phys. Lett.* 156, 312 (1989).
- R. Liu, R. E. Huie, M. J. Kurylo, and O. J. Nielsen, *Chem. Phys. Lett.* 167, 519 (1990).
- O. J. Nielsen, O. Jørgensen, M. Donlon, H. W. Sidebottom, D. J. O'Farrell, and J. Treacy, *Chem. Phys. Lett.* 168, 319 (1990).
- A. J. Hynes and P. H. Wine, *J. Phys. Chem.* 95, 1232 (1991).
- E. C. Tuazon, J. Arey, R. Atkinson, and S. M. Aschmann, *Environ. Sci. Technol.* 27, 1832 (1993).
- E. S. C. Kwok, R. Atkinson, and J. Arey, *Environ. Sci. Technol.* 26, 1798 (1992).
- J. A. Kerr and D. W. Stocker, *J. Atmos. Chem.* 4, 253 (1986).
- J. S. Gaffney, R. Fajer, G. I. Senum, and J. H. Lee, *Int. J. Chem. Kinet.* 18, 399 (1986).
- R. Atkinson and S. M. Aschmann, *Int. J. Chem. Kinet.* 21, 1123 (1989).



Reaction Scheme (16)

- <sup>15</sup>R. Atkinson, S. M. Aschmann, W. P. L. Carter, and A. M. Winer, *Int. J. Chem. Kinet.* **14**, 919 (1982).
- <sup>16</sup>R. Atkinson, S. M. Aschmann, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., *Int. J. Chem. Kinet.* **16**, 1085 (1984).
- <sup>17</sup>E. C. Tuazon, W. P. L. Carter, R. Atkinson, and J. N. Pitts, Jr., *Int. J. Chem. Kinet.* **15**, 619 (1983).
- <sup>18</sup>I. M. Campbell and K. Goodman, *Chem. Phys. Lett.* **36**, 382 (1975).
- <sup>19</sup>G. J. Audley, D. L. Baulch, I. M. Campbell, D. J. Waters, and G. Watling, *J. Chem. Soc. Faraday Trans. 1*, **78**, 611 (1982).
- <sup>20</sup>D. L. Baulch, I. M. Campbell, and S. M. Saunders, *Int. J. Chem. Kinet.* **17**, 355 (1985).
- <sup>21</sup>O. J. Nielsen, H. W. Sidebottom, D. J. O'Farrell, M. Donlon, and J. Treacy, *Chem. Phys. Lett.* **146**, 197 (1988).
- <sup>22</sup>S. Zabarnick, J. W. Fleming, and M. C. Lin, *Chem. Phys.* **120**, 319 (1988).
- <sup>23</sup>B. Fritz, K. Lorenz, W. Steinert, and R. Zellner, *Proc. 2nd European Symposium on the Physico-Chemical Behaviour of Atmospheric Pollutants*, D. Riedel Pub. Co., Dordrecht, The Netherlands, 1982, pp. 192-202.
- <sup>24</sup>C. Zetzsch, presented at Bunsen-Kolloquium, Frankfurt am Main, Germany, March 1983; data cited in Ref. 1.
- <sup>25</sup>M. J. Kurylo and G. L. Knable, *J. Phys. Chem.* **88**, 3305 (1984).
- <sup>26</sup>G. Poulet, G. Laverdet, J. L. Jourdain, and G. Le Bras, *J. Phys. Chem.* **88**, 6259 (1984).

### 3.9 Silicon-Containing Organic Compounds

The rate constants for the room temperature reactions of the OH radical with tetramethylsilane, a series of siloxanes and  $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_2\text{OH}$  determined by Atkinson<sup>1</sup> and Atkinson *et al.*<sup>2</sup> from relative rate studies are given in Table 45. The magnitude of these rate constants<sup>1,2</sup> indicates that these reactions proceed by H-atom abstraction:

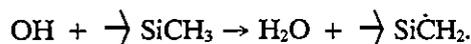


TABLE 45. Rate constants  $k$  for the gas-phase reactions of the OH radical with silicon-containing organic compounds

Organic	$10^{12} \times k$ ( $\text{cm}^3$ molecule <sup>-1</sup> s <sup>-1</sup> )	at $T$ (K)	Technique	Reference
Tetramethylsilane [(CH <sub>3</sub> ) <sub>4</sub> Si]	1.00 ± 0.09	297 ± 2	RR [relative to $k(\text{cyclohexane}) = 7.47 \times 10^{-12}$ ] <sup>a</sup>	Atkinson <sup>1</sup>
Hexamethyldisiloxane [(CH <sub>3</sub> ) <sub>3</sub> SiOSi(CH <sub>3</sub> ) <sub>3</sub> ]	1.38 ± 0.09	297 ± 2	RR [relative to $k(\text{cyclohexane}) = 7.47 \times 10^{-12}$ ] <sup>a</sup>	Atkinson <sup>1</sup>
Hexamethylcyclotrisiloxane [(−(CH <sub>3</sub> ) <sub>2</sub> SiO−) <sub>3</sub> ]	0.52 ± 0.11	297 ± 2	RR [relative to $k(\text{cyclohexane}) = 7.47 \times 10^{-12}$ ] <sup>a</sup>	Atkinson <sup>1</sup>
Octamethylcyclotetrasiloxane [(−CH <sub>3</sub> ) <sub>2</sub> SiO−] <sub>4</sub>	1.01 ± 0.20	297 ± 2	RR [relative to $k(\text{cyclohexane}) = 7.47 \times 10^{-12}$ ] <sup>a</sup>	Atkinson <sup>1</sup>
Decamethylcyclopentasiloxane [(−(CH <sub>3</sub> ) <sub>2</sub> SiO−) <sub>5</sub> ]	1.55 ± 0.30	297 ± 2	RR [relative to $k(\text{cyclohexane}) = 7.47 \times 10^{-12}$ ] <sup>a</sup>	Atkinson <sup>1</sup>
(CH <sub>3</sub> ) <sub>3</sub> SiOSi(CH <sub>3</sub> ) <sub>2</sub> OH	1.89 ± 0.36	297 ± 2	RR [relative to $k(\text{cyclohexane}) = 7.47 \times 10^{-12}$ ] <sup>a</sup>	Atkinson <i>et al.</i> <sup>2</sup>

<sup>a</sup>From present and previous<sup>3</sup> recommendations.

## References

- <sup>1</sup>R. Atkinson, *Environ. Sci. Technol.* **25**, 863 (1991).
- <sup>2</sup>R. Atkinson, S. M. Aschmann, and J. Arey, unpublished data (1993).
- <sup>3</sup>R. Atkinson, *J. Phys. Chem. Ref. Data Monograph* **1**, 1 (1989).

### 3.10. Selenium-Containing Organic Compounds

The room temperature rate constant determined for dimethyl selenide by Atkinson *et al.*<sup>1</sup> from a relative rate study is given in Table 46. The magnitude of this rate constant suggests that the reaction proceeds by initial addition of the OH radical to the Se atom,



where the products may include  $\text{H}_2\text{O} + \text{CH}_3\text{Se}\dot{\text{C}}\text{H}_2$ .

## References

- <sup>1</sup>R. Atkinson, S. M. Aschmann, D. Hasegawa, E. T. Thompson-Eagle, and W. T. Frankenberger, Jr., *Environ. Sci. Technol.* **24**, 1326 (1990).
- <sup>2</sup>R. Atkinson, *J. Phys. Chem. Ref. Data Monograph* **1**, 1 (1989).

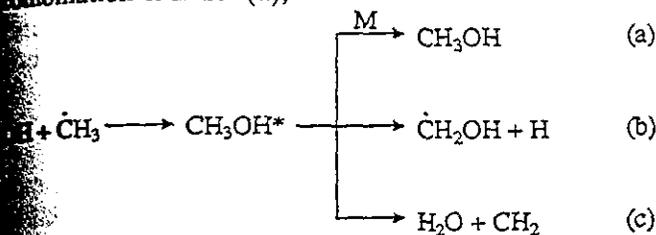
### 3.11. Aromatic Compounds

The rate constants reported since the review and evaluation of Atkinson<sup>1</sup> are given in Table 47. The study of Atkinson *et al.*<sup>7</sup> concerning the kinetics of the reactions of the OH radical with 1,4-benzodioxan, 2,3-dihydrobenzofuran and 2,3-benzofuran at  $298 \pm 2$  K, the data being given in the review of Atkinson,<sup>1</sup> has now been published.<sup>7</sup> In addition to the rate constants given in Table 47, Goumri *et al.*<sup>8</sup> have investigated the reaction of the OH radical with benzene at low total pressures (0.5–9 Torr) at  $297 \pm 3$  K and 353 K.

$k_a(\text{CH}_3) = 1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K,

which is applicable to a total pressure of air  $\geq 100$  Torr and has an estimated overall uncertainty of a factor of 2.

Bott and Cohen<sup>3</sup> derived a rate constant of  $(1.8 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 1212 K and  $\sim 800$  Torr total pressure of argon, and concluded that the major reaction pathway under the conditions employed was the combination channel (a),



with channels (b) and (c) possibly being of minor importance.

### References

- Anastasi, S. Beverton, T. Ellermann, and P. Pagsberg, *J. Chem. Soc. Faraday Trans. 87*, 2325 (1991).  
 Oser, N. D. Stothard, R. Humpfer, and H. H. Grotheer, *J. Phys. Chem. 96*, 5359 (1992).  
 F. Bott and N. Cohen, *Int. J. Chem. Kinet. 23*, 1017 (1991).  
 J. Sworski, C. J. Hochanadel and P. J. Ogren, *J. Phys. Chem. 84*, 129 (1980).

## 4. Kinetics and Mechanisms of the Gas-Phase Reactions of the $\text{NO}_3$ Radical with Organic Compounds

Recent kinetic and mechanistic data for the gas-phase reactions of the  $\text{NO}_3$  radical with organic compounds are presented and discussed in the following sections. Temperature-dependent rate constants are generally given in the recommendations using the Arrhenius expression  $k = A e^{-B/T}$ .

### 4.1. Alkanes

The rate constants reported since the previous review Atkinson<sup>1</sup> are given in Table 50 (the data of Bagley *et al.*<sup>3</sup> were reported in an Addendum in the Atkinson<sup>1</sup> review, but were not used in the recommendations). The

upper limits to the rate constants reported by Boyd *et al.*<sup>2</sup> for ethane, propane and 2-methylbutane were derived by assuming that the stoichiometry factors were  $\geq 2$  under the stopped-flow reaction conditions employed. For methane, no enhanced decay rate of the  $\text{NO}_3$  radical was observed,<sup>2</sup> and the upper limit reported was derived from the observed lack of an increased  $\text{NO}_3$  radical decay rate in the presence of methane.

**Ethane.** Absolute rate constants have been determined by Bagley *et al.*<sup>3</sup> over the temperature range 453–553 K, and an upper limit has been derived by Boyd *et al.*<sup>2</sup> at room temperature (Table 50). The extrapolated 298 K rate constant from the data of Bagley *et al.*<sup>3</sup> is  $2.0 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (subject to an uncertainty of a factor of  $\geq 2$ ), which is consistent with the upper limits to the rate constant of  $4 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  measured by Wallington *et al.*<sup>4</sup> (which may however be erroneously low due to removal of the ethane by reaction with  $\text{F}_2$  in the experimental system used) and  $2.9 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  by Boyd *et al.*<sup>2</sup> This extrapolated rate constant of Bagley *et al.*<sup>3</sup> of  $2.0 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K is also in reasonable agreement with the rate constant calculated using a group rate constant for H-atom abstraction from a  $-\text{CH}_3$  group of  $k_{\text{prim}} = 7.0 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K<sup>1</sup> [leading to  $k(\text{ethane}) = 1.4 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K]. However, Boyd *et al.*<sup>2</sup> also derived from modeling their data a lower limit to the rate constant of  $9 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 302 K, significantly higher than that obtained from extrapolation of the elevated temperature data of Bagley *et al.*<sup>3</sup> or the estimated<sup>1</sup> rate constant.

Because of the small, and elevated, temperature range for which apparently reliable absolute rate constants are available,<sup>3</sup> no recommendation is made for this reaction. The previously derived 298 K  $-\text{CH}_3$  group rate constant<sup>1</sup> of  $k_{\text{prim}} = 7.0 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  is unchanged.

**n-Butane.** The rate constants measured by Bagley *et al.*<sup>3</sup> over the temperature range 298–523 K are given in Table 50. The 298 K rate constant of Bagley *et al.*<sup>3</sup> of  $(4.5 \pm 0.6) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  is in agreement within the error limits with the relative rate constant of Atkinson *et al.*<sup>5</sup> of  $(6.6 \pm 1.7) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  but is a factor of  $\sim 2$  higher than the upper limit reported by Wallington *et al.*<sup>4</sup> At temperatures  $> 423$  K the Arrhenius plot exhibits upward curvature, especially above

TABLE 49. Rate constants  $k$  for the gas-phase reactions of the OH radical with organic radicals at  $\sim 1$  atmosphere total pressure

Organic radical	$10^{12} \times k$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	at $T$ (K)	Technique	Reference
	$94 \pm 13^a$	294	PR-Modeling	Anastasi <i>et al.</i> <sup>1</sup>
	$18 \pm 5^b$	1212	SH-RA	Bott and Cohen <sup>3</sup>

<sup>a</sup> 250 Torr total pressure of argon diluent.

<sup>b</sup>  $\sim 800$  Torr total pressure of argon.

TABLE 50. Rate constants  $k$  and temperature-dependent parameters,  $k = Ae^{-B/T}$ , for the gas-phase reactions of the  $\text{NO}_3$  radical with alkanes

Alkane	$10^{12} \times A$ ( $\text{cm}^3$ $\text{molecule}^{-1} \text{s}^{-1}$ )	$B$ (K)	$k$ ( $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ )	at $T$ (K)	Technique	Reference	Temperature range covered (K)
Methane			$\leq 8 \times 10^{-19}$	302	SF-A	Boyd <i>et al.</i> <sup>2</sup>	
Ethane	$5.7 \pm 4.0$	$4426 \pm 337$	$(3.0 \pm 0.5) \times 10^{-16}$ $(4.7 \pm 0.8) \times 10^{-16}$ $(1.4 \pm 0.3) \times 10^{-15}$ $(1.6 \pm 0.3) \times 10^{-15}$	453 473 523 553	DF-A	Bagley <i>et al.</i> <sup>3</sup>	453-553
Propane			$\leq 2.9 \times 10^{-17}$ $\leq 6.5 \times 10^{-17}$	302 298	SF-A SF-A	Boyd <i>et al.</i> <sup>2</sup> Boyd <i>et al.</i> <sup>2</sup>	
<i>n</i> -Butane			$(4.5 \pm 0.6) \times 10^{-17}$ $(1.44 \pm 0.12) \times 10^{-16}$ $(4.6 \pm 1.2) \times 10^{-16}$ $(1.12 \pm 0.12) \times 10^{-15}$ $(3.2 \pm 0.3) \times 10^{-15}$ $(9.0 \pm 0.4) \times 10^{-15}$	298 333 373 423 473 523	DF-A	Bagley <i>et al.</i> <sup>3</sup>	298-523
2-Methylpropane			$(1.1 \pm 0.2) \times 10^{-16}$ $(4.5 \pm 1.6) \times 10^{-16}$ $(8.0 \pm 0.8) \times 10^{-16}$ $(2.3 \pm 0.4) \times 10^{-15}$ $(5.4 \pm 1.2) \times 10^{-15}$ $(1.30 \pm 0.24) \times 10^{-14}$ $\leq 7.0 \times 10^{-16}$	298 348 373 423 473 523 298	DF-A SF-A	Bagley <i>et al.</i> <sup>3</sup> Boyd <i>et al.</i> <sup>2</sup>	298-523
2-Methylbutane			$(1.6 \pm 0.2) \times 10^{-16}$ $(3.9 \pm 1.4) \times 10^{-16}$ $(1.04 \pm 0.12) \times 10^{-15}$ $(2.5 \pm 0.4) \times 10^{-15}$ $(6.1 \pm 1.4) \times 10^{-15}$ $(1.29 \pm 0.37) \times 10^{-14}$	298 323 373 423 473 523	DF-A	Bagley <i>et al.</i> <sup>3</sup>	298-523

473 K.<sup>3</sup> A unit-weighted least-squares analysis of the absolute rate constants of Bagley *et al.*<sup>3</sup> obtained over the restricted temperature range 298–423 K yields the recommended Arrhenius expression of

$$k(n\text{-butane}) = (2.76 \pm_{-1.28}^{+2.30}) \times 10^{-12} e^{-(3279 \pm 211)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 298–423 K, where the indicated errors are two least-squares standard deviations, and

$$k(n\text{-butane}) = 4.59 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of a factor of 1.5. While the relative rate constant of Atkinson *et al.*<sup>5</sup> is in reasonable agreement with this recommendation, it is possible that the rate constant of Atkinson *et al.*<sup>5</sup> is somewhat high<sup>1</sup> due to secondary reactions involving OH radicals.<sup>6</sup>

**2-Methylpropane.** The rate constants determined by Bagley *et al.*<sup>3</sup> over the temperature range 298–523 K are given in Table 50, and are plotted in Arrhenius form in Fig. 44 together with the room temperature relative rate constant of Atkinson *et al.*<sup>5</sup> In addition, Boyd *et al.*<sup>2</sup> derived an upper limit to the rate constant of  $7.0 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K, consistent with the data of Bagley *et al.*<sup>3</sup> and Atkinson *et al.*<sup>5</sup> The room temperature rate constants of Atkinson *et al.*<sup>5</sup> and Bagley *et al.*<sup>2</sup> are in excellent agreement. Since the Arrhenius plot appears to exhibit a significant degree of curvature at temperatures >423 K, a unit-weighted least-squares analysis of the room temperature relative rate constant of Atkinson *et al.*<sup>5</sup> and the 298–423 K absolute rate constants of Bagley *et al.*<sup>3</sup> has been carried out to yield the recommended Arrhenius expression of

$$k(2\text{-methylpropane}) = (3.05 \pm_{-0.9\%}^{+1.0\%}) \times 10^{-12} e^{-(3060 \pm 99)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 296–423 K, where the indicated errors are two least-squares standard deviations, and

$$k(2\text{-methylpropane}) = 1.06 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of  $\pm 40\%$ .

**Other Alkanes.** The upper limit to the rate constant for the reaction of the NO<sub>3</sub> radical with methane of  $8 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 302 K reported by Boyd *et al.*<sup>2</sup> is consistent with the upper limit to the rate constant recommended by Atkinson<sup>1</sup> of  $1 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K. Since only a single study has been carried out for 2-methylbutane,<sup>3</sup> no recommendation is made for this reaction. However, the measured 298 K rate constant<sup>3</sup> of  $(1.6 \pm 0.2) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  is totally consistent with the rate constants for H-atom abstraction from primary, secondary and tertiary C–H bonds derived by

Bagley *et al.*<sup>3</sup> from their rate data for ethane, *n*-butane and 2-methylpropane, and is in excellent agreement with the rate constant of  $1.5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  calculated from the –CH<sub>3</sub>, –CH<sub>2</sub>– and >CH– group rate constants derived by Atkinson<sup>1</sup>. Moreover, the predicted 298 K rate constants for *n*-butane and 2-methylpropane of  $4.7 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $8.5 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively, are in good agreement with the recommended values, and the calculated rate constant for propane of  $1.7 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K<sup>1</sup> is reasonably consistent with the lower limit to the rate constant of  $2.0 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K derived by Boyd *et al.*<sup>2</sup> from modeling their data. These observations indicate that the group rate constants at 298 K (in  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  units) of:  $k_{\text{prim}} = 7.0 \times 10^{-19}$ ,  $k_{\text{sec}} = 1.5 \times 10^{-17}$ , and  $k_{\text{tert}} = 8.2 \times 10^{-17}$ , together with the substituent factors of  $F(-\text{CH}_3) = 1.00$  and  $F(-\text{CH}_2-) = F(>\text{CH}-) = F(>\text{C}<) = 1.5$ , all at 298 K, can be used to calculate room temperature rate constants for the gas-phase reactions of the NO<sub>3</sub> radical with alkanes. In addition to allowing the overall reaction rate constants to be calculated, the distribution of alkyl radicals formed can be calculated.

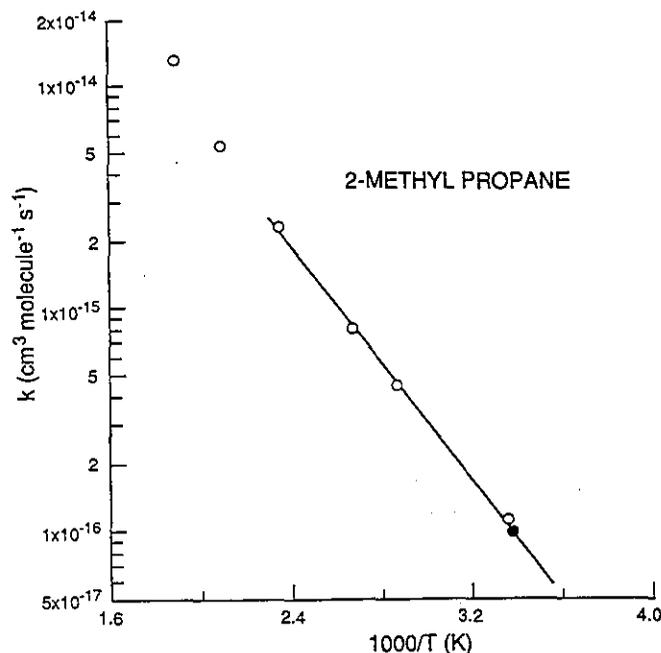


FIG. 44. Arrhenius plot of rate constants for the reaction of the NO<sub>3</sub> radical with 2-methylpropane. (○) Bagley *et al.*<sup>3</sup> (●) Atkinson *et al.*<sup>5</sup> (—) recommendation (see text).

## References

- <sup>1</sup>R. Atkinson, *J. Phys. Chem. Ref. Data* **20**, 459 (1991).
- <sup>2</sup>A. A. Boyd, C. E. Canosa-Mas, A. D. King, R. P. Wayne, and M. R. Wilson, *J. Chem. Soc. Faraday Trans.* **87**, 2913 (1991).
- <sup>3</sup>J. A. Bagley, C. Canosa-Mas, M. R. Little, A. D. Parr, S. J. Smith, S. J. Waygood, and R. P. Wayne, *J. Chem. Soc. Faraday Trans.* **86**, 2109 (1990).
- <sup>4</sup>T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., *J. Phys. Chem.* **90**, 4640 (1986).

<sup>5</sup>R. Atkinson, C. N. Plum, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., *J. Phys. Chem.* **88**, 2361 (1984).

<sup>6</sup>R. Atkinson, S. M. Aschmann, and J. N. Pitts, Jr., *J. Phys. Chem.* **92**, 3454 (1988).

## 4.2. Haloalkanes

The kinetic data reported since the review of Atkinson<sup>1</sup> are given in Table 51. The upper limits to the rate constants obtained by Boyd *et al.*<sup>2</sup> using a stopped flow system with optical absorption of the NO<sub>3</sub> radical assumed a minimum stoichiometric factor of 2 for reactions of the NO<sub>3</sub> radical under these conditions.

## References

<sup>1</sup>R. Atkinson, *J. Phys. Chem. Ref. Data* **20**, 459 (1991).

<sup>2</sup>A. A. Boyd, C. E. Canosa-Mas, A. D. King, R. P. Wayne, and M. R. Wilson, *J. Chem. Soc. Faraday Trans.* **87**, 2913 (1991).

## 4.3. Alkenes

The rate constants reported since the review and evaluation of Atkinson<sup>1</sup> are given in Table 52, with the data of Wille *et al.*<sup>6</sup> being obtained from observation of the oxirane product formation profiles. The rate constants for the reactions of the NO<sub>3</sub> radical with 2,3-dimethyl-2-butene, 1,3-butadiene, 2-methyl-1,3-butadiene (isoprene) and 2,3-dimethyl-1,3-butadiene reported by Poulet and Le Bras,<sup>10</sup> and used by Atkinson<sup>1</sup> in the evaluations of the rate constants for these reactions, have been published<sup>8,11</sup> (that for isoprene is included in the publication of Wille *et al.*<sup>6</sup> and is also given in Table 52).

*Ethene.* The room temperature rate constant of Biggs *et al.*,<sup>2</sup> of  $(1.7 \pm 0.5) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 300 K, is given in Table 52. This rate constant is in reasonable agreement with the recommended rate constant of Atkinson<sup>1</sup> of  $2.18 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at this temperature. Hence the previous recommendation,<sup>1</sup> of

$$k(\text{ethene}) = 4.88 \times 10^{-18} T^2 e^{-2282/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 295–523 K, with a 298 K rate constant of  $2.05 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , is unchanged.

*Propene.* The absolute rate constants of Canosa-Mas *et al.*<sup>3</sup> are given in Table 52 and are plotted, together with the room temperature relative rate constant of Atkinson *et al.*,<sup>12</sup> in Arrhenius form in Fig. 45. The agreement be-

tween the room temperature rate constants<sup>3,12</sup> is excellent. The Arrhenius plot exhibits distinct non-Arrhenius behavior above 423 K, and a unit-weighted least-squares analysis of the 298–423 K absolute rate constants of Canosa-Mas *et al.*<sup>3</sup> and the relative rate constant of Atkinson *et al.*<sup>12</sup> leads to the recommended Arrhenius expression of

$$k(\text{propene}) = (4.59 \pm_{-0.9\%}^{+1.22}) \times 10^{-13} e^{-(1156 \pm 79)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 296–423 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{propene}) = 9.49 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of  $\pm 35\%$ . This recommendation is in excellent agreement with, but supersedes, that of Atkinson<sup>1</sup> of

$$k(\text{propene}) = 9.45 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

*1-Butene.* The absolute rate constants of Canosa-Mas *et al.*<sup>4</sup> are given in Table 52 and are plotted, together with those of Atkinson *et al.*,<sup>12,13</sup> Andersson and Ljungström<sup>14</sup> and Barnes *et al.*,<sup>15</sup> in Arrhenius form in Fig. 46. The agreement between these studies is good, and a unit-weighted least-squares analysis of the absolute rate constants of Canosa-Mas *et al.*<sup>4</sup> and the relative rate constants of Atkinson *et al.*<sup>12,13</sup> and Barnes *et al.*<sup>15</sup> leads to the recommended Arrhenius expression of

$$k(1\text{-butene}) = (2.04 \pm_{-0.70\%}^{+1.06}) \times 10^{-13} e^{-(843 \pm 139)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 296–473 K, where the indicated errors are two least-squares standard deviations, and

$$k(1\text{-butene}) = 1.21 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of  $\pm 30\%$ . This recommendation is in excellent agreement with, but supersedes, that of Atkinson<sup>1</sup> of

$$k(1\text{-butene}) = 1.25 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

TABLE 51. Rate constants for the gas-phase reactions of the NO<sub>3</sub> radical with haloalkanes

Haloalkane	$k$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	at $T$ (K)	Technique	Reference
CH <sub>3</sub> Cl	$\leq 8 \times 10^{-19}$	300	SF-A	Boyd <i>et al.</i> <sup>2</sup>
CH <sub>2</sub> Cl <sub>2</sub>	$\leq 5.8 \times 10^{-18}$	300	SF-A	Boyd <i>et al.</i> <sup>2</sup>
CHCl <sub>3</sub>	$\leq 6.5 \times 10^{-17}$	304	SF-A	Boyd <i>et al.</i> <sup>2</sup>

TABLE 52. Rate constants and temperature-dependent parameters for the gas-phase reactions of the NO<sub>3</sub> radical with alkenes

Alkene	$10^{12} \times A$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$B$ (K)	$k$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	at $T$ (K)	Technique	Reference	Temperature range covered (K)
Ethene			$(1.7 \pm 0.5) \times 10^{-16}$	300	SF-A	Biggs <i>et al.</i> <sup>2</sup>	
Propene			$(9.3 \pm 1.2) \times 10^{-15}$	298	DF-A	Canosa-Mas <i>et al.</i> <sup>3</sup>	298–523
			$(1.45 \pm 0.36) \times 10^{-14}$	333			
			$(1.98 \pm 0.44) \times 10^{-14}$	373			
			$(3.06 \pm 0.84) \times 10^{-14}$	423			
			$(5.05 \pm 0.34) \times 10^{-14}$	473			
	$0.474 \pm 0.108$	$1171 \pm 66$ (298–423 K)	$(9.3 \pm 2.4) \times 10^{-14}$	523			
1-Butene			$(1.1 \pm 0.2) \times 10^{-14}$	299	DF-A	Canosa-Mas <i>et al.</i> <sup>4</sup>	299–473
			$(1.6 \pm 0.5) \times 10^{-14}$	323			
			$(1.8 \pm 0.4) \times 10^{-14}$	373			
			$(2.9 \pm 1.0) \times 10^{-14}$	423			
		0.25	940	$(3.6 \pm 0.8) \times 10^{-14}$			
2-Methylpropene			$(3.87 \pm 0.42) \times 10^{-13}$	298	DF-MS	Benter <i>et al.</i> <sup>5</sup>	
			$(3.6 \pm 0.4) \times 10^{-13}$	298	DF-MS	Wille <i>et al.</i> <sup>6</sup>	
<i>cis</i> -2-Butene			$(3.75 \pm 0.24) \times 10^{-13}$	298	DF-MS	Benter <i>et al.</i> <sup>5</sup>	
			$(3.3 \pm 0.8) \times 10^{-13}$	298	DF-MS	Wille <i>et al.</i> <sup>6</sup>	
<i>trans</i> -2-Butene			$(3.88 \pm 0.30) \times 10^{-13}$	298	DF-MS	Benter <i>et al.</i> <sup>5</sup>	
2-Methyl-2-butene			$(8.42 \pm 0.60) \times 10^{-12}$	298	DF-MS	Benter <i>et al.</i> <sup>5</sup>	
			$(7.0 \pm 2.0) \times 10^{-12}$	298	DF-MS	Wille <i>et al.</i> <sup>6</sup>	
2,3-Dimethyl-2-butene			$(4.07 \pm 0.40) \times 10^{-11}$	298	DF-MS	Benter <i>et al.</i> <sup>5</sup>	
			$(3.8 \pm 0.8) \times 10^{-11}$	298	DF-MS	Wille <i>et al.</i> <sup>6</sup>	
			$(5.71 \pm 0.28) \times 10^{-11}$	296 ± 2	RR [relative to $k$ (2-methyl-2-butene) = $9.37 \times 10^{-12}$ ] <sup>a</sup>	Atkinson <i>et al.</i> <sup>7</sup>	
2-Methyl-1,3-butadiene (isoprene)			$(8.26 \pm 0.60) \times 10^{-13}$	298	DF-MS	Wille <i>et al.</i> <sup>8</sup>	
			$(7.30 \pm 0.44) \times 10^{-13}$	298	DF-MS	Wille <i>et al.</i> <sup>8</sup>	
$\beta$ -Phellandrene			$(7.96 \pm 0.44) \times 10^{-12}$	297 ± 2	RR [relative to $k$ (2-methyl-2-butene) = $9.37 \times 10^{-12}$ ] <sup>a</sup>	Shorees <i>et al.</i> <sup>9</sup>	

<sup>a</sup>From present and previous<sup>1</sup> recommendations.

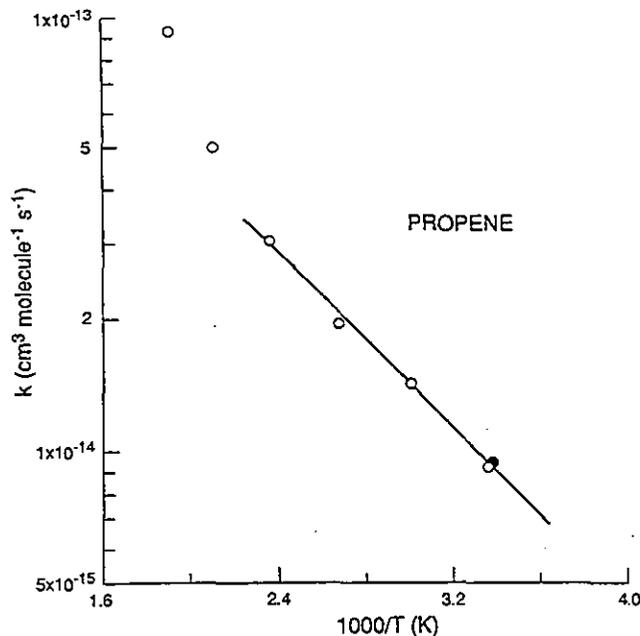


FIG. 45. Arrhenius plot of selected rate constants for the reaction of the  $\text{NO}_3$  radical with propene. (●) Atkinson *et al.*,<sup>12</sup> (○) Canosa-Mas *et al.*,<sup>3</sup> (—) recommendation (see text).

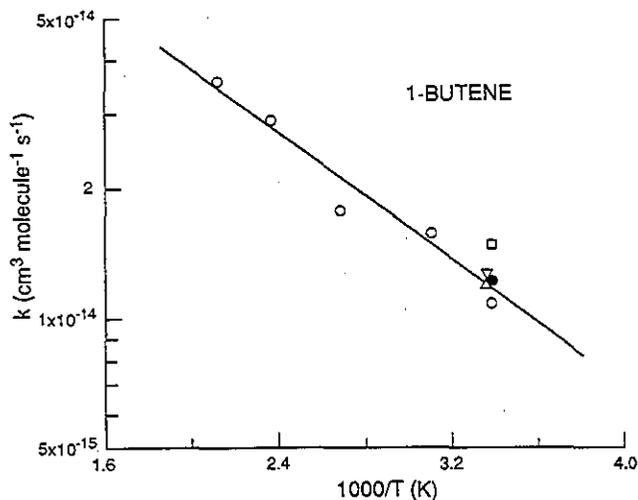


FIG. 46. Arrhenius plot of selected rate constants for the reaction of the  $\text{NO}_3$  radical with 1-butene. ( $\Delta$ ) Atkinson *et al.*,<sup>13</sup> (●) Atkinson *et al.*,<sup>12</sup> ( $\square$ ) Andersson and Ljungström,<sup>14</sup> ( $\nabla$ ) Barnes *et al.*,<sup>15</sup> (○) Canosa-Mas *et al.*,<sup>4</sup> (—) recommendation (see text).

**2-Methylpropene.** The rate constants determined by Benter *et al.*<sup>5</sup> and Wille *et al.*<sup>6</sup> (the latter from the oxirane product formation rate) are given in Table 52. These rate constants<sup>5,6</sup> are in good agreement with the previous recommendation of Atkinson<sup>1</sup> of

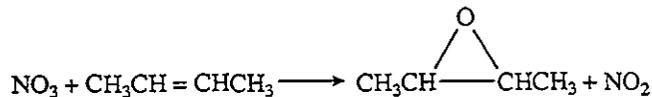
$$k(2\text{-methylpropene}) = 3.32 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

which is therefore unchanged.

**cis-2-Butene.** The rate constants determined by Benter *et al.*<sup>5</sup> and Wille *et al.*<sup>6</sup> (the latter from the oxirane product formation rate) are given in Table 52. These rate constants<sup>5,6</sup> are in excellent agreement with the previous recommendation of Atkinson<sup>1</sup> of

$$k(\text{cis-2-butene}) = 3.50 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

which is therefore unchanged. Wille *et al.*<sup>6</sup> showed that at 298 K and 2.2–7.5 Torr total pressure that the pathway



accounted for  $90 \pm 10\%$  of the overall reaction. This observation is in agreement with the previous results of Diugokencky and Howard<sup>16</sup> for the  $\text{NO}_3$  radical reaction with *trans*-2-butene at low total pressures.

**trans-2-Butene.** The rate constant reported by Benter *et al.*<sup>5</sup> is given in Table 52. This rate constant is in excellent agreement with the previous recommendation of Atkinson<sup>1</sup> of

$$k(\text{trans-2-butene}) = 3.90 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

which is therefore unchanged.

**2-Methyl-2-butene.** The rate constants reported by Benter *et al.*<sup>5</sup> and Wille *et al.*<sup>6</sup> (the latter from the oxirane product formation rate) are given in Table 52. The more precise rate constant of Benter *et al.*<sup>5</sup> is 20% lower than the previous recommendation of Atkinson<sup>1</sup> of

$$k(2\text{-methyl-2-butene}) = 9.37 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K. Until further absolute rate constant studies confirm a lower rate constant for this reaction, the previous recommendation<sup>1</sup> is unchanged.

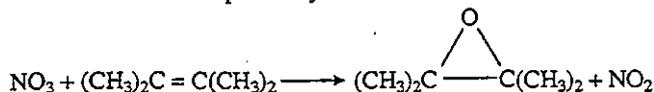
**2,3-Dimethyl-2-butene.** The rate constants obtained by Benter *et al.*<sup>5</sup> and Wille *et al.*<sup>6</sup> at low total pressures (2.3 Torr) are given in Table 52 (the rate constant of Wille *et al.*<sup>6</sup> was obtained from the oxirane product formation rate). These absolute rate constants<sup>5,6</sup> are  $\sim 30\%$  lower than the previous recommendation of Atkinson<sup>1</sup> of

$$k(2,3\text{-dimethyl-2-butene}) = 5.72 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

In contrast, the relative rate constant of Atkinson *et al.*<sup>7</sup> is in excellent agreement with the previous recommendation of Atkinson.<sup>1</sup>

However, the rate constants of Benter *et al.*<sup>5</sup> and Wille *et al.*<sup>6</sup> are in good agreement with the previously reported low pressure absolute rate constants of Rahman *et al.*<sup>17</sup> and Lancar *et al.*,<sup>11</sup> also obtained using discharge flow-mass spectrometry techniques. Until this discrepancy is resolved, possibly through the use of other experimental approaches, the previous recommendation is unchanged.

It should also be noted that the rate constant ratio of  $k(2,3\text{-dimethyl-2-butene})/k(2\text{-methyl-2-butene}) = 4.83 \pm 0.59$  at 298 K derived from the rate constants of Benter *et al.*<sup>5</sup> is significantly lower than the ratios of  $6.10 \pm 0.16$  at  $298 \pm 1$  K,<sup>13</sup>  $6.13 \pm 0.16$  at  $295 \pm 1$  K<sup>18</sup> and  $6.09 \pm 0.29$  at  $296 \pm 2$  K<sup>7</sup> obtained by Atkinson *et al.*<sup>7,13,18</sup> from relative rate studies conducted at atmospheric pressure of air. Wille *et al.*<sup>6</sup> observed the formation of the oxirane from the reaction pathway



to account for  $90 \pm 10\%$  of the overall reaction.

*2-Methyl-1,3-butadiene (isoprene)*. The rate constants reported by Wille *et al.*<sup>8</sup> at 298 K originate from studies conducted at two laboratories, with that of Lancar *et al.*<sup>11</sup> being reported previously<sup>10</sup> and used in the review and evaluation of Atkinson.<sup>1</sup> The rate constant determined at Kiel, Germany<sup>8</sup> of  $(7.30 \pm 0.44) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K is in good agreement with the recommendation of Atkinson<sup>1</sup> of

$$k(\text{isoprene}) = 6.78 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

and hence this previous recommendation<sup>1</sup> of

$$k(\text{isoprene}) = 3.03 \times 10^{-12} e^{-446/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 251–381 K is unchanged.

## References

- <sup>1</sup>R. Atkinson, *J. Phys. Chem. Ref. Data* **20**, 459 (1991).
- <sup>2</sup>P. Biggs, A. A. Boyd, C. E. Canosa-Mas, D. M. Joseph, and R. P. Wayne, *Meas. Sci. Technol.* **2**, 675 (1991).
- <sup>3</sup>C. E. Canosa-Mas, S. J. Smith, S. J. Waygood, and R. P. Wayne, *J. Chem. Soc. Faraday Trans.* **87**, 3473 (1991).
- <sup>4</sup>C. E. Canosa-Mas, P. S. Monks, and R. P. Wayne, *J. Chem. Soc. Faraday Trans.* **88**, 11 (1992).
- <sup>5</sup>Th. Benter, E. Becker, U. Wille, M. M. Rahman, and R. N. Schindler, *Ber. Bunsenges. Phys. Chem.* **96**, 769 (1992).
- <sup>6</sup>U. Wille, M. M. Rahman, and R. N. Schindler, *Ber. Bunsenges. Phys. Chem.* **96**, 833 (1992).
- <sup>7</sup>R. Atkinson, S. M. Aschmann, and J. Arey, *Environ. Sci. Technol.* **26**, 1397 (1992).
- <sup>8</sup>U. Wille, E. Becker, R. N. Schindler, I. T. Lancar, G. Poulet, and G. Le Bras, *J. Atmos. Chem.* **13**, 183 (1991).
- <sup>9</sup>B. Shorees, R. Atkinson, and J. Arey, *Int. J. Chem. Kinet.* **23**, 897 (1991).
- <sup>10</sup>G. Poulet and G. Le Bras, 2nd LACTOZ Report (a joint EUROTRAC/Cost 611 project), 1989; cited in Ref. 1.
- <sup>11</sup>I. T. Lancar, V. Daele, G. Le Bras, and G. Poulet, *J. Chim. Phys.* **88**, 1777 (1991).
- <sup>12</sup>R. Atkinson, S. M. Aschmann, and J. N. Pitts, Jr., *J. Phys. Chem.* **92**, 3454 (1988).
- <sup>13</sup>R. Atkinson, C. N. Plum, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., *J. Phys. Chem.* **88**, 1210 (1984).
- <sup>14</sup>Y. Andersson and E. Ljungström, *Atmos. Environ.* **23**, 1153 (1989).
- <sup>15</sup>I. Barnes, V. Bastian, K. H. Becker, and Z. Tong, *J. Phys. Chem.* **94**, 2413 (1990).
- <sup>16</sup>E. J. Dlugokencky and C. J. Howard, *J. Phys. Chem.* **93**, 1091 (1989).
- <sup>17</sup>M. M. Rahman, E. Becker, Th. Benter, and R. N. Schindler, *Ber. Bunsenges. Phys. Chem.* **92**, 91 (1988).

<sup>18</sup>R. Atkinson, S. M. Aschmann, A. M. Winer, and J. N. Pitts, Jr., *Environ. Sci. Technol.* **18**, 370 (1984).

## 4.4. Haloalkenes

The rate constants reported since the review and evaluation of Atkinson<sup>1</sup> are given in Table 53 (the data of Wängberg *et al.*<sup>3</sup> were included in the Addendum in Atkinson<sup>1</sup>). The rate constants for the reaction of the  $\text{NO}_3$  radical with 2-chloro-1-butene at room temperature<sup>2,3</sup> are in good agreement. The trends in the rate constants for the reactions of the  $\text{NO}_3$  radical with haloalkenes with the number and configuration of the halogen substituent(s) around the  $>\text{C}=\text{C}<$  bond are discussed by Aird *et al.*<sup>2</sup>

## References

- <sup>1</sup>R. Atkinson, *J. Phys. Chem. Ref. Data* **20**, 459, (1991).
- <sup>2</sup>R. W. S. Aird, C. E. Canosa-Mas, D. J. Cook, G. Marston, P. S. Monks, R. P. Wayne, and E. Ljungström, *J. Chem. Soc. Faraday Trans.* **88**, 1093 (1992).
- <sup>3</sup>I. Wängberg, E. Ljungström, J. Hjorth and G. Ottobri, *J. Phys. Chem.* **94**, 8036 (1990).

## 4.5. Alkynes

The rate constants reported since the review and evaluation of Atkinson<sup>1</sup> are given in Table 54.

## References

- <sup>1</sup>R. Atkinson, *J. Phys. Chem. Ref. Data* **20**, 459 (1991).
- <sup>2</sup>Th. Benter, E. Becker, U. Wille, R. N. Schindler, C. E. Canosa-Mas, S. J. Smith, S. J. Waygood, and R. P. Wayne, *J. Chem. Soc. Faraday Trans.* **87**, 2141 (1991).

## 4.6. Oxygen-Containing Organic Compounds

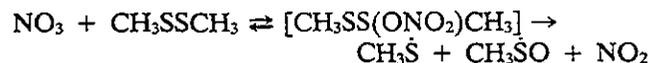
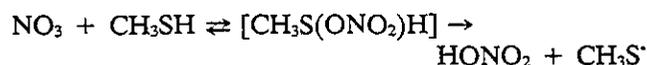
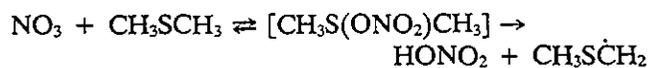
The kinetic data reported since the review and evaluation of Atkinson<sup>1</sup> are given in Table 55.

## References

- <sup>1</sup>R. Atkinson, *J. Phys. Chem. Ref. Data* **20**, 459 (1991).
- <sup>2</sup>A. A. Boyd, C. E. Canosa-Mas, A. D. King, R. P. Wayne, and M. R. Wilson, *J. Chem. Soc. Faraday Trans.* **87**, 2913 (1991).
- <sup>3</sup>R. Atkinson and S. M. Aschmann, *J. Atmos. Chem.* **16**, 337 (1993).

## 4.7. Sulfur-Containing Organic Compounds

Jensen *et al.*<sup>1,2</sup> have conducted product studies of the gas-phase reactions of the  $\text{NO}_3$  radical with  $\text{CH}_3\text{SCH}_3$ ,<sup>1,2</sup>  $\text{CD}_3\text{SCD}_3$ ,<sup>2</sup>  $\text{CH}_3\text{SH}$ <sup>2</sup> and  $\text{CH}_3\text{SSCH}_3$ ,<sup>2</sup> using Fourier transform infrared (FT-IR) absorption spectroscopy to monitor the reactants and products. By monitoring the relative disappearance rates of  $\text{CH}_3\text{SCH}_3$  and  $\text{CD}_3\text{SCD}_3$ , a rate constant ratio of  $k(\text{CH}_3\text{SCH}_3)/k(\text{CD}_3\text{SCD}_3) = 3.8 \pm 0.6$  at  $295 \pm 2$  K was determined,<sup>2</sup> in excellent agreement with the absolute rate constants of Daykin and Wine<sup>3</sup> for  $\text{CH}_3\text{SCH}_3$  and  $\text{CD}_3\text{SCD}_3$ . This deuterium isotope effect<sup>2</sup> and the products observed<sup>1,2</sup> led Jensen *et al.*<sup>1,2</sup> to conclude that these  $\text{NO}_3$  radical reactions proceed exclusively (or mainly) by,



in agreement with previous discussions.<sup>4</sup>

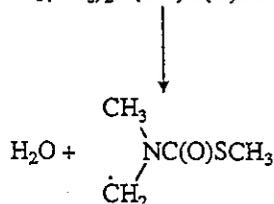
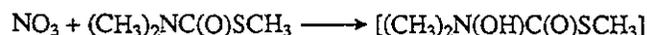
Analogous product studies have been conducted by Jensen *et al.*<sup>5</sup> for the gas-phase reactions of the NO<sub>3</sub> radical with CH<sub>3</sub>CH<sub>2</sub>SH, CH<sub>3</sub>CH<sub>2</sub>SCH<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>SCH<sub>2</sub>CH<sub>3</sub> and CH<sub>3</sub>CH<sub>2</sub>SSCH<sub>2</sub>CH<sub>3</sub> in air at 295 ± 2 K. Jensen *et al.*<sup>5</sup> concluded that the reaction mechanisms for these organosulfur compounds were analogous to those for CH<sub>3</sub>SH, CH<sub>3</sub>SCH<sub>3</sub> and CH<sub>3</sub>SSCH<sub>3</sub>.<sup>1,2,4</sup>

## References

- <sup>1</sup>N. R. Jensen, J. Hjorth, C. Lohse, H. Skov, and G. Restelli, *Atmos. Environ.* **25A**, 1897 (1991).
- <sup>2</sup>N. R. Jensen, J. Hjorth, C. Lohse, H. Skov, and G. Restelli, *J. Atmos. Chem.* **14**, 95 (1992).
- <sup>3</sup>E. P. Daykin and P. H. Wine, *Int. J. Chem. Kinet.* **22**, 1083 (1990).
- <sup>4</sup>R. Atkinson, *J. Phys. Chem. Ref. Data* **20**, 459 (1991).
- <sup>5</sup>N. R. Jensen, J. Hjorth, C. Lohse, H. Skov, and G. Restelli, *Int. J. Chem. Kinet.* **24**, 839 (1992).

## 4.8. Nitrogen- and Silicon-Containing Organic Compounds

The rate constants reported since the review and evaluation of Atkinson<sup>1</sup> are given in Table 56. From a product study, Kwok *et al.*<sup>2</sup> showed that the major reaction pathway for the NO<sub>3</sub> radical reaction with (CH<sub>3</sub>)<sub>2</sub>NC(O)SCH<sub>3</sub> proceeds by overall H-atom abstraction to form the CH<sub>2</sub>(CH<sub>3</sub>)NC(O)SCH<sub>3</sub> radical (presumably by initial NO<sub>3</sub> radical interaction with the N atom), ultimately leading to the formation of CH<sub>3</sub>(CHO)NC(O)SCH<sub>3</sub> in 87 ± 13% yield.



## References

- <sup>1</sup>R. Atkinson, *J. Phys. Chem. Ref. Data* **20**, 459 (1991).
- <sup>2</sup>E. S. C. Kwok, R. Atkinson, and J. Arey, *Environ. Sci. Technol.* **26**, 1798 (1992).
- <sup>3</sup>R. Atkinson, S. M. Aschmann, and J. Arey, unpublished data (1993).

## 4.9. Aromatic Compounds

The rate constants reported since the review and evaluation of Atkinson<sup>1</sup> are given in Table 57.

*Phenol, o-Cresol, m-Cresol and p-Cresol.* The room temperature rate constants of Atkinson *et al.*<sup>2</sup> are given in Table 57. These rate constants are in general agreement (within ±40%) with the relative rate constants of Carter *et al.*,<sup>3</sup> and that for phenol<sup>2</sup> is also in excellent agreement with the rate constant of Atkinson *et al.*<sup>4</sup> determined relative to the rate constant for the reaction of the NO<sub>3</sub> radical with 2-methyl-2-butene. There are, however, significant discrepancies between the rate constants for *o*-, *m*- and *p*-cresol obtained from the two studies of Atkinson *et al.*<sup>2,4</sup> (the rate constants for *o*- and *p*-cresol<sup>4</sup> were relative to that for *m*-cresol, which in turn was relative to that for phenol,<sup>4</sup> all determined using FT-IR absorption spectroscopy).<sup>4</sup>

A unit-weighted average of the rate constants for phenol of Atkinson *et al.*<sup>2,4</sup> leads to the recommendation of

$$k(\text{phenol}) = 3.78 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty of ±35%. This recommendation supersedes that of Atkinson<sup>1</sup> of

$$k(\text{phenol}) = 3.64 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

which was based on the study of Atkinson *et al.*<sup>4</sup> For the three cresol isomers, the rate constants of Atkinson *et al.*<sup>2</sup> are recommended:

$$k(o\text{-cresol}) = 1.37 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}$$

with an estimated overall uncertainty of ±35%,

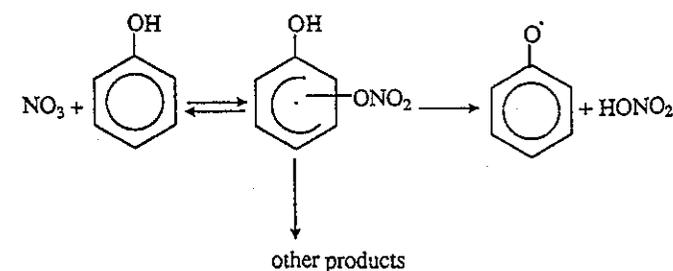
$$k(m\text{-cresol}) = 9.74 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}$$

with an estimated overall uncertainty of ±35%, and

$$k(p\text{-cresol}) = 1.07 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}$$

with an estimated overall uncertainty of a factor of 1.5.

Atkinson *et al.*<sup>2</sup> also measured the nitrophenol and nitrocresol yields from these NO<sub>3</sub> radical reactions, and observed yields significantly lower than unity for phenol and *o*- and *m*-cresol (Sec. 2.4). These product data suggest that these NO<sub>3</sub> radical reactions proceed by,



with the phenoxy radicals reacting with NO<sub>2</sub> to form the nitrophenols.<sup>2</sup>

## Miscellaneous

Rindone *et al.*<sup>5</sup> have investigated the gas-phase reactions of the NO<sub>3</sub> radical with *o*-xylene-*h*<sub>10</sub>, *o*-xylene-*d*<sub>10</sub>,

TABLE 53. Rate constants  $k$  for the gas-phase reactions of the  $\text{NO}_3$  radical with haloalkenes

Haloalkene	$10^{12} \times A$ ( $\text{cm}^3$ $\text{molecule}^{-1} \text{s}^{-1}$ )	$B$ (K)	$k$ ( $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ )	at $T$ (K)	Technique	Reference	Temperature range covered (K)
1-Chloro-1-butene [ $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCl}$ ]			$(1.2 \pm 0.4) \times 10^{-14}$	298	DF-A	Aird <i>et al.</i> <sup>2</sup>	
2-Chloro-1-butene [ $\text{CH}_3\text{CH}_2\text{CCl}=\text{CH}_2$ ]			$(1.73 \pm 0.31) \times 10^{-14}$	299	DF-A	Wängberg <i>et al.</i> <sup>3</sup>	
			$(2.21 \pm 0.53) \times 10^{-14}$	296	RR [relative to $k(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5)$ $= 4.40 \times 10^{-11}$ ] <sup>a</sup>	Wängberg <i>et al.</i> <sup>3</sup>	
			$(1.7 \pm 0.3) \times 10^{-14}$	299	DF-A	Aird <i>et al.</i> <sup>2</sup>	
3-Chloro-1-butene [ $\text{CH}_3\text{CHClCH}=\text{CH}_2$ ]	$2.4 \times 10^{-12}$	$1992 \pm 241$	$(3.0 \pm 0.7) \times 10^{-15}$	296	DF-A	Aird <i>et al.</i> <sup>2</sup>	296-473
			$(1.2 \pm 0.1) \times 10^{-14}$	373			
			$(3.5 \pm 1.2) \times 10^{-14}$	473			
1-Chloro-2-butene [ $\text{CH}_3\text{CH}=\text{CHCH}_2\text{Cl}$ ]	$6.0 \times 10^{-13}$	$981 \pm 349$	$(2.0 \pm 0.7) \times 10^{-14}$	298	DF-A	Aird <i>et al.</i> <sup>2</sup>	298-473
			$(5.0 \pm 1.7) \times 10^{-14}$	373			
			$(7.0 \pm 5.5) \times 10^{-14}$	473			
2-Chloro-2-butene [ $\text{CH}_3\text{CH}=\text{CClCH}_3$ ]			$(1.10 \pm 0.40) \times 10^{-13}$	298	DF-A	Aird <i>et al.</i> <sup>2</sup>	
1-Chloro-2-methylpropene [ $(\text{CH}_3)_2\text{C}=\text{CHCl}$ ]			$(9.0 \pm 2.3) \times 10^{-14}$	298	DF-A	Aird <i>et al.</i> <sup>2</sup>	
2-Chloromethylpropene [ $\text{CH}_3\text{C}(\text{CH}_2\text{Cl})=\text{CH}_2$ ]	$1.6 \times 10^{-12}$	$1277 \pm 205$	$(2.5 \pm 0.4) \times 10^{-14}$	298	DF-A	Aird <i>et al.</i> <sup>2</sup>	298-473
			$(4.7 \pm 0.5) \times 10^{-14}$	373			
			$(1.23 \pm 0.06) \times 10^{-13}$	473			
3-Bromo-1-butene [ $\text{CH}_3\text{CHBrCH}=\text{CH}_2$ ]			$(4 \pm 1) \times 10^{-15}$	298	DF-A	Aird <i>et al.</i> <sup>2</sup>	
4-Bromo-1-butene [ $\text{CH}_2\text{BrCH}_2\text{CH}=\text{CH}_2$ ]			$(5 \pm 1) \times 10^{-15}$	298	DF-A	Aird <i>et al.</i> <sup>2</sup>	
2-Bromo-2-butene [ $\text{CH}_3\text{CH}=\text{CBrCH}_3$ ]			$(1.34 \pm 0.01) \times 10^{-13}$	298	DF-A	Aird <i>et al.</i> <sup>2</sup>	

<sup>a</sup>From present and previous<sup>1</sup> recommendations.

TABLE 54. Rate constants  $k$  for the gas-phase reactions of the  $\text{NO}_3$  radical with alkynes

Alkyne	$k$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	at $T$ (K)	Technique	Reference
2-Hexyne	$(2.8 \pm 0.1) \times 10^{-14}$	298	DF-MS	Benter <i>et al.</i> <sup>2</sup>
	$\sim 3 \times 10^{-13}$	433	DF-A	Benter <i>et al.</i> <sup>2</sup>

TABLE 55. Rate constants  $k$  for the gas-phase reactions of the  $\text{NO}_3$  radical with oxygen-containing organic compounds

Oxygenate	$k$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	at $T$ (K)	Technique	Reference
Acetone	$\leq 1.1 \times 10^{-17}$	302	SF-A	Boyd <i>et al.</i> <sup>2</sup>
4-Acetyl-1-methylcyclohexene	$(1.05 \pm 0.08) \times 10^{-11}$	$296 \pm 2$	RR [relative to $k$ (2-methyl-2-butene) = $9.37 \times 10^{-12}$ ] <sup>a</sup>	Atkinson and Aschmann <sup>3</sup>

<sup>a</sup>From present and previous<sup>1</sup> recommendation.

TABLE 56. Rate constants  $k$  for the gas-phase reactions of the  $\text{NO}_3$  radical with nitrogen- and silicon-containing organic compounds

Organic	$k$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	at $T$ (K)	Technique	Reference
<i>Nitrogen-containing</i>				
$(\text{CH}_3)_2\text{NC}(\text{O})\text{SCH}_3$	$(7.10 \pm 0.31) \times 10^{-15}$	$298 \pm 2$	RR [relative to $k$ (1-butene) = $1.21 \times 10^{-14}$ ] <sup>a</sup>	Kwok <i>et al.</i> <sup>2</sup>
$(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{NC}(\text{O})\text{SCH}_2\text{CH}_3$	$(8.94 \pm 0.45) \times 10^{-15}$	$298 \pm 2$	RR [relative to $k$ (1-butene) = $1.21 \times 10^{-14}$ ] <sup>a</sup>	Kwok <i>et al.</i> <sup>2</sup>
$\text{CH}_3\text{CH}_2(\text{c-C}_6\text{H}_{11})\text{NC}(\text{O})\text{SCH}_2\text{CH}_3$	$(3.18 \pm 0.26) \times 10^{-14}$	$298 \pm 2$	RR [relative to $k$ (1-butene) = $1.21 \times 10^{-14}$ ] <sup>a</sup>	Kwok <i>et al.</i> <sup>2</sup>
<i>Silicon-containing</i>				
$(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_2\text{OH}$	$< 1.7 \times 10^{-16}$	$297 \pm 2$	RR [relative to $k$ ( $n$ -heptane) = $1.37 \times 10^{-16}$ ] <sup>a</sup>	Atkinson <i>et al.</i> <sup>3</sup>

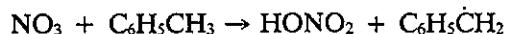
<sup>a</sup>From present and previous<sup>1</sup> recommendations.

TABLE 57. Rate constants  $k$  for the gas-phase reactions of the  $\text{NO}_3$  radical with aromatic compounds

Aromatic	$k$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	at $T$ (K)	Technique	Reference
Phenol	$(3.92 \pm 0.25) \times 10^{-12}$	$296 \pm 2$	RR [relative to $k(2\text{-methyl-2-butene}) = 9.37 \times 10^{-12}]^a$	Atkinson <i>et al.</i> <sup>2</sup>
<i>o</i> -Cresol	$(1.37 \pm 0.09) \times 10^{-11}$	$296 \pm 2$	RR [relative to $k(2\text{-methyl-2-butene}) = 9.37 \times 10^{-12}]^a$	Atkinson <i>et al.</i> <sup>2</sup>
<i>m</i> -Cresol	$(9.74 \pm 0.47) \times 10^{-12}$	$296 \pm 2$	RR [relative to $k(2\text{-methyl-2-butene}) = 9.37 \times 10^{-12}]^a$	Atkinson <i>et al.</i> <sup>2</sup>
<i>p</i> -Cresol	$(1.07 \pm 0.10) \times 10^{-11}$	$296 \pm 2$	RR [relative to $k(2\text{-methyl-2-butene}) = 9.37 \times 10^{-12}]^a$	Atkinson <i>et al.</i> <sup>2</sup>
2-Nitrophenol	$< 1.2 \times 10^{-14}$	$296 \pm 2$	RR [relative to $k(\textit{trans}\text{-2-butene}) = 3.89 \times 10^{-13}]^a$	Atkinson <i>et al.</i> <sup>2</sup>

<sup>a</sup>From present and previous<sup>1</sup> recommendations.

*p*-xylene- $h_{10}$ , *p*-xylene- $d_{10}$  and *p*-xylene- $d_6$  [ $\text{C}_6\text{H}_4(\text{CD}_3)_2$ ] at room temperature, and observed a significant deuterium isotope effect on the rate constants, with the deuterated xylenes reacting slower than the non-deuterated compounds by factors of 1.48–1.87. In agreement with the rate constants of Atkinson and Aschmann,<sup>6</sup> these kinetic data of Rindone *et al.*<sup>5</sup> confirm that the  $\text{NO}_3$  radicals with the alkyl-substituted benzenes proceed by H-atom abstraction from the C–H (or C–D) bonds



## References

- <sup>1</sup>R. Atkinson, *J. Phys. Chem. Ref. Data* **20**, 459 (1991).
- <sup>2</sup>R. Atkinson, S. M. Aschmann, and J. Arey, *Environ. Sci. Technol.* **26**, 1397 (1992).
- <sup>3</sup>W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., *Environ. Sci. Technol.* **15**, 829 (1981).
- <sup>4</sup>R. Atkinson, W. P. L. Carter, C. N. Plum, A. M. Winer, and J. N. Pitts, Jr., *Int. J. Chem. Kinet.* **16**, 887 (1984).
- <sup>5</sup>B. Rindone, F. Cariati, G. Restelli, and J. Hjorth, *Fres. J. Anal. Chem.* **339**, 673 (1991).
- <sup>6</sup>R. Atkinson and S. M. Aschmann, *Int. J. Chem. Kinet.* **20**, 513 (1988).

## 5. Kinetics and Mechanisms of the Gas-Phase Reactions of Ozone with Organic Compounds

In this section, the previous review and evaluation of Atkinson and Carter<sup>1</sup> is updated.

### 5.1. Haloalkanes

Since the review and evaluation of Atkinson and Carter,<sup>1</sup> Tuazon *et al.*<sup>2</sup> have determined an upper limit

to the rate constant for the reaction of  $\text{O}_3$  with 1,2-dibromo-3-chloropropane ( $\text{CH}_2\text{BrCHBrCH}_2\text{Cl}$ ) of  $k(\text{CH}_2\text{BrCHBrCH}_2\text{Cl}) < 3 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at  $296 \pm 2 \text{ K}$ .

## References

- <sup>1</sup>R. Atkinson and W. P. L. Carter, *Chem. Rev.* **84**, 437 (1984).
- <sup>2</sup>E. C. Tuazon, R. Atkinson, S. M. Aschmann, J. Arey, A. M. Winer, and J. N. Pitts, Jr., *Environ. Sci. Technol.* **20**, 1043 (1986).

### 5.2. Alkenes

The rate constants reported since the review and evaluation of Atkinson and Carter<sup>1</sup> are given in Table 58. Also included in this table are the corrected rate constants of Herron and Huie<sup>4</sup> for propene. The study of Treacy *et al.*<sup>3</sup> is taken to supersede the data previously reported by Donlon *et al.*<sup>14</sup>

*Ethene.* The rate constants of Bahta *et al.*<sup>2</sup> and Treacy *et al.*<sup>3</sup> are given in Table 58 (the rate constants of Bahta *et al.*<sup>2</sup> have been averaged at each of the four temperatures studied). Since Treacy *et al.*<sup>3</sup> did not tabulate the individual rate constants at the various temperatures studied, only the Arrhenius expression and 298 K rate constants can be included in Table 58. These two kinetic studies<sup>2,3</sup> obtained room temperature rate constants in the range  $(1.37\text{--}1.45) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , which are somewhat lower than many of the previous rate constant data,<sup>1</sup> including those of Su *et al.*<sup>15</sup> and Kan *et al.*<sup>16</sup> The rate constants of Bahta *et al.*<sup>2</sup> and Treacy *et al.*<sup>3</sup> are plotted in Arrhenius form in Fig. 47, together with the rate constants of DeMore,<sup>17</sup> Stedman *et al.*,<sup>18</sup> Herron and Huie,<sup>4</sup> Japar *et al.*,<sup>19,20</sup> Toby *et al.*<sup>21</sup> and Atkinson *et al.*<sup>22</sup> A unit-weighted least-squares analysis of the rate constants of DeMore,<sup>17</sup> Stedman *et al.*,<sup>18</sup> Herron and Huie,<sup>4</sup> Japar *et al.*,<sup>19,20</sup> Toby *et al.*,<sup>21</sup> Atkinson *et al.*,<sup>22</sup> Bahta *et al.*<sup>2</sup> and

the 298 K rate constant of Treacy *et al.*<sup>3</sup> leads to the recommended Arrhenius expression of

$$k(\text{ethene}) = (9.14^{+3.13}_{-2.33}) \times 10^{-15} e^{-(2580 \pm 71)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 178–362 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{ethene}) = 1.59 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of  $\pm 30\%$ .

This recommendation supersedes the previous recommendation of Atkinson and Carter<sup>1</sup> (which was also used by the NASA<sup>23</sup> and IUPAC<sup>24</sup> evaluations) of

$$k(\text{ethene}) = 1.2 \times 10^{-14} e^{-2630/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the same temperature range of 178–362 K, with a 298 K rate constant of  $1.75 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

**Propene.** The rate constants of Treacy *et al.*<sup>3</sup> are given in Table 58, together with the corrected rate constants of Herron and Huie<sup>4</sup> (the lowest temperature studied was 235.0 K and not 250.0 K as given by Herron and Huie<sup>4</sup> and used in the evaluation of Atkinson and Carter<sup>1</sup>). The rate constants of Herron and Huie<sup>4</sup> and Treacy *et al.*<sup>3</sup> are plotted in Arrhenius form in Fig. 48, together with the apparently reliable<sup>1</sup> rate constants of Cox and Penkett,<sup>25</sup> Stedman *et al.*,<sup>18</sup> Japar *et al.*<sup>19,20</sup> and Atkinson *et al.*<sup>22</sup> The rate constants determined by Herron and Huie<sup>4</sup> and Treacy *et al.*<sup>3</sup> for propene [and ethene (Fig. 47)] are in excellent agreement over the temperature range common to both studies (240–324 K). The rate constants obtained by Huie and Herron<sup>26</sup> and Treacy *et al.*<sup>3</sup> for 1-butene, *cis*-2-butene, *trans*-2-butene, 2-methylpropene and 2-methyl-2-butene are also in excellent agreement over the temperature range common to both studies (240–324 K).

In addition to these studies, Greene and Atkinson<sup>5</sup> have carried out a relative rate study of the reactions of O<sub>3</sub> with a series of alkenes at  $296 \pm 2$  K. Greene and Atkinson<sup>5</sup> obtained relative rate constants for propene, 1-butene, 2-methylpropene, *cis*- and *trans*-2-butene, 2-methyl-2-butene, 2,3-dimethyl-2-butene and 2-methyl-1,3-butadiene,<sup>5</sup> and these relative rate constants are in generally excellent agreement with the absolute rate constants of Herron and Huie,<sup>4</sup> Huie and Herron<sup>26</sup> and Treacy *et al.*<sup>3</sup> From a unit-weighted average of the 298 K rate constants of Herron and Huie<sup>4</sup> and Treacy *et al.*<sup>3</sup> a rate constant of

$$k(\text{propene}) = 1.01 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}$$

is recommended. Combination of this 298 K rate constant with the temperature dependence of  $B = 1878$  K, obtained from a unit-weighted average of the temperature dependencies of Herron and Huie<sup>4</sup> and Treacy *et al.*<sup>3</sup> leads to the recommended Arrhenius expression of

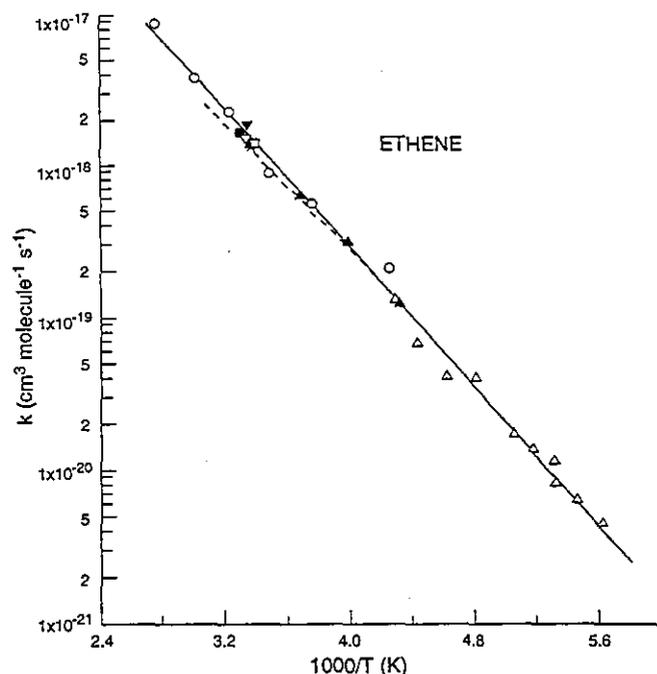


FIG. 47. Arrhenius plot of selected rate constants for the reaction of O<sub>3</sub> with ethene. ( $\Delta$ ) DeMore;<sup>17</sup> ( $\nabla$ ) Stedman *et al.*;<sup>18</sup> ( $\circ$ ) Herron and Huie;<sup>4</sup> ( $\blacktriangledown$ ) Japar *et al.*;<sup>19,20</sup> ( $\blacksquare$ ) Toby *et al.*;<sup>21</sup> ( $\square$ ) Atkinson *et al.*;<sup>22</sup> ( $\blacktriangle$ ) Bahta *et al.*;<sup>2</sup> ( $-X-$ ) Treacy *et al.*;<sup>3</sup> ( $-$ ) recommendation (see text).

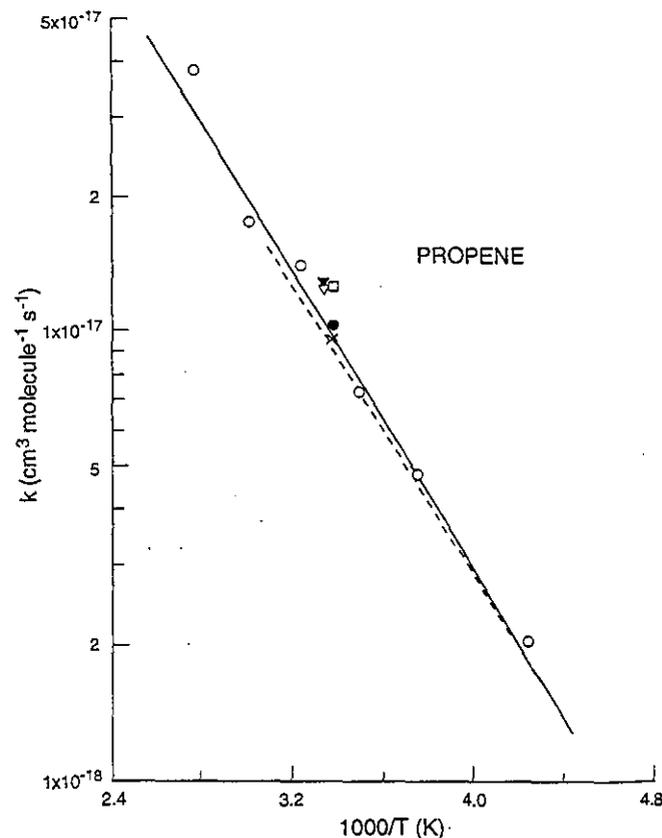


FIG. 48. Arrhenius plot of selected rate constants for the reaction of O<sub>3</sub> with propene. ( $\square$ ) Cox and Penkett,<sup>25</sup> ( $\nabla$ ) Stedman *et al.*;<sup>18</sup> ( $\circ$ ) Herron and Huie;<sup>4</sup> ( $\blacktriangledown$ ) Japar *et al.*;<sup>19,20</sup> ( $\bullet$ ) Atkinson *et al.*;<sup>22</sup> ( $-X-$ ) Treacy *et al.*;<sup>3</sup> ( $-$ ) recommendation (see text).

$$k(\text{propene}) = 5.51 \times 10^{-15} e^{-1878/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 235–362 K, with an estimated overall uncertainty at 298 K of  $\pm 25\%$ .

This recommendation supersedes the IUPAC<sup>24</sup> recommendation of

$$k(\text{propene}) = 6.5 \times 10^{-15} e^{-1880/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 230–370 K, with a 298 K rate constant of  $1.2 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

*1-Butene*. The rate constants of Treacy *et al.*<sup>3</sup> and Greene and Atkinson<sup>5</sup> are given in Table 58 and are plotted, together with the rate constants of Japar *et al.*<sup>19</sup> and Huie and Herron,<sup>26</sup> in Arrhenius form in Fig. 49. The agreement of the room temperature rate constants between the studies of Huie and Herron,<sup>26</sup> Treacy *et al.*<sup>3</sup> and Greene and Atkinson<sup>5</sup> is excellent. From a unit-weighted average of the 298 K rate constants of Huie and Herron,<sup>26</sup> Treacy *et al.*<sup>3</sup> and Greene and Atkinson<sup>5</sup> (corrected from 296 K to 298 K using the recommended temperature dependence), the rate constant of

$$k(1\text{-butene}) = 9.64 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}$$

is recommended. Combining this recommended 298 K rate constant with the unit-weighted average of the temperature dependences of Huie and Herron<sup>26</sup> and Treacy *et al.*,<sup>3</sup> of  $B = 1744 \text{ K}$ , leads to the recommendation of

$$k(1\text{-butene}) = 3.36 \times 10^{-15} e^{-1744/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 225–363 K, with an estimated overall uncertainty at 298 K of  $\pm 25\%$ . This recommendation supersedes that of Atkinson and Carter<sup>1</sup> of

$$k(1\text{-butene}) = 3.46 \times 10^{-15} e^{-1713/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the same temperature range of 225–363 K, with a 298 K rate constant of  $1.10 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

*2-Methylpropene*. The rate constants of Treacy *et al.*<sup>3</sup> and Greene and Atkinson<sup>5</sup> are given in Table 58 and are plotted, together with the rate constants of Japar *et al.*<sup>19</sup> and Huie and Herron,<sup>26</sup> in Arrhenius form in Fig. 50. The rate constants of Huie and Herron,<sup>26</sup> Treacy *et al.*<sup>3</sup> and Greene and Atkinson<sup>5</sup> are in excellent agreement, and a unit-weighted average of the 298 K rate constants of Huie and Herron,<sup>26</sup> Treacy *et al.*<sup>3</sup> and Greene and Atkinson<sup>5</sup> (corrected to 298 K as described for 1-butene above) leads to the recommended 298 K rate constant of

$$k(2\text{-methylpropene}) = 1.13 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Combining this 298 K rate constant with the temperature dependence of  $B = 1632 \text{ K}$  obtained from a unit-weighted average of the temperature dependencies of Huie and Herron<sup>26</sup> and Treacy *et al.*<sup>3</sup> leads to the recommendation of

$$k(2\text{-methylpropene}) = 2.70 \times 10^{-15} e^{-1632/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 225–363 K, with an estimated overall uncertainty at 298 K of  $\pm 30\%$ . This recommendation supersedes that of Atkinson and Carter<sup>1</sup> of

$$k(2\text{-methylpropene}) = 3.55 \times 10^{-15} e^{-1693/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the same temperature range of 225–363 K, with a 298 K rate constant of  $1.21 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

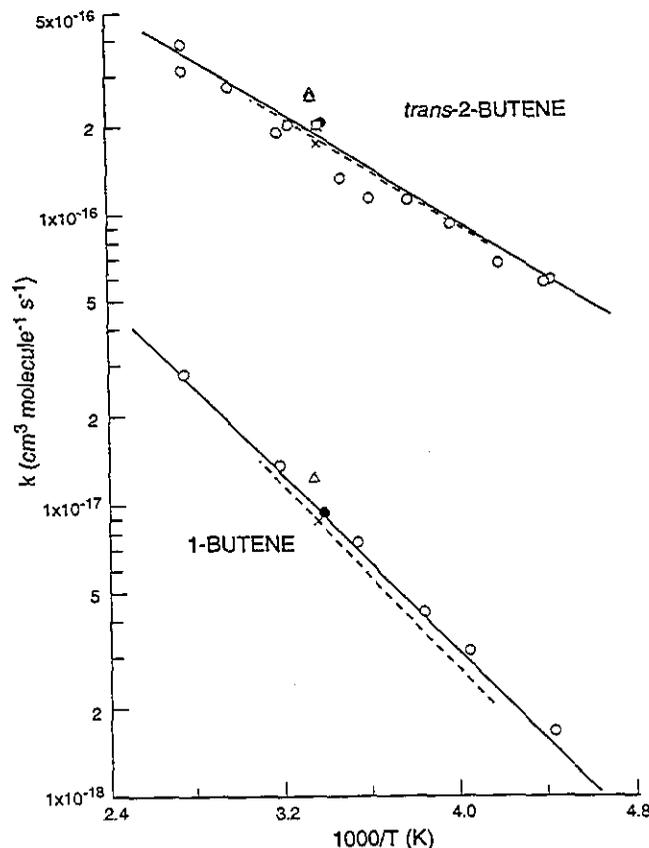


FIG. 49. Arrhenius plots of selected rate constants for the reactions of  $\text{O}_3$  with 1-butene and *trans*-2-butene. ( $\Delta$ ) Japar *et al.*,<sup>19</sup> (1-butene) and Japar *et al.*,<sup>19,20</sup> (*trans*-2-butene); ( $\circ$ ) Huie and Herron,<sup>26</sup> ( $\square$ ) Nolting *et al.*,<sup>6</sup> ( $-X-$ ) Treacy *et al.*,<sup>3</sup> ( $\bullet$ ) Greene and Atkinson,<sup>5</sup> (—) recommendations (see text).

*cis*-2-Butene. The rate constants of Treacy *et al.*<sup>3</sup> and Greene and Atkinson<sup>5</sup> are given in Table 58 and are plotted in Arrhenius form, together with the rate constants of Japar *et al.*,<sup>19</sup> Huie and Herron<sup>26</sup> and Atkinson *et al.*,<sup>27</sup> in Fig. 50. The room temperature rate constants of Huie and Herron,<sup>26</sup> Treacy *et al.*<sup>3</sup> and Greene and Atkinson<sup>5</sup> are in excellent agreement, and agree well with the literature rate constants of Cox and Penkett,<sup>25</sup> Japar *et al.*,<sup>19</sup> and Atkinson *et al.*<sup>27</sup> A unit-weighted average of the 298 K rate constants of Huie and Herron,<sup>26</sup> Treacy *et al.*<sup>3</sup> and Greene and Atkinson<sup>5</sup> (corrected to 298 K as described above for 1-butene) leads to the recommended 298 K rate constant of

TABLE 58. Rate constants  $k$  and temperature-dependent parameters,  $k = Ae^{-B/T}$ , for the gas-phase reactions of  $O_3$  with alkenes

Alkene	$10^{12} \times A$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$B$ (K)	$k$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	at $T$ (K)	Technique	Reference	Temperature range covered (K)
Ethene			$(1.34 \pm 0.37) \times 10^{-19}$	232 ± 4	S-UV	Bahta <i>et al.</i> <sup>2</sup>	228-301
			$(3.31 \pm 0.88) \times 10^{-19}$	251 ± 4			
			$(6.60 \pm 1.75) \times 10^{-19}$	272 ± 3			
			$(1.45 \pm 0.25) \times 10^{-18}$	298 ± 3			
	$(7.72 \pm 0.89) \times 10^{-15}$	2557 ± 31					
	$(5.1 \pm 1.0) \times 10^{-15}$	2446 ± 91	$(1.37 \pm 0.08) \times 10^{-18}$	298	S-UV	Treacy <i>et al.</i> <sup>3</sup>	240-324
Propene			$(2.08 \pm 0.02) \times 10^{-18}$	235.0	SF-MS	Herron and Huie <sup>4</sup>	235-362
			$(4.83 \pm 0.10) \times 10^{-18}$	266.9			
			$(7.37 \pm 0.15) \times 10^{-18}$	286.2			
			$(1.41 \pm 0.02) \times 10^{-17}$	309.4			
			$(1.76 \pm 0.02) \times 10^{-17}$	332.4			
			$(3.82 \pm 0.05) \times 10^{-17}$	362.0			
	$6.14 \times 10^{-15}$	1897 ± 109					
	$(4.9 \pm 1.0) \times 10^{-15}$	1858 ± 70	$(9.6 \pm 0.4) \times 10^{-18}$	298	S-UV	Treacy <i>et al.</i> <sup>3</sup>	240-324
1-Butene	$(3.7 \pm 1.0) \times 10^{-15}$	1801 ± 156	$(8.8 \pm 0.6) \times 10^{-18}$	298	S-UV	Treacy <i>et al.</i> <sup>3</sup>	240-324
			$(9.44 \pm 0.30) \times 10^{-18}$	296 ± 2	RR [relative to $k$ (propene) = $9.68 \times 10^{-18}$ ] <sup>a</sup>	Greene and Atkinson <sup>5</sup>	
2-Methylpropene	$(2.5 \pm 0.5) \times 10^{-15}$	1592 ± 115	$(1.09 \pm 0.18) \times 10^{-17}$	298	S-UV	Treacy <i>et al.</i> <sup>3</sup>	240-324
			$(1.10 \pm 0.04) \times 10^{-17}$	296 ± 2	RR [relative to $k$ (propene) = $9.68 \times 10^{-18}$ ] <sup>a</sup>	Greene and Atkinson <sup>5</sup>	
<i>cis</i> -2-Butene	$(3.4 \pm 0.7) \times 10^{-15}$	979 ± 22	$(1.23 \pm 0.18) \times 10^{-16}$	298	S-UV	Treacy <i>et al.</i> <sup>3</sup>	240-324
			$(1.24 \pm 0.08) \times 10^{-16}$	296 ± 2	RR [relative to $k$ (propene) = $9.68 \times 10^{-18}$ ] <sup>a</sup>	Greene and Atkinson <sup>5</sup>	
<i>trans</i> -2-Butene	$(6.7 \pm 1.3) \times 10^{-15}$	1066 ± 115	$(2.02 \pm 0.10) \times 10^{-16}$	297 ± 2	RR [relative to $k$ ( <i>cis</i> -2-butene) = $1.24 \times 10^{-16}$ ] <sup>a</sup>	Nolting <i>et al.</i> <sup>6</sup>	
			$(1.81 \pm 0.06) \times 10^{-16}$	298	S-UV	Treacy <i>et al.</i> <sup>3</sup>	240-324
			$(2.08 \pm 0.15) \times 10^{-16}$	296 ± 2	RR [relative to $k$ (propene) = $9.68 \times 10^{-18}$ ] <sup>a</sup>	Greene and Atkinson <sup>5</sup>	

TABLE 58. Rate constants  $k$  and temperature-dependent parameters,  $k = Ae^{-B/T}$ , for the gas-phase reactions of  $O_3$  with alkenes — Continued

Alkene	$10^{12} \times A$ ( $cm^3$ molecule $^{-1}$ s $^{-1}$ )	$B$ (K)	$k$ ( $cm^3$ molecule $^{-1}$ s $^{-1}$ )	at $T$ (K)	Technique	Reference	Temperature range covered (K)
1-Pentene.	$(1.7 \pm 0.5) \times 10^{-15}$	$1579 \pm 81$	$(9.2 \pm 0.5) \times 10^{-18}$	298	S-UV	Treacy <i>et al.</i> <sup>3</sup>	240–324
2-Methyl-2- butene	$(6.5 \pm 1.3) \times 10^{-15}$	$831 \pm 44$	$(3.97 \pm 0.12) \times 10^{-16}$	298	S-UV	Treacy <i>et al.</i> <sup>3</sup>	240–324
			$(3.81 \pm 0.04) \times 10^{-16}$	$298 \pm 2$	RR [relative to $k(2,3\text{-dimethyl-}2\text{-butene}) =$ $1.13 \times 10^{-15}]^a$	Atkinson <i>et al.</i> <sup>7</sup>	
			$(4.08 \pm 0.28) \times 10^{-16}$	$296 \pm 2$	RR [relative to $k(\text{propene}) =$ $9.68 \times 10^{-18}]^a$	Greene and Atkinson <sup>5</sup>	
1-Hexene	$(1.4 \pm 0.5) \times 10^{-15}$	$1479 \pm 70$	$(1.02 \pm 0.06) \times 10^{-17}$	298	S-UV	Treacy <i>et al.</i> <sup>3</sup>	240–324
<i>cis</i> -3-Methyl- 2-pentene			$(4.50 \pm 0.17) \times 10^{-16}$	$297 \pm 2$	RR [relative to $k(\text{cis-2-butene}) =$ $1.24 \times 10^{-16}]^a$	Nolting <i>et al.</i> <sup>6</sup>	
2,3-Dimethyl-2-butene			$(1.19 \pm 0.11) \times 10^{-15}$	$296 \pm 2$	RR [relative to $k(\text{propene}) =$ $9.68 \times 10^{-18}]^a$	Greene and Atkinson <sup>5</sup>	
1-Heptene			$(1.44 \pm 0.85) \times 10^{-17}$	293–298	S-UV/GC	Grosjean <sup>8</sup>	
1,2-Propadiene			$1.3 \times 10^{-20}$	231	S-UV	Bahta <i>et al.</i> <sup>2</sup>	231–298
			$1.4 \times 10^{-20}$	236			
			$2.4 \times 10^{-20}$	240			
			$2.7 \times 10^{-20}$	243			
			$3.9 \times 10^{-20}$	252			
			$4.3 \times 10^{-20}$	257			
			$4.9 \times 10^{-20}$	258			
			$4.6 \times 10^{-20}$	259			
			$4.9 \times 10^{-20}$	261			
			$5.0 \times 10^{-20}$	261			
			$4.6 \times 10^{-20}$	261			
			$5.0 \times 10^{-20}$	263			
			$6.4 \times 10^{-20}$	265			
			$6.6 \times 10^{-20}$	266			
			$7.0 \times 10^{-20}$	268			
			$7.1 \times 10^{-20}$	268			
		$8.7 \times 10^{-20}$	275				
		$1.03 \times 10^{-19}$	278				
		$1.08 \times 10^{-19}$	280				
		$1.02 \times 10^{-19}$	280				
	$(1.54 \pm 0.25) \times 10^{-15}$	$2689 \pm 44$	$(1.80 \pm 0.18) \times 10^{-19}$	$297 \pm 1$			

TABLE 58. Rate constants  $k$  and temperature-dependent parameters,  $k = Ae^{-B/T}$ , for the gas-phase reactions of  $O_3$  with alkenes -- Continued

Alkene	$10^{12} \times A$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$B$ (K)	$k$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	at $T$ (K)	Technique	Reference	Temperature range covered (K)
1,3-Butadiene			$1.48 \times 10^{-18}$	254	S-UV	Bahta <i>et al.</i> <sup>2</sup>	254-299
			$1.63 \times 10^{-18}$	256			
			$1.61 \times 10^{-18}$	257			
			$1.73 \times 10^{-18}$	257			
			$1.79 \times 10^{-18}$	257			
			$1.67 \times 10^{-18}$	258			
			$1.96 \times 10^{-18}$	260			
			$1.78 \times 10^{-18}$	261			
			$1.86 \times 10^{-18}$	262			
			$2.12 \times 10^{-18}$	263			
			$1.93 \times 10^{-18}$	264			
			$2.63 \times 10^{-18}$	266			
			$2.83 \times 10^{-18}$	267			
			$2.74 \times 10^{-18}$	268			
			$2.99 \times 10^{-18}$	269			
			$2.73 \times 10^{-18}$	270			
			$2.78 \times 10^{-18}$	270			
			$3.27 \times 10^{-18}$	271			
			$3.35 \times 10^{-18}$	271			
			$3.16 \times 10^{-18}$	272			
		$3.05 \times 10^{-18}$	273				
		$3.48 \times 10^{-18}$	274				
		$3.44 \times 10^{-18}$	275				
		$3.27 \times 10^{-18}$	276				
		$3.29 \times 10^{-18}$	279				
		$3.37 \times 10^{-18}$	279				
		$3.31 \times 10^{-18}$	280				
	$(2.20 \pm 0.44) \times 10^{-14}$	$2430 \pm 55$	$(6.27 \pm 0.63) \times 10^{-18}$	$297 \pm 2$			
	$(8.2 \pm 1.6) \times 10^{-15}$	$2136 \pm 106$	$(6.3 \pm 0.4) \times 10^{-18}$	298	S-UV	Treacy <i>et al.</i> <sup>3</sup>	240-324
<i>trans</i> -1,3- Pentadiene			$6.3 \times 10^{-18}$	238	S-UV	Bahta <i>et al.</i> <sup>2</sup>	238-298
			$8.1 \times 10^{-18}$	242			
			$7.1 \times 10^{-18}$	243			
			$8.6 \times 10^{-18}$	245			
			$9.1 \times 10^{-18}$	247			
			$6.6 \times 10^{-18}$	248			
			$8.5 \times 10^{-18}$	249			
			$9.9 \times 10^{-18}$	249			
			$1.03 \times 10^{-17}$	251			
			$1.25 \times 10^{-17}$	253			
			$1.06 \times 10^{-17}$	253			
			$1.20 \times 10^{-17}$	254			
			$1.49 \times 10^{-17}$	255			

TABLE 58. Rate constants  $k$  and temperature-dependent parameters,  $k = Ae^{-B/T}$ , for the gas-phase reactions of  $O_3$  with alkenes — Continued

Alkene	$10^{12} \times A$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$B$ (K)	$k$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	at $T$ (K)	Technique	Reference	Temperature range covered (K)
			$1.59 \times 10^{-17}$	255			
			$1.50 \times 10^{-17}$	256			
			$1.21 \times 10^{-17}$	256			
			$1.21 \times 10^{-17}$	256			
			$1.06 \times 10^{-17}$	257			
			$1.30 \times 10^{-17}$	258			
			$1.44 \times 10^{-17}$	258			
			$1.48 \times 10^{-17}$	259			
			$1.50 \times 10^{-17}$	260			
			$1.75 \times 10^{-17}$	260			
			$1.15 \times 10^{-17}$	260			
			$1.50 \times 10^{-17}$	261			
			$1.36 \times 10^{-17}$	261			
			$1.61 \times 10^{-17}$	266			
			$1.70 \times 10^{-17}$	266			
			$1.98 \times 10^{-17}$	270			
			$2.35 \times 10^{-17}$	271			
			$(4.42 \pm 0.51) \times 10^{-17}$	297–298			
1,3-Pentadiene	$(1.07 \pm 0.25) \times 10^{-13}$	$2319 \pm 62$	$(4.24 \pm 0.12) \times 10^{-17}$	298	S-UV	Treacy <i>et al.</i> <sup>3</sup>	240–324
1,4-Pentadiene	$(2.1 \pm 0.4) \times 10^{-15}$	$1158 \pm 101$	$(1.45 \pm 0.20) \times 10^{-17}$	$298 \pm 2$	S-UV	Treacy <i>et al.</i> <sup>3</sup>	
2-Methyl-1,3-butadiene (isoprene)	$(7.8 \pm 1.6) \times 10^{-15}$	$1913 \pm 139$	$(1.28 \pm 0.12) \times 10^{-17}$	298	S-UV	Treacy <i>et al.</i> <sup>3</sup>	240–324
			$(1.17 \pm 0.02) \times 10^{-17}$	$296 \pm 2$	RR [relative to $k(\text{propene}) = 9.68 \times 10^{-18}$ ] <sup>a</sup>	Greene and Atkinson <sup>5</sup>	
2-Methyl-1,4-pentadiene			$(1.32 \pm 0.20) \times 10^{-17}$	$298 \pm 2$	S-UV	Treacy <i>et al.</i> <sup>3</sup>	
2,3-Dimethyl-1,3-butadiene	$(6.9 \pm 1.3) \times 10^{-15}$	$1668 \pm 42$	$(2.65 \pm 0.08) \times 10^{-17}$	298	S-UV	Treacy <i>et al.</i> <sup>3</sup>	240–324
2,4-Dimethyl-1,3-butadiene			$(8.0 \pm 1.4) \times 10^{-17}$	$298 \pm 2$	S-UV	Treacy <i>et al.</i> <sup>3</sup>	
2,5-Dimethyl-1,5-hexadiene			$(1.42 \pm 0.20) \times 10^{-17}$	$298 \pm 2$	S-UV	Treacy <i>et al.</i> <sup>3</sup>	
3-Methylene-7-methyl-1,6-octadiene (myrcene)			$(4.74 \pm 0.76) \times 10^{-16}$	$296 \pm 2$	RR [relative to $k(\alpha\text{-pinene}) = 8.52 \times 10^{-17}$ ] <sup>a</sup>	Atkinson <i>et al.</i> <sup>9</sup>	

TABLE 58. Rate constants  $k$  and temperature-dependent parameters,  $k = Ae^{-B/T}$ , for the gas-phase reactions of  $O_3$  with alkenes -- Continued

Alkene	$10^{12} \times A$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$B$ (K)	$k$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	at $T$ (K)	Technique	Reference	Temperature range covered (K)
<i>trans</i> -3,7-Dimethyl- 1,3,6-octatriene ( <i>trans</i> -ocimene) <sup>b</sup>			$(5.44 \pm 0.83) \times 10^{-16}$	296 $\pm$ 2	RR [relative to $k(\alpha\text{-pinene}) =$ $8.52 \times 10^{-17}$ ] <sup>a</sup>	Atkinson <i>et al.</i> <sup>9</sup>	
Cyclopentene			$(4.97 \pm 0.30) \times 10^{-16}$	291.5	S-CL	Bennett <i>et al.</i> <sup>10</sup>	
			$(5.95 \pm 0.34) \times 10^{-16}$	297 $\pm$ 2	RR [relative to $k(\textit{cis}\text{-2-butene}) =$ $1.24 \times 10^{-16}$ ] <sup>a</sup>	Nolting <i>et al.</i> <sup>6</sup>	
			$(6.28 \pm 0.42) \times 10^{-16}$	296 $\pm$ 2	RR [relative to $k(\textit{propene}) =$ $9.68 \times 10^{-18}$ ] <sup>a</sup>	Greene and Atkinson <sup>5</sup>	
Cyclohexene			$(1.51 \pm 0.10) \times 10^{-16}$	295	S-CL	Bennett <i>et al.</i> <sup>10</sup>	
			$(7.44 \pm 0.48) \times 10^{-17}$	297 $\pm$ 2	RR [relative to $k(\textit{cis}\text{-2-butene}) =$ $1.24 \times 10^{-16}$ ] <sup>a</sup>	Nolting <i>et al.</i> <sup>6</sup>	
			$(9.93 \pm 0.21) \times 10^{-17}$	303 $\pm$ 1	S-CL	Izumi <i>et al.</i> <sup>11</sup>	
			$(7.14 \pm 0.47) \times 10^{-17}$	296 $\pm$ 2	RR [relative to $k(\textit{propene}) =$ $9.68 \times 10^{-18}$ ] <sup>a</sup>	Greene and Atkinson <sup>5</sup>	
1,4-Cyclohexadiene			$(4.60 \pm 0.23) \times 10^{-17}$	296 $\pm$ 2	RR [relative to $k(\textit{propene}) =$ $9.68 \times 10^{-18}$ ] <sup>a</sup>	Greene and Atkinson <sup>5</sup>	
Cycloheptene			$(2.70 \pm 0.15) \times 10^{-16}$	297 $\pm$ 2	RR [relative to $k(\textit{cis}\text{-2-butene}) =$ $1.24 \times 10^{-16}$ ] <sup>a</sup>	Nolting <i>et al.</i> <sup>6</sup>	
$\alpha$ -Pinene			$(8.20 \pm 1.24) \times 10^{-17}$	297 $\pm$ 2	RR [relative to $k(\textit{cis}\text{-2-butene}) =$ $1.24 \times 10^{-16}$ ] <sup>a</sup>	Nolting <i>et al.</i> <sup>6</sup>	
			$(9.71 \pm 1.06) \times 10^{-17}$	296 $\pm$ 2	S-CL	Atkinson <i>et al.</i> <sup>9</sup>	
$\beta$ -Pinene			$(1.34 \pm 0.20) \times 10^{-17}$	297 $\pm$ 2	RR [relative to $k(\textit{cis}\text{-2-butene}) =$ $1.24 \times 10^{-16}$ ] <sup>a</sup>	Nolting <i>et al.</i> <sup>6</sup>	

TABLE 58. Rate constants  $k$  and temperature-dependent parameters,  $k = Ae^{-B/T}$ , for the gas-phase reactions of  $O_3$  with alkenes — Continued

Alkene	$10^{12} \times A$ ( $\text{cm}^3$ $\text{molecule}^{-1} \text{s}^{-1}$ )	$B$ (K)	$k$ ( $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ )	at $T$ (K)	Technique	Reference	Temperature range covered (K)
			$(1.48 \pm 0.17) \times 10^{-17}$	$296 \pm 2$	S-CL	Atkinson <i>et al.</i> <sup>9</sup>	
			$(1.64 \pm 0.20) \times 10^{-17}$	$296 \pm 2$	RR [relative to $k(\alpha\text{-pinene}) =$ $8.52 \times 10^{-17}]^a$	Atkinson <i>et al.</i> <sup>9</sup>	
2-Carene			$(2.32 \pm 0.30) \times 10^{-16}$	$296 \pm 2$	S-CL	Atkinson <i>et al.</i> <sup>9</sup>	
			$(2.31 \pm 0.24) \times 10^{-16}$	$296 \pm 2$	RR [relative to $k(\alpha\text{-pinene}) =$ $8.52 \times 10^{-17}]^a$	Atkinson <i>et al.</i> <sup>9</sup>	
3-Carene			$(5.20 \pm 0.56) \times 10^{-17}$	$296 \pm 2$	S-CL	Atkinson <i>et al.</i> <sup>9</sup>	
			$(3.71 \pm 0.40) \times 10^{-17}$	$296 \pm 2$	RR [relative to $k(\alpha\text{-pinene}) =$ $8.52 \times 10^{-17}]^a$	Atkinson <i>et al.</i> <sup>9</sup>	
Camphene			$(9.0 \pm 1.7) \times 10^{-19}$	$296 \pm 2$	S-CL	Atkinson <i>et al.</i> <sup>12</sup>	
Sabinene			$(8.07 \pm 0.83) \times 10^{-17}$	$296 \pm 2$	S-CL	Atkinson <i>et al.</i> <sup>12</sup>	
			$(8.61 \pm 0.94) \times 10^{-17}$	$296 \pm 2$	RR [relative to $k(\alpha\text{-pinene}) =$ $8.52 \times 10^{-17}]^a$	Atkinson <i>et al.</i> <sup>9</sup>	
Limonene			$(2.04 \pm 0.22) \times 10^{-16}$	$296 \pm 2$	RR [relative to $k(\alpha\text{-pinene}) =$ $8.52 \times 10^{-17}]^a$	Atkinson <i>et al.</i> <sup>9</sup>	
$\alpha$ -Phellandrene			$(1.85 \pm 0.40) \times 10^{-15}$	$296 \pm 2$	RR [relative to $k(\alpha\text{-pinene}) =$ $8.52 \times 10^{-17}]^a$	Atkinson <i>et al.</i> <sup>9</sup>	
$\beta$ -Phellandrene			$(4.71 \pm 0.28) \times 10^{-17}$	$297 \pm 2$	RR [relative to $k(\alpha\text{-pinene}) =$ $8.59 \times 10^{-17}]^a$	Shorees <i>et al.</i> <sup>13</sup>	
$\alpha$ -Terpinene			$(8.47 \pm 2.24) \times 10^{-15}$	$296 \pm 2$	RR [relative to $k(\alpha\text{-pinene}) =$ $8.52 \times 10^{-17}]^a$	Atkinson <i>et al.</i> <sup>9</sup>	

TABLE 58. Rate constants  $k$  and temperature-dependent parameters,  $k = Ae^{-B/T}$ , for the gas-phase reactions of  $O_3$  with alkenes - Continued

Alkene	$10^{12} \times A$ ( $\text{cm}^3$ $\text{molecule}^{-1} \text{s}^{-1}$ )	$B$ (K)	$k$ ( $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ )	at $T$ (K)	Technique	Reference	Temperature range covered (K)
$\gamma$ -Terpinene			$(1.40 \pm 0.16) \times 10^{-16}$	$296 \pm 2$	RR [relative to $k(\alpha\text{-pinene}) =$ $8.52 \times 10^{-17}]^a$	Atkinson <i>et al.</i> <sup>9</sup>	
Terpinolene			$(1.38 \pm 0.24) \times 10^{-15}$	$296 \pm 2$	RR [relative to $k(\alpha\text{-pinene}) =$ $8.52 \times 10^{-17}]^a$	Atkinson <i>et al.</i> <sup>9</sup>	
Azulene			$< 7 \times 10^{-17}$	$298 \pm 2$	RR [relative to $k(2,3\text{-dimethyl-}$ $2\text{-butene}) =$ $1.13 \times 10^{-15}]^a$	Atkinson <i>et al.</i> <sup>7</sup>	

<sup>a</sup>From present recommendations (see text).

<sup>b</sup>*cis*-isomer has a rate constant  $10 \pm 10\%$  lower than that for the *trans*-isomer.<sup>9</sup>

$$k(\text{cis-2-butene}) = 1.25 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

Combination of this 298 K rate constant with the temperature dependence of  $B = 968 \text{ K}$  determined from a unit-weighted average of the temperature dependencies of Huie and Herron<sup>26</sup> and Treacy *et al.*<sup>3</sup> leads to the recommendation of

$$k(\text{cis-2-butene}) = 3.22 \times 10^{-15} e^{-968/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 225–364 K, with an estimated overall uncertainty at 298 K of  $\pm 25\%$ . This recommendation supersedes that of Atkinson and Carter<sup>1</sup> of

$$k(\text{cis-2-butene}) = 3.52 \times 10^{-15} e^{-983/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the same temperature range of 225–364 K, with a 298 K rate constant of  $1.30 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

*trans-2-Butene*. The absolute rate constants of Treacy *et al.*<sup>3</sup> and the relative rate constants of Nolting *et al.*<sup>6</sup> and Greene and Atkinson<sup>5</sup> are given in Table 58 and are plotted, together with the rate constants of Japar *et al.*<sup>19,20</sup> and Huie and Herron,<sup>26</sup> in Arrhenius form in Fig. 49. The rate constants of Nolting *et al.*<sup>6</sup> and Greene and Atkinson<sup>5</sup> are in excellent agreement and are in reasonable agreement with the room temperature rate constants of Huie and Herron<sup>26</sup> and Treacy *et al.*<sup>3</sup> A unit-weighted average of the 298 K rate constants of Huie and Herron,<sup>26</sup> Treacy *et al.*<sup>3</sup> and Greene and Atkinson<sup>5</sup> (corrected to 298 K as described above for 1-butene) leads to the recommended 298 K rate constant of

$$k(\text{trans-2-butene}) = 1.90 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

Combination of this 298 K rate constant with the temperature dependence of  $B = 1059 \text{ K}$  determined from a unit-weighted average of the temperature dependencies of Huie and Herron<sup>26</sup> and Treacy *et al.*<sup>3</sup> leads to the recommendation of

$$k(\text{trans-2-butene}) = 6.64 \times 10^{-15} e^{-1059/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 225–364 K, with an estimated overall uncertainty at 298 K of  $\pm 35\%$ .

This recommendation supersedes that of Atkinson and Carter<sup>1</sup> of

$$k(\text{trans-2-butene}) = 9.08 \times 10^{-15} e^{-1136/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the same temperature range of 225–364 K, with a 298 K rate constant of  $2.00 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

*1-Pentene*. The rate constants of Treacy *et al.*<sup>3</sup> are given in Table 58. The room temperature rate constant of Treacy *et al.*<sup>3</sup> is in reasonable agreement with that of Japar *et al.*<sup>19</sup> of  $(1.07 \pm 0.04) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at  $299 \pm 2 \text{ K}$ . A unit-weighted average of the rate constants of Treacy *et al.*<sup>3</sup> and Japar *et al.*<sup>18</sup> leads to the recommendation of

$$k(1\text{-pentene}) = 1.00 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty of  $\pm 30\%$ .

*2-Methyl-2-butene*. The rate constants of Treacy *et al.*<sup>3</sup>, Atkinson *et al.*<sup>7</sup> and Greene and Atkinson<sup>5</sup> are given in Table 58 and those of Treacy *et al.*<sup>3</sup> and Green and Atkinson<sup>5</sup> are plotted, together with the rate constants of Japar *et al.*<sup>19</sup> and Huie and Herron,<sup>26</sup> in Arrhenius form in Fig. 50. The rate constants of Atkinson *et al.*<sup>7</sup> and Greene and Atkinson<sup>5</sup> are self-consistent and are in good agreement with the room temperature rate constants of Huie and Herron<sup>26</sup> and Treacy *et al.*<sup>3</sup> A unit-weighted average of the 298 K rate constants of Huie and Herron,<sup>26</sup> Treacy *et al.*<sup>3</sup> and Greene and Atkinson<sup>5</sup> (corrected to 298 K as described above for 1-butene) leads to the recommended 298 K rate constant of

$$k(2\text{-methyl-2-butene}) = 4.03 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

Combination of this 298 K rate constant with the temperature dependence of  $B = 829 \text{ K}$  determined from a unit-weighted average of the temperature dependencies of Huie and Herron<sup>26</sup> and Treacy *et al.*<sup>3</sup> leads to the recommendation of

$$k(2\text{-methyl-2-butene}) = 6.51 \times 10^{-15} e^{-829/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 227–363 K, with an estimated overall uncertainty at 298 K of  $\pm 35\%$ . This recommendation supersedes that of Atkinson and Carter<sup>1</sup> of

$$k(2\text{-methyl-2-butene}) = 6.17 \times 10^{-15} e^{-798/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the same temperature range of 227–363 K, with a 298 K rate constant of  $4.23 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

*1-Hexene*. The rate constants of Treacy *et al.*<sup>3</sup> are given in Table 58. These absolute rate constants are in good agreement with the previous room temperature rate constants of Stedman *et al.*,<sup>18</sup> Japar *et al.*,<sup>19</sup> Adeniji *et al.*<sup>28</sup> and Atkinson *et al.*<sup>22</sup> A unit-weighted average of the room temperature constants of Stedman *et al.*,<sup>18</sup> Japar *et al.*,<sup>19</sup> Adeniji *et al.*,<sup>28</sup> Atkinson *et al.*<sup>22</sup> and Treacy *et al.*<sup>3</sup> leads to the recommendation of

$$k(1\text{-hexene}) = 1.10 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty of  $\pm 30\%$ . This recommendation is similar to, but supersedes, that of Atkinson and Carter<sup>1</sup> of

$$k(1\text{-hexene}) = 1.17 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

*2,3-Dimethyl-2-butene*. The relative rate constant of Greene and Atkinson<sup>5</sup> is given in Table 58 and is plotted, together with the rate constants of Japar *et al.*<sup>19</sup> and Huie and Herron,<sup>26</sup> in Arrhenius form in Fig. 50. The room temperature rate constant of Greene and Atkinson<sup>5</sup> is in

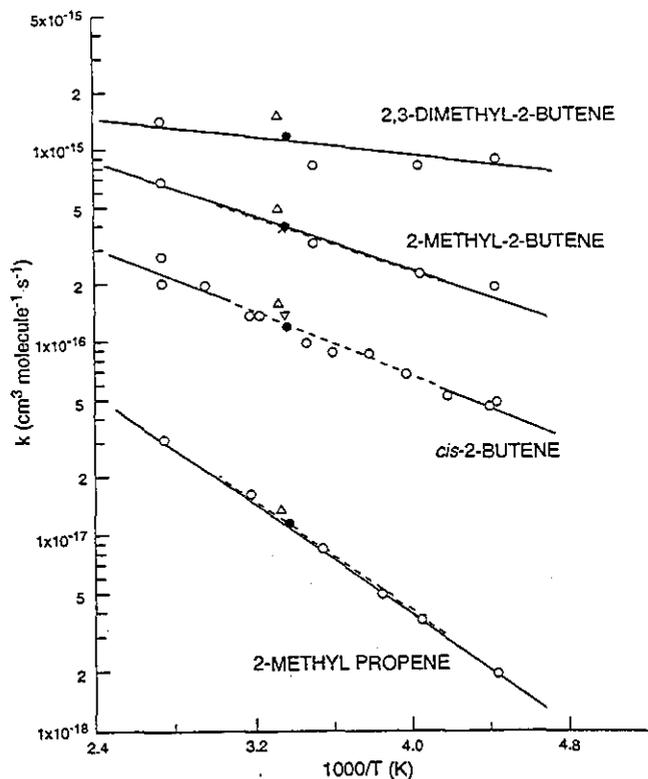


FIG. 50. Arrhenius plots of selected rate constants for the reactions of  $O_3$  with 2-methylpropene, *cis*-2-butene, 2-methyl-2-butene and 2,3-dimethyl-2-butene. ( $\Delta$ ) Japar *et al.*,<sup>19</sup> ( $\circ$ ) Huie and Herron;<sup>26</sup> ( $\nabla$ ) Atkinson *et al.*,<sup>27</sup> ( $-X-$ ) Treacy *et al.*,<sup>3</sup> ( $\bullet$ ) Greene and Atkinson;<sup>5</sup> (—) recommendations (see text). For *cis*-2-butene, the recommendation and Arrhenius line of Treacy *et al.*<sup>3</sup> are indistinguishable.

good agreement with the Arrhenius expression of Huie and Herron.<sup>26</sup> A unit-weighted average of the 298 K rate constants of Huie and Herron<sup>26</sup> and Greene and Atkinson<sup>5</sup> (corrected to 298 K as described above for 1-butene) leads to the recommended 298 K rate constant of

$$k(2,3\text{-dimethyl-2-butene}) = 1.13 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

Combination of this 298 K rate constant with the temperature dependence of  $B = 294$  K of Huie and Herron<sup>26</sup> leads to the recommendation of

$$k(2,3\text{-dimethyl-2-butene}) = 3.03 \times 10^{-15} e^{-294/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 227–363 K, with an estimated overall uncertainty at 298 K of  $\pm 35\%$ . This recommendation is similar to, but supersedes, that of Atkinson and Carter<sup>1</sup> of

$$k(2,3\text{-dimethyl-2-butene}) = 3.71 \times 10^{-15} e^{-347/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the same temperature range of 227–363 K, with a 298 K rate constant of  $1.16 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

*cis*-3-Methyl-2-pentene. The room temperature relative rate constant of Nolting *et al.*<sup>6</sup> (Table 58) is in good agreement with that of Japar *et al.*,<sup>19</sup> of  $(4.56 \pm 0.08) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at  $299 \pm 2$  K, and a unit-weighted average of these two rate constants<sup>6,19</sup> leads to the recommendation of

$$k(\textit{cis}\text{-3-methyl-2-pentene}) = 4.5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K},$$

with an estimated overall uncertainty of  $\pm 35\%$ .

*1,2-Propadiene*. The rate constants of Bahta *et al.*<sup>2</sup> are given in Table 58, and are in good agreement with the Arrhenius expression reported by Toby and Toby.<sup>29</sup> Accordingly, the Arrhenius expression of Bahta *et al.*<sup>2</sup> is preferred.

*1,3-Butadiene*. The rate constants of Bahta *et al.*<sup>2</sup> and Treacy *et al.*<sup>3</sup> are given in Table 58. The room temperature rate constants determined by Bahta *et al.*<sup>2</sup> and Treacy *et al.*<sup>3</sup> are lower than the previous rate constant of Japar *et al.*,<sup>19</sup> and the temperature dependencies of Bahta *et al.*<sup>2</sup> and Treacy *et al.*<sup>3</sup> are lower than that reported by Toby and Toby.<sup>30</sup> The data of Bahta *et al.*<sup>2</sup> and Treacy *et al.*<sup>3</sup> are in reasonably good agreement, especially at around room temperature, and are hence preferred. A unit-weighted average of the 298 K rate constants of Bahta *et al.*<sup>2</sup> and Treacy *et al.*<sup>3</sup> yields the recommendation of

$$k(1,3\text{-butadiene}) = 6.3 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K},$$

with an estimated overall uncertainty of  $\pm 30\%$ . From a unit-weighted average of the temperature dependencies of Bahta *et al.*<sup>2</sup> and Treacy *et al.*,<sup>3</sup> a temperature dependence of  $B = 2283$  K is recommended, leading to

$$k(1,3\text{-butadiene}) = 1.34 \times 10^{-14} e^{-2283/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 231–324 K. This recommendation differs significantly from that of Atkinson and Carter<sup>1</sup> of

$$k(1,3\text{-butadiene}) = 8.8 \times 10^{-14} e^{-2768/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

with a 298 K rate constant of  $8.1 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

*2-Methyl-1,3-butadiene*. The rate constants of Treacy *et al.*<sup>3</sup> and Greene and Atkinson<sup>5</sup> are given in Table 58 and are plotted in Arrhenius form in Fig. 51, together with the data of Arnts and Gay,<sup>31</sup> Adeniji *et al.*<sup>28</sup> and Atkinson *et al.*<sup>32</sup> The room temperature rate constants from these studies<sup>3,5</sup> are in excellent agreement with those of Arnts and Gay<sup>31</sup> ( $1.27 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at  $295 \pm 1$  K) and Atkinson *et al.*<sup>32</sup> [ $(1.25 \pm 0.20) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at  $296 \pm 1$  K and  $(1.17 \pm 0.19) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at  $296 \pm 2$  K], but are significantly lower than the room temperature rate constant of Adeniji *et al.*<sup>28</sup> Combination of the 295–298 K rate con-

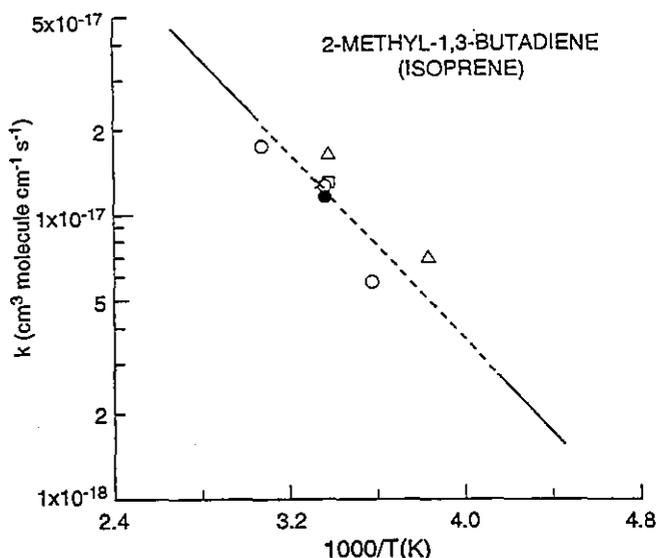


FIG. 51. Arrhenius plot of rate constants for the reaction of  $O_3$  with 2-methyl-1,3-butadiene (isoprene). ( $\square$ ) Arnts and Gay,<sup>31</sup> ( $\Delta$ ) Adeniji *et al.*,<sup>28</sup> ( $\circ$ ) Atkinson *et al.*,<sup>32</sup> ( $-X-$ ) Treacy *et al.*,<sup>3</sup> ( $\bullet$ ) Greene and Atkinson,<sup>5</sup> ( $-$ ) recommendation (see text). [The recommendation and the Arrhenius expression of Treacy *et al.*<sup>3</sup> are indistinguishable].

stants of Arnts and Gay,<sup>31</sup> Atkinson *et al.*,<sup>32</sup> Treacy *et al.*<sup>3</sup> and Greene and Atkinson<sup>5</sup> with the temperature dependence of  $B = 1913$  K determined by Tracy *et al.*<sup>3</sup> leads to the recommendation of

$$k(2\text{-methyl-1,3-butadiene}) = 7.86 \times 10^{-15} e^{-1913/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 240–324 K, and

$$k(2\text{-methyl-1,3-butadiene}) = 1.28 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of  $\pm 25\%$ . This recommendation supersedes that of Atkinson and Carter<sup>1</sup> of

$$k(2\text{-methyl-1,3-butadiene}) = 1.23 \times 10^{-14} e^{-2013/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

with a 298 K rate constant of  $1.43 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

**Cyclopentene.** The rate constants of Bennett *et al.*,<sup>10</sup> Nolting *et al.*,<sup>6</sup> and Greene and Atkinson<sup>5</sup> are given in Table 58. As discussed previously, the previous room temperature rate constants for this reaction<sup>19,27,28</sup> range over a factor of 3.5. The room temperature relative rate constants of Nolting *et al.*<sup>6</sup> and Greene and Atkinson<sup>5</sup> are in excellent agreement and, based mainly on the rate constant of Greene and Atkinson,<sup>5</sup> it is recommended that

$$k(\text{cyclopentene}) = 6.3 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty of  $\pm 35\%$ .

**Cyclohexene.** The room temperature rate constants of Bennett *et al.*,<sup>10</sup> Nolting *et al.*,<sup>6</sup> Izumi *et al.*<sup>11</sup> and Greene and Atkinson<sup>5</sup> are given in Table 58. Somewhat analogous to the situation for cyclopentene, these<sup>5,6,10,11</sup> and previous<sup>19,27,28</sup> literature room temperature rate constants exhibit a significant degree of scatter, covering a range of  $\sim 2.7$  in this case. Again, the relative rate constants of Nolting *et al.*<sup>6</sup> and Greene and Atkinson<sup>5</sup> are in good agreement and, based mainly on the rate constant of Greene and Atkinson,<sup>5</sup> it is recommended that

$$k(\text{cyclohexene}) = 7.2 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty of  $\pm 30\%$ .

**1,4-Cyclohexadiene.** The relative rate constant of Greene and Atkinson<sup>5</sup> is given in Table 58. This rate constant is 28% lower than that of Atkinson *et al.*<sup>27</sup> The rate constant of Greene and Atkinson<sup>5</sup> is recommended, of

$$k(1,4\text{-cyclohexadiene}) = 4.6 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty of  $\pm 35\%$ .

**Cycloheptene.** The relative rate constant of Nolting *et al.*<sup>6</sup> is given in Table 58. This rate constant of Nolting *et al.*<sup>6</sup> is in reasonable agreement with that of Atkinson *et al.*<sup>27</sup> of  $(3.19 \pm 0.36) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at  $297 \pm 1$  K. A unit-weighted average of these rate constants<sup>6,27</sup> leads to the recommendation of

$$k(\text{cycloheptene}) = 2.9 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty of  $\pm 35\%$ .

**$\alpha$ -Pinene.** The rate constants of Nolting *et al.*<sup>6</sup> and Atkinson *et al.*<sup>9</sup> are given in Table 58. In addition, the relative rate constant for sabinene relative to that for  $\alpha$ -pinene determined in the study of Atkinson *et al.*<sup>9</sup> can be combined with the absolute rate constant for sabinene<sup>12</sup> to obtain a rate constant for  $\alpha$ -pinene of  $7.99 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at  $296 \pm 2$  K.<sup>9</sup> The absolute rate constants of Atkinson *et al.*<sup>9,32</sup> and the relative rate constants of Nolting *et al.*<sup>6</sup> and Atkinson *et al.*<sup>9</sup> are in good agreement, and a unit-weighted average of these rate constants<sup>6,9,32</sup> leads to the recommendation of

$$k(\alpha\text{-pinene}) = 8.52 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 296 \pm 1 \text{ K.}$$

Combining this 296 K rate constant with the temperature dependence of Atkinson *et al.*<sup>32</sup> of  $B = 731 \pm 174$  K leads to the recommendation of

$$k(\alpha\text{-pinene}) = 1.01 \times 10^{-15} e^{-732/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 276–324 K, and

$$k(\alpha\text{-pinene}) = 8.66 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of  $\pm 30\%$ .

**$\beta$ -Pinene.** The room temperature rate constants of Nolting *et al.*<sup>6</sup> and Atkinson *et al.*<sup>9</sup> are given in Table 58. The rate constants from these studies<sup>6,9</sup> are in good agreement, and agree reasonably well with the rate constant of  $(2.1 \pm 0.5) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at  $296 \pm 2 \text{ K}$  determined previously by Atkinson *et al.*<sup>32</sup> A unit-weighted average of the absolute and relative rate constants of Nolting *et al.*<sup>6</sup> and Atkinson *et al.*<sup>9</sup> leads to the recommendation of

$$k(\beta\text{-pinene}) = 1.5 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty of  $\pm 35\%$ .

**2-Carene, 3-Carene and Sabinene.** The absolute and relative rate constants of Atkinson *et al.*<sup>9,12</sup> are given in Table 58. The relative rate constants are preferred,<sup>9</sup> leading to the recommendations of

$$k(2\text{-carene}) = 2.3 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$k(3\text{-carene}) = 3.7 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

and

$$k(\text{sabinene}) = 8.6 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

all at 298 K and with estimated overall uncertainties of  $\pm 35\%$ .

**Other Terpenes.** The rate constants of Atkinson *et al.*<sup>9,12</sup> and Shorees *et al.*<sup>13</sup> are given in Table 58. As discussed previously,<sup>1,9</sup> these rate constants are significantly lower than the previous literature data, but are preferred. The rate constants of Atkinson *et al.*<sup>9,12</sup> and Shorees *et al.*<sup>13</sup> should therefore be used.

**Other Alkenes.** For the other alkenes for which data are given in Table 58, these are the first reported data, apart from 1,3-pentadiene for which the studies of Bahta *et al.*<sup>2</sup> and Treacy *et al.*<sup>3</sup> give very different temperature dependencies (but similar room temperature rate constants).

## References

- <sup>1</sup>R. Atkinson and W. P. L. Carter, *Chem. Rev.* **84**, 437 (1984).
- <sup>2</sup>A. Bahta, R. Simonaitis, and J. Heicklen, *Int. J. Chem. Kinet.* **16**, 1227 (1984).
- <sup>3</sup>J. Treacy, M. El Hag, D. O'Farrell, and H. Sidebottom, *Ber. Bunsenges. Phys. Chem.* **96**, 422 (1992).
- <sup>4</sup>J. T. Herron and R. E. Huie, *J. Phys. Chem.* **78**, 2085 (1974).
- <sup>5</sup>C. R. Greene and R. Atkinson, *Int. J. Chem. Kinet.* **24**, 803 (1992).
- <sup>6</sup>F. Nolting, W. Behnke, and C. Zetzsch, *J. Atmos. Chem.* **6**, 47 (1988).
- <sup>7</sup>R. Atkinson, J. Arey, and S. M. Aschmann, *Int. J. Chem. Kinet.* **24**, 467 (1992).
- <sup>8</sup>D. Grosjean, *Sci. Total Environ.* **37**, 195 (1984).
- <sup>9</sup>R. Atkinson, D. Hasegawa, and S. M. Aschmann, *Int. J. Chem. Kinet.* **22**, 871 (1990).
- <sup>10</sup>P. J. Bennett, S. J. Harris, and J. A. Kerr, *Int. J. Chem. Kinet.* **19**, 609 (1987).

- <sup>11</sup>K. Izumi, K. Murano, M. Mizuochi, and T. Fukuyama, *Environ. Sci. Technol.* **22**, 1207 (1988).
- <sup>12</sup>R. Atkinson, S. M. Aschmann, and J. Arey, *Atmos. Environ.* **24A**, 2647 (1990).
- <sup>13</sup>B. Shorees, R. Atkinson, and J. Arey, *Int. J. Chem. Kinet.* **23**, 897 (1991).
- <sup>14</sup>M. Donlon, D. J. O'Farrell, J. J. Treacy, and H. W. Sidebottom, *Proc. 5th European Symposium on the Physico-Chemical Behaviour of Atmospheric Pollutants*, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1990, pp. 359–363.
- <sup>15</sup>F. Su, J. G. Calvert, and J. H. Shaw, *J. Phys. Chem.* **84**, 239 (1980).
- <sup>16</sup>C. S. Kan, F. Su, J. G. Calvert, and J. H. Shaw, *J. Phys. Chem.* **85**, 2359 (1981).
- <sup>17</sup>W. B. DeMore, *Int. J. Chem. Kinet.* **1**, 209 (1969).
- <sup>18</sup>D. H. Stedman, C. H. Wu, and H. Niki, *J. Phys. Chem.* **77**, 2511 (1973).
- <sup>19</sup>S. M. Japar, C. H. Wu, and H. Niki, *J. Phys. Chem.* **78**, 2318 (1974).
- <sup>20</sup>S. M. Japar, C. H. Wu, and H. Niki, *J. Phys. Chem.* **80**, 2057 (1976).
- <sup>21</sup>F. S. Toby, S. Toby, and H. E. O'Neal, *Int. J. Chem. Kinet.* **8**, 25 (1976).
- <sup>22</sup>R. Atkinson, S. M. Aschmann, D. R. Fitz, A. M. Winer, and J. N. Pitts, Jr., *Int. J. Chem. Kinet.* **14**, 13 (1982).
- <sup>23</sup>W. B. DeMore, S. P. Sander, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, A. R. Ravishankara, C. E. Kolb, and M. J. Molina, "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling," NASA Panel for Data Evaluation, Evaluation No. 10, Jet Propulsion Laboratory Publication 92-20, August 15, 1992.
- <sup>24</sup>R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, and J. Troe, *J. Phys. Chem. Ref. Data* **21**, 1125 (1992).
- <sup>25</sup>R. A. Cox and S. A. Penkett, *J. Chem. Soc. Faraday Trans. 1*, **68**, 1735 (1972).
- <sup>26</sup>R. E. Huie and J. T. Herron, *Int. J. Chem. Kinet. Symp.* **1**, 165 (1975).
- <sup>27</sup>R. Atkinson, S. M. Aschmann, W. P. L. Carter, and J. N. Pitts, Jr., *Int. J. Chem. Kinet.* **15**, 721 (1983).
- <sup>28</sup>S. A. Adeniji, J. A. Kerr, and M. R. Williams, *Int. J. Chem. Kinet.* **13**, 209 (1981).
- <sup>29</sup>F. S. Toby and S. Toby, *Int. J. Chem. Kinet.* **6**, 417 (1974).
- <sup>30</sup>F. S. Toby and S. Toby, *Int. J. Chem. Kinet. Symp.* **1**, 197 (1975).
- <sup>31</sup>R. R. Arnts and B. W. Gay, Jr., "Photochemistry of Some Naturally Emitted Hydrocarbons," EPA-600/3-79-081, September 1979, Research Triangle Park, NC.
- <sup>32</sup>R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., *Atmos. Environ.* **16**, 1017 (1982).

## 5.3. Haloalkenes

The rate constants reported since the review and evaluation of Atkinson and Carter<sup>1</sup> are given in Table 59. The rate constant of Toby and Toby<sup>2</sup> for  $\text{CF}_2 = \text{CF}_2$  was inadvertently omitted from the previous evaluation.<sup>1</sup> This room temperature rate constant of Toby and Toby<sup>2</sup> for  $\text{CF}_2 = \text{CF}_2$  is lower by factors of  $\sim 3$  and 20 than the measurements of Adeniji *et al.*<sup>5</sup> and Heicklen,<sup>6</sup> respectively.

**3-Chloro-1-propene (allyl chloride).** The rate constants of Edney *et al.*<sup>3</sup> and Tuazon *et al.*<sup>4</sup> are given in Table 59. These rate constants<sup>3,4</sup> are in good agreement, and a unit-weighted average leads to the recommendation of

$$k(\text{allyl chloride}) = 1.55 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty of  $\pm 30\%$ . Product studies were also conducted by Edney *et al.*<sup>3</sup> and Tuazon *et al.*<sup>4</sup> and these references should be consulted for further details.

## References

- <sup>1</sup>R. Atkinson and W. P. L. Carter, *Chem. Rev.* **84**, 437 (1984).  
<sup>2</sup>F. S. Toby and S. Toby, *J. Phys. Chem.* **80**, 2313 (1976).  
<sup>3</sup>E. O. Edney, P. B. Shepson, T. E. Kleindienst, and E. W. Corse, *Int. J. Chem. Kinet.* **18**, 597 (1986).  
<sup>4</sup>E. C. Tuazon, R. Atkinson, and S. M. Aschmann, *Int. J. Chem. Kinet.* **22**, 981 (1990).  
<sup>5</sup>A. Adeniji, J. A. Kerr, and M. R. Williams, *Int. J. Chem. Kinet.* **13**, 209 (1981).  
<sup>6</sup>J. Heicklen, *J. Phys. Chem.* **70**, 477, 4101 (1966).

## 5.4. Oxygen-Containing Organic Compounds

The kinetic data reported since the review and evaluation of Atkinson and Carter<sup>1</sup> are given in Table 60. As expected, no evidence for any reaction of 1,8-cineole (a cyclic saturated ether) was observed.<sup>2</sup>

**Acrolein.** The rate constant measured by Treacy *et al.*<sup>3</sup> at 298 ± 2 K is given in Table 60. This rate constant of Treacy *et al.*<sup>3</sup> is in excellent agreement with that of Atkinson *et al.*<sup>5</sup> of (2.8 ± 0.5) × 10<sup>-19</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 296 ± 2 K. A unit-weighted average of the rate constants of Atkinson *et al.*<sup>5</sup> and Treacy *et al.*<sup>3</sup> leads to the recommended rate constant of

$$k(\text{acrolein}) = 2.9 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty of ±35%.

**Methacrolein.** The 298 K rate constant and Arrhenius expression reported by Treacy *et al.*<sup>3</sup> are given in Table 60 (the individual rate constants at the temperatures studied were not tabulated). The 298 K rate constant of Treacy *et al.*<sup>3</sup> is in good agreement with the room temperature rate constants of Atkinson *et al.*<sup>5</sup> of (1.12 ± 0.13) × 10<sup>-18</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 296 ± 2 K, and Kamens *et al.*<sup>6</sup> of 1.1 × 10<sup>-18</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at an unspecified room temperature.

A unit-weighted average of the room temperature rate constants of Atkinson *et al.*<sup>5</sup> and Treacy *et al.*<sup>3</sup> combined with the temperature dependence of Treacy *et al.*<sup>3</sup> leads to the recommended Arrhenius expression of

$$k(\text{methacrolein}) = 1.36 \times 10^{-15} e^{-2112/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 240–324 K, and

$$k(\text{methacrolein}) = 1.14 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

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

**Methyl vinyl ketone.** The 298 K rate constant and Arrhenius expression reported by Treacy *et al.*<sup>3</sup> are given in Table 60. The 298 K rate constant of Treacy *et al.*<sup>3</sup> is in reasonable agreement with the rate constants of Atkinson *et al.*<sup>5</sup> of (4.77 ± 0.59) × 10<sup>-18</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 296 ± 2 K, and Kamens *et al.*<sup>6</sup> of 4.0 × 10<sup>-18</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at an unspecified room temperature. A unit-weighted average of the room temperature rate con-

stants of Atkinson *et al.*<sup>5</sup> and Treacy *et al.*<sup>3</sup> combined with the temperature dependence of Treacy *et al.*<sup>3</sup> leads to the recommended Arrhenius expression of

$$k(\text{methyl vinyl ketone}) = 7.51 \times 10^{-16} e^{-1521/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 240–324 K, and

$$k(\text{methyl vinyl ketone}) = 4.56 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

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

## References

- <sup>1</sup>R. Atkinson and W. P. L. Carter, *Chem. Rev.* **84**, 437 (1984).  
<sup>2</sup>R. Atkinson, D. Hasegawa, and S. M. Aschmann, *Int. J. Chem. Kinet.* **22**, 871 (1990).  
<sup>3</sup>J. Treacy, M. El Hag, D. O'Farrell, and H. Sidebottom, *Ber. Bunsenges. Phys. Chem.* **96**, 422 (1992).  
<sup>4</sup>R. Atkinson and S. M. Aschmann, *J. Atmos. Chem.* **16**, 337 (1993).  
<sup>5</sup>R. Atkinson, S. M. Aschmann, A. M. Winer, and J. N. Pitts, Jr., *Int. J. Chem. Kinet.* **13**, 1133 (1981).  
<sup>6</sup>R. M. Kamens, M. W. Gery, H. E. Jeffries, M. Jackson, E. I. Cole, *Int. J. Chem. Kinet.* **14**, 955 (1982).

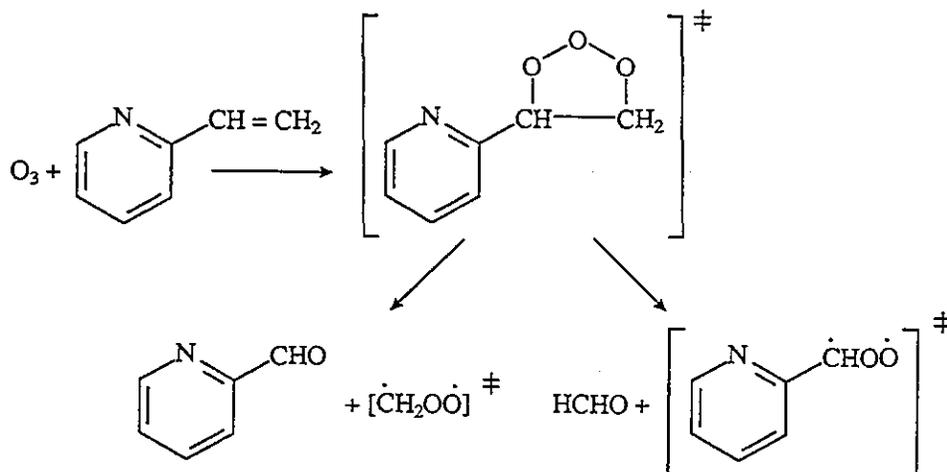
## 5.5. Nitrogen-Containing Organic Compounds

The rate constants reported since the review and evaluation of Atkinson and Carter<sup>1</sup> are given in Table 61. The rate constants of Tuazon *et al.*<sup>2</sup> for the aliphatic amines and tetramethylhydrazine are all lower, by factors of ~1.2–3, than the unpublished data of Tuazon, Atkinson, Carter and Pitts, cited in Atkinson and Carter.<sup>1</sup> The rate constants of Tuazon *et al.*<sup>2</sup> given in Table 61 are preferred.

The rate constant for 2-vinylpyridine<sup>4</sup> is very similar to that for styrene (see Sec. 5.7. below), indicating that the O<sub>3</sub> reaction proceeds by initial O<sub>3</sub> addition to the -CH=CH<sub>2</sub> substituent group. Under atmospheric conditions, the major products of the O<sub>3</sub> reaction with 2-vinylpyridine were determined to be 2-pyridinecarboxaldehyde and HCHO, with yields of 0.80 ± 0.09 and 0.34 ± 0.05, respectively,<sup>4</sup> together with minor amounts of pyridine, HCOOH and HC(O)OOH.<sup>4</sup> (See Reaction Scheme (17) on the next page.)

## References

- <sup>1</sup>R. Atkinson and W. P. L. Carter, *Chem. Rev.* **84**, 437 (1984).  
<sup>2</sup>E. C. Tuazon, R. Atkinson, S. M. Aschmann, and J. Arey, *Res. Chem. Intermed.*, in press (1993).  
<sup>3</sup>R. Atkinson, E. C. Tuazon, T. J. Wallington, S. M. Aschmann, J. Arey, A. M. Winer, and J. N. Pitts, Jr., *Environ. Sci. Technol.* **21**, 64 (1987).  
<sup>4</sup>E. C. Tuazon, J. Arey, R. Atkinson, and S. M. Aschmann, *Environ. Sci. Technol.* **27**, 1832 (1993).  
<sup>5</sup>E. S. C. Kwok, R. Atkinson, and J. Arey, *Environ. Sci. Technol.* **26**, 1798 (1992).



Reaction Scheme (17)

### 5.6. Phosphorus-, Silicon- and Selenium-Containing Organic Compounds

The rate constants reported since the review and evaluation of Atkinson and Carter<sup>1</sup> are given in Table 62. Only for dimethyl selenide ( $\text{CH}_3\text{SeCH}_3$ ) was a reaction observed.<sup>8</sup>

### References

- <sup>1</sup>R. Atkinson and W. P. L. Carter, *Chem. Rev.* **84**, 437 (1984).
- <sup>2</sup>E. C. Tuazon, R. Atkinson, S. M. Aschmann, J. Arey, A. M. Winer, and J. N. Pitts, Jr., *Environ. Sci. Technol.* **20**, 1043 (1986).
- <sup>3</sup>M. A. Goodman, S. M. Aschmann, R. Atkinson, and A. M. Winer, *Arch. Environ. Contam. Toxicol.* **17**, 281 (1988).
- <sup>4</sup>R. Atkinson, S. M. Aschmann, M. A. Goodman, and A. M. Winer, *Int. J. Chem. Kinet.* **20**, 273 (1988).
- <sup>5</sup>M. A. Goodman, S. M. Aschmann, R. Atkinson, and A. M. Winer, *Environ. Sci. Technol.* **22**, 578 (1988).
- <sup>6</sup>R. Atkinson, *Environ. Sci. Technol.* **25**, 863 (1991).
- <sup>7</sup>R. Atkinson, S. M. Aschmann, and J. Arey, unpublished data (1992).
- <sup>8</sup>R. Atkinson, S. M. Aschmann, D. Hasegawa, E. T. Thompson-Eagle, and W. T. Frankenberger, Jr., *Environ. Sci. Technol.* **24**, 1326 (1990).

### 5.7. Aromatic Compounds

The rate constants reported since the review and evaluation of Atkinson and Carter<sup>1</sup> are given in Table 63. In most cases, only upper limits to the rate constants have been obtained.

**Benzene and Alkyl-Substituted Benzenes.** The rate constants of Toby *et al.*<sup>2</sup> for benzene, toluene and the xylenes and of Atkinson *et al.*<sup>3</sup> for 1-methyl-4-isopropylbenzene are given in Table 63. These reactions are extremely slow at room temperature and, consistent with the conclusions of Atkinson and Carter,<sup>1</sup> an upper limit of

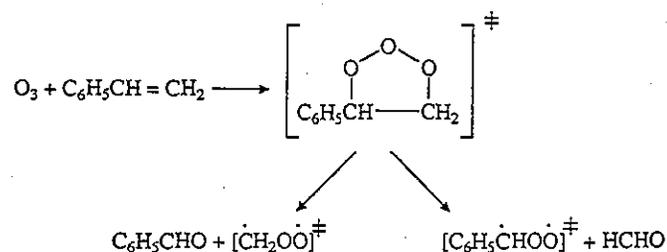
$$k(\text{benzene and alkyl-benzenes}) < 1 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}$$

is recommended.

**Styrene.** The rate constant of Tuazon *et al.*<sup>6</sup> is given in Table 63. This room temperature rate constant is in good agreement with that of Atkinson *et al.*<sup>13</sup> of  $(2.16 \pm 0.46) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at  $296 \pm 2 \text{ K}$ . The study of Tuazon *et al.*<sup>6</sup> supersedes that of Atkinson *et al.*<sup>13</sup> and the rate constant of Tuazon *et al.*<sup>6</sup> is used to recommend that

$$k(\text{styrene}) = 1.71 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K},$$

with an estimated overall uncertainty of  $\pm 35\%$ . This reaction proceeds by initial addition of  $\text{O}_3$  to the  $-\text{CH}=\text{CH}_2$  substituent group,



and both  $\text{HCHO}$  and  $\text{C}_6\text{H}_5\text{CHO}$  were observed by Tuazon *et al.*<sup>6</sup> in yields of  $0.37 \pm 0.05$  and  $0.41 \pm 0.05$ , respectively.

**2,3-Benzofuran and Acenaphthylene.** In contrast to most of the other aromatic compounds studied (Table 63 and Atkinson and Carter<sup>1</sup>), these two compounds react with  $\text{O}_3$ . These  $\text{O}_3$  reactions proceed by initial  $\text{O}_3$  addition to the  $>\text{C}=\text{C}<$  bonds in the 5-membered ring systems.<sup>7,11</sup>

TABLE 59. Rate constants  $k$  and temperature-dependent parameters,  $k = Ae^{-B/T}$ , for the gas-phase reactions of  $O_3$  with haloalkenes

Haloalkene	$10^{12} \times A$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	$B$ (K)	$k$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	at $T$ (K)	Technique	Reference	Temperature range covered (K)
Tetrafluoroethene	$0.26 \pm 0.18$	$4781 \pm 353$	$2.8 \times 10^{-20}$ <sup>a</sup>	298	S-UV	Toby and Toby <sup>2</sup>	273-383
3-Chloro-1-propene (allyl chloride)			$(1.5 \pm 0.23) \times 10^{-18}$	298	S-UV	Edney <i>et al.</i> <sup>3</sup>	
			$(1.60 \pm 0.18) \times 10^{-18}$	$298 \pm 2$	S-CL	Tuazon <i>et al.</i> <sup>4</sup>	

<sup>a</sup>Calculated from Arrhenius expression.TABLE 60. Rate constants  $k$  and temperature-dependent parameters for the gas-phase reactions of  $O_3$  with oxygen-containing compounds

Oxygenate	$A$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	$B$ (K)	$k$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	at $T$ (K)	Technique	Reference	Temperature range covered (K)
1,8-Cineole			$< 1.5 \times 10^{-19}$	$296 \pm 2$	S-CL	Atkinson <i>et al.</i> <sup>2</sup>	
Acrolein [ $\text{CH}_2=\text{CHCHO}$ ]			$(3.0 \pm 0.4) \times 10^{-19}$	$298 \pm 2$	S-UV	Treacy <i>et al.</i> <sup>3</sup>	
Methacrolein [ $\text{CH}_2=\text{C}(\text{CH}_3)\text{CHO}$ ]	$(1.3 \pm 0.2) \times 10^{-15}$	$2112 \pm 131$	$(1.1 \pm 0.2) \times 10^{-18}$	298	S-UV	Treacy <i>et al.</i> <sup>3</sup>	240-324
Methyl vinyl ketone [ $\text{CH}_2=\text{CHC}(\text{O})\text{CH}_3$ ]	$(6.9 \pm 1.4) \times 10^{-16}$	$1521 \pm 78$	$(4.2 \pm 0.4) \times 10^{-18}$	298	S-UV	Treacy <i>et al.</i> <sup>3</sup>	240-324
4-Acetyl-1- methylcyclohexene			$(1.50 \pm 0.04) \times 10^{-16}$	$296 \pm 2$	RR [relative to $k(2\text{-methyl-2-}$ $\text{butene}) = 3.96$ $\times 10^{-16}$ ] <sup>a</sup>	Atkinson and Aschmann <sup>4</sup>	

<sup>a</sup>From present recommendation.

TABLE 61. Rate constants  $k$  for the gas-phase reactions of  $O_3$  with nitrogen-containing organic compounds

Organic	$k$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	at $T$ (K)	Technique	Reference
Methylamine	$(7.4 \pm 2.4) \times 10^{-21}$	298 $\pm$ 2	S-CL	Tuazon <i>et al.</i> <sup>2</sup>
Dimethylamine	$(1.67 \pm 0.20) \times 10^{-18}$	298 $\pm$ 2	S-CL	Tuazon <i>et al.</i> <sup>2</sup>
Trimethylamine	$(7.84 \pm 0.87) \times 10^{-18}$	298 $\pm$ 2	S-CL	Tuazon <i>et al.</i> <sup>2</sup>
2-(Dimethylamino)ethanol [(CH <sub>3</sub> ) <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> OH]	$(6.76 \pm 0.83) \times 10^{-18}$	298 $\pm$ 2	S-CL	Tuazon <i>et al.</i> <sup>2</sup>
Tetramethylhydrazine	$(5.21 \pm 0.60) \times 10^{-18}$	298 $\pm$ 2	S-CL	Tuazon <i>et al.</i> <sup>2</sup>
Pyridine	$< 1.1 \times 10^{-20}$	296 $\pm$ 2	S-CL	Atkinson <i>et al.</i> <sup>3</sup>
2-Vinylpyridine	$(1.46 \pm 0.17) \times 10^{-17}$	298 $\pm$ 2	S-CL	Tuazon <i>et al.</i> <sup>4</sup>
1,3,5-Triazine	$< 4 \times 10^{-21}$	296 $\pm$ 2	S-CL	Atkinson <i>et al.</i> <sup>3</sup>
(CH <sub>3</sub> ) <sub>2</sub> NC(O)SCH <sub>3</sub>	$< 4 \times 10^{-20}$	298 $\pm$ 2	S-GC	Kwok <i>et al.</i> <sup>5</sup>
(CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> NC(O)SCH <sub>2</sub> CH <sub>3</sub>	$< 1.3 \times 10^{-19}$	298 $\pm$ 2	S-GC	Kwok <i>et al.</i> <sup>5</sup>
CH <sub>3</sub> CH <sub>2</sub> ( <i>c</i> -C <sub>6</sub> H <sub>11</sub> )NC(O)SCH <sub>2</sub> CH <sub>3</sub>	$< 3 \times 10^{-19}$	298 $\pm$ 2	S-GC	Kwok <i>et al.</i> <sup>5</sup>

TABLE 62. Rate constants  $k$  for the gas-phase reactions of  $O_3$  with phosphorus-, selenium- and silicon- containing organic compounds

Organic	$k$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	at $T$ (K)	Technique	Reference
<i>Phosphorus-Containing</i>				
(CH <sub>3</sub> O) <sub>3</sub> PO	$< 6 \times 10^{-20}$	296 $\pm$ 2	S-IR	Tuazon <i>et al.</i> <sup>2</sup>
(CH <sub>3</sub> O) <sub>2</sub> P(O)SCH <sub>3</sub>	$< 2 \times 10^{-19}$	298 $\pm$ 2	S-GC	Goodman <i>et al.</i> <sup>3</sup>
(CH <sub>3</sub> S) <sub>2</sub> P(O)OCH <sub>3</sub>	$< 1 \times 10^{-19}$	298 $\pm$ 2	S-GC	Goodman <i>et al.</i> <sup>3</sup>
(CH <sub>3</sub> O) <sub>3</sub> PS	$< 3 \times 10^{-19}$	298 $\pm$ 2	S-GC	Goodman <i>et al.</i> <sup>3</sup>
(CH <sub>3</sub> O) <sub>2</sub> P(S)SCH <sub>3</sub>	$< 2 \times 10^{-19}$	298 $\pm$ 2	S-GC	Goodman <i>et al.</i> <sup>3</sup>
(CH <sub>3</sub> O) <sub>3</sub> P(S)Cl	$< 2 \times 10^{-19}$	296 $\pm$ 2	S-GC	Atkinson <i>et al.</i> <sup>4</sup>
(CH <sub>3</sub> O) <sub>2</sub> P(O)N(CH <sub>3</sub> ) <sub>2</sub>	$< 2 \times 10^{-19}$	296 $\pm$ 2	S-GC	Goodman <i>et al.</i> <sup>5</sup>
(CH <sub>3</sub> O) <sub>2</sub> P(S)N(CH <sub>3</sub> ) <sub>2</sub>	$< 2 \times 10^{-19}$	296 $\pm$ 2	S-GC	Goodman <i>et al.</i> <sup>5</sup>
(CH <sub>3</sub> O) <sub>2</sub> P(S)NHCH <sub>3</sub>	$< 2 \times 10^{-19}$	296 $\pm$ 2	S-GC	Goodman <i>et al.</i> <sup>5</sup>
(CH <sub>3</sub> O) <sub>2</sub> P(S)NH <sub>2</sub>	$< 4 \times 10^{-19}$	296 $\pm$ 2	S-GC	Goodman <i>et al.</i> <sup>5</sup>
<i>Silicon-Containing</i>				
Tetramethylsilane [(CH <sub>3</sub> ) <sub>4</sub> Si]	$< 7 \times 10^{-21}$	297 $\pm$ 2	S-GC	Atkinson <sup>6</sup>
Hexamethyldisiloxane [(CH <sub>3</sub> ) <sub>2</sub> SiOSi(CH <sub>3</sub> ) <sub>3</sub> ]	$< 7 \times 10^{-21}$	297 $\pm$ 2	S-GC	Atkinson <sup>6</sup>
Hexamethylcyclotrisiloxane [-(CH <sub>3</sub> ) <sub>2</sub> SiO-] <sub>3</sub>	$< 3 \times 10^{-20}$	297 $\pm$ 2	S-GC	Atkinson <sup>6</sup>
Octamethylcyclotetrasiloxane [-(CH <sub>3</sub> ) <sub>2</sub> SiO-] <sub>4</sub>	$< 3 \times 10^{-20}$	297 $\pm$ 2	S-GC	Atkinson <sup>6</sup>
Decamethylcyclopentasiloxane [-(CH <sub>3</sub> ) <sub>2</sub> SiO-] <sub>5</sub>	$< 3 \times 10^{-20}$	297 $\pm$ 2	S-GC	Atkinson <sup>6</sup>
(CH <sub>3</sub> ) <sub>3</sub> SiOSi(CH <sub>3</sub> ) <sub>2</sub> OH	$< 7 \times 10^{-20}$	297 $\pm$ 2	S-GC	Atkinson <i>et al.</i> <sup>7</sup>
<i>Selenium-Containing</i>				
Dimethyl selenide (CH <sub>3</sub> ) <sub>2</sub> Se	$(6.80 \pm 0.72) \times 10^{-17}$	296 $\pm$ 2	S-CL	Atkinson <i>et al.</i> <sup>8</sup>

TABLE 63. Rate constants  $k$  and temperature dependent parameters,  $k = Ae^{-B/T}$ , for the gas-phase reactions of  $O_3$  with aromatic compounds

Aromatic	$10^{12} \times A$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$B$ (K)	$k$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	at $T$ (K)	Technique	Reference	Temperature range covered (K)
Benzene	$10.5 \pm 1.9$	$7398 \pm 353$	$1.7 \times 10^{-22}$ <sup>a</sup>	298	S-UV	Toby <i>et al.</i> <sup>2</sup>	298-423
Toluene	$2.34 \pm 1.28$	$6694 \pm 403$	$4.1 \times 10^{-22}$ <sup>a</sup>	298	S-UV	Toby <i>et al.</i> <sup>2</sup>	298-398
<i>o</i> -Xylene	$0.240 \pm 0.032$	$5586 \pm 453$	$1.7 \times 10^{-21}$ <sup>a</sup>	298	S-UV	Toby <i>et al.</i> <sup>2</sup>	298-423
<i>m</i> -Xylene	$0.537 \pm 0.033$	$6039 \pm 202$	$8.5 \times 10^{-22}$ <sup>a</sup>	298	S-UV	Toby <i>et al.</i> <sup>2</sup>	298-423
<i>p</i> -Xylene	$0.191 \pm 0.028$	$5586 \pm 302$	$1.4 \times 10^{-21}$ <sup>a</sup>	298	S-UV	Toby <i>et al.</i> <sup>2</sup>	298-423
1-Methyl-4-isopropylbenzene ( <i>p</i> -cymene)			$< 5 \times 10^{-20}$	$296 \pm 2$	S-CL	Atkinson <i>et al.</i> <sup>3</sup>	
			$\leq 2.1 \times 10^{-18}$	$296 \pm 2$	RR [relative to $k(\alpha\text{-pinene}) = 8.52 \times 10^{-17}$ ] <sup>b</sup>	Atkinson <i>et al.</i> <sup>3</sup>	
Benzylchloride			$< 6 \times 10^{-20}$	$298 \pm 2$	S-CL	Tuazon <i>et al.</i> <sup>4</sup>	
Nitrobenzene			$< 7 \times 10^{-21}$	$296 \pm 2$	S-CL	Atkinson <i>et al.</i> <sup>5</sup>	
Aniline			$(1.12 \pm 0.14) \times 10^{-18}$	$296 \pm 2$	S-CL	Atkinson <i>et al.</i> <sup>5</sup>	
<i>N,N</i> -Dimethylaniline			$(9.1 \pm 1.0) \times 10^{-18}$	$296 \pm 2$	S-CL	Atkinson <i>et al.</i> <sup>5</sup>	
Styrene			$(1.71 \pm 0.18) \times 10^{-17}$	$296 \pm 2$	S-CL	Tuazon <i>et al.</i> <sup>6</sup>	
1,4-Benzodioxan			$< 1.2 \times 10^{-20}$	$298 \pm 2$	S-CL	Atkinson <i>et al.</i> <sup>7</sup>	
2,3-Dihydrobenzofuran			$< 1 \times 10^{-19}$	$298 \pm 2$	S-CL	Atkinson <i>et al.</i> <sup>7</sup>	
2,3-Benzofuran			$(1.83 \pm 0.21) \times 10^{-18}$	$298 \pm 2$	S-CL	Atkinson <i>et al.</i> <sup>7</sup>	
1,4-Naphthoquinone			$< 2 \times 10^{-19}$	$298 \pm 2$	S-GC	Atkinson <i>et al.</i> <sup>8</sup>	
Naphthalene			$< 3 \times 10^{-19}$	$295 \pm 1$	S-GC	Atkinson and Aschmann <sup>9</sup>	
1-Methylnaphthalene			$< 1.3 \times 10^{-19}$	$298 \pm 2$	S-GC	Atkinson and Aschmann <sup>10</sup>	
2-Methylnaphthalene			$< 4 \times 10^{-19}$	$295 \pm 1$	S-GC	Atkinson and Aschmann <sup>9</sup>	
2,3-Dimethylnaphthalene			$< 4 \times 10^{-19}$	$295 \pm 1$	S-GC	Atkinson and Aschmann <sup>9</sup>	
Acenaphthene			$< 5 \times 10^{-19}$	$296 \pm 2$	S-GC	Atkinson and Aschmann <sup>11</sup>	
Acenaphthylene			$(5.5 \pm 1.5) \times 10^{-16}$	$296 \pm 2$	S-GC	Atkinson and Aschmann <sup>11</sup>	
1-Nitronaphthalene			$< 6 \times 10^{-19}$	$298 \pm 2$	S-GC	Atkinson <i>et al.</i> <sup>8</sup>	
2-Nitronaphthalene			$< 6 \times 10^{-19}$	$298 \pm 2$	S-GC	Atkinson <i>et al.</i> <sup>8</sup>	
2-Methyl-1-nitronaphthalene			$< 3 \times 10^{-19}$	$298 \pm 2$	S-GC	Arey <i>et al.</i> <sup>12</sup>	

<sup>a</sup>Calculated from cited Arrhenius expression.

<sup>b</sup>From present recommendation.

## References

- <sup>1</sup>R. Atkinson and W. P. L. Carter, *Chem. Rev.* **84**, 437 (1984).  
<sup>2</sup>S. Toby, L. J. Van de Burgt and F. S. Toby, *J. Phys. Chem.* **89**, 1982 (1985).  
<sup>3</sup>R. Atkinson, D. Hasegawa and S. M. Aschmann, *Int. J. Chem. Kinet.* **22**, 871 (1990).  
<sup>4</sup>E. C. Tuazon, R. Atkinson, and S. M. Aschmann, *Int. J. Chem. Kinet.* **22**, 981 (1990).  
<sup>5</sup>R. Atkinson, E. C. Tuazon, T. J. Wallington, S. M. Aschmann, J. Arey, A. M. Winer, and J. N. Pitts, Jr., *Environ. Sci. Technol.* **21**, 64 (1987).  
<sup>6</sup>E. C. Tuazon, J. Arey, R. Atkinson, and S. M. Aschmann, *Environ. Sci. Technol.* **27**, 1832 (1993).  
<sup>7</sup>R. Atkinson, J. Arey, E. C. Tuazon, and S. M. Aschmann, *Int. J. Chem. Kinet.* **24**, 345 (1992).  
<sup>8</sup>R. Atkinson, S. M. Aschmann, J. Arey, B. Zielinska, and D. Schuetzle, *Atmos. Environ.* **23**, 2679 (1989).  
<sup>9</sup>R. Atkinson and S. M. Aschmann, *Int. J. Chem. Kinet.* **18**, 569 (1986).  
<sup>10</sup>R. Atkinson and S. M. Aschmann, *Atmos. Environ.* **21**, 2323 (1987).  
<sup>11</sup>R. Atkinson and S. M. Aschmann, *Int. J. Chem. Kinet.* **20**, 513 (1988).  
<sup>12</sup>J. Arey, R. Atkinson, S. M. Aschmann, and D. Schuetzle, *Polycyclic Aromatic Compounds*, **1**, 33 (1990).  
<sup>13</sup>R. Atkinson, S. M. Aschmann, D. R. Fitz, A. M. Winer, and J. N. Pitts, Jr., *Int. J. Chem. Kinet.* **14**, 13 (1982).

## 6. Acknowledgments

The author gratefully thanks the U. S. Environmental Protection Agency, through Cooperative Agreement No. CR-815699-01-0 (Marcia C. Dodge, Project Officer) and the California Air Resources Board, through Contract No. A032-055 (Ralph Propper, Project Monitor) for financial assistance, and thanks Drs. J. Alistair Kerr, Suzanne E. Paulson, John H. Seinfeld and Timothy J. Wallington for communicating their data prior to publication and Ms. Christy J. LaClaire for her excellent work in assembling this manuscript. While this work has been funded by the U. S. EPA and the California Air Resources Board, it has not been subjected to these agencies reviews and therefore no official endorsement should be inferred.

7. Addendum  
Updated literature

In this section, literature data appearing since the final version of this article was prepared are presented and discussed. The format of this Addendum follows that of the article.

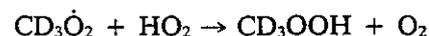
7.1. Gas-Phase Tropospheric Chemistry  
of Organic Compounds

## 7.1.1. Alkanes

Kinetic data concerning the OH radical reactions with the alkanes which have appeared since the final version of this article was prepared are presented and discussed in Sec. 7.2.1 (this addendum). In this section, new data concerning the reaction mechanisms and products of the reactions subsequent to the initial OH radical and/or NO<sub>3</sub> radical reactions are given.

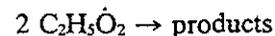
Reactions of Alkyl Radicals with HO<sub>2</sub> Radicals

Wallington and Hurley<sup>1</sup> have used FT-IR absorption spectroscopy to study the products of the gas-phase reaction of the CD<sub>3</sub>Ö<sub>2</sub> radical with the HO<sub>2</sub> radical at 295 ± 2 K over the total pressure range 10–700 Torr of O<sub>2</sub> or O<sub>2</sub> + N<sub>2</sub>. CD<sub>3</sub>Ö<sub>2</sub> and HO<sub>2</sub> radicals were generated<sup>1</sup> by the photolysis of F<sub>2</sub>-CD<sub>4</sub>-H<sub>2</sub>-O<sub>2</sub>-N<sub>2</sub> mixtures at wavelengths > 290 nm. CD<sub>3</sub>OOH was the major product observed and, taking into account the self-reaction of CD<sub>3</sub>Ö<sub>2</sub> radicals (calculated to be 9–11% of the overall removal of CD<sub>3</sub>Ö<sub>2</sub> radicals), then a formation yield of CD<sub>3</sub>OOH from the reaction of HO<sub>2</sub> radicals with CD<sub>3</sub>Ö<sub>2</sub> radicals of 1.00 ± 0.04 was obtained.<sup>1</sup> These data show that the CD<sub>3</sub>Ö<sub>2</sub> radical reaction with the HO<sub>2</sub> radical proceeds through the single channel,



in agreement with the data presented in Sec. 2.1.

Fenter *et al.*<sup>2</sup> have used a flash photolysis system with ultraviolet absorption spectroscopy to determine rate constants for the reactions



and



The rate constant obtained for the self reaction of ethyl peroxy radicals of  $(6.7 \pm 0.6) \times 10^{-14} e^{(60 \pm 40)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 248–460 K is in good agreement with that recommended in Sec. 2.1 from the IUPAC recommendation.<sup>3</sup> For the reaction of the C<sub>2</sub>H<sub>5</sub>Ö<sub>2</sub> radical with the HO<sub>2</sub> radical, however, Fenter *et al.*<sup>2</sup> obtained a rate constant at atmospheric pressure of

$$k(\text{C}_2\text{H}_5\dot{\text{O}}_2 + \text{HO}_2) = (1.60 \pm 0.40) \times 10^{-13} e^{(1260 \pm 130)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

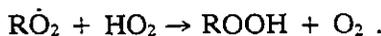
over the temperature range 248–480 K, with  $k(\text{C}_2\text{H}_5\dot{\text{O}}_2 + \text{HO}_2) = (1.10 \pm 0.21) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.<sup>2</sup> This rate constant is a factor of ~2 higher than previous measurements (Sec. 2.1) but is close to the general recommendation made in Sec. 2.1 of

$$k(\text{RO}_2 + \text{HO}_2) = 1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Rowley *et al.*<sup>4</sup> have studied the kinetics and products of the gas-phase reaction of the neopentyl peroxy [(CH<sub>3</sub>)<sub>3</sub>CCH<sub>2</sub>Ö<sub>2</sub>] radical with the HO<sub>2</sub> radical. A rate constant  $k$  of  $k = (1.43 \pm 0.46) \times 10^{-13} e^{(1380 \pm 100)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was determined over the temperature range 248–365 K, with  $k = (1.5 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.<sup>4</sup> This rate constant is similar to those determined by Rowley *et al.*<sup>5</sup> for the reactions of the HO<sub>2</sub> radical with cyclopentyl peroxy and cyclohexyl peroxy radicals of  $2.1 \times 10^{-13} e^{1323/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $2.6 \times 10^{-13} e^{1245/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively.

Using FT-IR absorption spectroscopic analysis at  $296 \pm 2$  K and 700 Torr total pressure of  $O_2 + N_2$ , Rowley *et al.*<sup>4</sup> observed neopentyl hydroperoxide,  $(CH_3)_3CCH_2OOH$ , to be the major product of the  $HO_2$  radical reaction with the neopentyl peroxy radical, with a formation yield of  $0.92 \pm 0.15$ .

These data<sup>4</sup> again show that the reactions of the alkyl peroxy radicals with the  $HO_2$  radical proceed by



Based on the rate constants for the alkyl peroxy radicals other than methyl peroxy, the recommendation for the reaction of  $HO_2$  radicals with  $R\dot{O}_2$  radicals given in Sec. 2.1 of

$$k(HO_2 + R\dot{O}_2) = 3.5 \times 10^{-13} e^{1000/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

with  $k(HO_2 + R\dot{O}_2) = 1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K, uncertain by a factor of 2, is revised to

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

uncertain to a factor of 2, and

$$k(HO_2 + R\dot{O}_2) = 1.9 \times 10^{-13} e^{1300/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 250–370 K. Obviously, the data for the individual alkyl peroxy radicals should be used, when available.

#### Reactions of Alkyl Peroxy Radicals with $R\dot{O}_2$ Radicals

Rowley *et al.*<sup>6</sup> have carried out a kinetic and product study of the self-reaction of cyclopentyl peroxy radicals. At  $295 \pm 2$  K and 700 Torr total pressure of  $N_2 + O_2$ , cyclopentanone and cyclopentanol were observed with

similar yields ( $0.18 \pm 0.01$  and  $0.16 \pm 0.02$ , respectively), independent of the  $O_2$  partial pressure over the range 5–700 Torr.<sup>6</sup> These data, together with the small yield of hydroperoxide(s) observed [ $0.07 \pm 0.02$ ], indicate that the major reaction pathway involves formation of the cyclopentoxy radical with subsequent ring cleavage<sup>6</sup> [see Reaction Scheme (18)] followed by the various reactions of the  $\dot{C}H_2CH_2CH_2CH_2CHO$  radical, as discussed in Sec. 2.1.

Rate constants  $k_{obs}$  were determined<sup>6</sup> over the temperature range 243–373 K from the flash photolysis of  $Cl_2$ -cyclopentane- $O_2$ - $N_2$  mixtures by monitoring the second-order decays of the cyclopentyl peroxy radical absorption. At a given temperature, values of  $k_{obs}$  was observed to depend on the  $O_2/Cl_2$  concentration ratios used, increasing with the  $O_2/Cl_2$  concentration ratio.<sup>6</sup> This behavior was explained<sup>6</sup> by reaction of the  $\dot{C}H_2CH_2CH_2CH_2CHO$  radical with  $Cl_2$  in competition with reaction of the  $\dot{C}H_2CH_2CH_2CH_2CHO$  radical with  $O_2$  (and possibly isomerization). From these data, Rowley *et al.*<sup>6</sup> obtained rate constants for the reaction pathways of

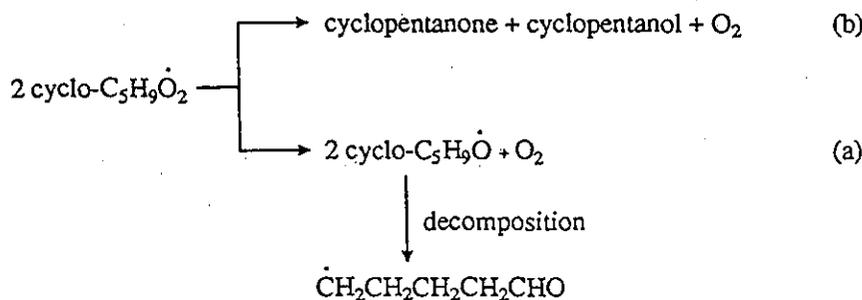
$$k_b = (1.3 \pm 0.4) \times 10^{-14} e^{(188 \pm 83)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$(k_b = 2.19 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}), \text{ and}$$

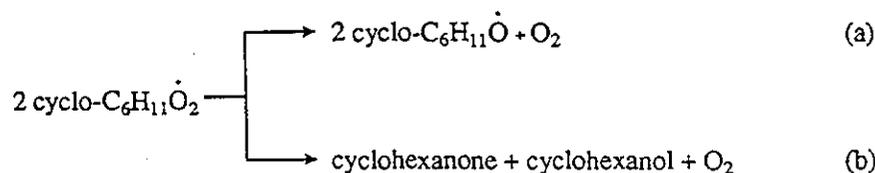
$$k_a + k_b \leq (2.9 \pm 0.8) \times 10^{-13} e^{-(555 \pm 77)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$(k_a + k_b \leq 6.73 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}).$$

Additional kinetic experiments for the self-reactions of cyclohexyl peroxy radicals were also conducted by Rowley *et al.*,<sup>6</sup> to augment those previously reported.<sup>7</sup> For the reactions shown by Reaction Scheme (19), rate constants of



Reaction Scheme (18)



Reaction Scheme (19)

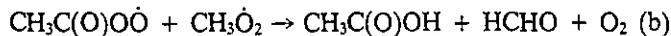
$$k_b = (1.3 \pm 0.3) \times 10^{-14} e^{(185 \pm 15)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 253–323 K and

$$k_a + k_b = 7.7 \times 10^{-14} e^{-184/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 253–373 K were obtained.<sup>6</sup> The overall rate constant ( $k_a + k_b$ )<sup>6</sup> is similar to that previously reported.<sup>7</sup>

Horie and Moortgat<sup>8</sup> have carried out a product study of the reaction of  $\text{CH}_3\dot{\text{O}}_2$  radicals with the acetylperoxy ( $\text{CH}_3\text{C}(\text{O})\text{O}\dot{\text{O}}$ ) radical over the temperature range 263–333 K, using matrix-isolation FT-IR spectroscopy.



A rate constant ratio of  $k_a/k_b = 2.2 \times 10^6 e^{-(3870 \pm 950)/T}$  ( $k_a/k_b = 5.0$  at 298 K) was obtained.<sup>8</sup> This rate constant ratio is a factor of  $\sim 5$  higher than the 298 K IUPAC recommendation<sup>3</sup> given in Sec. 2.1.

Heimann and Warneck<sup>9</sup> have investigated the products of the OH radical-initiated reaction of 2,3-dimethylbutane in the presence of 750 Torr total pressure of air at 297 K. OH radicals were produced by the photolysis of  $\text{H}_2\text{O}_2$ , and the products observed were consistent with expectations. The data obtained<sup>9</sup> allowed derivation of rate constant ratios  $k_a/k$  ( $k = k_a + k_b$ ) for the reactions



of  $k_a/k = 0.39 \pm 0.08$  for the self-reaction of 2-propyl peroxy radicals (in good agreement with the IUPAC recommendation<sup>3</sup> of  $k_a/k = 0.34$  at 298 K) and  $k_a/k = 0.44 \pm 0.07$  for the self-reaction of 2,3-dimethyl-2-butyl peroxy radicals. Rate constants for the cross-combination reactions of 2,3-dimethyl-2-butyl peroxy radicals with 2-propyl peroxy and 2,3-dimethyl-1-butyl peroxy radicals were also derived from computer simulations.<sup>9</sup>

## References

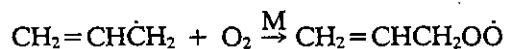
1. T. J. Wallington and M. D. Hurley, *Chem. Phys. Lett.* **193**, 84 (1992).
2. F. F. Fenter, V. Catoire, R. Lesclaux, and P. D. Lightfoot, *J. Phys. Chem.* **97**, 3530 (1993).
3. R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, and J. Troe, *J. Phys. Chem. Ref. Data* **21**, 1125 (1992).
4. D. M. Rowley, R. Lesclaux, P. D. Lightfoot, K. J. Hughes, M. D. Hurley, S. Rudy, and T. J. Wallington, *J. Phys. Chem.* **96**, 7043 (1992).
5. D. M. Rowley, R. Lesclaux, P. D. Lightfoot, B. Nozière, T. J. Wallington, and M. D. Hurley, *J. Phys. Chem.* **96**, 4889 (1992).
6. D. M. Rowley, P. D. Lightfoot, R. Lesclaux, and T. J. Wallington, *J. Chem. Soc. Faraday Trans.* **88**, 1369 (1992).
7. D. M. Rowley, P. D. Lightfoot, R. Lesclaux, and T. J. Wallington, *J. Chem. Soc. Faraday Trans.* **87**, 3221 (1991).
8. O. Horie and G. K. Moortgat, *J. Chem. Soc. Faraday Trans.* **88**, 3305 (1992).
9. G. Heimann and P. Warneck, *J. Phys. Chem.* **96**, 8403 (1992).

## 7.1.2. Alkenes

Kinetic data concerning the OH radical,  $\text{NO}_3$  radical and  $\text{O}_3$  reactions with the alkenes which have appeared since the final version of this article was prepared are given in Secs. 7.2.3, 7.3.1 and 7.4.1 (this addendum). In this section, new data concerning the products and reaction mechanisms of these reactions are given.

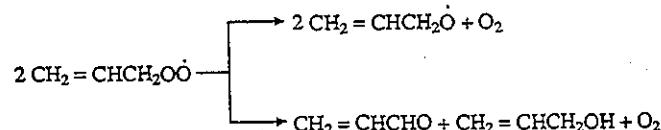
### OH Radical Reactions

Jenkin *et al.*<sup>1</sup> have measured a rate constant at  $296 \pm 2$  K and 740–800 Torr total pressure for the addition of  $\text{O}_2$  to the allyl radical

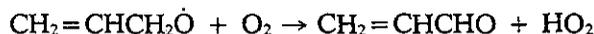


of  $(6 \pm 2) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . This room temperature rate constant is similar to that of  $\sim 4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  measured by Morgan *et al.*<sup>2</sup> at 380 K and 50 Torr total pressure of Ar diluent, suggesting that the rate constant for this addition reaction is essentially independent of temperature over the range  $\sim 290$ –400 K.

Jenkin *et al.*<sup>1</sup> also investigated the kinetics and products of the self-reaction of the allyl peroxy ( $\text{CH}_2=\text{CHCH}_2\text{O}\dot{\text{O}}$ ) radical, and concluded that the rate constants for the reactions

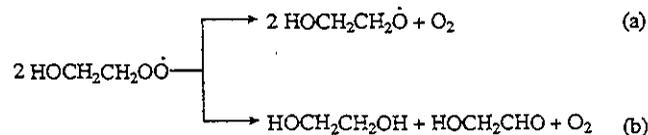


are  $(k_a + k_b) = (6.8 \pm 1.3) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k_a/(k_a + k_b) = 0.61 \pm 0.07$  at  $296 \pm 2$  K. FT-IR absorption spectroscopy showed<sup>1</sup> that, as expected, the alkoxy radical  $\text{CH}_2=\text{CHCH}_2\dot{\text{O}}$  reacts with  $\text{O}_2$ ,

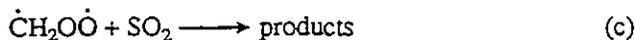
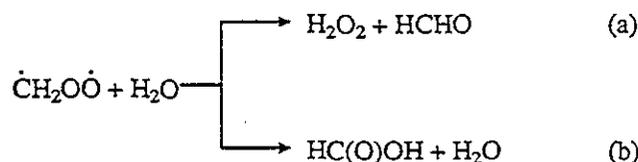
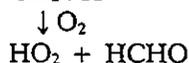
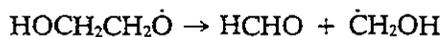


and no evidence for decomposition of this alkoxy radical was observed.<sup>1</sup>

Barnes *et al.*<sup>3</sup> have used FT-IR absorption spectroscopy to study the products of the self-reaction of  $\beta$ -hydroxyethyl peroxy ( $\text{HOCH}_2\text{CH}_2\text{O}\dot{\text{O}}$ ) radicals at  $295 \pm 3$  K as a function of total pressure (11–675 Torr) and  $\text{O}_2$  concentration. The major products observed<sup>3</sup> were glycolaldehyde ( $\text{HOCH}_2\text{CHO}$ ), HCHO and  $\text{HOCH}_2\text{CH}_2\text{OH}$ . Barnes *et al.*<sup>3</sup> concluded that the reactions involved are:



followed by



with  $k_a/(k_a + k_b) = 0.50 \pm 0.06$ . Furthermore, the rate constant ratio for reaction with  $\text{O}_2$  versus decomposition of the  $\text{HOCH}_2\text{CH}_2\dot{\text{O}}$  radical was in excellent agreement with the ratio measured by Niki *et al.*<sup>4</sup> from a product study of the OH radical reaction with ethene in the presence of  $\text{NO}_x$ .

Grosjean *et al.*<sup>5</sup> studied the products formed during  $\text{NO}_x$ -air irradiations of isoprene, and observed HCHO, methyl vinyl ketone and methacrolein to be the major products formed during the OH radical-dominated reaction period. The reported yields of these three products, which were not corrected for secondary reactions with the OH radical, were 0.50, 0.22 and 0.31, respectively.<sup>5</sup> These yields are consistent with the more extensive product data of Tuazon and Atkinson<sup>6</sup> and Paulson *et al.*<sup>7</sup>

Aerosol formation from the OH radical-initiated reactions of  $\alpha$ - and  $\beta$ -pinene in air has been further studied by Zhang *et al.*<sup>8</sup>

### $\text{O}_3$ Reactions

Hatakeyama and Akimoto<sup>9</sup> has investigated the oxidation of  $\text{SO}_2$  in reacting  $\text{O}_3$ -ethene- $\text{SO}_2$ - $\text{H}_2\text{O}$ -air systems through the formation of formic acid ( $\text{HC(O)OH}$ ). The  $\text{HC(O)OH}$  formation yield data obtained<sup>9</sup> were in accord with Reaction Scheme (20), and a rate constant ratio  $k_b/k_a = 6.0 \times 10^{-3}$  was derived.<sup>9</sup>

Becker *et al.*<sup>10</sup> have reinvestigated the formation of  $\text{H}_2\text{O}_2$  in the reactions of  $\text{O}_3$  with a series of alkenes using tunable diode laser absorption spectroscopy and FT-IR absorption spectroscopy in 130–1080 liter volume reaction chambers. The  $\text{H}_2\text{O}_2$  yields of Becker *et al.*<sup>10</sup> are in agreement with their previous data,<sup>11</sup> being (on a molar basis) 0.001 for ethene and isoprene, 0.0015 for  $\beta$ -pinene, 0.0028 for propene, 0.005 for *trans*-2-butene and  $\alpha$ -pinene, 0.006 for 3-carene, 0.018 for limonene and 0.027 for 2,3-dimethyl-2-butene. These yields are in approximate agreement with those reported in the gas-phase by Hewitt and Kok,<sup>12</sup> but are much lower than those of Simonaitis *et al.*<sup>13</sup> From the  $\text{H}_2\text{O}_2$  formation yields obtained in experiments conducted in the presence and absence of  $\text{SO}_2$  at various water vapor concentrations, Becker *et al.*<sup>10</sup> derived rate constant ratios for the processes

of  $(k_a + k_b)/k_c = (8.3 \pm 3.6) \times 10^{-4}$  and  $k_a/(k_a + k_b) = 0.005$ . For the corresponding reactions of the  $(\text{CH}_3)_2\dot{\text{C}}\text{OO}$  biradical, values of  $(k_a + k_b)/k_c = (4.1 \pm 2.2) \times 10^{-4}$  and  $k_a/(k_a + k_b) = 0.13$  were derived.<sup>10</sup> These rate constant ratios  $(k_a + k_b)/k_c$  are within a factor of 4 of that reported by Suto *et al.*<sup>14</sup> for the  $\dot{\text{C}}\text{H}_2\text{O}\dot{\text{O}}$  biradical. The discrepancies between the  $\text{H}_2\text{O}_2$  yields measured in the studies of Becker *et al.*<sup>10,11</sup> and Simonaitis *et al.*<sup>13</sup> need to be resolved.

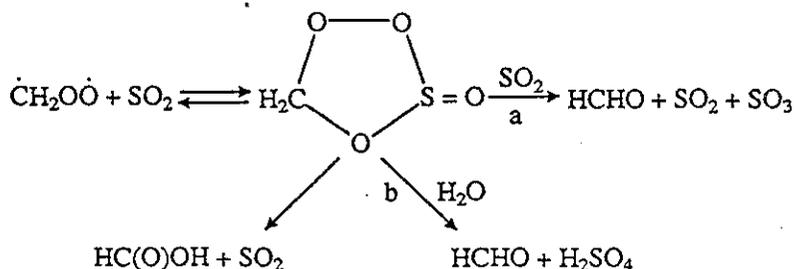
Grosjean *et al.*<sup>5</sup> have investigated the products formed from the gas-phase reaction of  $\text{O}_3$  with isoprene in the presence of an excess concentration of cyclohexane to scavenge the OH radicals formed from the  $\text{O}_3$ -isoprene reaction. The molar yields of HCHO, methyl vinyl ketone and methacrolein were 0.90, 0.17 and 0.44, respectively,<sup>5</sup> similar to those reported by Kamens *et al.*<sup>15</sup> and Niki *et al.*<sup>16</sup> in the absence of an OH radical scavenger but lower than the methyl vinyl ketone and methacrolein yields derived from the primary reaction by Paulson *et al.*<sup>17</sup> Further studies are clearly required.

Atkinson *et al.*<sup>18</sup> have carried out a product study of the reaction of  $\text{O}_3$  with isoprene in the presence of cyclohexane (to scavenge OH radicals) in  $\text{N}_2$  and air diluents, and shown that the epoxides observed by Paulson *et al.*<sup>17</sup> arise from a direct reaction (see Reaction Scheme (21) on next page) and not via the intermediary of  $\text{O}(^3\text{P})$  atoms. An  $\text{O}(^3\text{P})$  atom formation yield of  $< 0.1$ , and probably  $< 0.01$ , was obtained,<sup>18</sup> much lower than that of  $0.45 \pm 0.20$  derived by Paulson *et al.*<sup>17</sup>

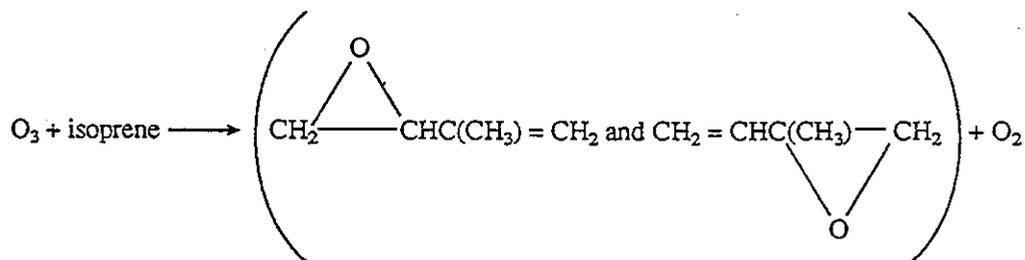
Aerosol formation from the  $\text{O}_3$  reactions with  $\alpha$ - and  $\beta$ -pinene has been investigated by Zhang *et al.*<sup>8</sup>

### $\text{NO}_3$ Radical Reactions

Skov *et al.*<sup>19</sup> have investigated the products and mechanisms of the gas-phase reactions of the  $\text{NO}_3$  radical with isoprene, 1,3-butadiene, 2,3-dimethyl-1,3-butadiene, 1,3-butadiene-1,1,4,4-*d*<sub>4</sub>, 1,3-butadiene-*d*<sub>6</sub> and 2-methyl-1,3-butadiene-4,4-*d*<sub>2</sub> in air at  $295 \pm 2$  K and  $740 \pm 5$  Torr total pressure. The products observed were in general accord with the reaction schemes discussed in Sec. 2.2, and



Reaction Scheme (20)



Reaction Scheme (21)

the article of Skov *et al.*<sup>19</sup> should be consulted for further details.

## References

- <sup>1</sup>M. E. Jenkin, T. P. Murrells, S. J. Shalliker, and G. D. Hayman, *J. Chem. Soc. Faraday Trans.* **89**, 433 (1993).
- <sup>2</sup>C. A. Morgan, M. J. Pilling, J. M. Tulloch, R. P. Ruiz, and K. D. Bayes, *J. Chem. Soc. Faraday Trans.* **2**, **78**, 1323 (1982).
- <sup>3</sup>I. Barnes, K. H. Becker, and L. Ruppert, *Chem. Phys. Lett.* **203**, 295 (1993).
- <sup>4</sup>H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, *Chem. Phys. Lett.* **80**, 499 (1981).
- <sup>5</sup>D. Grosjean, E. L. Williams II, and E. Grosjean, *Environ. Sci. Technol.* **27**, 830 (1993).
- <sup>6</sup>E. C. Tuazon and R. Atkinson, *Int. J. Chem. Kinet.* **22**, 1221 (1990).
- <sup>7</sup>S. E. Paulson, R. C. Flagan, and J. H. Seinfeld, *Int. J. Chem. Kinet.* **24**, 79 (1992).
- <sup>8</sup>S.-H. Zhang, M. Shaw, J. H. Seinfeld, and R. C. Flagan, *J. Geophys. Res.* **97**, 20717 (1992).
- <sup>9</sup>S. Hatakeyama and H. Akimoto, *Nippon Kagaku Kaishi* **785** (1992).
- <sup>10</sup>K. H. Becker, J. Bechara, and K. J. Brockmann, *Atmos. Environ.* **27A**, 57 (1993).
- <sup>11</sup>K. H. Becker, K. J. Brockmann, and J. Bechara, *Nature* **346**, 256 (1990).
- <sup>12</sup>C. N. Hewitt and G. L. Kok, *J. Atmos. Chem.* **12**, 181 (1991).
- <sup>13</sup>R. Simonaitis, K. J. Olszyna, and J. F. Meagher, *Geophys. Res. Lett.* **18**, 9 (1991).
- <sup>14</sup>M. Suto, E. R. Manzanares, and L. C. Lee, *Environ. Sci. Technol.* **19**, 815 (1985).
- <sup>15</sup>R. M. Kamens, M. W. Gery, H. E. Jeffries, M. Jackson, and E. I. Cole, *Int. J. Chem. Kinet.* **14**, 955 (1982).
- <sup>16</sup>H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, *Environ. Sci. Technol.* **17**, 312A (1983).
- <sup>17</sup>S. E. Paulson, R. C. Flagan, and J. H. Seinfeld, *Int. J. Chem. Kinet.* **24**, 103 (1992).
- <sup>18</sup>R. Atkinson, J. Arey, S. M. Aschmann, and E. C. Tuazon, *Res. Chem. Intermed.*, in press (1993).
- <sup>19</sup>H. Skov, J. Hjorth, C. Lohse, N. R. Jensen, and G. Restelli, *Atmos. Environ.* **26A**, 2771 (1992).

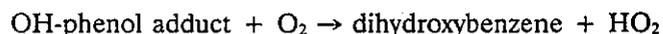
### 7.1.3. Aromatic Compounds

Kinetic data for the OH radical and NO<sub>3</sub> reactions with aromatic compounds which have appeared since the final version of this article was prepared are presented and discussed in Secs. 7.2.6 and 7.3.3. In this section, new data concerning the products and reaction mechanisms of these reactions are given.

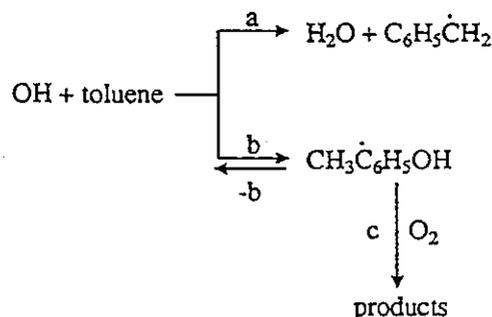
The rate constants for the reactions of the OH-phenol adduct with NO and NO<sub>2</sub> determined by Knispel *et al.*<sup>1</sup> were inadvertently omitted from Sec. 2.4. An upper limit for reaction of the OH-phenol adduct with NO of 7 ×

10<sup>-14</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 316–332 K was obtained.<sup>1</sup> Rate constants for reaction of the OH-phenol adduct with NO<sub>2</sub> of (2.8 ± 0.4) × 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 331 K and (3.6 ± 0.3) × 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 353 K were determined, these rate constants being similar to those for the corresponding reactions of NO<sub>2</sub> with the OH-benzene and OH-toluene adducts.<sup>1</sup>

Zetzsch and coworkers<sup>2</sup> have reported updated rate constants for the reactions of hydroxycyclohexadienyl and substituted-hydroxycyclohexadienyl radicals with O<sub>2</sub>. The rate constants (in units of 10<sup>-16</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 100 Torr total pressure of Ar diluent) are<sup>2</sup>: for the hydroxycyclohexadienyl radical formed from the OH radical reaction with benzene; 1.6 ± 0.6 at 299 K, 2.1 ± 0.4 at 314 K, 3.0 ± 0.3 at 333 K, and 3.7 ± 0.4 at 354 K; for the methylhydroxycyclohexadienyl radical(s) formed from the OH radical reaction with toluene; 5.6 ± 1.5 at 299 K, 5.6 ± 0.6 at 321 K, 5.6 ± 0.6 at 339 K, 5.3 ± 0.7 at 347 K, and 5.9 ± 0.8 at 354 K; and for the dihydroxycyclohexadienyl radical(s) formed from the OH radical reaction with phenol; 300 ± 70 at 323 K, 260 ± 60 at 333 K, 270 ± 50 at 337 K, 290 ± 60 at 343 K, 270 ± 60 at 353 K, and 360 ± 50 at 363 K. Additional experiments showed the formation of HO<sub>2</sub> radicals in >90% yield from reaction of the OH-phenol adduct with O<sub>2</sub> at room temperature,<sup>2</sup> although the reaction sequence was concluded<sup>2</sup> to be more complex than the direct formation of HO<sub>2</sub> radicals via



Using a 2400 liter volume reaction chamber at 300 K and atmospheric pressure of N<sub>2</sub>, Zetzsch *et al.*<sup>2</sup> used a relative rate technique to show that the rate constants for the reactions of benzene, toluene and *p*-xylene with the OH radical increased with increasing concentrations of O<sub>2</sub>, as expected from the reaction sequence (taking toluene as an example)



and the previously measured rate constants  $k_a$ ,  $k_b$ ,  $k_{-b}$  and  $k_c$ . For *p*-xylene, the experimental data allowed a rate constant  $k_c$  for reaction of  $O_2$  with the dimethylhydroxycyclohexadienyl radical of  $\sim 1.9 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  to be derived.<sup>2</sup>

Atkinson and Aschmann<sup>3</sup> have generated OH radicals from the dark  $O_3$  reactions with propene and  $\alpha$ -pinene at  $296 \pm 2 \text{ K}$  and atmospheric pressure of air (Sec. 2.2), and shown that *o*-cresol is formed from toluene with a slightly lower yield in the absence of  $NO_x$  than in the presence of  $NO_x$ . The formation yields of 2,3-butanedione (biacetyl) were also measured from the OH radical reactions with *o*-xylene and 1,2,3-trimethylbenzene in the presence and absence of  $NO_x$ . For 1,2,3-trimethylbenzene, the 2,3-butanedione formation yield<sup>3</sup> increased from  $\sim 0.18$  in the absence of  $NO_x$  to  $\sim 0.45$  in the presence of  $NO_2$  at concentrations  $\geq 5 \times 10^{12} \text{ molecule cm}^{-3}$ . The product data of Atkinson and Aschmann<sup>3</sup> are consistent with the kinetic data of Zetzsch and coworkers<sup>1,2</sup> and indicate that the OH-benzene, OH-toluene, OH-xylene and OH-trimethylbenzene adducts will react with  $O_2$  under most atmospheric conditions.

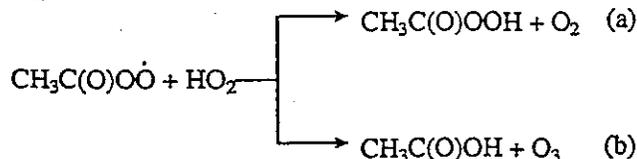
## References

- R. Knispel, R. Koch, M. Siese, and C. Zetzsch, Ber. Bunsenges. Phys. Chem. 94, 1375 (1990).
- C. Zetzsch, M. Elend, R. Knispel, R. Koch, J. Nowack and M. Siese, "Hydroxyl and Aromatics: Fate of the Adducts in the Presence of  $O_2$ ," EUROTRAC Annual Report, 1991, Part 8, LACTOZ, pp. 207-215, Commission of the European Communities.
- R. Atkinson and S. M. Aschmann, Int. J. Chem. Kinet., submitted for publication (1994).

### 87.1.4. Oxygen-Containing Organic Compounds

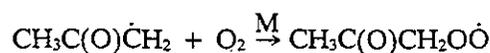
The kinetics of the OH radical,  $NO_3$  radical and  $O_3$  reactions with oxygen-containing organic compounds which have appeared since the final version of this article was prepared are presented and discussed in Secs. 7.2.5, 7.3.2 and 7.4.2. In this section new data concerning the products and reaction mechanisms of these reactions are given.

Horie and Moortgat<sup>1</sup> have obtained, from a product study of the reaction of the  $CH_3C(O)OO\cdot$  radical with  $HO_2$ ,

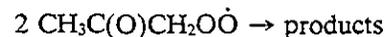


the rate constant ratio of  $k_a/k_b = 330 e^{-(1430 \pm 480)/T}$  over the temperature range 263–333 K ( $k_a/k_b = 2.7$  at 298 K). This rate constant ratio<sup>1</sup> is in agreement with the recommendation of Atkinson *et al.*<sup>2</sup> (Sec. 2.5) of  $k_a/k_b = 2.3$  at 298 K, but disagrees with the previous recommendation<sup>2</sup> that  $k_a/k_b = 2.3$ , independent of temperature over the range 250–370 K.

Cox *et al.*<sup>3</sup> have used a pulsed radiolysis technique to obtain rate constants for the reactions



and

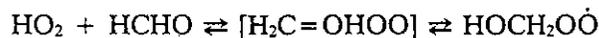


at 298 K and one atmosphere total pressure of  $SF_6$ , of  $(1.5 \pm 0.3) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $(8.3 \pm 1.6) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively. The  $O_2$  addition reaction to the  $CH_3C(O)\dot{C}H_2$  radical has a rate constant of a similar magnitude to the reactions of  $O_2$  with alkyl radicals (Sec. 2.1), as expected.

Grosjean *et al.*<sup>4</sup> have shown that the atmospheric photooxidation of *cis*-3-hexen-1-ol ( $CH_3CH_2CH = CHCH_2CH_2OH$ ) leads to the formation of propanal and peroxypropionyl nitrate, as expected.<sup>5</sup> Based on analogy with the reaction of propene with OH radicals and  $O_3$ , propanal is expected to be a first-generation product, with subsequent OH radical reaction with propanal in the presence of  $NO_x$  leading to the formation of peroxypropionyl nitrate ( $CH_3CH_2C(O)OONO_2$ ) [Sec. 2.6].

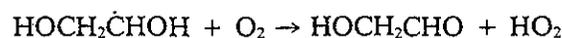
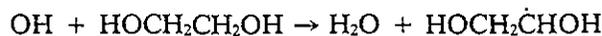
Wallington *et al.*<sup>6</sup> have used FT-IR absorption spectroscopy to investigate the products formed from the OH radical and Cl atom-initiated reactions of di-isopropyl ether at  $295 \pm 2 \text{ K}$  and 700 Torr total pressure of air. The major product of both the OH radical (in the presence of  $NO_x$ ) and Cl atom reactions was isopropyl acetate [ $(CH_3)_2CHOC(O)CH_3$ ], with a yield of  $1.05 \pm 0.06$  from the OH radical reaction.<sup>6</sup> An isopropyl acetate yield of  $0.92 \pm 0.13$  was obtained from the Cl atom-initiated reaction in the presence of  $NO_x$  and a yield of the products arising from the reactions of the  $CH_3\dot{O}$  radical ( $HCHO$ ,  $CH_3ONO$  and  $CH_3ONO_2$ ) of  $\sim 1.1$  was determined. The OH radical reaction is expected to proceed mainly at the  $>CH-$  group,<sup>6,7</sup> and hence the OH radical reaction in the presence of  $NO_x$  must proceed by Reaction Scheme (22). Temperature-dependent absorption cross-sections for acetone and 2-butanone have been measured by Hynes *et al.*<sup>8</sup>

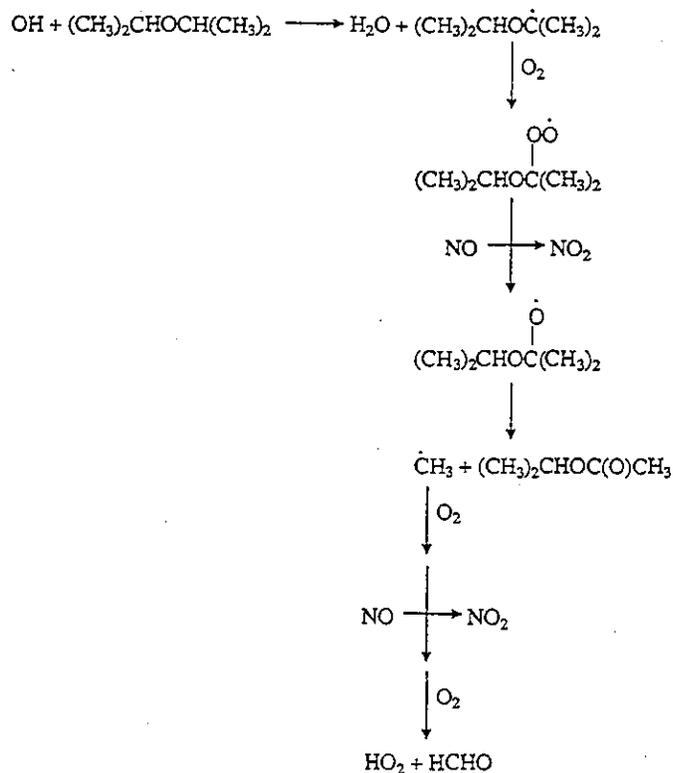
The gas-phase reaction of the  $HO_2$  radical with  $HCHO$  has been theoretically investigated by Evleth *et al.*,<sup>9</sup> and it was concluded that the reaction proceeds by



and that the intermediate alkoxy radical  $HOCH_2\dot{O}$  is not involved.

Barnes *et al.*<sup>10</sup> have studied the products of the OH radical reaction with  $HOCH_2CH_2OH$  and shown that glycolaldehyde ( $HOCH_2CHO$ ) is the major product, together with lesser yields of  $HCHO$  and  $HC(O)OH$ . The reaction then proceeds mainly by<sup>10</sup>





Reaction Scheme (22)

## References

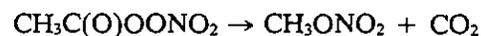
- <sup>1</sup>O. Horie and G. K. Moortgat, *J. Chem. Soc. Faraday Trans.* **88**, 3305 (1992).
- <sup>2</sup>R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, and J. Troe, *J. Phys. Chem. Ref. Data* **21**, 1125 (1992).
- <sup>3</sup>R. A. Cox, J. Munk, O. J. Nielsen, P. Pagsberg, and E. Ratajczak, *Chem. Phys. Lett.* **173**, 206 (1990).
- <sup>4</sup>D. Grosjean, E. L. Williams II, and E. Grosjean, *Environ. Sci. Technol.* **27**, 979 (1993).
- <sup>5</sup>J. Arey, A. M. Winer, R. Atkinson, S. M. Aschmann, W. D. Long, and C. L. Morrison, *Atmos. Environ.* **25A**, 1063 (1991).
- <sup>6</sup>T. J. Wallington, J. M. Andino, A. R. Potts, S. J. Rudy, W. O. Siegl, Z. Zhang, M. J. Kurylo, and R. E. Huie, *Environ. Sci. Technol.* **27**, 98 (1993).
- <sup>7</sup>R. Atkinson, *Int. J. Chem. Kinet.* **19**, 799 (1987).
- <sup>8</sup>A. J. Hynes, E. A. Kenyon, A. J. Pounds, and P. H. Wine, *Spectrochimica Acta.* **48A**, 1235 (1992).
- <sup>9</sup>E. M. Evleth, C. F. Melius, M. T. Rayez, J. C. Rayez, and W. Forst, *J. Phys. Chem.* **97**, 5040 (1993).
- <sup>10</sup>I. Barnes, K. H. Becker, and L. Ruppert, *Chem. Phys. Lett.* **203**, 295 (1993).

### 7.1.5. Nitrogen-Containing Organic Compounds

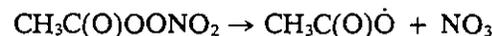
Kinetic data for the gas-phase reactions of O<sub>3</sub> with nitrogen-containing organic compounds which has appeared since the finalization of this article are presented in Sec. 7.4.3 below. The product and mechanistic data for nitrogen-containing organic compounds are presented below.

Langer *et al.*<sup>1</sup> and Orlando *et al.*<sup>2</sup> have investigated the thermal decomposition of peroxyacetyl nitrate (PAN) in

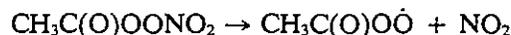
the presence of NO<sub>2</sub>. Orlando *et al.*<sup>2</sup> showed that the reaction channels



and



are of negligible importance compared to the reaction pathway,



and that the thermal decomposition of PAN is not a significant source of CH<sub>3</sub>ONO<sub>2</sub> in the atmosphere. Langer *et al.*<sup>1</sup> concluded that the heterogeneous decomposition of PAN is not important under atmospheric conditions.

## References

- <sup>1</sup>S. Langer, I. Wängberg, and E. Ljungström, *Atmos. Environ.* **26A**, 3089 (1992).
- <sup>2</sup>J. J. Orlando, G. S. Tyndall, and J. G. Calvert, *Atmos. Environ.* **26A**, 3111 (1992).

### 7.2. Kinetics and Mechanisms of the Gas-Phase Reactions of the OH Radical with Organic Compounds

The rate constants for the reactions of the OH radical with organic compounds reported since Sec. 3 of this article was finalized are presented and discussed in the sections below.

#### 7.2.1. Alkanes

The rate constants reported since Table 36 was finalized are given in Table 64.

**Methane.** The absolute rate constants reported by Lancar *et al.*<sup>1</sup> and Sharkey and Smith<sup>2</sup> at 378–422 K<sup>1</sup> and 298 K<sup>2</sup> are within ±20% of the recommendation given in Sec. 3.1, of  $k(\text{CH}_4) = 7.44 \times 10^{-18} T^2 e^{-1361/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 223–1512 K. The upper limit obtained by Sharkey and Smith<sup>2</sup> at 178 K is also consistent with this recommended rate constant. However, the rate constant reported by Sharkey and Smith<sup>2</sup> at 216 K is a factor of 2.6 higher than the recommended rate constant. The recommended rate constant from Sec. 3.1 is unchanged. The 378 and 422 K rate constants of Lancar *et al.*<sup>1</sup> together with the 295–420 K data of Vaghjani and Ravishankara<sup>6</sup> and the 333–378 K data of Finlayson-Pitts *et al.*<sup>7</sup> may indicate that the value of  $n$  in the three-parameter expression  $k(\text{CH}_4) = CT^n e^{-D/T}$  is  $>2$ , leading to slightly lower rate constants in the range ~330–600 K than presently recommended.

**Ethane.** The absolute rate constants reported by Sharkey and Smith<sup>2</sup> at 178–298 K are  $9 \pm 6$  to  $20 \pm 10\%$  higher than those calculated from the recommendation of Sec. 3.1, of  $k(\text{ethane}) = 1.51 \times 10^{-17} T^2 e^{-492/T} \text{ cm}^3$

Table 64. Rate constants  $k$  for the gas-phase reactions of the OH radical with alkanes

Alkane	$10^{12} \times k$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	at $T$ (K)	Technique	Reference
Methane	$0.0262 \pm 0.0027$	378	DF-EPR	Lancar <i>et al.</i> <sup>1</sup>
	$0.0427 \pm 0.0018$	422		
	$<0.0003$	178	LP-LIF	Sharkey and Smith <sup>2</sup>
	$0.00165 \pm 0.0002$	216		
	$0.0076 \pm 0.0003$	298		
Ethane	$0.013 \pm 0.002$	138	LP-LIF	Sharkey and Smith <sup>2</sup>
	$0.025 \pm 0.003$	178		
	$0.0785 \pm 0.004$	216		
	$0.295 \pm 0.014$	298		
	$0.291 \pm 0.007$	298	RR [relative to $k(\text{propane}) = 1.50 \times 10^{-17} T^2 e^{-44/T}$ ]	Finlayson-Pitts <i>et al.</i> <sup>3</sup>
	$0.285 \pm 0.013$	298		
	$0.377 \pm 0.014$	323		
	$0.480 \pm 0.013$	348		
	$0.590 \pm 0.010$	373		
Propane	$1.15 \pm 0.06$	298	RR [relative to $k(n\text{-butane}) = 2.54 \times 10^{-12}$ ]	Finlayson-Pitts <i>et al.</i> <sup>3</sup>
	$1.15 \pm 0.06$	298		
	$1.04 \pm 0.07$	298	RR [relative to $k(2\text{-methylpropane}) = 2.33 \times 10^{-12}$ ]	Finlayson-Pitts <i>et al.</i> <sup>3</sup>
	$1.22 \pm 0.04$	298		
	$1.16 \pm 0.06$	298		
$n$ -Pentane	$4.22 \pm 0.05$	302	RR [relative to $k(2\text{-methylpropane}) = 2.36 \times 10^{-12}$ ]	Donaghy <i>et al.</i> <sup>4</sup>
$n$ -Hexane	$5.55 \pm 0.20$	$301 \pm 2$	RR [relative to $k(n\text{-pentane}) = 3.99 \times 10^{-12}$ ]	McLoughlin <i>et al.</i> <sup>5</sup>

\*From recommendations in Sec. 3.1.

molecule<sup>-1</sup> s<sup>-1</sup> over the temperature range 226–800 K. The rate constant reported by Sharkey and Smith<sup>2</sup> at 138 K is  $60 \pm 25\%$  higher than the present recommendation. Finlayson-Pitts *et al.*<sup>3</sup> have employed a relative rate method, using the dark reaction of O<sub>3</sub> in the presence of alkanes and the photolysis of O<sub>3</sub>-H<sub>2</sub>O-alkane mixtures to generate OH radicals, to obtain rate constants for ethane versus propane. The rate constants obtained by Finlayson-Pitts *et al.*<sup>3</sup> over the temperature range 298–373 K (Table 64) are within 13% of the recommendation given in Sec. 3.1, which is hence unchanged.

**Propane.** Finlayson-Pitts *et al.*<sup>3</sup> have used relative rate methods to obtain rate constants for the OH radical reaction with propane relative to those for the OH radical reactions with  $n$ -butane and 2-methylpropane. For the measurements relative to 2-methylpropane, OH radicals were generated from the dark reactions of O<sub>3</sub> in alkane-O<sub>2</sub> or alkane-H<sub>2</sub>O-O<sub>2</sub> mixtures, the photolysis of O<sub>3</sub>-H<sub>2</sub>O-alkane-O<sub>2</sub> mixtures, and the photolysis of CH<sub>3</sub>ONO-NO-alkane-air mixtures.<sup>3</sup> The three methods of OH radical generation led to essentially identical results (Table 64).<sup>3</sup> The rate constants for propane obtained by Finlayson-Pitts *et al.*<sup>3</sup> are in excellent agreement with the recommended 298 K rate constant of

$1.15 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Sec. 3.1), and hence this recommendation is unchanged.

**$n$ -Pentane and  $n$ -Hexane.** The relative rate constants of Donaghy *et al.*<sup>4</sup> ( $n$ -pentane) and McLoughlin *et al.*<sup>5</sup> ( $n$ -hexane) are given in Table 64. These rate constants are in good agreement (within 5% for  $n$ -pentane and 2% for  $n$ -hexane) with the recommendations given in Sec. 3.1 and by Atkinson.<sup>8</sup> These recommendations (Sec. 3.1 and Ref. 8) are hence unchanged.

## References

- <sup>1</sup>I. T. Lancar, G. Le Bras, and G. Poulet, C. R. Acad. Sci. Paris, Series II, 1487 (1992).
- <sup>2</sup>P. Sharkey and I. W. M. Smith, J. Chem. Soc. Faraday Trans. **89**, 631 (1993).
- <sup>3</sup>B. J. Finlayson-Pitts, S. K. Hernandez, and H. N. Berko, J. Phys. Chem. **97**, 1172 (1993).
- <sup>4</sup>T. Donaghy, I. Shanahan, M. Hande, and S. Fitzpatrick, Int. J. Chem. Kinet. **25**, 273 (1993).
- <sup>5</sup>P. McLoughlin, R. Kane, and I. Shanahan, Int. J. Chem. Kinet. **25**, 137 (1993).
- <sup>6</sup>G. L. Vaghjani and A. R. Ravishankara, Nature **350**, 406 (1991).
- <sup>7</sup>B. J. Finlayson-Pitts, M. J. Ezell, T. M. Jayaweera, H. N. Berko, and C. C. Lai, Geophys. Res. Lett. **19**, 1371 (1992).
- <sup>8</sup>R. Atkinson, J. Phys. Chem. Ref. Data Monograph **1**, 1 (1989).

## 7.2.2. Haloalkanes

The rate constants reported since Table 37 was finalized was given in Table 65.

$\text{CH}_3\text{F}$ . The rate constants obtained by Wallington and Hurley<sup>1</sup> from relative rate measurements are given in Table 65. These rate constants are in excellent agreement with that of  $1.62 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 296 K calculated from the recommendation of Atkinson<sup>15</sup> of

$$k(\text{CH}_3\text{F}) = 5.51 \times 10^{-18} T^2 e^{-1005/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 292–480 K. This recommendation<sup>15</sup> is hence unchanged.

$\text{CH}_3\text{Cl}$ . Taylor *et al.*<sup>2</sup> have reinvestigated the kinetics of the OH radical reaction with  $\text{CH}_3\text{Cl}$  at elevated temperatures (742–955 K) to check that previous measurements<sup>16</sup> were not influenced by photolysis of the  $\text{CH}_3\text{Cl}$  reactant. This was shown to be generally the case, and the rate constants determined at 742–955 K<sup>2</sup> are given in Table 65. These rate constants<sup>2</sup> and those of Taylor *et al.*,<sup>16</sup> as listed by Taylor *et al.*<sup>2</sup> (with the rate constants of Taylor *et al.*<sup>16</sup> being averaged at 473 and 475 K, 524 and 525 K, 667 K, and 695 K, and the rate constant at 735 K being omitted), are used in the evaluation of the rate constant for this reaction. A unit-weighted least-squares analysis of the absolute rate constants of Howard and Evenson,<sup>17</sup> Perry *et al.*,<sup>18</sup> Davis *et al.*,<sup>19</sup> Paraskevopoulos *et al.*,<sup>20</sup> Jeong and Kaufman<sup>21</sup> and the absolute rate constants listed by Taylor *et al.*<sup>2</sup> (see above), using the expression  $k = CT^2 e^{-D/T}$ , yields the recommendation of

$$k(\text{CH}_3\text{Cl}) = (7.33^{+1.09}_{-0.94}) \times 10^{-18} T^2 e^{-(809 \pm 54)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 250–955 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{CH}_3\text{Cl}) = 4.31 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of  $\pm 20\%$ . This recommendation supersedes that of Atkinson<sup>15</sup> of

$$k(\text{CH}_3\text{Cl}) = 3.50 \times 10^{-18} T^2 e^{-585/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 250–483 K, with a 298 K rate constant of  $4.36 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , and leads to a rate constant at 250 K 15% lower than calculated from the previous<sup>15</sup> recommendation.

$\text{CH}_3\text{Br}$ . The absolute rate constants obtained by Mellouki *et al.*<sup>3</sup> and Zhang *et al.*<sup>4</sup> are given in Table 65. These rate constants are significantly lower than the previous data of Howard and Evenson<sup>17</sup> and Davis *et al.*<sup>19</sup> over a similar temperature range. A unit-weighted least-squares analysis of the rate constants of Mellouki *et al.*<sup>3</sup> and Zhang *et al.*,<sup>4</sup> using the expression  $k = CT^2 e^{-D/T}$ , yields the recommendation of

$$k(\text{CH}_3\text{Br}) = (3.62^{+0.77}_{-0.63}) \times 10^{-18} T^2 e^{-(711 \pm 56)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 233–400 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{CH}_3\text{Br}) = 2.96 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of  $\pm 20\%$ . This recommendation supersedes that of Atkinson<sup>15</sup> of

$$k(\text{CH}_3\text{Br}) = 2.60 \times 10^{-18} T^2 e^{-521/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 244–2000 K, with a 298 K rate constant of  $4.02 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

$\text{CH}_2\text{Cl}_2$ . Taylor *et al.*<sup>2</sup> have re-investigated the kinetics of this reaction, and the rate constants obtained<sup>2</sup> are given in Table 65. These rate constants<sup>2</sup> supersede those reported previously.<sup>16</sup> A unit-weighted least-squares analysis of the absolute rate constants of Howard and Evenson,<sup>17</sup> Perry *et al.*,<sup>18</sup> Davis *et al.*,<sup>19</sup> Jeong and Kaufman<sup>21</sup> and Taylor *et al.*,<sup>2</sup> using the expression  $k = CT^2 e^{-D/T}$ , yields the recommendation of

$$k(\text{CH}_2\text{Cl}_2) = (6.14^{+1.16}_{-0.97}) \times 10^{-18} T^2 e^{-(389 \pm 66)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 245–955 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{CH}_2\text{Cl}_2) = 1.48 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of  $\pm 20\%$ . This recommendation supersedes that of Atkinson<sup>15</sup> of

$$k(\text{CH}_2\text{Cl}_2) = 8.54 \times 10^{-18} T^2 e^{-500/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 245–455 K, with a 298 K rate constant of  $1.42 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

$\text{CHF}_2\text{Cl}$ . The absolute rate constants determined by Orkin and Khamaganov<sup>5</sup> are given in Table 65. These rate constants<sup>5</sup> are in good agreement (within 12% from 298–370 K and within 21% at 460 K) with the recommendation of Atkinson,<sup>15</sup> of

$$k(\text{CHF}_2\text{Cl}) = 1.51 \times 10^{-18} T^2 e^{-1000/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 250–482 K, and

$$k(\text{CHF}_2\text{Cl}) = 4.68 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

The previous recommendation<sup>15</sup> is therefore unchanged.

$\text{CHF}_2\text{Br}$ . The absolute rate constants of Orkin and Khamaganov<sup>6</sup> are given in Table 65. These rate constants<sup>6</sup> are in excellent agreement with the recommendation in Sec. 3.2 (being 1–9% higher at 314–460 K and 14% higher at 298 K) of

$$k(\text{CHF}_2\text{Br}) = 1.48 \times 10^{-18} T^2 e^{-779/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 233–432 K, and

$$k(\text{CHF}_2\text{Br}) = 9.63 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

This recommendation from Sec. 3.2 is hence unchanged, although the estimated overall uncertainty at 298 K is now reduced to  $\pm 30\%$ .

$\text{CHCl}_3$ . Taylor *et al.*<sup>2</sup> have reinvestigated the kinetics of this reaction, and observed that at temperatures  $\geq 400$  K laser photolysis of the  $\text{CHCl}_3$  reactant led to erroneously high measured rate constants unless the laser photolysis intensities were kept low. The rate constants obtained at low laser photolysis intensities, and shown to be independent of the laser photolysis intensity,<sup>2</sup> are given in Table 65. These rate constants supersede those of Taylor *et al.*<sup>16</sup> reported earlier. The rate constants of Taylor *et al.*<sup>2</sup> at temperatures of 360–480 K are significantly (up to a factor of  $\sim 1.7$ ) lower than the rate constants of Jeong and Kaufman.<sup>21</sup> A unit-weighted least-squares analysis of the absolute rate constants of Howard and Evenson,<sup>17</sup> Davis *et al.*<sup>19</sup> and Taylor *et al.*,<sup>2</sup> using the expression  $k = CT^2 e^{-D/T}$ , leads to the recommendation of

$$k = (1.80_{-0.32}^{+0.38}) \times 10^{-18} T^2 e^{-(129 \pm 75)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 245–775 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{CHCl}_3) = 1.04 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of  $\pm 20\%$ . [Inclusion of the rate constants of Jeong and Kaufman<sup>21</sup> into the data set used for evaluation of this rate constant leads to  $k(\text{CHCl}_3) = 2.11 \times 10^{-18} T^2 e^{-169/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the same temperature range, with a 298 K rate constant of  $1.06 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .]

The present recommendation supersedes the previous recommendation of Atkinson<sup>15</sup> of

$$k(\text{CHCl}_3) = 6.30 \times 10^{-18} T^2 e^{-504/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the more restricted temperature range of 245–487 K, with a 298 K rate constant of  $1.03 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The present recommendation leads to significantly higher rate constants for temperatures  $\leq 290$  K than calculated from the previous recommendation.<sup>15</sup> In particular, the present recommendation leads to rate constants which are 20–45% higher than those measured by Davis *et al.*<sup>19</sup> at 245 K and Jeong and Kaufman<sup>21</sup> at 249 K. Clearly, further absolute rate constant studies are needed, particularly at temperatures in the range  $\sim 230$ –270 K, to resolve these discrepancies.<sup>2,19,21</sup>

$\text{CF}_4$ ,  $\text{CF}_3\text{Br}$  and  $\text{CF}_2\text{BrCF}_2\text{Br}$ . The upper limits to the rate constants reported by Ravishankara *et al.*<sup>7</sup> ( $\text{CF}_4$ ) and Orkin and Khamaganov<sup>6</sup> ( $\text{CF}_3\text{Br}$  and  $\text{CF}_2\text{BrCF}_2\text{Br}$ ) are given in Table 65. The upper limit to the rate constant for  $\text{CF}_4$  reported by Ravishankara *et al.*<sup>7</sup> is consistent with,

but a factor of 200 lower, than the recommendation of Atkinson<sup>15</sup> based on the data of Howard and Evenson.<sup>17</sup> Accordingly, a rate constant of

$$k(\text{CF}_4) < 2 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}$$

is recommended.

The upper limits to the rate constants for  $\text{CF}_3\text{Br}$  and  $\text{CF}_2\text{BrCF}_2\text{Br}$  of Orkin and Khamaganov<sup>6</sup> are consistent with the upper limits recommended at 298 K in Sec. 3.2 of  $< 1 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $< 1.5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively.

$\text{CH}_3\text{CH}_2\text{Cl}$ . The absolute rate constants determined by Markert and Nielsen<sup>8</sup> are given in Table 65. The 295 K rate constant reported by Markert and Nielsen<sup>8</sup> is identical to that reported by Markert and Nielsen<sup>22</sup> and used in the evaluation of the rate constant for this reaction in Sec. 3.2. However, the rate constants of Markert and Nielsen<sup>8</sup> at 307–360 K are 45–77% higher than calculated from the recommendation given in Sec. 3.2 of

$$k(\text{CH}_3\text{CH}_2\text{Cl}) = 7.71 \times 10^{-18} T^2 e^{-152/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 294–789 K, with a 298 K rate constant of  $4.11 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (the 295 K rate constant of Markert and Nielsen<sup>8,22</sup> is only 7% higher than the recommended value). The recommendation of Sec. 3.2 is unchanged.

$\text{CH}_3\text{CH}_2\text{Br}$ . The relative rate constant of Donaghy *et al.*<sup>9</sup> is given in Table 9. This 300 K rate constant of Donaghy *et al.*<sup>9</sup> is 25% lower than that calculated from the Arrhenius expression of Xing *et al.*<sup>23</sup> and Qiu *et al.*<sup>24</sup> (Sec. 3.2), although within the combined uncertainties cited.<sup>9,23,24</sup> From a unit-weighted average of the room temperature rate constants of Xing *et al.*<sup>23</sup> and Qiu *et al.*<sup>24</sup> and Donaghy *et al.*,<sup>9</sup> the recommendation of

$$k(\text{CH}_3\text{CH}_2\text{Br}) = 2.7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}$$

is obtained, with an estimated overall uncertainty at 298 K of  $\pm 40\%$ .

$\text{CH}_3\text{CHCl}_2$ . The absolute rate constants determined by Jiang *et al.*<sup>10</sup> are given in Table 65. The only previous rate constant for  $\text{CH}_3\text{CHCl}_2$  is that measured at 296 K by Howard and Evenson,<sup>25</sup> and the agreement is excellent. A unit-weighted least-squares analysis of the absolute rate constants of Howard and Evenson<sup>25</sup> and Jiang *et al.*,<sup>10</sup> using the expression  $k = CT^2 e^{-D/T}$ , leads to the recommendation of

$$k(\text{CH}_3\text{CHCl}_2) = (2.50 \pm 0.16) \times 10^{-18} T^2 e^{(63 \pm 27)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 294–800 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{CH}_3\text{CHCl}_2) = 2.74 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of  $\pm 30\%$ .

$\text{CH}_3\text{CCl}_3$ . The absolute rate constants of Jiang *et al.*<sup>11</sup> are given in Table 65. These rate constants of Jiang *et al.*<sup>11</sup> are systematically higher than the recommendation of Sec. 3.2 based on the absolute rate constants of Finlayson-Pitts *et al.*<sup>26</sup> and Talukdar *et al.*<sup>27</sup> This discrepancy increases with temperature, with the rate constants of Jiang *et al.*<sup>11</sup> being 15% higher than the recommendation of Sec. 3.2 at 298 K, increasing to 34% higher at 400 K. Accordingly, the recommendation of Sec. 3.2 of

$$k(\text{CH}_3\text{CCl}_3) = 2.25 \times 10^{-18} T^2 e^{-910/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 243–379 K, with a 298 K rate constant of  $9.43 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , is unchanged.

$\text{CH}_2\text{FCF}_3$ . The absolute rate constants of Orkin and Khamaganov<sup>5</sup> are given in Table 65. These rate constants are in excellent agreement (within 14%) with the recommendation of Sec. 3.2 based on the rate constants of Martin and Parakevopoulos,<sup>28</sup> Liu *et al.*<sup>29</sup> and Gierczak *et al.*<sup>30</sup> Accordingly, the recommendation of Sec. 3.2 of

$$k(\text{CH}_2\text{FCF}_3) = 1.61 \times 10^{-18} T^2 e^{-1005/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 223–450 K, with a 298 K rate constant of  $4.90 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , is unchanged.

$\text{CH}_2\text{BrCF}_3$ . The absolute rate constants of Nelson *et al.*<sup>12</sup> and Orkin and Khamaganov<sup>6</sup> are given in Table 65. The rate constants of Nelson *et al.*<sup>12</sup> are uniformly lower, by  $\sim 20\%$ , than those of Orkin and Khamaganov<sup>6</sup> over the temperature range common to both studies (298–353 K). A unit-weighted least-squares analysis of the absolute rate constants of Nelson *et al.*<sup>12</sup> and Orkin and Khamaganov,<sup>6</sup> using the Arrhenius expression  $k = A e^{-B/T}$ , yields the recommendation of

$$k(\text{CH}_2\text{BrCF}_3) = (1.44^{+1.14}_{-0.64}) \times 10^{-12} e^{-(1337 \pm 192)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 280–460 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{CH}_2\text{BrCF}_3) = 1.62 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of  $\pm 40\%$ .

$\text{CHCl}_2\text{CHCl}_2$ . The absolute rate constants of Jiang *et al.*<sup>13</sup> are given in Table 65. These rate constants are a factor of  $\sim 2$  lower than those of Xing *et al.*<sup>23</sup> and Qiu *et al.*<sup>24</sup> No recommendation is made.

$\text{CHFBrCF}_3$ . The rate constants of Orkin and Khamaganov<sup>6</sup> are given in Table 65. These rate constants are in good agreement with the absolute rate constants of

Brown *et al.*<sup>31</sup> A unit-weighted least-squares analysis of the rate constants of Brown *et al.*<sup>31</sup> and Orkin and Khamaganov,<sup>6</sup> using the Arrhenius expression  $k = A e^{-B/T}$ , yields the recommendation of

$$k(\text{CHFBrCF}_3) = (8.09^{+2.87}_{-2.12}) \times 10^{-13} e^{-(1157 \pm 105)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 279–460 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{CHFBrCF}_3) = 1.67 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an overall estimated uncertainty at 298 K of  $\pm 35\%$ .

$\text{CHClBrCF}_3$ . The absolute rate constants of Orkin and Khamaganov<sup>6</sup> are given in Table 65. This is the first temperature-dependence study. The previous rate constant of Brown *et al.*<sup>32,33</sup> at 303 K is  $\sim 25\%$  higher than that calculated from the Arrhenius expression of Orkin and Khamaganov.<sup>6</sup> A unit-weighted least-squares analysis of the absolute rate constants of Orkin and Khamaganov,<sup>6</sup> using the Arrhenius expression  $k = A e^{-B/T}$ , yields the recommendation of

$$k(\text{CHClBrCF}_3) = (1.20^{+0.23}_{-0.20}) \times 10^{-12} e^{-(970 \pm 63)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 298–460 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{CHClBrCF}_3) = 4.63 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of  $\pm 40\%$ .

$\text{CH}_3\text{CH}_2\text{Cl}$  and  $\text{CH}_3\text{CHClCH}_3$ . The rate constants of Markert and Nielsen<sup>8</sup> and Donaghy *et al.*<sup>9</sup> are given in Table 65. For both chloropropanes, the room temperature rate constants exhibit a significant amount of scatter. Furthermore, the absolute rate constant data of Markert and Nielsen<sup>8</sup> are quite scattered for both compounds. Based on the relative rate constants of Donaghy *et al.*,<sup>9</sup> rate constants of

$$k(\text{CH}_3\text{CH}_2\text{Cl}) = 1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

and

$$k(\text{CH}_3\text{CHClCH}_3) = 9.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K are recommended, both with estimated overall uncertainties of  $\pm 40\%$ .

*Other Haloalkanes.* For the other haloalkanes listed in Table 65, only single studies (or studies conducted by one research group) have been carried out and no recommendations are made.

Table 65. Rate constants  $k$  and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkanes

Haloalkane	$10^{12} \times A$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	n	B (K)	$10^{14} \times k$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	at T (K)	Technique	Reference	Temperature range covered (K)
CH <sub>3</sub> F				1.61 ± 0.08	296 ± 2	RR [relative to $k(\text{acetylene}) = 7.99 \times 10^{-13}$ ] <sup>a</sup>	Wallington and Hurley <sup>1</sup>	
				1.51 ± 0.08	296 ± 2	RR [relative to $k(\text{methane}) = 6.57 \times 10^{-15}$ ] <sup>a</sup>	Wallington and Hurley <sup>1</sup>	
CH <sub>3</sub> Cl				146.3 ± 4.8	742	LP-LIF	Taylor <i>et al.</i> <sup>2</sup>	742-955
				167.0 ± 4.6	775			
				217.0 ± 10.3	875			
				247.1 ± 11.9	925			
				267.0 ± 31.7	955			
	2.90 × 10 <sup>-2</sup>	0.89	1447 ± 75 <sup>b</sup>					
CH <sub>3</sub> Br				0.98 ± 0.04	233	LP-LIF	Mellouki <i>et al.</i> <sup>3</sup>	233-379
				1.22 ± 0.02	243			
				1.55 ± 0.03	251			
				1.39 ± 0.06	253			
				1.43 ± 0.04	253			
				1.48 ± 0.06	253			
				1.70 ± 0.05	263			
				1.99 ± 0.04	273			
				2.08 ± 0.11	273			
				1.97 ± 0.08	273			
				2.31 ± 0.05	284			
				2.84 ± 0.06	296			
				2.82 ± 0.06	296			
				2.71 ± 0.05	296			
				3.03 ± 0.11	296			
				3.51 ± 0.06	313			
				3.80 ± 0.08	321			
				4.08 ± 0.13	322			
				4.40 ± 0.10	326			
				4.63 ± 0.10	337			
5.75 ± 0.20	350							
5.62 ± 0.12	352							
6.34 ± 0.25	364							
6.67 ± 0.40	366							
8.00 ± 0.08	378							
	2.35		1300 ± 150	7.66 ± 0.22	379			

Table 65. Rate constants  $k$  and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkanes – Continued

Haloalkane	$10^{12} \times A$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$n$	$B$ (K)	$10^{14} \times k$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	at $T$ (K)	Technique	Reference	Temperature range covered (K)
				1.17 ± 0.29	250	FP-RF	Zhang <i>et al.</i> <sup>4</sup>	250-400
				1.33 ± 0.19	250			
				1.68 ± 0.30	270			
				2.25 ± 0.56	283			
				2.81 ± 0.31	295			
				2.77 ± 0.74	296			
				2.96 ± 0.83	298			
				6.51 ± 0.97	340			
				12.3 ± 1.3	400			
				5.79				
CH <sub>2</sub> Cl <sub>2</sub>				14.7 ± 1.8	295	LP-LIF	Taylor <i>et al.</i> <sup>2</sup>	295-955
				16.1 ± 3.0	309			
				24.8 ± 2.3	335			
				24.2 ± 4.6	340			
				29.4 ± 5.6	376			
				43.9 ± 5.8	415			
				43.3 ± 4.2	425			
				61.5 ± 13.8	455			
				65.1 ± 10.6	474			
				85.8 ± 11.8	495			
				81.8 ± 10.0	535			
				101.4 ± 7.6	575			
				135.3 ± 13.0	615			
				148.1 ± 8.3	655			
				165.6 ± 11.6	695			
				184.5 ± 13.3	735			
				213.0 ± 12.8	775			
				259.0 ± 11.7	896			
4.01 × 10 <sup>-3</sup>	1.09	771 ± 48	316.0 ± 39.2	955				
CH <sub>2</sub> Br <sub>2</sub>				6.0 ± 0.2	243	LP-LIF	Mellouki <i>et al.</i> <sup>3</sup>	243-380
				6.8 ± 0.2	253			
				7.0 ± 0.3	253			
				6.8 ± 0.4	253			
				8.4 ± 0.4	268			
				9.5 ± 0.5	283			
				10.6 ± 0.3	296			
				11.1 ± 0.4	296			
				12.0 ± 0.7	297			
				10.7 ± 0.3	298			
				11.3 ± 0.6	298			
				12.0 ± 0.2	300			
				13.5 ± 1.0	324			
				17.4 ± 1.0	350			
				1.91				

Table 65. Rate constants  $k$  and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkanes -- Continued

Haloalkane	$10^{12} \times A$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$n$	$B$ (K)	$10^{14} \times k$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	at $T$ (K)	Technique	Reference	Temperature range covered (K)
CHF <sub>2</sub> Cl	$0.81 \pm 0.12$		$1516 \pm 53$	$0.49 \pm 0.045$	298	DF-EPR	Orkin and Khamaganov <sup>5</sup>	298-460
				$0.72 \pm 0.051$	318			
				$0.89 \pm 0.064$	330			
				$1.32 \pm 0.096$	370			
				$3.00 \pm 0.22$	460			
CHF <sub>2</sub> Br	$0.93 \pm 0.09$		$1326 \pm 33$	$1.10 \pm 0.09$	298	DF-EPR	Orkin and Khamaganov <sup>6</sup>	298-460
				$1.32 \pm 0.09$	314			
				$1.64 \pm 0.12$	329			
				$2.07 \pm 0.15$	350			
				$2.62 \pm 0.19$	370			
				$4.03 \pm 0.28$	410			
CHCl <sub>3</sub>	$4.65 \times 10^{-5}$	1.52	$261 \pm 42$	$5.80 \pm 0.5$	460	LP-LIF	Taylor <i>et al.</i> <sup>2</sup>	295-775
				$11.2 \pm 1.0$	295			
				$14.2 \pm 2.7$	327			
				$17.1 \pm 2.0$	360			
				$20.4 \pm 1.2$	390			
				$24.2 \pm 1.3$	429			
				$28.9 \pm 4.5$	452			
				$29.8 \pm 1.8$	456			
				$32.6 \pm 1.8$	480			
				$44.0 \pm 3.1$	540			
				$47.9 \pm 3.7$	600			
				$65.6 \pm 6.1$	670			
				$68.1 \pm 5.0$	700			
				$70.2 \pm 4.3$	730			
$84.7 \pm 5.0$	775							
CF <sub>4</sub>				$<0.0002$	c	d	Ravishankara <i>et al.</i> <sup>7</sup>	
CF <sub>3</sub> Br				$<0.04$	298	DF-EPR	Orkin and Khamaganov <sup>6</sup>	298-460
				$<0.04$	460			
CH <sub>3</sub> CH <sub>2</sub> Cl	$24 \pm 4$		$1083 \pm 361$	$43 \pm 5$	295	PR-RA	Markert and Nielsen <sup>8</sup>	295-360
				$66 \pm 4$	307			
				$83 \pm 8$	315			
				$82 \pm 16$	333			
				$95 \pm 13$	360			

Table 65. Rate constants  $k$  and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkanes — Continued

Haloalkane	$10^{12} \times A$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$n$	$B$ (K)	$10^{14} \times k$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	at $T$ (K)	Technique	Reference	Temperature range covered (K)
CH <sub>3</sub> CH <sub>2</sub> Br				23.4 ± 0.8	300	RR [relative to $k(\text{ethane}) = 2.64 \times 10^{-13}$ ] <sup>a</sup>	Donaghy <i>et al.</i> <sup>9</sup>	
CH <sub>3</sub> CHCl <sub>2</sub>				28.2 ± 1.4	294	LP-LIF	Jiang <i>et al.</i> <sup>10</sup>	294–800
				30.9 ± 2.0	321			
				35.8 ± 1.9	338			
				39.2 ± 0.6	362			
				46.5 ± 1.9	401			
				54.2 ± 1.2	441			
				64.5 ± 2.1	482			
				75.8 ± 2.2	521			
				89.1 ± 3.8	560			
				97.8 ± 2.7	602			
				114 ± 4.4	640			
				122 ± 9.4	680			
				134 ± 12.1	719			
162 ± 18.0	760							
188 ± 7.6	800							
	$2.02 \times 10^{-8}$	2.67	$-378 \pm 18$					
CH <sub>3</sub> CCl <sub>3</sub>				1.1 ± 0.1	298	LP-LIF	Jiang <i>et al.</i> <sup>11</sup>	298–761
				2.9 ± 0.6	350			
				5.0 ± 1.0	400			
				9.4 ± 0.6	457			
				10.9 ± 2.9	460			
				12.2 ± 1.2	495			
				12.7 ± 0.9	513			
				18.5 ± 1.3	527			
				20.2 ± 1.0	535			
				21.8 ± 2.8	560			
				23.5 ± 3.8	601			
				33.1 ± 8.1	642			
				36.8 ± 3.6	671			
				54.5 ± 2.0	720			
				72.6 ± 3.9	761			
	$2.78 \times 10^{-6}$	2.08	$1068 \pm 108$					
CH <sub>2</sub> FCF <sub>3</sub>				0.50 ± 0.044	298	DF-EPR	Orkin and Khamaganov <sup>5</sup>	298–460
				0.83 ± 0.066	330			
				1.14 ± 0.08	360			
				1.42 ± 0.11	370			
				3.31 ± 0.24	460			
	$1.03 \pm 0.18$		$1588 \pm 52$					

Table 65. Rate constants  $k$  and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkanes — Continued

Haloalkane	$10^{12} \times A$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$n$	$B$ (K)	$10^{14} \times k$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	at $T$ (K)	Technique	Reference	Temperature range covered (K)					
CH <sub>2</sub> BrCF <sub>3</sub>	1.39 ± 0.6		1350 ± 195	1.08 ± 0.08	280	DF-LIF	Nelson <i>et al.</i> <sup>12</sup>	280–353					
				1.45 ± 0.13	294								
				1.99 ± 0.07	318								
				2.35 ± 0.15	328								
				3.01 ± 0.10	353								
	0.85 ± $\frac{0.09}{0.08}$		1113 ± 35	2.05 ± 0.16	298	DF-EPR	Orkin and Khamaganov <sup>6</sup>	298–460					
				3.06 ± 0.21	338								
				4.81 ± 0.34	389								
				7.65 ± 0.55	460								
CH <sub>2</sub> ClCCl <sub>3</sub>				2.0 ± 0.4 <sup>e</sup>	295	LP-LIF	Jiang <i>et al.</i> <sup>13</sup>	295–882					
				3.1 ± 0.5 <sup>e</sup>	326								
				3.9 ± 0.8 <sup>e</sup>	335								
				5.8 ± 1.3 <sup>e</sup>	362								
				9.2 ± 1.4 <sup>e</sup>	403								
				15.3 ± 3.6 <sup>3</sup>	452								
				16.6 ± 1.7 <sup>e</sup>	460								
				24.2 ± 3.2	480								
				26.2 ± 7.2	501								
				39.9 ± 6.5	544								
				57.8 ± 11	575								
				60.4 ± 4.8	579								
				66.1 ± 3.9	623								
				85.0 ± 6.6	663								
				118 ± 34	696								
				84.6 ± 18	701								
				119 ± 33	737								
				153 ± 20	777								
				148 ± 12	783								
				171 ± 15	832								
215 ± 30	882												
CHCl <sub>2</sub> CHCl <sub>2</sub>	3.38 × 10 <sup>-3</sup>	1.21	1553 ± 92	10.9 ± 2.7	295	LP-LIF	Jiang <i>et al.</i> <sup>13</sup>	295–701					
				13.8 ± 2.0	316								
				15.4 ± 1.9	326								
				19.8 ± 2.6	340								
				27.1 ± 1.0	382								
				30.6 ± 2.1	402								
				32.0 ± 2.1	422								
				37.4 ± 3.4	442								
				52.2 ± 5.7	520								
				63.6 ± 6.3	562								
				80.6 ± 7.8	640								
				89.6 ± 8.1	701								
				0.776	0.22				915 ± 62				

Table 65. Rate constants  $k$  and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkanes — Continued

Haloalkane	$10^{12} \times A$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$n$	$B$ (K)	$10^{14} \times k$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	at $T$ (K)	Technique	Reference	Temperature range covered (K)
CHFClCF <sub>2</sub> Cl	$0.92 \pm 0.25$		$1281 \pm 85$	$1.23 \pm 0.10$	298	DF-EPR	Orkin and Khamaganov <sup>5</sup>	298–460
				$1.67 \pm 0.12$	313			
				$1.81 \pm 0.13$	330			
				$2.19 \pm 0.16$	344			
				$2.74 \pm 0.22$	360			
				$2.68 \pm 0.19$	370			
				$5.63 \pm 0.41$	460			
CHFBrCF <sub>3</sub>	$0.72 \pm 0.07$		$1111 \pm 32$	$1.75 \pm 0.17$	298	DF-EPR	Orkin and Khamaganov <sup>6</sup>	298–460
				$2.02 \pm 0.14$	314			
				$2.35 \pm 0.16$	330			
				$2.96 \pm 0.27$	350			
				$3.61 \pm 0.43$	370			
				$4.60 \pm 0.32$	410			
				$6.22 \pm 0.48$	460			
CHCl <sub>2</sub> CF <sub>2</sub> Cl	$1.13 \pm 0.16$		$918 \pm 52$	$5.30 \pm 0.41$	298	DF-EPR	Orkin and Khamaganov <sup>5</sup>	298–460
				$6.75 \pm 0.48$	330			
				$9.38 \pm 0.72$	370			
				$15.90 \pm 1.10$	460			
CHClBrCF <sub>3</sub>	$1.28 \pm 0.12$		$995 \pm 38$	$4.50 \pm 0.40$	298	DF-EPR	Orkin and Khamaganov <sup>6</sup>	298–460
				$5.82 \pm 0.41$	317			
				$7.15 \pm 0.5$	341			
				$8.64 \pm 0.6$	370			
				$9.53 \pm 0.67$	389			
				$11.10 \pm 0.78$	410			
				$14.90 \pm 1.4$	460			
CF <sub>2</sub> BrCF <sub>2</sub> Br				$<0.04$	298	DF-EPR	Orkin and Khamaganov <sup>6</sup>	298–460
				$<0.04$	460			
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> Cl	$100 \pm 30$		$1443 \pm 482$	$96 \pm 4$	295	PR-RA	Markert and Nielsen <sup>8</sup>	295–353
				$68 \pm 7$	295			
				$147 \pm 6$	317			
				$176 \pm 2$	328			
				$116 \pm 7$	331			
				$180 \pm 20$	333			
				$160 \pm 3$	353			
				$111 \pm 3$	305			

Table 65. Rate constants  $k$  and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkanes — Continued

Haloalkane	$10^{12} \times A$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$n$	$B$ (K)	$10^{14} \times k$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	at $T$ (K)	Technique	Reference	Temperature range covered (K)
				87.1 ± 2.5	308	RR [relative to $k(n\text{-pentane})$ $= 4.11 \times 10^{-12}$ ]	Donaghy <i>et al.</i> <sup>9</sup>	
				112 ± 10	303	RR [relative to $k(\text{cyclohexane})$ $= 7.60 \times 10^{-12}$ ]	Donaghy <i>et al.</i> <sup>9</sup>	
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> Br				118 ± 7	300	RR [relative to $k(\text{cyclohexane})$ $= 7.54 \times 10^{-12}$ ]	Donaghy <i>et al.</i> <sup>9</sup>	
CH <sub>3</sub> CHClCH <sub>3</sub>				43 ± 4	295	PR-RA	Markert and Nielsen <sup>8</sup>	295-353
			104 ± 7	313				
			95 ± 3	333				
	50 ± 6		1323 ± 842	101 ± 4	353			
				92.0 ± 4.6	303	RR [relative to $k(\text{cyclohexane})$ $= 7.60 \times 10^{-12}$ ]	Donaghy <i>et al.</i> <sup>9</sup>	
CH <sub>3</sub> CHBrCH <sub>3</sub>				87.6 ± 11.3	298	RR [relative to $k(\text{cyclohexane})$ $= 7.49 \times 10^{-12}$ ]	Donaghy <i>et al.</i> <sup>9</sup>	
CH <sub>2</sub> ClCH <sub>2</sub> CH <sub>2</sub> Cl				77.9 ± 3.1	305	RR [relative to $k(\text{cyclohexane})$ $= 7.64 \times 10^{-12}$ ]	Donaghy <i>et al.</i> <sup>9</sup>	
CF <sub>3</sub> CHFCl <sub>2</sub>				0.144 ± 0.012	294	DF-LIF	Nelson <i>et al.</i> <sup>12</sup>	294-369
			0.165 ± 0.028	295				
			0.166 ± 0.06	297				
			0.241 ± 0.013	321				
			0.253 ± 0.011	323				
			0.323 ± 0.024	343				
			0.332 ± 0.020	343				
			0.325 ± 0.063	346				
			0.493 ± 0.061	368				
	3.7 ± 1.1		1615 ± 190	0.472 ± 0.033	369			

Table 65. Rate constants  $k$  and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkanes - Continued

Haloalkane	$10^{12} \times A$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$n$	$B$ (K)	$10^{14} \times k$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	at $T$ (K)	Technique	Reference	Temperature range covered (K)
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Cl	28 ± 9		842 ± 482	169 ± 9	295	PR-RA	Markert and Nielsen <sup>8</sup>	295-353
				210 ± 10	295			
				114 ± 6	295			
				128 ± 5	295			
				231 ± 7	320			
				234 ± 9	331			
				214 ± 6	353			
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Br				246 ± 8	299	RR [relative to $k$ (cyclohexane) = $7.51 \times 10^{-12}$ ] <sup>a</sup>	Donaghy <i>et al.</i> <sup>9</sup>	
(CH <sub>3</sub> ) <sub>3</sub> CCl				41.2 ± 4.5	298	RR [relative to $k$ (cyclohexane) = $7.49 \times 10^{-12}$ ] <sup>a</sup>	Donaghy <i>et al.</i> <sup>9</sup>	
CHF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CHF <sub>2</sub>	0.780 ± 0.340		1510 ± 260	0.126 ± 0.050	245	FP-RF	Zhang <i>et al.</i> <sup>14</sup>	245-419
				0.322 ± 0.033	266			
				0.279 ± 0.024	266			
				0.418 ± 0.030	296			
				0.780 ± 0.120	335			
				1.12 ± 0.17	380			
				2.53 ± 0.26	419			
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Cl	17 ± 3		481 ± 361	336 ± 7	295	PR-RA	Markert and Nielsen <sup>8</sup>	295-353
				275 ± 8	295			
				450 ± 20	319			
				390 ± 30	331			
				380 ± 20	353			
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Br				396 ± 14	304	RR [relative to $k$ (cyclohexane) = $7.62 \times 10^{-12}$ ] <sup>a</sup>	Donaghy <i>et al.</i> <sup>9</sup>	
CF <sub>3</sub> CHFCHFCF <sub>2</sub> CF <sub>3</sub>	0.421 ± 0.128		1400 ± 180	0.156 ± 0.039	250	FP-RF	Zhang <i>et al.</i> <sup>14</sup>	250-400
				0.194 ± 0.029	270			
				0.267 ± 0.036	270			
				0.387 ± 0.038	295			
				0.630 ± 0.097	330			
				0.887 ± 0.103	365			
				1.28 ± 0.23	400			

Table 65. Rate constants  $k$  and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkanes — Continued

Haloalkane	$10^{12} \times A$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$n$	$B$ (K)	$10^{14} \times k$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> ) at $T$ (K)	Technique	Reference	Temperature range covered (K)	
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Cl	$16 \pm 2$		$361 \pm 241$	$360 \pm 30$	295	PR-RA	Markert and Nielsen <sup>8</sup>	295–353
				$400 \pm 30$	295			
				$470 \pm 10$	319			
				$510 \pm 50$	333			
				$470 \pm 40$	333			
				$570 \pm 40$	339			
				$500 \pm 40$	339			
				$380 \pm 30$	339			
				$520 \pm 10$	343			
				$410 \pm 20$	353			
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Br				$585 \pm 21$	306	RR [relative to $k(\text{cyclohexane})$ $= 7.67 \times 10^{-12}$ ] <sup>a</sup>	Donaghy <i>et al.</i> <sup>9</sup>	

<sup>a</sup>From present (Section 3.2) and previous<sup>15</sup> recommendations.<sup>b</sup>Combined with the previous measurements of Taylor *et al.*<sup>16</sup><sup>c</sup>Not reported, expected to be room temperature.<sup>d</sup>Not reported, expected to be LP-LIF.<sup>e</sup>Corrected for the presence of CHCl=CCl<sub>2</sub> impurity.<sup>13</sup>

## References

- <sup>1</sup>T. J. Wallington and M. D. Hurley, *Environ. Sci. Technol.* **27**, 1448 (1993).
- <sup>2</sup>P. H. Taylor, Z. Jiang, and B. Dellinger, *Int. J. Chem. Kinet.* **25**, 9 (1993).
- <sup>3</sup>A. Mellouki, R. K. Talukdar, A.-M. Schmoltner, T. Gierczak, M. J. Mills, S. Solomon, and A. R. Ravishankara, *Geophys. Res. Lett.* **19**, 2059 (1992).
- <sup>4</sup>Z. Zhang, R. D. Saini, M. J. Kurylo, and R. E. Huie, *Geophys. Res. Lett.* **19**, 2413 (1992).
- <sup>5</sup>V. L. Orkin and V. G. Khamaganov, *J. Atmos. Chem.* **16**, 157 (1993).
- <sup>6</sup>V. L. Orkin and V. G. Khamaganov, *J. Atmos. Chem.* **16**, 169 (1993).
- <sup>7</sup>A. R. Ravishankara, S. Solomon, A. A. Turnipseed, and R. F. Warren, *Science* **259**, 194 (1993).
- <sup>8</sup>F. Markert and O. J. Nielsen, *Chem. Phys. Lett.* **194**, 123 (1992).
- <sup>9</sup>T. Donaghy, I. Shanahan, M. Hande, and S. Fitzpatrick, *Int. J. Chem. Kinet.* **25**, 273 (1993).
- <sup>10</sup>Z. Jiang, P. H. Taylor, and B. Dellinger, *J. Phys. Chem.* **96**, 8964 (1992).
- <sup>11</sup>Z. Jiang, P. H. Taylor, and B. Dellinger, *J. Phys. Chem.* **96**, 8961 (1992).
- <sup>12</sup>D. D. Nelson, Jr., M. S. Zahniser, and C. E. Kolb, *Geophys. Res. Lett.* **20**, 197 (1993).
- <sup>13</sup>Z. Jiang, P. H. Taylor, and B. Dellinger, *J. Phys. Chem.* **97**, 5050 (1993).
- <sup>14</sup>Z. Zhang, R. D. Saini, M. J. Kurylo, and R. E. Huie, *Chem. Phys. Lett.* **200**, 230 (1992).
- <sup>15</sup>R. Atkinson, *J. Phys. Chem. Ref. Data, Monograph 1,1* (1989).
- <sup>16</sup>P. H. Taylor, J. A. D'Angelo, M. C. Martin, J. H. Kasner, and B. Dellinger, *Int. J. Chem. Kinet.* **21**, 829 (1989).
- <sup>17</sup>C. J. Howard and K. M. Evenson, *J. Chem. Phys.* **64**, 197 (1976).
- <sup>18</sup>R. A. Perry, R. Atkinson, and J. N. Pitts, Jr., *J. Chem. Phys.* **64**, 1618 (1976).
- <sup>19</sup>D. D. Davis, G. Machado, B. Conaway, Y. Oh, and R. Watson, *J. Chem. Phys.* **65**, 1268 (1976).
- <sup>20</sup>G. Paraskevopoulos, D. L. Singleton, and R. S. Irwin, *J. Phys. Chem.* **85**, 561 (1981).
- <sup>21</sup>K.-M. Jeong and F. Kaufman, *J. Phys. Chem.* **86**, 1808 (1982).
- <sup>22</sup>F. Markert and O. J. Nielsen, *Chem. Phys. Lett.* **189**, 171 (1992).
- <sup>23</sup>S.-B. Xing, S.-H. Shi, and L.-X. Qiu, *Int. J. Chem. Kinet.* **24**, 1 (1992).
- <sup>24</sup>L. X. Qiu, S. H. Shi, S. B. Xing, and X. G. Chen, *J. Phys. Chem.* **96**, 685 (1992).
- <sup>25</sup>C. J. Howard and K. M. Evenson, *J. Chem. Phys.* **64**, 4303 (1976).
- <sup>26</sup>B. J. Finlayson-Pitts, M. J. Ezell, T. M. Jayaweera, H. N. Berko, and C. C. Lai, *Geophys. Res. Lett.* **19**, 1371 (1992).
- <sup>27</sup>R. K. Talukdar, A. Mellouki, A.-M. Schmoltner, T. Watson, S. Montzka, and A. R. Ravishankara, *Science* **257**, 227 (1992).
- <sup>28</sup>J.-P. Martin and G. Paraskevopoulos, *Can. J. Chem.* **61**, 861 (1983).
- <sup>29</sup>R. Liu, R. E. Huie, and M. J. Kurylo, *J. Phys. Chem.* **94**, 3247 (1990).
- <sup>30</sup>T. Gierczak, R. Talukdar, G. L. Vaghjani, E. R. Lovejoy, and A. R. Ravishankara, *J. Geophys. Res.* **96**, 5001 (1991).
- <sup>31</sup>A. C. Brown, C. E. Canosa-Mas, A. D. Parr, K. Rothwell, and R. P. Wayne, *Nature* **347**, 541 (1990).
- <sup>32</sup>A. C. Brown, C. E. Canosa-Mas, A. D. Parr, and R. P. Wayne, *Atmos. Environ.* **24A**, 2499 (1990).
- <sup>33</sup>A. C. Brown, C. E. Canosa-Mas, A. D. Parr, J. M. T. Pierce, and R. P. Wayne, *Nature* **341**, 635 (1989).

## 7.2.3. Haloalkenes

The rate constants reported for the reactions of the OH radicals with haloalkenes since Table 39 was finalized are given in Table 66.

$\text{CHCl}=\text{CCl}_2$ . The absolute rate constants of Jiang *et al.*,<sup>1</sup> measured at 740 Torr total pressure of helium diluent, are given in Table 66. At room temperature, the rate constant of Jiang *et al.*<sup>1</sup> is 65–70% higher than the

recommendation of Atkinson,<sup>3</sup> although the discrepancy decreases with increasing temperature. While this effect could be due to the rate constant being pressure-dependent at total pressures up to several hundred Torr, the temperature dependence of the rate constants measured by Jiang *et al.*,<sup>1</sup> of  $B = -1000$  K, appears anomalously high. In the absence of further confirmation of these data of Jiang *et al.*,<sup>1</sup> the previous recommendation<sup>3</sup> is unchanged.

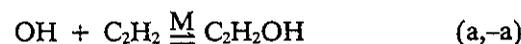
$\text{CF}_3\text{CF}=\text{CF}_2$ . McIlroy and Tully<sup>2</sup> have measured rate constants for the reaction of the OH radical with  $\text{CF}_3\text{CF}=\text{CF}_2$  over the temperature range 293–831 K. At 293 K, the rate constant is independent of total pressure of helium over the range 75–750 Torr. The reaction is assumed to proceed by OH radical addition at temperatures  $\leq 500$  K.<sup>2</sup> Non-exponential decays of the OH radical concentration were observed<sup>2</sup> over the temperature range 528–641 K, indicating either thermal decomposition of the  $\text{HOC}_3\text{F}_6$  adduct back to reactants or generation of an F atom which reacted with the  $\text{H}_2\text{O}$  present to reform OH radicals. At temperatures  $> 736$  K, the measured rate constant exceeds that for the OH radical addition pathway extrapolated from the 293–489 K temperature range, indicating a direct reaction process.<sup>2</sup>

## References

- <sup>1</sup>Z. Jiang, P. H. Taylor, and B. Dellinger, *J. Phys. Chem.* **97**, 5050 (1993).
- <sup>2</sup>A. McIlroy and F. P. Tully, *J. Phys. Chem.* **97**, 610 (1993).
- <sup>3</sup>R. Atkinson, *J. Phys. Chem. Ref. Data Monograph 1, 1* (1989).

## 7.2.4. Alkynes

Lai *et al.*<sup>1</sup> have measured the forward and reverse rate constants for the reaction of the OH radical with acetylene over the temperature range 627–713 K at 414–864 Torr total pressure of He.



Under these temperature and pressure conditions, the rate constants  $k_a$  and  $k_{-a}$  are in the fall-off regime between second- and third-order kinetics and first- and second-order kinetics, respectively.<sup>2</sup> For 760 Torr of Ar diluent, Atkinson<sup>2</sup> used the Troe fall-off model to calculate rate constants  $k_a$  for the addition of the OH radical to  $\text{C}_2\text{H}_2$  (H-atom abstraction is of no importance at 627–713 K) of  $\sim 8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 710 K and  $\sim 1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 625 K. The rate constants  $k_a$  obtained by Lai *et al.*<sup>1</sup> are in accord with these calculations,<sup>2</sup> with  $k_a = (1.1 \pm 0.2) \times 10^{-13} e^{(1460 \pm 500)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the restricted set of pressure and temperature conditions employed.

## References

- <sup>1</sup>L.-H. Lai, Y.-C. Hsu, and Y.-P. Lee, *J. Chem. Phys.* **97**, 3092 (1992).
- <sup>2</sup>R. Atkinson, *J. Phys. Chem. Ref. Data Monograph 1, 1* (1989).

Table 66. Rate constants  $k$  and temperature-dependent parameters,  $k = A e^{-B/T}$ , for the gas-phase reactions of the OH radical with haloalkenes at, or close to, the high pressure limit

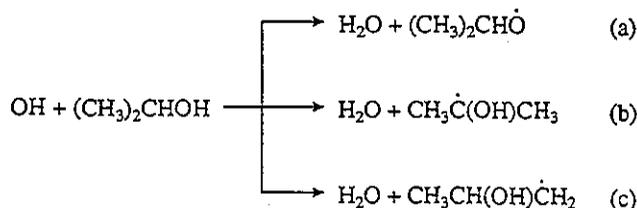
Haloalkene	$10^{12} \times A$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$B$ (K)	$10^{12} \times k$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	at $T$ (K)	Technique	Reference	Temperature range covered (K)
CHCl=CCl <sub>2</sub>			3.97 ± 0.45	295	LP-LIF	Jiang <i>et al.</i> <sup>1</sup>	295-460
			3.08 ± 0.23	326			
			2.84 ± 0.29	335			
			2.17 ± 0.21	362			
			1.58 ± 0.16	403			
			1.23 ± 0.12	452			
			1.18 ± 0.11	460			
Hexafluoropropene* (CF <sub>3</sub> CF=CF <sub>2</sub> )			2.32 ± 0.10	293	LP-LIF	McIlroy and Tully <sup>2</sup>	293-831
			2.10 ± 0.09	326			
			1.87 ± 0.08	378			
			1.74 ± 0.09	438			
	0.99 ± 0.064	-245 ± 23 (293-489 K)	1.66 ± 0.08	489			
			1.16 ± 0.07	656			
			1.32 ± 0.08	713			
			1.56 ± 0.10	736			
			1.61 ± 0.10	753			
			1.72 ± 0.11	794			
		1.74 ± 0.11	831				

\*All rate constants at 750 Torr total pressure of helium diluent.

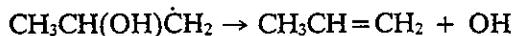
## 7.2.5. Oxygen-Containing Organic Compounds

The rate constants reported since Table 41 was finalized are given in Table 67.

**2-Propanol.** The absolute rate constants determined by Dunlop and Tully<sup>2</sup> for  $(\text{CH}_3)_2\text{CHOH}$ ,  $(\text{CH}_3)_2\text{CHOD}$ ,  $(\text{CH}_3)_2\text{CDOH}$ ,  $(\text{CD}_3)_2\text{CHOH}$  and  $(\text{CD}_3)_2\text{CDOD}$  are given in Table 67. For the reaction of  $^{16}\text{OH}$  radicals with  $(\text{CH}_3)_2\text{CHOH}$ , non-exponential decays of the  $^{16}\text{OH}$  radical were observed over the temperature range 504–600 K.<sup>2</sup> Above 600 K, exponential decays of the  $^{16}\text{OH}$  radical were observed, with the rate constants being significantly lower than expected from extrapolation of the lower temperature data.<sup>2</sup> At 548 and 587 K, rate constants were obtained from the exponential decays of  $^{18}\text{OH}$  radicals. These observations are expected<sup>2,10</sup> from the reaction sequence



with the  $\text{CH}_3\text{CH}(\text{OH})\dot{\text{C}}\text{H}_2$  radical formed in channel (c) being identical to that formed from OH radical addition to propene, and undergoing thermal decomposition at temperatures  $\geq 600$  K.<sup>9</sup>



Thus at temperatures  $\leq 500$  K the measured rate constant for reaction with  $^{16}\text{OH}$  radicals is  $k_a + k_b + k_c$ , while for temperatures  $> 600$  K the measured rate constant for  $^{16}\text{OH}$  radical reaction is  $k_a + k_b$  (the  $^{18}\text{OH}$  radical reaction leads to a measured rate constant for  $k_a + k_b + k_c$  since  $^{16}\text{OH}$  radicals and not  $^{18}\text{OH}$  radicals are regenerated). Because of expected rapid exchange of the H and D atoms on the  $-\text{OH}$  or  $-\text{OD}$  groups, the rate constants for  $(\text{CH}_3)_2\text{CHOD}$  and  $(\text{CH}_3)_2\text{CHOH}$  are identical (note that H or D atom abstraction from the  $-\text{OH}$  or  $-\text{OD}$  groups is also of minor importance) [Table 67]. From the rate constants obtained for  $(\text{CH}_3)_2\text{CHOH}$  and the partially or fully deuterated species, Dunlop and Tully<sup>2</sup> obtained a rate constant ratio of  $k_d/(k_a + k_b + k_c)$  for  $(\text{CH}_3)_2\text{CHOH}$  of

$$k_d/(k_a + k_b + k_c) = 0.698 e^{-521/T}$$

over the temperature range 293–502 K.

The rate constants of Dunlop and Tully<sup>2</sup> for  $(\text{CH}_3)_2\text{CHOH}$  are lower than those of Wallington and Kurylo<sup>11</sup> by  $\sim 10$ – $20\%$  over the temperature range common to both studies (293–440 K). A unit-weighted least squares analysis of the  $^{16}\text{OH}$  and  $^{18}\text{OH}$  radical reaction rate constants of Dunlop and Tully<sup>2</sup>, using the expression  $k = CT^2 e^{-D/T}$ , leads to the recommendation of

$$k(2\text{-propanol}) = (4.06 \pm 0.11) \times 10^{-18} T^2 e^{(788 \pm 11)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 293–587 K, where the indicated errors are two least-squares standard deviations, and

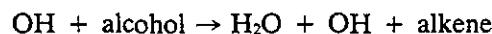
$$k(2\text{-propanol}) = 5.07 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of  $\pm 20\%$ . This recommendation supersedes that in Sec. 3.6 of

$$k(2\text{-propanol}) = 7.32 \times 10^{-18} T^2 e^{620/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 240–440 K, with a 298 K rate constant of  $5.21 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

**2,2-Dimethylpropan-1-ol (Neopentyl alcohol).** The absolute rate constants determined by Tully<sup>3</sup> for the reactions of  $^{16}\text{OH}$  and  $^{18}\text{OH}$  radicals with  $(\text{CH}_3)_3\text{CCH}_2\text{OH}$  are given in Table 67. For the  $^{18}\text{OH}$  radical reaction, exponential  $^{18}\text{OH}$  radical decays were observed at all temperatures,<sup>3</sup> while for the  $^{16}\text{OH}$  radical reactions non-exponential  $^{16}\text{OH}$  radical decays were observed<sup>3</sup> over the temperature range 437–572 K (the rate constants obtained from the initial portions of these non-exponential decays are given in Table 67). While non-exponential decays of  $^{16}\text{OH}$  radicals were observed over a fairly limited temperature range,<sup>3</sup> indicating some (slow) reformation of  $^{16}\text{OH}$  radicals,<sup>3</sup> the data obtained show that the previously observed reaction scheme of



at temperatures  $\geq 500$  K<sup>10</sup> does not occur to any significant extent for neopentyl alcohol. This lack of significant regeneration of OH radicals from the OH radical reaction with neopentyl alcohol is expected, since neopentyl alcohol does not contain any abstractable  $\beta$ -H atoms (see above discussion for 2-pentanol).

**Di-isopropyl ether.** The absolute and relative rate constants of McLaughlin *et al.*<sup>4</sup> and Wallington *et al.*<sup>5,6</sup> are given in Table 67. The room temperature absolute and relative rate constants of McLoughlin *et al.*<sup>4</sup> and Wallington *et al.*<sup>5,6</sup> are in excellent agreement with those of Nelson *et al.*<sup>12</sup> given in Table 41 of Sec. 3.6. Over the temperature range employed by Wallington *et al.*,<sup>5</sup> the rate constants were well fit by an Arrhenius expression and no evidence for curvature in the Arrhenius plot was observed.<sup>5</sup> Accordingly, a unit-weighted least-squares analysis of the absolute rate constants of Nelson *et al.*<sup>12</sup> and Wallington *et al.*<sup>5</sup> and the relative rate constants of Nelson *et al.*,<sup>12</sup> McLoughlin *et al.*,<sup>4</sup> and Wallington *et al.*,<sup>5,6</sup> using the Arrhenius expression  $k = A e^{-B/T}$ , yields the recommendation of

$$k(\text{di-isopropyl ether}) = (2.20_{-0.73}^{+1.08}) \times 10^{-12} e^{(457 \pm 120)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 240–400 K, where the indi-

errors are two least-squares standard deviations,

$$\begin{aligned} & \text{di-isopropyl ether) =} \\ & 1.02 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K,} \end{aligned}$$

with an estimated overall uncertainty at 298 K of  $\pm 25\%$ . The relative rate constants of Wallington *et al.*<sup>5,6</sup> given in Table 67 are in excellent agreement with the recommended rate constant from Table 3.6 of

$$\begin{aligned} & k(\text{ethyl } t\text{-butyl ether) =} \\ & 8.84 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K.} \end{aligned}$$

This recommendation is hence unchanged, although the estimated overall uncertainties are reduced to  $\pm 30\%$ .

*Methyl t-amyl ether.* The absolute and relative rate constants of Wallington *et al.*<sup>6</sup> are given in Table 67. These room temperature rate constants<sup>6</sup> are  $\sim 30\%$  lower than the previously reported absolute room temperature rate constant of Wallington *et al.*,<sup>13</sup> and reanalysis<sup>6</sup> of the ether sample used by Wallington *et al.*<sup>13</sup> showed the presence of a reactive alkene impurity. An Arrhenius plot of the absolute rate constants of Wallington *et al.*<sup>6</sup> showed no evidence of curvature.<sup>6</sup> Hence, a unit-weighted least-squares of the absolute and relative rate constants of Wallington *et al.*,<sup>6</sup> using the Arrhenius expression  $k = A e^{-B/T}$ , yields the recommendation of

$$\begin{aligned} & k(\text{methyl } t\text{-amyl ether) =} \\ & (6.49^{+1.45}_{-1.18}) \times 10^{-12} e^{(48 \pm 61)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \end{aligned}$$

over the temperature range 240–400 K, where the indicated errors are two least-squares standard deviations, and

$$\begin{aligned} & k(\text{methyl } t\text{-amyl ether) =} \\ & 5.52 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K,} \end{aligned}$$

with an estimated overall uncertainty at 298 K of  $\pm 35\%$ .

*n-Propyl acetate and n-butyl acetate.* The relative rate constants of Williams *et al.*<sup>8</sup> are given in Table 67. For *n*-propyl acetate, the rate constants of Williams *et al.*<sup>8</sup> are in good agreement with the previous recommendation of Atkinson<sup>9</sup> of

$$k(n\text{-propyl acetate}) = 3.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K,}$$

which is therefore unchanged.

For *n*-butyl acetate, the rate constants of Williams *et al.*<sup>8</sup> are  $\sim 35\%$  higher than the previous absolute rate constants of Hartmann *et al.*<sup>14</sup> and Wallington *et al.*<sup>15</sup> A

unit-weighted average of the absolute and relative room temperature rate constants of Hartmann *et al.*,<sup>14</sup> Wallington *et al.*<sup>15</sup> and Williams *et al.*<sup>8</sup> leads to the recommendation of

$$k(n\text{-butyl acetate}) = 4.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K,}$$

with an estimated overall uncertainty of  $\pm 50\%$ . This recommendation supersedes that of Atkinson<sup>9</sup> of

$$k(n\text{-butyl acetate}) = 4.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K.}$$

*1-Acetoxy-2-ethoxyethane.* The relative rate constants of Williams *et al.*<sup>8</sup> given in Table 67 are in good agreement with the room temperature rate constant of Hartmann *et al.*,<sup>14</sup> of  $(1.3 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K. Accordingly, a unit-weighted average of the room temperature rate constants of Hartmann *et al.*<sup>14</sup> and Williams *et al.*<sup>8</sup> leads to the recommendation of

$$\begin{aligned} & k(1\text{-acetoxy-2-ethoxyethane) =} \\ & 1.14 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K,} \end{aligned}$$

with an estimated overall uncertainty of  $\pm 40\%$ .

## References

- 1 T. J. Wallington and M. D. Hurley, *Environ. Sci. Technol.* **27**, 1448 (1993).
- 2 J. R. Dunlop and F. P. Tully, *J. Phys. Chem.* **97**, 6457 (1993).
- 3 F. P. Tully, 23rd International Symposium on Combustion, 1990; The Combustion Institute, Pittsburgh, PA, 1991, pp. 147–153.
- 4 P. McLoughlin, R. Kane, and I. Shanahan, *Int. J. Chem. Kinet.* **25**, 137 (1993).
- 5 T. J. Wallington, J. M. Andino, A. R. Potts, S. J. Rudy, W. O. Siegl, Z. Zhang, M. J. Kurylo, and R. E. Huie, *Environ. Sci. Technol.* **27**, 98 (1993).
- 6 T. J. Wallington, A. R. Potts, J. M. Andino, W. O. Siegl, Z. Zhang, M. J. Kurylo, and R. E. Huie, *Int. J. Chem. Kinet.* **25**, 265 (1993).
- 7 Z. Zhang, R. D. Saini, M. J. Kurylo, and R. E. Huie, *J. Phys. Chem.* **96**, 9301 (1992).
- 8 D. C. Williams, L. N. O'Rji, and D. A. Stone, *Int. J. Chem. Kinet.* **25**, 539 (1993).
- 9 R. Atkinson, *J. Phys. Chem. Ref. Data Monograph* **1**, 1 (1989).
- 10 W. P. Hess and F. P. Tully, *Chem. Phys. Lett.* **152**, 183 (1988).
- 11 T. J. Wallington and M. J. Kurylo, *Int. J. Chem. Kinet.* **19**, 1015 (1987).
- 12 L. Nelson, O. Rattigan, R. Neavyn, H. Sidebottom, J. Treacy, and O. J. Nielsen, *Int. J. Chem. Kinet.* **22**, 1111 (1990).
- 13 T. J. Wallington, P. Dagaut, R. Liu, and M. J. Kurylo, *Int. J. Chem. Kinet.* **20**, 541 (1988).
- 14 D. Hartmann, A. Gedra, D. Rhäsa, and R. Zellner, *Proc. 4th European Symposium on the Physico-Chemical Behaviour of Atmospheric Pollutants*, D. Reidel Publishing Co., Dordrecht, The Netherlands, 1987, pp. 225–235.
- 15 T. J. Wallington, P. Dagaut, R. Liu, and M. J. Kurylo, *Int. J. Chem. Kinet.* **20**, 177 (1988).

Table 67. Rate constants  $k$  and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organic compounds

Oxygenate	$10^{12} \times A$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> ) n	$B$ (K)	$10^{12} \times k$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> ) at $T$ (K)	Technique	Reference	Temperature range covered (K)		
<i>Aldehydes</i>								
Formyl fluoride [HC(O)F]			<0.0041 296 ± 2	RR [relative to $k(\text{CH}_3\text{F}) = 1.62$ $\times 10^{-14}$ ] <sup>a</sup>	Wallington and Hurley <sup>1</sup>			
<i>Alcohols</i>								
2-Propanol [(CH <sub>3</sub> ) <sub>2</sub> CHOH]	1.044 × 10 <sup>-5</sup>	1.86	736 (293-587 K)	5.10 ± 0.21	293	LP-LIF	Dunlop and Tully <sup>2</sup>	293-745
				4.89 ± 0.20	326			
				4.68 ± 0.20	378			
				4.73 ± 0.22	438			
				4.86 ± 0.24	502			
				5.16 ± 0.27 <sup>b</sup>	548			
				5.37 ± 0.47 <sup>b</sup>	587			
				3.93 ± 0.29	624			
				3.96 ± 0.27	643			
				4.06 ± 0.26	653			
4.42 ± 0.38	745							
2-Propanol- <i>d</i> <sub>1</sub> [(CH <sub>3</sub> ) <sub>2</sub> CHOD]				5.13 ± 0.22	293	LP-LIF	Dunlop and Tully <sup>2</sup>	293-502
				4.88 ± 0.20	326			
				4.68 ± 0.20	378			
				4.82 ± 0.23	438			
				4.86 ± 0.25	502			
2-Propanol- <i>d</i> <sub>1</sub> [(CH <sub>3</sub> ) <sub>2</sub> CDOH]				3.23 ± 0.13	293	LP-LIF	Dunlop and Tully <sup>2</sup>	293-502
				3.13 ± 0.13	326			
				3.21 ± 0.14	378			
				3.38 ± 0.16	438			
				3.58 ± 0.19	502			
2-Propanol- <i>d</i> <sub>6</sub> [(CD <sub>3</sub> ) <sub>2</sub> CHOH]				4.68 ± 0.20	293	LP-LIF	Dunlop and Tully <sup>2</sup>	293-502
				4.37 ± 0.18	326			
				4.12 ± 0.17	378			
				4.04 ± 0.18	438			
				4.13 ± 0.20	502			
2-Propanol- <i>d</i> <sub>8</sub> [(CD <sub>3</sub> ) <sub>2</sub> CDOD]				2.71 ± 0.11	293	LP-LIF	Dunlop and Tully <sup>2</sup>	293-587
				2.60 ± 0.11	326			
				2.64 ± 0.11	378			
				2.76 ± 0.13	438			

Table 67. Rate constants  $k$  and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organic compounds — Continued

Oxygenate	$10^{12} \times A$ ( $\text{cm}^3$ molecule $^{-1}$ s $^{-1}$ ) n	$B$ (K)	$10^{12} \times k$ ( $\text{cm}^3$ molecule $^{-1}$ s $^{-1}$ ) at $T$ (K)	Technique	Reference	Temperature range covered (K)			
			2.89 $\pm$ 0.14						
			3.30 $\pm$ 0.21 <sup>b</sup>						
2,2-Dimethylpropan-1-ol [(CH <sub>3</sub> ) <sub>3</sub> CCH <sub>2</sub> OH]			5.53 $\pm$ 0.24	LP-LIF	Tully <sup>3</sup>	293-764			
			5.41 $\pm$ 0.24						
			5.41 $\pm$ 0.25						
			5.66 $\pm$ 0.35 <sup>c</sup>						
			5.62 $\pm$ 0.27 <sup>b</sup>						
			5.78 $\pm$ 0.37 <sup>c</sup>						
			5.73 $\pm$ 0.27 <sup>b</sup>						
			6.11 $\pm$ 0.38 <sup>c</sup>						
			5.90 $\pm$ 0.30 <sup>b</sup>						
			6.08 $\pm$ 0.38 <sup>c</sup>						
			6.25 $\pm$ 0.40 <sup>c</sup>						
			6.42 $\pm$ 0.40 <sup>c</sup>						
			6.52 $\pm$ 0.34 <sup>b</sup>						
			6.89 $\pm$ 0.37 <sup>c</sup>						
			7.42 $\pm$ 0.41						
			6.97 $\pm$ 0.39 <sup>b</sup>						
		7.47 $\pm$ 0.42							
		7.83 $\pm$ 0.48							
		8.82 $\pm$ 0.58							
		9.08 $\pm$ 0.57							
		10.4 $\pm$ 0.67							
		11.6 $\pm$ 0.75							
<i>Ethers</i>									
Di-isopropyl ether [(CH <sub>3</sub> ) <sub>2</sub> CHOCH(CH <sub>3</sub> ) <sub>2</sub> ]			10.6 $\pm$ 0.5	RR [relative to $k$ (diethyl ether) $= 1.31 \times 10^{-11}$ ] <sup>a</sup>	McLoughlin <i>et al.</i> <sup>4</sup>	240-400			
			12.9 $\pm$ 1.4						
			12.4 $\pm$ 1.7	FP-RF	Wallington <i>et al.</i> <sup>5</sup>				
			10.6 $\pm$ 0.9						
			10.8 $\pm$ 0.9						
			8.67 $\pm$ 1.16						
			6.51 $\pm$ 1.02						
			6.98 $\pm$ 1.38						
	2.2 $\pm$ 0.4	-445 $\pm$ 145	9.81 $\pm$ 0.23				295 $\pm$ 2	RR [relative to $k$ (cyclohexane) $= 7.43 \times 10^{-12}$ ] <sup>a</sup>	Wallington <i>et al.</i> <sup>5</sup>

Table 67. Rate constants  $k$  and temperature-dependent

Parameters for the gas-phase reactions of the OH radical with oxygen-containing organic compounds

Oxygenate	$10^{12} \times A$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> ) n	$B$ (K)	$\ln k$ at $T$ (K)	Technique	Reference	Temperature range covered (K)
Ethyl <i>t</i> -butyl ether [CH <sub>3</sub> CH <sub>2</sub> OC(CH <sub>3</sub> ) <sub>3</sub> ]			8.6	RR [relative to CH <sub>3</sub> F] = 1.62 <sup>147a</sup>	Wallington and Hurley <sup>1</sup>	293-745
			8.62 ± 0.3	RR [relative to $k$ (cyclohexane) = 7.43 × 10 <sup>-13</sup> ]	Wallington et al. <sup>5</sup>	
Methyl <i>t</i> -amyl ether [CH <sub>3</sub> OC(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ]	6.32 ± 0.72	40 ± 70	5.12 ± 0.48			240-400
			5.76 ± 0.43			
			5.68 ± 0.36			
			5.66 ± 0.38			
			5.45 ± 0.48	36		
			5.85 ± 0.62	400		
CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> Cl			5.33 ± 0.24	295 ±		
CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> Cl			4.69 ± 0.28	300 ± 3		
CH <sub>3</sub> OCH <sub>2</sub> CHCl <sub>2</sub>			2.27 ± 0.11	300 ± 3	R. $k$ (a. = 1..	
CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> Br			6.64 ± 0.23	300 ± 3	RR [rel. $k$ (diethyl = 1.31 ×	Wallington et al. <sup>5</sup>
CH <sub>3</sub> CHFOCF <sub>2</sub> CH <sub>2</sub> Cl			<0.3	300 ± 3	RR [relative to $k$ (diethyl ether) = 1.31 × 10 <sup>-11</sup> ]	McLoughlin et al. <sup>4</sup>
CHF <sub>2</sub> OCHClCF <sub>3</sub>			<0.3	300 ± 3	RR [relative to $k$ (diethyl ether) = 1.31 × 10 <sup>-11</sup> ]	McLoughlin et al. <sup>4</sup>

Table 67. Rate constants  $k$  and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organic compounds -- Continued

Oxygenate	$10^{12} \times A$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> ) <sup>n</sup>	$B$ (K)	$10^{12} \times k$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	at $T$ (K)	Technique	Reference	Temperature range covered (K)
CHF <sub>2</sub> OCF <sub>2</sub> CHFCI			<0.3	300 ± 3	RR [relative to $k$ (diethyl ether) = $1.31 \times 10^{-11}$ ] <sup>a</sup>	McLoughlin <i>et al.</i> <sup>4</sup>	
CH <sub>3</sub> OCF <sub>3</sub>			0.0214 ± 0.0015	296	FP-RF	Zhang <i>et al.</i> <sup>7</sup>	
CHF <sub>2</sub> OCF <sub>3</sub>			0.00338 ± 0.00041 0.00356 ± 0.00062	296 296	FP-RF	Zhang <i>et al.</i> <sup>7</sup>	
CHF <sub>2</sub> OCHF <sub>2</sub>			0.0253 ± 0.0024 0.0241 ± 0.0016	296 296	FP-RF	Zhang <i>et al.</i> <sup>7</sup>	
CH <sub>3</sub> OCH <sub>2</sub> CF <sub>3</sub>			0.624 ± 0.067	296	FP-RF	Zhang <i>et al.</i> <sup>7</sup>	
CHF <sub>2</sub> OCH <sub>2</sub> CF <sub>3</sub>			0.0125 ± 0.0009 0.0120 ± 0.0016	296 296	FP-RF	Zhang <i>et al.</i> <sup>7</sup>	
cyclo-CF <sub>2</sub> CHFCF <sub>2</sub> O-			0.00251 ± 0.00035 0.00240 ± 0.00030	296 296	FP-RF	Zhang <i>et al.</i> <sup>7</sup>	
cyclo-(CF <sub>2</sub> ) <sub>3</sub> O-			<0.0002	296	FP-RF	Zhang <i>et al.</i> <sup>7</sup>	
<i>Esters</i>							
<i>n</i> -Propyl acetate [CH <sub>3</sub> C(O)OCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ]			3.45 ± 0.88	297 ± 2	RR [relative to $k$ (propene) = $2.65 \times 10^{-11}$ ] <sup>a</sup>	Williams <i>et al.</i> <sup>8</sup>	
			3.56 ± 0.85	297 ± 2	RR [relative to $k$ ( <i>n</i> -butane) = $2.53 \times 10^{-12}$ ] <sup>a</sup>	Williams <i>et al.</i> <sup>8</sup>	
<i>n</i> -Butyl acetate [CH <sub>3</sub> C(O)OCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ]			5.75 ± 0.96	297 ± 2	RR [relative to $k$ (propene) = $2.65 \times 10^{-11}$ ] <sup>a</sup>	Williams <i>et al.</i> <sup>8</sup>	
			5.53 ± 0.86	297 ± 2	RR [relative to $k$ ( <i>n</i> -butane) = $2.53 \times 10^{-12}$ ] <sup>a</sup>	Williams <i>et al.</i> <sup>8</sup>	
<i>n</i> -Pentyl acetate [CH <sub>3</sub> C(O)OCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ]			7.58 ± 0.48	297 ± 2	RR [relative to $k$ (propene) = $2.65 \times 10^{-11}$ ] <sup>a</sup>	Williams <i>et al.</i> <sup>8</sup>	

Table 67. Rate constants  $k$  and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organic compounds — Continued

Oxygenate	$10^{12} \times A$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> ) <sup>a</sup>	$B$ (K)	$10^{12} \times k$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> ) at $T$ (K)	Technique	Reference	Temperature range covered (K)
			$7.51 \pm 0.56$	$297 \pm 2$	RR [relative to $k(n\text{-butane}) =$ $2.53 \times 10^{-12}$ ] <sup>a</sup>	Williams <i>et al.</i> <sup>8</sup>
1-Acetoxy-2-ethoxyethane [CH <sub>3</sub> C(O)OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>3</sub> ]			$10.7 \pm 1.4$	$297 \pm 2$	RR [relative to $k(\text{propene}) =$ $2.65 \times 10^{-11}$ ] <sup>a</sup>	Williams <i>et al.</i> <sup>8</sup>
			$10.6 \pm 0.7$	$297 \pm 2$	RR [relative to $k(n\text{-butane}) =$ $2.53 \times 10^{-12}$ ] <sup>a</sup>	Williams <i>et al.</i> <sup>8</sup>
2-Ethoxyethyl isobutyrate [(CH <sub>3</sub> ) <sub>2</sub> CHC(O)OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>3</sub> ]			$13.6 \pm 2.4$	$297 \pm 2$	RR [relative to $k(\text{propene}) =$ $2.65 \times 10^{-11}$ ] <sup>a</sup>	Williams <i>et al.</i> <sup>8</sup>
			$13.0 \pm 1.1$	$297 \pm 2$	RR [relative to $k(n\text{-butane}) =$ $2.53 \times 10^{-12}$ ] <sup>a</sup>	Williams <i>et al.</i> <sup>8</sup>
			$13.7 \pm 1.7$	$297 \pm 2$	RR [relative to $k(\text{trans-2-butene}) =$ $6.44 \times 10^{-11}$ ] <sup>a</sup>	Williams <i>et al.</i> <sup>8</sup>
2-Ethoxyethyl methacrylate [CH <sub>2</sub> =C(CH <sub>3</sub> )C(O)OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>3</sub> ]			$27.4 \pm 2.1$	$297 \pm 2$	RR [relative to $k(\text{propene}) =$ $2.65 \times 10^{-11}$ ] <sup>a</sup>	Williams <i>et al.</i> <sup>8</sup>
			$28.2 \pm 3.5$	$297 \pm 2$	RR [relative to $k(\text{trans-2-butene}) =$ $6.44 \times 10^{-11}$ ] <sup>a</sup>	Williams <i>et al.</i> <sup>8</sup>
4-Penten-1-yl acetate [CH <sub>3</sub> C(O)OCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> ]			$43.7 \pm 3.9$	$297 \pm 2$	RR [relative to $k(\text{propene}) =$ $2.65 \times 10^{-11}$ ] <sup>a</sup>	Williams <i>et al.</i> <sup>8</sup>
			$43.1 \pm 2.9$	$297 \pm 2$	RR [relative to $k(\text{trans-2-butene}) =$ $6.44 \times 10^{-11}$ ] <sup>a</sup>	Williams <i>et al.</i> <sup>8</sup>
Ethyl 3-ethoxy-2-propenoate [CH <sub>3</sub> CH <sub>2</sub> OCH=CHC(O)OCH <sub>2</sub> CH <sub>3</sub> ]			$33.2 \pm 1.3$	$297 \pm 2$	RR [relative to $k(\text{trans-2-butene}) =$ $6.44 \times 10^{-11}$ ] <sup>a</sup>	Williams <i>et al.</i> <sup>8</sup>

<sup>a</sup>From present or previous<sup>9</sup> recommendations.<sup>b</sup>Reaction of <sup>18</sup>OH radical.<sup>c</sup>Non-exponential <sup>16</sup>OH radical decays observed. Rate constant obtained from the initial portion of the decay curve.

## 7.2.6. Aromatic Compounds

The rate constants reported for the gas-phase reactions of OH radicals with aromatic compounds since Table 47 was finalized are given in Table 68.

*Toluene*. The rate constant obtained by Finlayson-Pitts *et al.*,<sup>1</sup> using a relative rate method and ozone as a dark source of OH radicals,<sup>1</sup> of  $(6.00 \pm 0.29) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K (Table 68), is in excellent agreement with the recommendation of Atkinson<sup>3</sup> of

$$k(\text{toluene}) = 5.96 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

which is therefore unchanged.

*Hexafluorobenzene*. The absolute rate constants determined by McIlroy and Tully<sup>2</sup> over the temperature 244–830 K are given in Table 68. No evidence for OH radical reformation was observed<sup>2</sup> at elevated temperatures, consistent with either a larger C–OH bond dissociation energy in the HO–C<sub>6</sub>F<sub>6</sub> adduct<sup>3</sup> or with an exothermic reaction pathway to products other than the reactants.<sup>2</sup>

The room temperature rate constant of McIlroy and Tully<sup>2</sup> is in reasonable or good agreement, respectively, with the previous absolute rate constants of Ravishankara *et al.*<sup>4</sup> and Wallington *et al.*<sup>5</sup> The rate constants of Wallington *et al.*<sup>5</sup> over the temperature range 234–438 K are in reasonable agreement with those of McIlroy and Tully,<sup>2</sup> although the data of Wallington *et al.*<sup>5</sup> lead to a significantly lower Arrhenius activation energy  $B$  of  $B = 610 \pm 80$  K.

A unit-weighted least-squares analysis of the absolute rate constants of Ravishankara *et al.*,<sup>4</sup> Wallington *et al.*<sup>5</sup> and McIlroy and Tully,<sup>2</sup> using the Arrhenius expression  $k = A e^{-B/T}$ , leads to the recommendation of

$$k(\text{hexafluorobenzene}) = (3.88_{-0.79}^{+0.98}) \times 10^{-12} e^{-(931 \pm 78)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 234–830 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{hexafluorobenzene}) = 1.71 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of  $\pm 30\%$ .

This recommendation supersedes that of Atkinson<sup>3</sup> of

$$k(\text{hexafluorobenzene}) = 1.46 \times 10^{-12} e^{-638/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 234–438 K, with a 298 K rate constant of  $1.72 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

## References

- <sup>1</sup>B. J. Finlayson-Pitts, S. K. Hernandez, and H. N. Berko, *J. Phys. Chem.* **97**, 1172 (1993).
- <sup>2</sup>A. McIlroy and F. P. Tully, *J. Phys. Chem.* **97**, 610 (1993).
- <sup>3</sup>R. Atkinson, *J. Phys. Chem. Ref. Data Monograph* **1**, 1 (1989).
- <sup>4</sup>A. R. Ravishankara, S. Wagner, S. Fischer, G. Smith, R. Schiff, R. T. Watson, G. Tesi, and D. D. Davis, *Int. J. Chem. Kinet.* **10**, 783 (1978).
- <sup>5</sup>T. J. Wallington, D. M. Neuman, and M. J. Kurylo, *Int. J. Chem. Kinet.* **19**, 725 (1987).

## 7.2.7. Organic Radicals

Rate constants reported for the gas-phase reactions of the OH radical with organic radicals since Table 49 was finalized are given in Table 69.

*CH<sub>3</sub>*. The absolute room temperature rate constants of Hughes *et al.*<sup>1</sup> and Fagerström *et al.*<sup>2</sup> are given in Table 69. Hughes *et al.*<sup>1</sup> observed no pressure dependence of the rate constant over the total pressure range 7.4–700 Torr of helium diluent, while Fagerström *et al.*<sup>2</sup> observed the rate constant to increase from  $(9.6 \pm 0.5) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 64 Torr total pressure of SF<sub>6</sub> to  $(1.30 \pm 0.12) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 750 torr total pressure of SF<sub>6</sub>. The absolute room temperature rate constants from these two studies<sup>1,2</sup> and those of Anastasi *et al.*<sup>4</sup> and Osner *et al.*<sup>5</sup> exhibit discrepancies of a factor of  $\sim 2$ . The recommendation of Sec. 3.13 of

$$k_{\infty}(\text{CH}_3) = 1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

applicable to total pressures of air  $\geq 100$  Torr and with an estimated overall uncertainty of a factor of 2, is unchanged.

## References

- <sup>1</sup>K. J. Hughes, A. R. Pereira, and M. J. Pilling, *Ber. Bunsenges. Phys. Chem.* **96**, 1352 (1992).
- <sup>2</sup>K. Fagerström, A. Lund, G. Mahmoud, J. T. Jodkowski, and E. Ratajczak, *Chem. Phys. Lett.* **204**, 226 (1993).
- <sup>3</sup>K. Fagerström, A. Lund, G. Mahmoud, J. T. Jodkowski, and E. Ratajczak, *Chem. Phys. Lett.* **208**, 321 (1993).
- <sup>4</sup>C. Anastasi, S. Beverton, T. Ellermann, and P. Pagsberg, *J. Chem. Soc. Faraday Trans.* **87**, 2325 (1991).
- <sup>5</sup>H. Osner, N. D. Stothard, R. Humpfer, and H. H. Grotheer, *J. Phys. Chem.* **96**, 5359 (1992).

Table 68. Rate constants  $k$  and temperature-dependent parameters,  $k = A e^{-B/T}$ , for the gas-phase reactions of the OH radical with aromatic compounds

Aromatic	$10^{12} \times A$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$B$ (K)	$10^{12} \times k$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> ) at $T$ (K)	Technique	Reference	Temperature range covered (K)
Toluene			6.00 ± 0.29 298	RR [relative to $k(n\text{-hexane})$ $= 5.61 \times 10^{-12}$ ]	Finlayson-Pitts <i>et al.</i> <sup>1</sup>	
Hexafluorobenzene (C <sub>6</sub> F <sub>6</sub> )			0.0790 ± 0.0042 0.109 ± 0.006 0.136 ± 0.008 0.152 ± 0.009 0.215 ± 0.012 0.300 ± 0.018 0.413 ± 0.028 0.532 ± 0.031 0.703 ± 0.050 0.838 ± 0.048 1.05 ± 0.069 1.30 ± 0.15 1.31 ± 0.10	244 260 275 294 327 377 420 467 529 586 637 709 830	LP-LIF	McIlroy and Tully <sup>2</sup> 244-830
	4.78 ± 0.90	1005 ± 116				

\*From previous recommendation.<sup>3</sup>

TABLE 69. Rate constants  $k$  for the gas-phase reactions of the OH radical with organic radicals at, or close to, the high-pressure limit

Radical	$10^{12} \times k$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	at $T$ (K)	Technique	Reference
CH <sub>3</sub>	$76 \pm 8$	290	LP-RA	Hughes <i>et al.</i> <sup>1</sup>
	$144 \pm 15^a$	298	PR-RA	Fagerström <i>et al.</i> <sup>2</sup>
C <sub>2</sub> H <sub>5</sub>	$118 \pm 17^b$	298	PR-RA	Fagerström <i>et al.</i> <sup>3</sup>

<sup>1</sup>Extrapolated high-pressure limit<sup>2</sup>; see text.

<sup>2</sup>Independent of total pressure of SF<sub>6</sub> diluent over the range 188–750 Torr.

### 7.3. Kinetics and Mechanisms of the Gas-Phase Reactions of the NO<sub>3</sub> Radical with Organic Compounds

#### 7.3.1. Alkanes

Since Table 50 was finalized, Langer *et al.*<sup>1</sup> have used a discharge flow system with optical absorption detection of NO<sub>3</sub> radicals at 662 nm to obtain a rate constant of  $(2.8 \pm 0.3) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at  $296 \pm 2 \text{ K}$  for the reaction of the NO<sub>3</sub> radical with *n*-hexane. Due to the expected occurrence of secondary reactions leading to a stoichiometry of  $\sim 2$  for disappearance of NO<sub>3</sub> radicals,<sup>1</sup> this rate constant is an upper limit and is consistent with the discussion given in Sec. 4.1.

#### Reference

<sup>1</sup>S. Langer, E. Ljungström and I. Wängberg, *J. Chem. Soc. Faraday Trans. 89*, 425 (1993).

#### 7.3.2. Alkenes

The rate constants reported since Table 52 was finalized are given in Table 70. For 1,3-butadiene, isoprene and 2,3-dimethyl-1,3-butadiene, the absolute rate constants of Ellermann *et al.*<sup>1</sup> are higher than the recommendations of Atkinson<sup>2</sup> at 298 K of

$$k(1,3\text{-butadiene}) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$k(2\text{-methyl-1,3-butadiene}) = 6.78 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

and

$$k(2,3\text{-dimethyl-1,3-butadiene}) = 2.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

with estimated overall uncertainties of factors of 3 (1,3-butadiene) and 2 (2-methyl-1,3-butadiene and 2,3-dimethyl-1,3-butadiene). The recommendations of Atkinson<sup>2</sup> are unchanged (see also Sec. 4.3 for isoprene).

The absolute rate constant for 1,3-cyclohexadiene of  $(1.2 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 295 K is in excellent agreement with the recommendation of Atkinson<sup>2</sup> of

$$k(1,3\text{-cyclohexadiene}) = 1.16 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K},$$

which is therefore unchanged.

#### References

<sup>1</sup>T. Ellermann, O. J. Nielsen, and H. Skov, *Chem. Phys. Lett.* **200**, 224 (1992).

<sup>2</sup>R. Atkinson, *J. Phys. Chem. Ref. Data* **20**, 459 (1991).

#### 7.3.3. Oxygen-Containing Organic Compounds

The rate constants reported since Table 55 was finalized are given in Table 71. The duplicate sets of experiments at  $296 \pm 2 \text{ K}$  for several of the esters studied are for ester samples obtained from different commercial sources.<sup>1</sup> Because of the slowness of these reactions, the rate constants given in Table 71 should be considered to be upper limits to the elementary rate constants.<sup>1</sup>

#### References

<sup>1</sup>S. Langer, E. Ljungström and I. Wängberg, *J. Chem. Soc. Faraday Trans. 89*, 425 (1993).

#### 7.3.4. Aromatic Compounds

The rate constants reported since Table 57 was finalized are given in Table 72, where the rate constants  $k_{\text{abs}}$ ,  $k_a$ ,  $k_b$ ,  $k_c$  and  $k_d$  are those for the reactions (abs), (a), (b), (c) and (d), respectively.

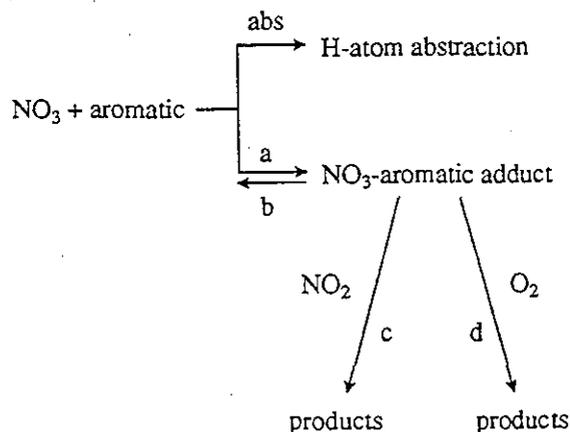


Table 70. Rate constants  $k$  for the gas-phase reactions of the  $\text{NO}_3$  radical with alkenes

Alkene	$k$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	at $T$ (K)	Technique	Reference
1,3-Butadiene	$(1.8 \pm 0.4) \times 10^{-13}$	295	PR-A	Ellermann <i>et al.</i> <sup>1</sup>
2-Methyl-1,3-butadiene (isoprene)	$(1.07 \pm 0.20) \times 10^{-12}$	295	PR-A	Ellermann <i>et al.</i> <sup>1</sup>
2,3-Dimethyl-1,3-butadiene	$(2.7 \pm 0.2) \times 10^{-12}$	295	PR-A	Ellermann <i>et al.</i> <sup>1</sup>
<i>cis</i> -1,3-Pentadiene	$(1.4 \pm 0.1) \times 10^{-12}$	295	PR-A	Ellermann <i>et al.</i> <sup>1</sup>
<i>trans</i> -1,3-Pentadiene	$(1.6 \pm 0.1) \times 10^{-12}$	295	PR-A	Ellermann <i>et al.</i> <sup>1</sup>
1,3-Cyclohexadiene	$(1.2 \pm 0.2) \times 10^{-11}$	295	PR-A	Ellermann <i>et al.</i> <sup>1</sup>
<i>trans,trans</i> -2,4-Hexadiene	$(1.6 \pm 0.3) \times 10^{-11}$	295	PR-A	Ellermann <i>et al.</i> <sup>1</sup>

These rate constant data are from the relative rate constant study of Kwok *et al.*<sup>1</sup> Of particular interest is the determination of the rate constant  $k_a = 6.8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 297 K for the addition reaction of the  $\text{NO}_3$  radical with dibenzo-*p*-dioxin. Assuming that the rate constant  $k_c$  for the reaction of  $\text{NO}_2$  with the  $\text{NO}_3$ -dibenzo-*p*-dioxin adduct is similar to those determined by Knispel *et al.*<sup>3</sup> for the reactions of  $\text{NO}_2$  with the OH-benzene, OH-toluene and OH-phenol adducts, of  $\sim 3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , than a rate constant for the thermal decomposition of  $\text{NO}_3$ -dibenzo-*p*-dioxin back to reactants of  $k_b \sim 520 \text{ s}^{-1}$  at  $297 \pm 2 \text{ K}$  was obtained.<sup>1</sup> Furthermore, with the same assumption,  $k_d < 1.2 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at  $297 \pm 2 \text{ K}$ , approximately an order of magnitude (or greater) less than the room temperature rate constants determined by Knispel *et al.*<sup>3</sup> for the corresponding reactions of OH-benzene and OH-toluene adducts with  $\text{O}_2$ .

## References

- <sup>1</sup>E. S. C. Kwok, R. Atkinson, and J. Arey, *Int. J. Chem. Kinet.*, in press (1994).  
<sup>2</sup>R. Atkinson, *J. Phys. Chem. Ref. Data* **20**, 459 (1991).  
<sup>3</sup>R. Knispel, R. Koch, M. Siese, and C. Zetzsch, *Ber. Bunsenges. Phys. Chem.* **94**, 1375 (1990).

### 7.4. Kinetics and Mechanisms of the Gas-Phase Reactions of Ozone with Organic Compounds

The kinetic and mechanistic data reported since Sec. 5 was finalized are presented and briefly discussed in the sections below.

#### 7.4.1. Alkenes

The rate constants reported since Table 58 was finalized are given in Table 73. In addition to the rate constants given in Table 73, Munshi *et al.*<sup>3</sup> have reported lower limits to the (unspecified) room temperature rate constants for  $\alpha$ -pinene,  $\beta$ -pinene, limonene and  $\alpha$ -phellandrene of (in  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  units)  $> 8.0 \times 10^{-17}$ ,  $> 9.6 \times 10^{-18}$ ,  $> 5.0 \times 10^{-18}$  and  $> 4.1 \times 10^{-17}$ , respectively.

*2-Methyl-1,3-butadiene (isoprene)*. The absolute rate constant of Grosjean *et al.*<sup>1</sup> is given in Table 73. This rate constant of Grosjean *et al.*<sup>1</sup> is in reasonable agreement with that of  $1.15 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  calculated from the recommendation of Sec. 5.2 of

$$k(2\text{-methyl-1,3-butadiene}) = 7.86 \times 10^{-15} e^{-1913/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 240–324 K, which is unchanged.

*Cycloheptene*. The rate constant of Greene and Atkinson<sup>2</sup> supersedes that of Atkinson *et al.*<sup>4</sup> (and is 30% lower), and is in good agreement with the relative rate constant of Nolting *et al.*<sup>5</sup> of  $(2.70 \pm 0.15) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at  $297 \pm 2 \text{ K}$ . A unit-weighted average of the relative rate constants of Nolting *et al.*<sup>5</sup> and Greene and Atkinson<sup>2</sup> leads to the recommendation of

$$k(\text{cycloheptene}) = 2.48 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty of  $\pm 40\%$ .

*Other Alkenes*. The rate constants measured by Greene and Atkinson<sup>2</sup> using a relative rate method are given in Table 73. These rate constants of Greene and Atkinson<sup>2</sup> supersede those of Atkinson *et al.*<sup>4,6</sup>

## References

- <sup>1</sup>D. Grosjean, E. L. Williams II, and E. Grosjean, *Environ. Sci. Technol.* **27**, 830 (1993).  
<sup>2</sup>C. R. Greene and R. Atkinson, *Int. J. Chem. Kinet.* **26**, 37 (1994).  
<sup>3</sup>H. B. Munshi, K. V. S. R. Rao, and R. M. Iyer, *Atmos. Environ.* **23**, 1971 (1989).  
<sup>4</sup>R. Atkinson, S. M. Aschmann, W. P. L. Carter, and J. N. Pitts, Jr., *Int. J. Chem. Kinet.* **15**, 721 (1983).  
<sup>5</sup>F. Nolting, W. Behnke, and C. Zetzsch, *J. Atmos. Chem.* **6**, 47 (1988).  
<sup>6</sup>R. Atkinson, S. M. Aschmann, and W. P. L. Carter, *Int. J. Chem. Kinet.* **16**, 967 (1984).

#### 7.4.2. Oxygen-Containing Organic Compounds

The rate constants reported since Table 60 was finalized are given in Table 74 (those of Hatakeyama *et al.*<sup>3</sup> and Munshi *et al.*<sup>4</sup> were inadvertently omitted from Sec. 5.4).

Table 71. Rate constants  $k$  and temperature-dependent parameters,  $k = A e^{-B/T}$ , for the gas-phase reactions of the  $\text{NO}_3$  radical with oxygen-containing compounds

Organic	$10^{12} \times A$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	$B$ (K)	$k$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	at $T$ (K)	Technique	Reference	Temperature range covered (K)
Methyl formate [ $\text{HC(O)OCH}_3$ ]			$(3 \pm 1) \times 10^{-18}$	296 $\pm$ 2	DF-A	Langer <i>et al.</i> <sup>1</sup>	
			$(4.1 \pm 0.6) \times 10^{-18}$	296 $\pm$ 2			
Methyl acetate [ $\text{CH}_3\text{C(O)OCH}_3$ ]			$(7 \pm 2) \times 10^{-18}$	296 $\pm$ 2	DF-A	Langer <i>et al.</i> <sup>1</sup>	
			$(7.2 \pm 0.4) \times 10^{-17}$	296 $\pm$ 2			
Methyl propionate [ $\text{CH}_3\text{CH}_2\text{C(O)OCH}_3$ ]			$(3.3 \pm 0.8) \times 10^{-17}$	296 $\pm$ 2	DF-A	Langer <i>et al.</i> <sup>1</sup>	
Methyl butyrate [ $\text{CH}_3\text{CH}_2\text{CH}_2\text{C(O)OCH}_3$ ]			$(4.8 \pm 0.5) \times 10^{-17}$	296 $\pm$ 2	DF-A	Langer <i>et al.</i> <sup>1</sup>	
Ethyl formate [ $\text{HC(O)CH}_2\text{CH}_3$ ]			$(1.7 \pm 0.3) \times 10^{-17}$	296 $\pm$ 2	DF-A	Langer <i>et al.</i> <sup>1</sup>	
			$(2.2 \pm 0.4) \times 10^{-17}$	296 $\pm$ 2			
Ethyl acetate [ $\text{CH}_3\text{C(O)OCH}_2\text{CH}_3$ ]	0.133	2795 $\pm$ 962	$(5 \pm 3) \times 10^{-18}$	273	DF-A	Langer <i>et al.</i> <sup>1</sup>	273-373
			$(1.4 \pm 0.3) \times 10^{-17}$	296 $\pm$ 2			
			$(1.1 \pm 0.2) \times 10^{-17}$	296 $\pm$ 2			
			$(1.6 \pm 0.4) \times 10^{-17}$	313			
			$(1.8 \pm 0.5) \times 10^{-17}$	328			
			$(4.2 \pm 0.4) \times 10^{-17}$	353			
Ethyl propionate [ $\text{CH}_3\text{CH}_2\text{C(O)OCH}_2\text{CH}_3$ ]			$(3.3 \pm 0.4) \times 10^{-17}$	296 $\pm$ 2	DF-A	Langer <i>et al.</i> <sup>1</sup>	
			$(3.8 \pm 0.1) \times 10^{-17}$	296 $\pm$ 2			
Propyl formate [ $\text{HC(O)OCH}_2\text{CH}_2\text{CH}_3$ ]			$(5.4 \pm 0.9) \times 10^{-17}$	296 $\pm$ 2	DF-A	Langer <i>et al.</i> <sup>1</sup>	
Propyl acetate [ $\text{CH}_3\text{C(O)OCH}_2\text{CH}_2\text{CH}_3$ ]			$(5 \pm 2) \times 10^{-17}$	296 $\pm$ 2	DF-A	Langer <i>et al.</i> <sup>1</sup>	

*Methacrolein and Methyl Vinyl Ketone.* The absolute rate constants of Grosjean *et al.*<sup>1</sup> are given in Table 74. These rate constants are in good agreement, to within 6% for methacrolein and 17% for methyl vinyl ketone, with the rate constants calculated from the recommendations given in Sec. 5.4 of

$$k(\text{methacrolein}) = 1.36 \times 10^{-15} e^{-2112/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

and

$$k(\text{methyl vinyl ketone}) = 7.51 \times 10^{-16} e^{-1521/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

both over the temperature range 240–324 K. These previous recommendations are unchanged.

*2-Cyclohexen-1-one.* The upper limit to the rate constant obtained by Greene and Atkinson<sup>2</sup> from a relative rate study is consistent with the absolute rate constant of Atkinson *et al.*<sup>6</sup>

*3-Penten-2-one.* The relative rate constant of Greene and Atkinson<sup>2</sup> supersedes the previous absolute rate constant of Atkinson *et al.*<sup>6</sup>

## References

- <sup>1</sup>D. Grosjean, E. L. Williams II, and E. Grosjean, *Environ. Sci. Technol.* **27**, 830 (1993).  
<sup>2</sup>C. R. Greene and R. Atkinson, *Int. J. Chem. Kinet.* **26**, 37 (1994).  
<sup>3</sup>S. Hatakeyama, S. Honda, and H. Akimoto, *Bull. Chem. Soc. Jpn.* **58**, 2411 (1985).  
<sup>4</sup>H. B. Munshi, K. V. S. R. Rao, and R. M. Iyer, *Atmos. Environ.* **23**, 1971 (1989).  
<sup>5</sup>R. Atkinson, J. Arey, S. M. Aschmann, and E. C. Tuazon, *Res. Chem. Intermed.*, in press (1993).  
<sup>6</sup>R. Atkinson, S. M. Aschmann, A. M. Winer, and J. N. Pitts, Jr., *Int. J. Chem. Kinet.* **13**, 1133 (1981).

## 7.4.3. Nitrogen-Containing Organic Compounds

Blatchley *et al.*<sup>1</sup> have used a static system with ultraviolet absorption spectroscopy to investigate the kinetics of the gas-phase reaction of pyridine, 2-, 3- and 4-methylpyridine, and 2,5- and 2,6-dimethylpyridine with O<sub>3</sub>. Due to spectroscopic interferences between O<sub>3</sub> and the pyridine and/or pyridine reaction products, only semi-quantitative data were obtained, indicating that these reactions were slow, with room temperature rate constants of  $\sim(5-50) \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  being reported.

Munshi *et al.*<sup>2</sup> used a flow technique with ultraviolet absorption spectroscopy to measure rate constants at room temperature (unspecified) for the gas phase reactions of O<sub>3</sub> with acrylonitrile (CH<sub>2</sub>=CHCN) and methacrylonitrile (CH<sub>2</sub>=C(CH<sub>3</sub>)CN) of  $1.38 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $3.52 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively. Decidedly non-unit stoichiometry was observed for the O<sub>3</sub> reaction with acrylonitrile<sup>2</sup> ( $\Delta\text{O}_3/\Delta\text{acrylonitrile} = 0.33$ ), and the rate constant obtained<sup>2</sup> is marginally inconsistent with the upper limit of  $k(\text{acrylonitrile}) < 1 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  determined by Atkinson *et al.*<sup>3</sup> at  $296 \pm 2 \text{ K}$ .

## References

- <sup>1</sup>E. R. Blatchley, III, C. R. Daughton, and J. F. Thomas, *Atmos. Environ.* **27A**, 113 (1993).  
<sup>2</sup>H. B. Munshi, K. V. S. R. Rao, and R. M. Iyer, *Atmos. Environ.* **23**, 1971 (1989).  
<sup>3</sup>R. Atkinson, S. M. Aschmann, D. R. Fitz, A. M. Winer, and J. N. Pitts, Jr., *Int. J. Chem. Kinet.* **14**, 13 (1982).

Table 72. Rate constants  $k_{\text{abs}}$  and  $k_a$ , and rate constant ratios  $k_a k_c/k_b$  and  $k_a k_d/k_b$  for the gas-phase reactions of the NO<sub>3</sub> radical with aromatic compounds at  $297 \pm 2 \text{ K}$ <sup>1</sup>

Aromatic	$k_a$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> ) <sup>a</sup>	$k_{\text{abs}}$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> ) <sup>a</sup>	$k_a k_c/k_b$ (cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> ) <sup>a</sup>	$k_a k_d/k_b$ (cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> ) <sup>a</sup>
Methoxybenzene		$< 1.6 \times 10^{-15}$	$< 7 \times 10^{-30}$	
1,2-Dimethoxybenzene		$(9.8 \pm 4.8) \times 10^{-15}$	$(1.02 \pm 0.18) \times 10^{-28}$	
1,3-Dimethoxybenzene		$(1.02 \pm 0.35) \times 10^{-14}$	$(3.3 \pm 0.6) \times 10^{-29}$	
1,4-Dimethoxybenzene		$(8.8 \pm 0.6) \times 10^{-15}$	$(1.34 \pm 0.03) \times 10^{-28}$	
Dibenzofuran		$< 1.6 \times 10^{-15}$	$< 7 \times 10^{-30}$	
Dibenzo- <i>p</i> -dioxin	$6.8 \times 10^{-14}$ <sup>b</sup>	$< 8 \times 10^{-15}$	$3.9 \times 10^{-27}$ <sup>b</sup>	$< 1.6 \times 10^{-33}$

<sup>a</sup>Relative to  $k(1\text{-butene}) = 1.19 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,<sup>2</sup>

<sup>b</sup>Estimated overall uncertainty of a factor of  $\sim 2$ .

Table 73. Rate constants  $k$  for the gas-phase reaction of  $O_3$  with alkenes

Alkene	$k$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	at $T$ (K)	Technique	Reference
2-Methyl-1,3-butadiene (isoprene)	$(8.95 \pm 0.25) \times 10^{-18}$	$293 \pm 2$	S-UV	Grosjean <i>et al.</i> <sup>1</sup>
1,3-Cyclohexadiene	$(1.22 \pm 0.05) \times 10^{-15}$	$296 \pm 2$	RR [relative to $k(2,3\text{-dimethyl-2-}$ $\text{butene}) = 1.12 \times 10^{-15}]^a$	Greene and Atkinson <sup>2</sup>
Cycloheptene	$(2.26 \pm 0.04) \times 10^{-16}$	$296 \pm 2$	RR [relative to $k(cis\text{-2-butene})$ $= 1.22 \times 10^{-16}]^a$	Greene and Atkinson <sup>2</sup>
1,3-Cycloheptadiene	$(1.54 \pm 0.03) \times 10^{-16}$	$296 \pm 2$	RR [relative to $k(cis\text{-2-butene})$ $= 1.22 \times 10^{-16}]^a$	Greene and Atkinson <sup>2</sup>
Bicyclo[2.2.1]-2-heptene	$(1.55 \pm 0.05) \times 10^{-15}$	$296 \pm 2$	RR [relative to $k(2,3\text{-dimethyl-2-}$ $\text{butene}) = 1.12 \times 10^{-15}]^a$	Greene and Atkinson <sup>2</sup>
Bicyclo[2.2.1]-2,5- heptadiene	$(3.55 \pm 0.07) \times 10^{-15}$	$296 \pm 2$	RR [relative to $k(2,3\text{-dimethyl-2-}$ $\text{butene}) = 1.12 \times 10^{-15}]^a$	Greene and Atkinson <sup>2</sup>
Bicyclo[2.2.2]-2-octene	$(7.09 \pm 0.10) \times 10^{-17}$	$296 \pm 2$	RR [relative to $k(cis\text{-2-butene})$ $= 1.22 \times 10^{-16}]^a$	Greene and Atkinson <sup>2</sup>

<sup>a</sup>From previous recommendations.

Table 74. Rate constants  $k$  for the gas-phase reactions of  $O_3$  with oxygen-containing organic compounds

Organic	$k$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	at $T$ (K)	Technique	Reference
Methacrolein [ $\text{CH}_2 = \text{C}(\text{CH}_3)\text{CHO}$ ]	$(1.02 \pm 0.05) \times 10^{-18}$	$291 \pm 2$	S-UV	Grosjean <i>et al.</i> <sup>1</sup>
Methyl vinyl ketone [ $\text{CH}_3\text{C}(\text{O})\text{CH} = \text{CH}_2$ ]	$(4.72 \pm 0.09) \times 10^{-18}$	$291 \pm 2$	S-UV	Grosjean <i>et al.</i> <sup>1</sup>
3-Penten-2-one [ $\text{CH}_3\text{C}(\text{O})\text{CH} = \text{CHCH}_3$ ]	$(3.50 \pm 0.16) \times 10^{-17}$	$296 \pm 2$	RR [relative to $k(\text{propene}) =$ $9.68 \times 10^{-18}]^a$	Greene and Atkinson <sup>2</sup>
2-Cyclohexene-1-one	$< 1.9 \times 10^{-18}$	$296 \pm 2$	RR [relative to $k(\text{propene}) =$ $9.68 \times 10^{-18}]^a$	Greene and Atkinson <sup>2</sup>
Ketene [ $\text{CH}_2 = \text{C} = \text{O}$ ]	$< 1 \times 10^{-21}$	b	S-IR	Hatakeyama <i>et al.</i> <sup>3</sup>
Methylketene [ $\text{CH}_3\text{CH} = \text{C} = \text{O}$ ]	$< 7 \times 10^{-19}$	$303 \pm 1$	S-IR	Hatakeyama <i>et al.</i> <sup>3</sup>
Ethylketene [ $\text{CH}_3\text{CH}_2\text{CH} = \text{C} = \text{O}$ ]	$< 1 \times 10^{-18}$	$303 \pm 1$	S-IR	Hatakeyama <i>et al.</i> <sup>3</sup>
Dimethylketene [ $(\text{CH}_3)_2\text{C} = \text{C} = \text{O}$ ]	$< 4 \times 10^{-17}$	$303 \pm 1$	S-IR	Hatakeyama <i>et al.</i> <sup>3</sup>
Methyl acrylate [ $\text{CH}_2 = \text{CHC}(\text{O})\text{OCH}_3$ ]	$2.91 \times 10^{-18}$	b	F-UV	Munshi <i>et al.</i> <sup>4</sup>
Ethyl acrylate [ $\text{CH}_2 = \text{CHC}(\text{O})\text{OCH}_2\text{CH}_3$ ]	$5.70 \times 10^{-18}$	b	F-UV	Munshi <i>et al.</i> <sup>4</sup>
1,2-Epoxy-2-methyl- 3-butene	$(2.49 \pm 0.15) \times 10^{-18}$	$296 \pm 2$	RR [relative to $k(\text{propene}) =$ $9.68 \times 10^{-18}]^a$	Atkinson <i>et al.</i> <sup>5</sup>

<sup>a</sup>From previous recommendations.

<sup>b</sup>Room temperature, not specified.