# **Supplement** to "Evaluated kinetic and photochemical data for atmospheric chemistry: Volume VIII - gas phase reactions of organic species with four, or more, carbon atoms ($\geq C_4$)":

Detailed data sheets for the gas phase reactions of organic species with four, or more, carbon atoms ($\geq C_4$), IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation (http://iupac.pole-ether.fr/), access date: May 2020.

## Contents

### Data sheets for OH reactions

**Data sheets for $NO_3$ reactions**

## HOx_VOC7

$$\mathbf{HO + CH_3CH_2CH_2CH_3 \rightarrow H_2O + CH_2CH_2CH_2CH_3} \quad \mathbf{(1)}$$

$$\mathbf{\rightarrow H_2O + CH_3CHCH_2CH_3} \quad \mathbf{(2)}$$

$\Delta H°(1) = -72.4\ \mathrm{kJ \cdot mol^{-1}}$

$\Delta H°(2) = -86.6\ \mathrm{kJ \cdot mol^{-1}}$

### Rate coefficient data ($k = k_1 + k_2$)

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $1.41 \times 10^{-11} \exp[-(524 \pm 93)/T]$ | 298-495 | Greiner, 1970 | FP-KS |
| $(2.56 \pm 0.08) \times 10^{-12}$ | 298 | | |
| $(2.35 \pm 0.35) \times 10^{-12}$ | 298 | Stuhl, 1973 | FP-RF |
| $(4.22 \pm 0.17) \times 10^{-12}$ | 298 | Gordon and Mulac, 1975 | PR-RA |
| $(4.15 \pm 0.17) \times 10^{-12}$ | 381 | | |
| $(4.98 \pm 0.17) \times 10^{-12}$ | 416 | | |
| $1.76 \times 10^{-11} \exp[-(559 \pm 151)/T]$ | 298-420 | Perry et al., 1976 | FP-RF |
| $(2.72 \pm 0.27) \times 10^{-12}$ | 298 | | |
| $(2.67 \pm 0.22) \times 10^{-12}$ | 297 ± 2 | Paraskevopoulos and Nip, 1980 | FP-RA |
| $(2.3 \pm 0.3) \times 10^{-12}$ | 295 | Schmidt et al., 1985 | PLP-LIF |
| $2.34 \times 10^{-17} T^{1.95} \exp(134/T)$ | 294-509 | Droege and Tully, 1986 | PLP-LIF |
| $(2.42 \pm 0.10) \times 10^{-12}$ | 294 | | |
| $(2.25 \pm 0.10) \times 10^{-12}$ | 297 ± 2 | Abbatt et al., 1990 | DF-LIF |
| $(2.32 \pm 0.08) \times 10^{-12}$ | ~298 | Schiffman et al., 1991 | PLP-IR |
| $2.04 \times 10^{-17} T^2 \exp[(85 \pm 8)/T]$ | 231-378 | Talukdar et al., 1994 | PLP-LIF |
| $(2.459 \pm 0.018) \times 10^{-12}$ | 299 | | |
| $(2.43 \pm 0.07) \times 10^{-12}$ | 300 | Donahue et al., 1998 | DF-LIF |
| $(2.74 \pm 0.08) \times 10^{-12}$ | 325 | | |
| $(2.87 \pm 0.09) \times 10^{-12}$ | 340 | | |
| $(3.48 \pm 0.10) \times 10^{-12}$ | 375 | | |
| $(3.54 \pm 0.11) \times 10^{-12}$ | 390 | | |
| $(2.6 \pm 0.5) \times 10^{-12}$ | 300 | Chuong and Stevens, 2002 | DF-LIF |
| $(2.6 \pm 0.2) \times 10^{-12}$ | 300 | | |
| $(1.00 \pm 0.03) \times 10^{-12}$ | 185 | Donahue and Clarke, 2004 | DF-LIF (a) |
| $(1.14 \pm 0.04) \times 10^{-12}$ | 195 | | |
| $(1.21 \pm 0.08) \times 10^{-12}$ | 205 | | |
| $(1.36 \pm 0.04) \times 10^{-12}$ | 215 | | |
| $(1.45 \pm 0.04) \times 10^{-12}$ | 225 | | |
| $(1.64 \pm 0.13) \times 10^{-12}$ | 235 | | |
| $(1.77 \pm 0.08) \times 10^{-12}$ | 245 | | |
| $(1.74 \pm 0.05) \times 10^{-12}$ | 255 | | |
| $(1.95 \pm 0.06) \times 10^{-12}$ | 265 | | |
| $(2.07 \pm 0.07) \times 10^{-12}$ | 275 | | |
| $(2.17 \pm 0.06) \times 10^{-12}$ | 285 | | |
| $(2.54 \pm 0.08) \times 10^{-12}$ | 295 | | |
| *Relative Rate Coefficients* | | | |
| $9.9 \times 10^{-12}$ | 753 | Baker et al., 1970; Baldwin and Walker, 1979 | RR (b) |
| $(9.3 \pm 0.8) \times 10^{-12}$ | 653 | Hucknall et al, 1975 | RR (c) |
| $(2.64 \pm 0.25) \times 10^{-12}$ | 299 ± 2 | Atkinson et al., 1981 | RR (d) |
| $(2.92 \pm 0.32) \times 10^{-12}$ | 295 ± 1 | Atkinson and Aschmann, 1984 | RR (d) |
| $(2.45 \pm 0.34) \times 10^{-12}$ | 300 ± 2 | Barnes et al., 1986 | RR (e) |
| $(2.36 \pm 0.04) \times 10^{-12}$ | 300 | Behnke et al., 1988 | RR (f) |

| | | | |
|---|---|---|---|
| $1.39 \times 10^{-11} \cdot \exp(-526/T)$ | 235-361 | DeMore and Bayes, 1999 | RR (g) |
| $2.33 \times 10^{-12}$ | 298 | | |

## Comments

(a) Indicated errors are one standard deviation. Overall uncertainties were assessed to be ±7.5% for temperatures >250 K and ±10% for temperatures <250 K.

(b) Derived from the effects of the addition of small amounts of *n*-butane to slowly reacting mixtures of $H_2 + O_2$. The loss of $H_2$ was followed by monitoring the pressure change due to the reaction $2H_2 + O_2 \rightarrow 2H_2O$, and the loss of *n*-butane was measured by GC. The rate coefficient ratio $k(\mathrm{HO} + n\text{-butane})/k(\mathrm{HO} + H_2) = 13.2$ is placed on an absolute basis using $k(\mathrm{HO} + H_2) = 7.87 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 753 K (Atkinson, 2003).

(c) HO radicals were generated by the decomposition of $H_2O_2$ in a boric acid-coated reaction vessel, and the concentrations of *n*-butane and propane (the reference compound) were measured by GC. The measured rate coefficient ratios of $k(\mathrm{HO} + n\text{-butane})/k(\mathrm{HO} + \text{propane}) = 1.54 \pm 0.13$ is placed on an absolute value using $k(\mathrm{HO} + \text{propane}) = 6.16 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 653 K (IUPAC, 2019).

(d) HO radicals were generated by the photolysis of $CH_3ONO$ in one atmosphere of air. The concentrations of *n*-butane and propene (the reference compound) were measured by GC. The measured rate coefficient ratios of $k(\mathrm{HO} + n\text{-butane})/k(\mathrm{HO} + \text{propene}) = 0.0962 \pm 0.0093$ at 299 ± 2 K (Atkinson et al., 1981) and 0.101 ± 0.012 at 295 ± 1 K (Atkinson and Aschmann, 1984) are placed on an absolute value using $k(\mathrm{HO} + \text{propene}) = 2.85 \times 10^{-11}$ at 299 K and $2.89 \times 10^{-11}$ at 295 K cm$^3$ molecule$^{-1}$ s$^{-1}$ at atmospheric pressure of air (IUPAC, 2019).

(e) HO radicals were generated by the photolysis of $H_2O_2$ in air at atmospheric pressure, and the concentrations of *n*-butane and ethene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\mathrm{HO} + n\text{-butane})/k(\mathrm{HO} + \text{ethene}) = 0.32 \pm 0.04$ is placed on an absolute basis using $k(\mathrm{HO} + \text{ethene}) = 7.78 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 300 K and atmospheric pressure of air (IUPAC, 2019).

(f) HO radicals were generated by the photolysis of $NO_x$-organic-air mixtures at atmospheric pressure. The concentrations of *n*-butane and *n*-octane (the reference compound) were measured by GC, and the measured rate coefficient ratio of $k(\mathrm{HO} + n\text{-butane})/k(\mathrm{HO} + n\text{-octane})$ is placed on an absolute basis using $k(\mathrm{HO} + n\text{-octane}) = 8.15 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 300 K (Atkinson, 2003).

(g) HO radicals were generated by the photolysis of $H_2O$ at 185 nm or, at low temperatures, by the photolysis of $N_2O$ at 185 nm in the presence of $H_2$. The concentrations of *n*-butane and propane (the reference compound) were measured by GC. The measured rate coefficient ratios $k(\mathrm{HO} + n\text{-butane})/k(\mathrm{HO} + \text{propane})$ are placed on an absolute basis using a rate coefficient of $k(\mathrm{HO} + \text{propane}) = 1.65 \times 10^{-17}\, T^2 \exp(87/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019).

### Preferred Values

| Parameter | Value | $T$/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $2.35 \times 10^{-12}$ | 298 |
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $9.8 \times 10^{-12}$ exp(-425/$T$) | 180-300 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.06 | 298 |
| $\Delta$ E/R | ± 100 | 180-300 |

*Comments on Preferred Values*

The preferred values are based on the absolute rate coefficients of Droege and Tully (1986), Abbatt et al. (1990), Talukdar et al. (1994), Donahue et al. (1998) and Donahue and Clarke (2004) and the relative rate coefficients of DeMore and Bayes (1999). An Arrhenius plot of the rate coefficients from these studies (Droege and Tully, 1986; Abbatt et al., 1990; Talukdar et al., 1994; Donahue et al., 1998; DeMore and Bayes, 1999; Donahue and Clarke, 2004) plus the higher temperature relative rate data of Baker et al. (1970) [as re-evaluated by Baldwin and Walker (1979)] and Hucknall et al. (1975), is clearly curved (see Arrhenius plot).

The rate coefficients from the studies of Droege and Tully (1986), Abbatt et al. (1990), Talukdar et al. (1994), Donahue et al. (1998), DeMore and Bayes (1999) and Donahue and Clarke (2004) are fitted using the three parameter expression, $k = CT^2 \exp(-D/T)$, resulting in $k = 2.03 \times 10^{-17}\, T^2 \exp(78/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ over the temperature range 185-509 K. This expression also fits the higher temperature rate coefficient of Hucknall et al. (1975) extremely well. An Arrhenius fit, $k = A \exp(-B/T)$, of the rate coefficients from Droege and Tully (1986), Abbatt et al. (1990), Talukdar et al. (1994), Donahue et al. (1998), DeMore and Bayes (1999) and Donahue and Clarke (2004) at temperatures ≤300 K results in $k = 9.82 \times 10^{-12} \exp(-427/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$. As shown in the Arrhenius plot, this is an excellent representation of the rate coefficients from these studies at ≤ 300 K, and is the recommended Arrhenius expression. The preferred values are in good agreement with the room temperature absolute and relative rate coefficients of Greiner (1970), Stuhl (1973), Perry et al. (1976), Paraskevopoulos and Nip (1980), Schmidt et al. (1985), Schiffman et al. (1991), Atkinson et al. (1981), Atkinson and Aschmann (1984), Barnes et al. (1986), Behnke et al. (1988) and Chuong and Stevens (2002) which were not used in the evaluation of the rate coefficient.

Note that the Arrhenius expression derived from the 3-parameter fit, centered at 225 K with $A = C\, e^2\, T^2$ and $B = D + 2T$, of $k = 7.59 \times 10^{-12} \exp(-372/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ results in predicted rate coefficients 8% lower at 300 K and 5% higher at 180 K than those calculated from the preferred Arrhenius fit of the rate coefficients at ≤ 300 K.

Droege and Tully (1986) also measured rate coefficients for the reaction of the HO radical with *n*-butane-d$_{10}$, and derived a value of $k_1/k_2 = 1.035 \exp(-536/T)$, leading to $k_1 = 3.4 \times 10^{-13}$ at 298 K and $k_2 = 2.00 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K. $k_1$ and $k_2$ being the rate coefficients for the D-atom abstraction from CD$_3$- and –CD$_2$- groups, respectively.

### References

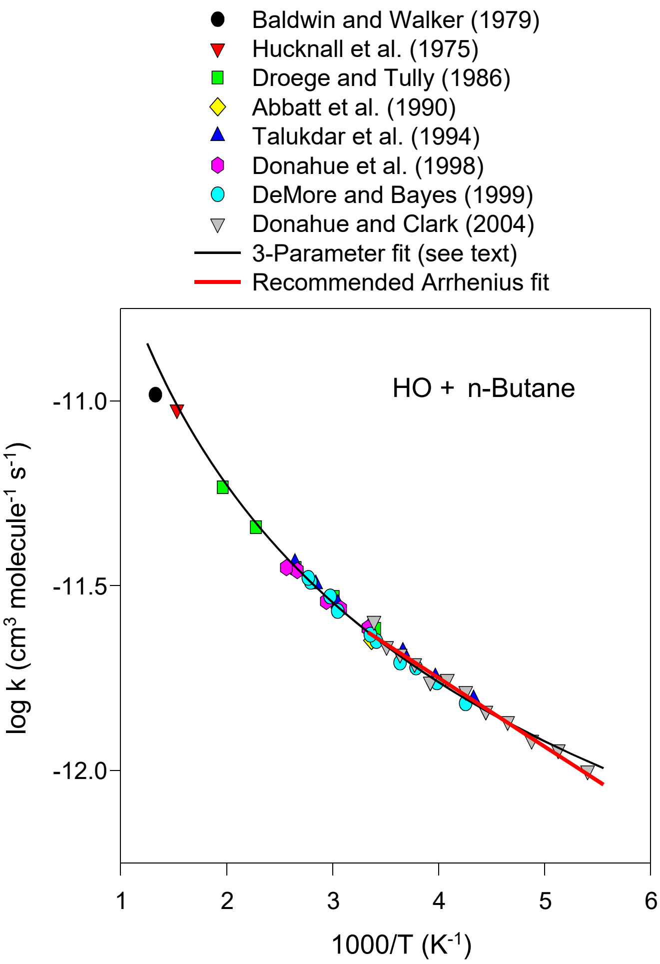
Abbatt, J. P. D., Demerjian, K. L. and Anderson, J. G.: J. Phys. Chem., 94, 4566, 1990.

Atkinson, R.: Atmos. Chem. Phys., 3, 2233, 2003.

Atkinson, R.: J. Phys. Chem. Ref. Data, 26, 215, 1997.

Atkinson, R. and Aschmann, S. M.: Int. J. Chem. Kinet., 16, 1175, 1984.

Atkinson, R., Carter, W. P. L., Winer, A. M. and Pitts Jr., J. N.: J. Air Pollut. Contr. Assoc., 31, 1090, 1981.
Baker, R. R., Baldwin, R. R. and Walker, R. W.: Trans. Faraday Soc., 66, 2812, 1970.
Baldwin, R. R. and Walker, R. W.: J. Chem. Soc. Faraday Trans. 1, 75, 140, 1979.
Barnes, I., Bastian, V., Becker, K. H., Fink, E. H. and Nelsen, W.: J. Atmos. Chem., 4, 445, 1986.
Behnke, W., Holländer, H., Koch, W., Nolting, F. and Zetzsch, C.: Atmos. Environ., 22, 1113, 1988.
Chuong, B. and Stevens, P. S.: J. Geophys. Res., 107 (D13), 4162, 2002.
DeMore, W. B. and Bayes, K. D.: J. Phys. Chem. A, 103, 2649, 1999.
Donahue, N. M. and Clarke, J. S.: Int. J. Chem. Kinet., 36, 259, 2004.
Donahue, N. M., Anderson, J. G. and Demerjian, K. L.: J. Phys. Chem. A, 102, 3121, 1998.
Droege, A. T. and Tully, F. P.: J. Phys. Chem., 90, 5937, 1986.
Gordon, S. and Mulac, W. A.: Int. J. Chem. Kinet. Symp. 1, 289, 1975.
Greiner, N. R.: J. Chem. Phys., 53, 1070, 1970.
Hucknall, D. J., Booth, D. and Sampson, R. J.: Int. J. Chem. Kinet. Symp. 1, 301, 1975.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Paraskevopoulos, G. and Nip, W. S.: Can. J. Chem., 58, 2146, 1980.
Perry, R. A., Atkinson, R. and Pitts Jr., J. N.: J. Chem. Phys., 64, 5314, 1976.
Schiffman, A., Nelson, Jr., D. D., Robinson, M. S. and Nesbitt, D. J.: J. Phys. Chem., 95, 2629, 1991.
Schmidt, V., Zhu, G. Y., Becker, K. H. and Fink, E. H.: Ber. Bunsenges. Phys. Chem., 89, 321, 1985.
Stuhl, F.: Z. Naturforsch., 28A, 1383, 1973.
Talukdar, R. K., Mellouki, A., Gierczak, T., Barone, S., Chiang, S.-Y. and Ravishankara, A. R.: Int. J. Chem. Kinet., 26, 973, 1994.



Rate coefficients for HO + n-Butane.

## HOx_VOC8

# HO + $CH_2$=C($CH_3$)CH=$CH_2$ (isoprene) → products

## Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $2.36 \times 10^{-11} \exp[(409 \pm 28)/T]$ | 299-422 | Kleindienst et al., 1982 | FP-RF |
| $(9.26 \pm 1.5) \times 10^{-11}$ | 299 | | |
| $9.7 \times 10^{-11} (T/298)^{-1.36}$ | 249-348 | Siese et al., 1994 | FP-RF |
| $9.7 \times 10^{-11}$ | 298 | | |
| $(1.10 \pm 0.05) \times 10^{-10}$ | 298 | Stevens et al., 1999 | DF-LIF |
| $2.70 \times 10^{-11} \exp[(336 \pm 74)/T]$ | 251-342 | Campuzano-Jost et al., 2000 | PLP-LIF (a) |
| $(8.56 \pm 0.26) \times 10^{-11}$ | 297 | | |
| $(1.10 \pm 0.04) \times 10^{-10}$ | 300 | Chuong and Stevens, 2000 | DF-LIF (b) |
| $(9.6 \pm 0.5) \times 10^{-11}$ | 295 | McGivern et al., 2000 | PLP-LIF (c) |
| $(1.01 \pm 0.08) \times 10^{-10}$ | 298 ± 2 | Zhang et al., 2000 | DF-CIMS (d) |
| $9.1 \times 10^{-11}$ | 298 ± 2 | Zhang et al., 2001 | DF-CIMS (e) |
| $(1.08 \pm 0.05) \times 10^{-10}$ | 300 | Chuong and Stevens, 2002 | DF-LIF (f) |
| $2.68 \times 10^{-11} \exp[(348 \pm 136)/T]$ | 251-342 | Campuzano-Jost et al., 2004 | PLP-LIF (g) |
| $(8.47 \pm 0.59) \times 10^{-11}$ | 297 | | |
| $(1.00 \pm 0.15) \times 10^{-10}$ | 293 | Spangenberg et al., 2004 | PLP-LIF (h) |
| $(1.00 \pm 0.12) \times 10^{-10}$ | 294 ± 1.1 | Karl et al., 2004 | (i) |
| $(1.02 \pm 0.09) \times 10^{-10}$ | 295 ± 1 | Poppe et al., 2007 | (i) |
| $(1.12 \pm 0.07) \times 10^{-10}$ | 296 ± 2 | | |
| $(1.07 \pm 0.08) \times 10^{-10}$ | 290.5 ± 2.5 | | |
| $(9.7 \pm 0.8) \times 10^{-11}$ | 291 ± 2 | | |
| $(9.9 \pm 0.8) \times 10^{-11}$ | 290 ± 1 | | |
| $1.93 \times 10^{-11} \exp[(466 \pm 12)/T]$ | 241-356 | Dillon et al., 2017 | PLP-LIF (j) |
| $(9.3 \pm 0.4) \times 10^{-11}$ | 297 | | |
| $1.80 \times 10^{-11} \exp[(522 \pm 28)/T]$ | 298-794 | Medeiros et al., 2018 | PLP-LIF (k),(l) |
| $(9.90 \pm 0.09) \times 10^{-11}$ | 298 | | (k),(l) |
| $(1.06 \pm 0.02) \times 10^{-10}$ | 298 | | (k),(m) |
| $(1.04 \pm 0.02) \times 10^{-10}$ | 298 | | (k),(n) |
| *Relative Rate Coefficients* | | | |
| $7.2 \times 10^{-11}$ | 300 | Cox et al., 1980 | RR (o) |
| $(1.08 \pm 0.05) \times 10^{-10}$ | 299 ± 2 | Atkinson et al., 1982 | RR (p) |
| $(9.90 \pm 0.27) \times 10^{-11}$ | 297 ± 2 | Ohta, 1983 | RR (q) |
| $(1.10 \pm 0.04) \times 10^{-10}$ | 295 ± 1 | Atkinson and Aschmann, 1984 | RR (r) |
| $(1.09 \pm 0.02) \times 10^{-10}$ | 297 ± 1 | Edney et al., 1986 | RR (s) |
| $(1.11 \pm 0.23) \times 10^{-10}$ | 298 | McQuaid et al., 2002 | RR (t) |
| $2.54 \times 10^{-11} \exp[(409 \pm 42)/T]$ | 298-363 | Gill and Hites, 2002 | RR (u) |
| $(1.00 \pm 0.05) \times 10^{-10}$ | 298 | | |
| $(1.06 \pm 0.04) \times 10^{-10}$ | 298 ± 2 | Iida et al., 2002 | RR (v) |
| $2.33 \times 10^{-11} \exp[(444 \pm 27)/T]$ | 240-340 | Singh and Li, 2007 | RR (w) |
| $(1.07 \pm 0.03) \times 10^{-10}$ | 298 | | RR (w,x) |
| $(1.11 \pm 0.02) \times 10^{-10}$ | 298 | | RR (w,y) |
| $3.97 \times 10^{-11} \exp[(249 \pm 20)/T]$ | 323-413 | Hites and Turner, 2009 | RR (u) |

## Comments

(a) Rate coefficients for the reactions of HO radicals with isoprene-d$_6$ and DO radicals with isoprene were also measured at 297 K, these being $(8.31 \pm 0.10) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and $(8.27 \pm 0.10) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively.

(b) Carried out at total pressures of 2-6 Torr (2.7-8.0 mbar) of helium diluent. No pressure dependence of the rate coefficient was observed at 300 K. However, at higher temperatures (321-423 K) the rate coefficient increased with increasing total pressure, with the effect being more pronounced at higher temperature.

(c) Carried out at total pressures of 0.5-20 Torr (0.7-27 mbar) of argon diluent. The rate coefficient was observed to be pressure dependent below 10 Torr total pressure; the value cited in the table is that measured at 20 Torr total pressure.

(d) Carried out at total pressures of 72.7-112.7 Torr (97-150 mbar) of $N_2$ diluent. The measured rate coefficient was independent of pressure over this range.

(e) Based on a very limited kinetic study carried out at a total pressure of 1.9 Torr (2.5 mbar) of helium diluent (the focus of the study was on formation of HO-isoprene adducts and their subsequent reactions).

(f) Carried out at total pressures of argon diluent of 100 Torr (133 mbar) and 150 Torr (200 mbar). The measured rate coefficient was independent of total pressure over this range.

(g) Rate coefficients for HO + isoprene-d$_6$ and DO + isoprene were also measured at 297 K, with values of $(8.27 \pm 0.17) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and $(8.43 \pm 0.18) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively. Isoprene and isoprene-d$_6$ concentrations in the gas flow stream were measured before and after the reaction cell by UV absorption at 228.9 nm. The data from this study are in excellent agreement with those previously reported by Campuzano-Jost et al. (2000) at the same temperatures, and are assumed to supersede the earlier study.

(h) Rate coefficients were also measured at 58, 71, 84, 104 and 114 K, with the rate coefficients of $(7.8 \pm 1.2) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, $(1.14 \pm 0.17) \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, $(9.8 \pm 1.5) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, $(1.88 \pm 0.28) \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and $(1.68 \pm 0.25) \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively.

(i) Carried out in a large volume (270 m$^3$) chamber. HO radicals were measured by LIF and isoprene was measured by GC (Karl et al., 2004; Poppe et al., 2007) or by proton-transfer-reaction mass spectrometry (Poppe et al., 2007) during irradiations of air mixtures containing low concentrations of isoprene and $NO_x$.

(j) Pulsed laser photolysis of $H_2O_2$ at 248 nm, in the presence of isoprene/$N_2$ or isoprene/air mixtures at total pressures in the range 3.8-165 Torr (5.1-220 mbar). Pseudo-first order decays of HO radical concentrations (monitored by LIF) were characterized in the presence of excess concentrations of isoprene (monitored by vacuum UV optical absorption at 184.95 nm). $k$ displayed no significant dependence on bath gas or on pressure over the studied range (N.B. The room temperature, 296-298 K, data points presented below were obtained at 3.8, 7.5, 42.9, 71.0, 103 and 165 Torr in $N_2$ and at 103 and 165 Torr in air. The reported value, tabulated above, is based on the average of the six $N_2$ determinations).

(k) Pulsed laser photolysis of $H_2O_2$ or $t$-$C_4H_9OOH$ at 248 nm, in the presence of isoprene/$N_2$ or isoprene/$N_2$/$O_2$ mixtures. Experiments carried out in either a high pressure apparatus, at total pressures of 1290-1670 Torr (1720-2230 mbar), or in a low pressure apparatus, at total pressures of 50-140 Torr (66-187 mbar). Decays of HO radical concentrations (monitored by LIF) were characterized in the presence of excess concentrations of isoprene. $k$ displayed no significant dependence pressure or HO radical source, and the tabulated temperature dependence expression is based on the combined dataset, also reported as $k = (10.4 \pm 0.4) \times 10^{-11} (T/298)^{-1.34\pm0.12}$. Evidence for H atom abstraction observed from [HO] decays at T > 700 K, when the reversible HO addition routes are equilibrated. Based on support from theoretical calculations, and from PTR-TOF-MS measurements of product formation at $m/z$ = 83 (attributed to 2-methylene-but-3-enal following abstraction from $CH_3$ group in the presence of $O_2$) at 298-473 K, the following expressions were also recommended for high-pressure limiting HO addition ($k_{add}$) and H abstraction ($k_{abs}$): $k_{add} = (9.5 \pm 0.2) \times 10^{-11} (T/298)^{-1.33\pm0.07}$; $k_{abs} = (1.3 \pm 0.3) \times 10^{-11} \exp(-3.61 \text{kJmol}^{-1}/RT)$; where $k = k_{add} + k_{abs}$.

(l) $k$ determined from high pressure measurements. HO generated by $H_2O_2$ photolysis.

(m) $k$ determined from low pressure measurements. HO generated by $H_2O_2$ photolysis.

(n) $k$ determined from low pressure measurements. HO generated by $t$-$C_4H_9OOH$ photolysis.

(o) Relative rate method carried out at atmospheric pressure of air. HO radicals were generated by photolysis of HONO at wavelengths >300 nm. The concentrations of isoprene and ethene (the reference compound) were measured by GC. The measured rate coefficient ratio $k$(HO + isoprene)/$k$(HO + ethene) is placed on an absolute basis by use of a rate coefficient of $k$(HO + ethene) = $7.78 \times 10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at 300 K and atmospheric pressure of air (IUPAC, 2019).

(p) Relative rate method carried out at atmospheric pressure of air. HO radicals were generated by photolysis of $CH_3ONO$ at wavelengths >300 nm. The concentrations of isoprene and propene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k$(HO + isoprene)/$k$(HO + propene) = $3.81 \pm 0.17$ is placed on an absolute basis by use of a rate coefficient of $k$(HO + propene) = $2.85 \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at 299 K and atmospheric pressure of air (IUPAC, 2019).

(q) Relative rate method carried out at atmospheric pressure of $N_2 + O_2$. HO radicals were generated by photolysis of $H_2O_2$ at 253.7 nm. The concentrations of isoprene and 1,3-butadiene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k$(HO + isoprene)/$k$(HO + 1,3-butadiene) = $1.48 \pm 0.04$ is placed on an absolute basis by use of a rate coefficient of $k$(HO + 1,3-butadiene) = $6.69 \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at 297 K and atmospheric pressure of air (Atkinson and Arey, 2003).

(r) Relative rate method carried out at atmospheric pressure of air. HO radicals were generated by photolysis of $CH_3ONO$ at wavelengths >300 nm. The concentrations of isoprene and propene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k$(HO + isoprene)/$k$(HO + propene) = $3.81 \pm 0.15$ is placed on an absolute basis by use of a rate coefficient of $k$(HO + propene) = $2.89 \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at 295 K and atmospheric pressure of air (IUPAC, 2019).

(s) Relative rate method carried out at atmospheric pressure of air. HO radicals were generated by photolysis of $CH_3ONO$ at wavelengths >300 nm. The concentrations of isoprene and propene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k$(HO + isoprene)/$k$(HO + propene) is placed on an absolute basis by use of a rate coefficient of $k$(HO + propene) = $2.87 \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at 297 K and atmospheric pressure of air (IUPAC, 2019).

(t) Relative rate method carried out at atmospheric pressure of air. HO radicals were generated by photolysis of $CH_3ONO$. The concentrations of isoprene and *trans*-2-butene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k$(HO + isoprene)/$k$(HO + *trans*-butene) = $1.74 \pm 0.14$ is placed on an absolute basis by use of a rate coefficient of $k$(HO + *trans*-2-butene) = $6.40 \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at 298 K and atmospheric pressure of air (IUPAC, 2019). The cited error limits are the 95% confidence intervals (McQuaid et al., 2002).

(u) Relative rate method carried out in a 192 $cm^3$ volume quartz reaction vessel at atmospheric pressure of helium diluent. HO radicals were generated by photolysis of $H_2O_2$. The concentrations of isoprene and 2-methylpropene (the reference compound) were measured by MS. Rate coefficients were measured over the temperature ranges 298-363 K by Gill and Hites (2002) and 323-413 K by Hites and Turner (2009). The measured rate coefficient ratios of $k$(HO + isoprene)/$k$(HO + 2-methylpropene) are placed on an absolute basis by use of a rate coefficient of $k$(HO + 2-methylpropene) = $9.4 \times 10^{-12}$ exp(505/$T$) $cm^3$ $molecule^{-1}$ $s^{-1}$ (IUPAC, 2019). The cited Arrhenius expression for the Hites and Turner (2009) study is an un-weighted least-squares fit to their data; the cited error in the temperature dependence is two standard deviations. Combination of the rate coefficients of Gill and Hites (2002) and Hites and Turner (2009) results in the Arrhenius expression $k = 3.12 \times 10^{-11} \exp[(339 \pm 19)/T]$ $cm^3$ $molecule^{-1}$ $s^{-1}$ or, because the combined data suggested a curved Arrhenius plot, $k = 3.44 \times 10^{-17} T^2 \exp[(1037 \pm 14)/T]$ $cm^3$ $molecule^{-1}$ $s^{-1}$ (Hites and Turner, 2009), both relative to $k$(HO + 2-methylpropene) = $9.4 \times 10^{-12}$ exp(505/$T$) $cm^3$ $molecule^{-1}$ $s^{-1}$ (IUPAC, 2019).

(v) Carried out at atmospheric pressure of air. HO radicals were generated by photolysis of $CH_3ONO$. The concentrations of isoprene and cyclohexane, di-*n*-butyl ether or propene (the reference compounds) were measured by FTIR spectroscopy. The measured rate coefficient ratios of $k$(HO + isoprene)/$k$(HO + cyclohexane) = 14.3 ± 1.2 and 1.49 ± 1.3, $k$(HO + isoprene)/$k$(HO + di-*n*-butyl ether) = 3.71 ± 0.14 and 3.61 ± 0.23, and $k$(HO + isoprene)/$k$(HO + propene) = 3.89 ± 0.20, 3.96 ± 0.18, 3.90 ± 0.15 and 3.98 ± 0.20 are placed on an absolute basis by use of rate coefficients at 298 K and atmospheric pressure of air of $k$(HO + cyclohexane) = $6.97 \times 10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ (Atkinson and Arey, 2003), $k$(HO + di-*n*-butyl ether) = $2.78 \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ (Mellouki et al., 1995) and $k$(HO + propene) = $2.86 \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ (IUPAC, 2019). The value in the table is the un-weighted average together with the two standard deviation error.

(w) Discharge flow system with MS detection of isoprene and the reference compounds dimethyl disulfide and ethanethiol. HO radicals generated by the reaction F + $H_2O$. Total pressure was in the range 1-3 Torr (1.3-4 mbar). The rate coefficient for the HO + isoprene reaction was independent of pressure over the range 1-3 Torr at 298 K, but was increased with increasing pressure over the range 1-3 Torr at 340 K. Temperature-dependent rate measurements were carried out at 1.0-1.1 Torr pressure, and hence the rate coefficient at 340 K would have been in the fall-off region. The measured rate coefficient ratios (which were tabulated only at 298 K) were placed on an absolute basis using $k$(HO + dimethyl disulfide) = $5.9 \times 10^{-11}$ exp(380/$T$) $cm^3$ $molecule^{-1}$ $s^{-1}$ (Wine et al., 1981) and $k$(HO + ethanethiol) = $1.23 \times 10^{-11}$ exp(396/$T$) $cm^3$ $molecule^{-1}$ $s^{-1}$ (Wine et al., 1984). The rate coefficient used for $k$(HO + dimethyl disulfide) is slightly different from the IUPAC recommendation of $7.0 \times 10^{-11}$ exp(350/$T$) $cm^3$ $molecule^{-1}$ $s^{-1}$ (IUPAC, 2019), but re-evaluation is only possible for the 298 K rate coefficient (see Comment (x) below).

(x) Relative to dimethyl disulfide. The measured rate coefficient ratio $k$(HO + isoprene)/$k$(HO + dimethyl disulfide) = 0.464 ± 0.010 at 298 K is placed on an absolute basis using $k$(HO + dimethyl disulfide) = $2.3 \times 10^{-10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ (IUPAC, 2019).

(y) Relative to ethanethiol. The measured rate coefficient ratio $k$(HO + isoprene)/$k$(HO + ethanethiol) = 2.398 ± 0.043 at 298 K is placed on an absolute basis using $k$(HO + ethanethiol) = $4.64 \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ (Wine et al., 1984).

## Preferred Values

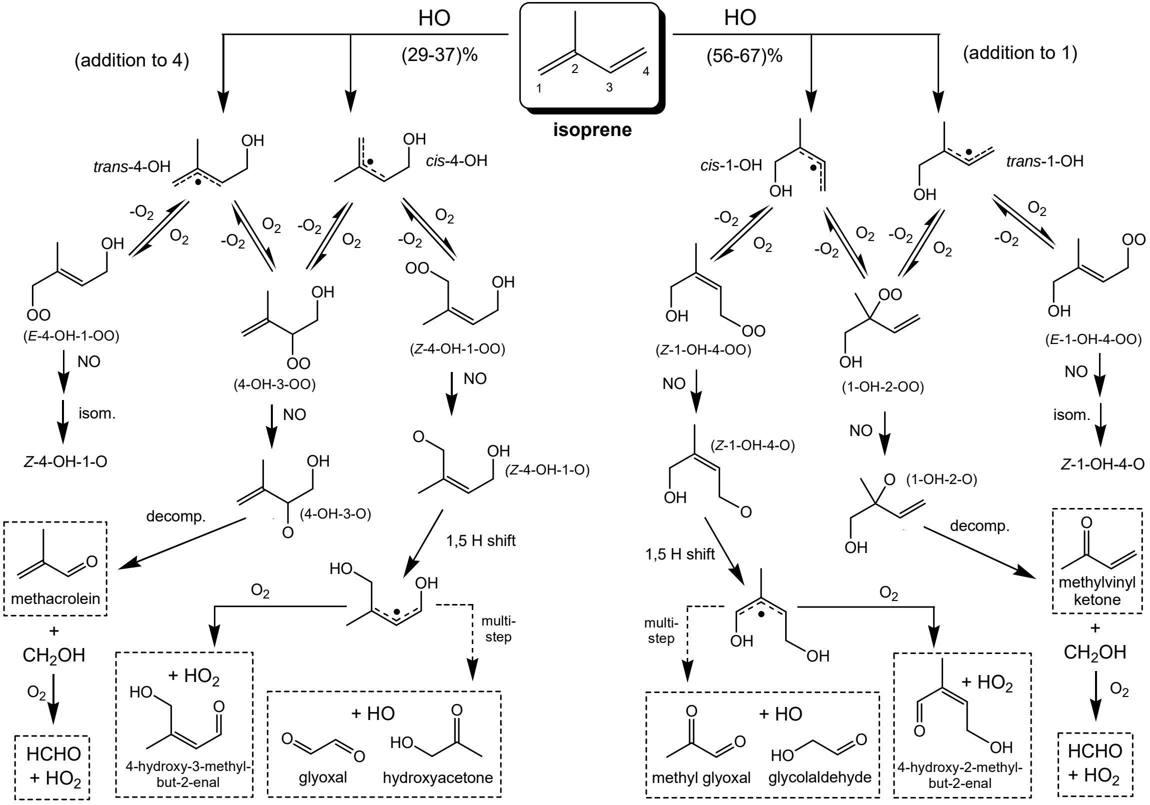
| Parameter | Value | $T$/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $1.0 \times 10^{-10}$ | 298 |
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $2.10 \times 10^{-11} \exp(465/T)$ | 240-630 |
| *Reliability* | | |
| $\Delta \log k$ | $\pm 0.06$ | 298 |
| $\Delta E/R$ | $\pm 150$ | |

*Comments on Preferred Values*

The reaction of HO radicals with isoprene has been studied extensively, and the room temperature values of $k$ in the reported absolute and relative rate studies are generally in very good agreement. The preferred value of $E/R$ is the average of those reported in the direct studies of Kleindienst et al. (1982), Dillon et al. (2017) and Medeiros et al. (2018), which collectively cover the complete temperature range of the recommendation. The slightly lower values of $E/R$ reported in the direct studies of Siese et al. (1994) and Campuzano-Jost et al. (2000; 2004), and those in the relative rate studies of Gill and Hites (2002) and Singh and Li (2007) also lie within the assigned uncertainty bounds. The 298 K preferred value of $k$ is an average of the room temperature values reported in the direct studies of Kleindienst et al. (1982), Siese et al. (1994), Stevens et al. (1999), Chuong and Stevens (2000; 2002), McGivern et al. (2000), Zhang et al. (2000; 2001), Karl et al. (2004)/Poppe et al. (2007), Dillon et al. (2017) and Medeiros et al. (2018), corrected to 298 K where necessary using the preferred temperature dependence. For each of the related pairs of studies, Chuong and Stevens (2000; 2002), Zhang et al. (2000; 2001) and Karl et al. (2004)/Poppe et al. (2007), a single unweighted average was applied in the above procedure. The rate coefficients reported by Campuzano-Jost et al. (2000; 2004) and Cox et al. (1980) are about 15 % and 27 % lower than the preferred value.

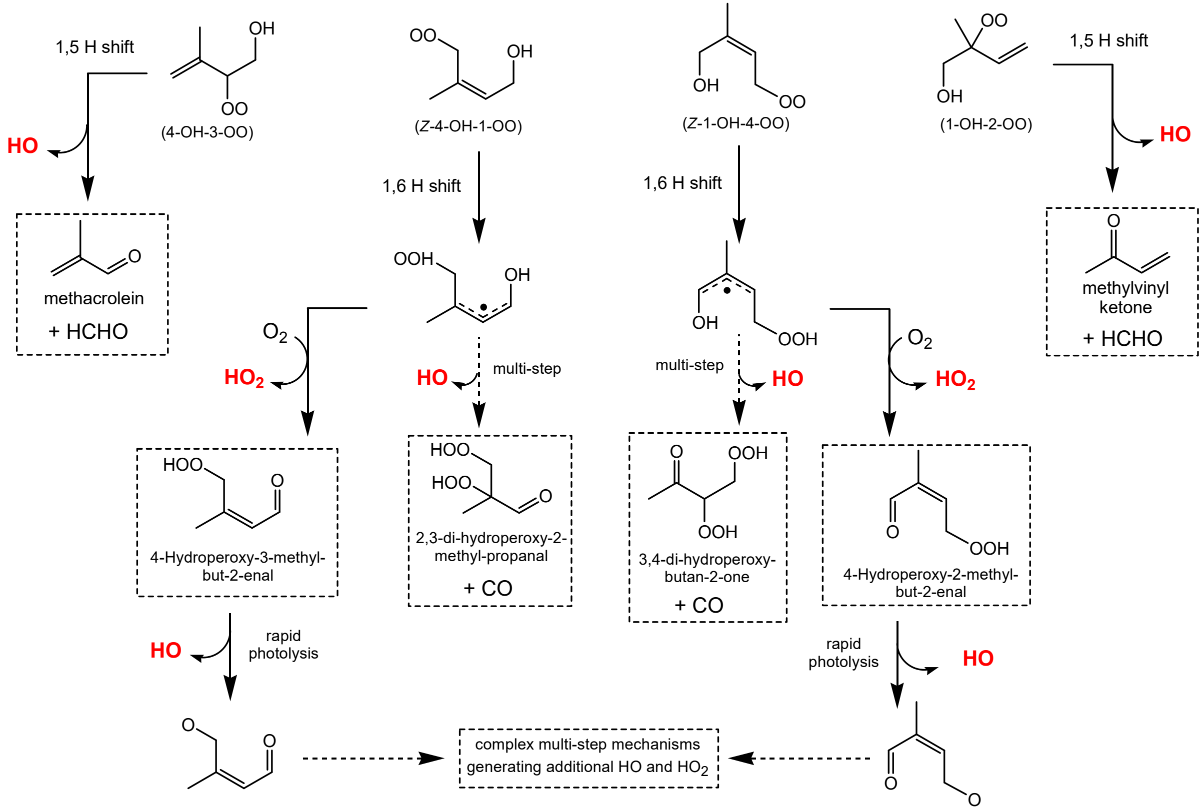
On the basis of theoretical studies (e.g. Vereecken and Peeters, 2001) and structure-activity relationship (SAR) methods (e.g. Jenkin et al., 2018), H atom abstraction has generally been estimated to account for only a very minor fraction (~0.3 %) of the reaction of HO with isoprene at 298 K and 1 bar pressure, with this occurring from the -$CH_3$ group. This is expected to increase at higher temperatures, and strong evidence for H atom abstraction at $T > 700$ K has been reported by Medeiros et al. (2018) (see comment (k)). They also tentatively suggested that H atom abstraction may account for as much as (3 ± 2) % of the reaction at 298 K, with support from PTR-TOF-MS measurements of product formation at $m/z = 83$, attributed to 2-methylene-but-3-enal. However, this observation may be complicated by formation of the isobaric species, 3-methylfuran, a reported minor product of the HO + isoprene reaction (see below).

The reaction thus proceeds almost exclusively by initial addition of HO to the C=C bonds. Theoretical calculations and SAR methods predict that the percentages of HO radical addition to the 1-, 2-, 3- and 4-position carbon atoms at 298 K lie in the ranges (56–67) %, (2–4) %, (2–5) % and (29–37)%, respectively (e.g. McGivern et al., 2000; Lei et al., 2000; Greenwald et al., 2007; Peeters et al., 2014; Jenkin et al., 2018), with these percentages being relatively insensitive to changes in temperature and pressure over the atmospheric ranges (Greenwald et al., 2007). Addition to the terminal carbon atoms therefore dominates, with subsequent (reversible) addition of $O_2$ leading to the formation of the six hydroxyallyl peroxy radicals shown in the schematic below (Peeters et al., 2009), with the species nomenclature also based on that study.



The subsequent chemistry has been reviewed in detail by Jenkin et al. (2015) and Wennberg et al. (2018). The majority of reported product studies have traditionally been carried out at atmospheric pressure in the presence of sufficient NO (> 500 ppb), so that the hydroxyallyl peroxy radicals react predominantly with NO at a rate that is much faster than their back decomposition rates. Under these conditions, the chemistry propagated by the reactions with NO forms a number of carbonyl and hydroxycarbonyl end products (shown in boxes), with the following molar yields, e.g. see Jenkin et al. (2015) and Wennberg et al. (2018), and references therein: methyl vinyl ketone, (32–44%), methacrolein (22–28%), formaldehyde (57–66%), 4-hydroxy-2-methyl-but-2-enal and 4-hydroxy-3-methyl-but-2-enal (10–20%), glyoxal (2.1–3%), glycolaldehyde (2.7–4.2%) and hydroxyacetone (2.9–3.8%). Minor formation (≤ 5%) of 3-methylfuran has also been reported (not shown in the schematic). This may be formed from isomerisation and dehydration of the product oxy radicals, Z-1-OH-4-O and Z-4-OH-1-O (Francisco-Márquez et al., 2003), but is also likely formed from secondary cyclisation and dehydration of 4-hydroxy-2-methyl-but-2-enal and 4-hydroxy-3-methyl-but-2-enal, possibly heterogeneously (Dibble, 2007). The reactions of the hydroxyallyl peroxy radicals with NO also partially form the corresponding hydroxy-nitrate products (not shown in the schematic), which have been reported to be formed with a collective yield of 4-15% (see data sheet ROO_50).

Other reactions of the hydroxyallyl peroxy radicals can compete with reaction with NO under atmospheric conditions, and in experimental studies with low $NO_x$ levels. These include bimolecular reactions with $HO_2$ and organic peroxy radicals, which can have propagating channels (leading to lower yields of the same end products discussed above) and terminating channels generating hydroxy-hydroperoxide, hydroxy-carbonyl and dihydroxy products (Ruppert and Becker, 2000; Benkelberg et al., 2000; Lee et al., 2005). However, a major advance in understanding in recent years has been the recognition of an important role for unimolecular isomerisation reactions of some of the hydroxyallyl peroxy radical isomers (e.g. Peeters et al., 2009; 2014), namely 1,5 H shift reactions for 1-OH-2-OO and 4-OH-3-OO and, more significantly, 1,6 H shift reactions *Z*-1-OH-4-OO and *Z*-4-OH-1-OO, as shown below.



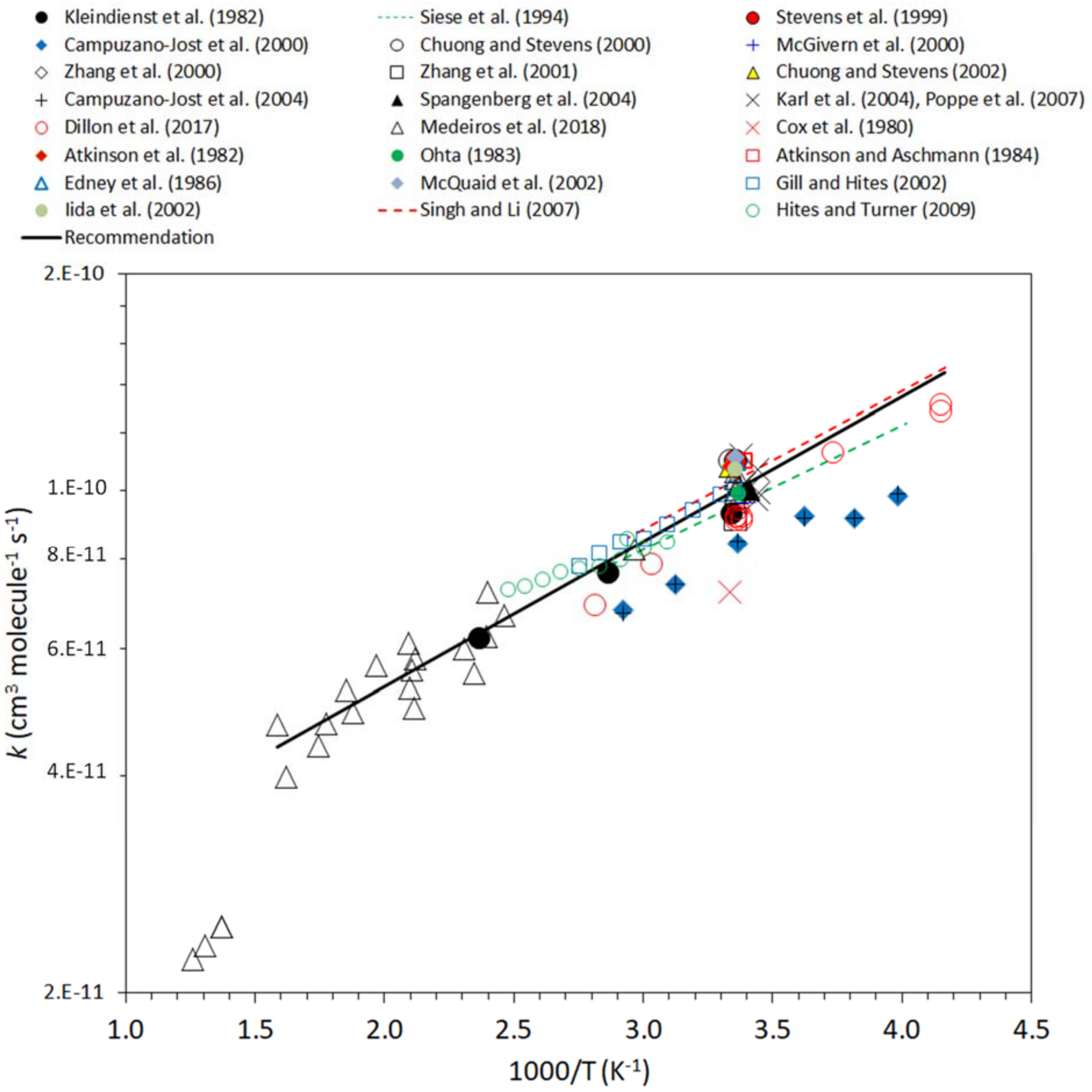
These reactions, in conjunction with interconversion of the hydroxyallyl peroxy radical isomers (*via* the reversible $O_2$ + OH-isoprene adduct reactions discussed above), provide significant routes for regeneration of $HO_x$ radicals under the low $NO_x$ conditions of the remote atmospheric boundary layer. Usually referred to as the Leuven Isoprene Mechanism (LIM), this subset of the chemistry was originally proposed and characterised in the theoretical studies of Peeters et al. (2009; 2014). It has been largely verified by laboratory experimental studies (Wennberg et al., 2018), and this mechanism and related chemistry continues to be a focus of ongoing experimental and theoretical studies.

## References

Atkinson, R. and Aschmann, S. M.: Int. J. Chem. Kinet., 16, 1175, 1984.
Atkinson, R., Aschmann, S. M., Tuazon, E.C., Arey, J. and Zielinska, B.: Int. J. Chem. Kinet., 21, 593, 1989.
Atkinson, R., Aschmann, S. M., Winer, A. M. and Pitts Jr., J. N.: Int. J. Chem. Kinet., 14, 507, 1982.
Benkelberg, H.-J., Böge, O., Seuwen, R., and Warneck, P.: Phys. Chem. Chem. Phys., 2, 4029, 2000. Campuzano-Jost, P., Williams, M. B., D'Ottone, L. and Hynes, A. J.: Geophys. Res. Lett., 27, 693, 2000.
Campuzano-Jost, P., Williams, M. B., D'Ottone, L. and Hynes, A. J.: J. Phys. Chem. A, 108, 1537, 2004.
Chuong, B. and Stevens, P. S.: J. Geophys. Res. 107 (D13), ACH 2-1, 2002.
Chuong, B. and Stevens, P. S.: J. Phys. Chem. A, 104, 5230, 2000.

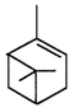
Cox, R. A., Derwent, R. G. and Williams, M. R.: Environ. Sci. Technol., 14, 57, 1980.
Dibble, T. S.: Chem. Phys. Lett., 447, 5, 2007.
Dillon, T. J., Dulitz, K., Groß, C. B. M., and Crowley, J. N.: Atmos. Chem. Phys., 17, 15137, https://doi.org/10.5194/acp-17-15137-2017, 2017.
Edney, E. O., Kleindienst, T. E. and Corse, E. W.: Int. J. Chem. Kinet., 18, 1355, 1986.
Francisco-Márquez, M., Alvarez-Idaboy, J. R., Galano, A. and Vivier-Bunge, A.: Phys. Chem. Chem. Phys., 5, 1392, 2003.
Gill, K. J. and Hites, R. A.: J. Phys. Chem. A, 106, 2538, 2002.
Greenwald, E. E., North, S. W., Georgievskii, Y. and Klippenstein, S. J.: J. Phys. Chem. A, 111, 5582, 2007.
Hites, R. A. and Turner, A. M.: Int. J. Chem. Kinet., 41, 407, 2009.
Iida, Y., Obi, K. and Imamura, T.: Chem. Lett., 792, 2002.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Jenkin, M. E., Young, J. C., and Rickard, A. R.: Atmos. Chem. Phys., 15, 11433, https://doi.org/10.5194/acp-15-11433-2015,2015.
Jenkin, M. E., Valorso, R., Aumont, B., Rickard, A. R., and Wallington, T. J.: Atmos. Chem. Phys., 18, 9297, https://doi.org/10.5194/acp-18-9297-2018, 2018.
Karl, M., Brauers, Th., Dorn, H.-P., Holland, F., Komenda, M., Poppe, D., Rohrer, F., Rupp, L., Schaub, A. and Wahner, A.: Geophys. Res. Lett., 31, L05117, doi:10.1029/2003GL019189, 2004.
Karl, M., Dorn, H.-P., Holland, F., Koppmann, R., Poppe, D., Rupp, L., Schaub, A. and Wahner, A.: J. Atmos. Chem., 55, 167, 2006.
Kleindienst, R. E., Harris, G. W. and Pitts Jr., J. N.: Environ. Sci. Technol., 16, 844, 1982.
Lee, W., Baasandorj, M., Stevens, P. S., and Hites, R. A.: Environ. Sci. Technol., 39, 1030, 2005.
Lei, W., Zhang, R., McGivern, W. S., Derecskei-Kovacs, A. and North, S. W.: Chem. Phys. Lett., 326, 109, 2000.
McGivern, W. S., Suh, I., Clinkenbeard, A. D., Zhang, R. and North, S. W.: J. Phys. Chem. A, 104, 6609, 2000.
McQuaid, J. B., Stocker, D. W. and Pilling, M. J.: Int. J. Chem. Kinet., 34, 7, 2002.
Medeiros, D. J., Blitz, M. A., James, L., Speak, T. H. and Seakins, P. W.: J. Phys. Chem. A, 122 (37), 7239, https://doi.org/10.1021/acs.jpca.8b04829, 2018.
Mellouki, A., Téton, S. and Le Bras, G.: Int. J. Chem. Kinet., 27, 791, 1995.
Ohta, T.: J. Phys. Chem., 87, 1209, 1983.
Peeters, J., Nguyen, T. L. and Vereecken, L.: Phys. Chem. Chem. Phys., 28, 5935, 2009.
Peeters, J., Müller, J.-F., Stavrakou, T. and Nguyen, V. S.: J. Phys. Chem. A, 118 (38), 8625, 2014.
Poppe, D., Brauers, T., Dorn, H.-P., Karl, M., Mentel, T., Schlosser, E., Tillmann, R., Wegener, R. and Wahner, A.: J. Atmos. Chem., 57, 203, 2007.
Ruppert, L. and Becker, K-H.: Atmos. Environ., 34, 1529, 2000.
Siese, M., Koch, R., Fittschen, C., and Zetzsch, C.: Proceedings of the EUROTRAC Symposium ’94, ed. P. M. Borrell, P. Borrell, T. Cvitaš, and W. Seiler, SPB Aacademic Publishing bv, Den Haag, The Netherlands, 115, 1994.
Singh, S. and Li, Z.: J. Phys. Chem. A, 111, 11843, 2007.
Spangenberg, T., Köhler, S., Hansmann, B., Wachsmuth, U., Abel, B. and Smith, M. A.: J. Phys. Chem. A, 108, 7527, 2004.
Sprengnether, M., Demerjian, K. L., Donahue, N. M. and Anderson, J. G.: J. Geophys. Res., 107(D15), 10.1029/2001JD000716, 2002.
Stevens, P., L’Esperance, D., Chuong, B. and Martin, G.: Int. J. Chem. Kinet., 31, 637, 1999.

Vereecken, L. and Peeters, J.: Chem. Phys. Lett., 333, 162, 2001.
Wennberg, P. O., Bates, K. H., Crounse, J. D., Dodson, L. G., McVay, R. C., Mertens, L. A., Nguyen, T. B., Praske, E., Schwantes, R. H., Smarte, M. D., St Clair, J. M., Teng A. P., Zhang, X., and Seinfeld, J. H.: Chem. Rev., 118, 3337, 2018.
Wine, P. H., Kreutter, N. M., Gump, C. A. and Ravishankara, A. R.: J. Phys. Chem., 85, 2660, 1981.
Wine, P. H., Thompson, R. J. and Semmes, D. H.: Int. J. Chem. Kinet., 16, 1623, 1984.
Zhang, D., Zhang, R., Church, C. and North, S. W.: Chem. Phys. Lett., 343, 49, 2001.
Zhang, R., Suh, I., Lei, W., Clinkenbeard, A. D. and North, S. W.: J. Geophys. Res., 105, 24627, 2000.



Rate coefficients for HO + Isoprene.

## HOx_VOC9

**HO +**  **α-pinene → products**

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $1.37 \times 10^{-11} \exp[(446 \pm 76)/T]$ | 298-422 | Kleindienst et al., 1982 | FP-RF (a) |
| $(6.01 \pm 0.82) \times 10^{-11}$ | 298 | | |
| $1.63 \times 10^{-12} \exp[(1080 \pm 50)/T]$ | 300-435 | Chuong et al., 2002 | DF-RF/LIF (b) |
| $(6.08 \pm 0.24) \times 10^{-11}$ | 300 | | |
| $(6.09 \pm 0.30) \times 10^{-11}$ | 300 | Davis and Stevens, 2005 | DF-LIF (c) |
| $1.83 \times 10^{-11} \exp[(330 \pm 6)/T]$ | 238-357 | Dillon et al., 2017 | PLP-LIF (d) |
| $(5.4 \pm 0.2) \times 10^{-11}$ | 296 | | |
| *Relative Rate Coefficients* | | | |
| $(5.6 \pm 1.7) \times 10^{-11}$ | 305 ± 2 | Winer et al., 1976 | RR/P-GC-FID (e) |
| $(5.36 \pm 0.31) \times 10^{-11}$ | 294 ± 1 | Atkinson et al., 1986 | RR/P-GC-FID (f) |
| $1.17 \times 10^{-11} \exp[(436 \pm 53)/T]$ | 295-364 | Gill and Hites, 2002 | RR/P-MS (g) |
| $(5.04 \pm 1.23) \times 10^{-11}$ | 298 | | |
| $1.40 \times 10^{-11} \exp[(387 \pm 46)/T]$ | 240-340 | Montenegro et al., 2012 | RR/DF-MS (h) |
| $(5.36 \pm 0.94) \times 10^{-11}$ | 298 | | |
| $(5.06 \pm 0.75) \times 10^{-11}$ | 298 | Dash et al. 2014 | RR/P-GC-FID (i) |

α-pinene is 2,6,6-trimethyl-bicyclo[3.1.1]hept-2-ene

### Comments

(a) Flash photolysis of $H_2O$/α-pinene mixtures in Ar (buffer gas) at total pressures in the range 50-200 Torr (67-270 mbar) under slow flow conditions. Pseudo-first order decays of HO radical concentrations (monitored by RF) were characterized in the presence of excess concentrations of α-pinene. $k$ displayed no dependence on pressure over the studied range.

(b) Pseudo-first order decays of HO radical concentrations (monitored by RF or LIF) were characterized in the presence of excess concentrations of α-pinene. Experiments carried out at a total pressure of 5 Torr (6.7 mbar) of either He or 90% He and 10% $O_2$.

(c) Pseudo-first order decays of HO radical concentrations (monitored by LIF) were characterized in the presence of excess concentrations of α-pinene. Experiments carried out at a total pressure of 5 Torr (6.7 mbar) of mainly He, with $O_2$ present at ~ 1-14% of the mixture.

(d) Pulsed laser photolysis of $H_2O_2$ at 248 nm, in the presence of α-pinene/$N_2$ or α-pinene/air mixtures at total pressures in the range 6-211 Torr (8-280 mbar). Pseudo-first order decays of HO radical concentrations (monitored by LIF) were characterized in the presence of excess concentrations of α-pinene (monitored by vacuum UV optical absorption at 184.95 nm). $k$ displayed no significant dependence on bath gas or on pressure over the studied range (N.B. The 296 K data points presented below were obtained at 7.5, 96 and 197 Torr in $N_2$ and at 97 Torr in air. The reported value, tabulated above, is based on the average of the four determinations).

(e) HO radicals were generated by the photolysis of $NO_x$ – organic – air mixtures in a 5870 L chamber at ~1 bar pressure. The concentrations of α-pinene and 2-methylpropene (the reference compound) were analyzed by GC. The measured rate coefficient ratio $k$(HO + α-pinene)/$k$(HO + 2-methylpropene) = 1.14 (± 30%) is placed on an absolute basis using $k$(HO

+ 2-methylpropene) = 4.92 × $10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at 305 K (IUPAC, 2019).

(f) HO radicals were generated by the photolysis of $CH_3ONO$ in air at wavelengths >300 nm in a 6400 L Teflon chamber at ~980 mbar pressure. The concentrations of α-pinene and 2,3-dimethyl-2-butene (the reference compound) were analyzed by GC during the $CH_3ONO$ – NO - α-pinene - 2,3-dimethyl-2-butene – air irradiations. The measured rate coefficient ratio *k*(HO + α-pinene)/*k*(HO + 2,3-dimethyl-2-butene) = 0.487 ± 0.028 is placed on an absolute basis using *k*(HO + 2,3-dimethyl-2-butene) = 1.10 × $10^{-10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ (Atkinson and Arey, 2003).

(g) HO radicals were generated by the photolysis of $H_2O_2$ in helium diluent in a 192 $cm^3$ volume quartz vessel. The concentrations of α-pinene and 1-butene, 2-methylpropene or *trans*-2-butene (the reference compounds) were analyzed by MS during the experiments. The measured rate coefficient ratios *k*(HO + α-pinene)/*k*(HO + 1-butene), *k*(HO + α-pinene)/*k*(HO + 2-methylpropene) and *k*(HO + α-pinene)/*k*(HO + *trans*-2-butene) are placed on an absolute basis using *k*(HO + 1-butene) = 6.6 × $10^{-12}$ exp(465/*T*) $cm^3$ $molecule^{-1}$ $s^{-1}$, *k*(HO + 2-methylpropene) = 9.4 × $10^{-12}$ exp(505/*T*) $cm^3$ $molecule^{-1}$ $s^{-1}$ and *k*(HO + *trans*-2-butene) = 1.0 × $10^{-11}$ exp(553/*T*) $cm^3$ $molecule^{-1}$ $s^{-1}$ (IUPAC, 2019).

(h) HO radicals were generated by the reaction of $H_2O$ with F atoms (formed from $F_2$ discharge), and added to flowing mixtures containing α-pinene and isoprene (the reference compound) in helium at a total pressure of 1-8 Torr (1.3-11 mbar). The measured rate coefficient ratios, *k*(HO + α-pinene)/*k*(HO + isoprene), are placed on an absolute basis using the rate coefficient expression *k*(HO + isoprene) = 2.7 × $10^{-11}$ exp(370/*T*) $cm^3$ $molecule^{-1}$ $s^{-1}$ (IUPAC, 2019).

(i) HO radicals were generated by the photolysis of $H_2O_2$ in nitrogen diluent at pressures in the range 800-850 Torr (1070-1130 mbar) in a 1750 $cm^3$ volume quartz vessel. The concentrations of α-pinene and propene (the reference compound) were analyzed by GC-FID. The measured rate coefficient ratio *k*(HO + α-pinene)/*k*(HO + propene) is placed on an absolute basis using *k*(HO + propene) = 2.86 × $10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at 298 K and 825 Torr (1100 mbar) (IUPAC, 2019).

## Preferred Values

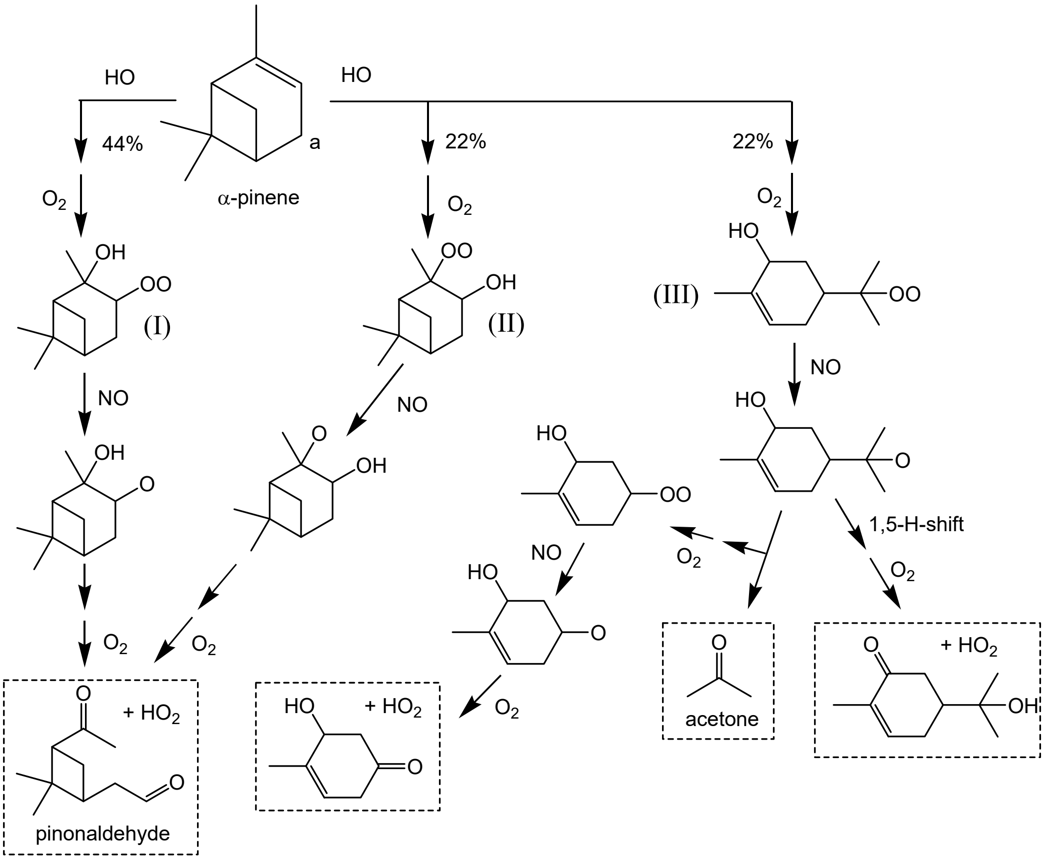
| Parameter | Value | T/K |
|---|---|---|
| *k* /$cm^3$ $molecule^{-1}$ $s^{-1}$ | 5.3 × $10^{-11}$ | 298 |
| *k* /$cm^3$ $molecule^{-1}$ $s^{-1}$ | 1.34 × $10^{-11}$ exp(410/T) | 240-360 |
| *Reliability* | | |
| Δ log *k* | ± 0.08 | 298 |
| Δ E/R | ± 100 | 240-360 |

*Comments on Preferred Values*

The room temperature values of *k* in the reported studies are in reasonable agreement. With the exception of the recent study of Dillon et al. (2017), those reported in the direct kinetics studies are consistently slightly higher (15% on average) than those reported in the relative rate studies. The direct studies of Chuong et al. (2002) and Davis and Stevens (2005) reported increased wall removal rates of HO when α-pinene was present, and initial deviations from pseudo-first order HO decay, which may contribute to the small systematic difference. Chuong et al. (2002) also report a temperature dependence that is significantly higher than those reported in other temperature dependence studies. Similar complications were not apparent in the recent direct study of Dillon et al. (2017), which reports a room temperature value of *k* that is comparable with those in the relative rate studies.

The preferred value of E/R is a rounded average of those reported in the relative rate studies of Gill and Hites (2002) and Montenegro et al. (2012), but is consistent with those reported in the direct studies of Kleindienst et al. (1982) and Dillon et al. (2017). The 298 K preferred value of *k* is an average of the room temperature values reported in all the tabulated relative rate studies, with those of Winer et al. (1976) and Atkinson et al. (1986) corrected to 298 K using the preferred temperature dependence. The pre-exponential factor is adjusted to fit the 298 K preferred value. However, the resultant expression also provides an excellent description of the recent direct kinetics data of Dillon et al. (2017) at temperatures below 300 K.

H atom abstraction has been estimated to account for about 12 % of the reaction of HO with α-pinene at 298 K (Peeters et al., 2001); with this being dominated by attack at position "a" in the schematic below, which forms a resonant radical. The reaction proceeds mainly by initial addition of the HO radical to the C=C bond, and the schematic illustrates some features of the established and predicted subsequent chemistry in air in the presence of $NO_x$.



The hydroxy-substituted peroxy radicals, (I), (II) and (III), are formed from sequential addition of HO and $O_2$, with (III) facilitated by competitive opening of the cyclobutyl ring in the intermediate chemically-activated HO-α-pinene adduct. The approximate contributions of the three pathways shown are based on the calculations of Vereecken and Peeters (2000) and Peeters et al. (2001) for 298 K and 1 bar. The subsequent chemistry, propagated by the reactions of intermediate peroxy radicals with NO, forms a number of carbonyl end products (as shown in boxes). The chemistry of (I) and (II) generates pinonaldehyde, which has been reported to be formed in yields in the range 28 ± 5% to 87 ± 20% in experimental studies in the presence of $NO_x$ (Arey et al., 1990; Hatakeyama et al., 1991; Hakola et al., 1994; Nozière et al., 1999; Wisthaler et al., 2001; Aschmann et al., 2002). Lower yields have generally been obtained by GC analyses

(Arey et al., 1990; Hakola et al., 1994; Aschmann et al., 2002) and by proton-transfer mass spectrometry (Wisthaler et al., 2001), with the higher values by *in situ* FTIR spectroscopy (Hatakeyama et al., 1991; Nozière et al., 1999). The chemistry of (III) partially generates acetone, which has been reported to be formed in yields in the range 5-11% (Aschmann et al., 1998; Reissell et al., 1999; Nozière et al., 1999; Orlando et al., 2000).

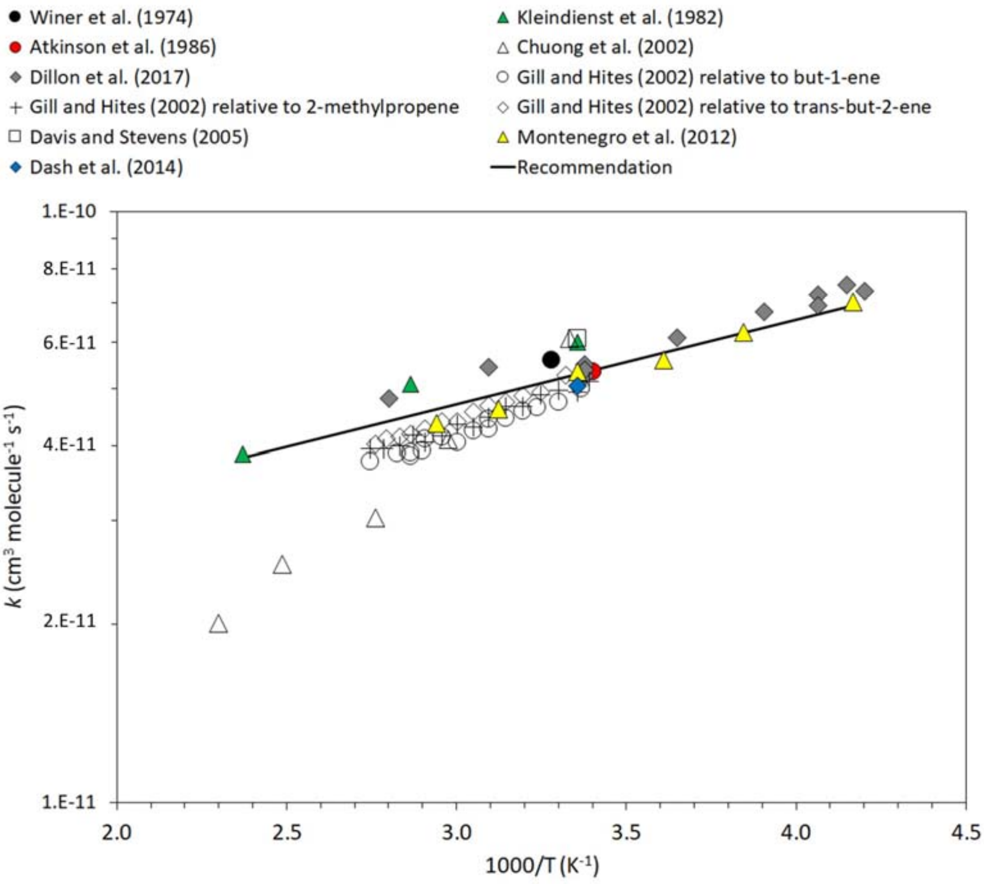
The reactions of all the peroxy radicals with NO also partially form the corresponding hydroxy-nitrate products (not shown in the schematic). There is some disagreement in the reported yields of nitrate products, with the *in situ* FTIR determinations of total nitrate products by Nozière et al. (1999), 18 ± 9%, and Rindelaub et al. (2015), 26 ± 7%, being much higher than those reported specifically for the $C_{10}$ hydroxynitrates by Aschmann et al. (2002), ~ 1 %, and Xu et al. (2019), 3.3 ± 1.5%, based on mass spectrometric methods (API-MS and GC−ToF-CIMS, respectively). Other products have also been observed, including formaldehyde (19%) and formic acid (7%) by Orlando et al. (2000); and product signals consistent with a number of higher molecular weight dihydroxycarbonyl, hydroxynitrate and dihydroxynitrate products by Aschmann et al. (1998; 2002).

Other reactions of the intermediate peroxy radicals can compete with reaction with NO under atmospheric conditions, and in experimental studies with low $NO_x$ levels. These include bimolecular reactions with $HO_2$ and organic peroxy radicals, which can have propagating channels (leading to lower yields of the same end products discussed above) and terminating channels generating hydroxy-hydroperoxide, hydroxy-carbonyl and dihydroxy products. Unimolecular isomerization reactions may also be available for complex peroxy radical intermediates. Capouet et al. (2004) calculated that peroxy radical (III) undergoes a ring closure reaction (forming a peroxide-bridged product) that dominates under most atmospheric conditions; and Berndt et al. (2016) have postulated that auto-oxidation reaction sequences, initiated by isomerization of peroxy radical (III) and involving a number of subsequent peroxy radical isomerization reactions, may account for the observed rapid formation of highly oxidized multifunctional organic compounds from the HO-initiated oxidation of α-pinene in chamber experiments. The role of unimolecular isomerization reactions has recently been confirmed by Xu et al. (2019), who experimentally and theoretically characterized a number of competitive ring-closure and H-atom shift reactions for peroxy radical (III).

## References

Arey, J., Atkinson, R. and Aschmann, S. M.: J. Geophys. Res., 95, 18546, 1990.
Aschmann, S. M., Reissell, A., Atkinson, R. and Arey, J.: J. Geophys. Res., 103, 25553, 1998.
Aschmann, S. M., Atkinson, R. and Arey, J.: J. Geophys. Res., 107 (D14), 4191, 2002.
Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
Atkinson, R., Aschmann, S. M. and Pitts Jr., J. N.: Int. J. Chem. Kinet., 18, 287, 1986.
Berndt, T., Richters, S., Jokinen, T., Hyttinen, N., Kurtén, T., Otkjær, R. V., Kjaergaard, H. G., Stratmann, F., Herrmann, H., Sipila, M., Kulmala, M. and Ehn, M.: Nat. Commun., 7, 13677, 2016.
Capouet, M., Peeters, J., Nozière, B. and Müller, J. F.: Atmos. Chem. Phys., 4, 2285, 2004.
Chuong, B., Davis, M., Edwards, M. and Stevens, P. S.: Int. J. Chem. Kinet., 34, 300, 2002.
Gill, K. J. and Hites, R. A.: J. Phys. Chem. A, 106, 2538, 2002.
Dash, M. R., Balaganesh, M. and Rajakumar, B.: Molecular Physics, 112(11), 1495, 2014.
Davis, M. E. and Stevens, P. S.: Atmos. Environ., 39, 1765, 2005.
Dillon, T. J., Dulitz, K., Groß, C. B. M., and Crowley, J. N.: Atmos. Chem. Phys., 17, 15137-15150, https://doi.org/10.5194/acp-17-15137-2017, 2017.
Hakola, H., Arey, J., Aschmann, S. M. and Atkinson, R.: J. Atmos. Chem., 18, 75, 1994.
Hatakeyama, S., Izumi, K., Fukuyama, T., Akimoto, H. and Washida, N.: J. Geophys. Res., 96, 947, 1991.

Kleindienst, T. E., Harris, G. W. and Pitts Jr., J. N.: Environ. Sci. Technol., 16, 844, 1982.
Montenegro, A., Ishibashi, J. S. A., Lam, P. and Li, Z.: J. Phys. Chem. A, 116, 12096, 2012.
Nozière, B., Barnes, I. and Becker, K.-H.: J. Geophys. Res., 104, 23645, 1999.
Orlando, J. J., Nozière, B., Tyndall, G. S., Orzechowska, G., Paulson, S. E. and Rudich, Y.: J. Geophys. Res., 105, 11561, 2000.
Peeters, J., Vereecken, L. and Fantechi, G.: Phys. Chem. Chem. Phys. 3, 5489, 2001.
Reissell, A., Harry, C., Aschmann, S. M., Atkinson, R. and Arey, J.: J. Geophys. Res., 104, 13869, 1999.
Rindelaub, J. D., McAvey, K. M. and Shepson, P. B.: Atmos. Environ., 100, 193, 2015.
Vereecken, L. and Peeters, J.: J. Phys. Chem. A, 104, 11140, 2000.
Winer, A. M., Lloyd, A. C., Darnall, K. R. and Pitts Jr., J. N.: J. Phys. Chem., 80, 1635, 1976.
Wisthaler, A., Jensen, N. R., Winterhalter, R., Lindinger, W. and Hjorth, J.: Atmos. Environ., 35, 618, 2001.
Xu, L., Møller, K. H., Crounse, J. D., Otkjær, R. V., Kjaergaard, H. G., and Wennberg, P. O.: J. Phys. Chem. A., 123, 1661, 2019.



Rate coefficients for HO + α-Pinene.

## HOx_VOC14

## HO + $CH_3CH_2CH_2CHO \rightarrow$ products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $5.7 \times 10^{-12} \exp[(411 \pm 164)/T]$ | 258-422 | Semmes et al., 1985 | FP-RF |
| $(2.06 \pm 0.30) \times 10^{-11}$ | 298 | | |
| $(2.88 \pm 0.26) \times 10^{-11}$ | 298 | Albaladejo et al., 2002 | PLP-LIF |
| *Relative Rate Coefficients* | | | |
| $(2.31 \pm 0.06) \times 10^{-11}$ | 298 ± 4 | Kerr and Sheppard, 1981 | RR (a) |
| $(2.45 \pm 0.15) \times 10^{-11}$ | 296 ± 2 | Papagni et al., 2000 | RR (b) |
| $(2.39 \pm 0.16) \times 10^{-11}$ | 298 ± 2 | D'Anna et al., 2001 | RR (c) |

## Comments

(a) HO radicals were generated by the photolysis of HONO in air and the concentrations of butanal and ethene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k$(HO + butanal)/$k$(HO + ethene) = 2.96 ± 0.07 is placed on an absolute basis using $k$(HO + ethene) = $7.8 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K and atmospheric pressure (IUPAC, 2019).

(b) HO radicals were generated by the photolysis of $CH_3ONO$ in air and the concentrations of butanal and methyl vinyl ketone (the reference compound) were measured by GC. The measured rate coefficient ratio of $k$(HO + butanal)/$k$(HO + methyl vinyl ketone) = 1.20 ± 0.07 is placed on an absolute basis using $k$(HO + methyl vinyl ketone) = $2.04 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 296 K (IUPAC, 2019).

(c) HO radicals were generated by the photolysis of an organic nitrite in air and the concentrations of butanal and 1-butene (the reference compound) were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k$(HO + butanal)/$k$(HO + 1-butene) = 0.76 ± 0.05 is placed on an absolute basis using $k$(HO + 1-butene) = $3.14 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K and atmospheric pressure of air (Atkinson, 1997; IUPAC, 2019).

## Preferred Values

| Parameter | Value | *T*/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $2.3 \times 10^{-11}$ | 298 |
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $5.8 \times 10^{-12} \exp(410/T)$ | 250-430 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.08 | 298 |
| $\Delta$ E/R | ± 250 | 250-430 |

*Comments on Preferred Values*

The preferred 298 K rate coefficient is the unweigthed mean of the room temperature absolute rate coefficient of Semmes et al. (1985) and the relative rate coefficients of Kerr and Sheppard (1981), Papagni et al. (2000) and D'Anna et al. (2001). The temperature dependence is that measured by Semmes et al. (1985), with the pre-exponential factor being adjusted to fit the 298 K preferred value. The room temperature rate coefficient of Albaladejo et al. (2002) is in good agreement with the preferred value. The relative rate coefficient of Audley et al. (1981) has not been used in the evaluation because, while it is in good agreement with the preferred 298 K rate coefficient, the rate coefficients of Audley et al. (1981) for 2-methyl-1-propanal, 1-pentanal and 2,2-dimethyl-1-propanal are significantly lower than the values of Semmes et al. (1985) and Kerr and Sheppard (1981). At room temperature and below, the reaction is expected to proceed primarily by H-atom abstraction from the -CHO group.

## References

Albaladejo, J., Ballesteros, B., Jiménez, E., Martin, P. and Martínez, E.: Atmos. Environ. 36, 3231, 2002.

Atkinson, R.: J. Phys. Chem. Ref. Data 26, 215, 1997.

Audley, G. J., Baulch, D. L. and Campbell, I. M.: J. Chem. Soc. Faraday Trans. 1 77, 2541, 1981.

D'Anna, B., Andresen, O., Gefen, Z. and Nielsen, C. J.: Phys. Chem. Chem. Phys. 3, 3057, 2001.

IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

Kerr, J. A. and Sheppard, D. W.: Environ. Sci. Technol. 15, 960, 1981.

Papagni, C., Arey, J. and Atkinson, R.: Int. J. Chem. Kinet. 32, 79, 2000.

Semmes, D. H., Ravishankara, A. R., Gump-Perkins, C. A. and Wine, P. H.: Int. J. Chem. Kinet. 17, 303, 1985.

## HOx_VOC15

## $HO + CH_2{=}C(CH_3)CHO \rightarrow$ products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $1.77 \times 10^{-11} \exp[(175 \pm 52)/T]$ | 300-423 | Kleindienst et al., 1982 | FP-RF |
| $(3.14 \pm 0.49) \times 10^{-11}$ | 300 | | |
| $7.73 \times 10^{-12} \exp[(379 \pm 46)/T]$ | 234-373 | Gierczak et al., 1997 | PLP-LIF |
| $(2.79 \pm 0.12) \times 10^{-11}$ | 298 | | |
| $9.8 \times 10^{-13} \exp[(1050 \pm 120)/T]$ | 300-422 | Chuong and Stevens, 2003 | DF-RF/LIF (a) |
| $(3.23 \pm 0.36) \times 10^{-11}$ | 300 | | |
| $(3.22 \pm 0.10) \times 10^{-11}$ | 300 | Chuong and Stevens, 2004 | DF-LIF (b) |
| *Relative Rate Coefficients* | | | |
| $(3.23 \pm 0.24) \times 10^{-11}$ | 299 ± 2 | Atkinson et al., 1983 | RR (c) |
| $(3.90 \pm 0.31) \times 10^{-11}$ | 298 ± 2 | Edney et al., 1986 | RR (d) |

## Comments

(a) No variation in the rate coefficient was observed over the pressure range 2.7-6.7 mbar (2-5 Torr) of He diluent at any of the temperatures studied (300-422 K). The cited temperature-dependent rate expression uses data at 6.7 mbar (5.0 Torr) pressure of He (Chuong and Stevens, 2003). Problems ascribed to reversible wall adsorption of methacrolein and heterogeneous wall reactions were observed; these were avoided or minimized by addition of ~10% $O_2$ or by conditioning the reactor with high F atom concentrations

(b) At 133 mbar (100 Torr) of $N_2$ diluent, using a turbulent flow reactor.

(c) Relative rate study carried out at atmospheric pressure of air. The concentrations of methacrolein and propene (the reference compound) were measured by GC. The measured rate coefficient ratio $k(HO + \text{methacrolein})/k(HO + \text{propene}) = 1.13 \pm 0.09$ is placed on an absolute basis by using a rate coefficient of $k(HO + \text{propene}) = 2.86 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 299 K and atmospheric pressure of air (IUPAC, 2019).

(d) Relative rate study carried out at atmospheric pressure of air. The concentrations of methacrolein and propene and *trans*-2-butene (the reference compounds) were measured by GC. The measured rate coefficient ratios are placed on an absolute basis using $k(HO + \text{propene}) = 2.63 \times 10^{-11}$ and $k(HO + trans\text{-2-butene}) = 6.40 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K and atmospheric pressure of air (UPAC, 2019). The indicated uncertainty is one standard deviation.

## Preferred Values

| Parameter | Value | $T$/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $3.0 \times 10^{-11}$ | 298 |
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $8.4 \times 10^{-12} \exp(380/T)$ | 230-380 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.08 | 298 |
| $\Delta E/R$ | ± 100 | 230-380 |

*Comments on Preferred Values*

The room temperature rate coefficients of Kleindienst et al. (1982), Atkinson et al. (1983), Gierczak et al. (1997) and Chuong and Stevens (2003, 2004) are in good agreement, with the relative rate measurement of Edney et al. (1986) being ~20-30% higher. The temperature dependencies obtained by Kleindienst et al. (1982) [300-423 K] and Chuong and Stevens (2003) [300-422 K] are respectively lower and higher than that determined by Gierczak et al. (1997) over the wider temperature range of 234-373 K. In the Chuong and Stevens (2003) study, the rate coefficients at 300, 328 and 361 K are in good agreement with the rate expression of Gierczak et al. (1997); those at 390 and 422 K (Chuong and Stevens, 2003) are lower than predicted from the Arrhenius expression of Gierczak et al. (1997). Because of the wider temperature range used by Gierczak et al. (1997) and the fact that it extends below room temperature, the temperature dependence of Gierczak et al. (1997) is accepted. The preferred 298 K rate coefficient is based on the room temperature rate coefficients of Atkinson et al. (1983) and Gierczak et al. (1997), and the pre-exponential factor is calculated from the preferred 298 K rate coefficient and the temperature dependence.

The products of the reaction of HO radicals with methacrolein in the presence of NO have been investigated by Tuazon and Atkinson (1990) and Orlando and Tyndall (1999). The reaction proceeds by two pathways: H-atom abstraction from the CHO group, and initial addition of the HO radical to the carbon atoms of the C=C bond. H-atom abstraction from the CHO group accounts for 50-55% of the overall reaction at room temperature (Tuazon and Atkinson, 1990; Orlando and Tyndall, 1999), forming the acyl radical $CH_2{=}C(CH_3)CO$ which then adds $O_2$ to form the acyl peroxy radical $CH_2{=}C(CH_3)C(O)OO$. This acyl peroxy radical reacts with $NO_2$, to form the peroxyacyl nitrate $CH_2{=}C(CH_3)C(O)OONO_2$ (MPAN), or with NO (Tuazon and Atkinson, 1990; Orlando and Tyndall, 1999):

$$CH_2{=}C(CH_3)C(O)OO + NO_2 \rightarrow CH_2{=}C(CH_3)C(O)OONO_2$$
$$CH_2{=}C(CH_3)C(O)OO + NO \rightarrow CH_2{=}CCH_3 + CO_2 + NO_2$$

The $CH_2{=}CCH_3$ radical reacts with $O_2$ to form HCHO, CO and $CO_2$ (Orlando and Tyndall, 1999).

Initial HO radical addition to the C=C bond leads (in the presence of NO) to the intermediate hydroxyalkoxy radicals $HOCH_2C(O)(CH_3)CHO$ and $OCH_2C(OH)(CH_3)CHO$, which decompose by the pathways (Tuazon and Atkinson, 1990; Orlando and Tyndall, 1999):

$$HOCH_2C(O)(CH_3)CHO \rightarrow CH_3C(O)CHO + CH_2OH$$
$$HOCH_2C(O)(CH_3)CHO \rightarrow HOCH_2C(O)CH_3 + HCO$$

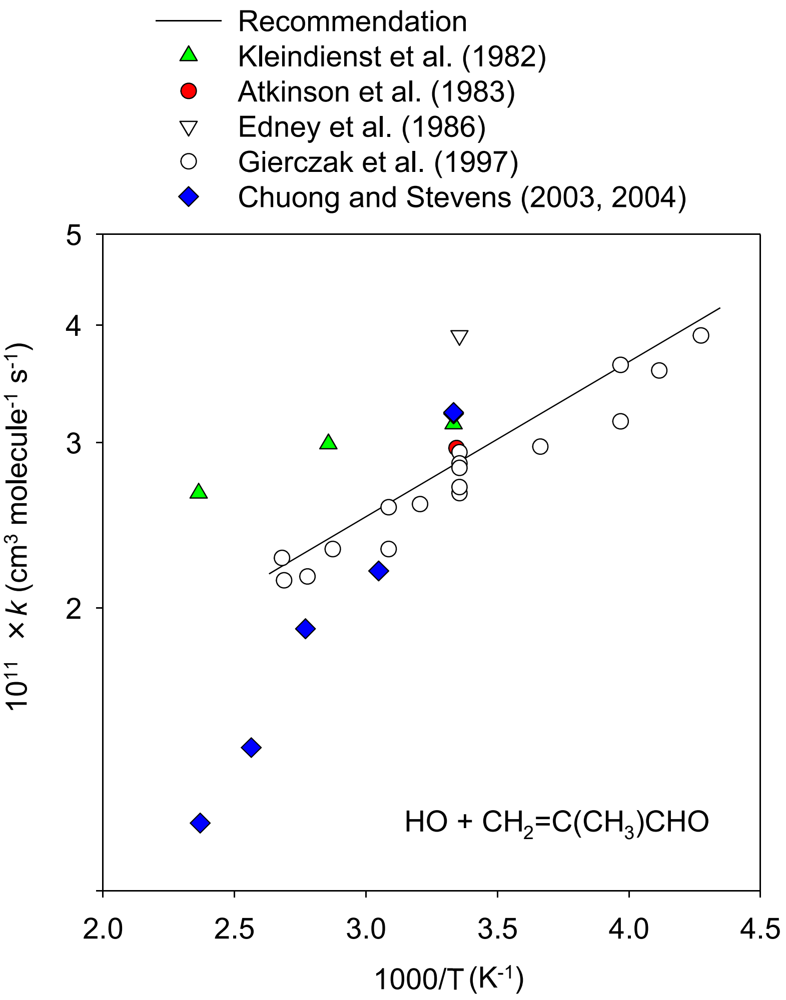
and

$$OCH_2C(OH)(CH_3)CHO \rightarrow HCHO + CH_3C(OH)CHO$$

followed by reactions of $CH_2OH$ and $CH_3C(OH)CHO$ radicals with $O_2$ to form $HCHO + HO_2$ and $CH_3C(O)CHO + HO_2$, respectively. The HO radical addition reaction appears to be in the high-pressure region above ~2.7 mbar (2 Torr) pressure (Gierczak et al., 1997; Chuong and Stevens, 2003). The first generation products from the HO radical addition pathways are therefore $HCHO + CH_3C(O)CHO$ and $HOCH_2C(O)CH_3 + CO$ (the CO arising from reaction of HCO with $O_2$). The studies of Tuazon and Atkinson (1990) and Orlando and Tyndall (1999) measured formation yields of methylglyoxal and hydroxyacetone of 8.4% and 44%, respectively, showing that initial HO radical addition occurs mainly at the terminal $CH_2$ moiety (Tuazon and Atkinson, 1990).

## References

Atkinson, R., Aschmann, S. M. and Pitts Jr., J. N.: Int. J. Chem. Kinet. 15, 75, 1983.
Chuong, B. and Stevens, P. S.: J. Phys. Chem. A 107, 2185, 2003.
Chuong, B. and Stevens, P. S.: Int. J. Chem. Kinet. 36, 12, 2004.
Edney, E. O., Kleindienst, T. E. and Corse, E. W.: Int. J. Chem. Kinet. 18, 1355, 1986.
Gierczak, T., Burkholder, J. B., Talukdar, R. K., Mellouki, A., Barone, S. B. and Ravishankara, A. R.: J. Photochem. Photobiol. A: Chem. 110, 1, 1997.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Kleindienst, T. E., Harris, G. W. and Pitts Jr., J. N.: Environ. Sci. Technol. 16, 844, 1982.
Orlando, J. J., Tyndall, G. S. and Paulson S. E.: Geophys. Res. Lett. 26, 2191, 1999.
Tuazon, E. C. and Atkinson, R.: Int. J. Chem. Kinet. 22, 591, 1990.



Rate coefficients for HO + CH$_2$=C(CH$_3$)CHO.

## HOx_VOC20

## $HO + CH_3C(O)CH_2CH_3 \rightarrow$ products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $2.3 \times 10^{-12} \exp[-(170 \pm 120)/T]$ | 240-440 | Wallington and Kurylo, 1987 | FP-RF |
| $(1.15 \pm 0.10) \times 10^{-12}$ | 296 | | |
| $1.51 \times 10^{-12} \exp[-(60 \pm 61)/T]$ | 243-372 | Le Calvé et al., 1998 | PLP-LIF |
| $(1.19 \pm 0.18) \times 10^{-12}$ | 298 | | |
| $1.35 \times 10^{-12} \exp[-(78 \pm 52)/T]$ | 228-388 | Jiménez et al., 2005 | PLP-LIF |
| $(1.04 \pm 0.07) \times 10^{-12}$ | 298 | | |
| $3.84 \times 10^{-24}\, T^4 \exp[(1038 \pm 11)/T]$ | 213-598 | Carr et al., 2008 | PLP-LIF |
| $(1.06 \pm 0.06) \times 10^{-12}$ | 298 | | |
| *Relative Rate Coefficients* | | | |
| $(3.4 \pm 1.0) \times 10^{-12}$ | 305 ± 2 | Winer et al., 1976 | RR (a) |
| $2.52 \times 10^{-12}$ | 300 | Cox et al., 1980 | RR (b) |
| $(8.7 \pm 0.9) \times 10^{-13}$ | 295 ± 2 | Cox et al., 1981 | RR (b) |
| $(9.1 \pm 1.6) \times 10^{-13}$ | 297 | Edney et al., 1986 | RR (c) |

## Comments

(a) HO radicals were generated by the photolysis of $NO_x$-organic-air mixtures, and the concentrations of 2-butanone and 2-methylpropene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k$(HO + 2-butanone)/$k$(HO + 2-methylpropene) = 0.07 (±30%) is placed on an absolute basis using $k$(HO + 2-methylpropene) = $4.92 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 305 K (IUPAC, 2019).

(b) HO radicals were generated by the photolysis of HONO in air, and the concentrations of 2-butanone and ethene (the reference compound) were measured by GC. The measured rate coefficient ratios $k$(HO + 2-butanone)/$k$(HO + ethene) are placed on an absolute basis by use of rate coefficients at atmospheric pressure of $k$(HO + ethene) = $7.78 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 300 K and $7.91 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 295 K (IUPAC, 2019).

(c) HO radicals were generated from the photolysis of $CH_3ONO$ in air, and the concentrations of 2-butanone and propane (the reference compound) were measured by GC. The measured rate coefficient ratio of $k$(HO + 2-butanone)/$k$(HO + propane) is placed on an absolute basis using $k$(HO + propane) = $1.07 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 297 K (IUPAC, 2019).

## Preferred Values

| **Parameter** | **Value** | ***T*/K** |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $1.1 \times 10^{-12}$ | 298 |
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $1.5 \times 10^{-12} \exp(-90/T)$ | 210-300 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.10 | 298 |
| Δ E/R | ± 200 | 210-300 |

*Comments on Preferred Values*

The measured rate coefficients exhibit a significant amount of scatter, ranging from ~9 × $10^{-13}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ to ~1.2 × $10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at 298 K. The absolute rate coefficients of Wallington and Kurylo (1987) and Le Calvé et al. (1998) are higher than those of Jiménez et al. (2005) and Carr et al. (2008), and this difference becomes more pronounced at lower temperatures (<295 K). Photolysis of 2-butanone may have contributed to the measured 2-butanone loss rates in the relative rate studies of Winer et al. (1976) and Cox et al. (1980). The rate coefficients of Wallington and Kurylo (1987), Le Calvé et al. (1998) and Carr et al. (2008) suggest curvature in the Arrhenius plot. An un-weighted least-squares analysis of the absolute rate coefficients of Wallington and Kurylo (1987), Le Calvé et al. (1998), Jiménez et al. (2005) and Carr et al. (2008), using the three-parameter expression $k = CT^2 \exp(-D/T)$, results in $k = 3.28 \times 10^{-18}\ T^2 \exp(402/T)$ $cm^3$ $molecule^{-1}$ $s^{-1}$ over the temperature range 213-598 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 245 K and is derived from the above three-parameter expression with $A = C\, e^2 T^2$ and $B = D + 2T$.

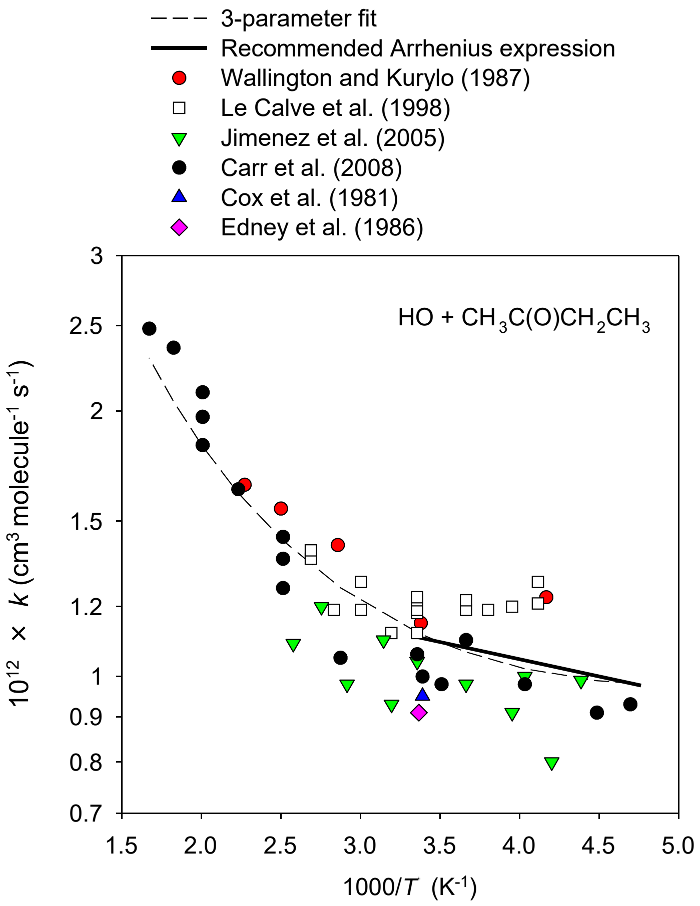
Cox et al. (1981) observed acetaldehyde as a product of the HO radical reaction with 2-butanone, with a formation yield of 0.62 ± 0.02. Acetaldehyde is expected to arise from 2-butanone after H-atom abstraction from the $CH_2$ group, and hence the fraction of the overall HO radical reaction with 2-butanone proceeding via

$$HO + CH_3C(O)CH_2CH_3 \rightarrow H_2O + CH_3C(O)CHCH_3$$

is ~0.62.

## References

Carr, S. A., Baeza-Romero, M. T., Blitz, M. A., Price, B. J. S. and Seakins, P. W.: Int. J. Chem. Kinet., 40, 504, 2008.
Cox, R. A., Derwent, R. G. and Williams, M. R.: Environ. Sci. Technol., 14, 57, 1980.
Cox, R. A., Patrick, K. F. and Chant, S. A.: Environ. Sci. Technol., 15, 587, 1981.
Edney, E. O., Kleindienst, R. E. and Corse, E. W.: Int. J. Chem. Kinet., 18, 1355, 1986.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Jiménez, E., Ballesteros, B., Martínez, E. and Albaladejo, J.: Environ. Sci. Technol., 39, 814, 2005.
Le Calvé, S., Hitier, D., Le Bras, G. and Mellouki, A.: J. Phys. Chem. A, 102, 4579, 1998.
Wallington, T. J. and Kurylo, M. J.: J. Phys. Chem., 91, 5050, 1987.
Winer, A. M., Lloyd, A. C., Darnall, K. R. and Pitts Jr., J. N.: J. Phys. Chem., 80, 1635, 1976.



Rate coefficients for HO + $CH_3C(O)CH_2CH_3$.

## HOx_VOC21

### $HO + CH_3C(O)CH=CH_2 \rightarrow$ products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $3.85 \times 10^{-12} \exp[(456 \pm 73)/T]$ | 298-424 | Kleindienst et al., 1982 | FP-RF |
| $(1.79 \pm 0.28) \times 10^{-11}$ | 298 | | |
| $2.67 \times 10^{-12} \exp[(612 \pm 49)/T]$ | 232-378 | Gierczak et al., 1997 | PLP-LIF |
| $(2.03 \pm 0.17) \times 10^{-11}$ | 298 | | |
| $(1.73 \pm 0.21) \times 10^{-11}$ | 300 | Chuong and Stevens, 2003 | DF-RF/LIF (a) |
| $(1.78 \pm 0.08) \times 10^{-11}$ | 300 | Chuong and Stevens, 2004 | DF-LIF (b) |
| $(1.86 \pm 0.12) \times 10^{-11}$ | 298 ± 2 | Holloway et al., 2005 | PLP-LIF (c) |
| *Relative Rate Coefficients* | | | |
| $1.36 \times 10^{-11}$ | 300 | Cox et al., 1980 | RR (d) |
| $(2.13 \pm 0.15) \times 10^{-11}$ | 299 ± 2 | Atkinson et al., 1983 | RR (e) |

## Comments

(a) At 300 K no measurable variation in the rate coefficient was observed over the pressure range 2.7-6.7 mbar (2-5 Torr) of He diluent; the cited rate coefficient is that obtained at 6.7 mbar (5 Torr) of He diluent. However, at the other temperatures studied (328, 361, 390 and 422 K) the measured rate coefficients increased with increasing pressure over the range 2.7-6.7 mbar (2-5 Torr) of He, showing that the reaction was in the fall-off regime under these temperature and pressure conditions. Problems ascribed to reversible wall adsorption of methyl vinyl ketone and heterogeneous wall reactions were observed; these were avoided or minimized by addition of ~10% $O_2$ or by conditioning the reactor with high F atom concentrations

(b) At 133 mbar (100 Torr) of $N_2$ diluent, using a turbulent flow reactor.

(c) The pulsed laser photolysis of 3-methyl-2,4-dione at 248 nm was used to generate HO radicals.

(d) Relative rate study carried out at atmospheric pressure of air. The concentrations of methyl vinyl ketone and ethene (the reference compound) were measured by GC. The measured rate coefficient ratio is placed on an absolute basis using $k$(HO + ethene) = $7.78 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 300 K and atmospheric pressure of air (IUPAC, 2019).

(e) Relative rate study carried out at atmospheric pressure of air. The concentrations of methyl vinyl ketone and propene (the reference compound) were measured by GC. The measured rate coefficient ratio $k$(HO + methyl vinyl ketone)/$k$(HO + propene) = 0.747 ± 0.055 is placed on an absolute basis using $k$(HO + propene) = $2.85 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 299 K and atmospheric pressure of air (IUPAC, 2019).

## Preferred Values

| Parameter | Value | *T*/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $2.0 \times 10^{-11}$ | 298 |
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $2.6 \times 10^{-12} \exp(610/T)$ | 230-380 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.10 | 298 |
| $\Delta$ E/R | ± 200 | 230-380 |

*Comments on Preferred Values*

The room temperature rate coefficients of Kleindienst et al. (1982), Atkinson et al. (1983), Gierczak et al. (1997), Chuong and Stevens (2003, 2004) and Holloway et al. (2005) are in good agreement, but are higher by ~20-35% than the earlier relative rate measurement of Cox et al. (1980). The preferred 298 K rate coefficient is based on the room temperature rate coefficients of Atkinson et al. (1983), Gierczak et al. (1997) and Holloway et al. (2005). The temperature dependence measured by Gierczak et al. (1997) is accepted and the pre-exponential factor is calculated from the preferred 298 K rate coefficient and the temperature dependence.

The products of the reaction of HO radicals with methyl vinyl ketone in the presence of NO have been investigated by Tuazon and Atkinson (1989). The reaction proceeds by initial addition of the HO radical to the carbon atoms of the C=C bond, forming (in the presence of NO) the intermediate hydroxyalkoxy radicals $CH_3C(O)CH(O)CH_2OH$ and $CH_3C(O)CH(OH)CH_2O$, which decompose by the pathways:

$$CH_3C(O)CH(O)CH_2OH \rightarrow CH_3C(O)CHO + CH_2OH$$
$$CH_3C(O)CH(O)CH_2OH \rightarrow CH_3CO + HOCH_2CHO$$

and

$$CH_3C(O)CH(OH)CH_2O \rightarrow HCHO + CH_3C(O)CHOH$$

followed by reactions of $CH_2OH$ and $CH_3C(O)CHOH$ radicals with $O_2$ to form HCHO + $HO_2$ and $CH_3C(O)CHO + HO_2$, respectively. The first generation products are therefore HCHO + $CH_3C(O)CHO$ and $HOCH_2CHO$ + $CH_3CO$ (with the acetyl radical reacting to form peroxyacetyl nitrate [$CH_3C(O)OONO_2$; PAN] or HCHO (Tuazon and Atkinson, 1989; IUPAC, 2019)). Tuazon and Atkinson (1989) measured formation yields of methylglyoxal and glycolaldehyde of 25 ± 8% and 64 ± 16%, respectively, showing that initial HO radical addition occurs mainly at the terminal $CH_2$ group (Tuazon and Atkinson, 1989).

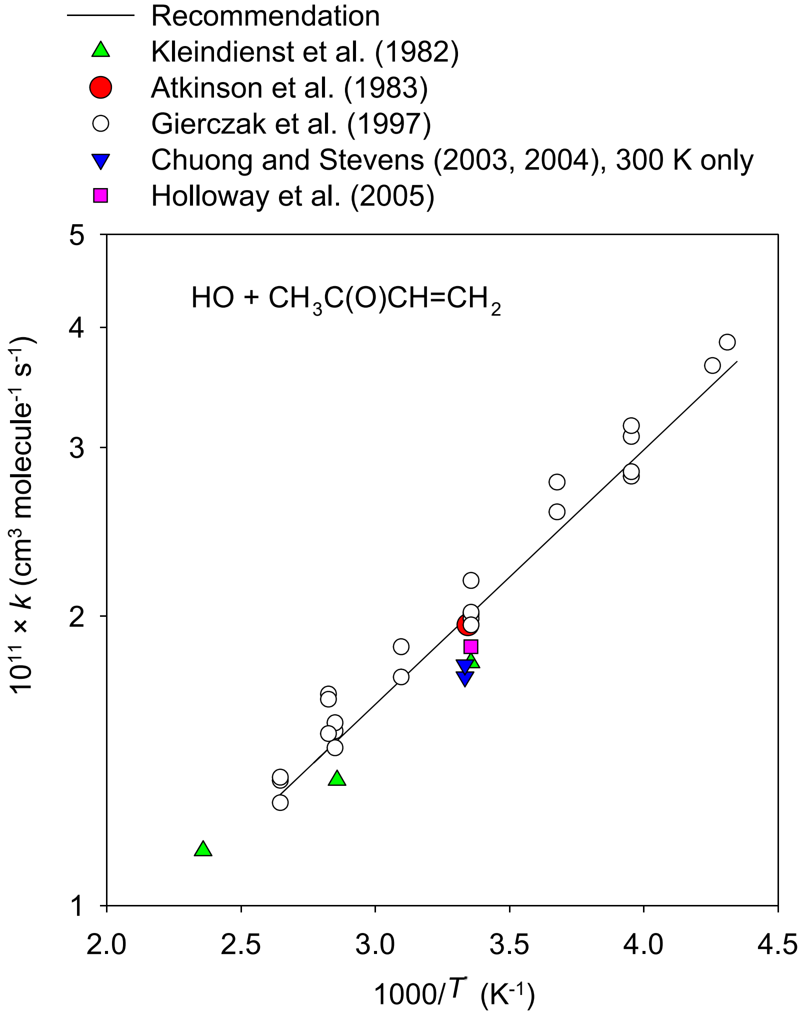
## References

Atkinson, R., Aschmann, S. M., and Pitts Jr., J. N.: Int. J. Chem. Kinet. 15, 75, 1983.
Chuong, B. and Stevens, P. S.: J. Phys. Chem. A 107, 2185, 2003.
Chuong, B. and Stevens, P. S.: Int. J. Chem. Kinet. 36, 12, 2004.
Edney, E. O., Kleindienst, T. E., and Corse, E. W.: Int. J. Chem. Kinet. 18, 1355, 1986.
Gierczak, T., Burkholder, J. B., Talukdar, R. K., Mellouki, A., Barone, S. B., and Ravishankara, A. R.: J. Photochem. Photobiol. A: Chem. 110, 1, 1997.
Holloway, A.-L., Treacy, J., Sidebottom, H., Mellouki, A., Daële, V., Le Bras, G. and Barnes, I.: J. Photochem. Photobiol. A: Chem. 176, 183, 2005.

IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

Kleindienst, T. E., Harris, G. W., and Pitts Jr., J. N.: Environ. Sci. Technol. 16, 844, 1982.

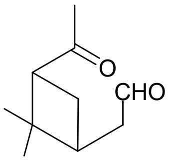
Tuazon, E. C. and Atkinson, R.: Int. J. Chem. Kinet. 21, 1141, 1989.



Rate coefficients for HO + $CH_3C(O)CH=CH_2$.

## HOx_VOC22

### HO + Pinonaldehyde → products



### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | *Reference* | Technique/ Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $4.5 \times 10^{-12} \exp[(600 \pm 100)/T]$ | 297-374 | Davis et al., 2007 | PLP-LIF (a) |
| $(3.46 \pm 0.52) \times 10^{-11}$ | 297 | | |
| *Relative Rate Coefficients* | | | |
| $(9.48 \pm 1.14) \times 10^{-11}$ | 298 ± 2 | Hallquist et al., 1997 | RR (b) |
| $(8.9 \pm 2.6) \times 10^{-11}$ | 300 ± 5 | Glasius et al., 1997 | RR (c,d) |
| $(9.0 \pm 1.3) \times 10^{-11}$ | 300 ± 5 | Glasius et al., 1997 | RR (c,e) |
| $(4.5 \pm 0.8) \times 10^{-11}$ | 296 ± 2 | Alvarado et al., 1998 | RR (f,g) |
| $(4.9 \pm 1.1) \times 10^{-11}$ | 296 ± 2 | Alvarado et al., 1998 | RR (f,h) |
| $(5.4 \pm 0.9) \times 10^{-11}$ | 296 ± 2 | Alvarado et al., 1998 | RR (f,i) |
| $(3.0 \pm 0.8) \times 10^{-11}$ | 295 ± 3 | Nozière et al., 1999 | RR (d,j) |
| $(5.5 \pm 1.5) \times 10^{-11}$ | 295 ± 3 | Nozière et al., 1999 | RR (e,j) |
| $(4.7 \pm 0.6) \times 10^{-11}$ | 295 ± 3 | | |
| $(2.8 \pm 1.0) \times 10^{-11}$ | 295 ± 3 | | |
| $(2.7 \pm 0.6) \times 10^{-11}$ | 295 ± 3 | Nozière et al., 1999 | RR (j,k) |
| $(3.3 \pm 0.3) \times 10^{-11}$ | 295 ± 3 | | |
| $(2.8 \pm 0.3) \times 10^{-11}$ | 295 ± 3 | | |
| $(3.9 \pm 0.4) \times 10^{-11}$ | 295 ± 3 | | |
| $(3.7 \pm 1.1) \times 10^{-11}$ | 299 ± 2 | Nozière et al., 1999 | RR (k,l) |
| $(4.2 \pm 1.1) \times 10^{-11}$ | 290 ± 2 | | |
| $(3.8 \pm 1.5) \times 10^{-11}$ | 288 ± 1 | | |
| $(4.4 \pm 0.8) \times 10^{-11}$ | 287 ± 1 | | |
| $(4.4 \pm 1.0) \times 10^{-11}$ | 289 ± 2 | | |

Pinonaldehyde is 3-acetyl-2,2-dimethyl-cyclobutaneacetaldehyde,

## Comments

(a) Pinonaldehyde was measured by UV absorption at 185 nm before and after gas mixtures flowed through the reaction vessel and by IR absorption before the reaction vessel. The cited error in the 297 K rate coefficient is the estimated overall uncertainty (±15%).

(b) HO radicals were generated by the photolysis of $CH_3ONO$-NO-air mixtures at 1013 ± 5 mbar (760 ± 3.8) pressure. The concentrations of pinonaldehyde and propene (the reference compound) were measured by FTIR spectroscopy. Wall losses of pinonaldehyde in the 153 L chamber were observed and measured in separate experiments and taken into account in the data analysis. The measured rate coefficient ratio of $k$(HO + pinonaldehyde)/$k$(HO + propene) is placed on an absolute basis using a rate coefficient at 298 K and atmospheric pressure of air of $k(\text{HO} + \text{propene}) = 2.86 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019).

(c) HO radicals were generated by the photolysis of $CH_3ONO$-NO-air or $H_2O_2$-air mixtures at

987 ± 7 mbar (740 ± 5 Torr) pressure. The concentrations of pinonaldehyde and isoprene or 1,3-butadiene (the reference compounds) were measured by FTIR spectroscopy. Decays of pinonaldehyde in the dark and due to photolysis were observed in the 480 L reaction chamber used and were taken into account in the data analysis. The measured rate coefficient ratios of *k*(HO + pinonaldehyde)/*k*(HO + isoprene) = 0.896 ± 0.260 and *k*(HO + pinonaldehyde)/*k*(HO + 1,3-butadiene) = 1.37 ± 0.19 are placed on an absolute basis using rate coefficients at 300 K of *k*(HO + isoprene) = $9.91 \times 10^{-11}$ (IUPAC, 2019) and *k*(HO + 1,3-butadiene) = $6.59 \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ (Atkinson and Arey, 2003).

(d) Relative to *k*(HO + isoprene).

(e) Relative to *k*(HO + 1,3-butadiene).

(f) HO radicals were generated by the photolysis of $CH_3ONO$-NO-air mixtures at 987 mbar (740 Torr) pressure. The concentrations of pinonaldehyde and propene, 1-butene or *m*-xylene (the reference compounds) were measured by GC. No measurable decays (<5%) of pinonaldehyde were observed due to dark decays to the walls of the 7000 L Teflon chamber used or due to photolysis at wavelengths >300 nm. The measured rate coefficient ratios of *k*(HO + pinonaldehyde)/*k*(HO + propene) = 1.70 ± 0.29, *k*(HO + pinonaldehyde)/*k*(HO + 1-butene) = 1.56 ± 0.33 and *k*(HO + pinonaldehyde)/*k*(HO + *m*-xylene) = 2.35 ± 0.35 are placed on an absolute basis using rate coefficients at 296 K and atmospheric pressure of air of *k*(HO + propene) = $2.88 \times 10^{-11}$, *k*(HO + 1-butene) = $3.17 \times 10^{-11}$, and *k*(HO + *m*-xylene) = $2.31 \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ (IUPAC, 2019).

(g) Relative to *k*(HO + propene).

(h) Relative to *k*(HO + 1-butene).

(i) Relative to *k*(HO + *m*-xylene).

(j) HO radicals were generated by the photolysis of $CH_3ONO$-NO-air or $H_2O_2$-air mixtures at 1013 mbar (760 Torr) pressure. The concentrations of pinonaldehyde and reference compound (isoprene, 1,3-butadiene or cyclohexane) were measured by FTIR spectroscopy. Wall losses and photolysis was observed in the various chambers used (ranging from 405 to 1080 L volume) and were taken into account in the data analysis. The measured rate coefficient ratios of *k*(HO + pinonaldehyde)/*k*(HO + isoprene), *k*(HO + pinonaldehyde)/*k*(HO + 1,3-butadiene) and *k*(HO + pinonaldehyde)/*k*(HO + cyclohexane) are placed on an absolute basis using rate coefficients at 295 K of *k*(HO + isoprene) = $1.01 \times 10^{-11}$ (IUPAC, 2019), *k*(HO + 1,3-butadiene) = $6.76 \times 10^{-11}$ (Atkinson and Arey, 2003), and *k*(HO + cyclohexane) = $6.90 \times 10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ (Atkinson, 2003; Atkinson and Arey, 2003).

(k) Relative to *k*(HO + cyclohexane).

(l) Experiments carried out in the ~180000 L volume EUPHORE chamber with HO radicals being generated by the dark reaction of ozone with 2,3-dimethyl-2-butene in air at ~1 bar pressure. The concentrations of pinonaldehyde and cyclohexane were monitored during the experiments by FTIR spectroscopy (pinonaldehyde and cyclohexane) and also by HPLC after derivatization for pinonaldehyde and by GC for cyclohexane. The measured rate coefficient ratios of *k*(HO + pinonaldehyde)/*k*(HO + cyclohexane) are placed on an absolute basis using *k*(HO + cyclohexane) = $3.26 \times 10^{-17} T^2 \exp(262/T)$ $cm^3$ $molecule^{-1}$ $s^{-1}$ (Atkinson, 2003; Atkinson and Arey, 2003).

## Preferred Values

| Parameter | Value | *T*/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $3.9 \times 10^{-11}$ | 298 |
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $5.2 \times 10^{-12} \exp(600/T)$ | 230-380 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.15 | 298 |
| $\Delta E/R$ | ± 300 | 230-380 |

*Comments on Preferred Values*

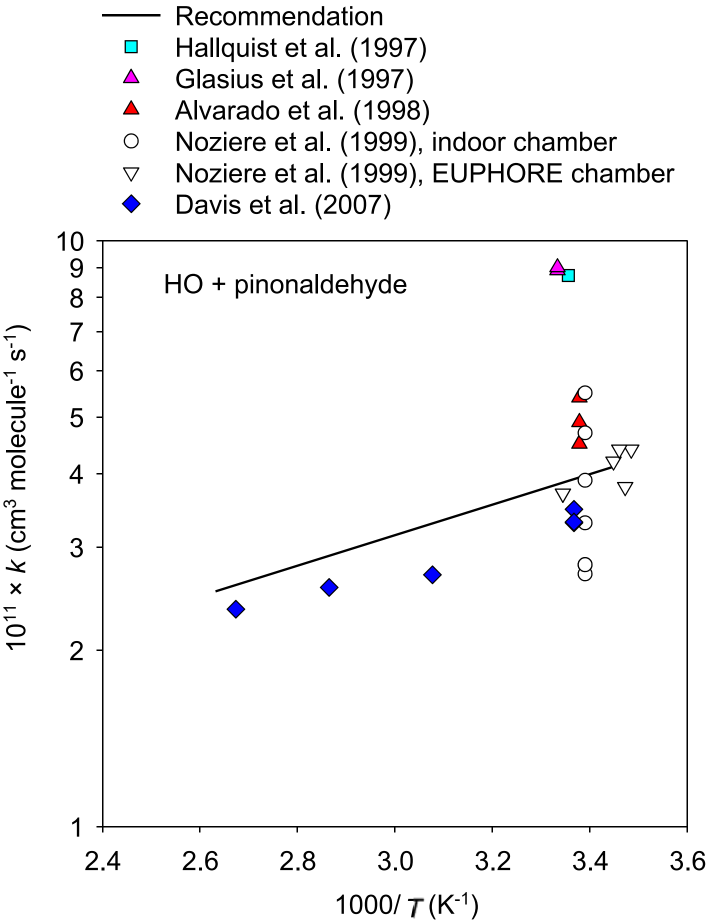
Pinonaldehyde is a low volatility product of the atmospheric reactions of α-pinene. Pinonaldehyde is prone to wall losses, making measurement of its reaction rate coefficients difficult. The available rate coefficients are from four relative rate studies carried out at around room temperature and a recent absolute rate study carried out over the temperature range 297-374 K (Hallquist et al., 1997; Glasius et al., 1997; Alvarado et al., 1998; Nozière et al., 1999; Davis et al., 2007). At room temperature the measured rate coefficients range over a factor of ~3, with those measured by Hallquist et al. (1997) and Glasius et al. (1997) being a factor of ~2 higher than those of Alvarado et al. (1998), Nozière et al. (1999) and Davis et al. (2007), possibly because of unresolved wall adsorption problems. The preferred values are based on the absolute rate study of Davis et al. (2007) and the relative rate studies of Alvarado et al. (1998), carried out in a large volume Teflon chamber, and Nozière et al. (1999), carried out in various chambers of volume ranging from 405 L to ~180000 L. After correction to 298 K using the temperature dependence of Davis et al. (2007), the rate coefficients measured by Alvarado et al. (1998) have been aggregated into an average of $4.9 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, and those measured in the extensive study of Nozière et al. (1999) have been aggregated into an average rate coefficient from the indoor chambers with photolytic production of HO radicals of $3.5 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and an average rate coefficient from the EUPHORE chamber study (with dark production of HO radicals) of $3.9 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. A simple average of these three relative rate coefficients and the absolute rate coefficient of Davis et al. (2007) (corrected to 298 K as described above), which are in agreement within their experimental uncertainties, leads to the preferred 298 K rate coefficient. The temperature dependence of Davis et al. (2007) is accepted and combined with the preferred 298 K rate coefficient to derive the pre-exponential factor.

The reaction proceeds by H-atom abstraction from the various C-H bonds, including from the CHO group. By analogy with other aldehydes (IUPAC, 2019), the negative temperature dependence suggests that a substantial fraction of the reaction proceeds by H-atom abstraction from the CHO group.

## References

Alvarado, A., Arey, J. and Atkinson, R.: J. Atmos. Chem., 31, 281, 1998.
Atkinson, R.: Atmos. Chem. Phys., 3, 2233, 2003.
Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
Davis, M. E., Talukdar, R. K., Notte, G., Ellison, G. B. and Burkholder, J. B.: Environ. Sci. Technol., 41, 3959, 2007.
Glasius, M., Calogirou, A., Jensen, N. R., Hjorth, J. and Nielsen, C. J.: Int. J. Chem. Kinet., 29, 527, 1997.
Hallquist, M., Wängberg, I. and Ljungström, E.: Environ. Sci. Technol., 31, 3166, 1997.

IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Nozière, B., Spittler, M., Ruppert, L., Barnes, I., Becker, K. H., Pons, M. and Wirtz, K.: Int. J. Chem. Kinet., 31, 291, 1999.



Rate coefficients for HO + Pinonaldehyde.

## HOx_VOC27

### HO + $CH_3CH_2CH_2CH_2OH \rightarrow$ products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $(8.31 \pm 0.63) \times 10^{-12}$ | 296 | Wallington and Kurylo, 1987 | FP-RF |
| $(7.80 \pm 0.20) \times 10^{-12}$ | 298 ± 2 | Nelson et al., 1990 | PR-RA |
| $5.30 \times 10^{-12} \exp[(146 \pm 92)/T]$ | 263-372 | Yujing and Mellouki, 2001 | PLP-LIF |
| $(8.47 \pm 0.34) \times 10^{-12}$ | 298 | | |
| *Relative Rate Coefficients* | | | |
| $(6.8 \pm 1.3) \times 10^{-12}$ | 292 | Campbell et al., 1976 | RR (a) |
| $(7.97 \pm 0.66) \times 10^{-12}$ | 298 ± 2 | Nelson et al., 1990 | RR (b) |
| $(1.03 \pm 0.05) \times 10^{-11}$ | 298 ± 2 | Oh and Andino, 2001 | RR (c) |
| $(7.67 \pm 0.14) \times 10^{-12}$ | 298 ± 2 | Cavalli et al., 2002 | RR (b) |
| $(8.58 \pm 0.66) \times 10^{-12}$ | 295 ± 2 | Wu et al., 2003 | RR (d) |

## Comments

(a) HO radicals were generated by the dark reaction of $H_2O_2$-$NO_2$ mixtures in the presence of CO and an organic compound. From sequential experiments using *n*-butane and 1-butanol, a rate coefficient ratio of $k$(HO + 1-butanol)/$k$(HO + *n*-butane) = 3.00 ± 0.56 (two standard deviations) was derived. This rate coefficient ratio is placed on an absolute basis using $k$(HO + *n*-butane) = $2.28 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 292 K (IUPAC, 2019).

(b) HO radicals were generated by the photolysis of $CH_3ONO$ in air, and the concentrations of 1-butanol and cyclohexane (the reference compound) were measured by GC. The measured rate coefficient ratio $k$(HO + 1-butanol)/$k$(HO + cyclohexane) is placed on an absolute basis using $k$(HO + cyclohexane) = $6.97 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (Atkinson, 2003) [Cavalli et al. (2002) measured a rate coefficient ratio of $k$(HO + 1-butanol)/$k$(HO + cyclohexane) = 1.10 ± 0.02].

(c) HO radicals were generated by the photolysis of $CH_3ONO$ in air, and the concentrations of 1-butanol and *p*-xylene (the reference compound) were measured by GC. The measured rate coefficient ratio $k$(HO + 1-butanol)/$k$(HO + *p*-xylene) = 0.72 ± 0.03 is placed on an absolute basis using $k$(HO + *p*-xylene) = $1.43 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (Calvert et al., 2002).

(d) HO radicals were generated by the photolysis of $H_2O_2$ in 1 atmosphere of air at 254 nm. The concentrations of 1-butanol and propane (the reference compound) were measured by GC. The measured rate coefficient ratio, $k$(HO + 1-butanol)/$k$(HO + propane), is placed on an absolute basis using $k$(HO + propane) = $1.07 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 295 K (Atkinson, 2003; IUPAC, 2019).

## Preferred Values

| Parameter | Value | *T*/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $8.5 \times 10^{-12}$ | 298 |
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $5.3 \times 10^{-12} \exp(140/T)$ | 260-380 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.06 | 298 |
| $\Delta$ E/R | ± 200 | 260-380 |

*Comments on Preferred Values*

The absolute rate study of Yujing and Mellouki (2001), the sole temperature-dependence study, is used to derive the preferred values. The 298 K coefficient from the study of Yujing and Mellouki (2001) is in good agreement with the room temperature absolute and relative rate coefficients of Wallington and Kurylo (1987), Nelson et al. (1990), Cavalli et al. (2002) and Wu et al. (2003), but is 18% lower than the relative rate coefficient of Oh and Andino (2001).

## References

Atkinson, R.: Atmos. Chem. Phys. 3, 2233, 2003.

Calvert, J. G., Atkinson, R., Becker, K. H., Kamens, R. M., Seinfeld, J. H., Wallington, T. J. and Yarwood, G.: The Mechanisms of Atmospheric Oxidation of Aromatic Hydrocarbons, Oxford University Press, New York, NY, 2002.

Campbell, I. M., McLaughlin, D. F. and Handy, B. J.: Chem. Phys. Lett. 38, 362, 1976.

Cavalli, F., Geiger, H., Barnes, I. and Becker, K. H.: Environ. Sci. Technol. 36, 1263, 2002.

IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

Nelson, L., Rattigan, O., Neavyn, R., Sidebottom, H., Treacy, J. and Nielsen, O. J.: Int. J. Chem. Kinet. 22, 1111, 1990.

Oh, S. and Andino, J. M.: Int. J. Chem. Kinet. 33, 422, 2001.

Wallington, T. J. and Kurylo, M. J.: Int. J. Chem. Kinet. 19, 1015, 1987.

Wu, H., Mu, Y., Zhang, X. and Jiang, G.: Int. J. Chem. Kinet. 35, 81, 2003.

Yujing, M. and Mellouki, A.: Chem. Phys. Lett. 333, 63, 2001.

## HOx_VOC28

## HO + $CH_3CH(OH)CH_2CH_3$ → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(8.58 \pm 0.49) \times 10^{-12}$ | 296 ± 2 | Chew and Atkinson, 1996 | RR (a) |
| $(8.80 \pm 0.14) \times 10^{-12}$ | 297 ± 3 | Baxley and Wells, 1998 | RR (b,c) |
| $(7.57 \pm 0.44) \times 10^{-12}$ | 297 ± 3 | Baxley and Wells, 1998 | RR (b,d) |

### Comments

(a) HO radicals were generated by the photolysis of $CH_3ONO$ in air, and the concentrations of 2-butanol and cyclohexane (the reference compound) were measured by GC. The measured rate coefficient ratio of $k$(HO + 2-butanol)/$k$(HO + cyclohexane) = 1.24 ± 0.07 is placed on an absolute basis using $k$(HO + cyclohexane) = $6.92 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 296 K (Atkinson, 2003).

(b) HO radicals were generated by the photolysis of $CH_3ONO$ in air, and the concentrations of 2-butanol and *n*-nonane and *n*-dodecane (the reference compounds) were measured by GC. The measured rate coefficient ratios of $k$(HO + 2-butanol)/$k$(HO + *n*-nonane) and $k$(HO + 2-butanol)/$k$(HO + *n*-dodecane) are placed on an absolute basis by use of rate coefficients at 297 K of $k$(HO + *n*-nonane) = $9.69 \times 10^{-12}$ and $k$(HO + *n*-dodecane) = $1.32 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson, 2003).

(c) Relative to HO + *n*-nonane.

(d) Relative to HO + *n*-dodecane.

### Preferred Values

| Parameter | Value | *T*/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $8.7 \times 10^{-12}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.08 | 298 |

*Comments on Preferred Values*

The preferred value is based on the relative rate coefficient of Chew and Atkinson (1996) and that of Baxley and Wells (1998) relative to HO + *n*-nonane, which are in excellent agreement. The rate coefficient of Baxley and Wells (1998) measured relative to that for HO + *n*-dodecane, while in agreement with the other two rate coefficients (Chew and Atkinson, 1996; Baxley and Wells, 1998), is more uncertain because of the small data-base for HO + *n*-dodecane (Atkinson, 2003), and hence this rate coefficient is not used in the evaluation.

### References

Atkinson, R.: Atmos. Chem. Phys. 3, 2233, 2003.
Baxley, J. S. and Wells, J. R.: Int. J. Chem. Kinet. 30, 745, 1998.
Chew, A. A. and Atkinson, R.: J. Geophys. Res. 101, 28649, 1996.

## HOx_VOC29

### $HO + (CH_3)_2C(OH)CH=CH_2 \rightarrow$ products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $8.2 \times 10^{-12} \exp[(610 \pm 50)/T]$ | 231-300 | Rudich et al., 1995 | PLP-LIF (a) |
| $(6.4 \pm 0.6) \times 10^{-11}$ | 298 | | |
| $(6.32 \pm 0.27) \times 10^{-11}$ | 300 | Baasandorj and Stevens, 2007 | DF-LIF (b) |
| *Relative Rate Coefficients* | | | |
| $(3.81 \pm 0.80) \times 10^{-11}$ | 298 ± 2 | Fantechi et al., 1998a | RR (c,d) |
| $(4.64 \pm 1.80) \times 10^{-11}$ | 298 ± 2 | Fantechi et al., 1998a | RR (c,e) |
| $(6.93 \pm 0.54) \times 10^{-11}$ | 295 ± 1 | Ferronato et al., 1998 | RR (e,f) |
| $(6.72 \pm 0.78) \times 10^{-11}$ | 295 ± 1 | Ferronato et al., 1998 | RR (f,g) |
| $(5.64 \pm 0.13) \times 10^{-11}$ | 296 ± 2 | Papagni et al., 2001 | RR (h) |
| $(7.01 \pm 0.28) \times 10^{-11}$ | 298 ± 2 | Imamura et al., 2004 | RR (i,j) |
| $(7.03 \pm 0.32) \times 10^{-11}$ | 298 ± 2 | Imamura et al., 2004 | RR (e,i) |
| $(5.6 \pm 0.2) \times 10^{-11}$ | 298 ± 2 | Carrasco et al., 2007 | RR (d,i) |

## Comments

(a) Rate coefficients for the reactions of HO, $H^{18}O$ and DO radicals with 2-methyl-3-buten-2-ol were measured, in the presence and absence of $O_2$ [up to 13.5 Torr (18 mbar) $O_2$ in the case of the HO radical reaction], over the temperature range 231-410 K. Above ~350 K the rate coefficients decreased with increasing temperature faster than predicted based on extrapolation of the lower temperature data. For the HO radical reaction, the rate coefficients in the presence of 2-13.5 Torr (2.7-18 mbar) of $O_2$ were up to 15-20% higher than in the absence of $O_2$, while the measured rate coefficients for the DO radical reaction were invariant to the presence or absence of $O_2$. HO radicals were observed to be formed in the DO radical reaction, and the rate coefficients of the DO radical and $H^{18}O$ radical reactions were essentially identical to those for the HO radical reactions in the presence of $O_2$. These data indicated that the measured rate coefficients from the HO radical reaction in the absence of $O_2$ are low because of HO radical regeneration, whereas $H^{18}O$ and DO radical regeneration does not occur from reactions of $H^{18}O$ and DO radicals with 2-methyl-3-buten-2-ol (HO radicals being formed by elimination of the –OH group in the 2-methyl-3-buten-2-ol in the absence of $O_2$). The rate coefficient cited is derived (Rudich et al., 1995) from the rate coefficients measured for the HO and DO radical reactions in the presence of $O_2$ over the temperature range 230-300 K, and is expected to be applicable to atmospheric conditions.

(b) Rate coefficients were measured over the temperature range 300-415 K at total pressures of helium diluent of 2-5 Torr (2.7-6.7 mbar), in the presence and absence of $O_2$. The room temperature rate coefficient measured in the presence of ~5-15% $O_2$ was ~15% higher than that measured in the absence of $O_2$ [as also observed by Rudich et al. (1995); see Comment (a)]. While the rate coefficient at 300 K was independent of total pressure over the range 2-5 Torr (2.7-6.7 mbar), at ≥335 K the measured rate coefficients in the presence of $O_2$ were pressure dependent. These observations indicate that at temperatures ≥335 K and pressures <5 Torr (6.7 mbar) the reaction is in the fall-off regime. Hence only the 300 K pressure-independent rate coefficient is listed in the table. Rate coefficients were also measured for the reaction of DO radicals with 2-methyl-3-buten-2-ol over the same temperature range, with a 300 K rate coefficient of (6.61 ± 0.66) × $10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$.

(c) HO radicals were generated by the photolysis of $H_2O_2$ at 253.7 nm in air at 987 ± 7 (740 ± 5) mbar pressure. The concentrations of 2-methyl-3-buten-2-ol and isoprene (or propene) [the reference compounds] were measured during the experiments by FTIR spectroscopy. The measured rate coefficient ratios *k*(HO + 2-methyl-3-buten-2-ol)/*k*(HO + isoprene) and *k*(HO + 2-methyl-3-buten-2-ol)/*k*(HO + propene) are placed on an absolute basis using rate coefficients at 298 K and atmospheric pressure of *k*(HO + isoprene) = 1.00 × $10^{-10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ (Atkinson and Arey, 2003; IUPAC, 2019) and *k*(HO + propene) = 2.86 × $10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ (IUPAC, 2019).

(d) Relative to *k*(HO + isoprene).

(e) Relative to *k*(HO + propene).

(f) HO radicals were generated by the photolysis (340-400 nm) of $^{13}CH_3ONO$-NO-$(CH_3)_2C(OH)CH{=}CH_2$-propene (or ethene) [the reference compounds]-air mixtures at 933 mbar (700 Torr) pressure. The concentrations of 2-methyl-3-buten-2-ol and propene (or ethene) were measured by FTIR spectroscopy. The measured rate coefficient ratios of *k*(HO + 2-methyl-3-buten-2-ol)/*k*(HO + propene) = 2.4 ± 0.2 and *k*(HO + 2-methyl-3-buten-2-ol)/*k*(HO + ethene) = 8.5 ± 0.9 are placed on an absolute basis using rate coefficients at 295 K and atmospheric pressure of air of *k*(HO + propene) = 2.89 × $10^{-11}$ and *k*(HO + ethene) = 7.91 × $10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ (IUPAC, 2019).

(g) Relative to *k*(HO + ethene).

(h) HO radicals were generated by the photolysis (at ≥300 nm) of $CH_3ONO$-NO-$(CH_3)_2C(OH)CH{=}CH_2$-1,3,5-trimethylbenzene (the reference compound)-air mixtures at 987 mbar (740 Torr) pressure. The concentrations of 2-methyl-3-buten-2-ol and 1,3,5-trimethylbenzene were measured by GC. The measured rate coefficient ratio of *k*(HO + 2-methyl-3-buten-2-ol)/*k*(HO + 1,3,5-trimethylbenzene) = 0.995 ± 0.022 is placed on an absolute basis using *k*(HO + 1,3,5-trimethylbenzene) = 5.67 × $10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at 296 K (Atkinson and Arey, 2003).

(i) HO radicals were generated by the photolysis of $CH_3ONO$-NO-$(CH_3)_2C(OH)CH{=}CH_2$-di-*n*-butyl ether, propene or isoprene (the reference compounds)-air mixtures at atmospheric pressure. The concentrations of 2-methyl-3-buten-2-ol and the reference compounds were measured by FTIR spectroscopy. The measured rate coefficient ratios of *k*(HO + 2-methyl-3-buten-2-ol)/*k*(HO + di-*n*-butyl ether) = 2.32 ± 0.10 (Imamura et al., 2004), *k*(HO + 2-methyl-3-buten-2-ol)/*k*(HO + propene) = 2.46 ± 0.12 (Imamura et al., 2004) and *k*(HO + 2-methyl-3-buten-2-ol)/*k*(HO + isoprene) = 0.56 ± 0.02 (Carrasco et al., 2007) are placed on an absolute basis using rate coefficients at 298 K and atmospheric pressure of air of *k*(HO + di-*n*-butyl ether) = 2.78 × $10^{-11}$ (Mellouki et al., 1995), *k*(HO + propene) = 2.86 × $10^{-11}$ (IUPAC, 2019), and *k*(HO + isoprene) = 1.00 × $10^{-10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ (Atkinson and Arey, 2003; IUPAC, 2019).

(j) Relative to *k*(HO + di-*n*-butyl ether).

**Preferred Values**

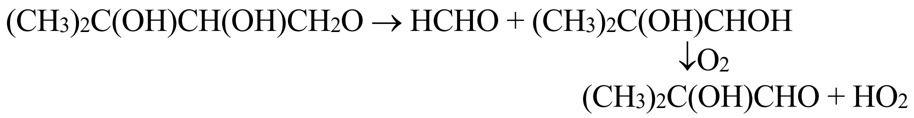
| Parameter | Value | *T*/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.5 \times 10^{-11}$ | 298 |
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $8.4 \times 10^{-12} \exp(610/T)$ | 230-300 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.08 | 298 |
| $\Delta E/R$ | ± 200 | 230-300 |

*Comments on Preferred Values*

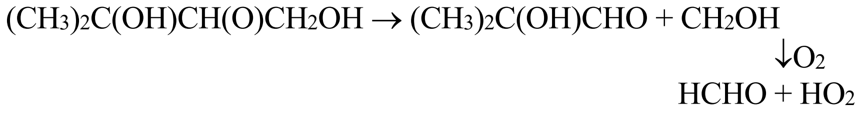
The room temperature rate coefficients of Rudich et al. (1995), Ferronato et al. (1998), Papagni et al. (2001), Imamura et al. (2004), Baasandorj and Stevens (2007) and Carrasco et al. (2007) are in reasonable agreement, although the rate coefficient of Ferronato et al. (1998) relative to ethene is somewhat higher than those of Rudich et al. (1995), Papagni et al. (2001), Imamura et al. (2004), Baasandorj and Stevens (2007) and Carrasco et al. (2007) and that of Ferronato et al. (1998) relative to propene. The two relative rate coefficients of Fantechi et al. (1998a) are significantly lower than the values measured by Rudich et al. (1995), Ferronato et al. (1998), Papagni et al. (2001), Imamura et al. (2004), Baasandorj and Stevens (2007) and Carrasco et al. (2007). The preferred 298 K rate coefficient is the average of the absolute and relative rate coefficients of Rudich et al. (1995), Ferronato et al. (1998), Papagni et al. (2001), Imamura et al. (2004) and Carrasco et al. (2007). The preferred temperature dependence is that reported by Rudich et al. (1995), and the pre-exponential factor is adjusted to fit the preferred 298 K rate coefficient.

The reaction proceeds almost totally by initial addition of HO to the C=C bond (Fantechi et al., 1998b; Ferronato et al., 1998; Alvarado et al., 1999; Spaulding et al., 2002; Reisen et al., 2003; Carrasco et al., 2007). In the presence of NO at atmospheric pressure of air the observed products are formaldehyde, acetone, glycolaldehyde, 2-hydroxy-2-methylpropanal [$(CH_3)_2C(OH)CHO$], and dihydroxynitrates [presumed to be $(CH_3)_2C(OH)CH(OH)CH_2ONO_2$ and $(CH_3)_2C(OH)CH(ONO_2)CH_2OH$] (Fantechi et al., 1998b; Ferronato et al., 1998; Alvarado et al., 1999; Spaulding et al., 2002; Reisen et al., 2003; Carraso et al., 2007). Based on the product studies of Ferronato et al. (1998), Alvarado et al. (1999), Reisen et al. (2003) and Carrasco et al. (2007) carried out in the presence of NO, the product yields are: formaldehyde, 35 ± 4% (Ferronato et al., 1998), 29 ± 3% (Alvarado et al., 1999) and 33 ± 8% (Carrasco et al., 2007); acetone, 52 ± 5% (Ferronato et al., 1998), 58 ± 4% (Alvarado et al., 1999) and 67 ± 5% (Carrasco et al., 2007); glycolaldehyde, 50 ± 5% (Ferronato et al., 1998), 61 ± 9% (Alvarado et al., 1999) and 78 ± 20% (Carrasco et al., 2007); 2-hydroxy-2-methylpropanal, 31 ± 4% (Reisen et al., 2003) and 31 ± 11% (Carrasco et al., 2007) [note that Carrasco et al. (2007) had a standard of 2-hydroxy-2-methylpropanal available, in contrast to Riesen et al. (2003)]; and dihydroxynitrates, 5 ± 2% (Alvarado et al., 1999).

The reaction mechanism is discussed in detail in Alvarado et al. (1999) and Carrasco et al. (2007). Reactions of the $(CH_3)_2C(OH)CH(OH)CH_2OO$ and $(CH_3)_2C(OH)CH(OO)CH_2OH$ peroxy radicals (formed after addition of $O_2$ to the initially formed $(CH_3)_2C(OH)CH(OH)CH_2$ and $(CH_3)_2C(OH)CHCH_2OH$ radicals) with NO lead to the formation of the dihydroxynitrates $(CH_3)_2C(OH)CH(OH)CH_2ONO_2$ and $(CH_3)_2C(OH)CH(ONO_2)CH_2OH$ or $NO_2$ plus the dihydroxyalkoxy radicals $(CH_3)_2C(OH)CH(OH)CH_2O$ and $(CH_3)_2C(OH)CH(O)CH_2OH$. At room temperature and atmospheric pressure of air the dominant fate of these dihydroxyalkoxy radicals is decomposition:

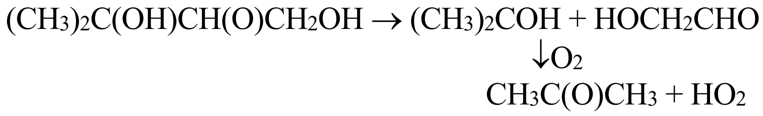


$$\begin{array}{l} (CH_3)_2C(OH)CH(OH)CH_2O \rightarrow HCHO + (CH_3)_2C(OH)CHOH \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow O_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad (CH_3)_2C(OH)CHO + HO_2 \end{array}$$



$$\begin{array}{l} (CH_3)_2C(OH)CH(O)CH_2OH \rightarrow (CH_3)_2C(OH)CHO + CH_2OH \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow O_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad HCHO + HO_2 \end{array}$$

and/or



$$\begin{array}{l} (CH_3)_2C(OH)CH(O)CH_2OH \rightarrow (CH_3)_2COH + HOCH_2CHO \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow O_2 \\ \qquad\qquad\qquad\qquad\qquad CH_3C(O)CH_3 + HO_2 \end{array}$$

Hence, as observed, it is expected that HCHO and $(CH_3)_2C(OH)CHO$ will be formed in the same yield [~31%], and that $HOCH_2CHO$ and $CH_3C(O)CH_3$ will be formed in the same yield [~60%] (Ferronato et al., 1998; Alvarado et al., 1999; Reisen et al., 2003; Carrasco et al., 2007). Fantechi et al. (1998b) and Carrasco et al. (2007) have investigated the reaction in the absence of NO (see Carrasco et al., 2007, for details).

## References

Alvarado, A., Tuazon, E. C., Aschmann, S. M., Arey, J. and Atkinson, R.: Atmos. Environ., 33, 2893, 1999.
Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
Baasandorj, M. and Stevens, P. S.: J. Phys. Chem A, 111, 640, 2007.
Carrasco, N., Doussin, J. F., O'Connor, M., Wenger, J. C., Picquet-Varrault, B., Durand-Jolibois, R. and Carlier, P.: J. Atmos. Chem., 56, 33, 2007.
Fantechi, G., Jensen, N. R., Hjorth, J. and Peeters, J.: Int. J. Chem. Kinet., 30, 589, 1998a.
Fantechi, G., Jensen, N. R., Hjorth, J. and Peeters, J.: Atmos. Environ., 32, 3547, 1998b.
Ferronato, C., Orlando, J. J. and Tyndall, G. S.: J. Geophys. Res., 103, 25579, 1998.
Imamura, T., Iida, Y., Obi, K., Nagatani, I., Nakagawa, K., Patroescu-Klotz, I., and Hatakeyama, S.: Int. J. Chem. Kinet., 36, 379, 2004.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation, (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.) http://iupac.pole-ether.fr/index.html., 2019.
Mellouki, A., Teton, S., Le Bras, G.: Int. J. Chem. Kinet. 27, 791, 1995.
Papagni, C., Arey, J. and Atkinson, R.: Int. J. Chem. Kinet., 33, 142, 2001.
Reisen, F., Aschmann, S. M., Atkinson, R. and Arey, J.: Environ. Sci. Technol., 37, 4664, 2003.
Rudich, Y., Talukdar, R. K., Burkholder, J. B. and Ravishankara, A. R.: J. Phys. Chem. 99, 12188, 1995.
Spaulding, R., Charles, M. J., Tuazon, E. C. and Lashley, M.: J. Am. Soc. Mass Spectrom., 13, 530, 2002.

**HOx_VOC31**

## HO + 3-methylfuran → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| Relative Rate Coefficients | | | |
| $(9.26 \pm 0.24) \times 10^{-11}$ | 296 ± 2 | Atkinson et al., 1989 | RR (a) |

### Comments

(a) Carried out at atmospheric pressure of air. HO radicals were generated by the photolysis of methyl nitrite-NO-air mixtures, and the concentrations of 3-methylfuran and 2,3-dimethyl-2-butene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k$(HO + 3-methylfuran)/$k$(HO + 2,3-dimethyl-2-butene) = $0.842 \pm 0.021$ is placed on an absolute basis using $k$(HO + 2,3-dimethyl-2-butene) = $1.10 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 296 K (Atkinson, 1997).

### Preferred Values

| Parameter | Value | *T*/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $9.3 \times 10^{-11}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.15 | 298 |

*Comments on Preferred Values*

The preferred value is based on the sole study of this reaction by Atkinson et al. (1989). The reaction of HO radicals with 3-methylfuran is expected to proceed almost exclusively by initial HO radical addition to the C=C bonds (Atkinson et al., 1989).

### References

Atkinson, R.: J. Phys. Chem. Ref. Data, 26, 215, 1997.
Atkinson, R., Aschmann, S. M., Tuazon, E. C., Arey, J. and Zielinska, B.: Int. J. Chem. Kinet., 21, 593, 1989.

## HOx_VOC33

### HO + $(CH_3)_2C(OH)CHO \rightarrow$ products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(1.49 \pm 0.21) \times 10^{-11}$ | 296 ± 2 | Baker et al., 2004 | RR (a) |
| $(1.36 \pm 0.14) \times 10^{-11}$ | 295 ± 2 | Carrasco et al., 2006 | RR (b) |
| $(1.23 \pm 0.06) \times 10^{-11}$ | 293 ± 2 | Carrasco et al., 2006 | RR (c) |

### Comments

(a) HO radicals were generated by the photolysis of $CH_3ONO$-NO-air mixtures at wavelengths >300 nm. $(CH_3)_2C(OH)CHO$ was generated in situ from the reaction of HO radicals with $(CH_3)_2C(OH)CH{=}CH_2$ and its concentration was measured during the reactions using solid phase microextraction fibers pre-coated with *o*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine for on-fiber derivatization of carbonyl compounds, with subsequent GC analyses. From the time-concentration behavior of $(CH_3)_2C(OH)CHO$ during the reactions, the rate coefficient ratio $k(HO + (CH_3)_2C(OH)CHO)/k(HO + (CH_3)_2C(OH)CH{=}CH_2) = 0.234 \pm 0.033$ was derived. This rate coefficient ratio is placed on an absolute basis using $k(HO + (CH_3)_2C(OH)CH{=}CH_2) = 6.36 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 296 K (IUPAC, 2019).

(b) HO radicals were generated by the photolysis of HONO at ~420 nm in synthetic air at atmospheric pressure. A synthesized sample of $(CH_3)_2C(OH)CHO$ was used, and the concentrations of $(CH_3)_2C(OH)CHO$ and isoprene (the reference compound) were monitored by FTIR spectroscopy. The measured rate coefficient ratio of $k(HO + (CH_3)_2C(OH)CHO)/k(HO + \text{isoprene}) = 0.135 \pm 0.014$ is placed on an absolute basis using $k(HO + \text{isoprene} = 1.01 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 296 K (IUPAC, 2019).

(c) HO radicals were generated by the photolysis of $H_2O_2$ in air by natural sunlight in the EUPHORE chamber at atmospheric pressure. A synthesized sample of $(CH_3)_2C(OH)CHO$ was used, and the concentrations of $(CH_3)_2C(OH)CHO$ and di-*n*-butyl ether (the reference compound) were monitored by FTIR spectroscopy. The measured rate coefficient ratio of $k(HO + (CH_3)_2C(OH)CHO)/k(HO + \text{di-}n\text{-butyl ether}) = 0.43 \pm 0.02$ is placed on an absolute basis using $k(HO + \text{di-}n\text{-butyl ether}) = 2.87 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 293 K (Mellouki et al., 1995).

### Preferred Values

| Parameter | Value | *T*/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $1.4 \times 10^{-11}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.10 | 298 |

*Comments on Preferred Values*

The two kinetic studies of this reaction are in good agreement, and the preferred value is the average of the three measurements, all of which are relative rate measurements using different reference compounds. Product studies show that acetone is formed in essentially 100% yield in both the presence and absence of NO, with molar yields of 1.06 ± 0.06 in the presence of NO and 1.10 ± 0.06 in the absence of NO (Carrasco et al., 2006). The reaction is expected to proceed mainly by H-atom abstraction from the –CHO group (Baker et al., 2004; Carrasco et al., 2006).

## References

Baker, J., Arey. J. and Atkinson, R.: J. Phys. Chem. A, 108, 7032, 2004.
Carrasco, N., Doussin, J.-F., Picquet-Varrault, B. and Carlier, P.: Atmos. Environ. 40, 2011, 2006.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Mellouki, A., Téton, S., Le Bras, G.: Int. J. Chem. Kinet. 27, 791, 1995.

**HOx_VOC42**

## HO + 1-$C_4H_9ONO_2$ → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $(1.74 \pm 0.19) \times 10^{-12}$ | 298 ± 2 | Nielsen et al., 1991 | PR-RA (a) |
| | | | |
| *Relative Rate Coefficients* | | | |
| $(1.31 \pm 0.10) \times 10^{-12}$ | 299 ± 2 | Atkinson et al., 1982 | RR (b,c) |
| $(1.65 \pm 0.18) \times 10^{-12}$ | 298 ± 2 | Atkinson and Aschmann, 1989 | RR (b,d) |
| $(1.47 \pm 0.08) \times 10^{-12}$ | 298 ± 2 | Nielsen et al., 1991 | RR (b,e) |

## Comments

(a) Carried out at a total pressure of 1 bar Ar.

(b) HO radicals were generated by the photolysis of $CH_3ONO$ in air at atmospheric pressure (0.97 bar to 1.0 bar). The concentrations of 1-butyl nitrate and the reference organic were measured by GC.

(c) The measured rate coefficient ratio of $k$(HO + 1-butyl nitrate)/$k$(HO + cyclohexane) = 0.187 ± 0.014 is placed on an absolute basis using $k$(HO + cyclohexane) = $7.00 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 299 K (Atkinson, 2003). Experiments were carried out in an ~75 liter Teflon chamber, and the data were interpreted as involving concurrent photolysis of 1-butyl nitrate.

(d) Experiments were carried out in a 6400 liter Teflon chamber, and irradiations were also carried out in the absence of $CH_3ONO$, allowing the photolysis rate to be accurately allowed for in the data analysis. The measured rate coefficient ratio of $k$(HO + 1-butyl nitrate)/$k$(HO + cyclohexane) = 0.237 ± 0.025 is placed on an absolute basis using $k$(HO + cyclohexane) = $6.97 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (Atkinson, 2003). These data supersede those of Atkinson et al. (1982).

(e) The measured rate coefficient ratio $k$(HO + 1-butyl nitrate)/$k$(HO + 2-methylpropane) is placed on an absolute basis using $k$(HO + 2-methylpropane) = $2.12 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (Atkinson, 2003).

## Preferred Values

| Parameter | Value | $T$/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $1.6 \times 10^{-12}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.06 | 298 |

*Comments on Preferred Values*

The absolute and relative rate coefficients of Atkinson and Aschmann (1989) (which supersedes the earlier data of Atkinson et al., 1982) and Nielsen et al. (1991) are in good agreement. The preferred value is an average of the absolute and relative rate constants of

Atkinson and Aschmann (1989) and Nielsen et al., (1991). By analogy with the reaction of the HO radical with 2-propyl nitrate (IUPAC, 2019), the temperature dependence of the rate coefficient at temperatures below 300 K is likely to be small.

## References

Atkinson, R.: Atmos. Chem. Phys. 3, 2233, 2003.
Atkinson, R. and Aschmann, S. M.: Int. J. Chem. Kinet. 21, 1123, 1989.
Atkinson, R., Aschmann, S. M., Carter, W. P. L. and Winer, A. M.: Int. J. Chem. Kinet. 14, 919, 1982.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Nielsen, O. J., Sidebottom, H. W., Donlon, M. and Treacy, J.: Chem. Phys. Lett. 178, 163, 1991.

**HOx_VOC43**

## HO + 2-$C_4H_9ONO_2$ → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(6.4 \pm 1.0) \times 10^{-13}$ | 299 ± 2 | Atkinson et al., 1982 | RR (a,b) |
| $(8.6 \pm 1.5) \times 10^{-13}$ | 298 ± 2 | Atkinson and Aschmann, 1989 | RR (a,c) |

### Comments

(a) HO radicals were generated by the photolysis of $CH_3ONO$ in one atmosphere of air. The concentrations of 2-butyl nitrate and the reference organic were measured by GC.

(b) Experiments were carried out in an ~75 liter Teflon chamber, and the data were interpreted as involving concurrent photolysis of 2-butyl nitrate. The measured rate constant ratio of $k$(HO + 2-butyl nitrate)/$k$(HO + cyclohexane) = 0.091 ± 0.013 is placed on an absolute basis using $k$(HO + cyclohexane) = $7.00 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 299 K (Atkinson, 2003).

(c) Experiments were carried out in a 6400 liter Teflon chamber, and irradiations were also carried out in the absence of $CH_3ONO$ allowing the loss of 2-butyl nitrate via photolysis rate to be measured and accounted for in the data analysis. The measured rate coefficient ratio of $k$(HO + 2-butyl nitrate)/$k$(HO + cyclohexane) = 0.123 ± 0.021 is placed on an absolute basis using $k$(HO + cyclohexane) = $6.97 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (Atkinson, 2003). These data supersede those of Atkinson et al. (1982).

### Preferred Values

| Parameter | Value | $T$/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $8.6 \times 10^{-13}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.15 | 298 |

*Comments on Preferred Values*

The preferred value is based on the rate coefficient of Atkinson and Aschmann (1989), which supersedes the earlier study of Atkinson et al. (1982). By analogy with the reaction of the HO radical with 2-propyl nitrate (IUPAC, 2019), the temperature dependence of the rate coefficient at temperatures below 300 K is likely to be small.

### References

Atkinson, R.: Atmos. Chem. Phys. 3, 2233, 2003.
Atkinson, R. and Aschmann, S. M.: Int. J. Chem. Kinet. 21, 1123, 1989.
Atkinson, R., Aschmann, S. M., Carter, W. P. L. and Winer, A. M.: Int. J. Chem. Kinet. 14, 919, 1982.

IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

## HOx_VOC46

## HO + $CH_3CH_2C(O)CH_2ONO_2$ → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | *Reference* | Technique/ Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(8.21 \pm 1.38) \times 10^{-13}$ | 298 ± 2 | Zhu et al., 1991 | RR (a) |

### Comments

(a) HO radicals were generated by the photolysis of $CH_3ONO$-NO-$N_2$-$O_2$ mixtures at 1 bar pressure. The concentrations of $CH_3CH_2C(O)CH_2ONO_2$ and *n*-butane were measured during the experiments by GC, and the measured rate constant ratio of $k$(HO + $CH_3CH_2C(O)CH_2ONO_2$)/$k$(HO + *n*-butane) = 0.357 ± 0.060 is placed on an absolute basis using $k$(HO + *n*-butane) = $2.3 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019).

### Preferred Values

| **Parameter** | **Value** | ***T*/K** |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $8.2 \times 10^{-13}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.30 | 298 |

*Comments on Preferred Values*

The preferred value is based on the sole study of Zhu et al. (1991), but with a higher uncertainty.

### References

IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Zhu, T., Barnes, I. and Becker, K. H.: J. Atmos. Chem. 13, 301, 1991.

## HOx_VOC47

## HO + $CH_3CH(ONO_2)C(O)CH_3 \rightarrow$ products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(1.15 \pm 0.13) \times 10^{-12}$ | 298 ± 2 | Zhu et al., 1991 | RR (a) |

### Comments

(a) HO radicals were generated by the photolysis of $CH_3ONO$-NO-$N_2$-$O_2$ mixtures at 1 bar pressure. The concentrations of $CH_3CH(ONO_2)C(O)CH_3$ and *n*-butane were measured during the experiments by GC, and the measured rate constant ratio of $k$(HO + $CH_3CH(ONO_2)C(O)CH_3$)/$k$(HO + *n*-butane) = $0.499 \pm 0.056$ is placed on an absolute basis using $k$(HO + *n*-butane) = $2.3 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019).

### Preferred Values

| Parameter | Value | ***T*/K** |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $1.2 \times 10^{-12}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.30 | 298 |

*Comments on Preferred Values*

The preferred value is based on the sole study of Zhu et al. (1991), but with a higher uncertainty.

### References

IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Zhu, T., Barnes, I. and Becker, K. H.: J. Atmos. Chem. 13, 301, 1991.

## HOx_VOC48

## HO + $CH_2=C(CH_3)C(O)OONO_2$ (MPAN) → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(3.33 \pm 0.40) \times 10^{-12}$ | 298 ± 2 | Grosjean et al., 1993 | RR (a) |
| $(3.31 \pm 0.51) \times 10^{-11}$ | 275 ± 3 | Orlando et al., 2002 | RR (b,c) |
| $(2.94 \pm 0.46) \times 10^{-11}$ | 275 ± 3 | Orlando et al., 2002 | RR (b,d) |

### Comments

(a) Relative rate method carried out at atmospheric pressure of air. HO radicals were generated by the photolysis (using natural sunlight) of ethyl nitrite-air mixtures, and the concentrations of $CH_2=C(CH_3)C(O)OONO_2$ (MPAN) and 1-butyl nitrate (the reference compound) were measured by GC with electron capture detection. The measured rate coefficient ratio of $k$(HO + MPAN)/$k$(HO + 1-butyl nitrate) = 2.08 ± 0.25 is placed on an absolute basis using $k$(HO + 1-butyl nitrate) = $1.6 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (IUPAC, 2019).

(b) Relative rate method carried out in synthetic air at 0.93-0.97 bar. HO radicals were generated by the photolysis of ethyl nitrite-NO-air mixtures, and the concentrations of $CH_2=C(CH_3)C(O)OONO_2$ (MPAN) and ethene and propene (the reference compounds) were measured by *in situ* FTIR spectroscopy. Experiments were carried out at 275 ± 3 K to decrease the rate of thermal decomposition of MPAN (IUPAC, 2019) in the presence of NO. The measured rate coefficient ratios of $k$(HO + MPAN)/$k$(HO + ethene) = 3.9 ± 0.6 and $k$(HO + MPAN)/$k$(HO + propene) = 0.95 ± 0.15 are placed on an absolute basis using rate coefficients at 275 K and atmospheric pressure of air of $k$(HO + ethene) = $8.48 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and $k$(HO + propene) = $3.1 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019).

(c) Relative to HO + ethene.

(d) Relative to HO + propene.

### Preferred Values

| Parameter | Value | $T$/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $2.9 \times 10^{-11}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | $^{+0.2}_{-0.5}$ | 298 |

*Comments on Preferred Values*

The rate coefficients measured in the two studies of Grosjean et al. (1993) and Orlando et al. (2002) disagree by a factor of ≈10, for reasons which are not known. The reaction of HO radicals with $CH_2=C(CH_3)C(O)OONO_2$ is expected to proceed almost exclusively by initial HO radical addition to the C=C bond (Grosjean et al., 1993; Orlando et al., 2002), and is expected to have a small (and probably negative) temperature dependence at around room temperature. Support for the Orlando et al. (2002) study arises from data for the structurally similar compound $CH_2=C(CH_3)C(O)OCH_3$ which has a rate coefficient for reaction with HO radicals of $(2.6 \pm 0.5) \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at 298 K (Saunders et al., 1994), which is similar to that measured by Orlando et al. (2002) for HO + MPAN. Accordingly, the preferred value is based on the rate coefficients measured by Orlando et al. (2002) at 275 K, adjusted to 298 K using the temperature dependence observed for HO + propene (IUPAC, 2019), and with appropriately large and asymmetric uncertainties. Formaldehyde and hydroxyacetone have been observed as products of this reaction (Grosjean et al., 1993; Orlando et al., 2002).

## References

Grosjean, D., Williams II, E. L. and Grosjean, E.: Int. J. Chem. Kinet. 25, 921, 1993.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Orlando, J. J., Tyndall, G. S., Bertman, S. B., Chen, W. and Burkholder, J. B.: Atmos. Environ. 36, 1895, 2002.
Saunders, S. M., Baulch, D. L., Cooke, K. M., Pilling, M. J. and Smurthwaite, P. I.: Int. J. Chem. Kinet. 26, 113, 1994.

## HOx_VOC60

$$HO + (CH_3)_3CH \rightarrow H_2O + (CH_3)_3C \quad (1)$$
$$\rightarrow H_2O + (CH_3)_2CHCH_2 \quad (2)$$

### Rate coefficient data ($k = k_1 + k_2$)

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $(2.13 \pm 0.12) \times 10^{-12}$ | $297 \pm 1$ | Greiner, 1967 | FP-KS |
| $8.7 \times 10^{-12} \exp[-(387 \pm 63)/T]$ | 297-498 | Greiner, 1970 | FP-KS |
| $(2.67 \pm 0.17) \times 10^{-12}$ | 298 | | |
| $(2.70 \pm 0.20) \times 10^{-12}$ | 267 | Trevor et al., 1982 | PLP-RF |
| $3.6 \times 10^{-12}$ | 298 | | |
| $(3.62 \pm 0.40) \times 10^{-12}$ | 324 | | |
| $(1.83 \pm 0.34) \times 10^{-12}$ | 296 | Böhland et al., 1984 | PLP-LMR |
| $(1.9 \pm 0.3) \times 10^{-12}$ | 295 | Schmidt et al., 1985 | PLP-LIF |
| $4.31 \times 10^{-17}\, T^{1.80} \exp(175/T)$ | 293-864 | Tully et al., 1986a | PLP-LIF |
| $(2.19 \pm 0.11) \times 10^{-12}$ | 293 | | |
| $(2.09 \pm 0.42) \times 10^{-11}$ | $1146 \pm 15$ | Bott and Cohen, 1989 | SH-RA |
| $(2.11 \pm 0.09) \times 10^{-12}$ | ~298 | Schiffman et al., 1991 | PLP-IR |
| $9.32 \times 10^{-18}\, T^2 \exp[(274 \pm 16)/T]$ | 231-372 | Talukdar et al., 1994 | PLP-LIF |
| $(2.10 \pm 0.16) \times 10^{-12}$ | 298 | | |
| $(2.09 \pm 0.06) \times 10^{-12}$ | 300 | Donahue et al., 1998 | DF-LIF |
| $(2.38 \pm 0.07) \times 10^{-12}$ | 325 | | |
| $(2.47 \pm 0.09) \times 10^{-12}$ | 340 | | |
| $(2.62 \pm 0.08) \times 10^{-12}$ | 375 | | |
| $(2.72 \pm 0.14) \times 10^{-12}$ | 390 | | |
| *Relative Rate Coefficients* | | | |
| $1.9 \times 10^{-11}$ | 793 | Baldwin and Walker, 1964 | RR (a) |
| $9.9 \times 10^{-12}$ | 753 | Baker et al., 1970; Baldwin and Walker, 1979 | RR (a) |
| $(3.43 \pm 0.86) \times 10^{12}$ | 298 | Gorse and Volman, 1972/73, 1974 | RR (b) |
| $(7.88 \pm 0.44) \times 10^{-12}$ | 653 | Hucknall et al., 1975 | RR (c) |
| $2.2 \times 10^{-12}$ | 303 | Wu et al., 1976 | RR (d) |
| $(2.19 \pm 0.05) \times 10^{-12}$ | $300 \pm 1$ | Darnall et al., 1978 | RR (e) |
| $(2.06 \pm 0.05) \times 10^{-12}$ | $297 \pm 2$ | Atkinson et al., 1984 | RR (f) |
| $(2.17 \pm 0.31) \times 10^{-12}$ | $297.8 \pm 0.4$ | Edney et al., 1986 | RR (e) |
| $6.33 \times 10^{-21}\, T^{3.125} \exp(540/T)$ | 229-403 | Wilson et al., 2006 | RR (g) |
| $2.09 \times 10^{-12}$ | 298 | | |

### Comments

(a) Derived from the effects of the addition of small amounts of 2-methylpropane to slowly reacting mixtures of $H_2 + O_2$. The loss of $H_2$ was followed by monitoring the pressure change due to the reaction $2H_2 + O_2 \rightarrow 2H_2O$, and the loss of 2-methylpropane was measured by GC. The rate coefficient ratios $k$(HO + 2-methylpropane)/$k$(HO + $H_2$) = 20 at 793 K (Baldwin and Walker, 1964) and 12.6 at 753 K (Baker et al., 1970; Baldwin and

Walker, 1979) are placed on an absolute basis using $k(HO + H_2) = 7.87 \times 10^{-13}$ at 753 K and $9.62 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 793 K (Atkinson, 2003).

(b) HO radicals were generated by the photolysis of $H_2O_2$ at 254 nm in $H_2O_2$-CO-$O_2$-2-methylpropane mixtures at total pressures of 16-21 Torr (21-28 mbar) (Gorse and Volman, 1972/73). The effect of varying the 2-methylpropane concentration on the $CO_2$ production rate was investigated (Gorse and Volman, 1972/73), and a rate coefficient ratio of $k$(HO + 2-methylpropane)/$k$(HO + CO) = 23.5 derived (Gorse and Volman, 1974). This rate coefficient ratio is placed on an absolute basis using $k(HO + CO) = 1.46 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019, using M = $N_2$).

(c) HO radicals were generated by the decomposition of $H_2O_2$ in a boric acid-coated reaction vessel, and the concentrations of 2-methylpropane and propane (the reference compound) were measured by GC. The measured rate coefficient ratios of $k$(HO + 2-methylpropane)/$k$(HO + propane) = 1.28 ± 0.07 is placed on an absolute value using $k$(HO + propane) = $6.16 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 653 K (IUPAC, 2019).

(d) HO radicals were generated by the photolysis of organic-$NO_x$-$O_2$-air mixtures at atmospheric pressure. 2-Methylpropane and *cis*-2-butene (the reference compound) were measured by GC, and the measured rate coefficient ratio $k$(HO + 2-methylpropane)/$k$(HO + *cis*-2-butene) = 0.04 is placed on an absolute basis using $k$(HO + *cis*-2-butane) = $5.45 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 303 K (IUPAC, 2019).

(e) HO radicals were generated by the photolysis of $CH_3ONO$ in one atmosphere of air. The concentrations of 2-methylpropane and *n*-butane (the reference compound) were measured by GC. The measured rate coefficient ratios $k$(HO + 2-methylpropane)/$k$(HO + *n*-butane) are placed on an absolute basis by using $k$(HO + *n*-butane) = $2.34 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K and $2.37 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 300 K (IUPAC, 2019).

(f) HO radicals were generated by the photolysis of $CH_3ONO$ in one atmosphere of air. The concentrations of 2-methylpropane and *n*-butane (the reference compound) were measured by GC. The measured rate coefficient ratio $k$(HO + 2-methylpropane)/$k$(HO + *n*-butane) = 0.886 ± 0.021 is placed on an absolute basis using $k$(HO + *n*-butane) = $2.33 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 297 K (IUPAC, 2019).

(g) HO radicals were generated by the photolysis of $H_2O$ at 185 nm or, at low temperatures, by the photolysis of $N_2O$ at 185 nm in the presence of $H_2$. The concentrations of 2-methylpropane and *n*-butane (the reference compound) were measured by GC/MS. The measured rate coefficient ratios $k$(HO + 2-methylpropane)/$k$(HO + *n*-butane) are placed on an absolute basis using $k$(HO + *n*-butane) = $2.03 \times 10^{-17} T^2 \exp(78/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019).

**Preferred Values**

| **Parameter** | **Value** | ***T*/K** |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $2.1 \times 10^{-12}$ | 298 |
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $5.4 \times 10^{-12} \exp(-285/T)$ | 210-300 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.04 | 298 |
| $\Delta E/R$ | ± 150 | 210-300 |

*Comments on Preferred Values*

The preferred values are based on the absolute rate coefficients of Tully et al. (1986a), Bott and Cohen (1989), Talukdar et al. (1994) and Donahue et al. (1998) and the relative rate coefficients of Baker et al. (1970) [as re-evaluated by Baldwin and Walker (1979)], Hucknall et al. (1975), Atkinson et al. (1984) [which is taken to supersede the earlier study of Darnall et al. (1978)] and Wilson et al. (2006). The three parameter expression, $k = CT^2 \exp(-D/T)$, was fitted to the rate coefficients from these studies, resulting in $k = 1.17 \times 10^{-17}\ T^2 \exp(213/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ over the temperature range 210-1150 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 250 K and is derived from the three parameter expression with $A = C\, e^2\, T^2$ and $B = D + 2T$. The preferred values are in good agreement with the room temperature absolute and relative rate coefficients of Greiner (1967, 1970), Böhland et al. (1984), Schmidt et al. (1985), Schiffman et al. (1991), Wu et al. (1976), Darnall et al. (1978) and Edney et al. (1986), which were not used in the evaluation of the rate coefficient.

Tully et al. (1986a) also measured rate coefficients for the reaction of the HO radical with 2-methylpropane-$d_1$, 2-methylpropane-$d_9$ and 2-methylpropane-$d_{10}$. Combining their rate coefficients for 2-methylpropane, 2-methylpropane-$d_1$, 2-methylpropane-$d_9$ and 2-methylpropane-$d_{10}$ with the deuterium isotope ratio $k_H/k_D$ for -$CH_3$/-$CD_3$ groups obtained from the 2,2-dimethylpropane (neopentane) reaction (Tully et al., 1985, 1986b), Tully et al. (1986a) derived rate coefficients for H-atom abstraction from the primary C-H bonds of the three $CH_3$ groups ($3k_{\text{primary}}$) and from the tertiary C-H bond in the CH group ($k_{\text{tertiary}}$), of $3k_{\text{primary}} = 3.81 \times 10^{-16}\ T^{1.53} \exp(-391/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ ($6.3 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K) and $k_{\text{tertiary}} = 9.52 \times 10^{-14}\ T^{0.51} \exp(-32/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ ($1.56 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K).

## References

Atkinson, R.: Atmos. Chem. Phys. 3, 2233, 2003.

Atkinson, R., Carter, W. P. L., Aschmann, S. M., Winer, A. M. and Pitts Jr., J. N.: Int. J. Chem. Kinet., 16, 469, 1984.

Baker, R. R., Baldwin, R. R. and Walker, R. W.: Trans. Faraday Soc., 66, 2812, 1970.

Baldwin, R. R. and Walker, R. W.: Trans. Faraday Soc., 60, 1236, 1964.

Baldwin, R. R. and Walker, R. W.: J. Chem. Soc. Faraday Trans. 1, 75, 140, 1979.

Böhland, T., Temps, F. and Wagner, H. Gg.: Zeit. Physik. Chemie Neue Folge, 142, S129, 1984.

Bott, J. F. and Cohen, N.: Int. J. Chem. Kinet., 21, 485, 1989.

Darnall, K. R., Atkinson, R. and Pitts Jr., J. N.: J. Phys. Chem., 82, 1581, 1978.

Donahue, N. M., Anderson, J. G. and Demerjian, K. L.: J. Phys. Chem. A, 102, 3121, 1998.

Edney, E. O., Kleindienst, T. E. and Corse, E. W.: Int. J. Chem. Kinet., 18, 1355, 1986.

Gorse, R. A. and Volman, D. H.: J. Photochem., 1, 1, 1972/73.

Gorse, R. A. and Volman, D. H.: J. Photochem., 3, 115, 1974.

Greiner, N. R.: J. Chem. Phys., 46, 3389, 1967.

Greiner, N. R.: J. Chem. Phys., 53, 1070, 1970.

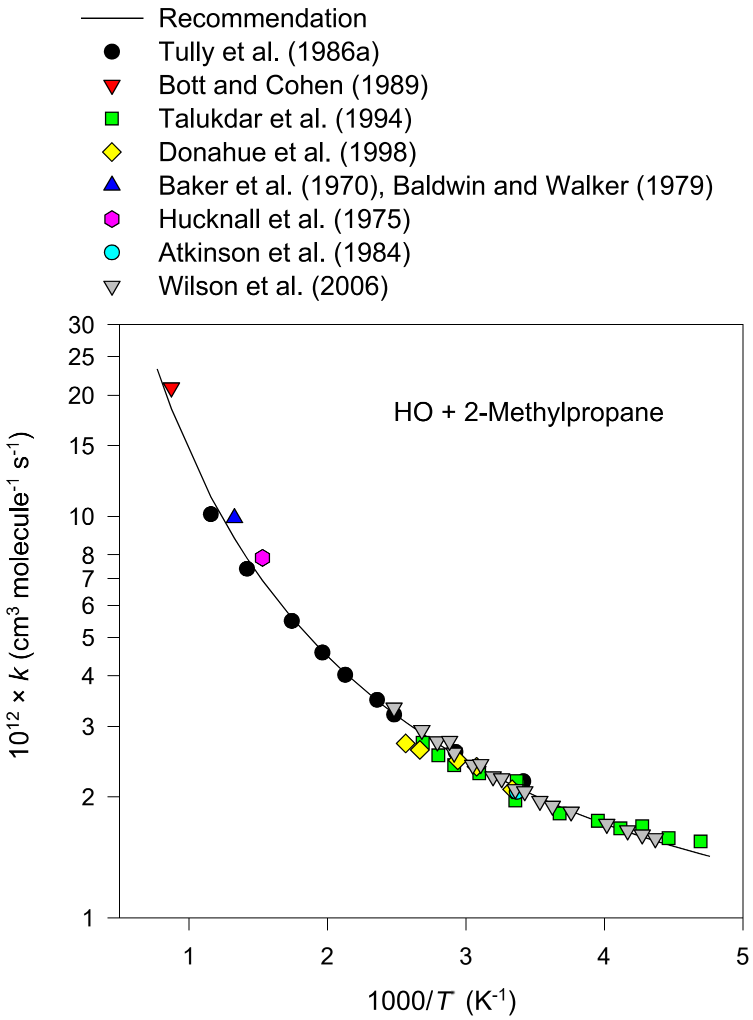
Hucknall, D. J., Booth, D. and Sampson, R. J.: Int. J. Chem. Kinet., Symp. 1, 301, 1975.

IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

Schiffman, A., Nelson Jr., D. D., Robinson, M. S. and Nesbitt, D. J.: J. Phys. Chem., 95, 2629, 1991.

Schmidt, V., Zhu, G. Y., Becker, K. H. and Fink, E. H.: Ber. Bunsenges. Phys. Chem., 89, 321, 1985.

Talukdar, R. K., Mellouki, A., Gierczak, T., Barone, S., Chiang, S.-Y. and Ravishankara, A. R.: Int. J. Chem. Kinet., 26, 973, 1994.
Trevor, P. L., Black, G. and Barker, J. R.: J. Phys. Chem., 86, 1661, 1982.
Tully, F. P., Koszykowski, M. L., and Binkley, J. S.: 20th International Symposium on Combustion, 1984; The Combustion Institute, Pittsburgh, PA, pp. 715-721, 1985.
Tully, F. P., Goldsmith, J. E. M. and Droege, A. T.: J. Phys. Chem., 90, 5932, 1986a.
Tully, F. P., Droege, A. T., Koszykowski, M. L., and Melius, C. F.: J. Phys. Chem., 90, 691, 1986b.
Wilson Jr., E. W., Hamilton, W. A., Kennington, H. R., Evans III, B., Scott, N. W. and DeMore, W. B.: J. Phys. Chem. A, 110, 3593, 2006.
Wu, C. H., Japar, S. M. and Niki, H.: J. Environ. Sci. Health, A11, 191, 1976.



Rate coefficients for HO + 2-Methylpropane.

## HOx_VOC61

### HO + 2-Methylpropene → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $9.2 \times 10^{-12} \exp[(503 \pm 151)/T]$ | 297-424 | Atkinson and Pitts, 1975 | FP-RF (a) |
| $(5.07 \pm 0.51) \times 10^{-11}$ | 297.2 | | |
| *Relative Rate Coefficients* | | | |
| $6.46 \times 10^{-11}$ | 298 | Morris and Niki, 1971a | DF-MS (b) |
| $5.01 \times 10^{-11}$ | 303 | Wu et al., 1976 | RR (c) |
| $5.68 \times 10^{-11}$ | 300 | Barnes et al., 1982 | RR (d) |
| $(5.47 \pm 0.09) \times 10^{-11}$ | 298 ± 2 | Ohta, 1984 | RR (e) |
| $(5.64 \pm 0.25) \times 10^{-11}$ | 295 ± 1 | Atkinson and Aschmann, 1984 | RR (f) |

## Comments

(a) Experiments carried out at 25 Torr (33 mbar) of Ar diluent.

(b) A rate coefficient for HO + 2-methylpropene was obtained relative to that for propene at 1 Torr (1.3 mbar) He diluent by monitoring the decays of 2-methylpropene and propene and the average HO radical concentrations under identical experimental conditions. The rate coefficient ratio $k$(HO + 2-methylpropene)/$k$(HO + propene) = 3.8 is placed on an absolute basis using $k$(HO + propene) = $1.7 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ under the experimental condition used (Morris and Niki, 1971b).

(c) HO radicals were generated by the photolysis of organic-$NO_x$-$O_2$-air mixtures at atmospheric pressure. 2-Methylpropene and *cis*-2-butene (the reference compound) were measured by GC. The measured rate coefficient ratio $k$(HO + 2-methylpropene)/$k$(HO + *cis*-2-butene) = 0.92 is placed on an absolute basis using $k$(HO + *cis*-2-butane) = $5.45 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 303 K (IUPAC, 2019).

(d) HO radicals were generated by decomposition of $HOONO_2$ in the dark in the presence of NO at atmospheric pressure of $N_2$ or air. 2-Methylpropene and ethene (the reference compound) were monitored by GC, and the measured rate coefficient ratio $k$(HO + 2-methylpropene)/$k$(HO + ethene) = 7.3 is placed on an absolute basis using a rate coefficient of $k$(HO + ethene) = $7.78 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 300 K and atmospheric pressure of air (IUPAC, 2019).

(e) HO radicals were generated by the photolysis of $H_2O_2$ at 253.7 nm in 760 Torr (1013 mbar) of $N_2$ or $O_2$ diluent in a quartz vessel. The concentrations of 2-methylpropene and 2-methyl-2-butene (the reference compound) were measured by GC during the experiments. The measured rate coefficient ratios $k$(HO + 2-methylpropene)/$k$(HO + 2-methyl-2-butene) = 0.63 ± 0.01 is placed on an absolute basis using $k$(HO + 2-methyl-2-butene) = $8.69 \times 10^{-11}$ at 298 K and atmospheric pressure of air (Atkinson and Arey, 2003).

(f) HO radicals were generated by the photolysis of $CH_3ONO$ in air at wavelengths >300 nm in a ~60 L Teflon chamber at atmospheric pressure of air. The concentrations of 2-methylpropene and propene (the reference compound) were monitored by GC during the experiments. The measured rate coefficient ratio $k$(HO + 2-methylpropene)/$k$(HO + propene) = 1.95 ± 0.09 is placed on an absolute basis using $k$(HO + propene) = $2.89 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 295 K and atmospheric pressure of air (IUPAC, 2019).

**Preferred Values**

| Parameter | Value | $T$/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $5.1 \times 10^{-11}$ | 298 |
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $9.4 \times 10^{-12} \exp(505/T)$ | 290-430 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.04 | 298 |
| $\Delta E/R$ | ± 200 | 290-430 |

*Comments on Preferred Values*

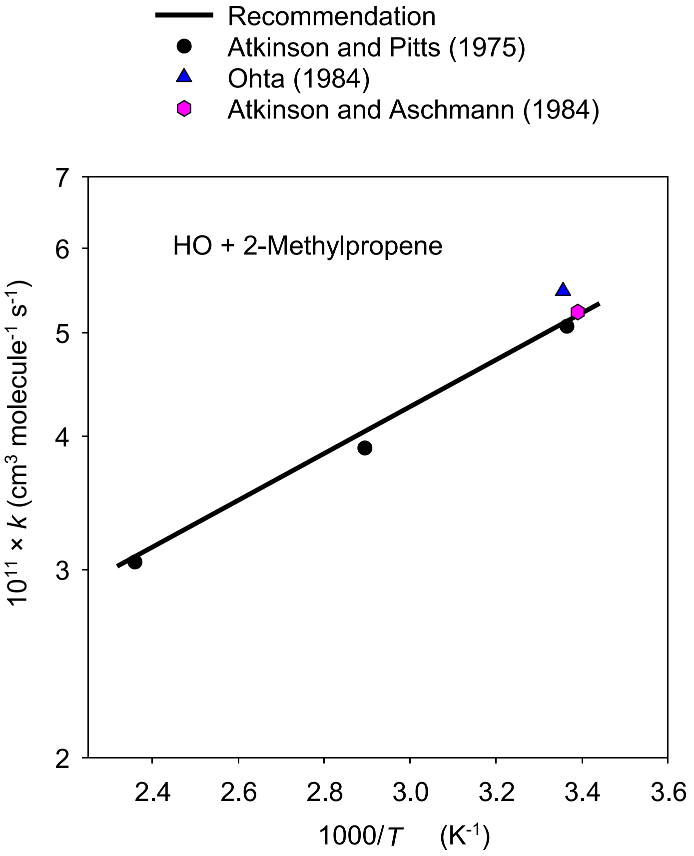
At room temperature, the absolute rate coefficient of Atkinson and Pitts (1975) and the relative rate coefficients of Wu et al. (1976), Barnes et al. (1982), Ohta (1984) and Atkinson and Aschmann (1984) are in reasonable agreement. Using propene as the reference compound, Atkinson and Aschmann (1984) measured rate coefficients for 1-butene, 3-methyl-1-butene, 2-methylpropene, *cis*-2-butene, *trans*-2-butene, 2-methyl-2-butene, 2,3-dimethyl-2-butene, propadiene, 1,3-butadiene and isoprene at 295 ± 1 K and atmospheric pressure of air. These relative rate data were fit by Atkinson (1989) to the absolute rate coefficients then available for propene, 1-butene, 3-methyl-1-butene, 2-methylpropene, *cis*-2-butene, *trans*-2-butene, 2-methyl-2-butene, propadiene and 1,3-butadiene (Atkinson and Pitts, 1975, 1978; Atkinson et al., 1977; Ravishankara et al., 1978; Nip and Paraskevopoulos, 1979; Tully and Goldsmith, 1985), using the observed temperature dependencies or $E/R$ = -500 K to adjust the measured rate coefficients to 295 K. The result of this fitting procedure (Atkinson, 1989) was that for 2-methylpropene, $k = 5.23 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 295 K. Combined with the temperature dependence of Atkinson and Pitts (1975), this leads to the preferred values.

At room temperature and below, the reaction proceeds dominantly by HO radical addition to the C=C bond. At elevated temperatures (>650 K), the HO-2-methylpropene adducts decompose rapidly back to reactants and the observed reaction is then H-atom abstraction (Atkinson, 1989).

**References**

Atkinson, R.: J. Phys. Chem. Ref. Data, Monograph 1, 1, 1989.
Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003a.
Atkinson, R. and Aschmann, S. M.: Int. J. Chem. Kinet., 16, 1175, 1984.
Atkinson, R. and Pitts Jr., J. N.: J. Chem. Phys., 63, 3591, 1975.
Atkinson, R. and Pitts Jr., J. N.: J. Chem. Phys., 68, 2992, 1978.
Atkinson, R., Perry, R. A. and Pitts Jr., J. N.: J. Chem. Phys., 67, 3170, 1977.
Barnes, I., Bastian, V., Becker, K. H., Fink, E. H. and Zabel, F.: Atmos. Environ., 16, 545, 1982.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Morris Jr., E. D. and Niki, H.: J. Phys. Chem., 75, 3640, 1971a.
Morris Jr., E. D. and Niki, H.: J. Am. Chem. Soc., 93, 3570, 1971b.
Nip, W. S. and Paraskevopoulos, G.: J. Chem. Phys., 71, 2170, 1979.
Ohta, T.: Int. J. Chem. Kinet., 16, 879, 1984.
Ravishankara, A. R., Wagner, S., Fischer, S., Smith, G., Schiff, R., Watson, R. T., Tesi, G. and Davis, D. D.: Int. J. Chem. Kinet., 10, 783, 1978.

Tully, F. P. and Goldsmith, J. E. M.: Chem. Phys. Lett., 116, 345, 1985.
Wu, C. H., Japar, S. M. and Niki, H.: J. Environ. Sci. Health, A11, 191, 1976.



Rate coefficients for HO + 2-Methylpropene.

**HOx_VOC62**

## HO + 1-Butene → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $(1.5 \pm 0.1) \times 10^{-11}$ | 300 | Pastrana and Carr, 1975 | DF-RF (a) |
| $7.6 \times 10^{-12} \exp[(468 \pm 151)/T]$ | 298-424 | Atkinson and Pitts, 1975 | FP-RF (b) |
| $(3.53 \pm 0.36) \times 10^{-11}$ | 297.7 | | |
| $(2.94 \pm 0.14) \times 10^{-11}$ | 298 | Ravishankara et al., 1978 | FP-RF (c) |
| $(3.34 \pm 0.25) \times 10^{-11}$ | 297 ± 2 | Nip and Paraskevopoulos, 1979 | FP-RA (d) |
| $(3.0 \pm 0.4) \times 10^{-11}$ | 298 | Biermann et al., 1982 | DF-MS (e) |
| $1.6 \times 10^{-11}$ | 478 | Liu et al., 1989 | PR-RA (f) |
| $(7.71 \pm 1.06) \times 10^{-11}$ | 170 | Sims et al., 1994 | PLP-LIF (g) |
| $(3.49 \pm 0.11) \times 10^{-11}$ | 295 | | |
| $(3.30 \pm 0.12) \times 10^{-11}$ | 295 | | |
| $(5.80 \pm 1.51) \times 10^{-11}$ | 165 ± 14 | Vakhtin et al., 2001, 2003 | PLP-LIF (h) |
| $(8.13 \pm 2.10) \times 10^{-11}$ | 165 ± 14 | | |
| $(3.0 \pm 0.2) \times 10^{-11}$ | 296 ± 2 | | |
| *Relative Rate Coefficients* | | | |
| $4.08 \times 10^{-11}$ | 298 | Morris and Niki, 1971a | DF-MS (i) |
| $2.83 \times 10^{-11}$ | 303 | Wu et al., 1976 | RR (j) |
| $2.96 \times 10^{-11}$ | 300 | Barnes et al., 1982 | RR (k) |
| $(3.40 \pm 0.08) \times 10^{-11}$ | 298 ± 2 | Ohta, 1984 | RR (l) |
| $(3.44 \pm 0.17) \times 10^{-11}$ | 295 ± 1 | Atkinson and Aschmann, 1984 | RR (m) |

## Comments

(a) Experiments carried out at 1 Torr (1.3 mbar) of He diluent.

(b) Experiments carried out at 25 Torr (33 mbar) of Ar diluent.

(c) Rate coefficients measured at 3 and 20 Torr (4 and 27 mbar) of helium diluent, with rate coefficients of $(2.96 \pm 0.19) \times 10^{-11}$ and $(2.94 \pm 0.14) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively. Value cited in the table is that at 20 Torr (26.7 mbar) He.

(d) Experiments carried out at 55 Torr (73 mbar) of (91% $H_2$ + 9% $N_2O$) diluent.

(e) 1-Butene was in ~10-fold excess of HO radical; concentrations, and the concentrations of 1-butene were monitored by photoionization mass spectrometry at m/z = 56. Experiments were carried out at ~2 Torr (~2.7 mbar) of He.

(f) Rate coefficients measured over the temperature range 478-853 K at 760 Torr (1.013 bar) of Ar diluent. Data were presented graphically and not tabulated.

(g) Experiments at 295 K were carried out at total pressures of Ar diluent of 14 and 23 Torr (19 and 31 mbar), with respective rate coefficients of $(3.49 \pm 0.11) \times 10^{-11}$ and $(3.30 \pm 0.12) \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. Rate coefficients of $(4.27 \pm 0.56) \times 10^{-10}$, $(3.15 \pm 0.40) \times 10^{-10}$ and $(2.73 \pm 0.16) \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ were also measured at 23, 44 and 75 K, respectively.

(h) Rate coefficients of $(1.74 \pm 0.28) \times 10^{-10}$, $(1.24 \pm 0.27) \times 10^{-10}$ and $(1.68 \pm 0.40) \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ were also measured at 96 ± 4, 103 ± 9 and 110 ± 7 K, respectively. The rate coefficient cited in the table for 296 ± 2 K is an average value of five measurements made over the pressure range 0.88-102 Torr (1.2-136 mbar) of $N_2$ diluent gas; no pressure dependence was observed over this pressure range.

(i) A rate coefficient for HO + 1-butene was obtained relative to that for propene at 1 Torr (1.3 mbar) He diluent by monitoring the decays of 1-butene and propene and the respective average HO radical concentrations under identical experimental conditions. The rate coefficient ratio *k*(HO + 1-butene)/*k*(HO + propene) = 2.4 is placed on an absolute basis using *k*(HO + propene) = $1.7 \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ under the experimental condition used (Morris and Niki, 1971b).

(j) HO radicals were generated by the photolysis of organic-$NO_x$-$O_2$-air mixtures at atmospheric pressure. 1-Butene and *cis*-2-butene (the reference compound) were measured by GC, and the measured rate coefficient ratio *k*(HO + 1-butene)/*k*(HO + *cis*-2-butene) = 0.52 is placed on an absolute basis using *k*(HO + *cis*-2-butane) = $5.45 \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at 303 K (IUPAC, 2019).

(k) HO radicals were generated by dark decomposition of $HOONO_2$ in the presence of NO at atmospheric pressure of $N_2$ or air. 1-Butene and ethene (the reference compound) were monitored by GC, and the measured rate coefficient ratio *k*(HO + 1-butene)/*k*(HO + ethene) = 3.8 is placed on an absolute basis using a rate coefficient of *k*(HO + ethene) = $7.78 \times 10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at 300 K and atmospheric pressure of air (IUPAC, 2019).

(l) HO radicals were generated by the photolysis of $H_2O_2$ at 253.7 nm in 760 Torr (1013 mbar) of $N_2$ or $O_2$ diluent in a quartz vessel. The concentrations of 1-butene and propene (the reference compound) were measured by GC during the experiments. The measured rate coefficient ratios *k*(HO + propene)/*k*(HO + 1-butene) = 0.84 ± 0.02 is placed on an absolute basis using *k*(HO + propene) = $2.86 \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at 298 K and atmospheric pressure of air (IUPAC, 2019).

(m) HO radicals were generated by the photolysis of $CH_3ONO$ in air at wavelengths >300 nm in a ~60 L Teflon chamber at atmospheric pressure of air. The concentrations of 1-butene and propene (the reference compound) were monitored by GC during the experiments. The measured rate coefficient ratio *k*(HO + 1-butene)/*k*(HO + propene) = 1.19 ± 0.06 is placed on an absolute basis using *k*(HO + propene) = $2.89 \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at 295 K and atmospheric pressure of air (IUPAC, 2019).

## Preferred Values

| Parameter | Value | *T*/K |
|---|---|---|
| $k$ /$cm^3$ $molecule^{-1}$ $s^{-1}$ | $3.1 \times 10^{-11}$ | 298 |
| $k$ /$cm^3$ $molecule^{-1}$ $s^{-1}$ | $6.6 \times 10^{-12}\exp(465/T)$ | 290-430 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.06 | 298 |
| Δ E/R | ± 150 | 290-430 |

*Comments on Preferred Values*

At room temperature, the absolute rate coefficients of Atkinson and Pitts (1975), Ravishankara et al. (1978), Biermann et al. (1982), Sims et al. (1994) and Vakhtin et al. (2001, 2003) and the relative rate coefficients of Wu et al. (1976), Barnes et al. (1982), Ohta (1984) and Atkinson and Aschmann (1984) are in reasonable agreement, with the relative rate studies of Ohta (1984) and Atkinson and Aschmann (1984) obtaining identical rate coefficient ratios of *k*(HO + 1-butene)/*k*(HO + propene) = 1.19 ± 0.03 at 298 ± 2 K and 1.19 ± 0.06 at 295 ± 1 K, respectively.

Using propene as the reference compound, Atkinson and Aschmann (1984) measured rate coefficients for 1-butene, 3-methyl-1-butene, 2-methylpropene, *cis*-2-butene, *trans*-2-butene, 2-methyl-2-butene, 2,3-dimethyl-2-butene, propadiene, 1,3-butadiene and isoprene at 295 ± 1 K and atmospheric pressure of air. These relative rate data for were fit by Atkinson (1989) to the absolute rate coefficients then available for propene, 1-butene, 3-methyl-1-butene, 2-methylpropene, *cis*-2-butene, *trans*-2-butene, 2-methyl-2-butene, propadiene and 1,3-butadiene (Atkinson and Pitts, 1975, 1978; Atkinson et al., 1977; Ravishankara et al., 1978; Nip and Paraskevopoulos, 1979; Tully and Goldsmith, 1985), using the observed temperature dependencies or $E/R$ = -500 K to adjust the measured rate coefficients to 295 K. The result of this fitting procedure (Atkinson, 1989) was that for 1-butene, $k = 3.19 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 295 K. Combined with the temperature dependence of Atkinson and Pitts (1975), this leads to the preferred values.

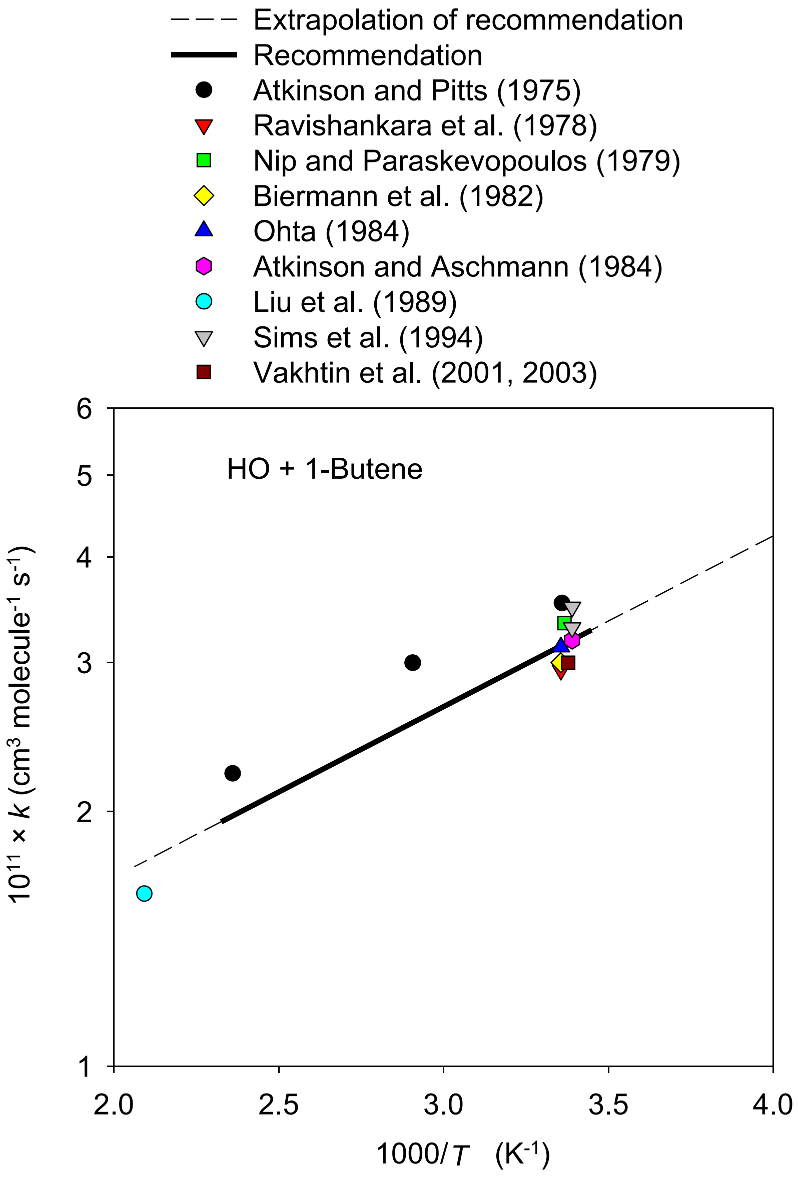
The more recent absolute rate coefficients of Sims et al. (1994) and Vakhtin et al. (2001, 2003) at 295-296 K are in good agreement with the preferred value, and the 478 K rate coefficient of Liu et al. (1989) is in good agreement with extrapolation of the recommended rate expression. The preferred Arrhenius expression should not be used much below room temperature; clearly extrapolation to 165-170 K leads to overprediction of the measured rate coefficients of Sims et al. (1994) and Vakhtin et al. (2001, 2003). Rather, the expression of the form $k = a \exp(-bT)$ appears to give a reasonable fit, with $a = 2.56 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and $b$ = 0.00705 (Atkinson and Arey, 2003).

At room temperature and below, the reaction proceeds by HO radical addition to the C=C bond, with H-atom abstraction accounting for <10% of the overall reaction at room temperature (Atkinson et al., 1985). At elevated temperatures (>650 K), the HO-1-butene adducts decompose rapidly back to reactants and the observed reaction is then H-atom abstraction (Atkinson, 1989).

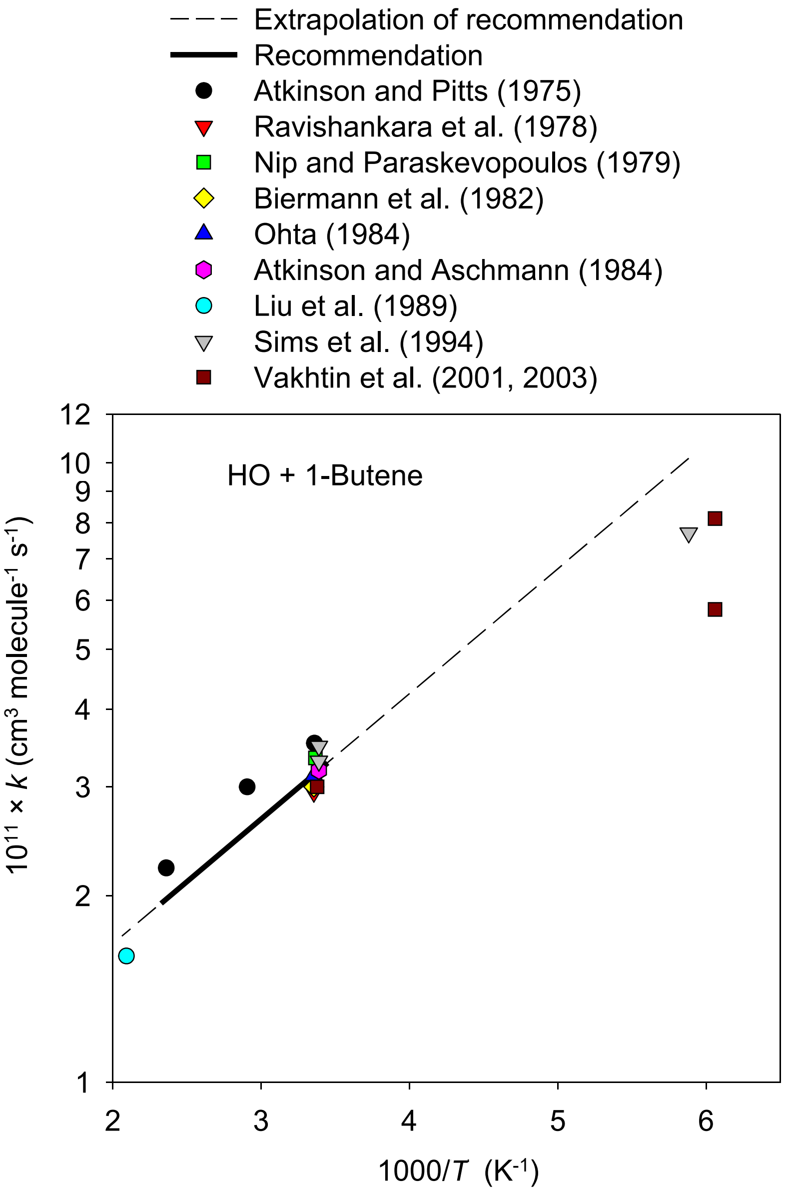
## References

Atkinson, R.: J. Phys. Chem. Ref. Data, Monograph 1, 1, 1989.
Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
Atkinson, R. and Aschmann, S. M.: Int. J. Chem. Kinet., 16, 1175, 1984.
Atkinson, R. and Pitts Jr., J. N.: J. Chem. Phys., 63, 3591, 1975.
Atkinson, R. and Pitts Jr., J. N.: J. Chem. Phys., 68, 2992, 1978.
Atkinson, R., Perry, R. A. and Pitts Jr., J. N.: J. Chem. Phys., 67, 3170, 1977.
Atkinson, R., Tuazon, E. C. and Carter, W. P. L.: Int. J. Chem. Kinet., 17, 725, 1985.
Barnes, I., Bastian, V., Becker, K. H., Fink, E. H. and Zabel, F.: Atmos. Environ., 16, 545, 1982.
Biermann, H. W., Harris, G. W. and Pitts Jr., J. N.: J. Phys. Chem., 86, 2958, 1982.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Liu, A., Jonah, C. D. and Mulac, W. A.: Radiat. Phys. Chem., 34, 687, 1989.
Morris Jr., E. D. and Niki, H.: J. Phys. Chem., 75, 3640, 1971a.
Morris Jr., E. D. and Niki, H.: J. Am. Chem. Soc., 93, 3570, 1971b.
Nip, W. S. and Paraskevopoulos, G.: J. Chem. Phys., 71, 2170, 1979.
Ohta, T.: Int. J. Chem. Kinet., 16, 879, 1984.
Pastrana, A. V. and Carr Jr., R. W.: J. Phys. Chem., 79, 765, 1975.
Ravishankara, A. R., Wagner, S., Fischer, S., Smith, G., Schiff, R., Watson, R. T., Tesi, G. and Davis, D. D.: Int. J. Chem. Kinet., 10, 783, 1978.
Sims, I. R., Smith, I. W. M., Bocherel, P., Defrance, A., Travers, D. and Rowe, B. R.: J. Chem. Soc. Faraday Trans., 90, 1473, 1994.
Tully, F. P. and Goldsmith, J. E. M.: Chem. Phys. Lett., 116, 345, 1985.
Vakhtin, A. B., Lee, S., Heard, D. E., Smith, I. W. M. and Leone, S. R.: J. Phys. Chem. A, 105,

7889, 2001.
Vakhtin, A. B., Murphy, J. E. and Leone, S. R.: J. Phys. Chem. A, 107, 10055, 2003.
Wu, C. H., Japar, S. M. and Niki, H.: J. Environ. Sci. Health, A11, 191, 1976.



Rate coefficients for HO + 1-Butene.



Rate coefficients for HO + 1-Butene.

## HOx_VOC63

### HO + *cis*-2-Butene → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $1.04 \times 10^{-11} \exp[(488 \pm 151)/T]$ | 298-425 | Atkinson and Pitts, 1975 | FP-RF (a) |
| $(5.37 \pm 0.54) \times 10^{-11}$ | 297.6 | | |
| $(4.26 \pm 0.25) \times 10^{-11}$ | 298 | Ravishankara et al., 1978 | FP-RF (b) |
| $(1.30 \pm 0.13) \times 10^{-10}$ | 170 | Sims et al., 1994 | PLP-LIF (c) |
| $(6.18 \pm 0.57) \times 10^{-11}$ | 295 | | |
| *Relative Rate Coefficients* | | | |
| $6.12 \times 10^{-11}$ | 298 | Morris and Niki, 1971a | DF-MS (d) |
| $(5.3 \pm 1.1) \times 10^{-11}$ | 305 ± 2 | Lloyd et al., 1976 | RR (e) |
| $(6.0 \pm 1.2) \times 10^{-11}$ | 305 ± 2 | Winer et al., 1976 | RR (f) |
| $(5.47 \pm 0.18) \times 10^{-11}$ | 298 ± 2 | Ohta, 1984 | RR (g) |
| $(6.16 \pm 0.14) \times 10^{-11}$ | 295 ± 1 | Atkinson and Aschmann, 1984 | RR (h) |

### Comments

(a) Experiments carried out at 25 Torr (33 mbar) of Ar.

(b) Rate coefficients measured at 3 and 20 Torr (4 and 27 mbar) of helium diluent, with rate coefficients of $(4.32 \pm 0.41) \times 10^{-11}$ and $(4.26 \pm 0.25) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively. Value cited in the table is that at 20 Torr He.

(c) Experiments at 295 K were carried out at a total pressure of Ar diluent of 14 Torr (19 mbar). Rate coefficients of $(3.89 \pm 0.23) \times 10^{-10}$, $(3.28 \pm 0.33) \times 10^{-10}$ and $(3.02 \pm 0.14) \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ were also measured at 23, 44 and 75 K, respectively.

(d) A rate coefficient for HO + *cis*-2-butene was obtained relative to that for propene at 1 Torr (1.3 mbar) He diluent by monitoring the decays of *cis*-2-butene and propene and the respective average HO radical concentrations under identical experimental conditions. The rate coefficient ratio $k$(HO + *cis*-2-butene)/$k$(HO + propene) = 3.6 is placed on an absolute basis using $k$(HO + propene) = $1.7 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Morris and Niki, 1971b).

(e) HO radicals generated by the photolysis of organic-$NO_x$ mixtures at atmospheric pressure in a 5870 L reaction chamber, with analyses of *cis*-2-butene and *n*-butane (the reference compound) by GC. The measured rate coefficient ratio $k$(HO + *cis*-2-butene)/$k$(HO + *n*-butane) = 21.8 ± 4.4 is placed on an absolute basis using $k$(HO + *n*-butane) = $2.44 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 305 K (IUPAC, 2019).

(f) HO radicals generated by the photolysis of organic-$NO_x$ mixtures at atmospheric pressure in a 5870 L reaction chamber, with analyses of *cis*-2-butene and 2-methylpropene (the reference compound) by GC. The measured rate coefficient ratio $k$(HO + *cis*-2-butene)/$k$(HO + 2-methylpropene) = 1.22 ± 0.25 is placed on an absolute basis using $k$(HO + 2-methylpropene) = $4.92 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 305 K (IUPAC, 2019).

(g) HO radicals were generated by the photolysis of $H_2O_2$ at 253.7 nm in 760 Torr (1013 mbar) of $N_2$ or $O_2$ diluent in a quartz vessel. The concentrations of *cis*-2-butene and 2-methyl-2-butene (the reference compound) were measured by GC during the experiments. The measured rate coefficient ratio $k$(HO + *cis*-2-butene)/$k$(HO + 2-methyl-2-butene) = 0.63 ± 0.02 is placed on an absolute basis using $k$(HO + 2-methyl-2-butene) = $8.69 \times 10^{-11}$ at 298 K and atmospheric pressure of air (Atkinson and Arey, 2003).

(h) HO radicals were generated by the photolysis of $CH_3ONO$ in air at wavelengths >300 nm in a ~60 L Teflon chamber at atmospheric pressure of air. The concentrations of 1-butene and propene (the reference compound) were monitored by GC during the experiments. The measured rate coefficient ratio $k$(HO + *cis*-2-butene)/$k$(HO + propene) = 2.13 ± 0.05 is placed on an absolute basis using $k$(HO + propene) = $2.89 \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at 295 K and atmospheric pressure of air (IUPAC, 2019).

## Preferred Values

| Parameter | Value | *T*/K |
|---|---|---|
| $k$ /$cm^3$ $molecule^{-1}$ $s^{-1}$ | $5.6 \times 10^{-11}$ | 298 |
| $k$ /$cm^3$ $molecule^{-1}$ $s^{-1}$ | $1.1 \times 10^{-11} \exp(485/T)$ | 290-430 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.10 | 298 |
| $\Delta E/R$ | ± 200 | 290-430 |

*Comments on Preferred Values*

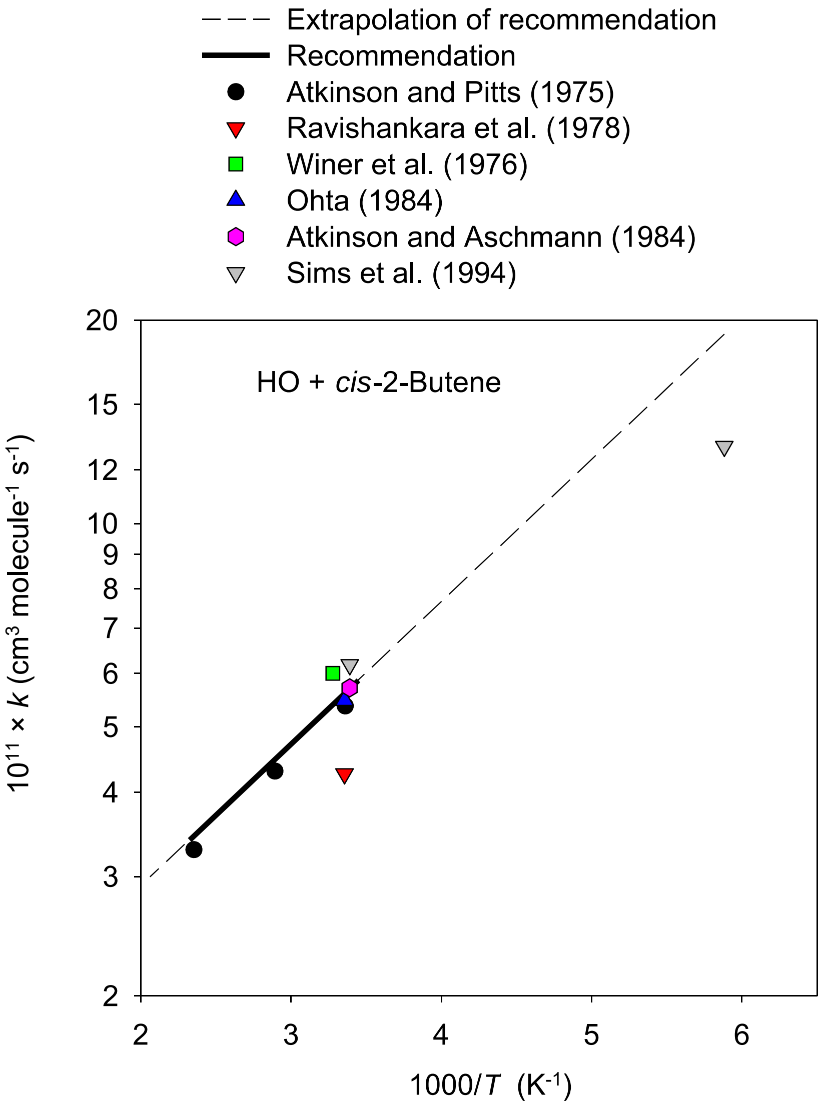
At room temperature, the absolute rate coefficients of Atkinson and Pitts (1975) and Sims et al. (1994) and the relative rate coefficients of Lloyd et al. (1976), Winer et al. (1976), Ohta (1984) and Atkinson and Aschmann (1984) are in reasonable agreement, with those of Lloyd et al. (1976) and Winer et al. (1976) having large associated uncertainties. The absolute rate coefficient of Ravishankara et al. (1978) is ~20% lower, possibly because of wall losses of *cis*-2-butene in the static reaction vessel used (Atkinson, 1989). Using propene as the reference compound, Atkinson and Aschmann (1984) measured rate coefficients for 1-butene, 3-methyl-1-butene, 2-methylpropene, *cis*-2-butene, *trans*-2-butene, 2-methyl-2-butene, 2,3-dimethyl-2-butene, propadiene, 1,3-butadiene and isoprene at 295 ± 1 K and atmospheric pressure of air. These relative rate data were fit by Atkinson (1989) to the absolute rate coefficients then available for propene, 1-butene, 3-methyl-1-butene, 2-methylpropene, *cis*-2-butene, *trans*-2-butene, 2-methyl-2-butene, propadiene and 1,3-butadiene (Atkinson and Pitts, 1975, 1978; Atkinson et al., 1977; Ravishankara et al., 1978; Nip and Paraskevopoulos, 1979; Tully and Goldsmith, 1985), using the observed temperature dependencies or $E/R = -500$ K to adjust the measured rate coefficients to 295 K. The result of this fitting procedure (Atkinson, 1989) was that for *cis*-2-butene, $k = 5.71 \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at 295 K. Combined with the temperature dependence of Atkinson and Pitts (1975), this leads to the preferred values.

The more recent absolute rate coefficient of Sims et al. (1994) at 295 K is in agreement with the preferred value within the experimental uncertainties. The preferred Arrhenius expression should not be used much below room temperature; clearly extrapolation to 170 K leads to overprediction of the measured rate coefficient of Sims et al. (1994). Rather, the expression of the form $k = a \exp(-bT)$ appears to give a reasonable fit, with $a = 4.0 \times 10^{-10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ and $b = 0.0066$, based on the preferred 295 K rate coefficient and the 170 K rate coefficient of Sims et al. (1994).

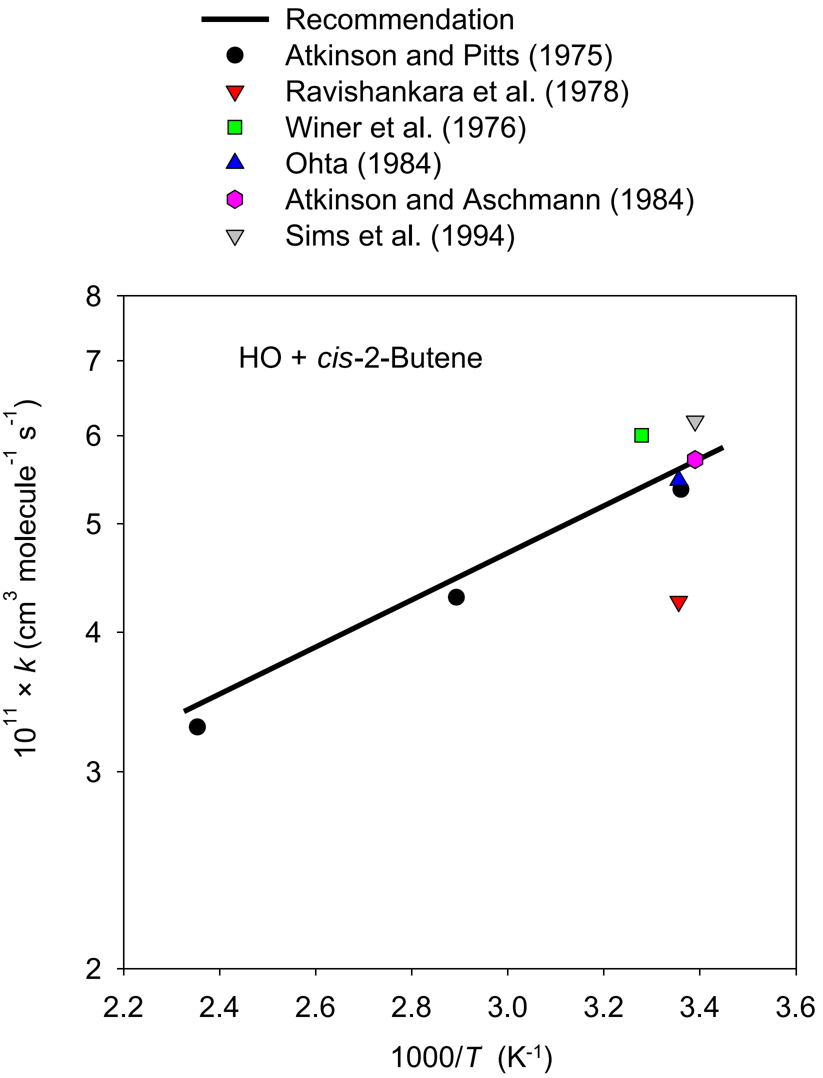
At room temperature and below, the reaction proceeds by HO radical addition to the C=C bond. At elevated temperatures (>650 K), the HO-*cis*-2-butene adduct is expected to decompose rapidly back to reactants and the observed reaction is then H-atom abstraction (Atkinson, 1989).

## References

Atkinson, R.: J. Phys. Chem. Ref. Data, Monograph 1, 1, 1989.
Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
Atkinson, R. and Aschmann, S. M.: Int. J. Chem. Kinet., 16, 1175, 1984.
Atkinson, R. and Pitts Jr., J. N.: J. Chem. Phys., 63, 3591, 1975.
Atkinson, R. and Pitts Jr., J. N.: J. Chem. Phys., 68, 2992, 1978.
Atkinson, R., Perry, R. A. and Pitts Jr., J. N.: J. Chem. Phys., 67, 3170, 1977.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Lloyd, A. C., Darnall, K. R., Winer, A. M. and Pitts Jr., J. N.: J. Phys. Chem., 80, 789, 1976.
Morris Jr., E. D. and Niki, H.: J. Phys. Chem., 75, 3640, 1971a.
Morris Jr., E. D. and Niki, H.: J. Am. Chem. Soc., 93, 3570, 1971b.
Nip, W. S. and Paraskevopoulos, G.: J. Chem. Phys., 71, 2170, 1979.
Ohta, T.: Int. J. Chem. Kinet., 16, 879, 1984.
Ravishankara, A. R., Wagner, S., Fischer, S., Smith, G., Schiff, R., Watson, R. T., Tesi, G. and Davis, D. D.: Int. J. Chem. Kinet., 10, 783, 1978.
Sims, I. R., Smith, I. W. M., Bocherel, P., Defrance, A., Travers, D. and Rowe, B. R.: J. Chem. Soc. Faraday Trans., 90, 1473, 1994.
Tully, F. P. and Goldsmith, J. E. M.: Chem. Phys. Lett., 116, 345, 1985.
Winer, A. M., Lloyd, A. C., Darnall, K. R. and Pitts Jr., J. N.: J. Phys. Chem., 80, 1635, 1976.



Rate coefficients for HO + *cis*-1-Butene.



Rate coefficients for HO + cis-2-Butene.

## HOx_VOC64

## HO + *trans*-2-Butene → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $(1.2 \pm 1) \times 10^{-11}$ | 300 | Pastrana and Carr, 1975 | DF-RA (a) |
| $1.12 \times 10^{-11} \exp[(549 \pm 151)/T]$ | 298-425 | Atkinson and Pitts, 1975 | FP-RF (b) |
| $(6.99 \pm 0.70) \times 10^{-11}$ | 297.8 | | |
| $(1.69 \pm 0.083) \times 10^{-10}$ | 170 | Sims et al., 1994 | PLP-LIF (c) |
| $(6.83 \pm 0.22) \times 10^{-11}$ | 295 | | |
| *Relative Rate Coefficients* | | | |
| $12.0 \times 10^{-11}$ | 298 | Morris and Niki, 1971 | DF-MS (d) |
| $7.09 \times 10^{-11}$ | 303 | Wu et al., 1976 | RR (e) |
| $(5.96 \pm 0.31) \times 10^{-11}$ | 298 ± 2 | Ohta, 1983 | RR (f) |
| $(7.02 \pm 0.14) \times 10^{-11}$ | 295 ± 1 | Atkinson and Aschmann, 1984 | RR (g) |
| $(7.9 \pm 1.3) \times 10^{-11}$ | 297.4 ± 1.7 | Edney et al., 1986 | RR (h) |
| $(7.87 \pm 0.38) \times 10^{-11}$ | 298 ± 3 | Rogers, 1989 | RR (i) |

### Comments

(a) Experiments carried out at 1 Torr (1.3 mbar) of He.

(b) Experiments carried out at 25 Torr (33 mbar) of Ar.

(c) Experiments at 295 K were carried out at a total pressure of Ar diluent of 14 Torr (19 mbar). Rate coefficients of $(4.52 \pm 0.32) \times 10^{-10}$, $(4.03 \pm 0.44) \times 10^{-10}$ and $(3.17 \pm 0.24) \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ were also measured at 23, 44 and 75 K, respectively.

(d) A rate coefficient for HO + *trans*-2-butene was obtained relative to that for propene at 1 Torr (1.3 mbar) He diluent by monitoring the decays of *trans*-2-butene and propene and the average HO radical concentrations under identical experimental conditions. The measured rate coefficient ratio $k$(HO + *trans*-2-butene)/$k$(HO + propene) = 4.2 is placed on an absolute basis using $k$(HO + propene) = $1.86 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019).

(e) HO radicals were generated by the photolysis of organic-$NO_x$-$O_2$-air mixtures at atmospheric pressure. *trans*-2-Butene and *cis*-2-butene (the reference compound) were measured by GC, and the measured rate coefficient ratio $k$(HO + *trans*-2-butene)/$k$(HO + *cis*-2-butene) = 1.3 is placed on an absolute basis using $k$(HO + *cis*-2-butene) = $5.45 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 303 K (IUPAC, 2019).

(f) HO radicals were generated by the photolysis of $H_2O_2$ at 253.7 nm in 760 Torr (1013 mbar) of $N_2$ or $O_2$ diluent in a quartz vessel. The concentrations of *trans*-2-butene and *cis*-1,3-pentadiene (the reference compound) were measured by GC during the experiments. The measured rate coefficient ratios $k$(HO + *trans*-2-butene)/$k$(HO + *cis*-1,3-pentadiene) = 0.59 ± 0.03 is placed on an absolute basis using $k$(HO + *cis*-1,3-pentadiene) = $1.01 \times 10^{-10}$ at 298 K and atmospheric pressure of air (Atkinson, 1989; Atkinson and Arey, 2003).

(g) HO radicals were generated by the photolysis of $CH_3ONO$ in air at wavelengths >300 nm in a ~60 L Teflon chamber at atmospheric pressure of air. The concentrations of *trans*-2-butene and propene (the reference compound) were monitored by GC. The measured rate coefficient ratio $k$(HO + *trans*-2-butene)/$k$(HO + propene) = 2.43 ± 0.05 is placed on an absolute basis using $k$(HO + propene) = $2.89 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 295 K and atmospheric pressure of air (IUPAC, 2019).

(h) HO radicals were generated by the photolysis of $CH_3ONO$ in one atmosphere of air. The concentrations of *trans*-2-butene and propene (the reference compound) were measured by GC. The measured rate coefficient ratio of *k*(HO + *trans*-2-butene)/*k*(HO + propene) is placed on an absolute basis using a rate coefficient at 297 K and atmospheric pressure of air of *k*(HO + propene) = $2.86 \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ (IUPAC, 2019).

(i) HO radicals were generated by the photolysis of HONO in one atmosphere of air in a 600 L stainless steel cell. The concentrations of *trans*-2-butene and propene (the reference compound) were measured by FTIR spectroscopy. The measured rate coefficient ratio *k*(HO + propene)/*k*(HO + *trans*-2-butene) = 0.365 ± 0.019 is placed on an absolute basis using rate coefficients at 298 K and atmospheric pressure of air of *k*(HO + propene) = $2.87 \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ (IUPAC, 2019).

## Preferred Values

| Parameter | Value | *T*/K |
|---|---|---|
| $k$ /$cm^3$ $molecule^{-1}$ $s^{-1}$ | $7.1 \times 10^{-11}$ | 298 |
| $k$ /$cm^3$ $molecule^{-1}$ $s^{-1}$ | $1.1 \times 10^{-11} \exp(553/T)$ | 290-430 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.06 | 298 |
| Δ E/R | ± 200 | 290-430 |

*Comments on Preferred Values*

At room temperature, the absolute rate coefficients of Atkinson and Pitts (1975), and Sims et al. (1994) and the relative rate coefficients of Wu et al. (1976), Ohta (1983), Atkinson and Aschmann (1984), Edney et al. (1986) and Rogers (1989) are in reasonable agreement, with that of Edney et al. (1986) having a large associated uncertainty. The preferred value is based on the relative studies and the absolute ones from Sims et al. (1994) at 295 K and Atkinson and Pitts (1975).

The preferred Arrhenius expression should not be used much below room temperature; clearly extrapolation to 170 K leads to overprediction of the measured rate coefficient of Sims et al. (1994). Rather, the expression of the form $k = a \exp(-bT)$ appears to give a reasonable fit, with $a = 6.1 \times 10^{-10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ and $b = 0.0076$, based on the preferred 295 K value and the 170 K rate coefficient of Sims et al. (1994).

At room temperature and below, the reaction proceeds by HO radical addition to the C=C bond. At elevated temperatures (>650 K), the HO-*trans*-2-butene adduct decomposes rapidly back to reactants and the observed reaction is then H-atom abstraction (Atkinson, 1989).

## References

Atkinson, R.: J. Phys. Chem. Ref. Data, Monograph 1, 1, 1989.

Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.

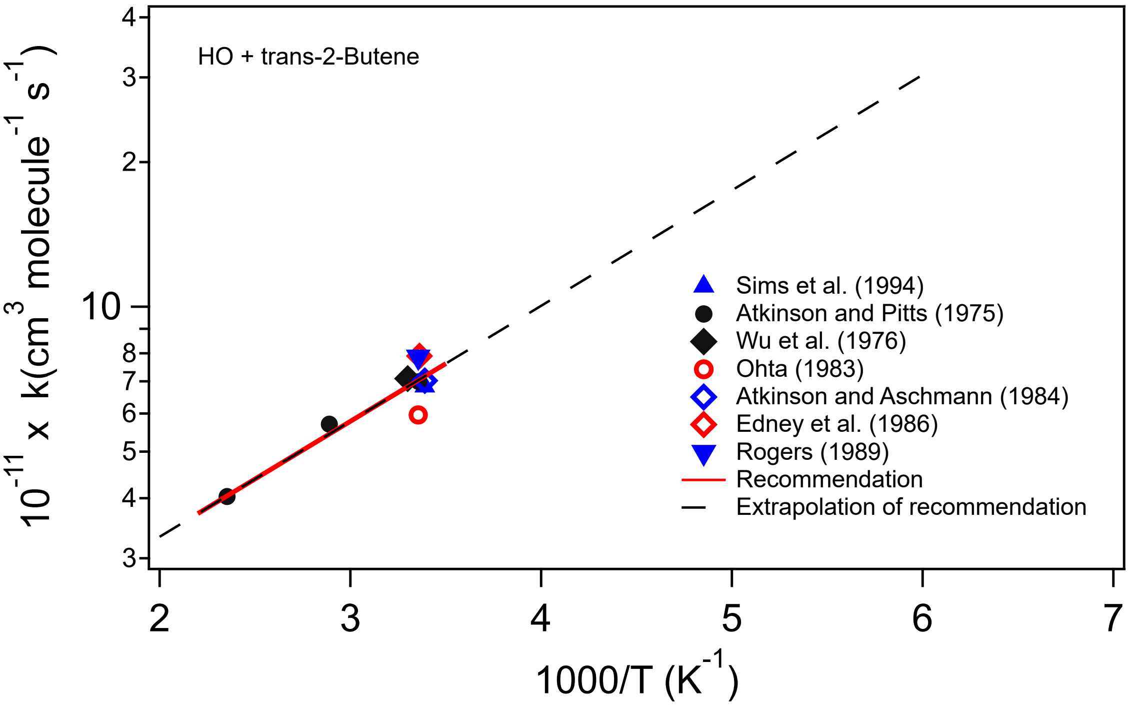
Atkinson, R. and Aschmann, S. M.: Int. J. Chem. Kinet., 16, 1175, 1984.

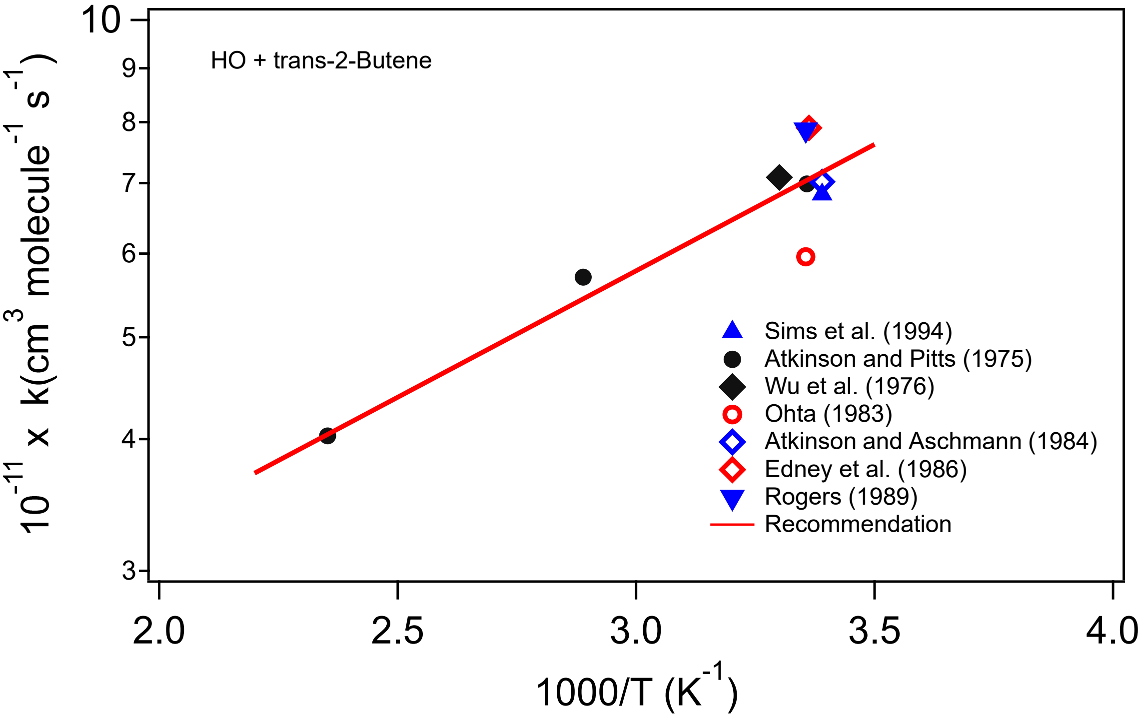
Atkinson, R. and Pitts Jr., J. N.: J. Chem. Phys., 63, 3591, 1975.

Edney, E. O., Kleindienst, T. E. and Corse, E. W.: Int. J. Chem. Kinet., 18, 1355, 1986.

IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluatio (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and

Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Morris Jr., E. D. and Niki, H.: J. Phys. Chem., 75, 3640, 1971.
Ohta, T.: J. Phys. Chem., 87, 1209, 1983.
Pastrana, A. V. and Carr Jr., R. W.: J. Phys. Chem., 79, 765, 1975.
Rogers, J. D.: Environ. Sci. Technol., 23, 177, 1989.
Sims, I. R., Smith, I. W. M., Bocherel, P., Defrance, A., Travers, D. and Rowe, B. R.: J. Chem. Soc. Faraday Trans., 90, 1473, 1994.
Wu, C. H., Japar, S. M. and Niki, H.: J. Environ. Sci. Health, A11, 191, 1976.





Rate coefficients for HO + *trans*-2-Butene.

## HOx_VOC66

### HO + $CH_3C(O)C(O)CH_3 \rightarrow$ products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | *Temp.*/K | Reference | Technique/Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $(2.4^{+0.8}_{-0.6}) \times 10^{-13}$ | 298 | Darnall et al., 1979 | FP-RF (a) |
| $(1.12 \pm 0.65) \times 10^{-12} \exp[-(450 \pm 90)/T]$ | 240-440 | Dagaut et al., 1988 | FP-RF (b) |
| $(2.3 \pm 0.2) \times 10^{-13}$ | 298 | | |

### Comments

(a) HO radicals were generated by the vacuum ultraviolet ($\lambda \geq 105$ nm) photolysis of $H_2O$ and monitored as function of time under pseudo-first order conditions by resonance fluorescence.

(b) HO radicals were generated by the vacuum ultraviolet ($\lambda \geq 165$ nm) photolysis of $H_2O$ and monitored as function of time under pseudo-first order conditions by resonance fluorescence.

### Preferred Values

| Parameter | Value | *T*/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $2.3 \times 10^{-13}$ | 298 |
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $5.25 \times 10^{-13} \exp(-243/T)$ | 240-350 |
| *Reliability* | | |
| $\Delta \log k$ | $\pm 0.06$ | 298 |
| $\Delta E/R$ | $\pm 50$ | 240-350 |

*Comments on Preferred Values*

The 298 K rate coefficient from the study of Darnall et al. (1979) is in excellent agreement with that of Dagaut et al. (1988). The combined data set of Darnall et al. at 298 K and those of Dagaut et al. below 350 K are used to derive the preferred values for the temperature dependence for atmospheric purposes.

The reaction of HO with 2,3-butanedione is assumed to proceed via H-atom abstraction from one of the methyl groups:

$$HO + CH_3C(O)C(O)CH_3 \rightarrow H_2O + CH_3C(O)C(O)CH_2$$

leading to a peroxy radical after reaction with $O_2$ which can at least partly react with NO to form an alkoxy radical, that can either dissociate or react with $O_2$:

$$CH_3C(O)C(O)CH_2O \rightarrow CH_3C(O)C(O) + HCHO$$

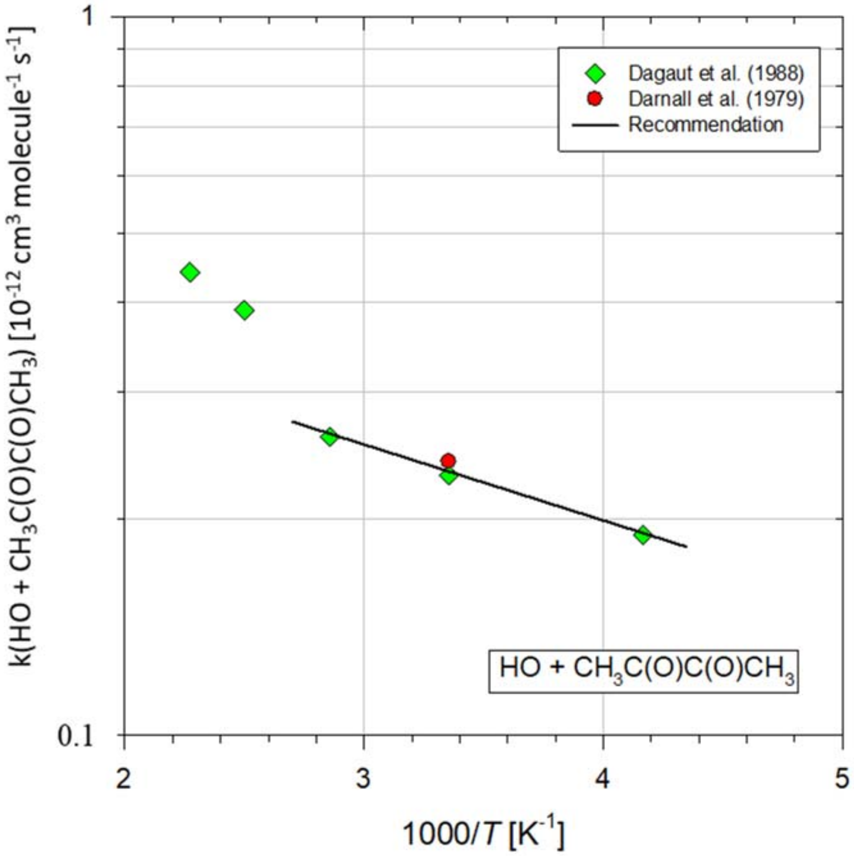
$$CH_3C(O)C(O)CH_2O + O_2 \rightarrow CH_3C(O)C(O)CHO + HO_2$$

Christensen et al. (1998) have reported that the atmospheric fate of $CH_3C(O)C(O)CH_2O$ formed from the Cl-initiated oxidation of 2,3-butanedione is decomposition to give HCHO, CO, and

$CH_3C(O)$ radicals. Hence, it is expected that the products of the reaction of HO with 2,3-butanedione under atmospheric conditions are $CH_3C(O)O_2$, HCHO and CO.

## References

Christensen, L. K., Sehested, J., Nielsen, O. J., Wallington, T. J., Guschin, A., and Hurley, M.D.: J. Phys. Chem. A, 102, 8913, 1998.
Dagaut, P., Wallington, T. J., Liu, R., and Kurylo, M. J.: J. Phys. Chem. 92**,** 4375, 1988.
Darnall, K. R., Atkinson, R., and Pitts Jr., J. N.: J. Phys. Chem. 83**,** 1943, 1979.



Rate coefficients for HO + $CH_3C(O)C(O)CH_3$.

## HOx_VOC67

## HO + $n$-$C_3H_7C(O)OH \rightarrow$ products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | $T$/K | Reference | Technique/ Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $(1.8 \pm 0.16) \times 10^{-12}$ | 298 | Zetzsch and Stuhl, 1982 | FP-RF (a) |

### Comments

(a) HO radicals were generated by the vacuum ultraviolet ($\lambda \geq 105$ nm) photolysis of $H_2O$ and monitored as function of time under pseudo-first order conditions by resonance fluorescence.

### Preferred Values

| Parameter | Value | $T$/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $1.8 \times 10^{-12}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | $\pm 0.15$ | 298 |

*Comments on Preferred Values*

The preferred rate coefficient value at 298 K is based on the sole study of Zetzsch and Stuhl (1982). This value is higher than those for the shorter chain organic acids ($CH_3C(O)OH$ and $C_2H_5C(O)OH$, respectively, $k = 7.4 \times 10^{-13}$ and $1.2 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson et al., 2006).

As with the other acids, it is expected that the reaction will occur both at the acidic site (–C(O)OH) and the alkyl site ($n$-$C_3H_7$-).

### References

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Atmos. Chem. Phys., 6, 3625, 2006.
Zetzsch, C., and Stuhl, F.: (1982), *Physico-chemical behaviour of atmospheric pollutants*, edited by B. Versino and H. Ott, D. Reidel Publishing Company, Dordrecht, 129,1982.

## HOx_VOC68

### HO + $i$-$C_3H_7CHO \rightarrow$ products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | *Temp.*/K | Reference | Technique/Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $(6.8\pm0.3) \times 10^{-12} \exp[(393 \pm 125)/T]$ | 255-423 | Semmes et al., 1985 | FP-RF (a) |
| $(2.42 \pm 0.33) \times 10^{-11}$ | 298 | | |
| $(15.8\pm0.5.0) \times 10^{-12} \exp[(313 \pm 145)/T]$ | 298-519 | Dóbé et al., 1989 | DF-RF (b) |
| $(4.63 \pm 0.73) \times 10^{-11}$ | 298 | | |
| $(7.3\pm1.9) \times 10^{-11} \exp[(390 \pm 78)/T]$ | 243-372 | Thévenet et al., 2000 | PLP-LIF (c) |
| $(2.6 \pm 0.4) \times 10^{-11}$ | 298 | | |
| | | | |
| *Relative Rate Coefficients* | | | |
| $(1.68 \pm 0.20) \times 10^{-11}$ | 298 | Audley et al., 1981 | RR (d, h) |
| $(2.69 \pm 0.52) \times 10^{-11}$ | 298 ± 4 | Kerr and Sheppard, 1981 | RR (e, i) |
| $(2.78 \pm 0.26) \times 10^{-11}$ | 297 ± 3 | Stemmler et al., 1997 | RR (f, j) |
| $(2.64 \pm 0.22) \times 10^{-11}$ | 298 ± 2 | D'Anna et al., 2001 | RR (g, k) |

## Comments

(a) HO radicals were generated by the vacuum ultraviolet ($\lambda \geq 165$ nm) photolysis of $H_2O$ and monitored as function of time under pseudo-first order conditions by resonance fluorescence.

(b) HO radicals were generated by the reaction H + $NO_2$ and monitored as function of time under pseudo-first order conditions by resonance fluorescence.

(c) HO radicals were generated by the photolysis of $H_2O_2$ and their concentration was measured by pulsed laser induced fluorescence.

(d) HO radicals were generated by the dark reaction of $H_2O_2$-$NO_2$ mixtures in the presence of CO and an organic compound. From sequential experiments using acetaldehyde and *iso*-butyraldehyde, a rate coefficient ratio of $k$(HO + *iso*-butyraldehyde)/$k$(HO + acetaldehyde) = 1.12 ± 0.13 (two standard deviations) was derived. This rate coefficient ratio is placed on an absolute basis using $k$(HO + acetaldehyde) = $1.5 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (IUPAC, 2019).

(e) HO radicals were generated by the photolysis of HONO at $\lambda$ = 300-450 nm in air at atmospheric pressure in a 220 L Tedlar chamber. The concentrations of *iso*-butyraldehyde and ethene (the reference compound) were measured by GC-FID. The measured rate coefficient ratio of $k$(HO + *iso*-butyraldehyde)/$k$(HO + ethene) = 3.40 ± 0.66 is placed on an absolute basis using $k$(HO + ethene) = $7.9 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K and atmospheric pressure (IUPAC, 2019).

(f) HO radicals were generated by the photolysis of $CH_3ONO$ at $\lambda$ = 350-450 nm in air at 725 ± 25 Torr (967 ± 33 mbar) pressure in a 200 L Teflon chamber. The concentrations of *iso*-butyraldehyde and di-n-propyl ether (the reference compound) were measured by GC. The measured rate coefficient ratio of $k$(HO + *iso*-butyraldehyde)/$k$(HO + di-n-propyl ether) = 1.39 ± 0.04 is placed on an absolute basis using $k$(HO + di-n-propyl ether) = $2.0 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K and atmospheric pressure (Calvert et al., 2010).

(g) HO radicals were generated by the photolysis of an organic nitrite in air at 1013 ± 10 mbar (760 ± 7.5 Torr) pressure in a 250 L electropolished stainless-steel reactor. The concentrations of *iso*-butyraldehyde and 1-butene (the reference compound) were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k$(HO + *iso*-butyraldehyde)/$k$(HO + 1-butene) = 0.85 ± 0.07 is placed on an absolute basis using $k$(HO + 1-butene) = $3.1 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K and atmospheric pressure of air (IUPAC, 2019).
(h) Relative to acetaldehyde
(i) Relative to ethene
(j) Relative to di-n-propyl ether
(k) Relative to isoprene

### Preferred Values

| Parameter | Value | *T*/K |
|---|---|---|
| $k$/ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $2.6 \times 10^{-11}$ | 298 |
| $k$/ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.8 \times 10^{-12}$ exp(410/$T$) | 240-425 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.04 | 298 |
| $\Delta$ E/R | ± 60 | 240-425 |

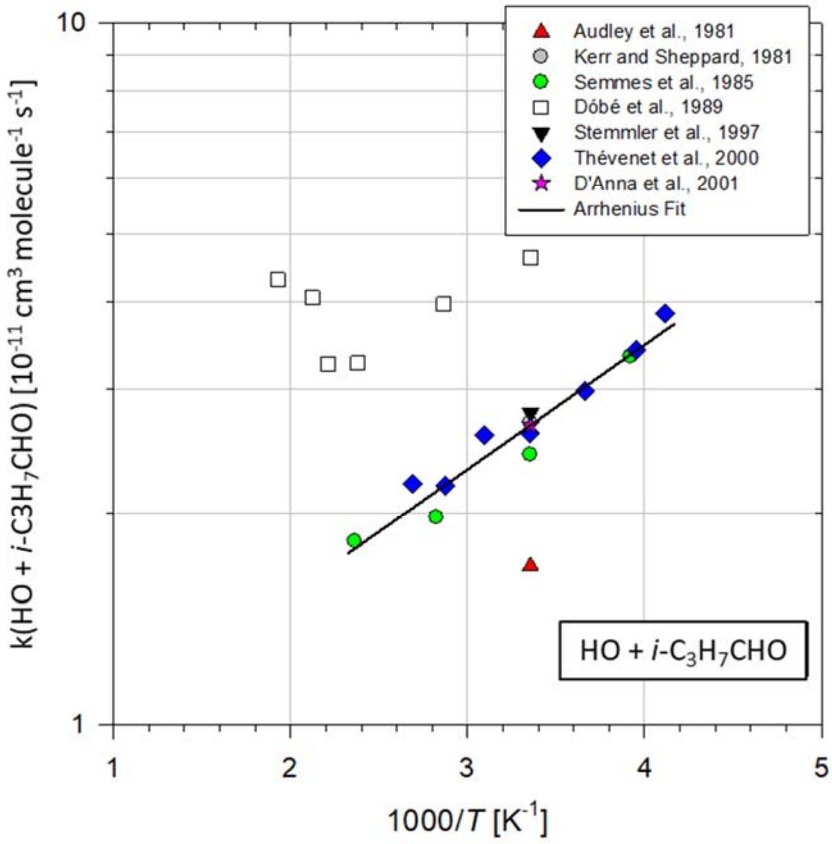
*Comments on Preferred Values*

The measurements of Kerr and Sheppard (1981), Semmes et al. (1985), Stemmler et al. (1997), Thévenet et al. (2000) and D'Anna et al. (2001) at 298 K are in very good agreement. The values reported by Audley et al. (1981) and Dóbé et al. (1989) are, respectively, ~ 40% lower and ~ 70% larger than the others. The preferred 298 K rate coefficient is derived from the mean of the room temperature rate coefficients of Kerr and Sheppard (1981), Semmes et al. (1985), Stemmler et al. (1997), Thévenet et al. (2000) and D'Anna et al. (2001). The temperature dependence is obtained from a fit to the data other than those Audley et al. (1981) and Dóbé et al. (1989). The relative rate coefficient of Audley et al. (1981) was not used in the evaluation, due to questions concerning the applicability of the experimental technique used (Semmes et al., 1985).

### References

Audley, G. J., Baulch, D. L., and Campbell, I. M.: J. Chem. Soc. Faraday Trans., 1 77, 2541, 1981.
Calvert, J. G., Mellouki, A., Orlando, J. J., Pilling, M., and Wallington T. J.: The Mechanisms of Atmospheric Oxidation of the Oxygenates, Oxford University Press, New York, NY, 2011.
D'Anna, B., Andresen, Ø., Gefen, Z. and Nielsen, C. J.: Phys. Chem. Chem. Phys., 3, 3057, 2001.
Dóbé, S., Khachatryan, L. A., and Bérces, T.: Ber. Bunsenges. Phys. Chem., 93, 847, 1989.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

Kerr, J. A., and Sheppard, D. W.: Environ. Sci. Technol., 15, 960, 1981.
Semmes, D. H., Ravishankara, A. R., Gump-Perkins, C. A., and Wine, P. H.: Int. J. Chem. Kinet. 17, 303, 1985.
Stemmler, K., Mengon, W., and Kerr, J., A.: J. Chem. Soc. Faraday Trans., 93, 2865, 1997.
Thévenet, R., Mellouki, A., and Le Bras, G.: Int. J. Chem. Kinet., 32, 676, 2000.



Rate coefficients for HO + i-$CH_3H_7CHO$.

## HOx_VOC69

### HO + $(CH_3)_2CHCH_2OH \rightarrow$ products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | *Temp.*/K | Reference | Technique/Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $(3.1\pm0.9) \times 10^{-12} \exp[(352 \pm 82)/T]$ | 241-370 | Mellouki et al., 2004 | PLP-LIF (a) |
| $(9.2 \pm 0.4) \times 10^{-12}$ | 298 | | |
| *Relative Rate Coefficients* | | | |
| $(8.8 \pm 0.3) \times 10^{-12}$ | 295 ± 2 | Wu et al., 2003 | RR (b, d) |
| $(9.2 \pm 0.4) \times 10^{-12}$ | 295 ± 2 | Wu et al., 2003 | RR (b, e) |
| $(8.5 \pm 0.1) \times 10^{-12}$ | 298 ± 2 | Mellouki et al., 2004 | RR (c, f) |
| $(8.8 \pm 0.3) \times 10^{-12}$ | 298 ± 2 | Mellouki et al., 2004 | RR (c, g) |

## Comments

(a) HO radicals were generated by the photolysis of $H_2O_2$ and their concentration measured by pulsed laser induced fluorescence.

(b) HO radicals were generated by the photolysis of $H_2O_2$ in 1 atmosphere of air at 254 nm. Experiments were carried out in a ~100 liter Teflon chamber, and the concentrations of 2-methyl-1-propanol (isobutyl alcohol), propane and cyclohexane (the reference organics) were measured by GC-FID. The measured rate coefficient ratios of $k(HO + (CH_3)_2CHCH_2OH)/k(HO + \text{propane})$ and $k(HO + (CH_3)_2CHCH_2OH)/k(HO + \text{cyclohexane})$ are placed on an absolute basis using $k(HO + \text{propane}) = 1.05 \times 10^{-12}$ (Atkinson et al., 2006) and $k(HO + \text{cyclohexane}) = 6.9 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 295 K (Calvert et al., 2008).

(c) HO radicals were generated by the photolysis of $H_2O_2$ in 1 atmosphere of air at 254 nm. Experiments were carried out in a ~120 liter Teflon chamber, and the concentrations of 2-methyl-1-propanol (isobutyl alcohol), 1-butanol and 1,3-dioxolane (the reference organics) were measured by GC-FID. The measured rate coefficient ratios of $k(HO + (CH_3)_2CHCH_2OH)/k(HO + \text{1-butanol}) = 1.00 \pm 0.01$ and $k(HO + (CH_3)_2CHCH_2OH)/k(HO + \text{1,3-dioxolane}) = 0.88 \pm 0.03$ are placed on an absolute basis using $k(HO + \text{1-butanol}) = 8.5 \times 10^{-12}$ at 298 K (IUPAC, 2019), and $k(HO + \text{1,3-dioxolane}) = 1.0 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Calvert et al., 2008).

(d) Relative to HO + propane

(e) Relative to HO + cyclohexane

(f) Relative to HO + 1-butanol

(g) Relative to HO + 1,3-dioxolane

## Preferred Values

| Parameter | Value | *T*/K |
|---|---|---|
| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | $8.9 \times 10^{-12}$ | 298 |
| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | $2.73 \times 10^{-12} \exp(352/T)$ | 240-370 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.08 | 298 |
| $\Delta$ E/R | ± 120 | 240-370 |

*Comments on Preferred Values*

The 298 K rate coefficients values from the absolute and relative studies of Mellouki et al. (2004) are in very good agreement with those from the relative determination of Wu et al. (2003). The preferred rate coefficient value at 298 K is derived from the average of the measurements reported in these two studies. The absolute rate study of Mellouki et al. (2004), the sole temperature-dependence study, combined with the preferred 298 K is used to derive E/R.

The reaction of HO with 2-methyl-1-propanol is expected to proceed via H-atom abstraction from $–CH_2–$ and $>CH–$ groups with a lower contribution from the $CH_3$–groups.

$HO + (CH_3)_2CHCH_2OH \rightarrow H_2O + (CH_3)_2CHCH_2O$ (a)

$HO + (CH_3)_2CHCH_2OH \rightarrow H_2O + (CH_3)_2CHCHOH$ (b)

$HO + (CH_3)_2CHCH_2OH \rightarrow H_2O + (CH_3)_2CCH_2OH$ (c)

$HO + (CH_3)_2CHCH_2OH \rightarrow H_2O + CH_2CH(CH_3)CH_2OH$ (d)

The $\alpha$-hydroxy alkyl radical formed by H-atom abstraction from $–CH_2–$ group (channel b) reacts with $O_2$ to form 2-methyl propanal ($(CH_3)_2CHCHO$). The hydroxyl alkyl radicals formed in channels (c) and (d) will add $O_2$ then react with NO to give the alkoxy radicals $(CH_3)_2C(O)CH_2OH$ and $OCH_2CH(CH_3)CH_2OH$. $(CH_3)_2C(O)CH_2OH$ radicals decompose to give acetone and formaldehyde. $OCH_2CH(CH_3)CH_2OH$ radicals react with $O_2$ to give $HC(O)CH(CH_3)CH_2OH$ and decompose to give $2HCHO + CH_3CHO$.

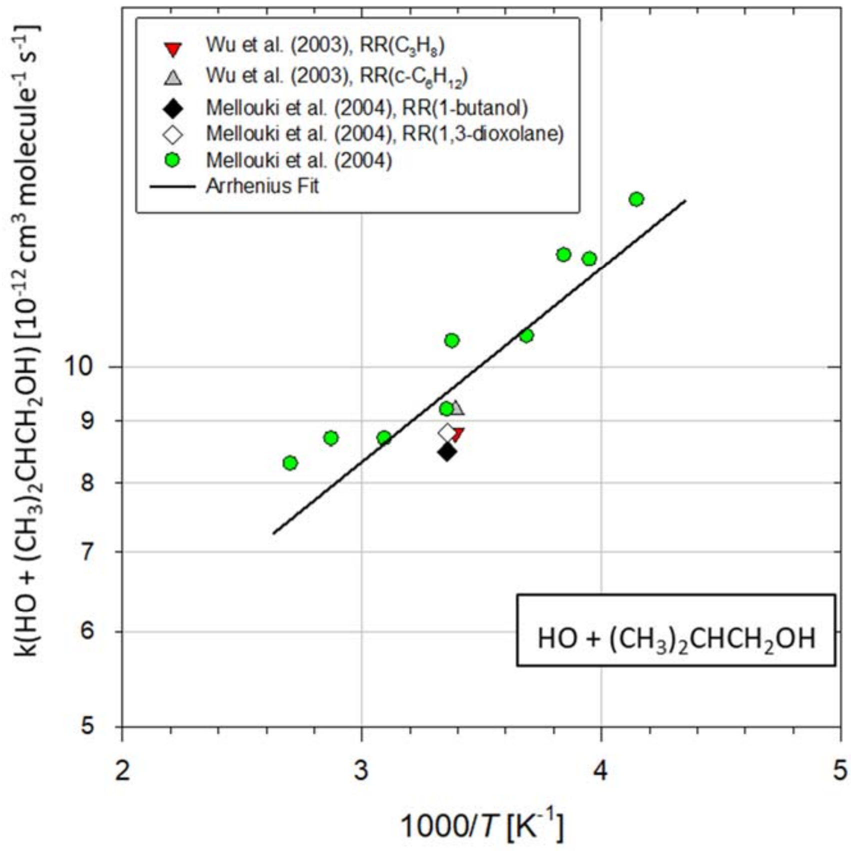
## References

Calvert, J. G., Derwent, R. G., Orlando, J. J., Tyndall, G. S., and Wallington T. J.: Mechanisms of Atmospheric Oxidation of the Alkanes, Oxford University Press, New York, NY, 2008.

IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

Mellouki, A., Oussar, F., Lun, X., and Chakir, A.: Phys. Chem. Chem. Phys., 6, 2951, 2004.

Wu, H., Mu, Y., Zhang, X., and Jiang, G.: Int. J. Chem. Kinet., 35, 81, 2003.



Rate coefficients for HO + $(CH_3)_2CHCH_2OH$.

## HOx_VOC70

## HO + $(CH_3)_3COH \rightarrow$ products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | *Temp.*/K | Reference | Technique/ Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $(3.3 \pm 1.6) \times 10^{-12} \exp[-(310 \pm 150)/T]$ | 240-440 | Wallington et al., 1988 | FP-RF (a) |
| $(1.07 \pm 0.08) \times 10^{-12}$ | 298 | | |
| $(8.1 \pm 1.7) \times 10^{-13}$ | 298 | Saunders et al., 1994 | DF-LIF (b) |
| $(2.66 \pm 0.48) \times 10^{-12} \exp[-(270 \pm 130)/T]$ | 253-372 | Téton et al., 1996 | PLP-LIF (c) |
| $(1.08 \pm 0.10) \times 10^{-12}$ | 298 | | |
| *Relative Rate Coefficients* | | | |
| $(1.08 \pm 0.07) \times 10^{-12}$ | 295 ± 2 | Wu et al., 2003 | RR (d) |

### Comments

(a) HO radicals were generated by the vacuum ultraviolet ($\lambda \geq 165$ nm) photolysis of $H_2O$ and monitored as function of time under pseudo-first order conditions by resonance fluorescence.

(b) HO radicals were generated by the H + $NO_2$ reaction and monitored under pseudo-first order conditions by laser induced fluorescence.

(c) HO radicals were generated by the photolysis of $H_2O_2$ and their concentration measured by pulsed laser induced fluorescence.

(d) HO radicals were generated by the photolysis of $H_2O_2$ in 1 atmosphere of air at 254 nm. Experiments were carried out in a ~100 liter Teflon chamber, and the concentrations of t-butyl alcohol and propane (the reference organic) were measured by GC-FID. The measured rate coefficient ratio of $k(HO + (CH_3)_3COH)/k(HO + \text{propane})$ is placed on an absolute basis using $k(HO + \text{propane}) = 1.05 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 295 K (IUPAC, 2019).

### Preferred Values

| Parameter | Value | *T*/K |
|---|---|---|
| $k$/ molecule$^{-1}$ s$^{-1}$ | $1.1 \times 10^{-12}$ | 298 |
| $k$/ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $1.6 \times 10^{-12} \exp(-121/T)$ | 240-314 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.06 | 298 |
| $\Delta E/R$ | ± 75 | 240-314 |

*Comments on Preferred Values*

The rate coefficient values obtained by Wallington et al. (1988), Téton et al. (1996) and Wu et al. (2003) near 298 K are in very good agreement. The room temperature value of Saunders et al. (1994) is ~25% lower than the others. The Arrhenius plots of the data of Wallington et al. (1988) and Téton et al. (1996) show curvature, fitting the expression $k$ = B +

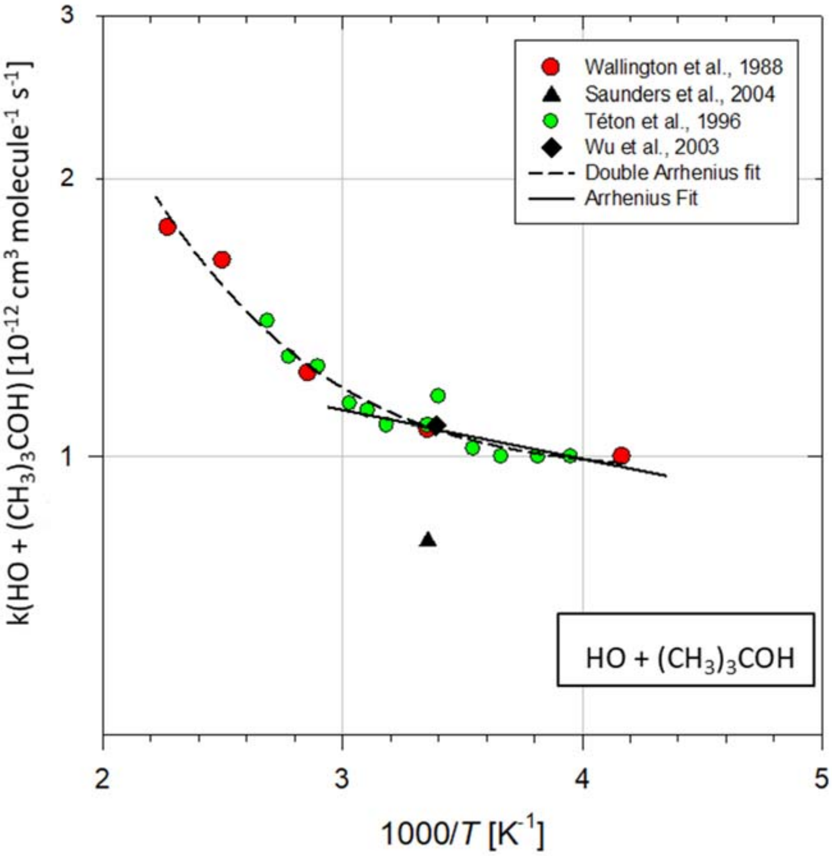
C exp(-D/T) to the rate coefficients reported by these authors gives $k = 9.57\times10^{-13} + 5.65\times10^{-11}$ exp (-1836/T) cm$^3$ molecule$^{-1}$ s$^{-1}$ over the temperature range 240-440 K. For atmospheric purposes, a fit to the data below 314 K of Wallington et al., Téton et al., and Wu et al. yields $k = 1.6 \times 10^{-12}$ exp(-121/$T$), giving $k = 1.1 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K.

The reaction of HO radicals with 2-methyl-2-propanol proceeds mainly by H-atom from $CH_3$- group. Under atmospheric conditions and in the presence of NO, the main degradation products expected are formaldehyde and acetone (Japar et al., 1990):

$$(CH_3)_3COH + HO + NO (+O_2) \rightarrow H_2CO + CH_3C(O)CH_3 + HO_2 + NO_2$$

## References

IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Japar, S. M., Wallington, T. J., Richert, J. F. O. and Ball, J. C.: Int. J. Chem. Kinet., 22, 1257, 1990.
Saunders, S. M., Baulch, D. L., Cooke, K. M., Pilling, M. J. and Smurthwaite, P. I.: Int. J. Chem. Kinet. 26, 113, 1994.
Téton, S., Mellouki, A., Le Bras, G. and Sidebottom, H.: Int. J. Chem. Kinet., 28, 291, 1996.
Wallington, T. J., Dagaut, P., Liu, R. and Kurylo, M. J.: Environ. Sci. Technol., 22, 842, 1988.
Wu, H., Mu, Y., Zhang, X. and Jiang, G.: Int. J. Chem. Kinet., 35, 81, 2003.



Rate coefficients for HO + $(CH_3)_3COH$.

## HOx_VOC76

$$\mathrm{HO + C_2H_5CH(OH)CHO \rightarrow H_2O + C_2H_5CH(OH)CO} \quad (1)$$
$$\mathrm{HO + C_2H_5CH(OH)CHO \rightarrow H_2O + C_2H_5C(OH)CHO} \quad (2)$$

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | *Temp.*/K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(2.37 \pm 0.23) \times 10^{-11}$ | 296 ± 2 | Baker et al., 2004 | RR-GC (a) |

### Comments

(a) HO radicals were generated by the photolysis of $CH_3ONO$-NO-air mixtures at 986 mbar (740 Torr) total pressure of purified air at > 300 nm. Experiments were carried out in a 7500 liter Teflon chamber. 2-hydroxybutanal was generated in situ from the HO radical-initiated reaction of 1,2-butanediol. The concentrations of 2-hydroxybutanal and its precursor, 1,2-butanediol, were measured by gas chromatography. From comparison of the measured time-concentration behaviour of $C_2H_5CH(OH)CHO$ and its precursor a rate coefficient ratio of $k$(HO + 2-hydroxybutanal)/$k$(HO + 1,2-butanediol) = 0.944 ± 0.074 was derived. This rate coefficient ratio is placed on an absolute basis using $k$(HO + 1,2-butanediol) = $2.51 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Calvert et al., 2011).

### Preferred Values

| Parameter | Value | $T$/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $2.4 \times 10^{-11}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.10 | 298 |

*Comments on Preferred Value*

The recommendation is based upon the relative study by Baker et al. (2004). The possible channels for reaction of $C_2H_5CH(OH)CHO$ with HO are:

$$\mathrm{HO + CH_3CH_2CH(OH)CHO \rightarrow CH_3CH_2CH(OH)CO + H_2O} \quad (1)$$
$$\mathrm{\rightarrow CH_3CH_2C(OH)CHO + H_2O} \quad (2)$$
$$\mathrm{\rightarrow CH_3CHCH(OH)CHO + H_2O} \quad (3)$$
$$\mathrm{\rightarrow CH_2CH_2CH(OH)CHO + H_2O} \quad (4)$$
$$\mathrm{\rightarrow CH_3CH_2CH(O)CHO + H_2O} \quad (5)$$

The channels (3), (4) and (5) are expected to be of minor importance compared to the channels (1) and (2). Hence, the reaction is expected to proceed mainly via abstraction of the aldehydic hydrogen to give $C_2H_5CH(OH)CO$ radicals (channel (1)) and through the H-atom abstraction from the >CH- group in the α-position to the hydroxyl group leading to $C_2H_5C(OH)CHO$ radicals (channel (2)) similarly to the reaction of HO with hydroxyacetaldehyde ($HOCH_2CHO$).

## References

Baker, J., Arey, J., and Atkinson, R.: J. Phys. Chem. A, 108, 7032, 2004.
Calvert, J. G., Mellouki, A., Orlando, J. J., Pilling, M. J., and Wallington T. J.: The Mechanisms of Atmospheric Oxidation of the Oxygenates, Oxford University Press, New York, NY, 2011.

## HOx_VOC77

## HO + $C_2H_5CH(OH)CH_2ONO_2$ → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | *Temp.*/K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(7.0 \pm 1.4) \times 10^{-12}$ | 296 ± 2 | Treves and Rudich, 2003 | RR (a, b) |

### Comments

(a) The rate coefficient was measured at atmospheric pressure of dry synthetic air in a photochemical reactor (100 L Tedlar chamber) by the relative rate technique using solid-phase microextraction (SPME) coupled to gas chromatography (GC) for the detection of the organic reactants. HO radicals were generated by the photolysis of $CH_3ONO$ (or $C_2H_5ONO$)-NO-air + 1-nitrooxy-2-butanol + 1-pentanol (or 1-octanol) mixtures at wavelengths > 300 nm. The measured rate coefficient ratios of $k$(HO + 1-nitrooxy-2-butanol)/$k$(HO + 1-pentanol) and $k$(HO + 1-nitrooxy-2-butanol)/$k$(HO + 1-octanol) were not given by the authors, they were placed on an absolute basis using $k$(HO + 1-pentanol) = $(1.12 \pm 0.15) \times 10^{-11}$ and $k$(HO + 1-octanol) = $(1.44 \pm 0.15) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Nelson et al., 1990).

(b) Average of the data obtained relative to HO + 1-pentanol and HO + 1-octanol.

### Preferred Values

| Parameter | Value | *T*/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $7.0 \times 10^{-12}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.20 | 298 |

*Comments on Preferred Values*

The preferred value is an average of the relative rate coefficients of Treves and Rudich (2003) obtained with two reference compounds. The reaction of HO with $C_2H_5CH(OH)CH_2ONO_2$ is expected to proceed mainly via H-atom abstraction from the CH group in the α-position to the hydroxyl group leading to $C_2H_5C(OH)CH_2ONO_2$ radicals which reacts with $O_2$ leading to $HO_2$ and the corresponding carbonyl ($C_2H_5C(O)CH_2ONO_2$).

$$HO + C_2H_5CH(OH)CH_2ONO_2 \rightarrow C_2H_5C(OH)CH_2ONO_2 + H_2O \quad (1)$$
$$O_2 + C_2H_5C(OH)CH_2ONO_2 \rightarrow C_2H_5C(O)CH_2ONO_2 + HO_2 \quad (2)$$

## References

Nelson, L., Rattigan, O., Neavyn, R., Sidebottom, H., Treacy, J., and Nielsen, O.J.: Int. J. Chem. Kinet., 22, 1111, 1990.
Treves, K., and Rudich, Y.: J. Phys. Chem. A, 107, 7809, 2003.

## HOx_VOC78

### HO + $C_2H_5CH(ONO_2)CH_2OH \rightarrow$ products

### Rate coefficient data

| *k*/cm$^3$ molecule$^{-1}$ s$^{-1}$ | *Temp.*/K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(7.4 \pm 1.5) \times 10^{-12}$ | 296 ± 2 | Treves and Rudich, 2003 | RR (a) |

### Comments

(a) The rate coefficient was measured at atmospheric pressure of dry synthetic air in a photochemical reactor (100 L Tedlar chamber) by the relative rate technique using solid-phase microextraction (SPME) coupled to gas chromatography (GC) for the detection of the organic reactants. HO radicals were generated by the photolysis of $CH_3ONO$ (or $C_2H_5ONO$)-NO-air + 2-nitrooxy-1-butanol + 1-pentanol (or 1-octanol) mixtures at wavelengths > 300 nm. The measured rate coefficient ratios of *k*(HO + 2-nitrooxy-1-butanol)/*k*(HO + 1-pentanol) and *k*(HO + 2-nitrooxy-1-butanol)/*k*(HO + 1-octanol) were not given by the authors, they were placed on an absolute basis using *k*(HO + 1-pentanol) = $(1.12 \pm 0.15) \times 10^{-11}$ and *k*(HO + 1-octanol) = $(1.44 \pm 0.15) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Nelson et al., 1990). The value in the table is the average of the data obtained relative to HO + 1-pentanol and HO + 1-octanol.

### Preferred Values

| Parameter | Value | *T*/K |
|---|---|---|
| *k* /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $7.4 \times 10^{-12}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.20 | 298 |

*Comments on Preferred Values*

The preferred value is an average of the relative rate coefficients of Treves and Rudich (2003) obtained with two reference compounds. The reaction of HO with $C_2H_5CH(ONO_2)CH_2OH$ is expected to proceed mainly via H-atom abstraction from the $CH_2$ group in the α-position to the hydroxyl group leading to $C_2H_5C(ONO_2)CH_2OH$ radicals which react with $O_2$ leading to $HO_2$ and the corresponding carbonyl ($C_2H_5C(ONO_2)CHO$).

$$HO + C_2H_5CH(ONO_2)CH_2OH \rightarrow C_2H_5CH(ONO_2)CHOH + H_2O \quad (1)$$
$$O_2 + C_2H_5CH(ONO_2)CHOH \rightarrow C_2H_5CH(ONO_2)CHO + HO_2 \quad (2)$$

## References

Nelson, L., Rattigan, O., Neavyn, R., Sidebottom, H., Treacy, J., and Nielsen, O.J.: Int. J. Chem. Kinet., 22, 1111, 1990.
Treves, K., and Rudich, Y.: J. Phys. Chem. A, 107, 7809, 2003.

## HOx_VOC79

$$\mathbf{HO + CH_3C(O)CH(OH)CH_3 \rightarrow H_2O + CH_3C(O)C(OH)CH_3 \quad (1)}$$
$$\mathbf{HO + CH_3C(O)CH(OH)CH_3 \rightarrow products \quad (2)}$$

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | $T$/K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(9.3 \pm 2.0) \times 10^{-12}$ | 296 ± 2 | Aschmann et al., 2000 | RR-GC (a) |
| $(2.25 \pm 0.20) \times 10^{-12} \exp[(612 \pm 50)/T]$ | 298-338 | Messaadia et al., 2013 | RR-FTIR (b) |
| $(10.1 \pm 3.2) \times 10^{-12}$ | 298 | | |

### Comments

(a) HO radicals were generated by the irradiation of $CH_3ONO$-NO-air mixtures at 986 mbar (740 Torr) total pressure of purified air at ~5% humidity at $\lambda > 300$ nm. Experiments were carried out in a 7900 liter Teflon chamber. The concentrations of 3-hydroxy-2-butanone and n-octane (the reference compound) were measured by gas chromatography. The measured rate coefficient ratio of $k$(HO + 3-hydroxy-2-butanone)/$k$(HO + n-octane) = 1.19 ± 0.05 is placed on an absolute basis using $k$(HO + n-octane) = $7.81 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 296 K and atmospheric pressure (Calvert et al., 2008).

(b) HO radicals were generated by the irradiation of HONO-air mixtures at 800-1013 mbar (600-760 Torr) of air at $400 > \lambda > 300$ nm. Experiments were carried out in a 63 liter triple-jacket Pyrex chamber. The concentrations of 3-hydroxy-2-butanone and benzaldehyde (the reference compound) were measured by FTIR. The measured rate coefficient ratio of $k$(HO + 3-hydroxy-2-butanone)/$k$(HO + benzaldehyde) = 0.80 ± 0.05 (at 298K), 0.70 ± 0.03 (at 313K), 0.72 ± 0.06 (at 338K) are placed on an absolute basis using $k$(HO + benzaldehyde) = $6.8 \times 10^{-12} \exp(185/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Calvert et al., 2011).

### Preferred Values

| Parameter | Value | $T$/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $9.7 \times 10^{-12}$ | 298 |
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $1.24 \times 10^{-12} \exp(612/T)$ | 280-350 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.10 | 298 |
| $\Delta E/R$ | ± 350 | 280-350 |

*Comments on Preferred Values*

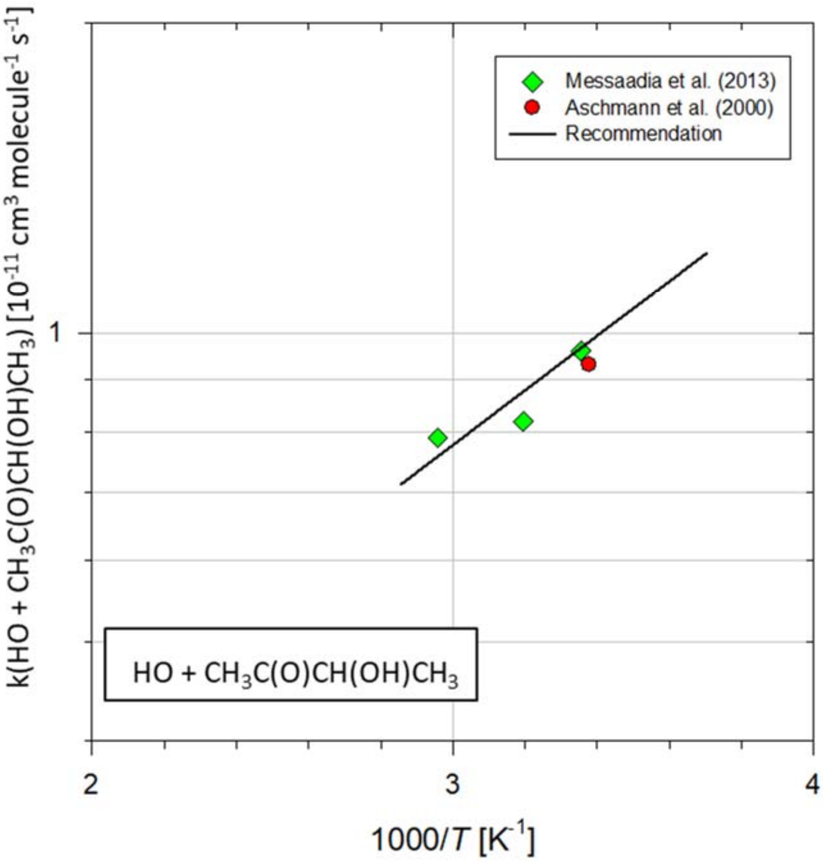
The results reported by Aschmann et al. (2000) and Messaadia et al. (2013) are in good agreement. Taking an average of the results from the two studies gives the recommended value of $k = 9.7 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K. Fitting the Arrhenius expression to the data from Messaadia et al. (2013) and adjusting the A-factor to reproduce the recommended value at 298 K gives $k(\mathrm{HO+CH_3C(O)CH(OH)CH_3}) = 1.24 \times 10^{-12} \exp(612/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$. In the product study by Aschmann et al. (2000) of the HO initiated oxidation of 3-hydroxy-2-butanone it was observed that 2,3-butanedione (biacetyl) was formed in a molar yield of 0.79 ± 0.14. The reaction proceeds mainly via hydrogen atom abstraction from the tertiary C-H bond:

$$\mathrm{HO + CH_3C(O)CH(OH)CH_3 \rightarrow CH_3C(O)C(OH)CH_3 + H_2O}$$
$$\mathrm{CH_3C(O)C(OH)CH_3 + O_2 \rightarrow CH_3C(O)C(O)CH_3 + HO_2}$$

The other possible channel is the H-atom abstraction from the methyl group which may account for about 20 %.

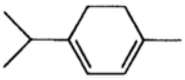
## References

Aschmann, S. M., Arey, J., and Atkinson, R.: J. Phys. Chem. A, 104, 3998, 2000.
Calvert, J. G., Derwent, R. G., Orlando, J. J., Tyndall, G. S., and Wallington, T. J.: *The Mechanisms of Atmospheric Oxidation of the Alkanes*, Oxford University Press, New York, 2008.
Calvert, J. G., Mellouki, A., Orlando, J. J., Pilling, M. J., and Wallington, T. J.: *The Mechanisms of Atmospheric Oxidation of the Oxygenates*, Oxford University Press, New York, 2011.
Messaadia, L., El Dib, G., Cazaunau, M., Roth, E., Ferhati, A., Mellouki, A., and Chakir, A.: Atmos. Env., 77, 951, 2013.



Rate coefficients for HO + $\mathrm{CH_3C(O)CH(OH)CH_3}$.

## HOx_VOC84

### HO +  (α-terpinene) → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(3.53 \pm 0.39) \times 10^{-10}$ | 294±1 | Atkinson et al., 1986 | RR (a) |
| $(3.4 \pm 0.4) \times 10^{-10}$ | 290 | Peeters et al., 1999 | FT-MS (b) |

α-terpinene is 1-isopropyl-4-methyl-cyclohexa-1,3-diene.

## Comments

(a) 6400 L Teflon chamber at 980 mbar (735 Torr) of air. HO radical was generated by the photolysis of $CH_3ONO$ at wavelengths > 300 nm. Correction made to the α-terpinene loss rate due to reaction with $NO_2$ was 24 to 65 % (generally ≈30%). α-terpinene and 2,3-dimethyl-2-butene (reference reactant) were monitored by GC-FID. The rate constant ratio, $k$(HO + α-terpinene) / $k$(HO + 2,3-dimethyl-2-butene) = 3.21 ± 0.35 is placed on an absolute basis using $k$(HO + 2,3-dimethyl-2-butene) = $1.1 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (Atkinson and Arey, 2003).

(b) Flow tube at ≈2.7 mbar (2 Torr) of He. HO was generated by the reaction $H+NO_2$. α-terpinene and isoprene (reference reactant) were monitored by mass spectrometry in excess of HO radicals. The rate constant ratio obtained, $k$(HO + α-terpinene) / $k$(HO + isoprene) is not provided by the authors. The rate coefficient value was placed on an absolute basis using $k$(HO + isoprene) = $1.0 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019).

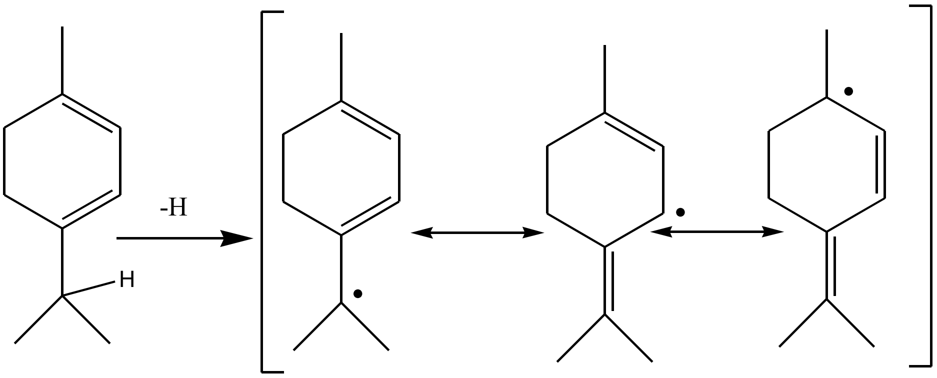
## Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $3.5 \times 10^{-10}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | 0.08 | 298 |

*Comments on Preferred Values*

The preferred value of the room temperature rate coefficient is based on the relative rate studies of Atkinson et al. (1986) and Peeters et al. (1999).

The reaction proceeds by addition of the HO radical to the >C=C< double bonds and by H-atom abstraction from the various C-H bonds with the HO radical addition channel expected to be the dominant channel. Reissell et al. (1999) have observed acetone (≈ 10%) as a reaction product but could not determine the reaction pathways leading to its formation. Both, HO-addition and H-abstraction could be involved. Peeters et al. (1999) reported a yield of (30±8)% for H-atom abstraction from all of the non-vinylic C-H bonds in the α-terpinene molecule. Hydrogen abstraction is facilitated by stabilization of the resulting radical by “super allyl” resonance delocalizing the unpaired electron over three C-atoms as shown in the scheme below (Vereecken and Peeters, 2001). Aschmann et al. (2011) suggested that H-abstraction from α-terpinene and γ-terpinene occur at similar rates. In their study of the HO reaction with γ-terpinene, they have shown that this reaction leads to p-cymene formation at least partly from H-atom abstraction from the two $CH_2$ groups in the 6-member ring. Lee at al. (2006) reported the following molar product yields from the HO-initiated oxidation of α-terpinene in the presence of $NO_x$: α-terpinaldehyde (19±2%), HCHO (7.8±2%), $CH_3CHO$ (0.7±0.1%), HCOOH (6.1±1%), $CH_3C(O)CH_3$ (3.1±4%) and $CH_3C(O)OH$ (2±0.3%).



## References

Aschmann, S. M., Arey, J., and Atkinson, R.: Atmos. Environ., 45, 4408-4411, 2011.
Atkinson, R., Aschmann, S. M., and Pitts, J. N.: Int. J. Chem. Kinet., 18, 287-299, 1986.
Atkinson, R., and Arey, J.: Chem. Rev., 103, 4605-4638, 2003.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Lee, A., Goldstein, A. H., Kroll, J. H., Ng, N. L., Varutbangkul, V., Flagan, R. C., and Seinfeld, J. H.: J. Geophys. Res., 111, D17305, 2006.
Peeters, J., Vandenberk, S., Piessens, E., and Pultau, V.: Chemosphere, 38, 1189-1195, 1999.
Reissell, A., Harry, C., Aschmann, S. M., Atkinson, R., and Arey, J.: J. Geophys. Res., 104, 13869-13879, 1999.

## HOx_VOC85

### HO +  (γ-terpinene) → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(1.73 \pm 0.18) \times 10^{-10}$ | 294±1 | Atkinson et al., 1986 | RR (a) |

γ-terpinene is 1-isopropyl-4-methyl-cyclohexa-1,4-diene.

### Comments

(a) 6400 L Teflon chamber at 980 mbar (735 Torr) of air. HO radical was generated by the photolysis of $CH_3ONO$ at wavelengths > 300 nm. γ-terpinene and 2,3-dimethyl-2-butene (reference reactant) were monitored by GC-FID. The rate constant ratio, $k$(HO + γ-terpinene) / $k$(HO + 2,3-dimethyl-2-butene) = 1.57 ± 0.16 is placed on an absolute basis using $k$(HO + 2,3-dimethyl-2-butene) = $1.1 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (Atkinson and Arey, 2003).

### Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $1.7 \times 10^{-10}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.10 | 298 |

*Comments on Preferred Values*

The preferred value of the room temperature rate coefficient is based on the relative rate study of Atkinson et al. (1986).

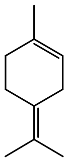
The reaction proceeds by addition of the HO radical to the >C=C< double bonds and by H-atom abstraction from the various C-H bonds with the addition channel being expected to be dominant. Rio et al. (2010) reported a branching ratio of (31±9%) for the H-atom abstraction channel. Reissell et al. (1999) observed acetone as a reaction product (10±3% molar yield) but could not ascribe the reaction pathways leading to its formation; HO-addition and H-abstraction could both be involved. Aschmann et al. (2011) observed p-cymene [1-methyl-4-(1-methylethyl)benzene or 4-isopropyltoluene] as a product from the reaction of HO with γ-terpinene with a molar yield of 13.6±2.5%. They suggested that p-cymene is formed after H-abstraction from the two ring $CH_2$ groups. Lee et al. (2006) observed γ-terpinaldehyde (57±6%), HCHO (17±2%), $CH_3CHO$ (1.2±0.2%), HCOOH (8.3±0.8%), $CH_3C(O)CH_3$ (5.3±0.5%) and

$CH_3C(O)OH$ (4.5±0.5%) as products of HO- radical initiated oxidation of γ-terpinene in the presence of $NO_x$.

## References

Aschmann, S. M., Arey, J., and Atkinson, R.: Atmos. Environ., 45, 4408-4411, 2011.
Atkinson, R., Aschmann, S. M., and Pitts, J. N.: Int. J. Chem. Kinet., 18, 287-299, 1986.
Atkinson, R., and Arey, J.: Chem. Rev., 103, 4605-4638, 2003.
Lee, A., Goldstein, A. H., Kroll, J. H., Ng, N. L., Varutbangkul, V., Flagan, R. C., and Seinfeld, J. H.: J. Geophys. Res., 111, D17305, 2006.
Reissell, A., Harry, C., Aschmann, S. M., Atkinson, R., and Arey, J.: J. Geophys. Res., 104, 13869-13879, 1999.
Rio, C., Flaud, P-M., Loison, J-C., and Villenave, E.: Chem. Phys. Chem., 11, 3962-3970, 2010.

## HOx_VOC86

**HO +**  **(terpinolene) → products**

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | *Reference* | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(2.21 \pm 0.56) \times 10^{-10}$ | 295 ± 2 | Corchnoy and Atkinson, 1990 | RR-GC (a) |

Terpinolene is 4-isopropylidene-1-methyl-cyclohexene

### Comments

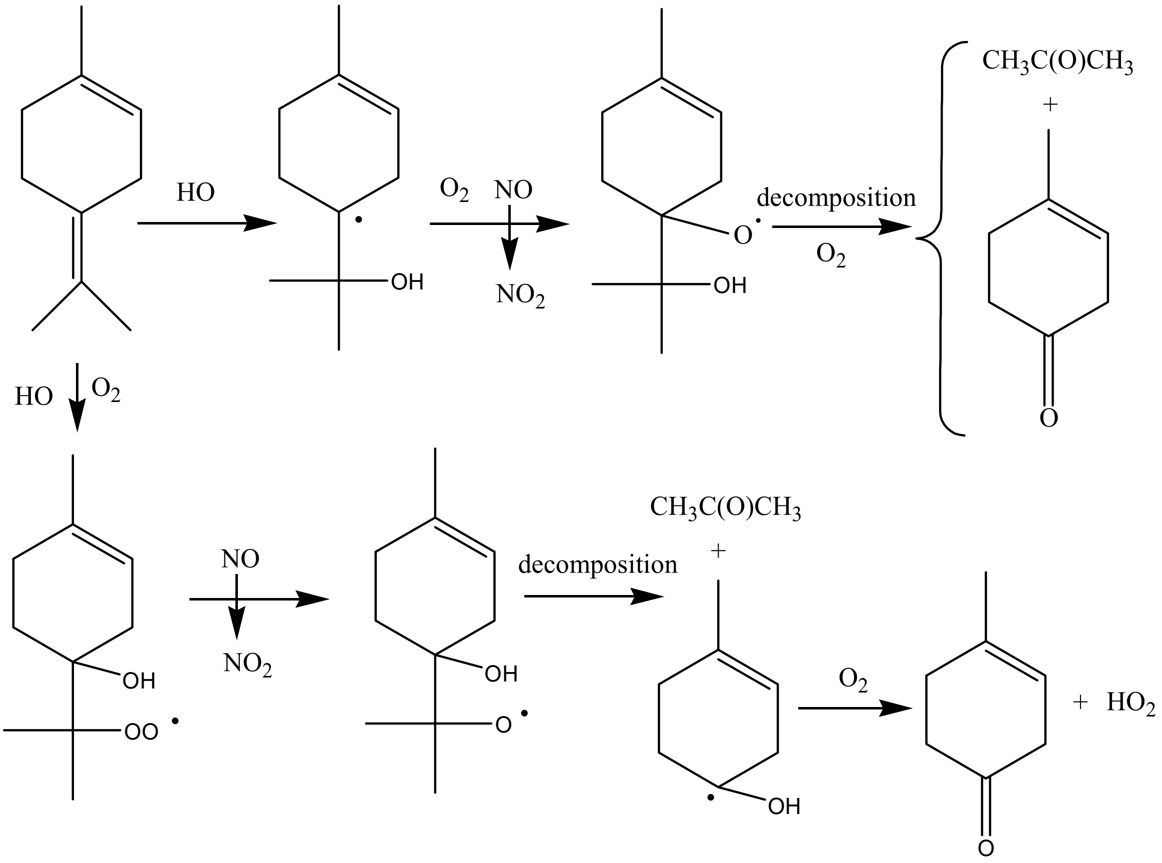
(a) 6400 L Teflon chamber at 735 Torr (980 mbar) of air. HO was generated using the photolysis of $CH_3ONO$ at wavelengths of >300 nm. Terpinolene and isoprene (reference reactant) were monitored by GC-FID. The rate constant ratio $k$(HO + terpinolene) / ($k$(HO + isoprene) = 2.21 ± 0.09 is placed on an absolute basis using $k$(HO + isoprene) = $1.0 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019).

### Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $2.2 \times 10^{-10}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.15 | 298 |

*Comments on Preferred Values*

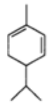
The preferred value of the room temperature rate coefficient is based on the single relative rate study of Corchnoy and Atkinson (1990). The error limits are expanded to reflect the single measurement. The reaction proceeds almost entirely by HO radical addition to the C=C bonds in terpinolene. Hakola et al. (1994) identified 4-methyl-3-cyclohexen-1-one as a major product from the reaction of HO radical with terpinolene in presence of NOx with a yield of (26±6) %. Acetone has been reported to be formed with a yield of 32-39 % (Reissell et al., 1999, Orlando et al., 2000) which is similar to the measured yield of the co-product 4-methyl-3-cyclohexen-1-one (reaction scheme given below). Hakola et al. (1994) observed another product with a minor yield of (8±2) % which was tentatively identified as a keto-aldehyde compound ($(CH_3)_2C{=}C(CH_2CHO)CH_2CH_2C(O)CH_3$) arising from the addition of HO to the endocyclic C=C bond (Hakola et al., 1994). Orlando et al. (2000) identified formaldehyde and formic acid as reaction products with yields of (29±6%) and (8±2%), respectively. Lee at al. (2006) reported a yield of 31% for secondary organic aerosol (SOA) formation along with organic compounds such as HCHO (23±3%), $CH_3CHO$ (0.7±0.1%), HCOOH (3.5±0.7%), $CH_3C(O)CH_3$ (20±2%) and $CH_3C(O)OH$ (1±0.2%).



## References

Corchnoy, S. B., and Atkinson, R., Env. Sci. Tech., 24, 1497-1502, 1990.
Hakola, H., Arey, J., Aschmann, S., and Atkinson, R., J. Atmos. Chem., 18, 75-102, 1994.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Lee, A., Goldstein, A.H., Kroll, J.H., Ng, N.L., Varutbangkul, V., Flagan, R.C., and Seinfeld, J.H., J. Geophys. Res., 111, D17305, doi:10.1029/2006JD007050, 2006.
Orlando, J.J., Nozière, B., Tyndall, G.S., Orzechowska, G.E., Paulson, S.E., Rudich, Y., J. Geophys. Res., 105, 11561-11572, 2000.
Reissell, A., Harry, C., Aschmann, S.M., Atkinson, R., and Arey, J., J. Geophys. Res., 104, 13869-13879, 1999.

## HOx_VOC87

HO +  (α-phellandrene) → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(3.05 \pm 0.70) \times 10^{-10}$ | 294±1 | Atkinson et al., 1986 | RR (a) |
| $(3.3 \pm 0.4) \times 10^{-10}$ | 290 | Peeters et al., 1999 | FT-MS (b) |

α-phellandrene is 2-methyl-5-(1-methylethyl)-1,3-cyclohexadiene.

### Comments

(a) 6400 L Teflon chamber at 980 mbar (735 Torr) of air. HO radical was generated by the photolysis of $CH_3ONO$ at wavelengths > 300 nm. α-phellandrene and 2,3-dimethyl-2-butene (reference reactant) were monitored by GC-FID. Correction made to the α-phellandrene loss rate due to reaction with $NO_2$ was 15 to 59 % (generally ≈50%). The rate constant ratio, $k$(HO + α- phellandrene) / $k$(HO + 2,3-dimethyl-2-butene) = 2.77 ± 0.63 is placed on an absolute basis using $k$(HO + 2,3-dimethyl-2-butene) = $1.1 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (Atkinson and Arey, 2003).

(b) Flow tube at ≈2.7 mbar (2 Torr) of He. HO was generated by the reaction H+$NO_2$. α-phellandrene and isoprene (reference reactant) were monitored by mass spectrometry in excess of HO radicals. The rate constant ratio obtained, $k$(HO + α-phellandrene) / $k$(OH + isoprene) is not provided by the authors. The rate coefficient value was placed on an absolute basis using $k$(HO + isoprene) = $1.0 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019).

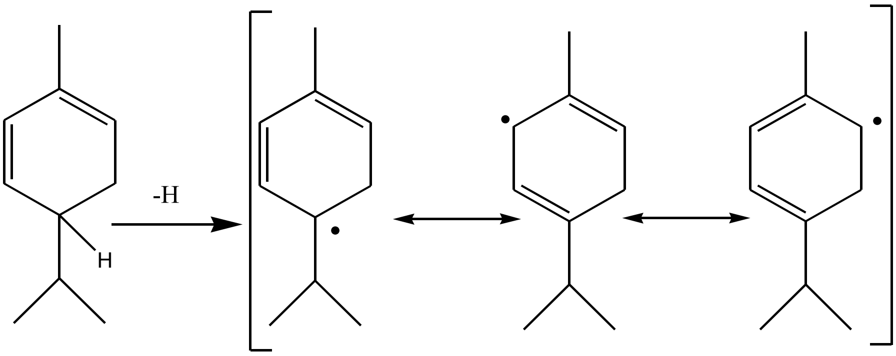
### Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $3.2 \times 10^{-10}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.08 | 298 |

*Comments on Preferred Values*

The preferred value of the room temperature rate coefficient is based on the relative rate studies of Atkinson et al. (1986) and Peeters et al. (1999).

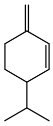
The reaction proceeds by initial addition of the HO radical to the carbon atoms of the C=C bonds and by H-atom abstraction from the various C-H bonds with the OH radical addition channel being expected to be dominant. Reissell et al. (1999) have observed acetone (8±4%) as a reaction product but could not determine the reaction pathways leading to its formation. Both, HO-addition and H-abstraction could be involved. Peeters et al. (1999) have reported a yield of (27±10)% for H-atom abstraction through the direct observation of $H_2O$ as reaction product. H-atom abstraction is expected to occur mainly from the non-vinylic C-H bonds and $CH_2$ group in the ring with H-atom abstraction from the methyl and isopropyl substituent groups being of minor importance since the tertiary C-H bond in the isopropyl group is not allylic. The hydrogen abstraction is facilitated by stabilization of the resulting radical by "super allyl" resonance delocalizing the unpaired electron over three C-atoms as shown in the scheme (Vereecken and Peeters, 2001, Aschmann et al., 2011).



## References

Aschmann, S. M., Arey, J., and Atkinson, R.: Atmos. Environ., 45, 4408-4411, 2011.
Atkinson, R., Aschmann, S. M., and Pitts, J. N.: Int. J. Chem. Kinet., 18, 287-299, 1986.
Atkinson, R., and Arey, J.: Chem. Rev., 103, 4605-4638, 2003.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Peeters, J., Vandenberk, S., Piessens, E., and Pultau, V.: Chemosphere, 38, 1189-1195, 1999.
Reissell, A., Harry, C., Aschmann, S. M., Atkinson, R., and Arey, J.: J. Geophys. Res., 104, 13869-13879, 1999.
Vereecken, L., and Peeters, J.: Chem. Phys. Letters, 333, 162-168, 2001.

## HOx_VOC88

**HO +**  **(β-phellandrene) → products**

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(1.66 \pm 0.41) \times 10^{-10}$ | 297±2 | Shorees et al., 1991 | RR (a) |

β-phellandrene is 3-isopropyl-6-methylene-cyclohexene.

### Comments

(a) 6400 L Teflon chamber at 980 mbar (735 Torr) of air. HO radical was generated by the photolysis of $CH_3ONO$ at wavelengths > 300 nm. β-phellandrene and 2,3-dimethyl-2-butene (reference reactant) were monitored by GC-FID. Correction made to the β-phellandrene loss rate due to reaction with $NO_2$ was <32 % (typically 10-20%). β-phellandrene concentrations were corrected to account for the presence of a co-eluting limonene impurity, initially present at 9.8 % of the β-phellandrene concentration. The rate constant ratio, $k$(HO + β-phellandrene) / $k$(HO + 2,3-dimethyl-2-butene) = $1.51 \pm 0.20$ is placed on an absolute basis using $k$(HO + 2,3-dimethyl-2-butene) = $1.1 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (Atkinson and Arey, 2003).

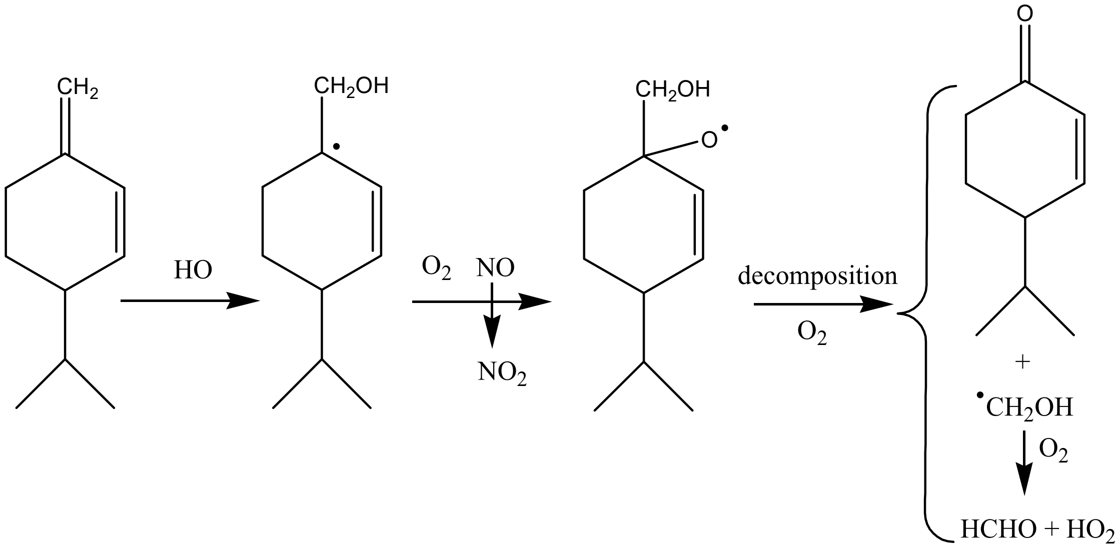
### Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $1.7 \times 10^{-10}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | $\pm 0.15$ | 298 |

*Comments on Preferred Values*

The preferred value of the rate coefficient at 298 K is based on the relative rate coefficient determination of Shorees et al. (1991) with increased uncertainties reflecting the difficulties of the experiment and the single measurement.

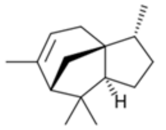
The reaction proceeds by initial addition of the HO radical to the carbon atoms of the C=C bonds and by H-atom abstraction from the various C-H bonds with the HO radical addition channel being expected to be the dominant. Hakola et al. (1999) have identified 4-isopropyl-2-cyclohexen-1-one as a product of the reaction with a formation yield of (29±7%). 4-Isopropyl-2-cyclohexen-1-one is expected to be produced through the initial HO addition at the acyclic >C=C< bond as shown below:



## References

Atkinson, R., and Arey, J.: Chem. Rev., 103, 4605-4638, 2003.
Hakola, H., Shorees, B., Arey, J., and Atkinson R.: Environ. Sci. Technol., 27, 278-283, 1993.
Shorees, B., Atkinson, R. and Arey, J.: Int. J. Chem. Kinet., 23, 897-906, 1991.

## HOx_VOC89

**HO +**  **(α-cedrene) → products**

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(6.7 \pm 1.4) \times 10^{-11}$ | 296±2 | Shu and Atkinson, 1995 | RR (a) |

α-Cedrene is (1S,2R,5S,7R)-2,6,6,8-tetramethyltricyclo[5.3.1.0$^{1,5}$]undec-8-ene

### Comments

(a) 6400 L Teflon chamber at 987 mbar (740 Torr) of air. HO radical was generated by the photolysis of $CH_3ONO$ at wavelengths > 300 nm. α-Cedrene and 2,3-dimethyl-2-butene (reference reactant) were monitored by GC-FID. The rate constant ratio, $k$(HO + α-cedrene) / $k$(HO + 2,3-dimethyl-2-butene) = 0.608 ± 0.017 is placed on an absolute basis using $k$(HO + 2,3-dimethyl-2-butene) = $1.1 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (Atkinson and Arey, 2003).

### Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.7 \times 10^{-11}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.10 | 298 |

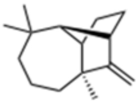
*Comments on Preferred Values*

The preferred value of the rate coefficient at 298 K is based on the relative rate coefficient determination of Shu and Atkinson (1995). The reaction is expected to proceed predominantly by addition to the >C=C< double bond.

### References

Atkinson, R., and Arey, J.: Chem. Rev., 103, 4605-4638, 2003.
Shu, Y., and Atkinson, R.: J. Geophys. Res., 100, 7275-7281, 1995.

## HOx_VOC90

**HO +**  **(longifolene) → products**

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(4.7 \pm 1.0) \times 10^{-11}$ | 296±2 | Shu and Atkinson, 1995 | RR (a) |

Longifolene is (1R,2S,7S,9S)- 3,3,7-trimethyl- 8-methylenetricyclo- [5.4.0.0$^{2,9}$]undecane

### Comments

(a) 6400 L Teflon chamber at 987 mbar (740 Torr) of air. HO radical was generated by the photolysis of $CH_3ONO$ at wavelengths > 300 nm. Longifolene and trans-2-butene (reference reactant) were monitored by GC-FID. The rate constant ratio, $k$(HO + longifolene) / $k$(HO + trans-2-butene) = 0.729 ± 0.025 is placed on an absolute basis using $k$(HO + trans-2-butene) = $6.4 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (IUPAC, 2019).

### Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $4.7 \times 10^{-11}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.10 | 298 |

*Comments on Preferred Values*

The preferred value of the rate coefficient at 298 K is based on the relative rate coefficient determination of Shu and Atkinson (1995). The reaction is expected to proceed predominantly by addition to the >C=C< double bond. The HO-initiated oxidation mechanism of longifolene is complex with many different pathways that produce a large number of organic compounds. Lee et al. (2006) reported molar product yields for HCHO (25±3%), $CH_3CHO$ (3.7±0.4%), HCOOH (31±3%), $CH_3C(O)CH_3$ (3.8±0.3%) and $CH_3C(O)OH$ (15±1%).

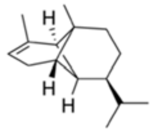
### References

IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

Lee, A. Allen H. Goldstein, A. H., Kroll, J. H., Ng, N. L., Varutbangkul, V., Flagan, R. C., and Seinfeld, J. H.: J. Geophys. Res., 111, D17305, doi:10.1029/2006JD007050, 2006.

Shu, Y., and Atkinson, R.: J. Geophys. Res., 100, 7275-7281, 1995.

## HOx_VOC91

**HO +**  **(α-copaene) → products**

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(9.0 \pm 1.9) \times 10^{-11}$ | 296±2 | Shu and Atkinson, 1995 | RR (a) |

α-Copaene is (1R,2S,6S,7S,8S)-8-isopropyl-1,3-dimethyltricyclo[4.4.0.0$^{2,7}$]dec-3-ene

### Comments

(a) 6400 L Teflon chamber at 987 mbar (740 Torr) of air. HO radical was generated by the photolysis of $CH_3ONO$ at wavelengths > 300 nm. α-Copaene and 2,3-dimethyl-2-butene (reference reactant) were monitored by GC-FID. The rate constant ratio, $k$(HO + α-copaene) / $k$(HO + 2,3-dimethyl-2-butene) = $0.817 \pm 0.044$ is placed on an absolute basis using $k$(HO + 2,3-dimethyl-2-butene) = $1.1 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (Atkinson and Arey, 2003).

### Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $9.0 \times 10^{-11}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.10 | 298 |

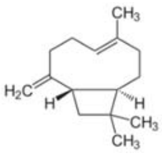
*Comments on Preferred Values*

The preferred value of the rate coefficient at 298 K is based on the relative rate coefficient determination of Shu and Atkinson (1995). The reaction is expected to proceed predominantly by addition to the >C=C< double bond.

### References

Atkinson, R., and Arey, J.: Chem. Rev., 103, 4605-4638, 2003.
Shu, Y., and Atkinson, R.: J. Geophys. Res., 100, 7275-7281, 1995.

## HOx_VOC92

**HO +**  **(β-caryophyllene) → products**

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(2.0\,^{+0.5}_{-0.9}) \times 10^{-10}$ | 296±2 | Shu and Atkinson, 1995 | RR (a) |

β-caryophyllene is 4,11,11-trimethyl-8-methylene-bicyclo[7.2.0]undec-4-ene

### Comments

(a) 6400 L Teflon chamber at 987 mbar (740 Torr) of air. HO radical was generated by the photolysis of $CH_3ONO$ at wavelengths > 300 nm. β-caryophyllene and 2,3-dimethyl-2-butene (reference reactant) were monitored by GC-FID. Corrections for the dark decay of β-caryophyllene were made. The rate constant ratio, $k$(HO + β-caryophyllene) / $k$(HO + 2,3-dimethyl-2-butene) = 1.79 ± 0.22 is placed on an absolute basis using $k$(HO + 2,3-dimethyl-2-butene) = $1.1 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (Atkinson and Arey, 2003).

### Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $2.0 \times 10^{-10}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.15 | 298 |

*Comments on Preferred Values*

The preferred value of the rate coefficient at 298 K is based on the relative rate coefficient determination of Shu and Atkinson (1995).

The reaction is expected to proceed predominantly by addition to both the exocyclic and endocyclic double bonds. A large yield (68%) of secondary organic aerosol was reported by Lee at al. (2006) along with gas phase organic species such as HCHO (42±10%), $CH_3CHO$ (0.6±0.2%), HCOOH (6.2±2%), $CH_3C(O)CH_3$ (1.5±0.4%) and $CH_3C(O)OH$ (8.7±2%). Hydroxy-hydroperoxides, dihydroxy compounds and hydroketones are expected to be among the first generation products (Jenkin et al., 2012).

## References

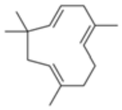
Atkinson, R., and Arey, J., Chem. Rev., 103, 4605-4638, 2003.

Jenkin, M. E., Wyche, K. P., Evans, C. J., Carr, T., Monks, P. S., Alfarra, M. R., Barley, M. H., McFiggans, G. B., Young, J. C., and Rickard, A. R.: Atmos. Chem. Phys., 12, 5275–5308, 2012.

Lee, A. Allen H. Goldstein,A. H., Kroll, J. H., Ng, N.L., Varutbangkul, V., Flagan, R. C., and Seinfeld, J. H.: J. Geophys. Res., 111, D17305, doi:10.1029/2006JD007050, 2006

Shu, Y., and Atkinson, R.: J. Geophys. Res., 100, 7275-7281, 1995.

# HOx_VOC93

**HO +**  **(α-humulene) → products**

## Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(2.9^{+0.7}_{-1}) \times 10^{-10}$ | 296±2 | Shu and Atkinson, 1995 | RR (a) |

α-Humulene is 2,6,6,9-Tetramethyl-1,4-8-cycloundecatriene

## Comments

(a) 6400 L Teflon chamber at 987 mbar (740 Torr) of air. HO radical was generated by the photolysis of $CH_3ONO$ at wavelengths > 300 nm. α-Humulene and 2,3-dimethyl-2-butene (reference reactant) were monitored by GC-FID. The rate constant ratio, $k$(HO + α-humulene) / $k$(HO + 2,3-dimethyl-2-butene) = 2.66 ± 0.27 is placed on an absolute basis using $k$(HO + 2,3-dimethyl-2-butene) = $1.1 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (Atkinson and Arey, 2003).

## Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $2.9 \times 10^{-10}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.10 | 298 |

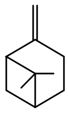
*Comments on Preferred Values*

The preferred value of the rate coefficient at 298 K is based on the relative rate coefficient determination of Shu and Atkinson (1995). The reaction is expected to proceed predominantly by addition to the >C=C< double bonds.

## References

Atkinson, R., and Arey, J.: Chem. Rev., 103, 4605-4638, 2003.
Shu, Y., and Atkinson, R.: J. Geophys. Res., 100, 7275-7281, 1995.

## HOx_VOC99

**HO +**  **(β-pinene) → products**

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $2.36 \times 10^{-11} \exp[(358 \pm 58)/T]$ | 297-423 | Kleindienst et al., 1982 | FP-RF (a) |
| $(7.76 \pm 1.10) \times 10^{-11}$ | 297 | | |
| $9.96 \times 10^{-12} \exp[(610 \pm 50)/T]$ | 300-435 | Chuong et al., 2002 | DF-RF/LIF (b) |
| $(7.72 \pm 0.44) \times 10^{-11}$ | 300 | | |
| $(7.68 \pm 0.72) \times 10^{-11}$ | 298 | Davis et al. 2005 | DF-LIF (c) |
| *Relative Rate Coefficients* | | | |
| $(6.54 \pm 0.99) \times 10^{-11}$ | 305 ± 2 | Winer et al., 1976 | RR/P-GC-FID (d) |
| $(7.81 \pm 0.51) \times 10^{-11}$ | 294 ± 1 | Atkinson et al., 1986 | RR/P-GC-FID (e) |
| $1.46 \times 10^{-11} \exp[(468 \pm 50)/T]$ | 295-364 | Gill and Hites, 2002 | RR/P-MS (f) |
| $(7.03 \pm 1.60) \times 10^{-11}$ | 298 | | |
| $1.91 \times 10^{-11} \exp[(416 \pm 17)/T]$ | 240-340 | Montenegro et al., 2012 | RR/DF-MS (g) |
| $(7.80 \pm 1.35) \times 10^{-11}$ | 298 | | |
| $(8.72 \pm 2.60) \times 10^{-11}$ | 298 | Dash and Rajakumar, 2013 | RR/P-GC-FID (h) |

β-pinene is 6,6-dimethyl-2-methylene-bicyclo[3.1.1]heptane

### Comments

(a) Flash photolysis of $H_2O$/β-pinene mixtures in Ar (buffer gas) at total pressures in the range 50-200 Torr (67-270 mbar) under slow flow conditions. Pseudo-first order decays of HO radical concentrations (monitored by RF) were characterized in the presence of excess concentrations of β-pinene. $k$ displayed no dependence on pressure over the studied range.

(b) Pseudo-first order decays of HO radical concentrations (monitored by RF or LIF) were characterized in the presence of excess concentrations of β-pinene. Experiments carried out at a total pressure of 5 Torr (6.7 mbar) of either He or 90% He/10% $O_2$.

(c) Pseudo-first order decays of HO radical concentrations (monitored by LIF) were characterized in the presence of excess concentrations of β-pinene. Experiments carried out at a total pressure of 5 Torr (6.7 mbar) of mainly He, with $O_2$ present at ~ 1-4% of the mixture.

(d) HO radicals were generated by the photolysis of $NO_x$ – organic – air mixtures in a 5870 L chamber at ~1 bar pressure. The concentrations of β-pinene and 2-methylpropene (the reference compound) were analyzed by GC during the experiments. The measured rate coefficient ratio $k$(HO + β-pinene)/$k$(HO + 2-methylpropene) = 1.33 (± 30%) is placed on an absolute basis using $k$(HO + 2-methylpropene) = $4.92 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 305 K (IUPAC, 2019).

(e) HO radicals were generated by the photolysis of $CH_3ONO$ in air at wavelengths >300 nm in a 6400 L Teflon chamber at ~980 mbar pressure. The concentrations of β-pinene and 2,3-dimethyl-2-butene (the reference compound) were analyzed by GC during UV irradiation of $CH_3ONO$ - NO - β-pinene - 2,3-dimethyl-2-butene - air mixtures. The measured rate coefficient ratio $k$(HO + β-pinene)/$k$(HO + 2,3-dimethyl-2-butene) = 0.710 ± 0.046 is placed on an absolute basis using k(HO + 2,3-dimethyl-2-butene) = 1.10 x $10^{-10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ (Atkinson and Arey, 2003).

(f) HO radicals were generated by the photolysis of $H_2O_2$ in helium diluent in a 192 $cm^3$ volume quartz vessel. The concentrations of β-pinene and 1-butene, 2-methylpropene or *trans*-2-butene (the reference compounds) were analyzed by MS during the experiments. The measured rate coefficient ratios *k*(HO + β-pinene)/*k*(HO + 1-butene), *k*(HO + β-pinene)/*k*(HO + 2-methylpropene) and *k*(HO + β-pinene)/*k*(HO + *trans*-2-butene) are placed placed on an absolute basis using *k*(HO + 1-butene) = 6.6 x $10^{-12}$ exp(465/*T*) $cm^3$ $molecule^{-1}$ $s^{-1}$, *k*(HO + 2-methylpropene) = 9.4 x $10^{-12}$ exp(505/*T*) $cm^3$ $molecule^{-1}$ $s^{-1}$ and *k*(HO + *trans*-2-butene) = 1.0 x $10^{-11}$ exp(553/*T*) $cm^3$ $molecule^{-1}$ $s^{-1}$ (IUPAC, 2019).

(g) HO radicals were generated by the reaction of $H_2O$ with F atoms (formed from $F_2$ discharge), and added to flowing mixtures containing β-pinene and isoprene (the reference compound) in helium at a total pressure of 1-8 Torr (1.3-11 mbar). The measured rate coefficient ratios, *k*(HO + β-pinene)/*k*(HO + isoprene), are placed on an absolute basis using the rate coefficient expression *k*(HO + isoprene) = 2.7 x $10^{-11}$ exp(370/*T*) $cm^3$ $molecule^{-1}$ $s^{-1}$ (IUPAC, 2019).

(h) HO radicals were generated by the photolysis of $H_2O_2$ in nitrogen diluent at pressures in the range 800 Torr (1070 mbar) in a 1750 $cm^3$ volume quartz vessel. The concentrations of β-pinene and 2-methylpropene (the reference compound) were analyzed by GC-FID. The measured rate coefficient ratio *k*(HO + β-pinene)/*k*(HO + 2-methylpropene) is placed on an absolute basis using *k*(HO + 2-methylpropene) = 5.1 x $10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at 298 K (IUPAC, 2019).

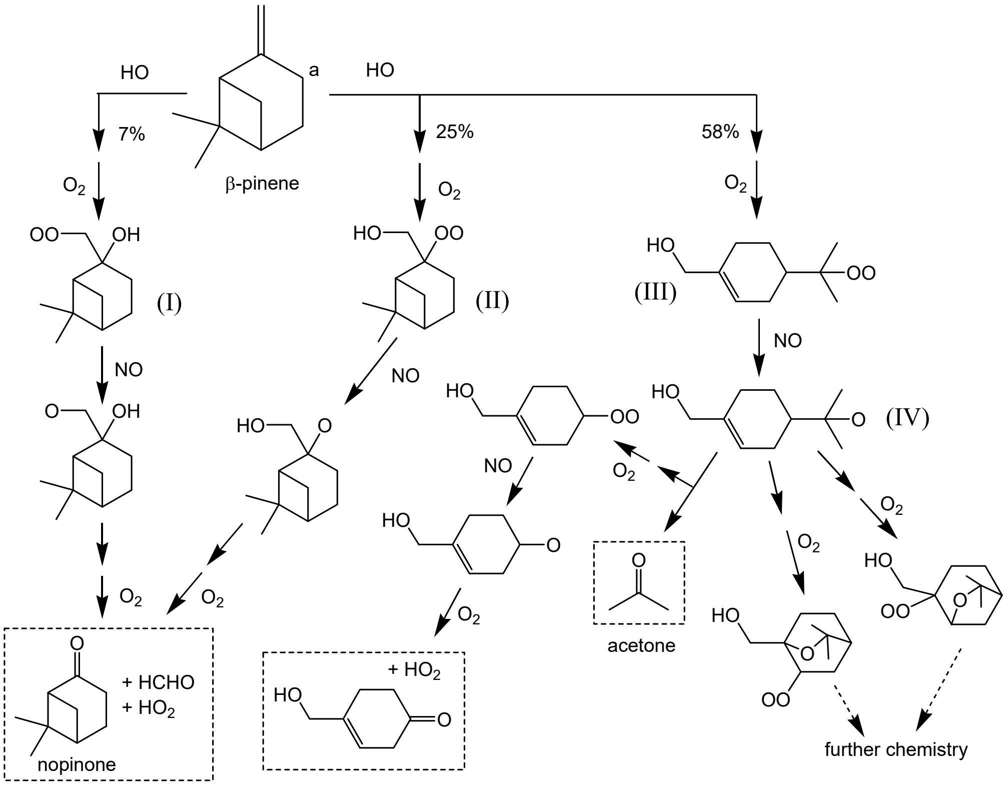
**Preferred Values**

| Parameter | Value | T/K |
|---|---|---|
| *k* /$cm^3$ $molecule^{-1}$ $s^{-1}$ | 7.6 × $10^{-11}$ | 298 |
| *k* /$cm^3$ $molecule^{-1}$ $s^{-1}$ | 1.62 × $10^{-11}$ exp(460/T) | 240-420 |
| *Reliability* | | |
| Δ log *k* | ± 0.05 | 298 |
| Δ E/R | ± 150 | 240-420 |

*Comments on Preferred Values*

The preferred value of E/R is a rounded average of those reported in the four tabulated temperature-dependence studies, with the assigned uncertainty range encompassing the set of values. The 298 K preferred value of *k* is the average of the room temperature values reported in all the tabulated studies, with those of Winer et al. (1976), Kleindienst et al. (1982), Atkinson et al. (1986) and Choung et al. (2002) corrected to 298 K using the preferred temperature dependence. The pre-exponential factor is adjusted to fit the 298 K preferred value.

H atom abstraction has been estimated to account for about 10 % of the reaction of HO with β-pinene at 298 K (Vereecken and Peeters, 2012); with position “a” in the schematic below (forming a resonant radical) being the most important attack site. The reaction proceeds mainly by initial addition of the HO radical to the C=C bond, and the schematic illustrates some established and predicted features of the subsequent chemistry in air in the presence of $NO_x$.



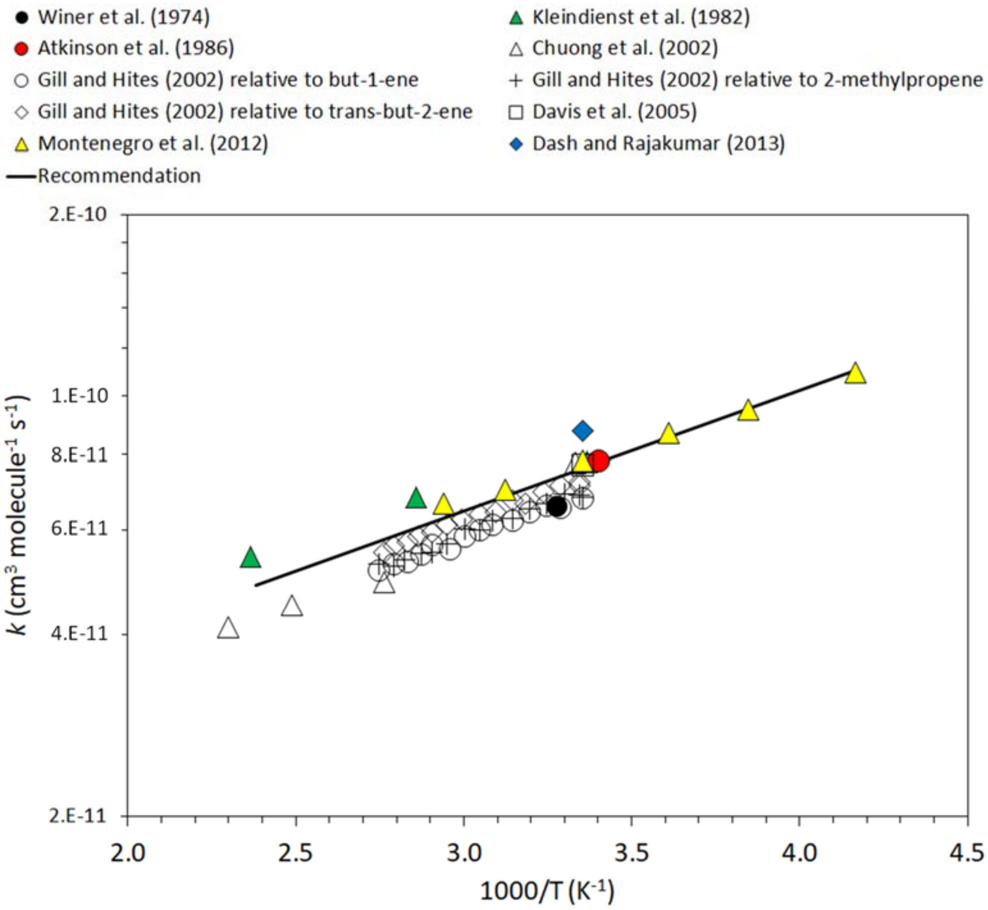
The hydroxy-substituted peroxy radicals, (I), (II) and (III), are formed from sequential addition of HO and $O_2$, with (III) facilitated by competitive opening of the cyclobutyl ring in the intermediate chemically-activated HO-β-pinene adduct. The approximate contributions of the three pathways shown are based on the calculations of Vereecken and Peeters (2012) for 298 K and 1 bar. The subsequent chemistry, propagated by the reactions of intermediate peroxy radicals with NO, forms a number of carbonyl end products (as shown in boxes). The chemistry of (I) and (II) generates nopinone, which has been reported to be formed with a yield of about 25-30% in experimental studies in the presence of $NO_x$ (Arey et al. 1990; Hakola et al., 1994; Wisthaler et al., 2001). Its co-product, formaldehyde, has been reported to be formed with a higher yield of 45 ± 8 % (Orlando et al., 2000), consistent with its additional formation from other sources in the system. The chemistry of (III) partially generates acetone, which has been reported to be formed in yields in the range 2-13% (Aschmann et al., 1998; Reissell et al., 1999; Nozière et al., 1999; Orlando et al., 2000). Its low yield may be explained by the operation of competing channels for oxy radical intermediate (IV), such as the illustrated ring closure reactions postulated by Vereecken and Peeters (2004; 2012).

The reactions of all the peroxy radicals with NO also partially form the corresponding hydroxy-nitrate products (not shown in the schematic), which have been reported to be formed with a collective yield of about 25% by Ruppert et al. (1999). Other products have also been observed, including formic acid (2%) by Orlando et al. (2000); and product signals consistent with a number of higher molecular weight dihydroxycarbonyl, hydroxynitrate and dihydroxynitrate products by Aschmann et al. (1998).

Other reactions of the intermediate peroxy radicals can compete with reaction with NO under atmospheric conditions, and in experimental studies with low $NO_x$ levels. These include bimolecular reactions with $HO_2$ and organic peroxy radicals, which can have propagating channels (leading to lower yields of the same end products discussed above) and terminating channels generating hydroxy-hydroperoxide, hydroxy-carbonyl and dihydroxy products. Unimolecular isomerization reactions may also be available for complex peroxy radical intermediates. Vereecken and Peeters (2004) calculated that peroxy radical (III) undergoes a ring closure reaction (forming a peroxide-bridged product) that dominates at ≤ 1 ppb NO; and Berndt et al. (2016) have postulated that auto-oxidation reaction sequences, initiated by isomerization of peroxy radical (III) and involving a number of subsequent peroxy radical isomerization reactions, may account for the observed rapid formation of highly oxidized multifunctional organic compounds from the HO-initiated oxidation of β-pinene in chamber experiments. The role of unimolecular isomerization reactions has recently been confirmed by Xu et al. (2019), who experimentally and theoretically characterized a number of competitive ring-closure and H-atom shift reactions for peroxy radical (III).

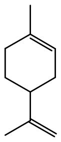
## References

Arey, J., Atkinson, R. and Aschmann, S. M.: J. Geophys. Res., 95, 18546, 1990
Aschmann, S. M., Reissell, A., Atkinson, R. and Arey, J.: J. Geophys. Res., 103, 25553, 1998.
Aschmann, S. M., Atkinson, R. and Arey, J.: J. Geophys. Res., 107 (D14), 4191, 10.1029/2001JD001098, 2002.
Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
Atkinson, R., Aschmann, S. M. and Pitts Jr., J. N.: Int. J. Chem. Kinet., 18, 287, 1986.
Berndt, T., Richters, S., Jokinen, T., Hyttinen, N., Kurtén, T., Otkjær, R. V., Kjaergaard, H. G., Stratmann, F., Herrmann, H., Sipila, M., Kulmala, M. and Ehn, M.: Nat. Commun., 7, 13677, 2016.
Chuong, B., Davis, M., Edwards, M. and Stevens, P. S.: Int. J. Chem. Kinet., 34, 300, 2002.
Gill, K. J. and Hites, R. A.: J. Phys. Chem. A, 106, 2538, 2002.
Dash, M. R. and Rajakumar, B.: Atmos. Environ., 79, 161, 2013.
Davis, M. E., Tapscott, C. and Stevens, P. S.: Int. J. Chem. Kinet., 37, 522, 2005.
Hakola, H., Arey, J., Aschmann, S. M. and Atkinson, R.: J. Atmos. Chem., 18, 75, 1994.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Kleindienst, T. E., Harris, G. W. and Pitts Jr., J. N.: Environ. Sci. Technol., 16, 844, 1982.
Montenegro, A., Ishibashi, J. S. A., Lam, P. and Li, Z.: J. Phys. Chem. A, 116, 12096, 2012.
Nozière, B., Barnes, I. and Becker, K.-H.: J. Geophys. Res., 104, 23645, 1999.
Orlando, J. J., Nozière, B., Tyndall, G. S., Orzechowska, G., Paulson, S. E. and Rudich, Y.: J. Geophys. Res., 105, (D9), 11561, 2000.
Reissell, A., Harry, C., Aschmann, S. M., Atkinson, R. and Arey, J.: J. Geophys. Res., 104, 13869, 1999.
Ruppert, L., Becker, K. H., Nozière, B., Spittler, M.: Development of monoterpene oxidation mechanisms: results from laboratory and smog chamber studies. Borrell, P.M., Borrell, P. (eds.) Transport and Chemical Transformation in the Troposphere. Proceedings of the EUROTRAC-2 Symposium '98, pp. 63–68. WIT, Southampton, UK, 1999.
Vereecken, L. and Peeters, J.: J. Phys. Chem. A, 108, 5197, 2004.
Vereecken, L. and Peeters, J.: Phys. Chem. Chem. Phys., 14, 3802, 2012.
Winer, A. M., Lloyd, A. C., Darnall, K. R. and Pitts Jr., J. N.: J. Phys. Chem., 80, 1635, 1976.
Wisthaler, A., Jensen, N. R., Winterhalter, R., Lindinger, W. and Hjorth, J.: Atmos. Environ., 35, 618, 2001.
Xu, L., Møller, K. H., Crounse, J. D., Otkjær, R. V., Kjaergaard, H. G., and Wennberg, P. O.: J. Phys. Chem. A., 123, 1661, 2019.



Rate coefficients for HO + β-Pinene.

## HOx_VOC100

**HO +**  **(limonene) → products**

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $4.59 \times 10^{-11} \exp[(382 \pm 154)/T]$ | 300-360 | Braure et al., 2014 | DF-MS (a) |
| $1.65 \times 10^{-10}$ | 300 | | |
| *Relative Rate Coefficients* | | | |
| $(1.45 \pm 0.22) \times 10^{-10}$ | 305 ± 2 | Winer et al., 1976 | RR (b) |
| $(1.66 \pm 0.50) \times 10^{-10}$ | 294 ± 1 | Atkinson et al., 1986 | RR (c) |
| $4.20 \times 10^{-11} \exp[(401 \pm 43)/T]$ | 295-364 | Gill and Hites, 2002 | RR (d) |
| $(1.61 \pm 0.31) \times 10^{-10}$ | 298 | | |
| $2.53 \times 10^{-11} \exp[(569 \pm 56)/T]$ | 220-355 | Braure et al., 2014 | DF-MS (a) |
| $1.70 \times 10^{-10}$ | 298* | | |

limonene is 4-isopropenyl-1-methyl-cyclohexene

### Comments

(a) Both absolute and relative rate determinations reported, carried out in 1 Torr (1.3 mbar) of He. Absolute rate coefficients determined mainly from observed decay of HO concentration in excess limonene, but with some experiments monitoring the decay of limonene concentration in excess HO. $k$ was also reported to be independent of pressure over the range 0.5-5 Torr (0.7-6.7 mbar). Relative rate determinations carried out using either the HO + $CH_3SSCH_3$ reaction or the HO + $Br_2$ reaction as a reference, with the latter monitored using the formation of the product HOBr. The measured rate coefficient ratios $k$(HO + limonene)/$k$(HO + $CH_3SSCH_3$) and $k$(HO + limonene)/$k$(HO + $Br_2$) are placed on an absolute basis using $k$(HO + $CH_3SSCH_3$) = $7.0 \times 10^{-11} \exp(350/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and $k$(HO + $Br_2$) = $1.9 \times 10^{-11} \exp(240/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019). The authors preferred to report a rate expression based on a combined analysis of all data. Applying the above reference rate coefficients, this results in the slightly adjusted expression, $k = 2.8 \times 10^{-11} \exp(543/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ over the temperature range 220-360 K, which is used here to represent their data. Almost identical temperature-dependent rate coefficients were also reported for the DO + limonene reaction, with the branching ratio for H atom abstraction described by $(0.07 \pm 0.03) \exp((460 \pm 140)/T)$ over the temperature range 253-355K, based on monitoring the formation of HDO.

(b) HO radicals were generated by the photolysis of $NO_x$ - organic - air mixtures in a 5870 L chamber at ~1 bar pressure. The concentrations of limonene and 2-methylpropene (the reference compound) were analyzed by GC. The measured rate coefficient ratio $k$(HO + limonene)/$k$(HO + 2-methylpropene) is placed on an absolute basis using $k$(HO + 2-methylpropene) = $4.92 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 305 K (IUPAC, 2019).

(c) HO radicals were generated by the photolysis of $CH_3ONO$ in air at wavelengths >300 nm in a 6400 L Teflon chamber at ~980 mbar pressure. The concentrations of limonene and 2,3-

dimethyl-2-butene (the reference compound) were analyzed by GC during UV irradiation of $CH_3ONO$ - NO - limonene - 2,3-dimethyl-2-butene - air mixtures. The measured rate coefficient ratio *k*(HO + limonene)/*k*(HO + 2,3-dimethyl-2-butene) = 1.51 ± 0.04 is placed on an absolute basis using *k*(HO + 2,3-dimethyl-2-butene) = $1.10 \times 10^{-10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ (Atkinson and Arey, 2003).

(d) HO radicals were generated by the photolysis of $H_2O_2$ in helium diluent in a 192 $cm^3$ volume quartz vessel. The concentrations of limonene and 1-butene, 2-methylpropene or *trans*-2-butene (the reference compounds) were analyzed by MS. The measured rate coefficient ratios *k*(HO + limonene)/*k*(HO + 1-butene), *k*(HO + limonene)/*k*(HO + 2-methylpropene) and *k*(HO + limonene)/*k*(HO + *trans*-2-butene) are placed on an absolute basis using *k*(HO + 1-butene) = $6.6 \times 10^{-12} \exp(465/T)$ $cm^3$ $molecule^{-1}$ $s^{-1}$, *k*(HO + 2-methylpropene) = $9.4 \times 10^{-12} \exp(505/T)$ $cm^3$ $molecule^{-1}$ $s^{-1}$ and *k*(HO + *trans*-2-butene) = $1.0 \times 10^{-11} \exp(553/T)$ $cm^3$ $molecule^{-1}$ $s^{-1}$ (IUPAC, 2019).

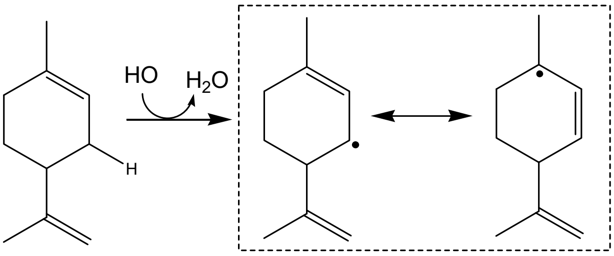
**Preferred Values**

| Parameter | Value | T/K |
|---|---|---|
| $k$ /$cm^3$ $molecule^{-1}$ $s^{-1}$ | $1.65 \times 10^{-10}$ | 298 |
| $k$ /$cm^3$ $molecule^{-1}$ $s^{-1}$ | $3.41 \times 10^{-11} \exp(470/T)$ | 220-360 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.05 | 298 |
| $\Delta$ E/R | ± 150 | 220-360 |

*Comments on Preferred Values*

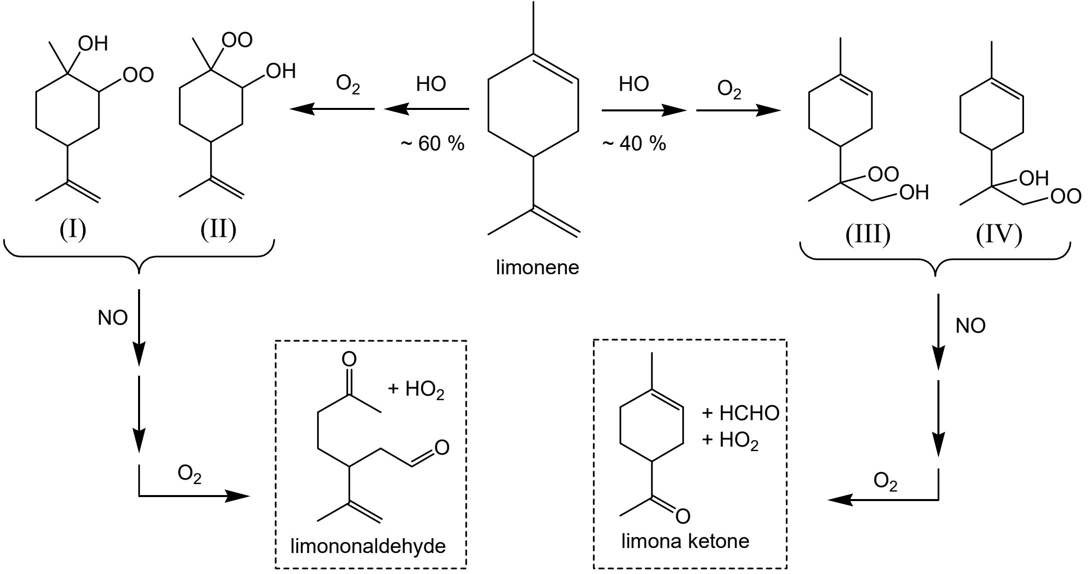
The preferred value of *E*/*R* is a rounded average of the values of Gill and Hites (2002) and Braure et al. (2014), with the latter based on the composite analysis of all their data (see comment (a)). The 298 K preferred value of *k* is the average of the room temperature values reported by Atkinson et al. (1986), corrected to 298 K using the preferred temperature dependence, Gill and Hites (2002) and Braure et al. (2014), based on the composite analysis of all their data (see comment (a)), which are in good agreement. The determination of Winer et al. (1974) is about 10 % lower than the preferred value, but within the assigned uncertainty bounds. The pre-exponential factor is adjusted to fit the 298 K preferred value.

H-atom abstraction has been reported to account for about 30 % of the reaction of HO (or DO) with limonene at 298 K (Rio et al., 2010; Braure et al., 2014). Rio et al. (2010) derived their value from analysis of the time-dependence of composite product peroxy radical absorptions (UV absorption) in air at atmospheric pressure, and from observation of product radical fragments (MS) at low pressure in the absence of $O_2$. Braure et al. (2014) derived their value from formation of HDO from the reaction of DO with limonene. They also observed an unexpected negative temperature dependence in the branching ratio (see comment (a)), suggesting a contribution of H-atom abstraction of over 40% at 250 K. A significant contribution of H-atom abstraction is expected to be facilitated by formation of resonant product radicals, following abstraction at five of the six available (saturated carbon) sites, e.g.:



However, theoretical (Dash and Rajakumar, 2015) and structure activity methods (Vereecken and Peeters, 2001), predict a much lower contribution of about 3-17 % from H-atom abstraction at 298 K, and a positive temperature dependence. Confirmatory experimental and theoretical studies would therefore be valuable.

HO addition is expected to occur significantly at both the endocyclic and exocyclic double bonds in limonene, and the schematic below illustrates some established features of the subsequent chemistry in air in the presence of $NO_x$.

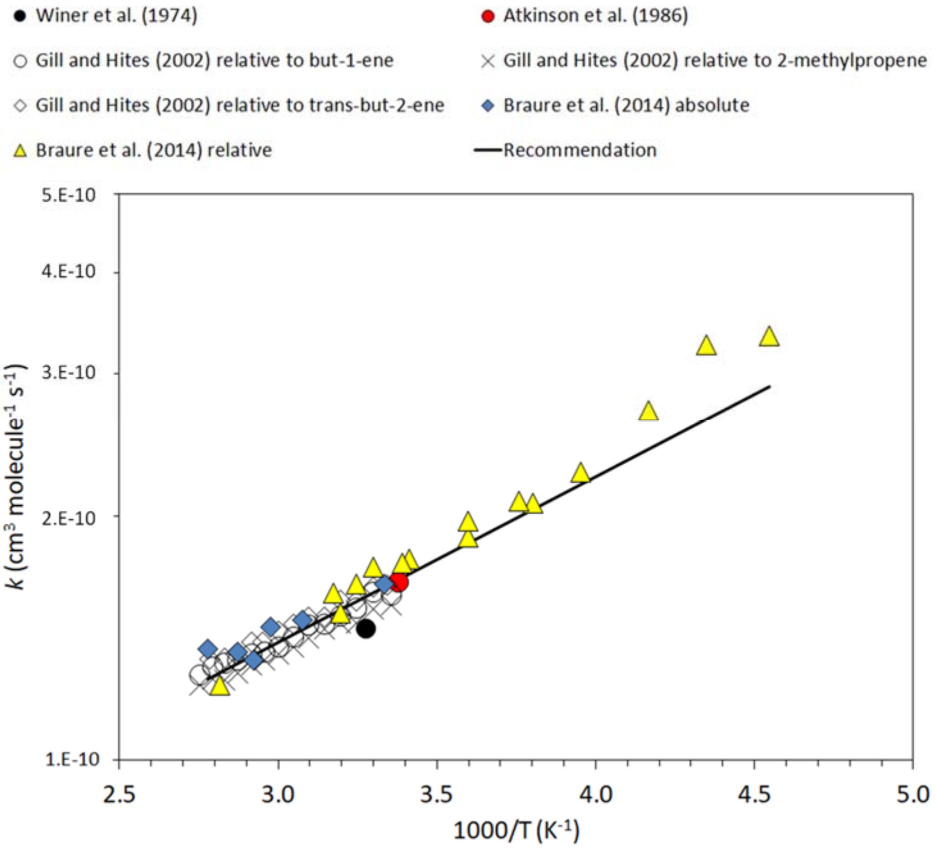


The hydroxy-substituted peroxy radicals, (I) and (II), are formed from sequential addition of HO and $O_2$ to the endocyclic bond, and (III) and (IV) are formed from addition to the exocyclic bond; with the approximate addition contributions shown based on structure activity methods (Peeters et al., 2007). The subsequent chemistry, propagated by the reactions of intermediate peroxy radicals with NO, forms a number of carbonyl end products (as shown in boxes). The chemistry of (I) and (II) generates limononaldehyde (3-isopropenyl-6-oxo-heptanal), for which yields of 28 % and 29 ± 6 % in the presence of $NO_x$ have been reported by Arey et al. (1990) and Hakola et al. (1994) respectively. The chemistry of (III) and (IV) generates limona ketone (4-acetyl-1-methyl-cyclohexene), for which the reported yields are 17.4 ± 2.8 % (Arey et al., 1990) and 20 ± 3 % (Hakola et al., 1994). Its co-product, formaldehyde, has been reported to be formed with a yield of 43 ± 5 % in photo-oxidation experiments (Lee et al., 2006), although limonene was partially reacting with $O_3$ under their experimental conditions. The reactions of all the peroxy radicals with NO also partially form the corresponding hydroxy-nitrate products (not shown in the schematic), which have been reported to be formed with a collective yield of about 23% by Ruppert et al. (1999).

Other reactions of the intermediate peroxy radicals can compete with reaction with NO under atmospheric conditions, and in experimental studies with low $NO_x$ levels. These include bimolecular reactions with $HO_2$ and organic peroxy radicals, which can have propagating channels (leading to lower yields of the same end products discussed above) and terminating channels generating hydroxy-hydroperoxide, hydroxy-carbonyl and dihydroxy products.

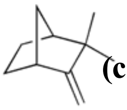
## References

Arey, J., Atkinson, R. and Aschmann, S. M.: J. Geophys. Res., 95, 18546, 1990.
Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
Atkinson, R., Aschmann, S. M. and Pitts Jr., J. N.: Int. J. Chem. Kinet., 18, 287, 1986.
Braure, T., Bedjanian, Y., Romanias, M. N., Morin, J., Riffault, V., Tomas, A. and Coddeville, P.: J. Phys. Chem. A, 118, 9482, 2014.
Dash, M. R. and Rajakumar, B.: Mol. Phys., 113(21), 3202, 2015.
Gill, K. J. and Hites, R. A.: J. Phys. Chem. A, 106, 2538, 2002.
Hakola, H., Arey, J., Aschmann, S. M. and Atkinson, R.: J. Atmos. Chem., 18, 75, 1994.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Lee, A., Goldstein, A. H., Kroll, J. H., Ng, N. L., Varutbangkul, V., Flagan, R. C., and Seinfeld, J. H: J. Geophys. Res., 111, D17305, doi:10.1029/2006JD007050, 2006.
Peeters, J., Boullart, W., Pultau, V., Vandenberk, S. and Vereecken, L.: J. Phys. Chem. A, 111, 1618, 2007.
Rio, C., Flaud, P-M, Loison, J-C. and Villenave, E.: Chem. Phys. Chem, 11, 3962, 2010.
Ruppert, L., Becker, K. H., Nozière, B., Spittler, M.: Development of monoterpene oxidation mechanisms: results from laboratory and smog chamber studies. Borrell, P.M., Borrell, P. (eds.) Transport and Chemical Transformation in the Troposphere. Proceedings of the EUROTRAC-2 Symposium '98, pp. 63–68. WIT, Southampton, UK, 1999.
Vereecken, L. and Peeters, J.: Chem. Phys. Lett., 333, 162, 2001.
Winer, A. M., Lloyd, A. C., Darnall, K. R. and Pitts Jr., J. N.: J. Phys. Chem., 80, 1635, 1976.



Rate coefficients for HO + Limonene.

## HOx_VOC101

**HO +**  **(camphene) → products**

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(5.28 \pm 0.20) \times 10^{-11}$ | 296 ± 2 | Atkinson et al., 1990 | RR-GC-FID (a) |
| $4.1 \times 10^{-12} \exp[(754 \pm 44)/T]$ | 288-311 | Gaona-Colman et al., 2017 | RR-FTIR (b, c) |
| $(5.1 \pm 1.1) \times 10^{-11}$ | 298 | Gaona-Colman et al., 2017 | (b, c) |
| $(5.1 \pm 0.3) \times 10^{-11}$ | 298 | Gaona-Colman et al., 2017 | (b, d) |

Camphene is 2,2-dimethyl-3-methylene-bicyclo[2.2.1]heptane.

### Comments

(a) HO radicals were generated by the photolysis of $CH_3ONO$ in air at wavelengths >300 nm in a 6400 L Teflon chamber at ~980 mbar pressure. The concentrations of camphene and isoprene (the reference compound) were analyzed by GC-FID during UV irradiation of $CH_3ONO$ - NO - camphene - isoprene - air mixtures. The measured rate coefficient ratio $k$(HO + camphene)/$k$(HO + isoprene) = 0.528 ± 0.019 is placed on an absolute basis using $k$(HO + isoprene) = $1.0 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019).

(b) HO radicals were generated by the photolysis of $H_2O_2$ in nitrogen at 254 nm in a 1080 L Teflon chamber at ~1000 mbar pressure. The concentrations of camphene and isoprene (the reference compound) were analyzed by long path FTIR during UV irradiation of $H_2O_2$ - camphene - reference - nitrogen mixtures. Two references were employed, 2,3-dimethyl-2-butene and isobutene at 298 K and isobutene in the temperature range 288-311 K. The measured rate coefficient ratios, $k$(HO + camphene)/$k$(HO + 2,3-dimethyl-2-butene) = 0.47 ± 0.01 and $k$(HO + camphene)/$k$(HO + isobutene) = 0.99 ± 0.02 are placed on an absolute basis using $k$(HO + 2,3-dimethyl-2-butene) = $1.09 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson et al., 1983) and $k$(HO + isobutene) = $5.14 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson, 1997). The measured rate coefficients in the temperature range 288-311 K are placed on an absolute basis using $k$(HO + isobutene) = $9.47 \times 10^{-12} \exp(504/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson, 1997).

(c) Relative to isobutene.

(d) Relative to 2,3-dimethyl-2-butene.

### Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $5.2 \times 10^{-11}$ | 298 |
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $4.14 \times 10^{-12} \exp(754/T)$ | 280-320 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.10 | 298 |
| $\Delta$ E/R | ± 100 | 280-320 |

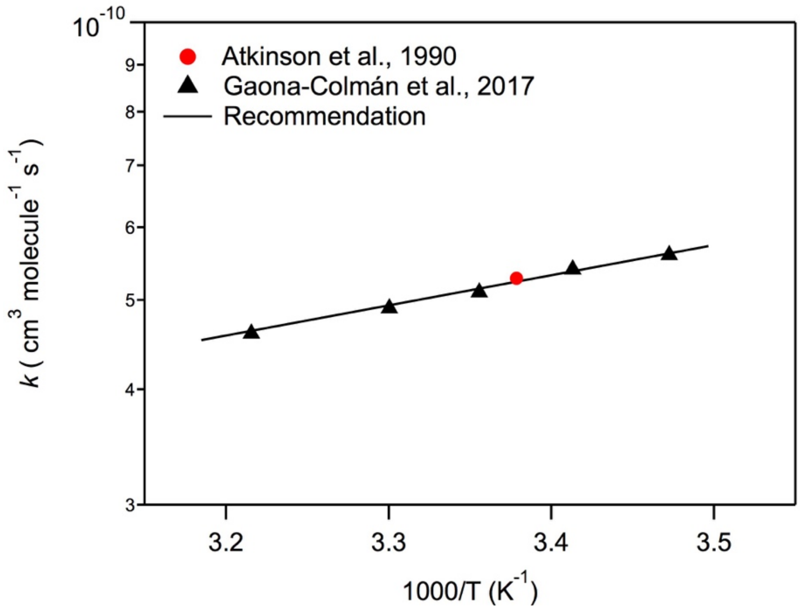
*Comments on Preferred Values*

The 298 K rate coefficients values from the absolute and relative studies of Gaona-Colman et al. (2017) are in very good agreement with the relative determination of Atkinson et al. (1990). Fitting the Arrhenius expression to the data from Gaona-Colman et al. (2017) and adjusting the A-factor slightly to reproduce the recommended value at 298 K gives the preferred temperature dependence expression.

The reaction of OH radical with camphene proceeds mainly by addition of OH to the double bond terminal carbon atom to form hydroxylalkyl radicals that will add $O_2$ to form hydroxyalkylperoxy radicals. In the presence of NO, hydroxyalkylperoxy radicals will be converted to hydroxyalkoxy radicals, which may either decompose or react with $O_2$. In absence of NOx, hydroxyalkylperoxy radicals undergo self-reaction and reactions with other peroxy radicals. Reissell et al (1999) and Gaona-Colman et al. (2017) have reported, respectively, (39±5)% and (33±6)% formation yields of acetone in presence of NOx. In absence of NOx, the yield of acetone reported by Gaona-Colman et al. (2017) was (10±2)%. The formaldehyde yields obtained by Gaona-Colman et al. (2017) were (3.6±0.7)% and (10±2)% in the absence and presence of NOx, respectively. Hakola et al. (1994) have observed the formation of camphenilone (3,3-dimethylbicyclo[2.2.1]heptan-2-one) and 6,6-dimethyl-3-caprolactone-2,5-methylene (4,4-dimethyl-3-oxabicyclo[3.2.1]octan-2-one) with very small yields (<0.02%).

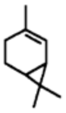
**References**

Atkinson, R., Aschmann, S. M. and Arey, J.: Atmos. Environ., 24, 2647, 1990.
Atkinson, R., Aschmann, S. M. and Carter, W. P., Int. J. Chem. Kinet., 15, 1161, 1983
Atkinson, R.: Phys. Chem. Ref. Data, 26, 215, 1997.
Gaona-Colman, E., Blanco, M. B., Barnes, I., Wiesen, P. and Turuel M. A.: RSC Adv., 7, 2733, 2017
Hakola, H., Arey, J., Aschmann, S. M. and Atkinson, R.: J. Atmos. Chem., 18, 75, 1994.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Reissell, A., Harry, C., Aschmann, S. M., Atkinson, R. and Arey, J.: J, Geophys. Res., 104, 13869, 1999.



Rate coefficients for HO + Camphene.

## HOx_VOC102

**HO +**  **(2-carene) → products**

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(7.95 \pm 2.00) \times 10^{-11}$ | 295 ± 2 | Corchnoy and Atkinson, 1990 | RR-GC-FID (a) |

2-carene is 3,7,7-trimethyl-bicyclo[4.1.0]hept-2-ene.

### Comments

(a) HO radicals were generated by the photolysis of $CH_3ONO$ in air at wavelengths >300 nm in a 6400 L Teflon chamber at ~980 mbar pressure. The concentrations of 2-carene and isoprene (the reference compound) were analyzed by GC-FID during UV irradiation of $CH_3ONO$ - NO - 2-carene - isoprene - air mixtures. The measured rate coefficient ratio $k$(HO + camphene)/$k$(HO + isoprene) = 0.779 ± 0.023 is placed on an absolute basis using $k$(HO + isoprene) = $1.0 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019).

### Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $8.0 \times 10^{-11}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.15 | 298 |

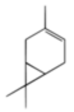
*Comments on Preferred Values*

The preferred value at 298 K is based on the relative rate study of Corchnoy and Atkinson (1990). The error limits have been expanded to reflect the fact that this is the only study available. The reaction is expected to proceed predominantly by addition to the >C=C< double bond.

### References

Corchnoy, S. B. and Atkinson, R.: Environ. Sci. Technol. 24, 1497, 1990.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

## HOx_VOC103

**HO +**  **(3-carene) → products**

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $2.48 \times 10^{-11} \exp[(357 \pm 17)/T]$ | 235-357 | Dillon et al., 2017 | PLP-LIF (a) |
| $(8.1 \pm 0.3) \times 10^{-11}$ | 297 | | |
| | | | |
| *Relative Rate Coefficients* | | | |
| $(8.55 \pm 0.42) \times 10^{-11}$ | 294 ± 1 | Atkinson et al., 1986 | RR-GC-FID (b) |

2-carene is 3,7,7-trimethyl-bicyclo[4.1.0]hept-2-ene.

### Comments

(a) HO radicals were generated by the photolysis of $H_2O_2$ at 248 nm in the presence of 3–carene/$N_2$ or 3-carene /air mixtures at total pressures in the range 9-281 mbar (7-211 Torr) and their concentration measured by pulsed laser induced fluorescence. Pseudo-first order decays of HO radical concentrations were characterized in the presence of excess concentrations of 3-carene (monitored by vacuum UV optical absorption at 185 nm). The rate constants were independent of the bath-gas pressure over the studied range or type ($N_2$ or air). The reported value is the mean of the results obtained under different conditions (pressure and bath-gas).

(b) HO radicals were generated by the photolysis of $CH_3ONO$ in air at wavelengths >300 nm in a 6400 L Teflon chamber at ~980 mbar pressure. The concentrations of 3-carene and 2,3-dimethyl-2-butene (the reference compound) were analyzed by GC-FID during UV irradiation of $CH_3ONO$ - NO - 3-carene - 2,3-dimethyl-2-butene - air mixtures. The measured rate coefficient ratio $k$(HO + 3-carene)/$k$(HO + 2,3-dimethyl-2-butene) = 0.777 ± 0.038 is placed on an absolute basis using $k$(HO + 2,3-dimethyl-2-butene) = $1.10 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson and Arey, 2003).

### Preferred Values

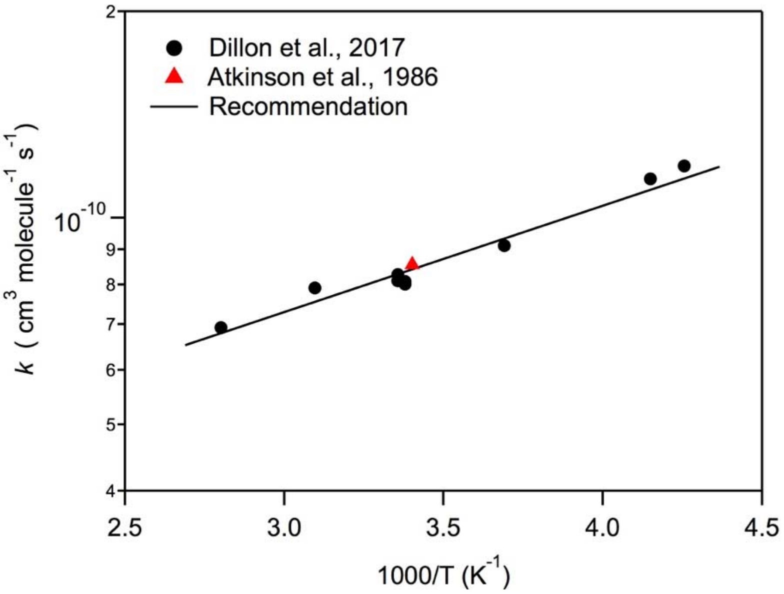
| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $8.3 \times 10^{-11}$ | 298 |
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $2.5 \times 10^{-11} \exp(357/T)$ | 230-360 |
| | | |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.06 | 298 |
| $\Delta$ E/R | ± 50 | 230-360 |

*Comments on Preferred Values*

The room temperature values of *k* in the reported studies are in agreement. The preferred rate coefficient value at 298 K is derived from the average of the two measurements. The absolute rate study of Dillon et al. (2017), the sole temperature-dependence study, combined with the preferred 298 K is used to derive the pre-exponential factor. The reaction is expected to proceed predominantly by addition to the >C=C< double bond. Reissell et al. (1999) have reported an acetone formation yield of (15±3)% in the presence of NO while Hakola et al. (1994) have identified 2,2-dimethyl-3-(2-oxopropyl)-cyclopropaneacetaldehyde with a yield of (34±8)%.

## References

Atkinson, R., Aschmann, S. M., Pitts, Jr. J. M.: Int. J. Chem. Kinet., 18, 287, 1986.
Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
Dillon, T. J., Dulitz, K., Groß, C. B. M., and Crowley, J. N.: Atmos. Chem. Phys., 17, 15137-15150, https://doi.org/10.5194/acp-17-15137-2017, 2017.
Hakola, H., Arey, J., Aschmann, S. M. and Atkinson, R.: J. Atmos. Chem., 18, 75, 1994.
Reissell, A., Harry, C., Aschmann, S. M., Atkinson, R. and Arey, J.: J. Geophys. Res., 104, 13869, 1999.



Rate coefficients for HO + 3-Carene.

## HOx_VOC104

HO +  (β-myrcene) → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(2.09 \pm 0.16) \times 10^{-10}$ | 294 ± 1 | Atkinson et al., 1986 | RR-GC-FID (a) |
| $9.19 \times 10^{-12} \exp[(1071 \pm 82)/T]$ | 313-423 | Hites and Turner, 2009 | RR-MS (b) |

Myrcene is 7-methyl-3-methylene-1,6-octadiene.

### Comments

(a) HO radicals were generated by the photolysis of $CH_3ONO$ in air at wavelengths >300 nm in a 6400 L Teflon chamber at ~980 mbar pressure. The concentrations of β-myrcene and 2,3-dimethyl-2-butene (the reference compound) were analyzed by GC-FID during UV irradiation of $CH_3ONO$ - NO - β-myrcene - 2,3-dimethyl-2-butene - air mixtures. The measured rate coefficient ratio $k$(HO + β-myrcene)/$k$(HO + 2,3-dimethyl-2-butene) = 1.90 ± 0.14 is placed on an absolute basis using $k$(HO + 2,3-dimethyl-2-butene) = $1.10 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson and Arey, 2003).

(b) HO radicals were generated by the photolysis of $H_2O_2$ in helium at wavelengths <360 nm in a 160 cm$^3$ volume quartz vessel at ~1 bar pressure. The concentrations of β-myrcene and isoprene (the reference compound) were monitored by MS. The measured rate coefficient ratios, $k$(HO + β-myrcene)/$k$(HO + isoprene), were placed on an absolute basis using $k$(HO + isoprene) = $3.14\times10^{-17}\, T^2 \times \exp(1036/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Hites and Turner, 2009), which agrees with the IUPAC recommendation over the studied temperature range (IUPAC, 2019).

### Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $2.1 \times 10^{-10}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.15 | 298 |

*Comments on Preferred Values*

The preferred rate coefficient value at 298 K is based on the relative rate measurement from Atkinson et al. (1986). Hites and Turner have not measured the rate coefficient at room temperature. An extrapolation of their data to room temperature using their Arrhenius expression leads to $k_{298} = 3.3\times10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ which is ≈ 50 % higher than that reported by Atkinson et al. (1986). Hites and Turner mentioned some possible experimental difficulties in deriving their values. Hence, no recommendation is made for the temperature dependence expression.

The reaction is expected to proceed predominantly by addition to the >C=C< double bonds. Reissell et al. (1999) have reported an acetone formation yield of (45±6)% in the presence of NO indicating that at least that fraction of the reaction occurs via addition of OH to $>C=C(CH_3)_2$.

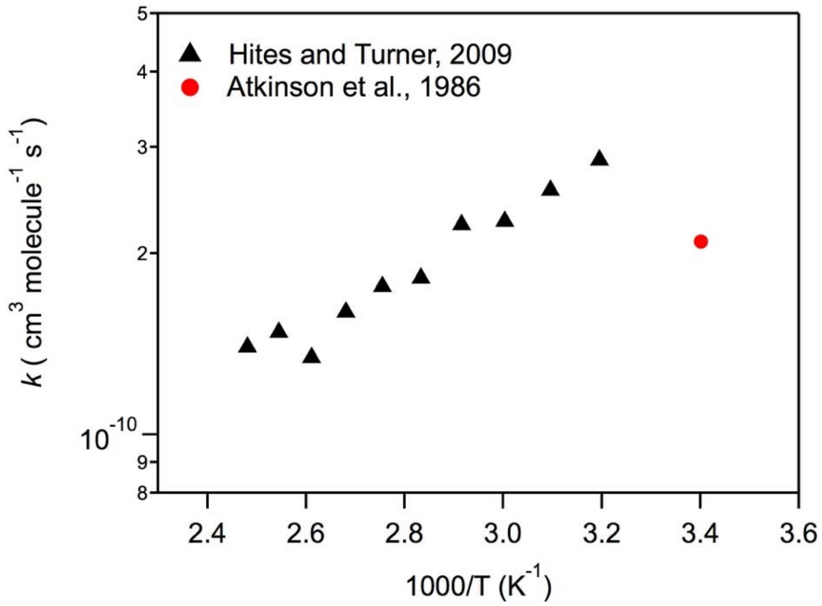
## References

Atkinson, R., Aschmann, S. M., Pitts, Jr. J. M.: Int. J. Chem. Kinet., 18, 287, 1986.

Hites, R. A. and Turner, A. M.: Int. J. Chem. Kinet., 41, 407, 2009.

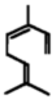
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

Reissell, A., Harry, C., Aschmann, S. M., Atkinson, R. and Arey, J.: J. Geophys. Res., 104, 13869, 1999.



Rate coefficients for HO + β-myrcene.

## HOx_VOC105

**HO +**  **(ocimene, cis and trans) → products**

**Rate coefficient data**

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(2.45 \pm 0.19) \times 10^{-10}$ | 294 ± 1 | Atkinson et al., 1986 | RR-GC-FID (a) |
| $4.35 \times 10^{-11} \exp[(579 \pm 59)/T]$ | 313-423 | Kim et al., 2011 | RR-MS (b) |

Ocimene is 3,7-dimethyl-1,3,6-octatriene.

### Comments

(a) HO radicals were generated by the photolysis of $CH_3ONO$ in air at wavelengths >300 nm in a 6400 L Teflon chamber at ~980 mbar pressure. The concentrations of β-ocimene and 2,3-dimethyl-2-butene (the reference compound) were analyzed by GC-FID during UV irradiation of $CH_3ONO$ - NO - β-ocimene - 2,3-dimethyl-2-butene - air mixtures. The measured rate coefficient ratio $k$(HO + β-ocimene)/$k$(HO + 2,3-dimethyl-2-butene) = 2.23 ± 0.17 is placed on an absolute basis using $k$(HO + 2,3-dimethyl-2-butene) = $1.10 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson and Arey, 2003).

(b) HO radicals were generated by the photolysis of $H_2O_2$ in helium at wavelengths <360 nm in a 160 cm$^3$ volume quartz vessel at ~1 bar pressure. The concentrations of β-ocimene and 2-methylpropene (the reference compound) were monitored by MS. The measured rate coefficient ratios, $k$(HO + β-ocimene)/$k$(HO + 2-methylpropene), were placed on an absolute basis using $k$(HO + 2-methylpropene) = $0.947\times10^{-11} \times \exp(504/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson, 1997).

### Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $2.8 \times 10^{-10}$ | 298 |
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $4.0 \times 10^{-11} \exp(579/T)$ | 310-430 |
| *Reliability* | | |
| Δ log $k$ | ± 0.15 | 298 |
| Δ E/R | ± 150 | 310-430 |

*Comments on Preferred Values*

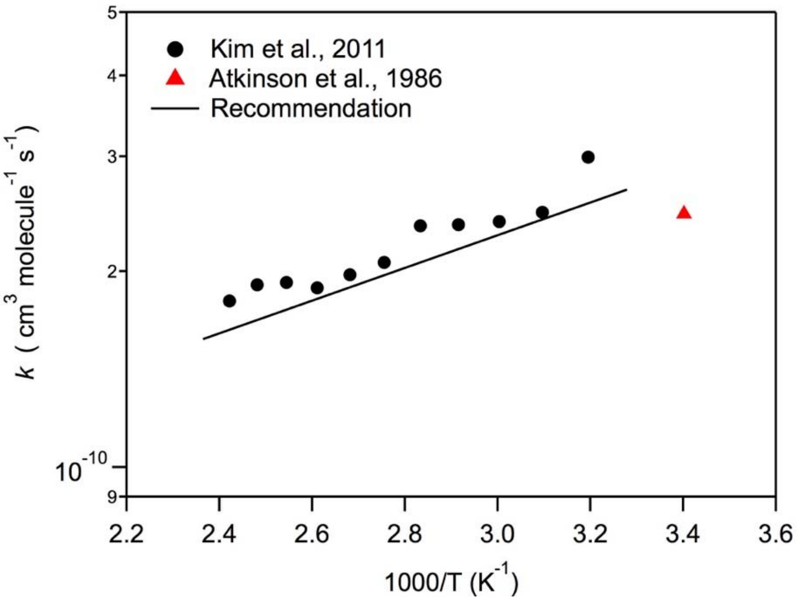
An extrapolation of the data from Kim et al. (2011) at 298K using their Arrhenius expression leads to $k_{298} = 3.04\times10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ which is ≈ 20 % higher than that reported by Atkinson et al. (1986). The preferred rate coefficient value at 298 K is the average of the measurement from Atkinson et al. (1986) and that from Kim et al. (2011) extrapolated to 298K.

The study of Kim et al. (2011), the sole temperature-dependence study, combined with the preferred 298 K is used to derive the pre-exponential factor.

The reaction is expected to proceed predominantly by addition to the >C=C< double bonds. Reissell et al. (1999) have reported an acetone formation yield of (20±15)% in the presence of NO indicating that at least that fraction of the overall reaction occurs via addition of OH to $>C=C(CH_3)_2$.

**References**

Atkinson, R., Aschmann, S. M., Pitts, Jr. J. M.: Int. J. Chem. Kinet., 18, 287, 1986.
Atkinson, R.,: Phys. Chem. Ref. Data, 26, 215, 1997.
Kim., D., Stevens, P. S., Hites, R. A. and Hites, R. A.: J. Phys. Chem. A, 115, 500, 2011.
Reissell, A., Harry, C., Aschmann, S. M., Atkinson, R. and Arey, J.: J. Geophys. Res., 104, 13869, 1999.



Rate coefficients for HO + Ocimene, cis and trans.

## HOx_VOC106

**HO +**  **(sabinene) → products**

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| (1.16± 0.05) × $10^{-10}$ | 296 ± 2 | Atkinson et al., 1990 | RR-GC-FID (a) |

Sabinene is 1-isopropyl-4-methylene-bicyclo[3.1.0]hexane.

### Comments

(a) HO radicals were generated by the photolysis of $CH_3ONO$ in air at wavelengths >300 nm in a 6400 L Teflon chamber at ~980 mbar pressure. The concentrations of camphene and isoprene (the reference compound) were analyzed by GC-FID during UV irradiation of $CH_3ONO$ - NO - sabinene - isoprene - air mixtures. The measured rate coefficient ratio $k$(HO + sabinene)/$k$(HO + isoprene) = 1.16 ± 0.04 is placed on an absolute basis using $k$(HO + isoprene) = 1.0 × $10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019).

### Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | 1.2 × $10^{-10}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.15 | 298 |

*Comments on Preferred Values*

The preferred value of the room temperature rate coefficient is based on the single study of Atkinson et al. (1990). The error limits are expanded to reflect the single measurement.

The reaction is expected to proceed mainly by addition of OH to the $CH_2$=C< bond with a non-negligible contribution from H-atom abstraction. Reissell et al. (1999) have reported (19±0.3)% formation yield of acetone in presence of NOx. Hakola et al. (1994) have observed the formation of sabinaketone with a yield of 7.3 %.

### References

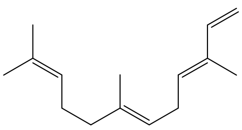
Atkinson, R., Aschmann, S. M. and Arey, J.: Atmos. Environ., 24, 2647, 1990.

Hakola, H., Arey, J., Aschmann, S. M. and Atkinson, R.: J. Atmos. Chem., 18, 75, 1994.

IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

Reissell, A., Harry, C., Aschmann, S. M., Atkinson, R. and Arey, J.: J. Geophys. Res., 104, 13869, 1999.

## HOx_VOC107

**HO +**  **(α-farnesene) → products**

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(2.19 \pm 0.11) \times 10^{-10}$ | 313-423 | Kim et al., 2011 | RR-MS (a) |

α-farnesene is 3,7,11-trimethyl-dodeca-1,3,6,10-tetraene

### Comments

(a) The concentrations of α-farnesene and 2-methylpropene (the reference compound) were monitored by MS during UV photolysis of $H_2O_2$ - α-farnesene - 2-methylpropene - He mixtures in a 160 cm$^3$ volume quartz vessel at ~1 bar pressure. The measured rate coefficient ratios, $k$(HO + α-farnesene)/$k$(HO + 2-methylpropene), were placed on an absolute basis using $k$(HO + 2-methylpropene) = $9.47 \times 10^{-12} \exp(504/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson, 1997), which agrees with the current IUPAC recommendation to within 0.5 % over the studied temperature range (IUPAC, 2019). The resultant values of $k$ displayed no significant temperature dependence, and the reported rate coefficient was based on the mean of the measured values.

### Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $2.2 \times 10^{-10}$ | 298 |
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $2.2 \times 10^{-10}$ | 298-430 |
| *Reliability* | | |
| $\Delta \log k$ | $\pm 0.30$ | 298 |
| $\Delta E/R$ | $\pm 200$ | 298-430 |

*Comments on Preferred Values*

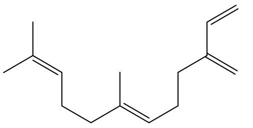
The preferred temperature-independent value of $k$ is based on the determination of Kim et al. (2011), with the lower bound of the temperature range extended to 298 K. This is the only reported investigation of the reaction, and confirmatory studies are required.

There have been no reported product or mechanistic investigations, and such studies are also required. However, structure-activity methods (e.g. Vereecken and Peeters, 2001; Peeters et al., 2007) suggest that the reaction should proceed mainly by addition of HO to the C=C bonds (with contributions from all sites); but with a non-negligible contribution from H-atom abstraction, which results in formation of resonance-stabilized allyl and superallyl radicals from attack at all (saturated carbon) sites.

## References

Atkinson, R.: Phys. Chem. Ref. Data, 26, 215, 1997.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Kim, D., Stevens, P. S. and Hites, R. A.: J. Phys. Chem. A, 115, 500, 2011.
Peeters, J., Boullart, W., Pultau, V., Vandenberk, S. and Vereecken, L.: J. Phys. Chem. A, 111, 1618, 2007.
Vereecken, L. and Peeters, J.: Chem. Phys. Lett., 333, 162, 2001.

## HOx_VOC108

**HO +**  **(β-farnesene) → products**

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | *Reference* | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(2.88 \pm 0.15) \times 10^{-10}$ | 313-423 | Kim et al., 2011 | RR-MS (a) |
| $(1.74 \pm 0.09) \times 10^{-10}$ | 296 ± 2 | Kourtchev et al., 2012 | RR-FTIR (b),(c) |
| $(1.61 \pm 0.18) \times 10^{-10}$ | 296 ± 2 | Kourtchev et al., 2012 | RR-FTIR (b),(d) |

β-farnesene is (6E)-7,11-dimethyl-3-methylene-1,6,10-dodecatriene

### Comments

(a) The concentrations of β-farnesene and 2-methylpropene (the reference compound) were monitored by MS during UV photolysis of $H_2O_2$ - β-farnesene - 2-methylpropene - He mixtures in a 160 cm$^3$ volume quartz vessel at ~1 bar pressure. The measured rate coefficient ratios, $k$(HO + β-farnesene)/$k$(HO + 2-methylpropene), were placed on an absolute basis using $k$(HO + 2-methylpropene) = $9.47 \times 10^{-12} \exp(504/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson, 1997), which agrees with the current IUPAC recommendation to within 0.5 % over the studied temperature range (IUPAC, 2019). The resultant values of $k$ displayed no significant temperature dependence, and the reported rate coefficient was based on the mean of the measured values.

(b) The concentrations of *trans*-β-farnesene and cyclohexa-1,3-diene or α-terpinene (the reference compounds), were monitored by long path FTIR during UV photolysis of $H_2O_2$ - *trans*-β-farnesene - reference compound mixtures in a 3.91 m$^3$ FEP chamber at 0.1–1 mbar above atmospheric pressure of purified air. The measured rate coefficient ratios, $k$(HO + *trans*-β-farnesene)/$k$(HO + cyclohexa-1,3-diene) = (1.06 ± 0.04) and $k$(HO + *trans*-β-farnesene)/$k$(HO + α-terpinene) = (0.46 ± 0.01), are placed on an absolute basis using $k$(HO + cyclohexa-1,3-diene) = $1.64 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson and Arey, 2003) and $k$($O_3$ + α-terpinene) = $3.5 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019)) at 296 K. Gas phase carbonyl products were also identified, following photolysis of HONO - *trans*-β-farnesene - air mixtures, as O-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine derivatives (GC-MS), by collection on denuders.

(c) Relative to cyclohexa-1,3-diene.

(d) Relative to α-terpinene.

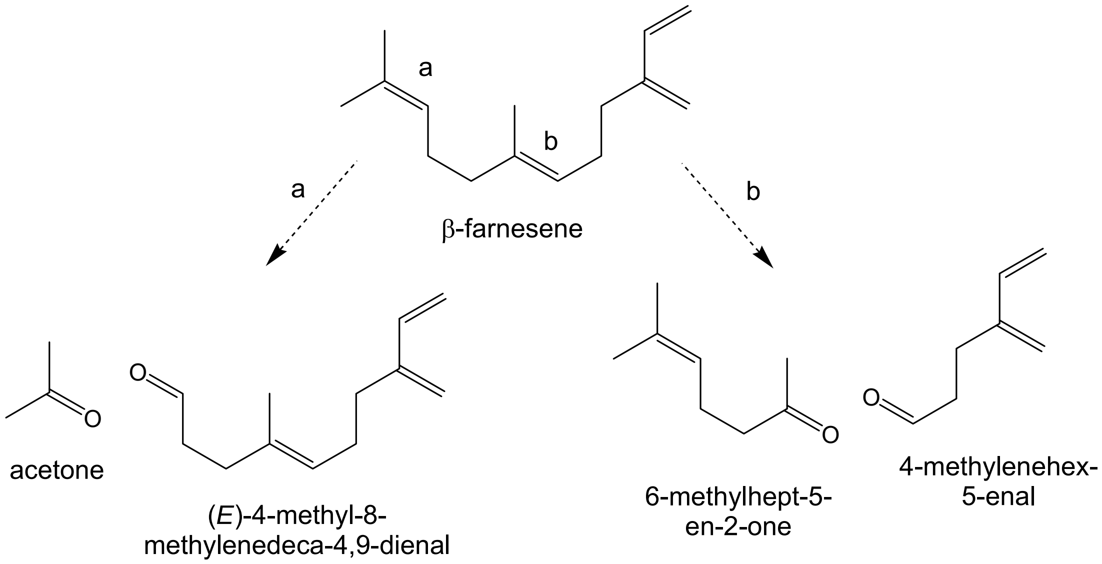
**Preferred Values**

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $2.3 \times 10^{-10}$ | 298 |
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $2.3 \times 10^{-10}$ | 296-430 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.30 | 298 |
| $\Delta$ E/R | ± 200 | 296-430 |

*Comments on Preferred Values*

The preferred value of $k$ is the average of the temperature-independent determination of Kim et al. (2011) and the room temperature determination of Kourtchev et al. (2012) (based on the mean of their two values), recommended for the temperature range 296-430 K. The reported values in the two studies differ by a factor of 1.7, and this is reflected in the assigned uncertainty. Additional studies are required to reduce this uncertainty.

Structure-activity methods (e.g. Vereecken and Peeters, 2001; Peeters et al., 2007) predict that the reaction should proceed mainly by addition of HO to the C=C bonds; but with a non-negligible contribution from H-atom abstraction, which results in formation of resonance-stabilized allyl radicals from attack at all (saturated carbon) sites. Kourtchev et al. (2012) reported evidence for HO addition to the two isolated C=C bonds ("a" and "b"), through detection of the corresponding carbonyl end products (acetone, (*E*)-4-methyl-8-methylenedeca-4,9-dienal, 4-methylenehex-5-enal and 6-methylhept-5-en-2-one), shown in the schematic below:

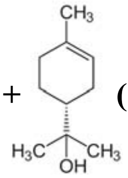


As presented by Kourtchev et al. (2012), these can be formed from the NO-catalyzed chemistry via intermediate β-hydroxy peroxy and oxy radical intermediates. They also reported detection of 4-oxopentanal, which may be formed from secondary oxidation of both (*E*)-4-methyl-8-methylenedeca-4,9-dienal and 6-methylhept-5-en-2-one. Addition of HO to the conjugated diene system is expected to be significant, although no evidence has been reported for the likely carbonyl end products (e.g. 6,10-dimethyl-2-methylene-undeca-5,9-dienal, 7,11-dimethyl-dodeca-1,6,10-trien-3-one and formaldehyde). Similarly, a significant contribution from H-atom abstraction chemistry also requires experimental confirmation.

## References

Atkinson, R.: Phys. Chem. Ref. Data, 26, 215, 1997.
Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Kim, D., Stevens, P. S. and Hites, R. A.: J. Phys. Chem. A, 115, 500, 2011.
Kourtchev, I., Bejan, I, Sodeau, J. R., and Wenger, J. C: Atmos. Environ., 46, 338, 2012.
Peeters, J., Boullart, W., Pultau, V., Vandenberk, S. and Vereecken, L.: J. Phys. Chem. A, 111, 1618, 2007.
Vereecken, L. and Peeters, J.: Chem. Phys. Lett., 333, 162, 2001.

## HOx_VOC109

**HO +**  **(α-terpineol) → products**

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(1.9 \pm 0.5) \times 10^{-10}$ | 297 ± 3 | Wells, 2005 | RR/GC-MS (a) |

(α-terpineol is: (2-(4-methyl-1-cyclohex-3-enyl)propan-2-ol).

### Comments

(a) HO radicals were generated by the photolysis of $CH_3ONO$ in air at wavelengths >300 nm in 60-100 L Teflon chamber in air at ~980 mbar pressure. Relative rate of loss of α-terpineol and either 2,5-dimethyl furan and isoprene was monitored by GC-MS. $k$(α-terpineol) / $k$(reference), not provided by the authors, was put on an absolute basis using $k$(isoprene) = $1.01 \times 10^{-10}$ and $k$(2,5-dimethyl furan) = $1.32 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Bierbach et al., 1992).

### Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $1.9 \times 10^{-10}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.30 | 298 |

*Comments on Preferred Values*

The preferred value at 298 K is an averge of the results from the relative rate studies of Wells (2005). The error limits have been expanded to reflect the fact that this is the only study available.

Wells (2005) positively identified acetone ($CH_3C(O)CH_3$), glyoxal (HC(O)C(O)H) and methylglyoxal ($CH_3C(O)C(O)H$) as the products of the reaction between HO and α-terpineol, concluding that both addition of HO to the double bond as well as abstraction of H-atom take place. Yields were not reported. Other products have been observed but not positively identified.

### References

Bierbach, A., Barnes, I. and Becker, K.H.: Atmos. Env. 26, 813, 1992.
Wells, J.R., Environ. Sci. Technol., 39, 6937, 2005.

## HOx_AROM1

$$\mathrm{HO} + \mathrm{C_6H_6}\ (\text{Benzene}) \rightarrow \mathrm{H_2O} + \mathrm{C_6H_5} \qquad (1)$$

$$\rightarrow \mathrm{HOC_6H_6} \qquad (2)$$

### Rate coefficient data ($k = k_1 + k_2$)

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $(1.59 \pm 0.12) \times 10^{-12}$ | 298 | Davis et al., 1975 | FP-RF (a) |
| $(1.24 \pm 0.12) \times 10^{-12}$ | 298 | Hansen et al., 1975 | FP-RF (b) |
| $(1.20 \pm 0.15) \times 10^{-12}$ | 297.6 | Perry et al., 1977 | FP-RF (c) |
| $(1.32 \pm 0.30) \times 10^{-12}$ | 304.4 | | |
| $(1.33 \pm 0.25) \times 10^{-12}$ | 305.8 | | |
| $(1.66 \pm 0.25) \times 10^{-12}$ | 322.7 | | |
| $(2.6 \pm 1.5) \times 10^{-13}$ | 396.2 | | |
| $(3.4 \pm 0.7) \times 10^{-13}$ | 396.4 | | |
| $(3.4 \pm 1.2) \times 10^{-13}$ | 405.8 | | |
| $(4.5 \pm 0.7) \times 10^{-13}$ | 422.0 | | |
| $3.1 \times 10^{-13} \exp[-(270 \pm 220)/T]$ | 250-298 | Tully et al., 1981 | FP-RF (d) |
| $(1.04 \pm 0.08) \times 10^{-12}$ | 250 | | |
| $(1.20 \pm 0.09) \times 10^{-12}$ | 270 | | |
| $(1.24 \pm 0.09) \times 10^{-12}$ | 298 | | |
| $(5.43 \pm 0.23) \times 10^{-13}$ | 542 | | |
| $(6.39 \pm 0.29) \times 10^{-13}$ | 621 | | |
| $(6.82 \pm 0.74) \times 10^{-13}$ | 630 | | |
| $(6.06 \pm 0.34) \times 10^{-13}$ | 653 | | |
| $(1.02 \pm 0.04) \times 10^{-12}$ | 715 | | |
| $(1.20 \pm 0.16) \times 10^{-12}$ | 742 | | |
| $(1.59 \pm 0.09) \times 10^{-12}$ | 817 | | |
| $(1.90 \pm 0.20) \times 10^{-12}$ | 895 | | |
| $(2.26 \pm 0.13) \times 10^{-12}$ | 917 | | |
| $(2.35 \pm 0.23) \times 10^{-12}$ | 981 | | |
| $(2.20 \pm 0.34) \times 10^{-12}$ | 1017 | | |
| $(7.6 \pm 1.5) \times 10^{-13}$ | 244 | Lorenz and Zellner, 1983 | PLP-RF (e) |
| $(1.15 \pm 0.25) \times 10^{-12}$ | $298 \pm 2$ | | |
| $(1.26 \pm 0.25) \times 10^{-12}$ | 336 | | |
| $(8.3 \pm 1.7) \times 10^{-13}$ | 373 | | |
| $(5.0 \pm 1.0) \times 10^{-13}$ | 384 | | |
| $(4.0 \pm 0.9) \times 10^{-13}$ | 453 | | |
| $(4.3 \pm 0.9) \times 10^{-13}$ | 523 | | |
| $(8.8 \pm 0.4) \times 10^{-13}$ | 295 | Wahner and Zetzsch, 1983 | FP-RF (f) |
| $(1.02 \pm 0.2) \times 10^{-12}$ | 296 | Rinke and Zetzsch, 1984 | FP-RF (f) |
| $3.5 \times 10^{-11} \exp[-(2300 \pm 100)/T]$ | 787-1409 | Madronich and Felder, 1985 | FP-RF |
| $2.3 \times 10^{-12} \exp[-(190 \pm 60)/T]$ | 239-354 | Witte et al., 1986 | FP-RF (g) |
| $(1.05 \pm 0.05) \times 10^{-12}$ | 299 | | |
| $(1.40 \pm 0.23) \times 10^{-12}$ | 234 | Wallington et al., 1987 | PF-RF (h) |
| $(1.30 \pm 0.19) \times 10^{-12}$ | 263 | | |
| $(1.29 \pm 0.14) \times 10^{-12}$ | 296 | | |
| $(1.93 \pm 0.37) \times 10^{-13}$ | 393 | | |

| | | | |
|---|---|---|---|
| $(2.58 \pm 0.34) \times 10^{-13}$ | 438 | | |
| $k_1 = (4.6 \pm 2.8) \times 10^{-14}$ | 298 | Knispel et al., 1990 | FP-RF (i) |
| $k_2 = (1.06 \pm 0.09) \times 10^{-12}$ | 298 | | |
| $k_1 = (1.9 \pm 1.2) \times 10^{-14}$ | 315 | | |
| $k_2 = (1.02 \pm 0.03) \times 10^{-12}$ | 315 | | |
| $k_1 = (1.2 \pm 0.6) \times 10^{-14}$ | 333 | | |
| $k_2 = (1.05 \pm 0.12) \times 10^{-12}$ | 333 | | |
| $k_1 = (2.1 \pm 0.9) \times 10^{-14}$ | 354 | | |
| $k_2 = (8.8 \pm 2.3) \times 10^{-13}$ | 354 | | |
| $2.0 \times 10^{-14} \exp[(1420 \pm 250)/T]$ | 345-385 | Lin et al., 1994 | PLP-LIF (j) |
| $(1.09 \pm 0.04) \times 10^{-12}$ | 345-361 | | |
| $(1.2 \pm 0.2) \times 10^{-12}$ | 298 | Bjergbakke et al., 1996 | PR-UVA (k) |
| $(1.10 \pm 0.07) \times 10^{-12}$ | 297 ± 2 | Bohn and Zetzsch, 1999 | PLP-UVA (l) |
| $(1.06 \pm 0.07) \times 10^{-12}$ | 297 ± 2 | | |
| $8.0 \times 10^{-11} \exp[-(3199 \pm 241)/T]$ | 908-1736 | Seta et al., 2006 | SH-LIF (m) |
| *Relative Rate Cofficients* | | | |
| $\leq 2.4 \times 10^{-12}$ | 304 ± 1 | Doyle et al., 1975 | RR (n) |
| $7.7 \times 10^{-13}$ | 300 | Cox et al., 1980 | RR (o) |
| $8.6 \times 10^{-13}$ | 300 | Barnes et al., 1982 | RR (p) |
| $(1.35 \pm 0.06) \times 10^{-12}$ | ~298 | Ohta and Ohyama, 1985 | RR (q) |
| $(1.19 \pm 0.44) \times 10^{-12}$ | 296 ± 1 | Edney et al., 1986 | RR (r) |
| $(1.19 \pm 0.47) \times 10^{-12}$ | 297 ± 2 | Sommerlade et al., 1993 | RR (s) |
| $2.93 \times 10^{-12} \exp[-(288.3 \pm 84.8)/T]$ | 274-363 | Semadeni et al., 1995 | RR (t) |
| $(1.12 \pm 0.06) \times 10^{-12}$ | 299 | | |

## Comments

(a) At 100 Torr (133 mbar) of He diluent. Lower rate coefficients were measured at 3 and 20 Torr (4 and 27 mbar) of He diluent.

(b) Measured rate coefficient was independent of the pressure of Ar diluent over the range 50-600 Torr (67-800 mbar).

(c) Non-exponential HO radical decays were observed at temperatures between 331 K and 381 K. Rate coefficients were measured at 100 Torr (133 mbar) of Ar diluent.

(d) Experiments were generally carried out at 100 Torr (133 mbar) pressure of Ar diluent. At 298 K, the rate coefficient was measured as a function of total pressure over the ranges 25-100 Torr (33-133 mbar) of He, 50-200 Torr (67-267 mbar) of Ar, and at 100 Torr (133 mbar) of $SF_6$, with no significant pressure dependence being observed over these ranges. Non-exponential HO radical decays were observed at temperatures between 320 K and 400 K.

(e) At 298 ± 2 K, rate coefficients were measured over the pressure range 1.5-112 mbar (1.1-84 Torr) of Ar diluent. The rate coefficients increased with increasing pressure up to ~40 mbar (30 Torr), with no observed effect of pressure above 40 mbar.

(f) Rate coefficients were measured over the pressure ranges 67-173 mbar (50-130 Torr) of Ar diluent (Wahner and Zetzsch, 1983) and 33-666 mbar (25-500 Torr) of He diluent (Rinke and Zetzsch, 1984), with a slight decrease in rate coefficient being observed below 133 mbar (100 Torr) pressure in both cases. The cited rate coefficients are at 133 mbar pressure.

(g) Rate coefficients were measured at 133 and/or 200 mbar pressure of Ar diluent (the 299 K rate coefficient cited in the table is at 133 mbar pressure). At 294 K, rate coefficients were also measured over the pressure range 1.3-533 mbar (1.0-400 Torr) of Ar diluent, with a decrease in rate coefficient being observed below ~67 mbar (50 Torr) pressure.

(h) No effect of pressure was observed over the range 25-50 Torr (33-67 mbar) of Ar diluent. Non-exponential HO radical decays were observed at 353 K.

(i) Rate coefficients $k_1$ and $k_2$ were derived from fitting the observed non-exponential HO radical decays, measured over time periods at a total pressure of 133 mbar of Ar, to reactions (1), (2), the back-decomposition of the HO-benzene adduct and accounting for diffusive and background losses of HO radicals and the HO-benzene adduct. Using the rate coefficients of Tully et al. (1981) at 500-1000 K and the expression $k_1 = C\,T^2 \exp(-D/T)$, a global fit to the experimental data resulted in rate coefficients $k_1$ of $6.6 \times 10^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K, $1.0 \times 10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 315 K, $1.5 \times 10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 333 K and $2.2 \times 10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 354 K.

*(j)* Rate coefficients k were derived from fitting the observed non-exponential HO radical decays, measured over time periods at total pressures of 250-500 Torr (333-667 mbar) of He, to reactions (1), (2), the back-decomposition of the HO-benzene adduct and accounting for diffusive and background losses of HO radicals and the HO-benzene adduct. The cited Arrhenius expression over the temperature range 345-385 K was obtained assuming that $k_1 = 0$.

(k) *k* was determined from the decay rates of HO radicals monitored by absorption at 309 nm.

(l) Experiments were carried out in $N_2$ and $O_2$ diluent at total pressures of 0.101-1.00 bar (75-750 Torr) of $N_2$ and 0.973-0.980 bar (730-735 Torr) of $O_2$, with measured rate coefficients of $(1.10 \pm 0.07) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ in $N_2$ and $(1.06 \pm 0.07) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ in $O_2$.

(m) HO radicals were generated by shock heating of nitric acid or *tert*-butyl hydroperoxide.

(n) HO radicals generated by the photolysis of organic-$NO_x$ mixtures at atmospheric pressure in a 5870 L reaction chamber, with analyses of benzene and *n*-butane (the reference compound) by GC. The measured rate coefficient ratio *k(*HO + benzene)/*k*(HO + *n*-butane) ≤ 1 is placed on an absolute basis using a rate coefficient of *k*(HO + *n*-butane) = $2.41 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 304 K (IUPAC, 2019).

(o) HO radicals generated by the photolysis of HONO at 300-450 nm in air at atmospheric pressure. Benzene and ethene (the reference compound) were monitored by GC, and the measured rate coefficient ratio *k*(HO + benzene)/*k*(HO + ethene) is placed on an absolute basis using a rate coefficient of *k*(HO + ethene) = $7.78 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 300 K and atmospheric pressure of air (IUPAC, 2019).

(p) HO radicals were generated by dark decomposition of $HOONO_2$ in the presence of NO at atmospheric pressure of $N_2$ or air. Benzene and ethene (the reference compound) were monitored by GC, and the measured rate coefficient ratio *k*(HO + benzene)/*k*(HO + ethene) = 0.11 is placed on an absolute basis using a rate coefficient of *k*(HO + ethene) = $7.78 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 300 K and atmospheric pressure of air (IUPAC, 2019).

(q) HO radicals generated by the photolysis of $H_2O_2$ at 254 nm at atmospheric pressure. Experiments were carried out at room temperature (the specific temperature not being noted). Benzene and *n*-hexane (the reference compound) were monitored by GC, and the measured rate coefficient ratio *k*(HO + benzene)/*k*(HO + *n*-hexane) = 0.26 ± 0.01 is placed on an absolute basis using a 298 K rate coefficient of *k*(HO + *n*-hexane) = $5.20 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson and Arey, 2003).

(r) HO radicals generated by the photolysis of $CH_3ONO$ in air at 1 bar pressure. Benzene and propane (the reference compound) were monitored by GC, and the measured rate coefficient ratio *k*(HO + benzene)/*k*(HO + propane) is placed on an absolute basis using a rate coefficient of *k*(HO + propane) = $1.08 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 296 K (IUPAC, 2019).

(s) HO radicals generated by the photolysis of $NO_x$ in the presence of organics in air at 70 Torr (93 mbar) pressure. Benzene and *n*-hexane (the reference compound) were monitored by MS, and the measured rate coefficient ratio $k$(HO + benzene)/$k$(HO + $n$-hexane) is placed on an absolute basis using a rate coefficient of $k$(HO + $n$-hexane) = $5.17 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 297 K (Atkinson and Arey, 2003).

(t) HO radicals generated by the photolysis of $CH_3ONO$ in air at atmospheric pressure. Benzene and toluene (the reference compound) were monitored by GC, and the measured rate coefficient ratio $k$(HO + benzene)/$k$(HO + toluene) = 1.625 exp[-(628.3 ± 84.8)/$T$] over the temperature range 274-363 K is placed on an absolute basis using a rate coefficient of $k$(HO + toluene) = $1.8 \times 10^{-12}$ exp(340/$T$) cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019).

**Preferred Values**

| Parameter | Value | $T$/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $1.2 \times 10^{-12}$ | 298 |
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $2.3 \times 10^{-12}$ exp(-190/$T$) | 230-350 |
| $k_1$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $8 \times 10^{-15}$ | 298 |
| $k_1$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $3.8 \times 10^{-11}$ exp(-2520/$T$) | 330-1410 |
| *Reliability* | | |
| Δ log $k$ | ± 0.06 | 298 |
| Δ E/R | ± 200 | 230-350 |
| Δ log $k_1$ | ± 0.5 | 298 |
| Δ $E_1$/R | ± 300 | 330-1410 |

*Comments on Preferred Values*

Absolute rate studies show that the reaction of HO radicals with benzene can be considered as comprising three temperature regimes (Perry et al., 1977; Tully et al., 1981). At temperatures <325-350 K the reaction proceeds by channels (1) and (2), with pathway (2) dominating and with the HO-benzene adduct, $HOC_6H_6$, being thermally stable against back-decomposition to reactants at total pressures above ~100 Torr. At total pressures <50-100 Torr, channel (2) is in the falloff regime at room temperature (Davis et al., 1975; Lorenz and Zellner, 1983; Wahner and Zetzsch, 1983; Rinke and Zetzsch, 1984; Witte and Zetzsch, 1986; Baulch et al., 1988; Goumri et al., 1991), with a limiting low-pressure rate coefficient at 297 ± 3 K of $k_0$(He) = $1.7 \times 10^{-29}$ cm$^6$ molecule$^{-2}$ s$^{-1}$ (Goumri et al., 1991). At temperatures >450 K, decomposition of the HO-benzene adduct back to reactants is sufficiently rapid that measured rate coefficients are then those for pathway (1). At temperatures in the range ~325-450 K, decomposition of the HO-benzene adduct is significant and the measured rate coefficients depend on the experimental conditions, and in absolute rate studies non-exponential HO radical decays are generally observed.

The >450 K rate coefficients of Tully et al. (1981), Lorenz and Zellner (1983) and Madronich and Felder (1985), which are attributed to those for pathway (1), and the values of $k_1$ derived by Knispel et al. (1990) from HO radical decay curves at 298-354 K indicate that an Arrhenius fit is adequate. The preferred values of $k_1$ are obtained from a least-squares fit of the >450 K rate coefficients of Tully et al. (1981), Lorenz and Zellner (1983) and Madronich and Felder (1985) and the rate coefficients $k_1$ of Knispel et al. (1990) at 333 K and 354 K (their rate coefficients $k_1$ at 298 K and 315 K have high associated uncertainties and are significantly higher than the rate coefficients $k_1$ derived by Knispel et al. (1990) from a global fit (see

Comment (i)), and are therefore not used in the evaluation of $k_1$). The shock tube data of Seta et al. (2006) at 908-1736 K are in excellent agreement with this preferred expression for $k_1$.

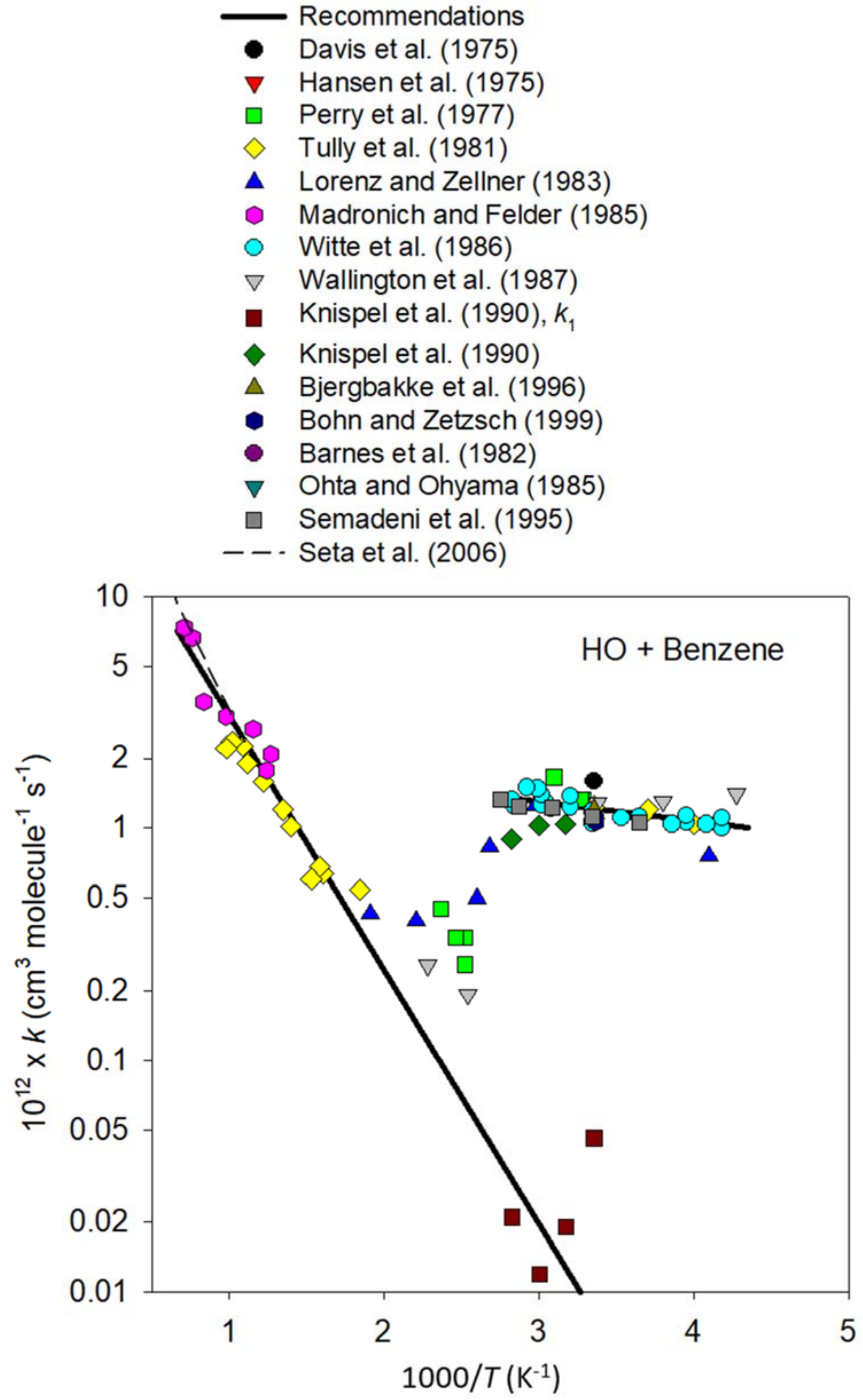
The preferred values of $k$ at ≤350 K are based on the absolute rate coefficients of Hansen et al. (1975), Perry et al. (1977), Tully et al. (1981), Lorenz and Zellner (1983), Witte et al. (1985) [which are judged to supersede the earlier room temperature studies of Wahner and Zetzsch (1983) and Rinke and Zetzsch (1984)], Wallington et al. (1987), Knispel et al. (1990) and Bohn and Zetzsch (1999). The rate coefficients at ≤350 K of Cox et al. (1981), Barnes et al. (1982), Wahner and Zetzsch (1983), Rinke and Zetzsch (1984), Ohta and Ohyama et al. (1985), Edney et al. (1986), Somerlade et al. (1993), Lin et al. (1994), Semadeni et al. (1995) and Bjergbakke et al. (1996) are in good agreement with the preferred ≤350 K rate expression. While the rate coefficients derived by Lin et al. (1994) from non-exponential HO radical decays over the restricted temperature range 345-385 K show a negative temperature dependence, this arises from the rate coefficients at ≥367 K and may be due to fall-off effects; their rate coefficients at 345-361 K are independent of temperature and ~20% lower than the preferred values. Particularly noteworthy is that the rate coefficients of Semadeni et al. (1995) measured relative to those for toluene are in excellent agreement with the preferred expression, indicating that the preferred values for HO + benzene and HO + toluene (IUPAC, 2019) are internally self-consistent.

At atmospherically-relevant temperatures, the reaction proceeds essentially totally by channel (2), with channel (1) accounting for <2% of the overall reaction at 298 K and even less at lower temperatures.

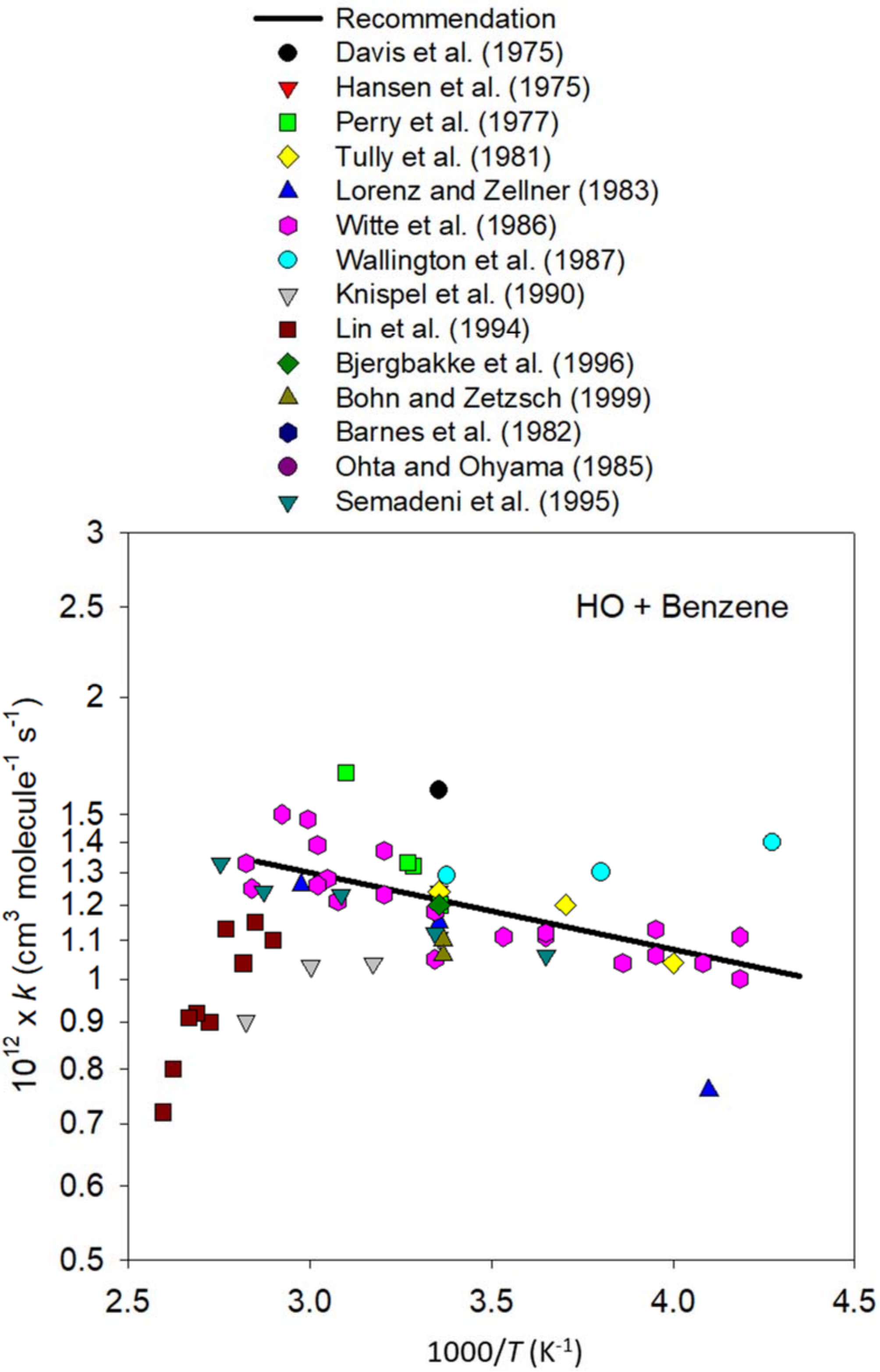
## References

Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
Baulch, D. L., Campbell, I. M. and Saunders, S. M.: J. Chem. Soc. Faraday Trans., 2, 84, 377, 1988.
Barnes, I., Bastian, V., Becker, K. H., Fink, E. H. and Zabel, F.: Atmos. Environ., 16, 545, 1982.
Bjergbakke, E., Sillesen, A. and Pagsberg, P.: J. Phys. Chem., 100, 5729, 1996.
Bohn, B. and Zetzsch, C.: Phys. Chem. Chem. Phys., 1, 5097, 1999.
Cox, R. A., Derwent, R. G. and Williams, M. R.: Environ. Sci. Technol., 14, 57, 1980.
Davis, D. D., Bollinger, W. and Fischer, S.: J. Phys. Chem., 79, 293, 1975.
Doyle, G. J., Lloyd, A. C., Darnall, K. R., Winer, A. M. and Pitts Jr., J. N.: Environ. Sci. Technol., 9, 237, 1975.
Edney, E. O., Kleindienst, T. E. and Corse, E. W.: Int. J. Chem. Kinet., 18, 1355, 1986.
Goumri, A., Pauwels, J. F. and Devolder, P.: Can. J. Chem.., 69, 1057, 1991.
Hansen, D. A., Atkinson, R. and Pitts Jr., J. N.: J. Phys. Chem., 79, 1763, 1975.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Knispel, R., Koch, R., Siese, M. and Zetzsch, C.: Ber. Bunsenges. Phys. Chem., 94, 1375, 1990.
Lin, S.-C., Kuo, T.-C. and Lee, Y.-P.: J. Chem. Phys., 101, 2098, 1994.
Lorenz, K. and Zellner, R.: Ber. Bunsenges. Phys. Chem., 87, 629, 1983.
Madronich, S. and Felder, W.: J. Phys. Chem., 89, 3556, 1985.
Ohta, T. and Ohyama, T.: Bull. Chem. Soc. Japn., 58, 3029, 1985.
Perry, R. A., Atkinson, R. and Pitts Jr., J. N.: J. Phys. Chem., 81, 296, 1977.
Rinke, M. and Zetzsch, C.: Ber. Bunsenges. Phys. Chem., 88, 55, 1984
Seta,T., Nakajima, M. and Miyoshi, A.: J. Phys. Chem. A, 110, 5081, 2006.
Semadeni, M., Stocker, D. W. and Kerr, J. A.: Int. J. Chem. Kinet., 27, 287, 1995.
Sommerlade, R., Parlar, H., Wrobel, D. and Kochs, P.: Environ. Sci. Technol., 27, 2435, 1993

Tully, F. P., Ravishankara, A. R., Thompson, R. L., Nicovich, J. M., Shah, R. C., Kreutter, N. M. and Wine, P. H.: J. Phys. Chem., 85, 2262, 1981.
Wahner, A. and Zetzsch, C.: J. Phys. Chem., 87, 4945, 1983.
Wallington, T. J., Neuman, D. M. and Kurylo, M. J.: Int. J. Chem. Kinet., 19, 725, 1987.
Witte, F., Urbanik, E. and Zetzsch, C.: J. Phys. Chem., 90, 3251, 1986.



Rate coefficients for HO + Benzene.



Rate coefficients for HO + Benzene.

# HOx_AROM2

$$\mathbf{HO + C_6H_5CH_3\ (Toluene) \rightarrow H_2O + C_6H_5CH_2} \qquad \mathbf{(1)}$$
$$\mathbf{\rightarrow HOC_6H_5CH_3} \qquad \mathbf{(2)}$$

## Rate coefficient data ($k = k_1 + k_2$)

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $(6.11 \pm 0.40) \times 10^{-12}$ | 298 | Davis et al., 1975 | FP-RF (a) |
| $(5.78 \pm 0.58) \times 10^{-12}$ | 298 | Hansen et al., 1975 | FP-RF (b) |
| $(6.40 \pm 0.64) \times 10^{-12}$ | 297.9 | Perry et al., 1977 | FP-RF (c) |
| $(4.90 \pm 0.6) \times 10^{-12}$ | 323.7 | | |
| $(1.49 \pm 0.22) \times 10^{-12}$ | 379.2 | | |
| $(1.58 \pm 0.24) \times 10^{-12}$ | 394.2 | | |
| $(1.69 \pm 0.25) \times 10^{-12}$ | 408.7 | | |
| $(1.76 \pm 0.18) \times 10^{-12}$ | 424.4 | | |
| $(1.71 \pm 0.20) \times 10^{-12}$ | 472.7 | | |
| $3.8 \times 10^{-12} \exp[(180 \pm 170)/T]$ | 213-298 | Tully et al., 1981 | FP-RF (d) |
| $(8.20 \pm 0.54) \times 10^{-12}$ | 213 | | |
| $(8.73 \pm 0.39) \times 10^{-12}$ | 231 | | |
| $(7.97 \pm 0.56) \times 10^{-12}$ | 250 | | |
| $(8.53 \pm 0.37) \times 10^{-12}$ | 260 | | |
| $(7.44 \pm 0.55) \times 10^{-12}$ | 270 | | |
| $(6.36 \pm 0.69) \times 10^{-12}$ | 298 | | |
| $(2.16 \pm 0.08) \times 10^{-12}$ | 504 | | |
| $(2.45 \pm 0.05) \times 10^{-12}$ | 568 | | |
| $(2.49 \pm 0.12) \times 10^{-12}$ | 568 | | |
| $(3.26 \pm 0.29) \times 10^{-12}$ | 666 | | |
| $(3.58 \pm 0.16) \times 10^{-12}$ | 694 | | |
| $(4.67 \pm 0.19) \times 10^{-12}$ | 793 | | |
| $(5.54 \pm 0.27) \times 10^{-12}$ | 868 | | |
| $(6.87 \pm 0.23) \times 10^{-12}$ | 958 | | |
| $(9.5 \pm 1.0) \times 10^{-12}$ | 1046 | | |
| $k_1 = (0 \pm 2.0) \times 10^{-13}$ | 299 | Knispel et al., 1990 | FP-RF (e) |
| $k_2 = (7.0 \pm 2.1) \times 10^{-12}$ | 299 | | |
| $k_1 = (4.5 \pm 2.1) \times 10^{-13}$ | 311 | | |
| $k_2 = (5.6 \pm 0.4) \times 10^{-12}$ | 311 | | |
| $k_1 = (5.0 \pm 0.6) \times 10^{-13}$ | 323 | | |
| $k_2 = (5.0 \pm 0.3) \times 10^{-12}$ | 323 | | |
| $k_1 = (6.2 \pm 0.9) \times 10^{-13}$ | 340 | | |
| $k_2 = (3.8 \pm 0.9) \times 10^{-12}$ | 340 | | |
| $(6.4 \pm 0.7) \times 10^{-12}$ | 338 | Markert and Pagsberg, 1993 | PR-UVA (f) |
| $(5.60 \pm 0.14) \times 10^{-12}$ | 299 ± 2 | Bohn, 2001 | PLP-UVA (g) |
| $(5.70 \pm 0.19) \times 10^{-12}$ | 299 ± 2 | | |
| *Relative Rate Cofficients* | | | |
| $(3.4 \pm 1.5) \times 10^{-12}$ | 304 ± 1 | Doyle et al., 1975 | RR (h) |
| $7.0 \times 10^{-12}$ | 300 | Cox et al., 1980 | RR (i) |
| $(5.62 \pm 0.16) \times 10^{-12}$ | ~298 | Ohta and Ohyama, 1985 | RR (j) |
| $(5.07 \pm 0.52) \times 10^{-12}$ | 297 | Edney et al., 1986 | RR (k) |

| | | | |
|---|---|---|---|
| $(5.93 \pm 0.16) \times 10^{-12}$ | 296 ± 2 | Atkinson and Aschmann, 1989 | RR (l) |
| $(6.35 \pm 1.50) \times 10^{-12}$ | 297 ± 2 | Sommerlade et al., 1993 | RR (m) |
| $(5.56 \pm 0.26) \times 10^{-12}$ | 298 | Finlayson-Pitts et al., 1993 | RR (n) |
| $2.09 \times 10^{-18}\ T^2 \exp[(207.4 \pm 113.5)/T]$ | 284-363 | Semadeni et al., 1995 | RR (o) |
| $(5.62 \pm 0.29) \times 10^{-12}$ | 299 | | |
| $(5.39 \pm 0.07) \times 10^{-12}$ | 276 | Anderson and Hites, 1996 | RR (p,q) |
| $(5.84 \pm 0.07) \times 10^{-12}$ | 285 | | |
| $(5.58 \pm 0.14) \times 10^{-12}$ | 285 | | |
| $(5.34 \pm 0.07) \times 10^{-12}$ | 293 | | |
| $(5.61 \pm 0.08) \times 10^{-12}$ | 303 | | |
| $(5.47 \pm 0.08) \times 10^{-12}$ | 310 | | |
| $(5.43 \pm 0.16) \times 10^{-12}$ | 323 | | |
| $(5.13 \pm 0.16) \times 10^{-12}$ | 323 | | |
| $(5.05 \pm 0.08) \times 10^{-12}$ | 323 | | |
| $(5.22 \pm 0.16) \times 10^{-12}$ | 324 | | |
| $(5.07 \pm 0.08) \times 10^{-12}$ | 324 | | |
| $(4.96 \pm 0.17) \times 10^{-12}$ | 344 | | |
| $(4.77 \pm 0.09) \times 10^{-12}$ | 363 | | |
| $(3.36 \pm 0.19) \times 10^{-12}$ | 371 | | |
| $(2.94 \pm 0.19) \times 10^{-12}$ | 383 | | |
| $(5.61 \pm 0.56) \times 10^{-12}$ | 296 | Anderson and Hites, 1996 | RR (p,r) |
| $(5.35 \pm 0.21) \times 10^{-12}$ | 297 | | |
| $(5.28 \pm 0.42) \times 10^{-12}$ | 297 | | |
| $(5.21 \pm 0.21) \times 10^{-12}$ | 297 | | |
| $(4.82 \pm 0.08) \times 10^{-12}$ | 323 | | |
| $(5.21 \pm 0.16) \times 10^{-12}$ | 323 | | |
| $(4.67 \pm 0.16) \times 10^{-12}$ | 323 | | |
| $(4.90 \pm 0.08) \times 10^{-12}$ | 323 | | |
| $(4.61 \pm 0.16) \times 10^{-12}$ | 324 | | |
| $(4.60 \pm 0.09) \times 10^{-12}$ | 363 | | |
| $(4.51 \pm 0.09) \times 10^{-12}$ | 363 | | |
| $(4.60 \pm 0.27) \times 10^{-12}$ | 363 | | |
| $(4.51 \pm 0.09) \times 10^{-12}$ | 363 | | |
| $(4.42 \pm 0.98) \times 10^{-12}$ | 363 | | |
| $(4.42 \pm 0.09) \times 10^{-12}$ | 363 | | |
| $(5.55 \pm 0.07) \times 10^{-12}$ | 296 ± 2 | Kramp and Paulson, 1998 | RR (s,t) |
| $(5.15 \pm 0.11) \times 10^{-12}$ | 296 ± 2 | Kramp and Paulson, 1998 | RR (s,t) |
| $(6.25 \pm 0.07) \times 10^{-12}$ | 296 ± 2 | Kramp and Paulson, 1998 | RR (s,u) |
| $(5.36 \pm 0.08) \times 10^{-12}$ | 296 ± 2 | Kramp and Paulson, 1998 | RR (s,v) |
| *Branching Ratios* | | | |
| $k_1/k = 0.728\ 0.082$ | 298 ± 2 | Atkinson et al., 1989 | (w) |
| $k_1/k_2 < 0.022$ | 299 | Knispel et al., 1990 | FP-RF (e) |
| $k_1/k_2 = 0.08 \pm 0.04$ | 311 | | |
| $k_1/k_2 = 0.10 \pm 0.02$ | 323 | | |
| $k_1/k_2 = 0.16 \pm 0.05$ | 340 | | |
| $k_1/k = 0.11 \pm 0.02$ | 338 | Markert and Pagsberg, 1993 | PR-UVA (x) |
| $k_1/k = 0.067 \pm 0.07$ | 298 | Smith et al., 1998 | (y) |
| $k_1/k = 0.065 \pm 0.09$ | ~298 | Klotz et al., 1998 | (z) |

## Comments

(a) At 100 Torr (133 mbar) of He diluent. Lower rate coefficients were measured at 3 and 20 Torr (4 and 27 mbar) of He diluent.

(b) Measured rate coefficient was independent of the pressure of Ar diluent over the range 100-619 Torr (133-825 mbar).

(c) Non-exponential HO radical decays were observed at temperatures between 325 K and 379 K. No effect of increasing the total pressure at 325 K, 378 K or 424 K from 100 Torr to 200 Torr (133-267 mbar) of argon diluent was observed on the measured rate coefficients (at 325 K and 378 K these were derived from the initial HO radical decay rates).

(d) Experiments were generally carried out at 100 Torr (133 mbar) pressure of Ar diluent. At 298 K, the rate coefficient was measured as a function of total pressure over the ranges 20-100 Torr (27-133 mbar) of He, 25-100 Torr (33-133 mbar) of Ar, and at 100 Torr (133 mbar) of $SF_6$, and the 298 K rate coefficient appeared to reach the high-pressure value at ~100 Torr pressure. Non-exponential HO radical decays were observed at temperatures between 320 K and 380 K.

(e) Rate coefficients $k_1$ and $k_2$ were derived from fitting the observed non-exponential HO radical decays, measured over time periods at a total pressure of 133 mbar of Ar, to reactions (1), (2), the back-decomposition of the HO-toluene adduct and accounting for diffusive and background losses of HO radicals and the HO-toluene adduct. Using the rate coefficients of Tully et al. (1981) at 500-1000 K and the expression $k_1 = C\,T^2 \exp(-D/T)$, a global fit to the experimental data resulted in rate coefficients $k_1$ of $4.3 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 299 K, $4.8 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 311 K, $5.3 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 323 K and $6.1 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 340 K.

(f) *k* was determined from the formation kinetics of the HO-toluene adduct monitored by UV absorption at 300 nm.

(g) Experiments were carried out in $N_2$ and $O_2$ diluent at a total pressure of 750 Torr (1 bar), with rate coefficients of $(5.70 \pm 0.19) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ in $N_2$ and $(5.60 \pm 0.14) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ in $O_2$.

(h) HO radicals generated by the photolysis of organic-$NO_x$ mixtures at atmospheric pressure in a 5870 L reaction chamber, with analyses of toluene and *n*-butane (the reference compound) by GC. The measured rate coefficient ratio *k(*HO + toluene)/*k*(HO + *n*-butane) = 1.4 ± 0.6 is placed on an absolute basis using a rate coefficient of *k*(HO + *n*-butane) = $2.41 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 304 K (IUPAC, 2019).

(i) HO radicals generated by the photolysis of HONO at 300-450 nm in air at atmospheric pressure. Toluene and ethene (the reference compound) were monitored by GC, and the measured rate coefficient ratio *k*(HO + toluene)/*k*(HO + ethene) is placed on an absolute basis using a rate coefficient of *k*(HO + ethene) = $7.78 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 300 K and atmospheric pressure of air (IUPAC, 2019).

(j) HO radicals generated by the photolysis of $H_2O_2$ at 254 nm at atmospheric pressure. Experiments were carried out at room temperature (the specific temperature not being noted). Toluene and *n*-hexane (the reference compound) were monitored by GC, and the measured rate coefficient ratio *k*(HO + toluene)/*k*(HO + *n*-hexane) = 1.08 ± 0.03 is placed on an absolute basis using a 298 K rate coefficient of *k*(HO + *n*-hexane) = $5.20 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson and Arey, 2003).

(k) HO radicals generated by the photolysis of $CH_3ONO$ in air at atmospheric pressure. Toluene and cyclohexane (the reference compound) were monitored by GC, and the measured rate coefficient ratio *k*(HO + toluene)/*k*(HO + cyclohexane) is placed on an absolute basis using a rate coefficient of *k*(HO + cyclohexane) = $6.95 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 297 K (Atkinson and Arey, 2003).

(l) HO radicals generated by the photolysis of $CH_3ONO$ in air at atmospheric pressure. Toluene and propene (the reference compound) were monitored by GC, and the measured rate coefficient ratio $k$(HO + toluene)/$k$(HO + propene) = 0.206 ± 0.006 is placed on an absolute basis using $k$(HO + propene) = $2.88 \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at 296 K and atmospheric pressure of air (IUPAC, 2019).

(m) HO radicals generated by the photolysis of $NO_x$ in the presence of organics in air at 70 Torr (93 mbar) pressure. Toluene and $n$-hexane (the reference compound) were monitored by MS, and the measured rate coefficient ratio $k$(HO + toluene)/$k$(HO + $n$-hexane) is placed on an absolute basis using $k$(HO + $n$-hexane) = $5.17 \times 10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at 297 K (Atkinson and Arey, 2003).

(n) HO radicals were generated from the dark reactions of $O_3$ with toluene and $n$-hexane (the reference compound) in $O_2$ diluent at 14.1-19.4 Torr (19-26 mbar) pressure. Toluene and $n$-hexane were monitored by GC, and the measured rate coefficient ratio $k$(HO + toluene)/$k$(HO + $n$-hexane) = 1.07 ± 0.05 is placed on an absolute basis using $k$(HO + $n$-hexane) = $5.20 \times 10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at 298 K (Atkinson and Arey, 2003).

(o) HO radicals generated by the photolysis of $CH_3ONO$ in air at atmospheric pressure. Toluene and 2,3-dimethylbutane (the reference compound) were monitored by GC, and the measured rate coefficient ratio $k$(HO + toluene)/$k$(HO + 2,3-dimethylbutane) = $0.126 \exp[(614.4 \pm 113.5)/T]$ over the temperature range 294-363 K is placed on an absolute basis using $k$(HO + 2,3-dimethylbutane) = $1.66 \times 10^{-17} T^2 \exp(407/T)$ $cm^3$ $molecule^{-1}$ $s^{-1}$ (Atkinson and Arey, 2003). Rate coefficients were also measured at 258 K, 264 K and 269 K but were not used by Semadeni et al. (1995) in their derivation of the Arrhenius expression.

(p) HO radicals generated by the photolysis of $O_3$ in the presence of water vapor at 254 nm in $N_2 + O_2$ or He diluent at atmospheric pressure. Toluene and cyclohexane (the reference compound) were monitored by MS, and the measured rate coefficient ratio $k$(HO + toluene)/$k$(HO + cyclohexane) are placed on an absolute basis using a rate coefficient of $k$(HO + cyclohexane) = $3.26 \times 10^{-17} T^2 \exp(262/T)$ $cm^3$ $molecule^{-1}$ $s^{-1}$ (Atkinson and Arey, 2003).

(q) In He diluent.

(r) In $N_2 + O_2$ diluent.

(s) HO radicals generated by the photolysis of $CH_3ONO$ in air at atmospheric pressure. Toluene and 1,3-butadiene, propene or cyclohexane (the reference compounds) were monitored by GC, and the measured rate coefficient ratios $k$(HO + toluene)/$k$(HO + reference compound) are placed on an absolute basis using rate coefficients at 296 K and atmospheric pressure of air of $k$(HO + 1,3-butadiene) = $6.72 \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ (Atkinson and Arey, 2003), $k$(HO + propene) = $2.88 \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ (IUPAC, 2019) and $k$(HO + cyclohexane) = $6.92 \times 10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ (Atkinson and Arey, 2003).

(t) Relative to 1,3-butadiene.

(u) Relative to propene.

(v) Relative to cyclohexane.

(w) Derived from the measured yields of benzaldehyde [$C_6H_5CHO$] plus benzyl nitrate [$C_6H_5CH_2ONO_2$] in irradiated $CH_3ONO$-NO-toluene-air mixtures at 298 ± 2 K and ~740 Torr of air. Benzaldehyde and benzyl nitrate are the first-generation products expected from reactions of benzyl radicals generated in channel (1).

(x) Pulse radiolysis study. Benzyl radicals were monitored at 253 nm and the derived benzyl radical concentration (calibrated using the Cl + toluene reaction to generate known concentrations of benzyl) were compared to the initial concentration of HO radicals generated in the reactions from the pulse radiolysis of Ar in the presence of $H_2O$.

(y) Derived from the measured yield of benzaldehyde [$C_6H_5CHO$] plus an estimated benzyl nitrate [$C_6H_5CH_2ONO_2$] yield in irradiated $CH_3ONO$-NO-toluene-air mixtures at 298 K and atmospheric pressure of air. Benzaldehyde and benzyl nitrate are the first-generation products expected from reactions of benzyl radicals generated in channel (1), and the benzyl nitrate yield is estimated using a yield ratio of benzyl nitrate/benzaldehyde = 0.12 (Hoshino et al., 1978; Atkinson et al., 1989).

(z) Derived from the measured yield of benzaldehyde [$C_6H_5CHO$] plus an estimated benzyl nitrate [$C_6H_5CH_2ONO_2$] yield in irradiated $NO_x$-toluene-air mixtures at ~298 K and atmospheric pressure of air. Benzaldehyde and benzyl nitrate are the first-generation products expected from reactions of benzyl radicals generated in channel (1), and the benzyl nitrate yield is estimated using a yield ratio of benzyl nitrate/benzaldehyde = 0.12 (Hoshino et al., 1978; Atkinson et al., 1989).

**Preferred Values**

| Parameter | Value | *T*/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $5.6 \times 10^{-12}$ | 298 |
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $1.8 \times 10^{-12} \exp(340/T)$ | 210-350 |
| $k_1$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $3.5 \times 10^{-13}$ | 298 |
| $k_1$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $2.5 \times 10^{-11} \exp(-1270/T)$ | 310-1050 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.06 | 298 |
| Δ E/R | ± 200 | 210-350 |
| $\Delta \log k_1$ | ± 0.20 | 298 |
| $\Delta E_1/R$ | ± 200 | 310-1050 |

*Comments on Preferred Values*

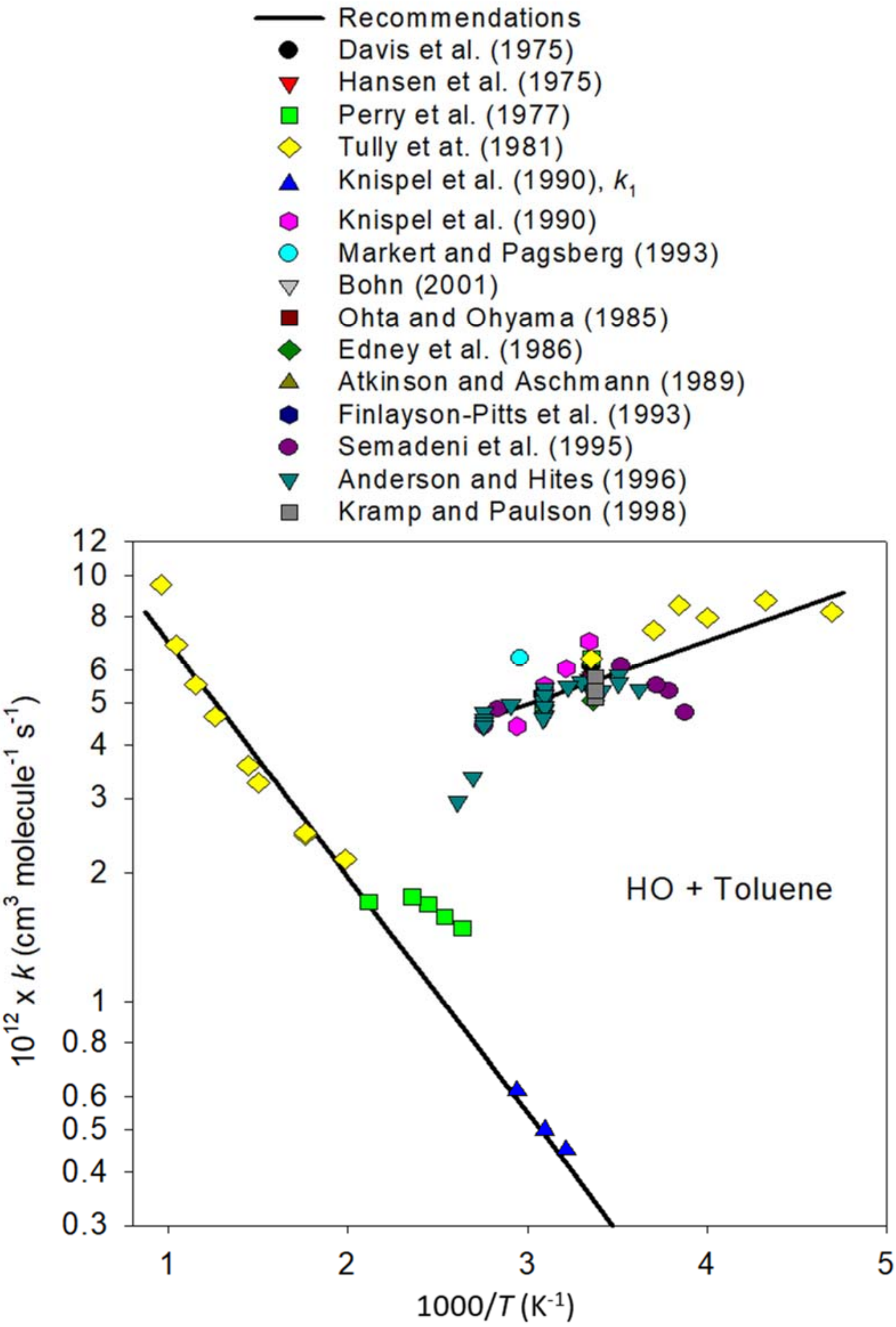
Absolute rate studies show that the reaction of HO radicals with toluene can be considered as comprising three temperature regimes (Perry et al., 1977; Tully et al., 1981). At temperatures <325-350 K the reaction proceeds by channels (1) and (2), with pathway (2) dominating and with the HO-toluene adducts, $HOC_6H_5CH_3$, being thermally stable against back-decomposition to reactants at total pressures above ~100 Torr. At total pressures <100 Torr, channel (2) is in the falloff regime (Davis et al., 1975; Tully et al., 1981; Bourmada et al., 1988a,b), with a limiting low-pressure rate coefficient at 295 ± 2 K of $k_o(\mathrm{He}) = 4.0 \times 10^{-28}$ cm$^6$ molecule$^{-2}$ s$^{-1}$ (Bourmada et al., 1988a,b). At temperatures >450 K, decomposition of the HO-toluene adducts back to reactants is sufficiently rapid that measured rate coefficients are then those for pathway (1). At temperatures in the range ~325-450 K, decomposition of the HO-toluene adducts is significant and the measured rate coefficients depend on the experimental conditions, and in absolute rate studies non-exponential HO radical decays are generally observed.

The >450 K rate coefficients of Perry et al. (1977) and Tully et al. (1981), which are attributed to those for pathway (1), and the values of $k_1$ derived by Knispel et al. (1990) from HO radical decay curves at 299-340 K indicate that an Arrhenius fit is adequate. The preferred values of $k_1$ are obtained from a least-squares fit of the >450 K rate coefficients of Perry et al. (1977) and Tully et al. (1981) and the rate coefficients $k_1$ of Knispel et al. (1990) at 323 K and

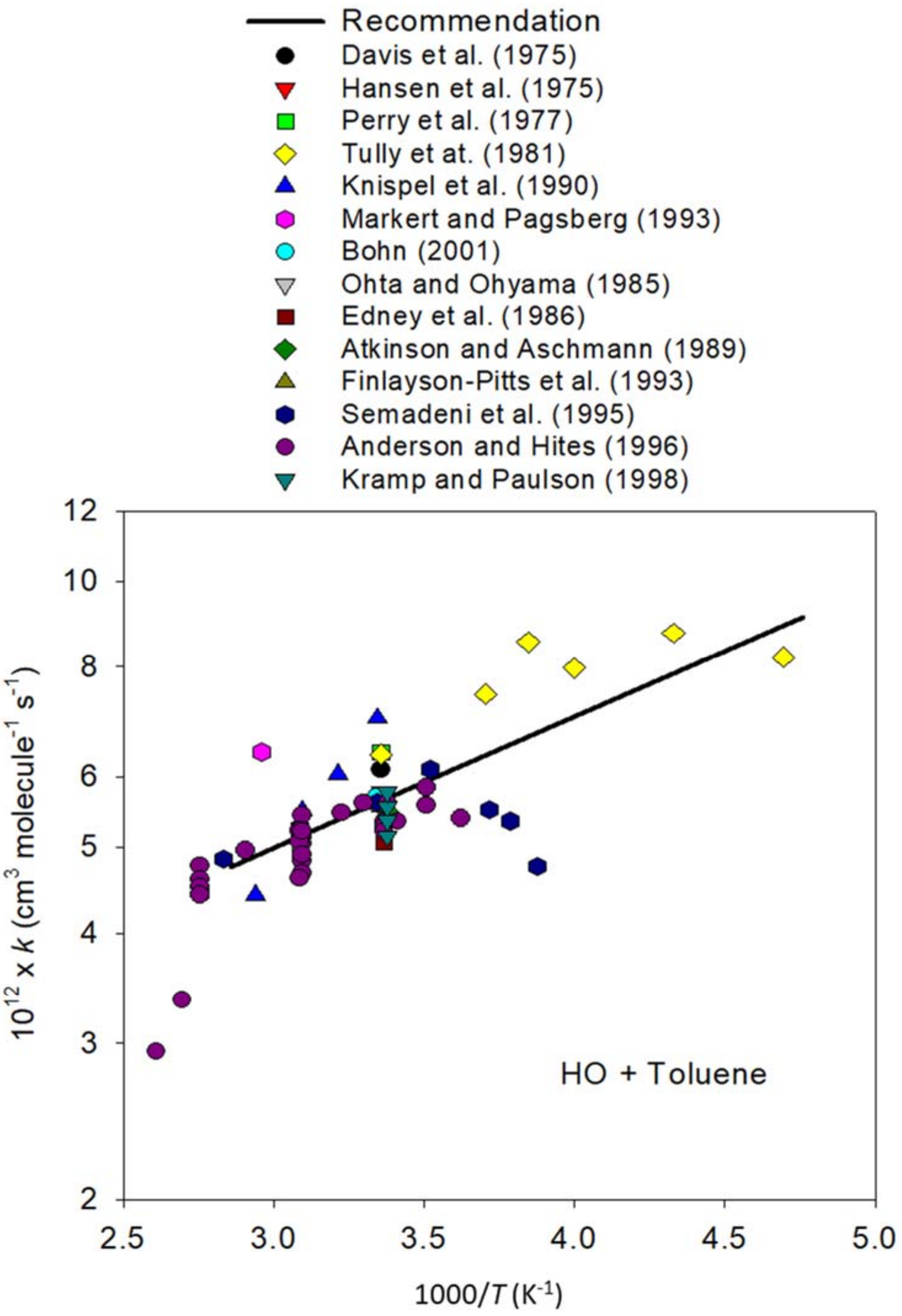
340 K (their rate coefficients $k_1$ at 299 K and 311 K have high associated uncertainties and are not used in the evaluation of $k_1$). The preferred values of $k$ at ≤350 K are based on the absolute rate coefficients of Hansen et al. (1975), Perry et al. (1977), Tully et al. (1981), Knispel et al. (1990) [omitting the 299 K rate coefficient which has a high associated uncertainty] and Bohn (2001) and the relative rate studies of Edney et al. (1986), Atkinson and Aschmann (1989), Finlayson-Pitts et al. (1993), Semadeni et al. (1995), Anderson and Hites (1996) and Kramp and Paulson (1998). The rate coefficient ratio $k_1/k$ derived from the preferred values (0.063 at 298 K) is in excellent agreement with the branching ratios obtained from product studies (Atkinson et al., 1989; Smith et al., 1998; Klotz et al., 1998).

## References

Anderson, P. N. and Hites, R. A. : Environ. Sci. Technol., 30, 301, 1996.
Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
Atkinson, R. and Aschmann, S. M.: Int. J. Chem. Kinet., 21, 355, 1989.
Atkinson, R., Aschmann, S. M., Arey, J. and Carter, W. P. L.: Int. J. Chem. Kinet., 21, 801, 1989.
Bohn, B.: J. Phys. Chem. A, 105, 6092, 2001.
Bourmada, M., Devolder, P. and Sochet, L.-R.: Chem. Phys. Lett., 149, 329, 1988a.
Bourmada, M., Carlier, M., Pauwels, J.-F. and Devolder, P.: J. Chim. Phys., 95, 881, 1988b.
Cox, R. A., Derwent, R. G. and Williams, M. R.: Environ. Sci. Technol., 14, 57, 1980.
Davis, D. D., Bollinger, W. and Fischer, S.: J. Phys. Chem., 79, 293, 1975.
Doyle, G. J., Lloyd, A. C., Darnall, K. R., Winer, A. M. and Pitts Jr., J. N.: Environ. Sci. Technol., 9, 237, 1975.
Edney, E. O., Kleindienst, T. E. and Corse, E. W.: Int. J. Chem. Kinet., 18, 1355, 1986.
Finlayson-Pitts, B. J., Hernandez, S. K. and Berko, H. N.: J. Phys. Chem., 97, 1172, 1993,
Hansen, D. A., Atkinson, R. and Pitts Jr., J. N.: J. Phys. Chem., 79, 1763, 1975.
Hoshino, M., Akimoto, H. and Okuda, M.: J. Chem. Soc. Jpn., 51, 718, 1978.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Klotz, B., Sørensen, S., Barnes, I., Becker, K. H., Etzkorn, T., Volkamer, R., Platt, U., Wirtz, K. and Martín-Reviejo, M.: J. Phys. Chem. A, 102, 10289, 1998.
Kramp, F. and Paulson, S. E. : J. Phys. Chem. A, 102, 2685, 1998.
Knispel, R., Koch, R., Siese, M. and Zetzsch, C.: Ber. Bunsenges. Phys. Chem., 94, 1375, 1990.
Markert, F. and Pagsberg, P.: Chem. Phys. Lett., 209, 445, 1993.
Ohta, T. and Ohyama, T.: Bull. Chem. Soc. Jpn., 58, 3029, 1985.
Perry, R. A., Atkinson, R. and Pitts Jr., J. N.: J. Phys. Chem., 81, 296, 1977.
Semadeni, M., Stocker, D. W. and Kerr, J. A.: Int. J. Chem. Kinet., 27, 287, 1995.
Smith, D. F., McIver, C. D. and Kleindienst, T. E.: J. Atmos. Chem., 30, 209, 1998.
Sommerlade, R., Parlar, H., Wrobel, D. and Kochs, P.: Environ. Sci. Technol., 27, 2435, 1993
Tully, F. P., Ravishankara, A. R., Thompson, R. L., Nicovich, J. M., Shah, R. C., Kreutter, N. M. and Wine, P. H.: J. Phys. Chem., 85, 2262, 1981.



Rate coefficients for HO + Toluene.



Rate coefficients for HO + Toluene.

## HOx_AROM3

$$\mathbf{HO + \textit{m}\text{-}CH_3C_6H_4OH\ (\textit{m}\text{-cresol}) \rightarrow H_2O + CH_3C_6H_4O} \quad (1)$$

$$\mathbf{\rightarrow H_2O + CH_2C_6H_4OH} \quad (2)$$

$$\mathbf{\rightarrow CH_3C_6H_4(OH)_2} \quad (3)$$

### Rate coefficient data ($k = k_1 + k_2 + k_3$)

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(5.77 \pm 0.33) \times 10^{-11}$ | $300 \pm 1$ | Atkinson et al., 1978 | RR (a) |
| $(7.34 \pm 0.43) \times 10^{-11}$ | $296 \pm 2$ | Atkinson and Aschmann, 1990 | RR (b) |
| $3.97 \times 10^{-12} \exp[(775.4 \pm 230.9)/T]$ | 299-373 | Semadeni et al., 1995 | RR (c) |
| $(5.42 \pm 0.54) \times 10^{-11}$ | 299 | | |
| $(5.78 \pm 0.91) \times 10^{-11}$ | $294 \pm 2$ | Coeur-Tourneur et al., 2006 | RR (d) |

## Comments

(a) HO radicals were generated by the photolysis of NO$_x$-organic-air mixtures in a ~5500 L Teflon chamber at wavelengths >300 nm at atmospheric pressure. The concentrations of *m*-cresol and *o*-cresol (the reference organics) were measured by GC. The measured rate coefficient ratio $k$(HO + *m*-cresol)/$k$(HO + *o*-cresol) = $1.42 \pm 0.08$ is placed on an absolute basis using a rate coefficient at 300 K of $k$(HO + *o*-cresol) = $4.06 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019).

(b) HO radicals generated by the photolysis of CH$_3$ONO in air at atmospheric pressure. The concentrations of *m*-cresol and propene (the reference compound) were monitored by GC. The measured rate coefficient ratio $k$(HO + *m*-cresol)/$k$(HO + propene) = $2.55 \pm 0.15$ is placed on an absolute basis using $k$(HO + propene) = $2.88 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 296 K and atmospheric pressure of air (IUPAC, 2019).

(c) HO radicals generated by the photolysis of CH$_3$ONO in air at atmospheric pressure in a ~200 L Teflon chamber. *m*-Cresol and *o*-cresol (the reference compound) were monitored by GC, and the measured rate coefficient ratio $k$(HO + *m*-cresol)/$k$(HO + *o*-cresol) = $2.482 \exp[-(194.6 \pm 230.9)/T]$ over the temperature range 299-373 K is placed on an absolute basis using $k$(HO + *o*-cresol) = $1.6 \times 10^{-12} \exp(970/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019).

(d) HO radicals generated by the photolysis of CH$_3$ONO in air at atmospheric pressure in a ~8000 L Plexiglas chamber. *m*-Cresol and 1,3,5-trimethylbenzene (the reference compound) were monitored by GC, and the measured rate coefficient ratios $k$(HO + *m*-cresol)/$k$(HO + 1,3,5-trimethylbenzene) = $1.02 \pm 0.16$ is placed on an absolute basis using $k$(HO + 1,3,5-trimethylbenzene) = $5.67 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson and Arey, 2003).

**Preferred Values**

| Parameter | Value | *T*/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.2 \times 10^{-11}$ | 298 |
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $2.4 \times 10^{-12} \exp(965/T)$ | 290-350 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.10 | 298 |
| $\Delta E/R$ | ± 600 | 290-350 |

*Comments on Preferred Values*

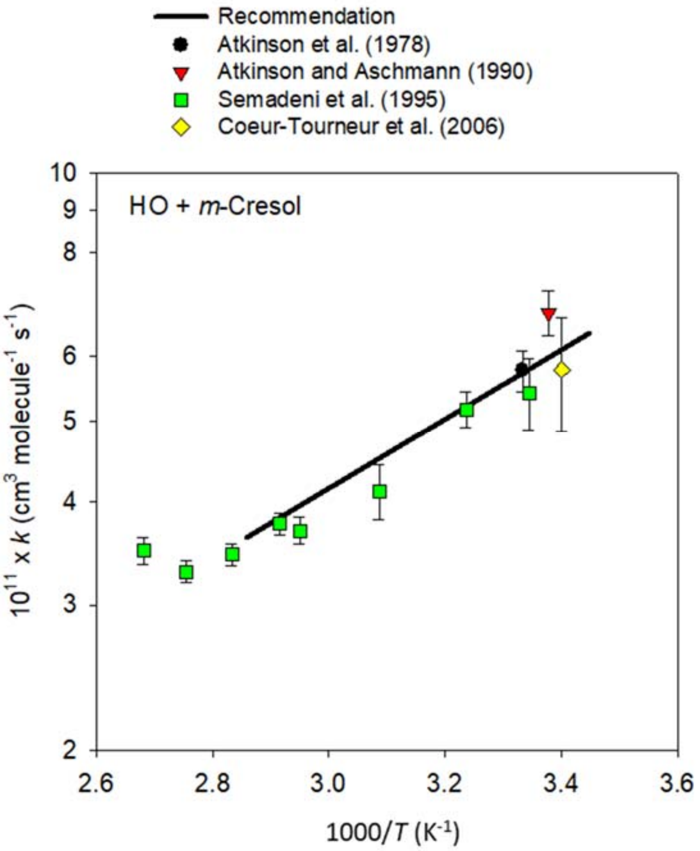
As for the reactions of HO radicals with benzene, toluene, phenol and *o*-cresol (IUPAC, 2019), the reaction of HO radicals with *m*-cresol can be considered as comprising three temperature regimes. At temperatures <325-350 K the reaction proceeds by channels (1-3), with pathway (3) dominating and with the HO-cresol adducts being thermally stable against back-decomposition to reactants at total pressures above ~30 Torr (based on the analogous HO + phenol reaction (IUPAC, 2019)). At temperatures >400-450 K, decomposition of the HO-cresol adducts back to reactants is sufficiently rapid that measured rate coefficients are then those for pathway (1) and (2). At temperatures in the range ~325-400 K, decomposition of the HO-cresol adducts is significant and the measured rate coefficients depend on the experimental conditions.

The available rate coefficients (Atkinson et al., 1978; Atkinson and Aschmann, 1990; Semadeni et al., 1995; Coeur-Tourneur et al., 2006) are all from relative rate studies, with only one study being carried out as a function of temperature (Semadeni et al., 1995). At room temperature, the relative rate data of Atkinson et al. (1978), Atkinson and Aschmann (1990), Semadeni et al. (1995) and Coeur-Tourneur et al. (2006) are in reasonable agreement. The preferred temperature dependence is obtained from a least-squares analysis of the rate coefficients of Semadeni et al. (1995) at temperatures <350 K. The preferred 298 K rate coefficient is an average of the room temperature rate coefficients of Atkinson and Aschmann (1990) [which is judged to supersede the earlier study of Atkinson et al. (1978)], Semadeni et al. (1995) and Coeur-Tourneur et al. (2006), using the preferred temperature dependence to correct the measured rate coefficients to 298 K. The pre-exponential factor is adjusted to fit the 298 K preferred value. Note that no rate coefficients have been measured below 294 K. Furthermore, the rate coefficients used to derive the preferred temperature dependence may have been influenced by thermal decomposition of the HO-cresol adducts, and hence the preferred rate expression should not be used below ~290 K

By analogy with the HO + *o*-cresol reaction (Perry et al., 1977; IUPAC, 2019), at atmospherically-relevant temperatures the HO + *m*-cresol reaction is expected to proceed almost entirely by channels (1) and (3), with channel (1) accounting for a minor fraction (~4%) of the overall reaction at 298 K and for less at lower temperatures. In the presence of $NO_x$, Atkinson et al. (1992), Olariu et al. (2002) and Coeur-Tourneur et al. (2006) measured 5-methyl-2-nitrophenol plus 3-methyl-2-nitrophenol formation yields from the HO radical-initiated reaction of *m*-cresol to be 3.2 ± 1.5% at 296 ± 2 K, 7.7 ± 2.2% at 298 ± 2 K, and 2.9 ± 0.5% at 294 ± 2 K, respectively. Since 3- and 5-methyl-2-nitrophenol formation is attributed to the reaction of 3-methylphenoxy radicals with $NO_2$, these observations indicate that at room temperature channel (1) accounts for least 3% of the overall reaction, consistent with the kinetic data.

## References

Atkinson, R. and Aschmann, S. M.: Int. J. Chem. Kinet., 22, 59, 1990.
Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
Atkinson, R., Darnall, K. R. and Pitts Jr., J. N.: J. Phys. Chem., 82, 2759, 1978.
Coeur-Tourneur, C., Henry, F., Janquin, M.-A. and Brutier, L.: Int. J. Chem. Kinet., 38, 553, 2006.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Olariu, R. I., Klotz, B., Barnes, I., Becker, K. H. and Mocanu, R.: Atmos. Environ., 36, 3685, 2002.
Perry, R. A., Atkinson, R. and Pitts Jr., J. N.: J. Phys. Chem., 81, 1607, 1977.
Semadeni, M., Stocker, D. W. and Kerr, J. A.: Int. J. Chem. Kinet., 27, 287, 1995.



Rate coefficients for HO + *m*-Cresol.

## HOx_AROM4

$$\begin{aligned}\textbf{HO} + \textbf{\textit{o}-CH}_3\textbf{C}_6\textbf{H}_4\textbf{OH (\textit{o}-cresol)} &\rightarrow \textbf{H}_2\textbf{O} + \textbf{CH}_3\textbf{C}_6\textbf{H}_4\textbf{O} \quad &\textbf{(1)}\\ &\rightarrow \textbf{H}_2\textbf{O} + \textbf{CH}_2\textbf{C}_6\textbf{H}_4\textbf{OH} \quad &\textbf{(2)}\\ &\rightarrow \textbf{CH}_3\textbf{C}_6\textbf{H}_4\textbf{(OH)}_2 \quad &\textbf{(3)}\end{aligned}$$

### Rate coefficient data ($k = k_1 + k_2 + k_3$)

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $1.6 \times 10^{-12} \exp[(906 \pm 1007)/T]$ | 299-335 | Perry et al., 1977 | FP-RF (a) |
| $(3.41 \pm 0.68) \times 10^{-11}$ | 299.4 | | |
| $(2.93 \pm 0.59) \times 10^{-11}$ | 310.6 | | |
| $(2.98 \pm 0.60) \times 10^{-11}$ | 322.0 | | |
| $(2.68 \pm 0.54) \times 10^{-11}$ | 330.7 | | |
| $(2.55 \pm 0.51) \times 10^{-11}$ | 335.4 | | |
| $5.0 \times 10^{-11} \exp[-(906 \pm 1007)/T]$ | 400-424 | | |
| $(5.6 \pm 1.1) \times 10^{-12}$ | 400.6 | | |
| $(5.4 \pm 1.1) \times 10^{-12}$ | 407.8 | | |
| $(6.2 \pm 1.2) \times 10^{-12}$ | 423.1 | | |
| *Relative Rate Cofficients* | | | |
| $(3.85 \pm 0.33) \times 10^{-11}$ | $300 \pm 1$ | Atkinson et al., 1978 | RR (b) |
| $(4.61 \pm 0.22) \times 10^{-11}$ | $296 \pm 2$ | Atkinson and Aschmann, 1990 | RR (c) |
| $1.01 \times 10^{-12} \exp[(1155.6 \pm 246.1)/T]$ | 301-373 | Semadeni et al., 1995 | RR (d) |
| $(4.65 \pm 0.40) \times 10^{-11}$ | 301 | | |
| $(4.25 \pm 0.52) \times 10^{-11}$ | $294 \pm 2$ | Coeur-Tourneur et al., 2006 | RR (e) |

## Comments

(a) Non-exponential HO radical decays were observed at temperatures between 344 K and 393 K. The total pressure was ~100 Torr (133 mbar) of argon diluent.

(b) HO radicals were generated by the photolysis of $NO_x$-organic-air mixtures in a ~5500 L Teflon chamber at wavelengths >300 nm at atmospheric pressure. The concentrations of *o*-cresol and *n*-butane and 2,2-dimethylpropane (the reference organics) were measured by GC. The measured rate coefficient ratio $k$(HO + *o*-cresol)/{$k$(HO + *n*-butane) - $k$(HO + 2,2-dimethylpropane)} is placed on an absolute basis using rate coefficients at 300 K of $k$(HO + *n*-butane) = $2.38 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019) and $k$(HO + 2,2,-dimethylpropane)} = $8.4 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Arey and Atkinson, 2003).

(c) HO radicals generated by the photolysis of $CH_3ONO$ in air at atmospheric pressure. The concentrations of *o*-cresol and propene (the reference compound) were monitored by GC. The measured rate coefficient ratio $k$(HO + *o*-cresol)/$k$(HO + propene) = $1.60 \pm 0.08$ is placed on an absolute basis using $k$(HO + propene) = $2.88 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 296 K and atmospheric pressure of air (IUPAC, 2019).

(d) HO radicals generated by the photolysis of $CH_3ONO$ in air at atmospheric pressure in a ~200 L Teflon chamber. *o*-Cresol and 1,3-butadiene (the reference compound) were monitored by GC, and the measured rate coefficient ratio $k$(HO + *o*-cresol)/$k$(HO + 1,3-

butadiene) = 0.068 exp[(707.6 ± 246.1)/$T$] over the temperature range 301-373 K is placed on an absolute basis using $k$(HO + 1,3-butadiene) = 1.48 × $10^{-11}$ exp(448/$T$) $cm^3$ $molecule^{-1}$ $s^{-1}$ (Atkinson and Arey, 2003).

(e) HO radicals generated by the photolysis of $CH_3ONO$ in air at atmospheric pressure in a ~8000 L Plexiglas chamber. *o*-Cresol and 1,3,5-trimethylbenzene (the reference compound) were monitored by GC, and the measured rate coefficient ratios $k$(HO + *o*-cresol)/$k$(HO + 1,3,5-trimethylbenzene) = 0.75 ± 0.09 is placed on an absolute basis using $k$(HO + 1,3,5-trimethylbenzene) = 5.67 × $10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ (Atkinson and Arey, 2003).

### Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /$cm^3$ $molecule^{-1}$ $s^{-1}$ | 4.2 × $10^{-11}$ | 298 |
| $k$ /$cm^3$ $molecule^{-1}$ $s^{-1}$ | 1.6 × $10^{-12}$ exp(970/$T$) | 290-350 |
| *Relability* | | |
| Δ log $k$ | ± 0.10 | 298 |
| Δ E/R | ± 600 | 290-350 |

*Comments on Preferred Values*

As for the reactions of HO radicals with benzene and toluene (IUPAC, 2019), the reaction of HO radicals with *o*-cresol can be considered as comprising three temperature regimes (Perry et al., 1977). At temperatures <325-350 K the reaction proceeds by channels (1-3), with pathway (3) dominating and with the HO-cresol adducts being thermally stable against back-decomposition to reactants at total pressures above ~30 Torr (based on the analogous HO + phenol reaction (IUPAC, 2019)). At temperatures >400-450 K, decomposition of the HO-cresol adducts back to reactants is sufficiently rapid that measured rate coefficients are then those for pathway (1) and (2). At temperatures in the range ~325-400 K, decomposition of the HO-cresol adducts is significant and the measured rate coefficients depend on the experimental conditions, and in absolute rate studies non-exponential HO radical decays are observed (Perry et al., 1977).

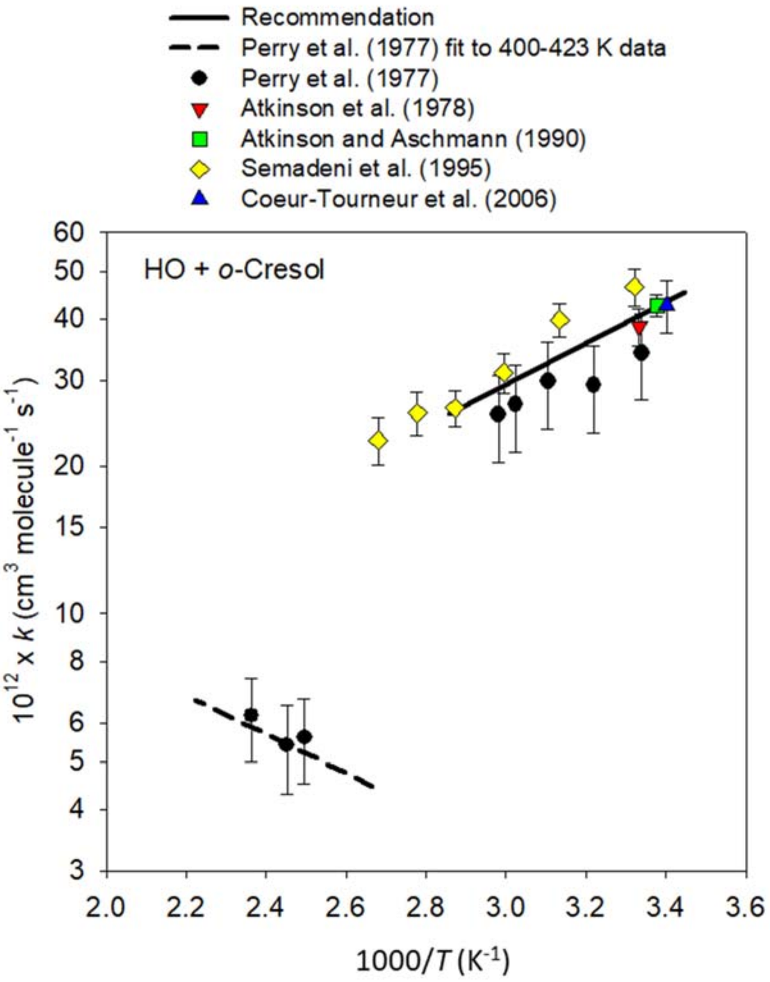
At room temperature, the absolute and relative rate data of Perry et al. (1977), Atkinson et al. (1978), Atkinson and Aschmann (1990), Semadeni et al. (1995) and Coeur-Tourneur et al. (2006) are in agreement within the experimental uncertainties. The preferred values of $k$ at ≤350 K are based on a least-squares analysis of the absolute rate coefficients of Perry et al. (1977) and the relative rate data of Atkinson and Aschmann (1990) [which is judged to supersede the earlier study of Atkinson et al. (1978)], Semadeni et al. (1995) and Coeur-Tourneur et al. (2006). Note that no rate coefficients have been measured below 294 K. Furthermore, the rate coefficients used to derive the preferred temperature dependence may have been influenced by fall-off effects and/or thermal decomposition of the HO-cresol adducts, and hence the preferred rate expression should not be used below ~290 K.

The rate coefficients of Perry et al. (1977) at 400-423 K suggest that H-atom abstraction, attributed to ($k_1$ + $k_2$), is minor at room temperature and below, accounting for ~6% of the overall reaction at 298 K to within a factor of ~2 using the Perry et al. (1977) fit to their 400-423 K data. The values of ($k_1$ + $k_2$) of Perry et al. (1977) at ~400 K are factors of ~200 and ~10 higher than the rate coefficients for H-atom abstraction from the ring C-H bonds in benzene and from the C-H bonds in the $CH_3$ substituent group in toluene, respectively (Knispel et al., 1990; IUPAC, 2019), indicating that for HO + *o*-cresol channel (1) dominates over channel (2) (i.e., $k_1 > k_2$). Moreover, the values of ($k_1 + k_2$) of Perry et al. (1977) for HO + *o*-cresol at ~400 K are similar to those of Knispel et al. (1990) for HO + phenol at 354 K and 374 K, again consistent with H-atom abstraction from the OH group dominating over H-atom abstraction from the ring C-H bonds or the C-H bonds of the $CH_3$ group.

At atmospherically-relevant temperatures, the reaction therefore proceeds almost entirely by channels (1) and (3), with channel (1) accounting for ~($6^{+6}_{-3}$)% of the overall reaction at 298 K and for less at lower temperatures. In the presence of $NO_x$, Atkinson et al. (1992), Olariu et al. (2002) and Coeur-Tourneur et al. (2006) measured 6-methyl-2-nitrophenol formation yields from the OH radical-initiated reaction of *o*-cresol to be 5.1 ± 1.5% at 296 ± 2 K, 6.8 ± 1.5% at 298 ± 2 K, and 4.7 ± 0.8% at 294 ± 2 K, respectively. Since 6-methyl-2-nitrophenol formation is attributed to the reaction of 2-methylphenoxy radicals with $NO_2$, these observations indicate that at room temperature channel (1) accounts for least 5% of the overall reaction, consistent with the kinetic data.

## References

Atkinson, R. and Aschmann, S. M.: Int. J. Chem. Kinet., 22, 59, 1990.
Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
Atkinson, R., Darnall, K. R. and Pitts Jr., J. N.: J. Phys. Chem., 82, 2759, 1978.
Coeur-Tourneur, C., Henry, F., Janquin, M.-A. and Brutier, L.: Int. J. Chem. Kinet., 38, 553, 2006.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Knispel, R., Koch, R., Siese, M. and Zetzsch, C.: Ber. Bunsenges. Phys. Chem., 94, 1375, 1990.
Olariu, R. I., Klotz, B., Barnes, I., Becker, K. H. and Mocanu, R.: Atmos. Environ., 36, 3685, 2002.
Perry, R. A., Atkinson, R. and Pitts Jr., J. N.: J. Phys. Chem., 81, 1607, 1977.
Semadeni, M., Stocker, D. W. and Kerr, J. A.: Int. J. Chem. Kinet., 27, 287, 1995.



Rate coefficients for HO + *o*-Cresol.

## HOx_AROM5

$$\mathbf{HO} + \boldsymbol{p}\text{-}\mathbf{CH_3C_6H_4OH}\ (\boldsymbol{p}\text{-}\mathbf{cresol}) \rightarrow \mathbf{H_2O + CH_3C_6H_4O} \quad \mathbf{(1)}$$

$$\rightarrow \mathbf{H_2O + CH_2C_6H_4OH} \quad \mathbf{(2)}$$

$$\rightarrow \mathbf{CH_3C_6H_4(OH)_2} \quad \mathbf{(3)}$$

### Rate coefficient data ($k = k_1 + k_2 + k_3$)

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(4.47 \pm 0.21) \times 10^{-11}$ | 300 ± 1 | Atkinson et al., 1978 | RR (a) |
| $(5.24 \pm 0.51) \times 10^{-11}$ | 296 ± 2 | Atkinson and Aschmann, 1990 | RR (b) |
| $1.12 \times 10^{-12} \exp[(1180.4 \pm 444.5)/T]$ | 301-373 | Semadeni et al., 1995 | RR (c) |
| $(5.42 \pm 0.54) \times 10^{-11}$ | 301 | | |
| $(4.38 \pm 0.69) \times 10^{-11}$ | 301 | Semadeni et al., 1995 | RR (d) |
| $(4.53 \pm 0.39) \times 10^{-11}$ | 314 | | |
| $(4.88 \pm 0.74) \times 10^{-11}$ | 294 ± 2 | Coeur-Tourneur et al., 2006 | RR (e) |

## Comments

(a) HO radicals were generated by the photolysis of $NO_x$-organic-air mixtures in a ~5500 L Teflon chamber at wavelengths >300 nm at atmospheric pressure. The concentrations of *p*-cresol and *o*-cresol (the reference organics) were measured by GC. The measured rate coefficient ratio $k$(HO + *p*-cresol)/$k$(HO + *o*-cresol) = 1.10 ± 0.05 is placed on an absolute basis using a rate coefficient at 300 K of $k$(HO + *o*-cresol) = $4.06 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019).

(b) HO radicals generated by the photolysis of $CH_3ONO$ in air at atmospheric pressure. The concentrations of *p*-cresol and propene (the reference compound) were monitored by GC. The measured rate coefficient ratio $k$(HO + *p*-cresol)/$k$(HO + propene) = 2.55 ± 0.15 is placed on an absolute basis using $k$(HO + propene) = $2.88 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 296 K and atmospheric pressure of air (IUPAC, 2019).

(c) HO radicals generated by the photolysis of $CH_3ONO$ in air at atmospheric pressure in a ~200 L Teflon chamber. *p*-Cresol and 1,3-butadiene (the reference compound) were monitored by GC, and the measured rate coefficient ratio $k$(HO + *p*-cresol)/$k$(HO + 1,3-butadiene) = $0.076 \exp[(732.4 \pm 444.5)/T]$ over the temperature range 301-373 K is placed on an absolute basis using $k$(HO + 1,3-butadiene) = $1.48 \times 10^{-11} \exp(448/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson and Arey, 2003).

(d) HO radicals generated by the photolysis of $CH_3ONO$ in air at atmospheric pressure in a ~200 L Teflon chamber. *p*-Cresol and *o*-cresol (the reference compound) were monitored by GC, and the measured rate coefficient ratios $k$(HO + *p*-cresol)/$k$(HO + *o*-cresol) = 1.09 ± 0.17 at 301 K and 1.29 ± 0.11 at 314 K are placed on an absolute basis using $k$(HO + *o*-cresol) = $1.6 \times 10^{-12} \exp(970/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019).

(e) HO radicals generated by the photolysis of $CH_3ONO$ in air at atmospheric pressure in a ~8000 L Plexiglas chamber. *p*-Cresol and 1,3,5-trimethylbenzene (the reference compound) were monitored by GC, and the measured rate coefficient ratios $k$(HO + *p*-cresol)/$k$(HO + 1,3,5-trimethylbenzene) = 0.86 ± 0.13 is placed on an absolute basis using $k$(HO + 1,3,5-trimethylbenzene) = $5.67 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson and Arey, 2003).

**Preferred Values**

| Parameter | Value | $T$/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $4.8 \times 10^{-11}$ | 298 |
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $1.9 \times 10^{-12} \exp(970/T)$ | 290-350 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.10 | 298 |
| $\Delta$ E/R | ± 600 | 290-350 |

*Comments on Preferred Values*

As for the reactions of HO radicals with benzene, toluene, phenol and *o*-cresol (IUPAC, 2019), the reaction of HO radicals with *p*-cresol can be considered as comprising three temperature regimes. At temperatures <325-350 K the reaction proceeds by channels (1-3), with pathway (3) dominating and with the HO-cresol adducts being thermally stable against back-decomposition to reactants at total pressures above ~30 Torr (based on the analogous HO + phenol reaction (IUPAC, 2019)). At temperatures >400-450 K, decomposition of the HO-cresol adducts back to reactants is sufficiently rapid that measured rate coefficients are then those for pathway (1) and (2). At temperatures in the range ~325-400 K, decomposition of the HO-cresol adducts is significant and the measured rate coefficients depend on the experimental conditions.

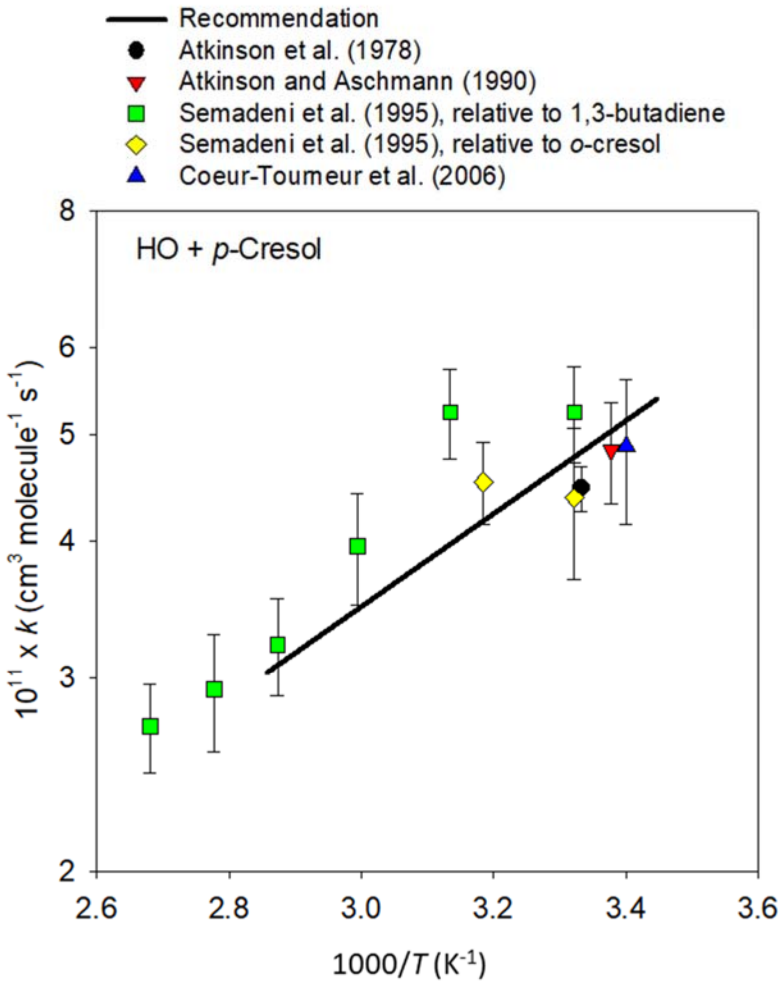
The available rate coefficients (Atkinson et al., 1978; Atkinson and Aschmann, 1990; Semadeni et al., 1995; Coeur-Tourneur et al., 2006) are all from relative rate studies, with only one study being carried out as a function of temperature (Semadeni et al., 1995). At room temperature, the relative rate data of Atkinson et al. (1978), Atkinson and Aschmann (1990), Semadeni et al. (1995) and Coeur-Tourneur et al. (2006) are in reasonable agreement. The temperature dependence obtained from the Semadeni et al. (1995) study (using rate coefficients at <350 K) has a large uncertainty, but is generally similar to those for HO + *o*-cresol ($E/R$ = -970 K) and HO + *m*-cresol ($E/R$ = -965 K) (IUPAC, 2019). Accordingly, a temperature dependence equal to that for the HO + *o*-cresol reaction is used. The preferred 298 K rate coefficient is an average of the room temperature rate coefficients of Atkinson and Aschmann (1990) [which is judged to supersede the earlier study of Atkinson et al. (1978)], Semadeni et al. (1995) [using only the rate coefficient measured relative to 1,3-butadiene] and Coeur-Tourneur et al. (2006), using the preferred temperature dependence to correct the measured rate coefficients to 298 K. The pre-exponential factor is adjusted to fit the 298 K preferred value. Note that no rate coefficients have been measured below 294 K. Furthermore, the rate coefficients used to derive the preferred temperature dependence may have been influenced by thermal decomposition of the HO-cresol adducts, and hence the preferred rate expression should not be used below ~290 K

By analogy with the HO + *o*-cresol reaction (Perry et al., 1977; IUPAC, 2019), at atmospherically-relevant temperatures the HO + *p*-cresol reaction is expected to proceed almost entirely by channels (1) and (3), with channel (1) accounting for a minor fraction (~5%) of the overall reaction at 298 K and for less at lower temperatures. In the presence of $NO_x$, Atkinson et al. (1992), Olariu et al. (2002) and Coeur-Tourneur et al. (2006) measured 4-methyl-2-nitrophenol formation yields from the HO radical-initiated reaction of *o*-cresol to be 10 ± 4% at 296 ± 2 K, 7.6 ± 2.2% at 298 ± 2 K, and 17.2 ± 2.5% at 294 ± 2 K, respectively. Since 4-methyl-2-nitrophenol formation is attributed to the reaction of 2-methylphenoxy radicals with $NO_2$, these observations indicate that at room temperature channel (1) accounts for least 5-6%

of the overall reaction, reasonably consistent with the approximate estimate from kinetic data from the *o*- and *p*-cresol reactions.

## References

Atkinson, R. and Aschmann, S. M.: Int. J. Chem. Kinet., 22, 59, 1990.
Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
Atkinson, R., Darnall, K. R. and Pitts Jr., J. N.: J. Phys. Chem., 82, 2759, 1978.
Coeur-Tourneur, C., Henry, F., Janquin, M.-A. and Brutier, L.: Int. J. Chem. Kinet., 38, 553, 2006.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Olariu, R. I., Klotz, B., Barnes, I., Becker, K. H. and Mocanu, R.: Atmos. Environ., 36, 3685, 2002.
Perry, R. A., Atkinson, R. and Pitts Jr., J. N.: J. Phys. Chem., 81, 1607, 1977.
Semadeni, M., Stocker, D. W. and Kerr, J. A.: Int. J. Chem. Kinet., 27, 287, 1995.



Rate coefficients for HO + *p*-Cresol.

## HOx_AROM6

$$\mathbf{HO + C_6H_5OH\ (phenol) \rightarrow H_2O + C_6H_5O \qquad (1)}$$
$$\mathbf{\rightarrow H_2O + C_6H_4OH \qquad (2)}$$
$$\mathbf{\rightarrow HOC_6H_5OH \qquad (3)}$$

### Rate coefficient data ($k = k_1 + k_2 + k_3$)

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $(2.83 \pm 0.57) \times 10^{-11}$ | 296 | Rinke and Zetzsch, 1984 | FP-RF (a) |
| $k_1 + k_2 = (0 \pm 0.5) \times 10^{-12}$ | 300 | Knispel et al., 1990 | FP-RF (b) |
| $k_3 = (2.9 \pm 0.3) \times 10^{-11}$ | 300 | | |
| $k_1 + k_2 = (0 \pm 0.5) \times 10^{-12}$ | 308 | | |
| $k_3 = (2.6 \pm 0.3) \times 10^{-11}$ | 308 | | |
| $k_1 + k_2 = (3.4 \pm 0.5) \times 10^{-12}$ | 323 | | |
| $k_3 = (1.9 \pm 0.2) \times 10^{-11}$ | 323 | | |
| $k_1 + k_2 = (4.6 \pm 0.5) \times 10^{-12}$ | 339 | | |
| $k_3 = (1.4 \pm 0.2) \times 10^{-11}$ | 339 | | |
| $k_1 + k_2 = (4.6 \pm 0.4) \times 10^{-12}$ | 354 | | |
| $k_3 = (1.3 \pm 0.2) \times 10^{-11}$ | 354 | | |
| $k_1 + k_2 = (5.1 \pm 0.4) \times 10^{-12}$ | 374 | | |
| $k_3 = (1.2 \pm 0.2) \times 10^{-11}$ | 374 | | |
| *Relative Rate Cofficients* | | | |
| $1.35 \times 10^{-11}$ | 1032 | He et al., 1988 | RR (c) |
| $2.66 \times 10^{-13} \exp[(1376.5 \pm 282.5)/T]$ | 301-373 | Semadeni et al., 1995 | RR (d) |
| $(2.56 \pm 0.27) \times 10^{-11}$ | 301 | | |
| $(2.41 \pm 0.21) \times 10^{-11}$ | 301 | Semadeni et al., 1995 | RR (e) |
| $(2.07 \pm 0.18) \times 10^{-11}$ | 314 | | |

## Comments

(a) Rate coefficients were measured over the pressure range 5-733 mbar (3.75-550 Torr) of He diluent, with no effect of pressure on the rate coefficient being observed at pressures ≥43 mbar (32 Torr). The cited rate coefficient is at 133 mbar pressure.

(b) Rate coefficients $k_1$ and $k_2$ were derived from fitting the observed non-exponential HO radical decays, measured at a total pressure of 133 mbar of Ar, to reactions (1) plus (2), (3), the back-decomposition of the HO-phenol adducts and accounting for diffusive and background losses of HO radicals and the HO-phenol adducts. Using the rate coefficient of He et al. (1988) at 1032 K and the expression $(k_1 + k_2) = C\,T^2 \exp(-D/T)$, a global fit to the experimental data resulted in rate coefficients $(k_1 + k_2)$ of $(3.97 \pm 0.03) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, essentially independent of temperature, over the range 300-374 K.

(c) Based on the effect of added CO on shocked 2,2,3,3-tetramethylbutane-phenol-Ar mixtures. The derived rate coefficient ratio $k$(HO + phenol)/$k$(HO + CO) = 33.2 (from the listed rate expressions) is placed on an absolute basis by use of $k$(HO + CO) = $4.08 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 1032 K and 3.75 ± 1.25 bar pressure (Atkinson, 2003). From comparison of their rate coefficient at 1032 K with those of Tully et al. (1981) for HO + benzene at ~1000 K, He et al. (1988) concluded that channel (1) was the dominant reaction pathway.

(d) HO radicals generated by the photolysis of $CH_3ONO$ in air at atmospheric pressure in a ~200 L Teflon chamber. Phenol and 1,3-butadiene (the reference compound) were monitored by GC, and the measured rate coefficient ratio $k$(HO + phenol)/$k$(HO + 1,3-butadiene) = 0.018 exp[(925.5 ± 282.5)/$T$] over the temperature range 301-373 K is placed on an absolute basis using a rate coefficient of $k$(HO + 1,3-butadiene) = $1.48 \times 10^{-11}$ exp(448/$T$) $cm^3$ $molecule^{-1}$ $s^{-1}$ (Atkinson and Arey, 2003).

(e) HO radicals generated by the photolysis of $CH_3ONO$ in air at atmospheric pressure in a ~200 L Teflon chamber. Phenol and *o*-cresol (the reference compound) were monitored by GC, and the measured rate coefficient ratios $k$(HO + phenol)/$k$(HO + *o*-cresol) = 0.60 ± 0.05 at 301 K and 0.59 ± 0.05 at 314 K are placed on an absolute basis using a rate coefficient of $k$(HO + o-cresol) = $1.6 \times 10^{-12}$ exp(970/$T$) $cm^3$ $molecule^{-1}$ $s^{-1}$ (IUPAC, 2019).

**Preferred Values**

| Parameter | Value | *T*/K |
|---|---|---|
| $k$ /$cm^3$ $molecule^{-1}$ $s^{-1}$ | $2.8 \times 10^{-11}$ | 298 |
| $k$ /$cm^3$ $molecule^{-1}$ $s^{-1}$ | $4.7 \times 10^{-13}$ exp(1220/$T$) | 290-350 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.08 | 298 |
| Δ E/R | ± 600 | 290-350 |

*Comments on Preferred Values*

As for the reactions of HO radicals with benzene and toluene (IUPAC, 2019), the reaction of HO radicals with phenol can be considered as comprising three temperature regimes. At temperatures <325-350 K the reaction proceeds by channels (1-3), with pathway (3) dominating and with the HO-phenol adduct, $HOC_6H_5OH$, being thermally stable against back-decomposition to reactants at total pressures above ~30 Torr (Rinke and Zetzsch, 1984). At temperatures >400-450 K, decomposition of the HO-phenol adduct back to reactants is sufficiently rapid that measured rate coefficients are then those for pathways (1) and/or (2). At temperatures in the range ~325-450 K, decomposition of the HO-phenol adduct is significant and the measured rate coefficients depend on the experimental conditions.

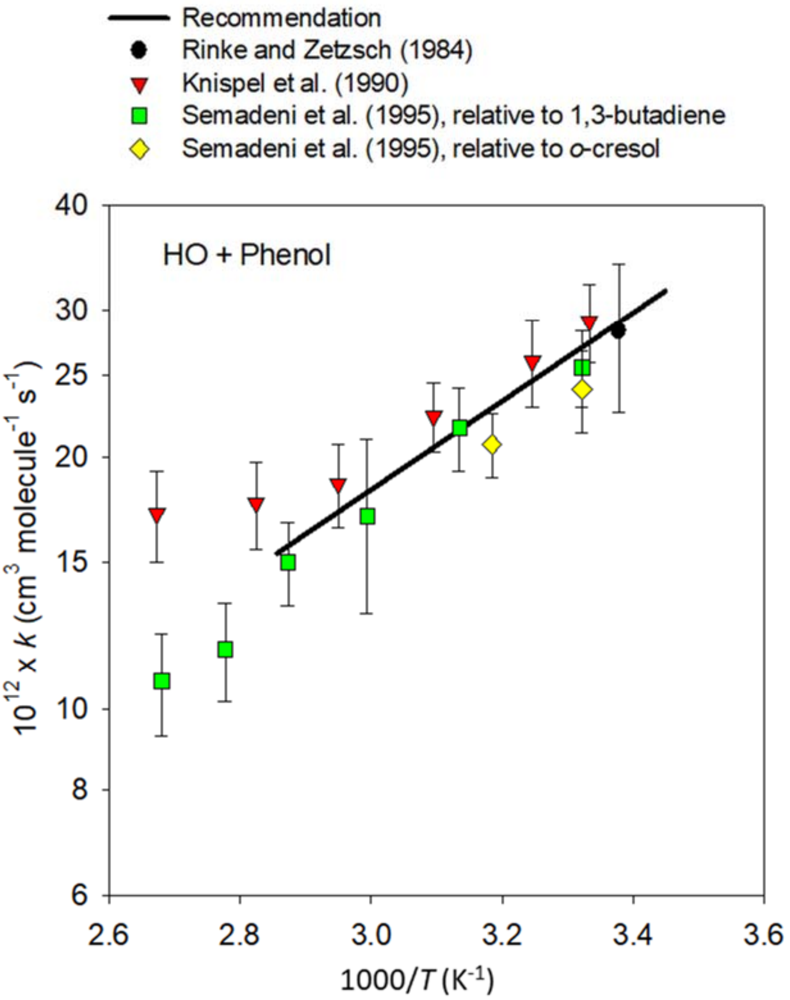
The preferred values of $k$ at ≤350 K are based on the absolute rate coefficients of Rinke and Zetzsch (1984) and Knispel et al. (1990) and the rate coefficients measured by Semadeni et al. (1995) relative to 1,3-butadiene. The rate coefficients measured by Semadeni et al. (1995) relative to *o*-cresol at 301 K and 314 K are in good agreement with the preferred values, indicating that the preferred values for HO + phenol and HO + *o*-cresol (IUPAC, 2019) are internally self-consistent. Note that no rate coefficients have been measured below 296 K. Furthermore, the rate coefficients used to derive the preferred temperature dependence may have been influenced by fall-off effects and/or thermal decomposition of the HO-phenol adducts, and hence the preferred rate expression should not be used below ~290 K.

An Arrhenius fit to the relative rate coefficient of He et al. (1988) at 1032 K (which is subject to significant uncertainty, in part due to uncertainties in the rate coefficient for the reaction of HO radicals with CO, the reference compound used) and the values of ($k_1$ + $k_2$) derived by Knispel et al. (1990) from HO radical decay curves at 323 K, 339 K, 354 K and 374 K results in ($k_1$ + $k_2$) ~ $2.4 \times 10^{-11}$ exp(-590/$T$) $cm^3$ $molecule^{-1}$ $s^{-1}$. The values of ($k_1$ + $k_2$) obtained by Knispel et al. (1990) at ~350 K are a factor of ~200 higher than the rate coefficient for H-atom abstraction from the ring C-H bonds in benzene (Knispel et al., 1990; IUPAC, 2019), indicating that for HO + phenol channel (1) dominates over channel (2) (i.e., $k_1 >> k_2$). Hence, as also concluded by He et al. (1988), channel (2) is of no importance and can be neglected at temperatures <1100 K.

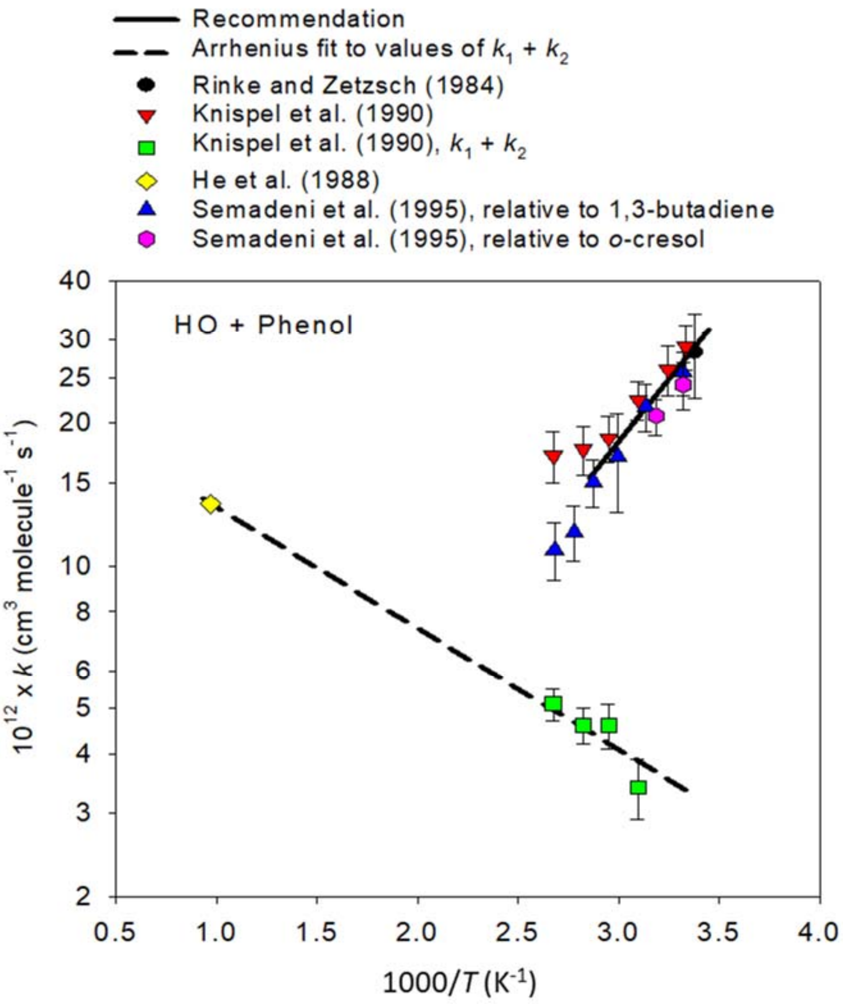
At atmospherically-relevant temperatures, the reaction proceeds almost entirely by channels (1) and (3), with channel (1) being estimated to account for ~12% of the overall reaction of HO radicals with phenol at 298 K, and for less at lower temperatures. In the presence of $NO_x$, Atkinson et al. (1992) and Olariu et al. (2002) measured 2-nitrophenol formation yields from the HO radical-initiated reaction of phenol to be 6.7 ± 1.5% at 296 ± 2 K and 5.8 ± 1.0% at 298 ± 2 K, respectively. Since 2-nitrophenol formation is attributed to the reaction of phenoxy radicals with $NO_2$, these observations indicate that at room temperature channel (1) accounts for least 6% of the overall reaction, consistent with the kinetic data.

## References

Atkinson, R.: Atmos. Chem. Phys., 3, 2233, 2003.
Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
He, Y. Z., Mallard, W. G. and Tsang, W.: J. Phys. Chem., 92, 2196, 1988.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Knispel, R., Koch, R., Siese, M. and Zetzsch, C.: Ber. Bunsenges. Phys. Chem., 94, 1375, 1990.
Olariu, R. I., Klotz, B., Barnes, I., Becker, K. H. and Mocanu, R.: Atmos. Environ., 36, 3685, 2002.
Rinke, M. and Zetzsch, C.: Ber. Bunsenges. Phys. Chem., 88, 55, 1984.
Semadeni, M., Stocker, D. W. and Kerr, J. A.: Int. J. Chem. Kinet., 27, 287, 1995.
Tully, F. P., Ravishankara, A. R., Thompson, R. L., Nicovich, J. M., Shah, R. C., Kreutter, N. M. and Wine, P. H.: J. Phys. Chem., 85, 2262, 1981.



Rate coefficients for HO + Phenol.



Rate coefficients for HO + Phenol.

## HOx_AROM7

### HO + 1,2-dihydroxybenzene ($1,2\text{-}C_6H_4(OH)_2$) → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(1.01 \pm 0.04) \times 10^{-10}$ | 300 ± 5 | Olariu et al., 2000 | RR (a,b) |
| $(1.06 \pm 0.04) \times 10^{-10}$ | 300 ± 5 | Olariu et al., 2000 | RR (a,c) |
| $(1.01 \pm 0.04) \times 10^{-10}$ | 300 ± 5 | Olariu et al., 2000 | RR (a,d) |

### Comments

(a) HO radicals were generated by the photolysis of $CH_3ONO$. Experiments were carried out in a 1080 L chamber at 1.013 bar of air. The concentrations of 1,2-dihydroxybenzene and isoprene, 1,3-butadiene or *trans*-2-butene (the reference compounds) were measured by FTIR spectroscopy. Wall losses of 1,2-dihydroxybenzene were measured and taken into account in the data analysis, and these contributed ~30% of the 1,2-dihydroxybenzene loss rate due to HO radical reaction during the experiments. The measured rate coefficient ratios of $k$(HO + 1,2-dihydroxybenzene)/$k$(HO + isoprene) = 1.024 ± 0.04, $k$(HO + 1,2-dihydroxybenzene)/$k$(HO + 1,3-butadiene) = 1.608 ± 0.052 and $k$(HO + 1,2-dihydroxybenzene)/$k$(HO + *trans*-2-butene) = 1.606 ± 0.05 are placed on an absolute basis using rate coefficients at 300 K of $k$(HO + isoprene) = $9.91 \times 10^{-11}$ (IUPAC, 2019), $k$(HO + 1,3-butadiene) = $6.59 \times 10^{-11}$ (Atkinson and Arey, 2003) and $k$(HO + *trans*-2-butene) = $6.32 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson and Arey, 2003).

(b) Relative to $k$(HO + isoprene).

(c) Relative to $k$(HO + 1,3-butadiene).

(d) Relative to $k$(HO + *trans*-2-butene).

### Preferred Values

| Parameter | Value | $T$/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $1.0 \times 10^{-10}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ±0.15 | 298 |

*Comments on Preferred Values*

The three rate coefficients measured by Olariu et al. (2000) at 300 ± 5 K using a relative rate method with three different reference compounds are in excellent agreement. The 298 K preferred value is an average of the three values of Olariu et al. (2000). The assigned uncertainty reflects the fact that all of the data are from a single study.

## Reference

Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Olariu, R. I., Barnes, I., Becker, K. H. and Klotz, B.: Int. J. Chem. Kinet., 32, 696, 2000.

## HOx_AROM8

### HO + 1,2-dihydroxy-3-methylbenzene → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(1.90 \pm 0.07) \times 10^{-10}$ | 300 ± 5 | Olariu et al., 2000 | RR (a,b) |
| $(1.99 \pm 0.06) \times 10^{-10}$ | 300 ± 5 | Olariu et al., 2000 | RR (a,c) |
| $(1.99 \pm 0.07) \times 10^{-10}$ | 300 ± 5 | Olariu et al., 2000 | RR (a,d) |

### Comments

(a) HO radicals were generated by the photolysis of $CH_3ONO$. Experiments were carried out in a 1080 L chamber at 1.013 bar of air. The concentrations of 1,2-dihydroxy-3-methylbenzene and isoprene, 1,3-butadiene or *trans*-2-butene (the reference compounds) were measured by FTIR spectroscopy. Wall losses of 1,2-dihydroxy-3-methylbenzene were measured and taken into account in the data analysis, and these contributed ~30% of the 1,2-dihydroxy-3-methylbenzene loss rate due to HO radical reaction during the experiments. The measured rate coefficient ratios of $k$(HO + 1,2-dihydroxy-3-methylbenzene)/$k$(HO + isoprene) = 1.92 ± 0.07, $k$(HO + 1,2-dihydroxy-3-methylbenzene)/$k$(HO + 1,3-butadiene) = 3.02 ± 0.09 and $k$(HO + 1,2-dihydroxy-3-methylbenzene)/$k$(HO + *trans*-2-butene) = 3.15 ± 0.1 are placed on an absolute basis by use of rate coefficients at 300 K of $k$(HO + isoprene) = $9.91 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019), $k$(HO + 1,3-butadiene) = $6.59 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson and Arey, 2003) and $k$(HO + *trans*-2-butene) = $6.32 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson and Arey, 2003).

(b) Relative to $k$(HO + isoprene).

(c) Relative to $k$(HO + 1,3-butadiene).

(d) Relative to $k$(HO + *trans*-2-butene).

### Preferred Values

| Parameter | Value | $T$/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $2.0 \times 10^{-10}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ±0.15 | 298 |

*Comments on Preferred Values*

The three rate coefficients measured by Olariu et al. (2000) at 300 ± 5 K using a relative rate method with three different reference compounds are in excellent agreement. The 298 K preferred value is an average of the three values of Olariu et al. (2000). The assigned uncertainty reflects the fact that all of the data are from a single study.

## References

Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Olariu, R. I., Barnes, I., Becker, K. H. and Klotz, B.: Int. J. Chem. Kinet., 32, 696, 2000.

## HOx_AROM9

### HO + 1,2-dihydroxy-4-methylbenzene → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(1.60 \pm 0.08) \times 10^{-10}$ | 300 ± 5 | Olariu et al., 2000 | RR (a,b) |
| $(1.52 \pm 0.04) \times 10^{-10}$ | 300 ± 5 | Olariu et al., 2000 | RR (a,c) |
| $(1.50 \pm 0.03) \times 10^{-10}$ | 300 ± 5 | Olariu et al., 2000 | RR (a,d) |

### Comments

(a) HO radicals were generated by the photolysis of $CH_3ONO$. Experiments were carried out in a 1080 L chamber at 1.013 bar of air. The concentrations of 1,2-dihydroxy-4-methylbenzene and isoprene, 1,3-butadiene or *trans*-2-butene (the reference compounds) were measured by FTIR spectroscopy. Wall losses of 1,2-dihydroxy-4-methylbenzene were measured and taken into account in the data analysis, and these contributed ~30% of the 1,2-dihydroxy-4-methylbenzene loss rate due to HO radical reaction during the experiments. The measured rate coefficient ratios of $k$(HO + 1,2-dihydroxy-4-methylbenzene)/$k$(HO + isoprene) = 1.61 ± 0.072, $k$(HO + 1,2-dihydroxy-4-methylbenzene)/$k$(HO + 1,3-butadiene) = 2.31 ± 0.048 and $k$(HO + 1,2-dihydroxy-4-methylbenzene)/$k$(HO + *trans*-2-butene) = 2.37 ± 0.047 are placed on an absolute basis by use of rate coefficients at 300 K of $k$(HO + isoprene) = $9.91 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019), $k$(HO + 1,3-butadiene) = $6.59 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson and Arey, 2003) and $k$(HO + *trans*-2-butene) = $6.32 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson and Arey, 2003).

(b) Relative to $k$(HO + isoprene).

(c) Relative to $k$(HO + 1,3-butadiene).

(d) Relative to $k$(HO + *trans*-2-butene).

### Preferred Values

| Parameter | Value | $T$/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $1.5 \times 10^{-10}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ±0.15 | 298 |

*Comments on Preferred Values*

The three rate coefficients measured by Olariu et al. (2000) at 300 ± 5 K using a relative rate method with three different reference compounds are in excellent agreement. The 298 K preferred value is an average of the three values of Olariu et al. (2000). The assigned uncertainty reflects the fact that all of the data are from a single study.

## References

Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Olariu, R. I., Barnes, I., Becker, K. H. and Klotz, B.: Int. J. Chem. Kinet., 32, 696, 2000.

## HOx_AROM10

### HO + 3-methyl-2-nitrophenol → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(3.39 \pm 0.18) \times 10^{-12}$ | $296 \pm 3$ | Bejan et al., 2007 | RR (a) |

### Comments

(a) HO radicals were generated by the photolysis of $CH_3ONO$. Experiments were carried out in a 1080 L chamber at 1.013 bar of air. The concentrations of 3-methyl-2-nitrophenol and ethene (the reference compound) were measured by FTIR spectroscopy. Wall losses and photolysis of 3-methyl-2-nitrophenol were measured and taken into account in the data analysis, and these contributed ~50-55% of the total measured 3-methyl-2-nitrophenol loss rate during the experiments. The measured rate coefficient ratio of $k$(HO + 3-methyl-2-nitrophenol)/$k$(HO + ethene) = $0.43 \pm 0.02$ is placed on an absolute basis by use of a rate coefficient at 296 K and atmospheric pressure of air of $k$(HO + ethene) = $7.78 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019).

### Preferred Values

| Parameter | Value | $T$/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $3.4 \times 10^{-12}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ±0.30 | 298 |

*Comments on Preferred Values*

The 298 K preferred value is based on the sole reported study of Bejan et al. (2007).

### References

Bejan, I., Barnes, I., Olariu, R., Zhou, S., Wiesen, P. and Benter, Th.: Phys. Chem. Chem. Phys., 9, 5686, 2007.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

## HOx_AROM11

### HO + 4-methyl-2-nitrophenol → products
### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(3.19 \pm 0.18) \times 10^{-12}$ | 296 ± 3 | Bejan et al., 2007 | RR (a,b) |
| $(3.60 \pm 0.54) \times 10^{-12}$ | 296 ± 3 | Bejan et al., 2007 | RR (a,c) |

### Comments

(a) HO radicals were generated by the photolysis of $CH_3ONO$. Experiments were carried out in a 1080 L chamber at 1.013 bar of air. The concentrations of 4-methyl-2-nitrophenol and ethene or *n*-butene (the reference compounds) were measured by FTIR spectroscopy. Wall losses and photolysis of 4-methyl-2-nitrophenol were measured and taken into account in the data analysis, and these contributed ~50-55% of the total measured 4-methyl-2-nitrophenol loss rate during the experiments. The measured rate coefficient ratios of $k$(HO + 4-methyl-2-nitrophenol)/$k$(HO + ethene) = $0.41 \pm 0.02$ and $k$(HO + 4-methyl-2-nitrophenol)/$k$(HO + *n*-butane) = $1.55 \pm 0.23$ are placed on an absolute basis by use of rate coefficients at 296 K and atmospheric pressure of air of $k$(HO + ethene) = $7.78 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019) and $k$(HO + *n*-butane) = $2.32 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019).

(b) Relative to $k$(HO + ethene).

(c) Relative to $k$(HO + *n*-butane).

### Preferred Values

| **Parameter** | **Value** | ***T*/K** |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $3.4 \times 10^{-12}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ±0.15 | 298 |

*Comments on Preferred Values*

The rate coefficients measured by Bejan et al. (2007) at 296 ± 3 K using a relative rate method with two different reference compounds are in good agreement. The 298 K preferred value is an un-weighted average of the two values of Bejan et al. (2007). The assigned uncertainty reflects the fact that all of the data are from a single study and the need to account for significant wall losses and photolysis of the 4-methyl-2-nitrophenol.

## References

IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

Bejan, I., Barnes, I., Olariu, R., Zhou, S., Wiesen, P. and Benter, Th.: Phys. Chem. Chem. Phys., 9, 5686, 2007.

## HOx_AROM12

### HO + 5-methyl-2-nitrophenol → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(5.15 \pm 0.35) \times 10^{-12}$ | 296 ± 3 | Bejan et al., 2007 | RR (a,b) |
| $(7.60 \pm 1.56) \times 10^{-12}$ | 296 ± 3 | Bejan et al., 2007 | RR (a,c) |

### Comments

(a) HO radicals were generated by the photolysis of $CH_3ONO$. Experiments were carried out in a 1080 L chamber at 1.013 bar of air. The concentrations of 5-methyl-2-nitrophenol and ethene or *n*-butene (the reference compounds) were measured by FTIR spectroscopy. Wall losses and photolysis of 5-methyl-2-nitrophenol were measured and taken into account in the data analysis, and these contributed 29-33% of the total measured 5-methyl-2-nitrophenol loss rate during the experiments. The measured rate coefficient ratios of $k$(HO + 5-methyl-2-nitrophenol)/$k$(HO + ethene) = 0.67 ± 0.04 and $k$(HO + 5-methyl-2-nitrophenol)/$k$(HO + *n*-butane) = 3.274 ± 0.67 (the rate coefficient ratio cited in Bejan et al. (2007) is in error (I. Barnes, private communication, 2008)) are placed on an absolute basis by use of rate coefficients at 296 K and atmospheric pressure of air of $k$(HO + ethene) = $7.78 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019) and $k$(HO + *n*-butane) = $2.32 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019).

(b) Relative to $k$(HO + ethene).

(c) Relative to $k$(HO + *n*-butane).

### Preferred Values

| Parameter | Value | *T*/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.4 \times 10^{-12}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ±0.20 | 298 |

*Comments on Preferred Values*

The rate coefficients measured by Bejan et al. (2007) at 296 ± 3 K using a relative rate method with two different reference compounds disagree by ≈30%. The 298 K preferred value is an un-weighted average of the two values of Bejan et al. (2007). The assigned uncertainty reflects the fact that all of the data are from a single study and the need to account for significant wall losses and photolysis of the 5-methyl-2-nitrophenol.

## References

Bejan, I., Barnes, I., Olariu, R., Zhou, S., Wiesen, P. and Benter, Th.: Phys. Chem. Chem. Phys., 9, 5686, 2007.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

## HOx_AROM13

### HO + 6-methyl-2-nitrophenol → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(2.49 \pm 0.18) \times 10^{-12}$ | $296 \pm 3$ | Bejan et al., 2007 | RR (a) |

### Comments

(a) HO radicals were generated by the photolysis of $CH_3ONO$. Experiments were carried out in a 1080 L chamber at 1.013 bar of air. The concentrations of 6-methyl-2-nitrophenol and ethene (the reference compound) were measured by FTIR spectroscopy. Wall losses and photolysis of 6-methyl-2-nitrophenol were measured and taken into account in the data analysis, and these contributed ~50-55% of the total measured 6-methyl-2-nitrophenol loss rate during the experiments. The measured rate coefficient ratio of $k$(HO + 6-methyl-2-nitrophenol)/$k$(HO + ethene) = $0.32 \pm 0.02$ is placed on an absolute basis by use of a rate coefficient at 296 K and atmospheric pressure of air of $k$(HO + ethene) = $7.78 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019).

### Preferred Values

| Parameter | Value | $T$/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $2.5 \times 10^{-12}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | $\pm 0.30$ | 298 |

*Comments on Preferred Values*

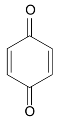
The 298 K preferred value is based on the sole reported study of Bejan et al. (2007).

### References

Bejan, I., Barnes, I., Olariu, R., Zhou, S., Wiesen, P. and Benter, Th.: Phys. Chem. Chem. Phys., 9, 5686, 2007.

IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

## HOx_AROM14

**HO +**  **1,4-Benzoquinone → products**

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(4.66 \pm 0.10) \times 10^{-12}$ | 300 ± 5 | Olariu et al., 2000 | RR (a,b) |
| $(4.55 \pm 0.14) \times 10^{-12}$ | 300 ± 5 | Olariu et al., 2000 | RR (a,c) |
| $(4.61 \pm 0.13) \times 10^{-12}$ | 300 ± 5 | Olariu et al., 2000 | RR (a,d) |

### Comments

(a) HO radicals were generated by the photolysis of $CH_3ONO$. Experiments were carried out in a 1080 L chamber at 1.013 bar of air. The concentrations of 1,4-benzoquinone and isoprene, 1,3-butadiene or *trans*-2-butene (the reference compounds) were measured by FTIR spectroscopy. Wall losses of 1,4-benzoquinone were measured and taken into account in the data analysis, and these contributed ~30% of the 1,4-benzoquinone loss rate due to HO radical reaction during the experiments. The measured rate coefficient ratios of $k$(HO + 1,4-benzoquinone)/$k$(HO + isoprene) = 0.047 ± 0.001, $k$(HO + 1,4-benzoquinone)/$k$(HO + 1,3-butadiene) = 0.069 ± 0.002 and $k$(HO + 1,4-benzoquinone)/$k$(HO + *trans*-2-butene) = 0.073 ± 0.002 are placed on an absolute basis by use of rate coefficients at 300 K of $k$(HO + isoprene) = $9.91 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019), $k$(HO + 1,3-butadiene) = $6.59 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson and Arey, 2003) and $k$(HO + *trans*-2-butene) = $6.32 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson and Arey, 2003).

(b) Relative to $k$(HO + isoprene).

(c) Relative to $k$(HO + 1,3-butadiene).

(d) Relative to $k$(HO + *trans*-2-butene).

### Preferred Values

| Parameter | Value | $T$/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $4.6 \times 10^{-12}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ±0.15 | 298 |

*Comments on Preferred Values*

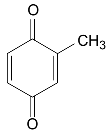
The three rate coefficients measured by Olariu et al. (2000) at 300 ± 5 K using a relative rate method with three different reference compounds are in excellent agreement. The 298 K preferred value is an average of the three values of Olariu et al. (2000). The assigned uncertainty reflects the fact that all of the data are from a single study.

## References

Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Olariu, R. I., Barnes, I., Becker, K. H. and Klotz, B.: Int. J. Chem. Kinet., 32, 696, 2000.

## HOx_AROM15

### HO + methyl-1,4-benzoquinone → products



### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(2.28 \pm 0.10) \times 10^{-11}$ | 300 ± 5 | Olariu et al., 2000 | RR (a,b) |
| $(2.37 \pm 0.07) \times 10^{-11}$ | 300 ± 5 | Olariu et al., 2000 | RR (a,c) |
| $(2.34 \pm 0.07) \times 10^{-11}$ | 300 ± 5 | Olariu et al., 2000 | RR (a,d) |

### Comments

(a) HO radicals were generated by the photolysis of $CH_3ONO$. Experiments were carried out in a 1080 L chamber at 1.013 bar of air. The concentrations of methyl-1,4-benzoquinone and isoprene, 1,3-butadiene or *trans*-2-butene (the reference compounds) were measured by FTIR spectroscopy. Wall losses of methyl-1,4-benzoquinone were measured and taken into account in the data analysis, and these contributed ~30% of the methyl-1,4-benzoquinone loss rate due to HO radical reaction during the experiments. The measured rate coefficient ratios of $k$(HO + methyl-1,4-benzoquinone)/$k$(HO + isoprene) = 0.23 ± 0.01, $k$(HO + methyl-1,4-benzoquinone)/$k$(HO + 1,3-butadiene) = 0.36 ± 0.01 and $k$(HO + methyl-1,4-benzoquinone)/$k$(HO + *trans*-2-butene) = 0.37 ± 0.01 are placed on an absolute basis by use of rate coefficients at 300 K of $k$(HO + isoprene) = $9.91 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019), $k$(HO + 1,3-butadiene) = $6.59 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson and Arey, 2003) and $k$(HO + *trans*-2-butene) = $6.32 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson and Arey, 2003).

(b) Relative to $k$(HO + isoprene).

(c) Relative to $k$(HO + 1,3-butadiene).

(d) Relative to $k$(HO + *trans*-2-butene).

### Preferred Values

| Parameter | Value | *T*/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $2.3 \times 10^{-11}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ±0.15 | 298 |

*Comments on Preferred Values*

The three rate coefficients measured by Olariu et al. (2000) at 300 ± 5 K using a relative rate method with three different reference compounds are in excellent agreement. The 298 K preferred value is an average of the three values of Olariu et al. (2000). The assigned uncertainty reflects the fact that all of the data are from a single study.

## References

Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Olariu, R. I., Barnes, I., Becker, K. H. and Klotz, B.: Int. J. Chem. Kinet., 32, 696, 2000.

## HOx_AROM16

### HO + $C_6H_5NO_2$ (nitrobenzene) → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $6 \times 10^{-13} \exp[-(440 \pm 80)/T]$ | 259-362 | Witte et al., 1986 | FP-RF (a) |
| $(1.37 \pm 0.14) \times 10^{-13}$ | 299 | | |
| *Relative Rate Cofficients* | | | |
| $<6.4 \times 10^{-13}$ | 296 ± 2 | Atkinson et al., 1987 | RR (b) |
| $<8.3 \times 10^{-13}$ | 296 ± 2 | Atkinson et al., 1987 | RR (c) |

### Comments

(a) At 100 Torr (133 mbar) of Ar diluent.

(b) HO radicals generated by the photolysis of $CH_3ONO$ in air at atmospheric pressure in a ~60 L Teflon chamber, with analyses of nitrobenzene and benzene (the reference compound) by GC. The measured rate coefficient ratio $k$(HO + nitrobenzene)/$k$(HO + benzene) <0.53 is placed on an absolute basis using a rate coefficient of $k$(HO + benzene) = $1.2 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 296 K (IUPAC, 2019).

(c) HO radicals generated by the dark reaction of $O_3 + N_2H_4$ in air at atmospheric pressure in a 5870 L reaction chamber. The concentrations of nitrobenzene and dimethyl ether (the reference compound) were monitored by FTIR spectroscopy, and the measured rate coefficient ratio $k$(HO + nitrobenzene)/$k$(HO + dimethyl ether) <0.3 is placed on an absolute basis using a rate coefficient of $k$(HO + dimethyl ether) = $2.76 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 296 K (IUPAC, 2019).

### Preferred Values

| Parameter | Value | $T$/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $1.4 \times 10^{-13}$ | 298 |
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.0 \times 10^{-13} \exp(-440/T)$ | 250-370 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.20 | 298 |
| $\Delta$ E/R | ± 300 | 250-370 |

*Comments on Preferred Values*

The upper limits to the rate coefficients obtained by Atkinson et al. (1987) are consistent with the absolute rate coefficients measured by Witte et al. (1986). The rate expression reported by Witte et al. (1986) is accepted as the preferred value. Since the Witte et al. (1986) study is the sole published study to report rate coefficients for this reaction (rather than upper limits), correspondingly large uncertainties are given. The reaction proceeds mainly by HO radical addition to the aromatic ring (Witte et al., 1986).

## References

Atkinson, R., Tuazon, E. C., Wallington, T. J., Aschmann, S. M., Arey, J., Winer, A. M. and Pitts Jr., J. N.: Environ. Sci. Technol., 21, 64, 1987.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Witte, F., Urbanik, E. and Zetzsch, C.: J. Phys. Chem., 90, 3251, 1986.

## HOx_AROM17

### HO + 3-nitrotoluene → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(1.22 \pm 0.82) \times 10^{-12}$ | 298 ± 2 | Atkinson et al., 1989 | RR (a) |

### Comments

(a) HO radicals generated by the photolysis of $CH_3ONO$ in air at atmospheric pressure in a ~6400 L Teflon chamber, with analyses of 3-nitrotoluene and benzene (the reference compound) by GC. The measured rate coefficient ratio $k$(HO + nitrobenzene)/$k$(HO + benzene) = 1.02 ± 0.68 is placed on an absolute basis using a rate coefficient of $k$(HO + benzene) = $1.2 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (IUPAC, 2019).

### Preferred Values

| Parameter | Value | *T*/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $1.2 \times 10^{-12}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ±0.50 | 298 |

*Comments on Preferred Values*

The preferred 298 K rate coefficient is based on the sole study reported to date.

### References

Atkinson, R., Aschmann, S. M., Arey, J. and Carter, W. P. L.: Int. J. Chem. Kinet., 21, 801, 1989.

IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

## HOx_AROM18

### HO + *cis*-CHOCH=CHCHO → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(5.73 \pm 0.12) \times 10^{-11}$ | 296 ± 2 | Bierbach et al., 1994 | RR-FTIR (a) |

### Comments

(a) HO radicals were generated by the photolysis of $H_2O_2$ in 1000 mbar of air at $\lambda = 254$ nm. Experiments were carried out in a 1080-L quartz-glass chamber, and the concentrations of *cis*-but-2-enedial and propene (the reference compound) were measured in situ by long-path FTIR using an optical path length of 492 m and a spectral resolution of 1 cm$^{-1}$. The measured rate coefficient ratio of $k$(HO + *cis*-but-2-enedial)/$k$(HO + propene) = 1.99 ± 0.04 is placed on an absolute basis using $k$(HO + propene) = $2.88 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019).

### Preferred Values

| Parameter | Value | *T*/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $5.7 \times 10^{-11}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.20 | 298 |

### *Comments on Preferred Value*

The preferred value is based on the sole study of Bierbach et al. (1994) in 1 bar of air. The reaction proceeds both by H-atom abstraction from the -CHO groups and via addition to the double bond. In their mechanistic study of the HO reaction with a mixture of *cis*/*trans*-butenedial isomers, Bierbach et al. (1994) have reported that slightly less than 50% of the reaction proceeds by H-atom abstraction from the aldehyde functional groups of butenedial leading to furan-2,5-dione (maleic anhydride). Glyoxal, expected to be major product of the HO addition, has been also observed as a reaction product but could not be quantified. The formation yield of 3*H*-furan-2-one was reported to be 4%.

### References

Bierbach, A., Barnes, I., Becker, K. H., and Wiesen E.: Environ. Sci. Technol., 28, 715, 1994.

IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

## HOx_AROM19

## HO + *trans*-CHOCH=CHCHO → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $\geq (2.67 \pm 0.87) \times 10^{-11}$ | 296 ± 2 | Bierbach et al., 1994 | RR-FTIR (a) |

### Comments

(a) HO radicals were generated by the photolysis of $H_2O_2$ in 1000 mbar of air at $\lambda = 254$ nm. Experiments were carried out in a 1080-L quartz-glass chamber, and the concentrations of *trans*-but-2-enedial and propene (the reference compound) were measured in situ by long-path FTIR using an optical path length of 492 m and a spectral resolution of 1 cm$^{-1}$. Because of difficulties in the analysis of the data caused by *trans*/*cis* isomerisation, only a lower limit for the rate coefficient ratio could be derived $k$(HO + trans-but-2-enedial)/$k$(HO + propene) $\geq 0.92$. This ratio is placed on an absolute basis using $k$(HO + propene) = $2.88 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019).

### Preferred Value

| Parameter | Value | $T$/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $\geq 2 \times 10^{-11}$ | 298 |

*Comments on Preferred Value*

The preferred value is based on the lower limit derived from the study of Bierbach et al. (1994) in 1 bar of air.

The reaction proceeds both by H-atom abstraction from the -CHO groups and via addition to the double bond. In their mechanistic study of the OH reaction with a mixture of *cis*/*trans*-butenedial isomers, Bierbach et al. (1994) have reported that slightly less than 50% of the reaction proceeds by H-atom abstraction from the aldehyde functional groups of butenedial leading to furan-2,5-dione (maleic anhydride). Glyoxal, expected to be major product of the OH addition, has been also observed as a reaction product but could not be quantified. The formation yield of 3*H*-furan-2-one was reported to be 4%.

### References

Bierbach, A., Barnes, I., Becker, K. H., and Wiesen, E.: Environ. Sci. Technol., 28, 715, 1994.

IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

## HOx_AROM20

## HO + 3*H*-furan-2-one → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(4.83 \pm 0.29) \times 10^{-11}$ | 296 ± 2 | Bierbach et al., 1994 | RR-FTIR (a) |

### Comments

(a) HO radicals were generated by the photolysis of $H_2O_2$ in 1000 mbar of air at $\lambda = 254$ nm. Experiments were carried out in a 1080-L quartz-glass chamber, and the concentrations of 3H-furan-2-one and propene (the reference compound) were measured in situ by long-path FTIR using an optical path length of 492 m and a spectral resolution of 1 cm$^{-1}$. The measured rate coefficient ratio of $k$(HO + 3H-furan-2-one)/$k$(HO + propene) = 1.68 ± 0.10 is placed on an absolute basis using $k$(HO + propene) = $2.88 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson et al., 2006).

### Preferred Value

| Parameter | Value | *T*/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $4.8 \times 10^{-11}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.2 | 298 |

*Comments on Preferred Value*

The preferred value is based on the sole study of Bierbach et al. (1994) in 1 bar of air but with higher uncertainty.

### References

Bierbach, A., Barnes, I., Becker, K. H., and Wiesen, E.: Environ. Sci. Technol., 28, 715, 1994.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

## HOx_AROM21

## HO + Furan-2,5-dione → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(1.36 \pm 0.07) \times 10^{-12}$ | 296 ± 2 | Bierbach et al., 1994 | RR-FTIR (a) |

### Comments

(a) HO radicals were generated by the photolysis of $H_2O_2$ in 1000 mbar of air at $\lambda = 254$ nm. Experiments were carried out in a 1080-L quartz-glass chamber, and the concentrations of furan-2,5-dione and n-butane (the reference compound) were measured in situ by long-path FTIR using an optical path length of 492 m and a spectral resolution of 1 cm$^{-1}$. The measured rate coefficient ratio of $k$(HO + furan-2,5-dione)/$k$(HO + n-butane) = 0.58 ± 0.03 is placed on an absolute basis using $k$(HO + butane) = $2.35 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019).

### Preferred Value

| Parameter | Value | *T*/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $1.4 \times 10^{-12}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.20 | 298 |

*Comments on Preferred Value*

The preferred value is based on the sole study of Bierbach et al. (1994) in 1 bar of air.

Bierbach et al. (1994) conducted a product analysis of the HO-initiated oxidation of furan-2,5-dione (maleic anhydride) using either photolysis of $H_2O_2$ or $CH_3ONO$/NO/air as the HO source. CO (20% yield) and HCOOH (3% yield) were observed as reaction products using both sources. Acetylene (5%) was observed only with $H_2O_2$ as the HO source. $CO_2$ was reported a major reaction products but could not be quantified. The product IR spectra showed two carbonyl absorptions in the region 1820-1720 cm$^{-1}$ but the identity of the compounds could not be determined. Bierbach et al. (1994) did not find evidence for the formation of PAN or other peroxynitrate type compounds.

### References

Bierbach, A., Barnes, I., Becker, K. H., and Wiesen, E.: Environ. Sci. Technol., 28, 715, 1994.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

## HOx_AROM22

### HO + $CH_3C(O)CH=CHCHO$ (*cis*/*trans*-4-oxopent-2-enal) → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(6.18 \pm 0.23) \times 10^{-11}$ | 296 ± 2 | Bierbach et al., 1994 | RR-FTIR (a) |

### Comments

(a) HO radicals were generated by the photolysis of $H_2O_2$ in 1000 mbar of air at $\lambda = 254$ nm. Experiments were carried out in a 1080-L quartz-glass chamber, and the concentrations of cis/trans-4-oxopent-2-enal and propene (the reference compound) were measured in situ by long-path FTIR using an optical path length of 492 m and a spectral resolution of 1 cm$^{-1}$. The measured rate coefficient ratio of $k$(HO + 4-oxopent-2-enal)/$k$(HO + propene) = $2.13 \pm 0.08$ is placed on an absolute basis using $k$(HO + propene) = $2.9 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019).

### Preferred Value

| Parameter | Value | *T*/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.2 \times 10^{-11}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.20 | 298 |

*Comments on Preferred Value*

The preferred value is based on the sole study of Bierbach et al. (1994) in 1 bar of air.

The reaction proceeds both by H-atom abstraction from the -CHO group and via addition to the double bond. Bierbach et al. (1994) reported that the HO reaction with a mixture of *cis*/*trans*-oxopent-2-enal isomers leading to formation of furan-2,5-dione (maleic anhydride) in a 40% yield which was taken as an indication that the abstraction channel plays an important role. Bierbach et al. (1994) also observed, but were not able to quantify, the formation of glyoxal and methylglyoxal which are expected to be major products following HO addition to the >C=C< double bond. The formation yield of 5-methyl-3*H*-furanone was reported to be 1%.

### References

Bierbach, A., Barnes, I., Becker, K. H., and Wiesen, E.: Environ. Sci. Technol., 28, 715, 1994.

IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

## HOx_AROM25

### HO + $C_6H_5CHO$ (benzaldehyde) → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Cofficients* | | | |
| $(1.26 \pm 0.08) \times 10^{-11}$ | 298 ± 2 | Niki et al., 1978 | RR (a, f) |
| $(1.1 \pm 0.2) \times 10^{-11}$ | 298 ± 4 | Kerr and Sheppard, 1981 | RR (b, f) |
| $5.7 \times 10^{-12} \exp[(225\pm57)/T)]$ | 294-343 | Semadeni et al., 1995 | RR (c, g) |
| $(1.22 \pm 0.07) \times 10^{-11}$ | 299 | | |
| $(1.20 \pm 0.14) \times 10^{-11}$ | 298 ± 2 | Thiault et al., 2002 | RR (d, g) |
| $(1.12 \pm 0.16) \times 10^{-11}$ | 298 ± 2 | Thiault et al., 2002 | RR (d, h) |
| $(1.15 \pm 0.13) \times 10^{-11}$ | 298 ± 2 | Thiault et al., 2002 | RR (d, i) |
| $(1.30 \pm 0.07) \times 10^{-11}$ | 295 ± 2 | Clifford et al., 2005 | RR (e, g) |
| $(1.31 \pm 0.12) \times 10^{-11}$ | 295 ± 2 | Clifford et al., 2005 | RR (e, j) |
| $(1.36 \pm 0.04) \times 10^{-11}$ | 295 ± 2 | Clifford et al., 2005 | RR (e, k) |
| $(1.46 \pm 0.20) \times 10^{-11}$ | 295 ± 2 | Clifford et al., 2005 | RR (e, l) |
| $(1.44 \pm 0.07) \times 10^{-11}$ | 295 ± 2 | Clifford et al., 2005 | RR (e, m) |

## Comments

(a) HO radicals were generated by the photolysis of HONO in air at atmospheric pressure in a 70 L Pyrex chamber. The concentrations of benzaldehyde and ethene (the reference compound) were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of $k$(HO + benzaldehyde)/$k$(HO + ethene) = 1.6 ± 0.1 is placed on an absolute basis using $k$(HO + ethene) = $7.9 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K and atmospheric pressure (IUPAC, 2019).

(b) HO radicals were generated by the photolysis of HONO at $\lambda$ = 300-450 nm in air at atmospheric pressure in a 220 L Tedlar chamber. The concentrations of benzaldehyde and ethene (the reference compound) were measured by GC-FID. The measured rate coefficient ratio of $k$(HO + benzaldehyde)/$k$(HO + ethene) = 1.39 ± 0.27 is placed on an absolute basis using $k$(HO + ethene) = $7.9 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K and atmospheric pressure (IUPAC, 2019).

(c) HO radicals were generated by the photolysis of $CH_3ONO$ in air at atmospheric pressure in a ~200 L Tedlar chamber. Benzaldehyde and diethyl ether (the reference compound) were monitored by GC, and the measured rate coefficient ratio $k$(HO + benzaldehyde)/$k$(HO + diethyl ether) = $0.721 \exp[(89.5 \pm 84.7)/T]$ over the temperature range 294-343 K is placed on an absolute basis using a rate coefficient of $k$(HO + diethyl ether) = $1.15 \times 10^{-17}\ T^2 \exp(743/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Calvert et al., 2009).

(d) HO radicals were generated by the photolysis of HONO at $\lambda$ = 300-460 nm in air at atmospheric pressure in a 200 L Teflon chamber. The concentrations of benzaldehyde, di-isopropyl ether, diethyl ether and 1,3-dioxolane (the reference compounds) were measured by GC-FID. The measured rate coefficient ratios of $k$(HO + benzaldehyde)/$k$(HO + di-isopropyl ether) = 1.12 ± 0.04, $k$(HO + benzaldehyde)/$k$(HO + diethyl ether) = 0.97 ± 0.02 and $k$(HO + benzaldehyde)/$k$(HO + 1,3-dioxolane) = 1.15 ± 0.02 are placed on an absolute basis by using $k$(HO + di-isopropyl ether) = $1.0 \times 10^{-11}$, $k$(HO + diethyl ether) = $1.24 \times 10^{-11}$ and $k$(HO + 1,3-dioxolane) = $1.0 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K and atmospheric pressure (Calvert et al., 2009).

(e) HO radicals generated by the photolysis of $CH_3ONO$ in air at atmospheric pressure in two different FEP Teflon chambers (350 L and 3910 L). The concentrations of benzaldehyde, di-n-butyl ether, tetrahydrofuran, 1,2,4-trimethylbenzene, diethyl ether and n-hexane (the reference compounds) were measured by GC-FID during the experiments. The measured rate coefficient ratios of $k$(HO + benzaldehyde)/$k$(HO + di-n-butyl ether) = 0.45 ± 0.04, $k$(HO + benzaldehyde)/$k$(HO + tetrahydrofuran) = 0.80 ± 0.02, $k$(HO + benzaldehyde)/$k$(HO + 1,2,4-trimethylbenzene) = 0.45 ± 0.06, $k$(HO + benzaldehyde)/$k$(HO + diethyl ether) = 1.05 ± 0.06 and $k$(HO + benzaldehyde)/$k$(HO + *n*-hexane) = 2.63 ± 0.12 are placed on an absolute basis using $k$(HO + di-n-butyl ether) = $2.9 \times 10^{-11}$, $k$(HO + tetrahydrofuran) = $1.7 \times 10^{-11}$, $k$(HO + diethyl ether) = $1.24 \times 10^{-11}$ (Calvert et al., 2009), $k$(HO + *n*-hexane) = $5.48 \times 10^{-12}$ (Calvert et al., 2008) and $k$(HO + 1,2,4-trimethylbenzene) = $3.25 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Calvert et al., 2002) at 298 K and atmospheric pressure and 295 K.

(f) Relative to HO + ethene

(g) Relative to HO + diethyl ether

(h) Relative to HO + di-isopropyl ether

(i) Relative to HO + 1,3-dioxolane

(j) Relative to HO + di-n-butyl ether

(k) Relative to HO + tetrahydrofuran

(l) Relative to 1,2,4-trimethylbenzene

(m) Relative to *n*-hexane

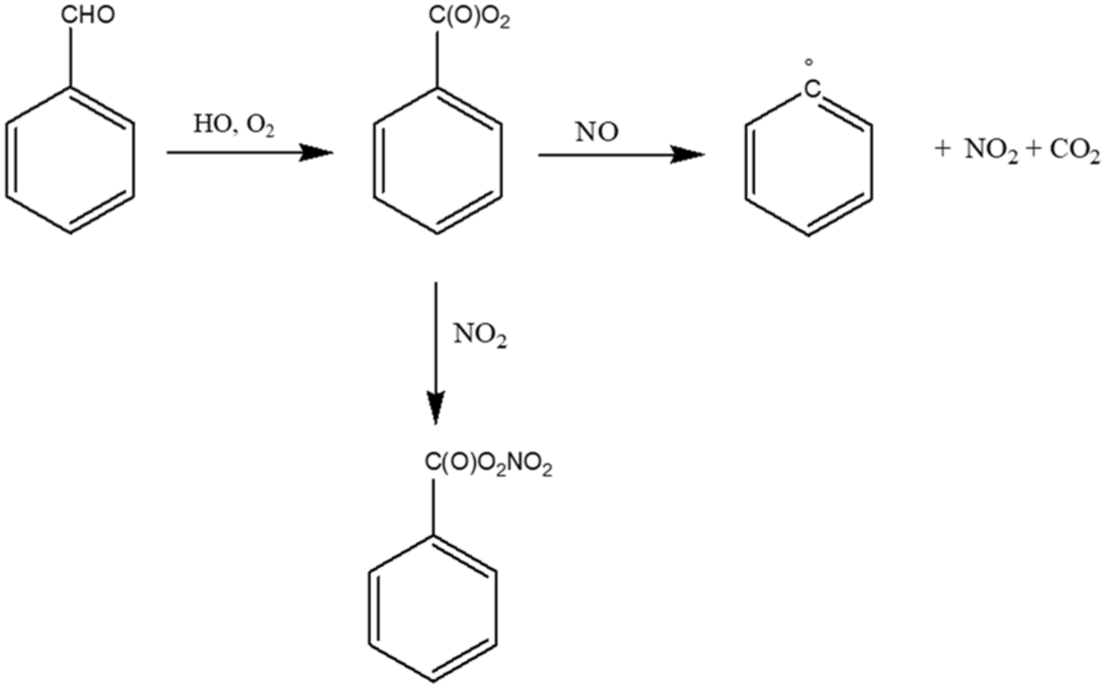
## Preferred Values

| Parameter | Value | *T*/K |
|---|---|---|
| $k$/ molecule$^{-1}$ s$^{-1}$ | $1.26 \times 10^{-11}$ | 298 |
| $k$/ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $5.9 \times 10^{-12} \exp(225/T)$ | 290-350 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.08 | 298 |
| $\Delta E/R$ | ± 170 | |

*Comments on Preferred Values*

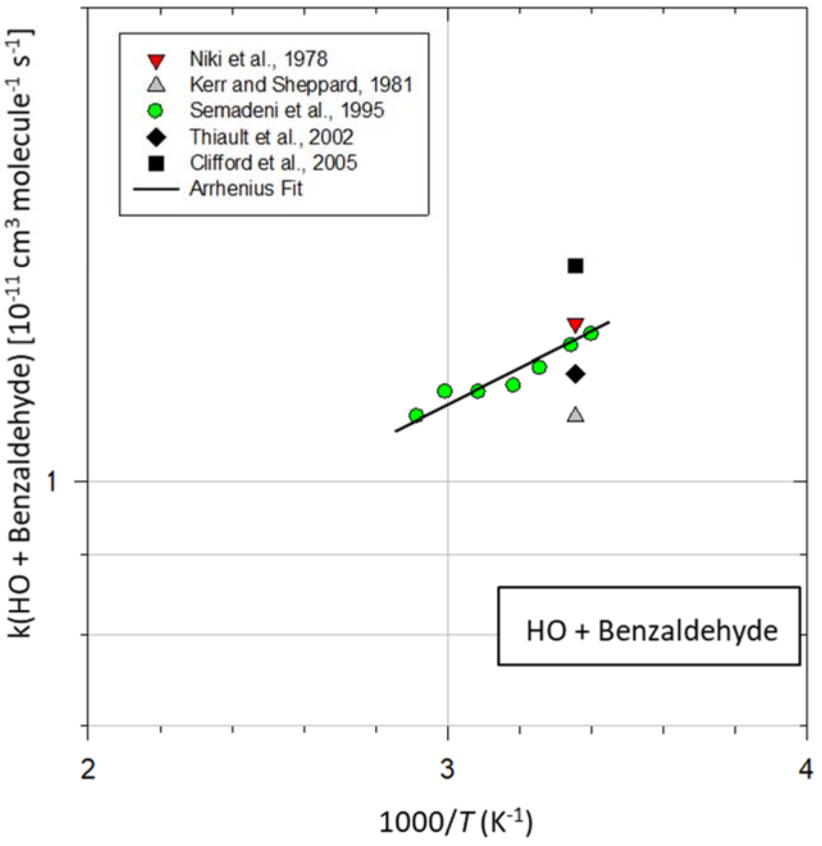
The rate coefficient values reported near 298 K by different authors are in agreement within the experimental uncertainties. The preferred value at 298 K is an average of these determinations. Semadeni et al. (1995) measured the temperature dependence using a relative method in the temperature range 289-373 K but used only the data in the range 294-343 K to derive their Arrhenius expression. The preferred temperature dependence values are obtained by combining the preferred $k$(298) value with the sole temperature dependence of Semadeni et al. in the restricted temperature range 294-343K.

Reaction of HO with benzaldehyde proceeds mainly by abstraction of the aldehydic H-atom to form benzoyl radical which adds $O_2$ to form benzoyl peroxy radical. In presence of NOx, benzoyl peroxy radical reacts with NO or $NO_2$:



## References

Calvert, J. G., Atkinson, R., Becker, K. H., Kamens, R. M., Seinfeld, J. H., Wallington, T. J., and Yarwood, G.: The Mechanisms of Atmospheric Oxidation of Aromatic Hydrocarbons, Oxford University Press, New York, NY, 2002.
Calvert, J. G., Derwent, R. G., Orlando, J. J., Tyndall, G. S., and Wallington T. J.: Mechanisms of Atmospheric Oxidation of the Alkanes, Oxford University Press, New York, NY, 2008.
Calvert, J. G., Mellouki, A., Orlando, J. J., Pilling, M., and Wallington T. J.: The Mechanisms of Atmospheric Oxidation of the Oxygenates, Oxford University Press, New York, NY, to appear, 2010.
Clifford, G. M., Thüner, L. P., Wenger, J. C., and Shallcross, D. E.: J. Photochem. Photobio. A: Chem., 176, 172, 2005.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Kerr, J. A., and Sheppard D. W.: Environ. Sci. Technol., 15, 960, 1981.
Niki, H., Maker, P. D., Savage, C. M., and Breitenbach, L. P.: J. Phys. Chem., 82, 132, 1978.
Semadeni, M., Stocker, D. W. and Kerr, J. A.: Int. J. Chem. Kinet., 27, 287, 1995.
Thiault, G., Mellouki, A., and Le Bras, G.: Phys. Chem. Chem. Phys., 4, 2194, 2002.



Rate coefficients for HO + Benzaldehyde.

# HOx_AROM26

## HO + $C_6H_5CH_2OH$ (benzyl alcohol) → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(2.75 \pm 0.66) \times 10^{-11}$ | 297 ± 3 | Harrison and Wells, 2009 | RR-GC (a, b) |
| $(2.61 \pm 0.58) \times 10^{-11}$ | 297 ± 3 | Harrison and Wells, 2009 | RR-GC (a, c) |
| $(2.7 \pm 0.7) \times 10^{-11}$ | 298 ± 2 | Bernard et al., 2013 | RR-FTIR (e, f) |
| $(2.7 \pm 0.8) \times 10^{-11}$ | 298 ± 2 | Bernard et al., 2013 | RR-FTIR (e, g) |
| $(2.9 \pm 0.4) \times 10^{-11}$ | 296 | Bernard et al., 2013 | RR-FTIR (h) |

## Comments

(a) HO radicals were generated by the photolysis of $CH_3ONO$-NO-air mixtures in 1 atmosphere of air at $\lambda > 300$ nm. Experiments were carried out in a ~50-80 liter Teflon chamber, and the concentrations of benzyl alcohol, n-decane and hexanal (the reference compounds) were measured during the experiments by gas chromatography. The measured rate coefficient ratios of $k$(HO + benzyl alcohol)/$k$(HO + n-decane) = 2.5 ± 0.6 and $k$(HO + benzyl alcohol)/$k$(HO + hexanal) = 0.9 ± 0.2 are placed on an absolute basis using $k$(HO + n-decane) = $1.1 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and $k$(HO + hexanal) = $2.9 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Calvert et al., 2008).

(b) Relative to HO + n-decane

(c) Relative to HO + hexanal

(e) HO radicals were generated by the photolysis of $CH_3ONO$-NO-air mixtures in 1013 mbar of air at $\lambda > 300$ nm (centered at 365 nm). Experiments were carried out in a ~7300 liter Teflon chamber, and the concentrations of benzyl alcohol, di-n-butyl ether and propene (the reference compounds) were measured during the experiments by FTIR. The measured rate coefficient ratios of $k$(HO + benzyl alcohol)/$k$(HO + di-n-butyl ether) = 0.96 ± 0.12 and $k$(HO + benzyl alcohol)/$k$(HO + propene) = 0.93 ± 0.06 are placed on an absolute basis using $k$(HO + di-n-butyl ether) = $2.8 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Calvert et al., 2011) and $k$(HO + propene) = $2.9 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019).

(f) Relative to HO + di-n-butyl ether

(g) Relative to HO + propene

(h) HO radicals were generated by the photolysis of $CH_3ONO$-NO-air mixtures in 933 mbar of air at $\lambda > 300$ nm. Experiments were carried out in a ~140 liter Pyrex chamber, and the concentrations of benzyl alcohol and ethene (the reference compound) were measured during the experiments by FTIR. The measured rate coefficient ratio of $k$(HO + benzyl alcohol)/$k$(HO + ethene) = 3.65 ± 0.18 are placed on an absolute basis using $k$(HO + ethene) = $7.9 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019).

## Preferred Values

| Parameter | Value | *T*/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $2.7 \times 10^{-11}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.08 | 298 |

*Comments on Preferred Values*

The results from Harrison and Wells (2009) and from Bernard et al. (2013) are in excellent agreement. The preferred value is an average of these two studies. The preferred value is in good agreement with the unpublished absolute measurement of Nolting et al., $k = (2.29\pm0.25) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K, cited in Atkinson (1989). Hippler et al. (1991) reported $k = 8.3 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at high temperature (1180-1450 K). This value was derived from a fit to the experimental profiles of stable products in shock-heated benzyl iodide/$HNO_3$/Ar mixtures.

The reaction proceeds both by H-atom abstraction from the $-CH_2OH$ group and via addition to the aromatic ring. H-atom abstraction from te $-CH_2OH$ group leads to the formation of benzaldehyde. In their mechanistic study, Harrison and Wells (2009) and Bernard et al. (2013) reported formation yied of ≈ 25% for benzaldehyde which reflects H-atom abstraction from $-CH_2OH$ group. According to these authors, the addition of HO radicals accounts to the aromatic ring accounts for ≈ 75% of the total reaction and leads to numereous species such as polyoxygenated aromatics (o-hydroxybenzyl alcohol, o-dihydroxybenzene, …), formaldehyde, glyoxal and 4-oxo-pentenal as products of the reaction. Bernard et al. (2013) have reported formation yields of (22±2)% for o-hydroxybenzyl alcohol and (10±3)% for o-dihydroxybenzene.

## References

Atkinson, R.: J. Phys. Chem. Ref. Data; Monograph 1, 246 pp., 1989.
Bernard, F., Magneron, I., Eyglunent, G., Daële, D., Wallington, T. J., Hurley, M. D., and Mellouki A.: Environ. Sci. Technol., 47, 3182, 2013.
Calvert, J. G., Derwent, R. G., Orlando, J. J., Tyndall, G. S., and Wallington, T. J.: Mechanisms of Atmospheric Oxidation of Alkanes, Oxford University Press, New York, NY, 2008.
Calvert, J. G., Mellouki, A., Orlando, J. J., Pilling, M., and Wallington T. J.: The Mechanisms of Atmospheric Oxidation of the Oxygenates, Oxford University Press, New York, NY, 2011.
Harrison, J. C., and Wells, J. R.: Atmos. Environ., 43, 798, 2009.
Hippler, H., Reihs, C., and Troe, J.: Symp. Int. Combust. Proc., 23, 37, 1991.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

## NO3_VOC26

### $NO_3$ + 2-methylpropane, $(CH_3)_3CH$ → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $(1.1 \pm 0.2) \times 10^{-16}$ | 298 | Bagley et al., 1990 | DF-A (a) |
| $(4.5 \pm 1.6) \times 10^{-16}$ | 348 | | |
| $(8.0 \pm 0.8) \times 10^{-16}$ | 373 | | |
| $(2.3 \pm 0.4) \times 10^{-15}$ | 423 | | |
| $(5.4 \pm 1.2) \times 10^{-15}$ | 473 | | |
| $(1.30 \pm 0.24) \times 10^{-14}$ | 523 | | |
| $\leq(6 \pm 1) \times 10^{-16}$ | 298 | Boyd et al., 1991 | SF-A (b) |
| *Relative Rate Coefficients* | | | |
| $(9.8 \pm 2.1) \times 10^{-17}$ | 296 ± 1 | Atkinson et al., 1984 | RR-GC (c) |
| $(1.18 \pm 0.25) \times 10^{-16}$ | 298 ± 2 | Barnes et al., 1990 | RR-GC (d) |

### Comments

(a) $NO_3$ radicals were generated by the reaction of F and $HNO_3$ in a discharge-flow system and monitored by optical absorption at 662 nm. The majority of experiments were conducted at a total pressure of 2.7 mbar (2 Torr).

(b) Stopped-flow technique with optical absorption of $NO_3$ radicals at 662 nm. Secondary reactions were expected to be significant, with a stoichiometry factor of ≥2. The cited upper limit to the rate coefficient includes a stoichiometry factor of 2.0.

(c) $NO_3$ radicals were produced by the thermal decomposition of $N_2O_5$, and the concentrations of 2-methylpropane and 2,3-dimethylbutane (the reference organic) were measured by GC at 987 mbar (740 Torr). A rate coefficient ratio of $k(NO_3 + \text{2-methylpropane})/k(NO_3 + \text{2,3-dimethylbutane}) = 0.24 \pm 0.05$ was obtained and is placed on an absolute basis using $k(NO_3 + \text{2,3-dimethylbutane}) = 4.08 \times 10^{-16}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 296 K (Atkinson, 1991).

(d) $NO_3$ radicals were produced by the thermal decomposition of $N_2O_5$, and the concentrations of 2-methylpropane and ethene were measured by GC at 1 bar total pressure. A rate coefficient ratio of $k(NO_3 + \text{ethene})/k(NO_3 + \text{2-methylpropane}) = 1.78 \pm 0.37$ was obtained and is placed on an absolute basis using $k(NO_3 + \text{ethene}) = 2.1 \times 10^{-16}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (IUPAC, 2019).

### Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $1.1 \times 10^{-16}$ | 298 |
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $3.0 \times 10^{-12} \exp(-3050/T)$ | 290-430 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.10 | 298 |
| $\Delta E/R$ | ± 300 | 290-430 |

*Comments on Preferred Values*

The preferred values are based on the absolute rate coefficients measured by Bagley et al. (1990) over the temperature range 298-423 K (at temperatures above 423 K the Arrhenius plot exhibits upward curvature). A least-squares analysis of the 298-423 K rate coefficients of Bagley et al. (1990) results in the preferred Arrhenius expression. The preferred room temperature rate coefficient is in excellent agreement with the relative rate coefficients of Atkinson et al. (1984) and Barnes et al. (1990). At room temperature and below the reaction proceeds almost totally by H-atom abstraction from the tertiary CH group (Bagley et al., 1990; Atkinson, 1991).

## References

Atkinson, R.: J. Phys. Chem. Ref. Data, 20, 459, 1991.

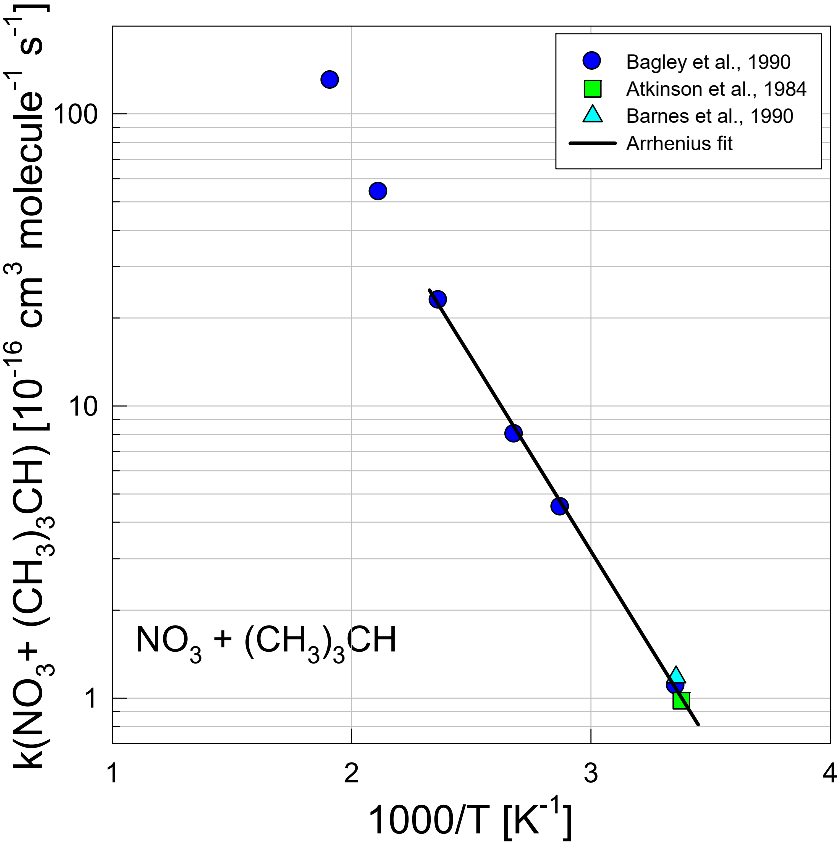
Atkinson, R., Plum, C. N., Carter, W. P. L., Winer, A. M., and Pitts Jr., J. N.: J. Phys. Chem., 88, 2361, 1984.

Bagley, J. A., Canosa-Mas, C., Little, M. R., Parr, A. D., Smith, S. J., Waygood, S. J., and Wayne, R. P.: J. Chem. Soc. Faraday Trans., 86, 2109, 1990.

Boyd, A. A., Canosa-Mas, C. E., King, A. D., Wayne, R. P., and Wilson, M. R.: J. Chem. Soc. Faraday Trans., 87, 2913, 1991.

Barnes, I., Bastian, V., Becker, K. H., and Tong, Z.: J. Phys. Chem., 94, 2413, 1990.

IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation, (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.) http://iupac.pole-ether.fr/index.html., 2019.



Rate coefficients for $NO_3$ + 2-methylpropane.

## Datasheet NO3_VOC27

### $NO_3$ + 2-Methylpropene ($(CH_3)_2C=CH_2$)$\rightarrow$ products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $(3.38 \pm 0.43) \times 10^{-13}$ | 298 | Ravishankara and Mauldin, 1985 | F-A (a) |
| $(3.4 \pm 0.7) \times 10^{-13}$ | 295 ± 2 | Canosa-Mas et al., 1988 | DF-A (b) |
| $(3.3 \pm 0.5) \times 10^{-13}$ | 298 | Rahman et al., 1988 | DF-MS (c) |
| $(3.87 \pm 0.42) \times 10^{-13}$ | 298 | Benter et al., 1992 | DF-MS (d) |
| $(3.6 \pm 0.4) \times 10^{-13}$ | 298 | Wille et al., 1992 | DF-MS (e) |
| *Relative Rate Coefficients* | | | |
| $(1.81 \pm 0.17) \times 10^{-13}$ | 300 | Japar and Niki, 1975 | RR-FTIR (f) |
| $(3.15 \pm 0.02) \times 10^{-13}$ | 298 ± 1 | Atkinson et al., 1984 | RR-GC (e) |
| $(3.35 \pm 0.51) \times 10^{-13}$ | 298 ± 2 | Barnes et al., 1990 | RR-GC (e) |

## Comments

(a) $NO_3$ radicals were generated by the thermal decomposition of $N_2O_5$, and monitored by diode laser absorption at 662 nm.

(b) $NO_3$ radicals were generated from reaction of F atoms (made in a microwave discharge through $F_2$/He) with $HNO_3$ in a flow system with uncoated Pyrex reactor in He gas at 2.7-6.7 mbar (2-5 Torr) and measured by optical absorption at 662 ± 2 nm. Rate coefficients derived from a second-order kinetic treatment of the experimental data with a 1:1 ($NO_3$:2-methylpropene) stoichiometry.

(c) $NO_3$ radicals were generated from reaction of F atoms (made in a microwave discharge through $F_2$/He) with $HNO_3$ in a flow system in He gas. The experiments were conducted in excess of $NO_3$ over 2-Methylpropene which was measured by MS.

(d) $NO_3$ radicals were generated from reaction of F atoms (made in a microwave discharge through $F_2$/He) with $HNO_3$ in a flow system in He gas at 2.38 mbar. The experiments were conducted in excess of $NO_3$ over 2-Methylpropene which was measured by MS.

(e) $NO_3$ radicals were generated from reaction of F atoms (made in a microwave discharge through $F_2$/He) with $HNO_3$ in a flow system in He gas at 3 mbar. The experiments were conducted in excess of 2-Methylpropene over $NO_3$ and the rate constant value determined from the oxirane product which was measured by MS.

(f) $NO_3$ radicals were generated from the thermal decomposition of $N_2O_5$. The experiments were conducted in 1000 mbar (750 Torr) (200 mbar (150 Torr) of $O_2$ + 800 mbar (600 Torr) of Ar) at 300 K. The experimental data were relative to the equilibrium coefficient $K$ for the $NO_3 + NO_2 \leftrightarrow N_2O_5$ reactions, and are placed on an absolute basis by use of $K = 2.15 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ at 300 K.

(g) $NO_3$ radicals were generated from the thermal decomposition of $N_2O_5$. The concentrations of 2-methylpropene and *trans*-2-butene (the reference compound) were measured by GC, and rate coefficient ratios of $k(NO_3$ + 2-methylpropene$)/k(NO_3$ + *trans*-2-butene$) = 0.808 \pm 0.005$ (Atkinson et al., 1984) and $0.86 \pm 0.13$ (Barnes et al., 1990) obtained. These rate coefficient ratios are placed on an absolute basis using $k(NO_3$ + *trans*-2-butene$) = 3.87 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (IUPAC, 2019).

## Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $3.4 \times 10^{-13}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | $\pm 0.10$ | 298 |

*Comments on Preferred Values*

Rate coefficients are only available at room temperature, and the absolute and relative rate coefficients of Atkinson et al. (1984), Ravishankara and Mauldin (1985), Canosa-Mas et al. (1988), Rahmann et al., (1988), Barnes et al. (1990), Benter et al. (1992) and Wille et al. (1992) are in excellent agreement. The rate coefficient of Japar and Niki (1975) relative to the equilibrium constant for the $N_2O_5 \leftrightarrow NO_3 + NO_2$ reactions, which is subject to significant uncertainties, is a factor of ~2 lower than the other rate coefficients and is not used in the evaluation of the rate coefficient $k$. The preferred value is obtained from an average of the rate coefficients of Atkinson et al. (1984), Ravishankara and Mauldin (1985), Canosa-Mas et al. (1988), Rahmann et al., (1988), Barnes et al. (1990), Benter et al. (1992) and Wille et al. (1992). The $NO_3$ radical reaction with 2-methylpropene proceeds by initial addition,

$NO_3 + (CH_3)_2C{=}CH_2 \rightarrow (CH_3)_2C^{\bullet}CH_2ONO_2^{*}$ or $(CH_3)_2C(ONO_2)C^{\bullet}H_2^{*}$

with the chemically-activated nitrooxyalkyl radicals decomposing to oxirane + $NO_2$ in competition with collisional stabilization; for example

$(CH_3)_2C^{\bullet}CH_2ONO_2^{*} \rightarrow$ 1,2-epoxy-2-methylpropane + $NO_2$
$(CH_3)_2C^{\bullet}CH_2ONO_2^{*} + M \rightarrow (CH_3)_2C^{\bullet}CH_2ONO_2 + M$

Under atmospheric conditions the thermalized nitrooxybutyl radicals react with $O_2$ to form the corresponding peroxy radicals $(CH_3)_2C(OO^{\bullet})CH_2ONO_2$ and $(CH_3)_2C(ONO_2)CH_2OO^{\bullet}$. At atmospheric pressure of air, the observed products and their formation yields are: HCHO, 80% (Barnes et al., 1990) and 24 ± 8% (Hjorth et al., 1990); acetone, 85% (Barnes et al., 1990), 24 ± 8% (Hjorth et al., 1990), and 88% (Berndt and Böge, 1995); $(CH_3)_2CHCHO$, ~5% (Berndt and Böge, 1995); 1,2-epoxy-2-methylpropane, 7% (Berndt and Böge, 1995); and total nitrates, ~25% (Barnes et al., 1990). Some of the differences in reported yields are likely due to the experimental conditions and procedures used, with Barnes et al. (1990) and Berndt and Böge (1995) adding NO after the reaction to promote thermal decomposition of peroxynitrates and concurrently convert peroxy radicals to alkoxy radicals.

## References

Atkinson, R., Plum, C. N., Carter, W. P. L., Winer, A. M., and Pitts Jr., J. N.: J. Phys. Chem., 88, 1210, 1984.
Barnes, I., Bastian, V., Becker, K. H., and Tong, Z.: J. Phys. Chem., 94, 2413, 1990.
Benter, Th., Becker, E., Wille, U., Rahman, M. M., and Schindler, R. N.: Ber. Bunsenges. Phys. Chem., 96, 769, 1992.
Berndt, T., and Böge, O.: J. Atmos. Chem., 21, 275, 1995.

Canosa-Mas, C., Smith, S. J., Toby, S., and Wayne, R. P.: J. Chem. Soc. Faraday Trans. 2, 84, 247, 1988.
Hjorth, J., Lohse, C., Nielsen, C. J., Skov, H., and Restelli, G.: J. Phys. Chem., 94, 7494, 1990.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Japar, S. M., and Niki, H.: J. Phys. Chem., 79, 1629, 1975.
Rahman, M. M., Becker, E., Benter, Th., and Schindler, R. N.: Ber. Bunsenges. Phys. Chem., 92, 91, 1988.
Ravishankara, A. R., and Mauldin III, R. L.: J. Phys. Chem., 89, 3144, 1985.
Wille, U., Rahman, M. M., and Schindler, R. N.: Ber. Bunsenges. Phys. Chem., 96, 833, 1992.

## Datasheet NO3_VOC28

## $NO_3$ + 1-Butene → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $2.5 \times 10^{-13} \exp[-(940 \pm 97)/T]$ | 299-473 | Canosa-Mas et al., 1992 | DF-A (a) |
| $(1.1 \pm 0.2) \times 10^{-14}$ | 299 | | |
| $5.2 \times 10^{-13} \exp[-(1067 \pm 31)/T]$ | 232-401 | Rudich et al., 1996 | F-A (b) |
| $(1.4 \pm 0.10) \times 10^{-14}$ | 298 | | |
| $(1.04 \pm 0.11) \times 10^{-14}$ | 298 ± 2 | Berndt et al., 1998 | F-LIF (b) |
| *Relative Rate Coefficients* | | | |
| $(1.29 \pm 0.14) \times 10^{-14}$ | 300 | Japar and Niki, 1975 | RR (c) |
| $(1.24 \pm 0.02) \times 10^{-14}$ | 298 ± 1 | Atkinson et al., 1984 | RR (d) |
| $(1.24 \pm 0.05) \times 10^{-14}$ | 296 ± 2 | Atkinson et al., 1988 | RR (e) |
| $(1.21 \pm 0.06) \times 10^{-14}$ | 296 ± 1 | Andersson and Ljungström, 1989 | RR (c) |
| $(1.27 \pm 0.19) \times 10^{-14}$ | 298 ± 2 | Barnes et al., 1990 | RR (d) |
| $(1.19 \pm 0.09) \times 10^{-14}$ | 298 ± 2 | Chew et al., 1998 | RR (d) |
| $(1.24 \pm 0.08) \times 10^{-14}$ | 296 ± 2 | Aschmann et al., 2008 | RR (e) |

### Comments

(a) $NO_3$ radicals generated by the thermal decomposition of $N_2O_5$.

(b) $NO_3$ radicals were generated by F + $HNO_3$ reaction in 2.7 mbar (2 Torr) total pressure of He and monitored by long path absorption at 662 nm; pseudo first order conditions.

(c) $NO_3$ radicals were generated from the thermal decomposition of $N_2O_5$. The experimental data were relative to the equilibrium coefficient $K$ for the $NO_3 + NO_2 \leftrightarrow N_2O_5$ reactions, and are placed on an absolute basis by use of $K = 2.15 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ at 300 K and $3.53 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ at 296 K ((IUPAC, 2019).

(d) $NO_3$ radicals were generated from the thermal decomposition of $N_2O_5$. The concentrations of 1-butene and propene (the reference compound) were measured by GC, and rate coefficient ratios of $k(NO_3$ + 1-butene)/$k(NO_3$ + propene) = 1.304 ± 0.012 (Atkinson et al., 1984), 1.34 ± 0.20 (Barnes et al., 1990) and 1.25 ± 0.09 (Chew et al., 1998) obtained. These rate coefficient ratios are placed on an absolute basis using $k(NO_3$ + propene) = $9.5 \times 10^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (IUPAC, 2019).

(e) $NO_3$ radicals were generated by the thermal decomposition of $N_2O_5$. The concentrations of 1-butene and thiophene (the reference compound) were measured by GC, and rate coefficient ratios of $k(NO_3$ + 1-butene)/$k(NO_3$ + thiophene) = 0.315 ± 0.011 (Atkinson et al., 1988) and 0.316 ± 0.020 (Aschmann et al., 2008) obtained. These rate coefficient ratios are placed on an absolute basis using $k(NO_3$ + thiophene) = $3.93 \times 10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 296 K (Atkinson, 1991).

## Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $1.3 \times 10^{-14}$ | 298 |
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $3.2 \times 10^{-13} \exp(-950/T)$ | 230-480 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.10 | 298 |
| $\Delta E/R$ | ± 200 | 230-480 |

*Comments on Preferred Values*

The available absolute and relative room temperature rate coefficients are in good agreement. The temperature dependencies measured by Canosa-Mas et al. (1992) and Rudich et al. (1996) are also in good agreement. The preferred values are derived from an un-weighted least-squares analysis of the absolute and relative rate coefficients of Atkinson et al. (1984, 1988), Barnes et al. (1990), Canosa-Mas et al. (1992), Rudich et al. (1996), Berndt et al. (1998), Chew et al. (1998) and Aschmann et al. (2008). Because of uncertainties in the equilibrium constant for the $N_2O_5 \leftrightarrow NO_3 + NO_2$ reactions, the data of Japar and Niki (1975) and Andersson and Ljungström (1989) are not used in the evaluation of the preferred values, although they are in agreement with the preferred value.

The $NO_3$ radical reaction with 1-butene proceeds by initial addition,

$NO_3 + CH_3CH_2CH{=}CH_2 \rightarrow CH_3CH_2C^{\bullet}HCH_2ONO_2^{*}$ or $CH_3CH_2CH(ONO_2)C^{\bullet}H_2^{*}$

with the chemically-activated nitrooxyalkyl radicals decomposing to 1,2-epoxybutane + $NO_2$ in competition with collisional stabilization; for example

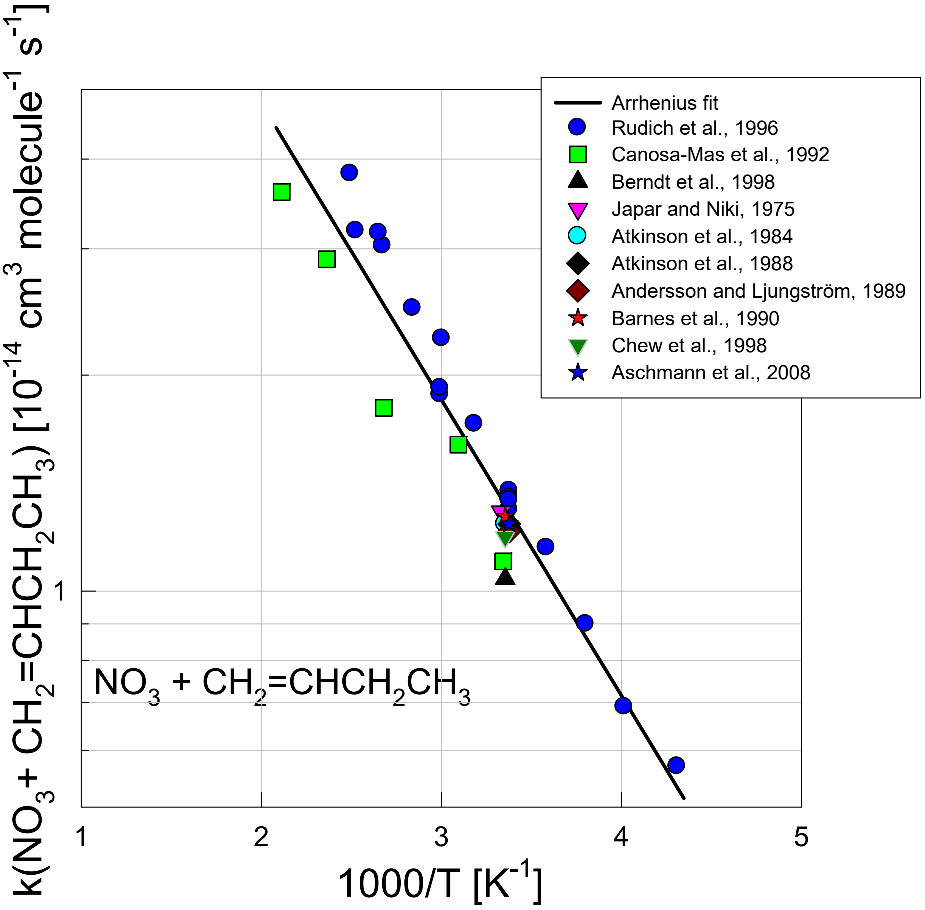
$CH_3CH_2C^{\bullet}HCH_2ONO_2^{*} \rightarrow$ 1,2-epoxybutane + $NO_2$
$CH_3CH_2C^{\bullet}HCH_2ONO_2^{*} + M \rightarrow CH_3CH_2C^{\bullet}HCH_2ONO_2 + M$

Under atmospheric conditions the thermalized nitrooxybutyl radicals react with $O_2$ to form the corresponding 1,2-nitrooxybutylperoxy radicals $CH_3CH_2CH(OO^{\bullet})CH_2ONO_2$ and $CH_3CH_2CH(ONO_2)CH_2OO^{\bullet}$. At atmospheric pressure of air, Barnes et al. (1990) observed HCHO, propanal, and total nitrates with yields (per reacted molecule of $CH_3CH_2CH{=}CH_2$ ) of 11%, 12% and ~60%, respectively. Berndt and Böge (1995) observed formation of 1,2-epoxybutane, propanal and $CH_3CH_2C(O)CH_2ONO_2$, with yields of 18%, 65% and ~17%, respectively, the yields in this case defined as ([product]/Σ[product]).

## References

Andersson, Y. and Ljungström, E.: Atmos. Environ., 23, 1153, 1989.
Aschmann, S. M., Tuazon, E. C., Long, W. D. and Atkinson, R.: J. Phys. Chem. A, 112, 13556, 2008.
Atkinson, R.: J. Phys. Chem. Ref. Data, 20, 459, 1991.
Atkinson, R., Plum, C. N., Carter, W. P. L., Winer, A. M. and Pitts Jr., J. N.: J. Phys. Chem., 88, 1210, 1984.
Atkinson, R., Aschmann, S. M. and Pitts Jr., J. N.: J. Phys. Chem., 92, 3454, 1988.

Barnes, I., Bastian, V., Becker, K. H. and Tong, Z.: J. Phys. Chem., 94, 2413, 1990.
Berndt, T. and Böge, O.: J. Atmos. Chem., 21, 275, 1995.
Berndt, T., Kind, I. and Karbach, H.-J.: Ber. Bunsenges. Phys. Chem., 102, 1486, 1998.
Canosa-Mas, C. E., Monks, P. S. and Wayne, R. P.: J. Chem. Soc. Faraday Trans., 88, 11, 1992.
Chew, A. A., Atkinson, R. and Aschmann, S. M.: J. Chem. Soc. Faraday Trans., 94, 1083, 1998.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Japar, S. M. and Niki, H.: J. Phys. Chem., 79, 1629, 1975.
Rudich, Y., Talukdar, R. K., Fox, R. W. and Ravishankara, A. R.: J. Phys. Chem., 100, 5374, 1996.



Rate coefficients for $NO_3$ + 1-butene

## Datasheet NO3_VOC29

## $NO_3$ + *cis*-2-Butene → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $(3.75 \pm 0.24) \times 10^{-13}$ | 298 | Benter et al., 1992 | DF-MS (a) |
| $(3.3 \pm 0.8) \times 10^{-13}$ | 298 | Wille et al., 1992 | DF-MS (a) |
| *Relative Rate Coefficients* | | | |
| $(2.97 \pm 0.33) \times 10^{-13}$ | 300 | Japar and Niki, 1975 | RR-FTIR (b) |
| $(3.50 \pm 0.01) \times 10^{-13}$ | 298 ± 1 | Atkinson et al., 1984 | RR-GC (c) |

### Comments

(a) $NO_3$ radicals were generated from reaction of F atoms (made in a microwave discharge through $F_2$/He) with $HNO_3$ in He carrier and monitored by MS.

(b) $NO_3$ radicals were generated from the thermal decomposition of $N_2O_5$. The experimental data were relative to the equilibrium coefficient $K$ for the $NO_3 + NO_2 \leftrightarrow N_2O_5$ reactions, and are placed on an absolute basis by use of $K = 2.15 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ at 300 K.

(c) $NO_3$ radicals were generated from the thermal decomposition of $N_2O_5$. The concentrations of *cis*-2-butene and *trans*-2-butene (the reference compound) were measured by GC, and rate coefficient ratios of $k$($NO_3$ + *cis*-2-butene)/$k$($NO_3$ + *trans*-2-butene) = 0.897 ± 0.003 (Atkinson et al., 1984) obtained. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k$($NO_3$ + *trans*-2-butene) = $3.9 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (IUPAC, 2019).

### Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $3.5 \times 10^{-13}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.10 | 298 |

*Comments on Preferred Values*

Rate coefficients are only available at room temperature, and the absolute and relative rate coefficients of Atkinson et al. (1984), Benter et al. (1992) and Wille et al. (1992) are in good agreement. While the rate coefficient of Japar and Niki (1975) is in good agreement with those of Atkinson et al. (1984), Benter et al. (1992) and Wille et al. (1992), it is not used in the rate coefficient evaluation because of uncertainties in the equilibrium constant for the $N_2O_5 \leftrightarrow NO_3 + NO_2$ reactions. The preferred value is obtained from an average of the rate coefficients of Atkinson et al. (1984), Benter et al. (1992) and Wille et al. (1992).

The $NO_3$ radical reaction with *cis*-2-butene proceeds by initial addition,

$NO_3$ + *cis*-$CH_3CH{=}CHCH_3 \rightarrow CH_3C^{\bullet}HCH(ONO_2)CH_3^{*}$

with the chemically-activated nitrooxyalkyl radicals decomposing to *cis*- or *trans*-2,3-epoxybutane + $NO_2$ in competition with collisional stabilization.

$CH_3C^{\bullet}HCH(ONO_2)CH_3^{*} \rightarrow$ 2,3-epoxybutane + $NO_2$
$CH_3C^{\bullet}HCH(ONO_2)CH_3^{*} + M \rightarrow CH_3C^{\bullet}HCH(ONO_2)CH_3 + M$

Under atmospheric conditions the thermalized nitrooxybutyl radical reacts with $O_2$ to form the peroxy radical $CH_3CH(OO^{\bullet})CH(ONO_2)CH_3$. At atmospheric pressure of air, the observed products and their molar formation yields are: $CH_3CHO$, 34 ± 12% (Hjorth et al., 1990); $CH_3C(O)CH(ONO_2)CH_3$, 41 ± 13% (Hjorth et al., 1990); $CH_3CH(OH)CH(ONO_2)CH_3$, 15 ± 5% (Hjorth et al., 1990); and 2,3-epoxybutane, ≤1% (Skov et al., 1994).

## References

Atkinson, R., Plum, C. N., Carter, W. P. L., Winer, A. M., and Pitts Jr., J. N.: J. Phys. Chem., 88, 1210, 1984.
Benter, Th., Becker, E., Wille, U., Rahman, M. M., and Schindler, R. N.: Ber. Bunsenges. Phys. Chem., 96, 769, 1992.
Hjorth, J., Lohse, C., Nielsen, C. J., Skov, H., and Restelli, G.: J. Phys. Chem., 94, 7494, 1990.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Japar, S. M., and Niki, H.: J. Phys. Chem., 79, 1629, 1975.
Skov, H., Benter, Th., Schindler, R. N., Hjorth, J., and Restelli, G.: Atmos. Environ., 28, 1583, 1994.
Wille, U., Rahman, M. M., and Schindler, R. N.: Ber. Bunsenges. Phys. Chem., 96, 833, 1992.

## Datasheet NO3_VOC30

## $NO_3$ + *trans*-2-Butene → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $(3.78 \pm 0.41) \times 10^{-13}$ | 298 | Raviskankara and Mauldin, 1985 | F-A/LIF (a) |
| $(1.78 \times 10^{-12} \exp[-(530 \pm 100)/T]) + (1.28 \times 10^{-14} \exp[(570 \pm 110)/T])$ | 204-378 | Dlugokencky and Howard, 1989 | F-LIF (b) |
| $(3.96 \pm 0.48) \times 10^{-13}$ | 298 | | |
| $(3.88 \pm 0.30) \times 10^{-13}$ | 298 | Benter et al., 1992 | DF-MS (c) |
| $(3.55 \pm 0.33) \times 10^{-13}$ | 267 | Rudich et al., 1996 | F-A (d) |
| $(4.06 \pm 0.36) \times 10^{-13}$ | 298 | | |
| $(3.74 \pm 0.45) \times 10^{-13}$ | 298 ± 2 | Berndt et al., 1998 | F-LIF (e) |
| $(3.78 \pm 0.17) \times 10^{-13}$ | 298 ± 2 | Kasyutich et al., 2002 | DF-A (f) |
| *Relative Rate Coefficients* | | | |
| $(2.31 \pm 0.17) \times 10^{-13}$ | 300 | Japar and Niki, 1975 | RR-FTIR (g) |
| $(3.09 \pm 0.27) \times 10^{-13}$ | 298 ± 1 | Atkinson et al., 1984 | RR-GC (g) |

### Comments

(a) $NO_3$ radicals generated by the thermal decomposition of $N_2O_5$ and were monitored by LIF at 662 nm, or were generated by the reaction F + $HNO_3$ and were monitored by long-path absorption at 662 nm at 0.53-1.47 mbar (0.4-1.1 Torr).

(b) $NO_3$ radicals were generated by the thermal decomposition of $N_2O_5$ at ~400 K and monitored by LIF. Experiments were carried out in a low-pressure flow tube at ~1.3-1.4 mbar (1.0-1.1 Torr) of He.

(c) $NO_3$ radicals were generated from reaction of F atoms (made in a microwave discharge through $F_2$/He) with $HNO_3$ in He carrier gas and monitored by MS.

(d) $NO_3$ radicals were generated by the thermal decomposition of $N_2O_5$ at 400 K in a flow system, and $NO_3$ radical concentrations were measured by visible tunable diode laser absorption at 661.9 nm at 2-4 mbar (1.5-3 Torr) of He.

(e) $NO_3$ radicals were generated by the thermal decomposition of $N_2O_5$ at ~400 K and monitored by LIF. Experiments were carried out in a low-pressure flow tube at ~ 3 mbar (2.5 Torr) of He.

(f) $NO_3$ radicals were generated by the reaction F + $HNO_3$ and were monitored by off-axis cavity-enhanced laser absorption spectroscopy at 662 nm.

(g) $NO_3$ radicals were generated from the thermal decomposition of $N_2O_5$. The experimental data were relative to the equilibrium coefficient $K$ for the $NO_3 + NO_2 \leftrightarrow N_2O_5$ reactions, and are placed on an absolute basis by use of $K = 2.15 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ at 300 K and $2.75 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ at 298 K (IUPAC, 2019).

## Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $3.9 \times 10^{-13}$ | 298 |
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $\{1.78 \times 10^{-12} \exp(-530/T) +$<br>$1.28 \times 10^{-14} \exp(570/T)\}$ | 200-380 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.08 | 200-380 |

*Comments on Preferred Values*

The available absolute 298 K rate coefficients are in excellent agreement, as are those of Dluokencky and Howard (1989) and Rudich et al. (1996) at 267 K. Because of uncertainties in the equilibrium constant for the $N_2O_5 \leftrightarrow NO_3 + NO_2$ reactions, the data of Japar and Niki (1975) and Atkinson et al. (1984) are not used in the evaluation of the preferred values. The temperature-dependent rate expression of Dlugokencky and Howard (1989) is accepted as the preferred value. There is no evidence for a pressure dependence of the room temperature rate constant over the pressure range 0.4-740 Torr as reported by the available studies.

The $NO_3$ radical reaction with *trans*-2-butene proceeds by initial addition,

$NO_3$ + *cis*-$CH_3CH{=}CHCH_3 \rightarrow CH_3C^{\bullet}HCH(ONO_2)CH_3^{*}$

with the chemically-activated nitrooxyalkyl radicals decomposing to *cis*- or *trans*-2,3-epoxybutane + $NO_2$ in competition with collisional stabilization.

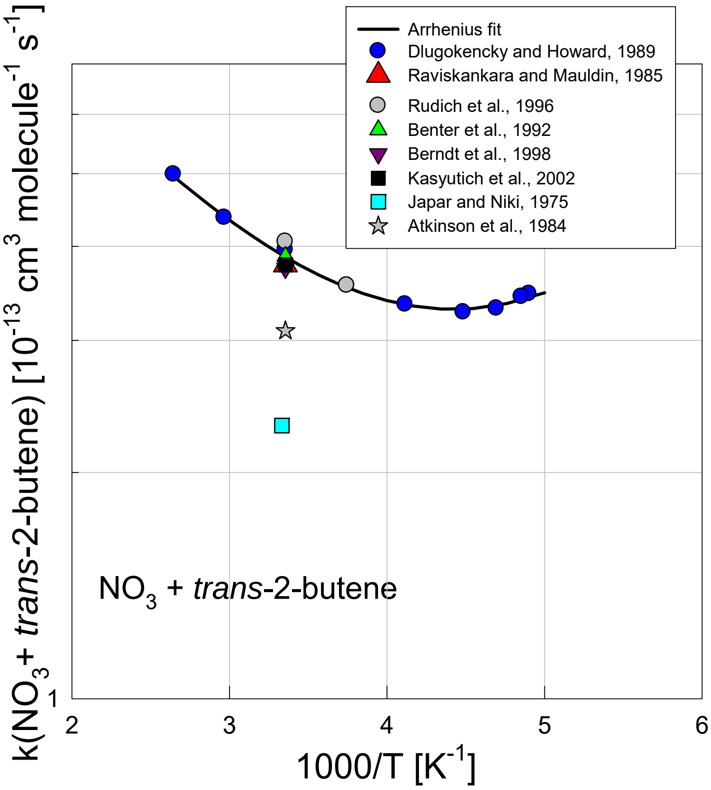
$CH_3C^{\bullet}HCH(ONO_2)CH_3^{*} \rightarrow$ 2,3-epoxybutane + $NO_2$
$CH_3C^{\bullet}HCH(ONO_2)CH_3^{*} + M \rightarrow CH_3C^{\bullet}HCH(ONO_2)CH_3 + M$

Under atmospheric conditions the thermalized nitrooxybutyl radical reacts with $O_2$ to form the peroxy radical $CH_3CH(OO^{\bullet})CH(ONO_2)CH_3$. At atmospheric pressure of air, the observed products and their molar formation yields are: $CH_3CHO$, 70% (Barnes et al., 1990), 34 ± 12% (Hjorth et al., 1990) and ~100% (Berndt and Böge, 1995); $CH_3C(O)CH(ONO_2)CH_3$, 55% (Barnes et al., 1990), 41 ± 13% (Hjorth et al., 1990) and 38% (Berndt and Böge, 1995); $CH_3CH(OH)CH(ONO_2)CH_3$, 15 ± 5% (Hjorth et al., 1990); $CH_3CH(ONO_2)CH(ONO_2)CH_3$, 4% (Barnes et al., 1990); and 2,3-epoxybutane, ≤1% (Skov et al., 1994) and 12% (Berndt and Böge, 1995). Some of these differences in reported yields are likely due to the experimental conditions and procedures used, with Barnes et al. (1990) and Berndt and Böge (1995) adding NO after the reaction to promote thermal decomposition of peroxynitrates and concurrently convert peroxy radicals to alkoxy radicals.

## References

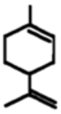
Atkinson, R., Plum, C. N., Carter, W. P. L., Winer, A. M., and Pitts Jr., J. N.: J. Phys. Chem., 88, 1210, 1984.
Barnes, I., Bastian, V., Becker, K. H., and Tong, Z.: J. Phys. Chem., 94, 2413, 1990.
Benter, Th., Becker, E., Wille, U., Rahman, M. M., and Schindler, R. N.: Ber. Bunsenges. Phys. Chem., 96, 769, 1992.

Berndt, T., and Böge, O.: J. Atmos. Chem., 21, 275, 1995.
Berndt, T., Kind, I., and Karbach, H.-J.: Ber. Bunsnges. Phys. Chem., 102, 1486, 1998.
Dlugokencky, E. J., and Howard, C. J.: J. Phys. Chem., 93, 1091, 1989.
Hjorth, J., Lohse, C., Nielsen, C. J., Skov, H., and Restelli, G.: J. Phys. Chem., 94, 7494, 1990.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Japar, S. M., and Niki, H.: J. Phys. Chem., 79, 1629, 1975.
Kasyutich, V. L., Canosa-Mas, C. E., Pfrang, C., Vaughan, S., and Wayne, R. P.: Appl. Phys. B, 75, 755, 2002.
Ravishankara, A. R., and Mauldin III, R. J.: J. Phys. Chem., 89, 3144, 1985.
Rudich, Y., Talukdar, R. K., Fox, R. W., and Ravishankara, A. R.: J. Phys. Chem., 100, 5374, 1996.
Skov, H., Benter, Th., Schindler, R. N., Hjorth, J., and Restelli, G.: Atmos. Environ., 28, 1583, 1994.



Rate coefficients for NO$_3$ + *trans*-2-butene

## Datasheet NO3_VOC33

**$NO_3$ +**  **(*d*-limonene) → products**

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $(9.4 \pm 0.9) \times 10^{-12}$ | 298 | Martínez et al., 1999 | DF-LIF (a) |
| $(5.8 \pm 0.7) \times 10^{-12}$ | 433 | | |
| *Relative Rate Coefficients* | | | |
| $(1.31 \pm 0.04) \times 10^{-11}$ | 295 | Atkinson et al., 1984 | RR (b) |
| $(1.12 \pm 0.17) \times 10^{-11}$ | 298 | Barnes et al., 1990 | RR (c) |

Limonene is 4-isopropenyl-1-methyl-cyclohexene.

### Comments

(a) $NO_3$ radicals ($6\text{-}30 \times 10^{11}$ molecule cm$^{-3}$) generated from reaction of F atoms (made in a microwave discharge through $F_2$/He) with $HNO_3$. Flow tube was operated at ~1.33 mbar (1 Torr) He. Limonene was present at similar concentrations (1-3 fold) to $NO_3$. So that absolute $NO_3$ concentrations (derived by titration with tetramethylethene) were necessary to derive the rate coefficient.

(b) 6400 L Teflon chamber at 295 K and 980 mbar (735 Torr) of air. $NO_3$ was generated by the thermal decomposition of $N_2O_5$. Limonene and 2-methyl-2-butene were monitored by GC. The rate constant ratio, $k(NO_3$ + limonene$)$ / $k(NO_3$ + 2-methyl-2-butene$) = 1.40 \pm 0.04$ is placed on an absolute basis by $k(NO_3$ + 2-methyl-2-butene$) = 9.37 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (Atkinson and Arey, 2003).

(c) 420 L glass chamber at 298 K and 980 mbar (735 Torr) of air. $NO_3$ was generated by the thermal decomposition of $N_2O_5$. Limonene and 2-methyl-2-butene were monitored by GC. The rate constant ratio, $k(NO_3$ + limonene$)$ / $k(NO_3$ + 2-methyl-2-butene$) = 1.20 \pm 0.18$ is placed on an absolute basis by $k(NO_3$ + 2-methyl-2-butene$) = 9.37 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (Atkinson and Arey, 2003).

### Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $1.2 \times 10^{-11}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | $\pm 0.12$ | 298 |

*Comments on Preferred Values*

The preferred value of the room temperature rate coefficient is based on the relative rate studies, which indicate a larger rate coefficient than observed in the single absolute study.

The difference between the rate coefficients obtained at 298 and 433 K (factor 1.6) was not considered large enough to warrant a more detailed investigation of the temperature dependence (Martínez et al., 1999).

The reaction mechanism involves the initial addition of $NO_3$ across a double bond to form a nitrooxyalkyl radical, which, in air, forms a nitrooxyalkyl peroxy radical. Product studies suggest that attack of $NO_3$ at the exocyclic double bond of limonene is insignificant (Spittler et al 2006), which is supported by theoretical calculations (Jiang et al., 2009).

The reaction products in air include endolim (yield of 29 %, Spittler et al., 2006) and organic nitrates (expected to include both mono- and dinitrates) with yields (per limonene reacted) between 30 and 67 % (Spittler et al. 2006; Hallquist et al., 1999; Fry et al 2011; Fry et al., 2014). Using thermal dissociation of alkyl nitrates and peroxynitrates coupled to LIF detection of $NO_2$, Fry et al., (2014) derived a molar organic nitrate yield (gas- and aerosol) of 0.54 with 83 % being located in the aerosol phase. Organonitrates comprised 82 % of the aerosol mass.

Secondary organic aerosol is formed efficiently in smog-chamber studies of the reaction between $NO_3$ and limonene with mass-based yields of between 17 and 57% reported (Hallquist et al., 1999; Fry et al., 2011; Fry et al., 2014). Spittler et al. (2006) suggest that much of the organic aerosol is formed from further reactions of endolim.

## References

Atkinson, R., Aschmann, S. M., Winer, A. M., and Pitts, J. N., Env. Sci. Tech., 18, 370-375, 1984.

Atkinson, R., and Arey, J., Chem. Rev., 103, 4605-4638, 2003.

Barnes, I., Bastian, V., Becker, K. H., and Tong, Z., J. Phys. Chem., 94, 2413-2419, 1990.

Fry, J. L., Kiendler-Scharr, A., Rollins, A. W., Brauers, T., Brown, S. S., Dorn, H. P., Dube, W. P., Fuchs, H., Mensah, A., Rohrer, F., Tillmann, R., Wahner, A., Wooldridge, P. J., and Cohen, R. C., Atmos. Chem. Phys., 11, 3879-3894, 2011.

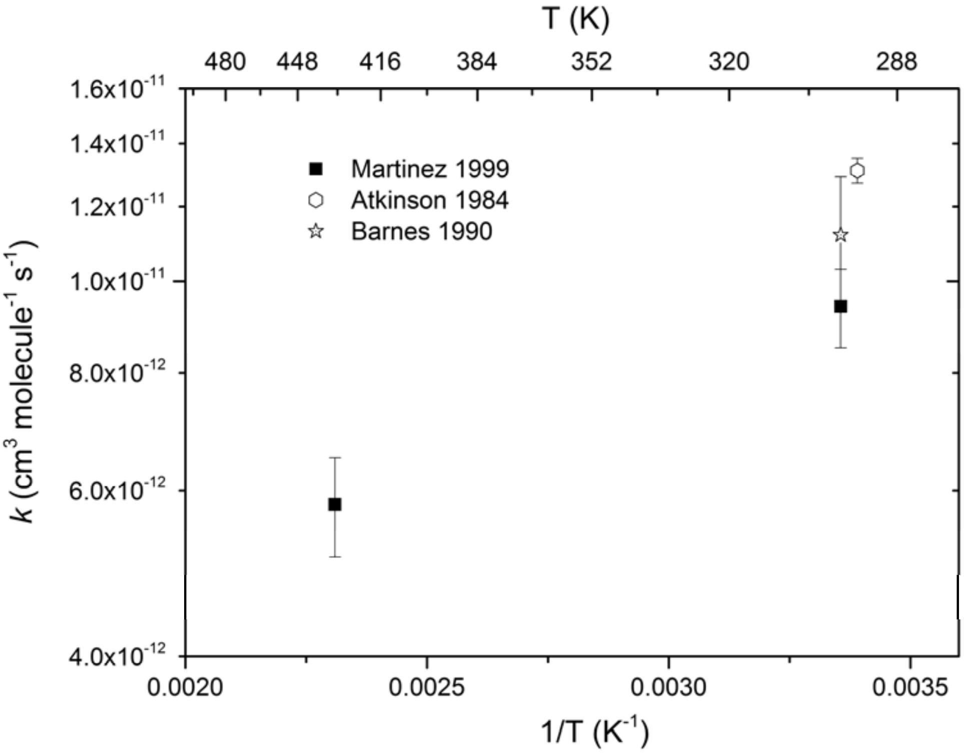
Fry, J. L., Draper, D. C., Barsanti, K. C., Smith, J. N., Ortega, J., Winkle, P. M., Lawler, M. J., Brown, S. S., Edwards, P. M., Cohen, R. C., and Lee, L., Env. Sci. Tech., 48, 11944-11953, 2014.

Hallquist, M., Wangberg, I., Ljungstrom, E., Barnes, I., and Becker, K. H., Env. Sci. Tech., 33, 553-559, 1999.

Jiang, L., Wang., W and Xu., Y. Int. J. Mol. Sci. 10, 3743-3754, 2009.

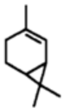
Martínez, E., Cabañas, B., Aranda, A., Martín, P., and Salgado, S., J. Atmos. Chem., 33, 265-282, 1999.

Spittler, M., Barnes, I., Bejan, I., Brockmann, K. J., Benter, T., and Wirtz, K., Atmos. Env., 40, S116-S127, 2006.



Rate coefficients for $NO_3$ + limonene

## Datasheet NO3_VOC34

**$NO_3$ +**  **(2-carene) → products**

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $(1.66 \pm 0.18) \times 10^{-11}$ | 298 | Martínez et al., 1999 | DF-LIF (a) |
| $1.4 \times 10^{-12} \exp[(741 \pm 190)/T]$ | 298-433 | | |
| *Relative Rate Coefficients* | | | |
| $(1.87 \pm 0.11) \times 10^{-11}$ | 295 | Corchnoy and Atkinson, 1990 | RR-GC (b) |
| $(2.16 \pm 0.36) \times 10^{-11}$ | 295 | Corchnoy and Atkinson, 1990 | RR-GC (c) |

2-carene is 3,7,7-trimethyl-bicyclo[4.1.0]hept-2-ene.

### Comments

(a) $NO_3$ radicals ($6\text{-}30 \times 10^{11}$ molecule cm$^{-3}$) generated from reaction of F atoms (made in a microwave discharge through $F_2$/He) with $HNO_3$. Flow tube was operated at ~1.33 mbar (1 Torr) He at 4 temperatures between 298 and 433 K. 2-carene was present at similar concentrations (1-3 fold) to $NO_3$. So that absolute $NO_3$ concentrations (derived by titration with tetramethylethene) were necessary to derive the rate coefficient.

(b) 6400 L Teflon chamber at 295 K and 980 mbar (735 Torr) of air. $NO_3$ was generated by the thermal decomposition of $N_2O_5$. 2-carene and 2-methyl-2-butene (reference reactant) were monitored by GC to obtain the rate constant ratio $k(NO_3$ + 2-carene) / $k(NO_3$ + 2-methyl-2-butene) = 2.00 ± 0.12. Using $k(NO_3$ + 2-methyl-2-butene) = $9.37 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (Atkinson and Arey, 2003) the absolute rate constants listed in the table is obtained.

(c) 6400 L Teflon chamber at 295 K and 980 mbar (735 Torr) of air. $NO_3$ was generated by the thermal decomposition of $N_2O_5$. 2-carene and 2,3-dimethyl-2-butene (reference reactant) were monitored by GC to obtain the rate constant ratio $k(NO_3$ + 2-carene) / $k(NO_3$ + 2,3-dimethyl-2-butene) = 0.377 ± 0.063. Using $k(NO_3$ + 2,3-dimethyl-2-butene) = $5.72 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson and Arey, 2003) the absolute rate constant listed in the table is obtained.

### Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $2.0 \times 10^{-11}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.12 | 298 |

*Comments on Preferred Values*

The three determinations of the room temperature rate coefficient agree to within ~30 % and the preferred value of the room temperature rate coefficient is based on the relative rate studies. The temperature dependence observed by Martínez et al. (1999) requires validation before a recommendation can be made.

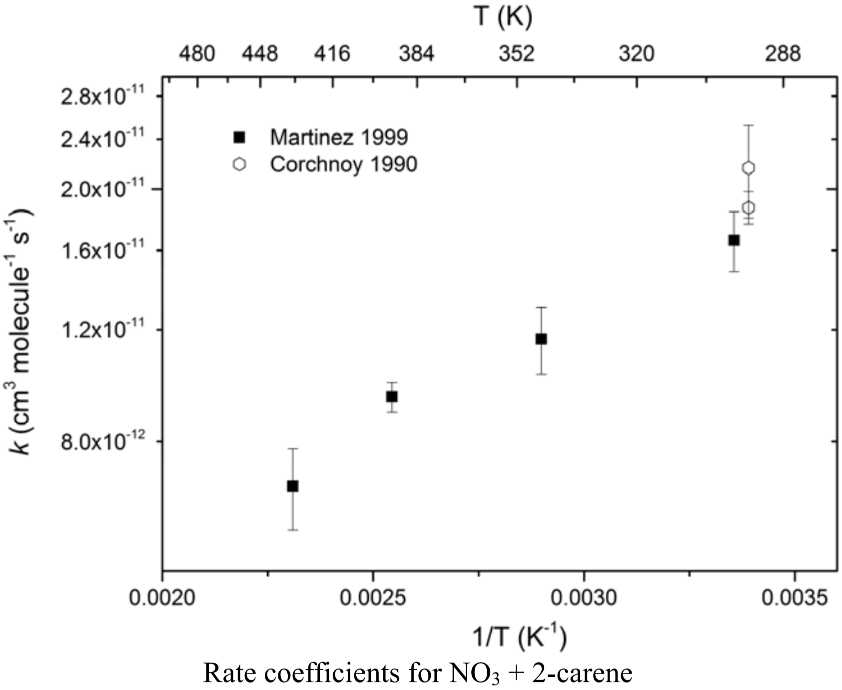
There are no product studies of this reaction, though the large rate constant indicates that the reaction proceeds mainly via addition of $NO_3$ across a double bond to form a chemically activated nitrooxyalkyl radical. At pressures found in the troposphere this adduct will undergo collisional stabilization prior to reaction with $O_2$ to form a nitrooxyalkyl peroxy radical or decompose to release $NO_2$. At atmospheric pressure the formation of the peroxy radical will generally dominate.

## References

Atkinson, R., and Arey, J., Chem. Rev., 103, 4605-4638, 2003.

Corchnoy, S. B., and Atkinson, R., Env. Sci. Tech., 24, 1497-1502, 1990.

Martínez, E., Cabañas, B., Aranda, A., Martín, P., and Salgado, S., J. Atmos. Chem., 33, 265-282, 1999.



Rate coefficients for $NO_3$ + 2-carene

## Datasheet NO3_VOC35

**NO$_3$ +**  **(3-carene) → products**

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(1.01 \pm 0.02) \times 10^{-11}$ | 295 | Atkinson et al., 1984 | RR (a) |
| $(8.2 \pm 1.2) \times 10^{-12}$ | 298 | Barnes et al., 1990 | RR (b) |

3-carene is 3,7,7-trimethyl-bicyclo[4.1.0]hept-3-ene.

### Comments

(a) 6400 L Teflon chamber at 295 K and 980 mbar (735 Torr) of air. NO$_3$ was generated by the thermal decomposition of N$_2$O$_5$. 3-carene and 2-methyl-2-butene were monitored by GC. The rate constant ratio, $k$(NO$_3$ + 3-carene) / $k$(NO$_3$ + 2-methyl-2-butene) = 1.08 ± 0.02 is placed on an absolute basis using $k$(NO$_3$ + 2-methyl-2-butene) = $9.37 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (Atkinson and Arey, 2003).

(b) 420 L glass chamber at 298 K and 1 bar of air. NO$_3$ was generated by the thermal decomposition of N$_2$O$_5$. 3-carene and 2-methyl-2-butene were monitored by GC. The rate constant ratio, $k$(NO$_3$ + 3-carene) / $k$(NO$_3$ + 2-methyl-2-butene) = 0.87 ± 0.13 is placed on an absolute basis using $k$(NO$_3$ + 2-methyl-2-butene) = $9.37 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (Atkinson and Arey, 2003).

### Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $9.1 \times 10^{-12}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.12 | 298 |

*Comments on Preferred Values*

The two relative rate studies of this reaction are at room temperature only. Both Atkinson et al. (1984) and Barnes et al. (1990) used the same reference reactant but derived rate coefficients which diverge by ~20 %. There is no obvious reason to favour either study and the preferred value of the 298 K rate coefficient is an unweighted average.

The reaction mechanism involves the addition of NO$_3$ across the double bond to form a nitrooxyalkyl radical, which, in air, forms a nitrooxyalkyl peroxy radical. Unstable nitrooxy peroxynitrates (from nitrooxyalkyl peroxy radical + NO$_2$) were observed at early reaction times (Hallquist et al. 1999). These authors also identified the end products caronaldehyde (molar yields of 2-3 %), carbonyls (estimated molar yield of 20-30 %) and nitrates (66-74 %). The atmospheric fate of caronaldehyde is expected to be reaction with OH and photolysis (Hallquist et al., 1997).

Using thermal dissociation of alkyl nitrates and peroxynitrates coupled to LIF detection of $NO_2$, Fry et al., (2014) derived a molar organic nitrate yield (gas- and aerosol) of 0.77 with 50 % being located in the aerosol phase. Organonitrates comprised 56 % of the aerosol mass.

Secondary organic aerosol has been observed in the smog-chamber studies of $NO_3$ + 3-carene (Hallquist et al., 1999; Griffin et al. 1999) with mass-based yields of up to 72 % depending on the amount of 3-carene reacted. Hallquist et al. provide evidence for the presence of condensable organics containing the $-ONO_2$ entity. A detailed mechanism of the potential routes to aerosol formation is presented by Colville et al. (2004).

## References

Atkinson, R., Aschmann, S. M., Winer, A. M., and Pitts, J. N., Env. Sci. Tech., 18, 370-375, 1984.

Atkinson, R., and Arey, J., Chem. Rev., 103, 4605-4638, 2003.

Barnes, I., Bastian, V., Becker, K. H., and Tong, Z., J. Phys. Chem., 94, 2413-2419, 1990.

Colville, C. J., and Griffin, R. J., Atmos. Env., 38, 4001-4012, 2004.

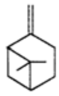
Fry, J. L., Draper, D. C., Barsanti, K. C., Smith, J. N., Ortega, J., Winkle, P. M., Lawler, M. J., Brown, S. S., Edwards, P. M., Cohen, R. C., and Lee, L., Env. Sci. Tech., 48, 11944-11953, 2014.

Griffin, R. J., Cocker, D. R., Flagan, R. C., and Seinfeld, J. H., J. Geophys. Res.-Atmos., 104, 3555-3567, 1999.

Hallquist, M., Wangberg, I., and Ljungstrom, E., Env. Sci. Tech., 31, 3166-3172, 1997

Hallquist, M., Wangberg, I., Ljungstrom, E., Barnes, I., and Becker, K. H., Env. Sci. Tech., 33, 553-559, 1999.

## Datasheet NO3_VOC36

### $NO_3$ +  (β-pinene) → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(2.36 \pm 0.10) \times 10^{-12}$ | 295 | Atkinson et al., 1984 | RR-GC (a) |
| $(2.38 \pm 0.05) \times 10^{-12}$ | 296 | Atkinson et al., 1988 | RR-GC (b) |
| $(1.1 \pm 0.4) \times 10^{-12}$ | 298* | Kotzias et al., 1989 | RR-FTIR (c) |
| $(2.81 \pm 0.47) \times 10^{-12}$ | 298 | Barnes et al., 1990 | RR-GC (d) |

β-pinene is 6,6-dimethyl-2-methylene-bicyclo[3.1.1]heptane.

## Comments

(a) 6400 L Teflon chamber at 295 K and 980 mbar (735 Torr) of air. $NO_3$ was generated by the thermal decomposition of $N_2O_5$. β-pinene and 2-methyl-2-butene (reference reactant) were monitored by GC. The rate constant ratio, $k(NO_3 + \beta\text{-pinene}) / k(NO_3 + \text{2-methyl-2-butene}) = 0.252 \pm 0.011$ is placed on an absolute basis using $k(NO_3 + \text{2-methyl-2-butene}) = 9.37 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (Atkinson and Arey, 2003).

(b) 6400 L Teflon chamber at 296 K and 980 mbar (735 Torr) of air. $NO_3$ was generated by the thermal decomposition of $N_2O_5$. β-pinene and trans-2-butene (reference reactant) were monitored by GC. The rate constant ratio, $k(NO_3 + \beta\text{-pinene}) / k(NO_3 + \text{trans-2-butene}) = 6.10 \pm 0.14$ is placed on an absolute basis using $k(NO_3 + \text{trans-2-butene}) = 3.9 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (IUPAC, 2019).

(c) 450 L Teflon-coated glass reactor, with β-pinene, $N_2O_5$ and $NO_2$ monitored by FTIR. $NO_3$, $NO_2$ and $N_2O_5$ were assumed to be in equilibrium and the $NO_3$ concentration was calculated from the equilibrium constant ($1.9 \times 10^{-11}$ molecule$^{-1}$ cm$^3$) and used to derive the rate constant from the β-pinene decay constant. The authors did not quote the temperature of these experiments, making re-assessment of their data via e.g. use of a more recently measured equilibrium constant difficult.

(d) 420 L glass chamber at 298 K and 1bar of air. $NO_3$ was generated by the thermal decomposition of $N_2O_5$. β-pinene and 2-methyl-2-butene were monitored by GC. The rate constant ratio, $k(NO_3 + \beta\text{-pinene}) / k(NO_3 + \text{2-methyl-2-butene}) = 0.30 \pm 0.05$ is placed on an absolute basis using $k(NO_3 + \text{2-methyl-2-butene}) = 9.37 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (Atkinson and Arey, 2003).

## Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $2.5 \times 10^{-12}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.12 | 298 |

*Comments on Preferred Values*

The relative rate studies of this reaction which employed either 2-methyl-2-butene or trans-2-butene as reference reactants are in broad agreement, though there is no obvious reason why Atkinson et al. (1984) and Barnes et al. (1990), who used the same reference reactant should derive rate coefficients which diverge by ~20 %. These studies are preferred over that of Kotzias et al. (1989), as there are greater uncertainties related to using the strongly temperature dependent equilibrium constant for the $NO_2 + NO_3 \rightleftharpoons N_2O_5$ reaction, which are compounded by the fact that authors did not cite their experimental temperature. The preferred value of the 298 K rate coefficient is thus an unweighted average of the results derived by Atkinson et al. (1984, 1988) and Barnes et al. (1990).

The reaction mechanism involves the addition of $NO_3$ across the double bond to form a nitrooxyalky radical, which, in air, forms a nitrooxyalkyl peroxy radical. Hallquist et al. (1999) identified the end products nopinone (molar yields of 1-2 %), carbonyls (estimated molar yield of 12-14 %) and organic nitrates (estimated molar yield of 61-74 %) which were also observed using FTIR and MS by Kotzias et al. (1989), but not quantified. Using thermal dissociation of alkyl nitrates and peroxynitrates coupled to LIF detection of $NO_2$, Fry et al., (2009) derived a molar organic nitrate yield of ~40 %. Hydroxynitrates (*m/z* = 215), hydroxycarbonyl nitrazes (*m/z* = 229) and dihydroxynitrates / hydroperoxides and cyclic ether hydroxynitrates (*m/z* = 231) have been observed as gas-phase products (Boyd et al., 2015), with altogether more than forty $C_7$-$C_{10}$ organic nitrates (in both gas and particle phase) possessing between 4 and 9 oxygen atoms detected (Boyd et al. 2015, Nah et al., 2016). Formation of peroxy radical that may perform intramolecular H-abstraction (auto-oxidation) has been proposed as a potential explanation for the high O-to-N ratios observed.

Secondary organic aerosol formation has been observed in the smog-chamber studies of $NO_3$ + β-pinene (Hallquist et al., 1999; Griffin et al. 1999; Fry et al., 2009, 2014: Boyd et al., 2015; Nah et al., 2016) with mass-based yields of up to 100 % depending on the amount of β-pinene reacted. The aerosol yield is not strongly influenced by relative humidity, seed-aerosol acidity or whether the fate of $RO_2$ is reaction with $NO_3$ or $HO_2$ (Boyd et al., 2015).

Organonitrates were found to comprise ≈ 45-75 % of the aerosol mass (Fry et al., 2014, Boyd et al., 2015: Nah et al., 2016) with evidence for particle-phase hydrolysis of tertiary nitrates (Boyd et al., 2015).

## References

Atkinson, R., Aschmann, S. M., Winer, A. M., and Pitts, J. N., Env. Sci. Tech., 18, 370-375, 1984.

Atkinson, R., and Arey, J., Chem. Rev., 103, 4605-4638, 2003.

Barnes, I., Bastian, V., Becker, K. H., and Tong, Z., J. Phys. Chem., 94, 2413-2419, 1990.

Boyd, C. M., Sanchez, J., Xu, L., Eugene, A. J., Nah, T., Tuet, W. Y., Guzman, M. I., and Ng, N. L., Atmos. Chem. Phys., 15, 7497-7522, 2015.

Fry, J. L., Kiendler-Scharr, A., Rollins, A. W., Wooldridge, P. J., Brown, S. S., Fuchs, H., Dube, W., Mensah, A., dal Maso, M., Tillmann, R., Dorn, H. P., Brauers, T., and Cohen, R. C., Atmos. Chem. Phys., 9, 1431-1449, 2009.

Fry, J. L., Kiendler-Scharr, A., Rollins, A. W., Wooldridge, P. J., Brown, S. S., Fuchs, H., Dube, W., Mensah, A., dal Maso, M., Tillmann, R., Dorn, H. P., Brauers, T., and Cohen, R. C., Atmos. Chem. Phys., 9, 1431-1449, 2009.

Fry, J. L., Draper, D. C., Barsanti, K. C., Smith, J. N., Ortega, J., Winkle, P. M., Lawler, M. J., Brown, S. S., Edwards, P. M., Cohen, R. C., and Lee, L., Env. Sci. Tech., 48, 11944-11953, 2014.

Griffin, R. J., Cocker, D. R., Flagan, R. C., and Seinfeld, J. H., J. Geophys. Res.-Atmos., 104, 3555-3567, 1999.

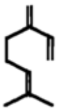
Hallquist, M., Wangberg, I., Ljungstrom, E., Barnes, I., and Becker, K. H., Env. Sci. Tech., 33, 553-559, 1999.

IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

Kotzias, D., Hjorth, J. L., and Skov, H., Toxicol. Environ. Chem., 20-1, 95-99, 1989.

Nah, T., Sanchez, J., Boyd, C. M., and Ng, N. L., Env. Sci. Tech., 50, 222-231, 2016.

## Datasheet NO3_VOC37

**$NO_3$ +**  **(myrcene) → products**

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $(1.28 \pm 0.11) \times 10^{-11}$ | 298 | Martínez et al., 1999 | DF-LIF (a) |
| $2.2 \times 10^{-12} \exp[(523 \pm 35)/T]$ | 298-433 | | |
| *Relative Rate Coefficients* | | | |
| $(1.06 \pm 0.02) \times 10^{-11}$ | 294 | Atkinson et al., 1985 | RR (b) |

Myrcene is 7-methyl-3-methylene-1,6-octadiene.

### Comments

(a) $NO_3$ radicals ($6\text{-}30 \times 10^{11}$ molecule cm$^{-3}$) generated from reaction of F atoms (made in a microwave discharge through $F_2$/He) with $HNO_3$. Flow tube was operated at ~1.33 mbar (1 Torr) He. Myrcene was present at similar concentrations (1-3 fold) to $NO_3$. So that absolute $NO_3$ concentrations (derived by titration with tetramethylethene) were necessary to derive the rate coefficient.

(b) 4000 L Teflon chamber at 294 K and 980 mbar (735 Torr) of air. $NO_3$ was generated by the thermal decomposition of $N_2O_5$. Correction made to the myrcene loss rate due to reaction with $NO_2$ was < 18 %. Myrcene and 2-methyl-2-butene were monitored by GC. The rate constant ratio, $k(NO_3 + \text{myrcene}) / k(NO_3 + \text{2-methyl-2-butene}) = 1.13 \pm 0.02$ is placed on an absolute basis using $k(NO_3 + \text{2-methyl-2-butene}) = 9.37 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (Atkinson and Arey, 2003).

### Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $1.1 \times 10^{-11}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.12 | 298 |

*Comments on Preferred Values*

The preferred value of the room temperature rate coefficient is based on the relative rate study of Atkinson et al. (1985) in which accurate determination of the reactant concentrations was not required. The error limits are expanded to reflect the necessity to correct for removal of myrcene by reaction with $NO_2$ and the ≈ 20 % difference to the absolute rate measurement (Martínez et al., 1999). The temperature dependence observed by Martínez et al. (1999) requires validation before a recommendation can be made.

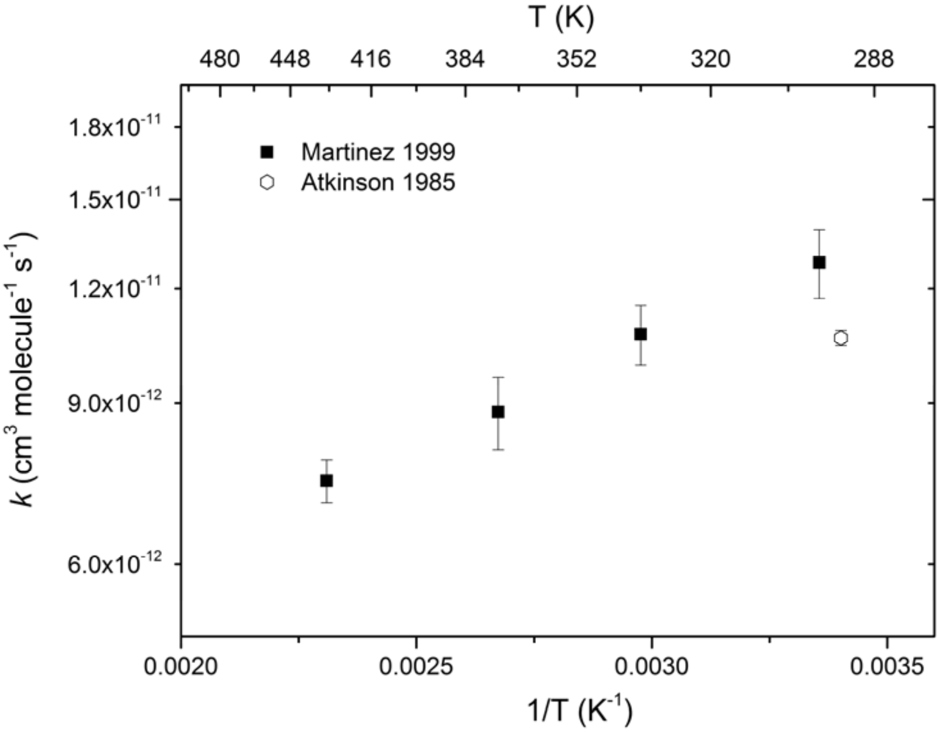
There are no product studies of this reaction, though the large rate constant indicates that the reaction proceeds mainly via addition of $NO_3$ across a double bond to form a chemically activated nitrooxyalkyl radical. At pressures found in the troposphere this adduct will undergo collisional stabilization prior to reaction with $O_2$ to form a nitrooxyalkyl peroxy radical or decompose to release $NO_2$. At atmospheric pressure the formation of the peroxy radical will generally dominate.

## References

Atkinson, R., Aschmann, S. M., Winer, A. M., and Pitts, J. N.: Env. Sci. Tech., 19, 159-163, 1985.

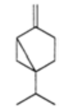
Atkinson, R., and Arey, J.: Chem. Rev., 103, 4605-4638, 2003.

Martínez, E., Cabañas, B., Aranda, A., Martín, P., and Salgado, S.: J. Atmos. Chem., 33, 265-282, 1999.



Rate coefficient for $NO_3$ + myrcene

## Datasheet NO3_VOC38

### $NO_3$ +  (sabinene) → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $(1.07 \pm 0.16) \times 10^{-11}$ | 298 | Martínez et al., 1999 | DF-LIF (a) |
| $2.3 \times 10^{-10} \exp[-(940 \pm 200)/T]$ | 298-393 | | |
| *Relative Rate Coefficients* | | | |
| $(1.01 \pm 0.03) \times 10^{-11}$ | 296 | Atkinson et al., 1990 | RR (b) |

Sabinene is 1-isopropyl-4-methylene-bicyclo[3.1.0]hexane.

## Comments

(a) $NO_3$ radicals ($6\text{-}30 \times 10^{11}$ molecule cm$^{-3}$) generated from reaction of F atoms (made in a microwave discharge through $F_2$/He) with $HNO_3$. Flow tube was operated at ~1.33 mbar (1 Torr) He at 4 temperatures between 298 and 393 K. Sabinene was present at similar concentrations (1-3 fold) to $NO_3$. So that absolute $NO_3$ concentrations (derived by titration with tetramethylethene) were necessary to derive the rate coefficient.

(b) Relative rate of loss of sabinene and 2-methyl-2-butene (reference reactant) in a 6400 L Teflon chamber at 980 mbar (735 Torr) of air was monitored by GC. $NO_3$ was generated by the thermal decomposition of $N_2O_5$. The rate constant ratio, $k(NO_3 + \text{sabinene}) / k(NO_3 + \text{2-methyl-2-butene}) = 1.08 \pm 0.03$ is placed on an absolute basis using $k(NO_3 + \text{2-methyl-2-butene}) = 9.37 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (Atkinson and Arey, 2003).

## Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $1.0 \times 10^{-11}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | $\pm 0.10$ | 298 |

*Comments on Preferred Values*

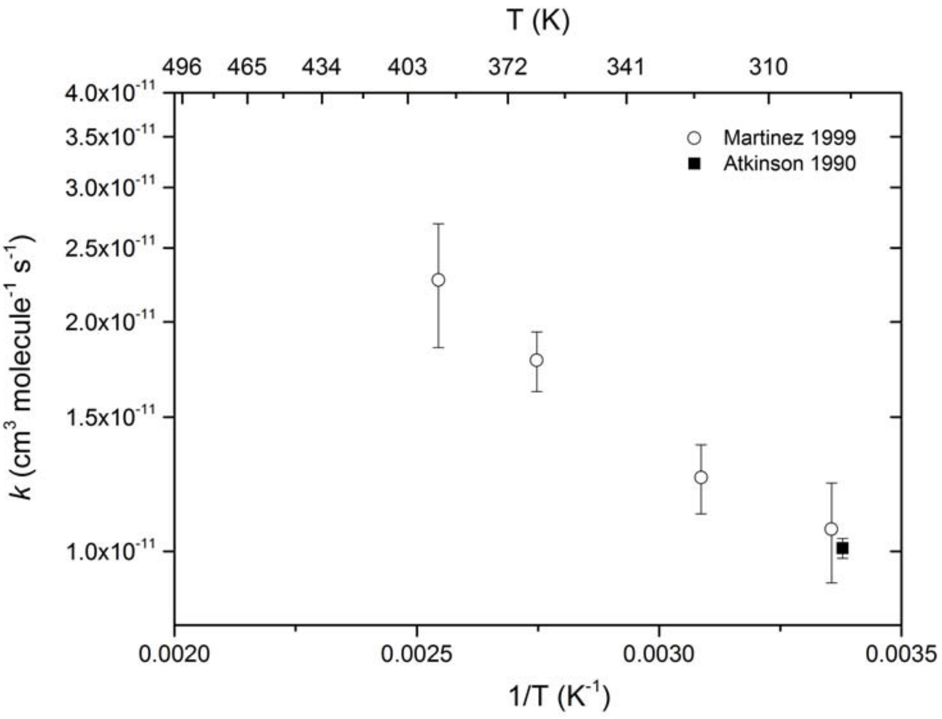
The preferred value at 298 K is based on the relative rate study of Atkinson et al. (1990). The significant, positive dependence of $k$ on temperature observed by Martínez et al. (1999) requires validation.

There are no product studies of this reaction, though the large rate constant indicates that the reaction proceeds mainly via addition of $NO_3$ across a double bond to form a chemically activated nitro-oxyalkyl radical. At pressures found in the troposphere this adduct will undergo collisional stabilization prior to reaction with $O_2$ to form a nitrooxyalkyl peroxy radical.

Secondary organic aerosol has been observed in the smog-chamber studies of $NO_3$ + sabinene (Fry et al., 2014) with mass-based yields of up to 45 % (at 10 µg $m^{-3}$ aerosol loading).

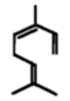
## References

Atkinson, R., Aschmann, S. M., and Arey, J., Atmos. Env., A, 24, 2647-2654, 1990.
Atkinson, R., and Arey, J., Chem. Rev., 103, 4605-4638, 2003.
Fry, J. L., Draper, D. C., Barsanti, K. C., Smith, J. N., Ortega, J., Winkle, P. M., Lawler, M. J., Brown, S. S., Edwards, P. M., Cohen, R. C., and Lee, L., Env. Sci. Tech., 48, 11944-11953, 2014.
Martínez, E., Cabañas, B., Aranda, A., Martín, P., and Salgado, S., J. Atmos. Chem., 33, 265-282, 1999.



Rate coefficients for $NO_3$ + sabinene

## Datasheet NO3_VOC39

**NO$_3$ +**  **(ocimene, cis and trans) → products**

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(2.23 \pm 0.06) \times 10^{-11}$ | 294 | Atkinson et al., 1985 | RR (a) |

Ocimene is 3,7-dimethyl-1,3,6-octatriene.

### Comments

(a) 4000 L Teflon chamber at 294 K and 980 mbar (735 Torr) of air. NO$_3$ was generated by the thermal decomposition of N$_2$O$_5$. Ocimene and 2-methyl-2-butene were monitored by GC. Correction made to the ocimene loss rate due to reaction with NO$_2$ was < 12 %. The rate constant ratio, $k$(NO$_3$ + ocimene) / $k$(NO$_3$ + 2-methyl-2-butene) = $2.38 \pm 0.06$ is placed on an absolute basis using $k$(NO$_3$ + 2-methyl-2-butene) = $9.37 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (Atkinson and Arey, 2003). The rate constants for the cis and trans-isomers of ocimene were indistinguishable within experimental uncertainty (8%).

### Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $2.2 \times 10^{-11}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | $\pm 0.15$ | 298 |

*Comments on Preferred Values*

The preferred value of the room temperature rate coefficient is based on the single study of Atkinson et al. (1985). The error limits are expanded to reflect the necessity to correct for removal of ocimene by reaction with NO$_2$ and because the results have not been confirmed.

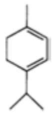
There are no product studies of this reaction, though the large rate constant indicates that the reaction proceeds mainly via addition of NO$_3$ across a double bond to form a chemically activated nitrooxyalkyl radical. At pressures found in the troposphere this adduct will undergo collisional stabilization prior to reaction with O$_2$ to form a nitrooxyalkyl peroxy radical or decompose to release NO$_2$. At atmospheric pressure the formation of the peroxy radical will generally dominate.

### References

Atkinson, R., Aschmann, S. M., Winer, A. M., and Pitts, J. N.: Env. Sci. Tech., 19, 159-163, 1985.

Atkinson, R., and Arey, J.: Chem. Rev., 103, 4605-4638, 2003.

## Datasheet NO3_VOC40

## $NO_3$ +  (α-terpinene) → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(1.82 \pm 0.07) \times 10^{-10}$ | 294 | Atkinson et al., 1985 | RR-GC (a) |
| $(1.03 \pm 0.06) \times 10^{-10}$ | 298 | Berndt et al., 1996 | RR (b) |

α-terpinene is 1-isopropyl-4-methyl-cyclohexa-1,3-diene.

### Comments

(a) 4000 L Teflon chamber at 980 mbar (735 Torr) of air. $NO_3$ was generated by the thermal decomposition of $N_2O_5$. Correction made to the α-terpinene loss rate due to reaction with $NO_2$ was 10 – 47 %. α-terpinene and 2,3-dimethyl-2-butene (reference reactant) were monitored by GC. The rate constant ratio, $k(NO_3$ + α-terpinene) / $k(NO_3$ + 2,3-dimethyl-2-butene) = 3.18 ± 0.13 is placed on an absolute basis using $k(NO_3$ + 2,3-dimethyl-2-butene) = $5.72 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (Atkinson and Arey, 2003).

(b) Flow tube at 15 mbar $N_2$. $NO_3$ was generated by the thermal decomposition of $N_2O_5$. Various detection schemes (electron impact MS, FTIR and GC-MS/FID) were available though it is not stated which was used for the relative rate analysis. The rate constant ratio obtained, $k(NO_3$ + α-terpinene) / $k(NO_3$ + 2,3-dimethyl-2-butene) = 1.796 ± 0.10 is placed on an absolute basis using $k(NO_3$ + 2,3-dimethyl-2-butene) = $5.72 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (Atkinson and Arey, 2003).

### Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $1.8 \times 10^{-10}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.25 | 298 |

*Comments on Preferred Values*

Despite use of the same reference reactant, the two relative rate studies derive rather different rate coefficients. It is not clear whether this is due to the different pressures and bath gases used. The preferred value of the room temperature rate coefficient is based on the relative rate study of Atkinson et al. (1985) in which the experiments were carried out at roughly atmospheric pressure and in air. The error limits are expanded to reflect the poor agreement between the two studies and the necessity to correct for removal of α-terpinene by reaction with $NO_2$.

The large rate constant indicates that addition of $NO_3$ across a double bond to form a nitrooxy- radical is the initial step. Organic nitrates (but not peroxy-nitrates or carbonyls) have been observed in $N_2/O_2$ bath gas and p-cymene is observed at yields of ~6 % at pressures of $N_2$ or air above 100 Torr (Berndt et al., 1996).

**References**

Atkinson, R., Aschmann, S. M., Winer, A. M., and Pitts, J. N., Env. Sci. Tech., 19, 159-163, 1985.
Atkinson, R., and Arey, J., Chem. Rev., 103, 4605-4638, 2003.
Berndt, T., Böge, O., Kind, I., and Rolle, W., Ber. Bunsen-Ges.Phys. Chem., 100, 462-469, 1996.

## Datasheet NO3_VOC41

**$NO_3$ +**  **(γ-terpinene) → products**

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $(2.4 \pm 0.7) \times 10^{-11}$ | 298 | Martínez et al., 1999 | DF-LIF (a) |
| $(3.6 \pm 0.7) \times 10^{-11}$ | 433 | | |
| *Relative Rate Coefficients* | | | |
| $(2.94 \pm 0.05) \times 10^{-11}$ | 294 | Atkinson et al., 1985 | RR (b) |

γ-terpinene is 1-isopropyl-4-methyl-cyclohexa-1,4-diene.

### Comments

(a) $NO_3$ radicals ($6\text{-}30 \times 10^{11}$ molecule cm$^{-3}$) generated from reaction of F atoms (made in a microwave discharge through $F_2$/He) with $HNO_3$. Flow tube was operated at ~1.33 mbar (1 Torr) He. γ-terpinene was present at similar concentrations (1-3 fold) to $NO_3$. So that absolute $NO_3$ concentrations (derived by titration with tetramethylethene) were necessary to derive the rate coefficient.

(b) 4000 L Teflon chamber at 980 mbar (735 Torr) of air. $NO_3$ was generated by the thermal decomposition of $N_2O_5$. γ-terpinene and 2-methyl-2-butene (reference reactant) were monitored by GC. Correction made to the γ -terpinene loss rate due to reaction with $NO_2$ was <1 %. The rate constant ratio, $k$($NO_3$ + γ-terpinene) / $k$($NO_3$ + 2-methyl-2-butene) = $3.14 \pm 0.05$ is placed on an absolute basis using $k$($NO_3$ + 2-methyl-2-butene) = $9.37 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (Atkinson and Arey, 2003).

### Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $2.9 \times 10^{-11}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | $\pm 0.12$ | 298 |

*Comments on Preferred Values*

The preferred value of the room temperature rate coefficient is based on the relative rate study of Atkinson et al. (1985) in which accurate determination of the reactant concentrations was not required. The error limits are expanded to reflect the necessity to correct for removal of γ-terpinene by reaction with $NO_2$ and the ≈ 20 % difference to the absolute rate measurement at the same temperature (Martínez et al., 1999). The difference between the rate coefficients obtained at 298 and 433 K (factor 1.5) was not considered large enough to warrant a more detailed investigation of the temperature dependence (Martínez et al., 1999).

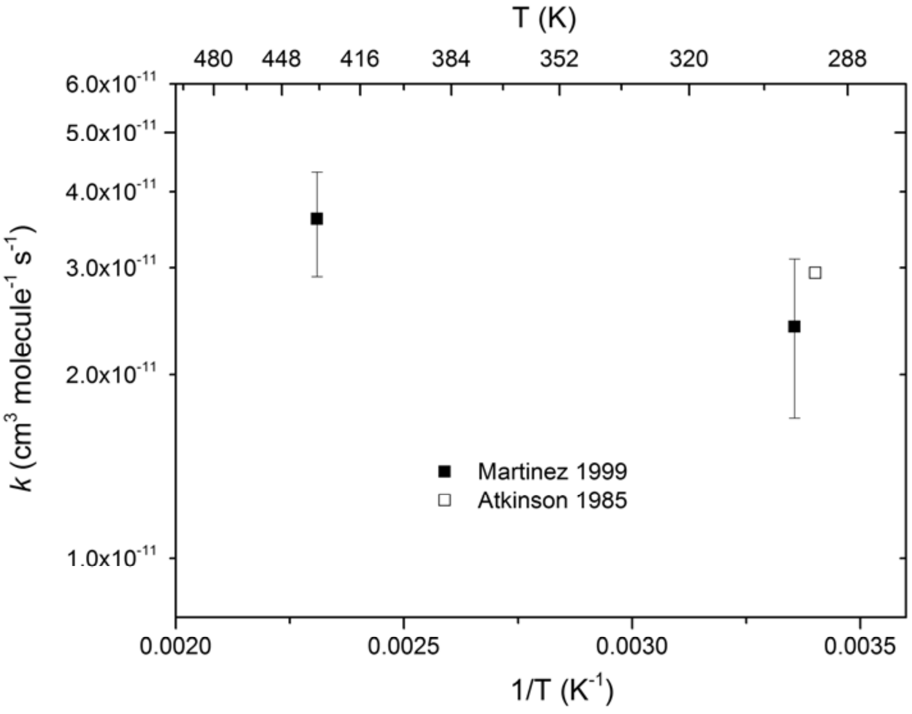
There are no product studies of this reaction, though the large rate constant indicates that the reaction proceeds mainly via addition of $NO_3$ across a double bond to form a chemically activated nitrooxyalkyl radical. At pressures found in the troposphere this adduct will undergo collisional stabilization prior to reaction with $O_2$ to form a nitrooxyalkyl peroxy radical or decompose to release $NO_2$. At atmospheric pressure the formation of the peroxy radical will generally dominate.

## References

Atkinson, R., Aschmann, S. M., Winer, A. M., and Pitts, J. N., Env. Sci. Tech., 19, 159-163, 1985.

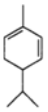
Atkinson, R., and Arey, J., Chem. Rev., 103, 4605-4638, 2003.

Martínez, E., Cabañas, B., Aranda, A., Martín, P., and Salgado, S., J. Atmos. Chem., 33, 265-282, 1999.



Rate coefficients for $NO_3$ + γ-terpinene

## Datasheet NO3_VOC42

## $NO_3$ +  (α-phellandrene) → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $(4.2 \pm 1.0) \times 10^{-11}$ | 298 | Martínez et al., 1999 | DF-LIF (a) |
| $1.9 \times 10^{-9} \exp[-(1158 \pm 270)/T]$ | 298-433 | | |
| *Relative Rate Coefficients* | | | |
| $(8.52 \pm 0.63) \times 10^{-11}$ | 294 | Atkinson et al., 1985 | RR (b) |
| $(5.98 \pm 0.20) \times 10^{-11}$ | 298 | Berndt et al., 1996 | RR (c) |

α-phellandrene is 2-methyl-5-(1-methylethyl)-1,3-cyclohexadiene.

## Comments

(a) $NO_3$ radicals ($6\text{-}30 \times 10^{11}$ molecule cm$^{-3}$) generated from reaction of F atoms (made in a microwave discharge through $F_2$/He) with $HNO_3$. Flow tube was operated at ~1.33 mbar (1 Torr) He. α-phellandrene was present at similar concentrations (1-3 fold) to $NO_3$. So that absolute $NO_3$ concentrations (derived by titration with tetramethylethene) were necessary to derive the rate coefficient.

(b) 4000 L Teflon chamber at 980 mbar (735 Torr) of air. $NO_3$ was generated by the thermal decomposition of $N_2O_5$. Correction made to the α-phellandrene loss rate due to reaction with $NO_2$ was 29 – 46 %. α-phellandrene and 2,3-dimethyl-2-butene (reference reactant) were monitored by GC. The rate constant ratio, $k(NO_3$ + α-phellandrene) / $k(NO_3$ + 2,3-dimethyl-2-butene) = 1.49 ± 0.11 is placed on an absolute basis using $k(NO_3$ + 2,3-dimethyl-2-butene) = $5.72 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (Atkinson and Arey, 2003).

(c) Flow tube at 15 mbar $N_2$. $NO_3$ was generated by the thermal decomposition of $N_2O_5$, 2,3-dimethyl-2-butene was used as reference reactant. Various detection schemes (electron impact MS, FTIR and GC-MS/FID) were available though it is not stated which was used for the relative rate analysis. The rate constant ratio obtained, $k(NO_3$ + α-phellandrene) / $k(NO_3$ + 2,3-dimethyl-2-butene) = 1.046 ± 0.035 is placed on an absolute basis using $k(NO_3$ + 2,3-dimethyl-2-butene) = $5.72 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (Atkinson and Arey, 2003).

## Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $7.3 \times 10^{-11}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.15 | 298 |

*Comments on Preferred Values*

The preferred value of the room temperature rate coefficient is an average of the two relative rate studies in which accurate determination of the reactant concentrations was not required. The error limits are expanded to reflect the necessity to correct for removal of α-phellandrene by reaction with $NO_2$ and the poor agreement between the three studies. The significant, positive dependence of *k* on temperature observed by Martínez et al. (1999) requires validation.

The large rate constant indicates that addition of $NO_3$ across a double bond to form a nitrooxyalkyl radical is the initial step. This can decompose to c-cymene, with a yield of ~ 20 % at pressures above 150 mbar $N_2$ or air (Berndt et al., 1996). Organic nitrates (but not peroxy-nitrates or carbonyls) have been observed in $N_2/O_2$ bath gas.

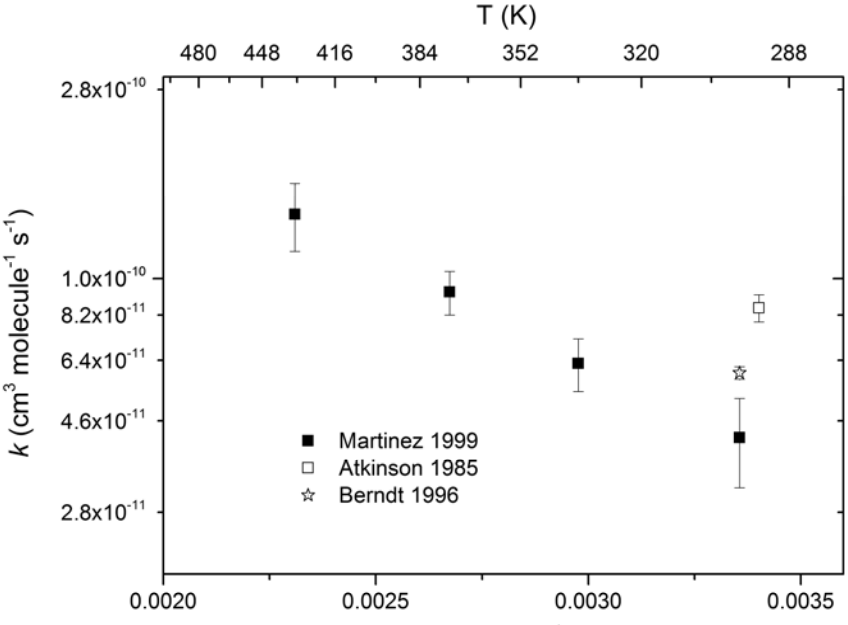
## References

Atkinson, R., Aschmann, S. M., Winer, A. M., and Pitts, J. N., Env. Sci. Tech., 19, 159-163, 1985.

Atkinson, R., and Arey, J., Chem. Rev., 103, 4605-4638, 2003.

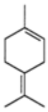
Berndt, T., Böge, O., Kind, I., and Rolle, W., Ber. Bunsen-Ges.Phys. Chem., 100, 462-469, 1996.

Martínez, E., Cabañas, B., Aranda, A., Martín, P., and Salgado, S., J. Atmos. Chem., 33, 265-282, 1999.



Rate coefficients for $NO_3$ + γ-phellandrene

## Datasheet NO3_VOC43

**$NO_3$ +**  **(terpinolene) → products**

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $(5.2 \pm 0.9) \times 10^{-11}$ | 298 | Martínez et al., 1999 | DF-LIF (a) |
| $(7.5 \pm 1.0) \times 10^{-11}$ | 433 | | |
| *Relative Rate Coefficients* | | | |
| $(9.67 \pm 0.51) \times 10^{-11}$ | 295 | Corchnoy and Atkinson, 1990 | RR (b) |
| $(6.12 \pm 0.52) \times 10^{-11}$ | 298 | Stewart et al., 2013 | RR (c) |

Terpinolene is 4-isopropylidene-1-methyl-cyclohexene.

### Comments

(a) $NO_3$ radicals ($6\text{-}30 \times 10^{11}$ molecule cm$^{-3}$) generated from reaction of F atoms (made in a microwave discharge through $F_2$/He) with $HNO_3$. Flow tube was operated at ~1.33 mbar (1 Torr) He. Terpinolene was present at similar concentrations (1-3 fold) to $NO_3$ and absolute $NO_3$ concentrations (derived by titration with tetramethylethene) were necessary to derive the rate coefficient.

(b) 6400 L Teflon chamber at 980 mbar (735 Torr) of air. $NO_3$ was generated by the thermal decomposition of $N_2O_5$. Terpinolene and 2,3-dimethyl-2-butene (reference reactant) were monitored by GC. The rate constant ratio $k$($NO_3$ + terpinolene) / ($k$($NO_3$ + 2,3-dimethyl-2-butene) = 1.69 ± 0.09 is placed on an absolute basis using $k$($NO_3$ + 2,3-dimethyl-2-butene) = $5.72 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson and Arey, 2003).

(c) 1 L glass vessel at 1013 mbar (760 Torr) of air. Relative changes in concentration of terpinolene and limonene (reference reactant) were monitored by GC. The rate constant ratio $k$($NO_3$ + terpinolene) / ($k$($NO_3$ + limonene) = 5.10 ± 0.43 is placed on an absolute basis using $k$($NO_3$ + limonene) = $1.2 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019).

### Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $9.7 \times 10^{-11}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.25 | 298 |

*Comments on Preferred Values*

The preferred value of the room temperature rate coefficient is based on the relative rate study of Corchnoy and Atkinson (1990) in which accurate determination of the reactant concentrations was not required. The error limits are expanded to reflect the poor agreement with the absolute rate measurement at the same temperature (Martínez et al., 1999) and the relative rate study of Stewart et al (2013). The difference between the rate coefficients obtained at 298 and 433 K (factor 1.44) was not considered large enough to warrant a more detailed investigation of the temperature dependence (Martínez et al., 1999).

There are no product studies of this reaction, though the large rate constant indicates that the reaction proceeds mainly via addition of $NO_3$ across a double bond to form a chemically activated nitrooxyalkyl radical. At pressures found in the troposphere this adduct will undergo collisional stabilization prior to reaction with $O_2$ to form a nitrooxyalkyl peroxy radical or decompose to release $NO_2$. At atmospheric pressure the formation of the peroxy radical will generally dominate.

## References

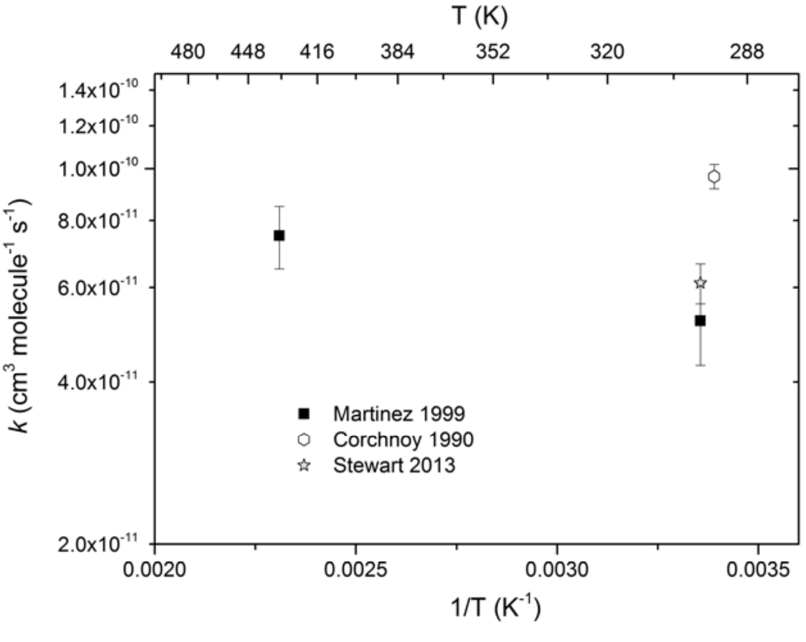
Atkinson, R., and Arey, J., Chem. Rev., 103, 4605-4638, 2003.

Corchnoy, S. B., and Atkinson, R., Env. Sci. Tech., 24, 1497-1502, 1990.

IUPAC, Task Group on Atmospheric Chemical kinetic data evaluation. (Ammann, M., Atkinson, R., Cox, R.A., Crowley, J.N., Hynes, R. G., Jenkin, M.E., Mellouki, W., Rossi, M. J., Troe, J. and Wallington, T. J.) Evaluated kinetic data: http://iupac.pole-ether.fr, 2019.

Martínez, E., Cabañas, B., Aranda, A., Martín, P., and Salgado, S., J. Atmos. Chem., 33, 265-282, 1999.

Stewart, D. J., Almabrok, S. H., Lockhart, J. P., Mohamed, O. M., Nutt, D. R., Pfrang, C., and Marston, G., Atmos. Env., 70, 227-235, 2013.



Rate coefficients for $NO_3$ + terpinolene

## Datasheet NO3_VOC46

### $NO_3$ +  (camphene) → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $(6.2 \pm 2.1) \times 10^{-13}$ | 298 | Martínez et al., 1998 | DF-LIF (a) |
| $3.1 \times 10^{-12} \exp[(-481 \pm 55)/T]$ | 298-433 | | |
| *Relative Rate Coefficients* | | | |
| $(6.59 \pm 0.16) \times 10^{-13}$ | 296 | Atkinson et al., 1990 | RR (b) |

Camphene is 2,2-dimethyl-3-methylene-bicyclo[2.2.1]heptane.

## Comments

(a) $NO_3$ radicals (≈ 3-6 × $10^{12}$ molecule cm$^{-3}$) generated from reaction of F atoms (made in a microwave discharge through $F_2$/He) with $HNO_3$. Flow tube was operated at ~1.33 mbar (1 Torr) He at 4 temperatures between 298 and 393 K. Camphene was present at similar concentrations (≈3-20 × $10^{12}$ molecule cm$^{-3}$) to $NO_3$. So that absolute $NO_3$ concentrations (derived by titration with tetramethylethene) were necessary to derive the rate coefficient.

(b) Loss of camphene and trans-2-butene (reference reactant) in a 6400 L Teflon chamber at 980 mbar (735 Torr) of air were monitored by GC following exposure to $NO_3$ radicalsVOC55 generated by the thermal decomposition of $N_2O_5$. The rate constant ratio, $k(NO_3 + \text{camphene}) / k(NO_3 + \text{trans-2-butene}) = 1.69 \pm 0.04$ required correction for an impurity in the camphene sample and is placed on an absolute basis using $k(NO_3 + \text{trans-2-butene}) = 3.9 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (IUPAC, 2019).

## Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.6 \times 10^{-13}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.10 | 298 |

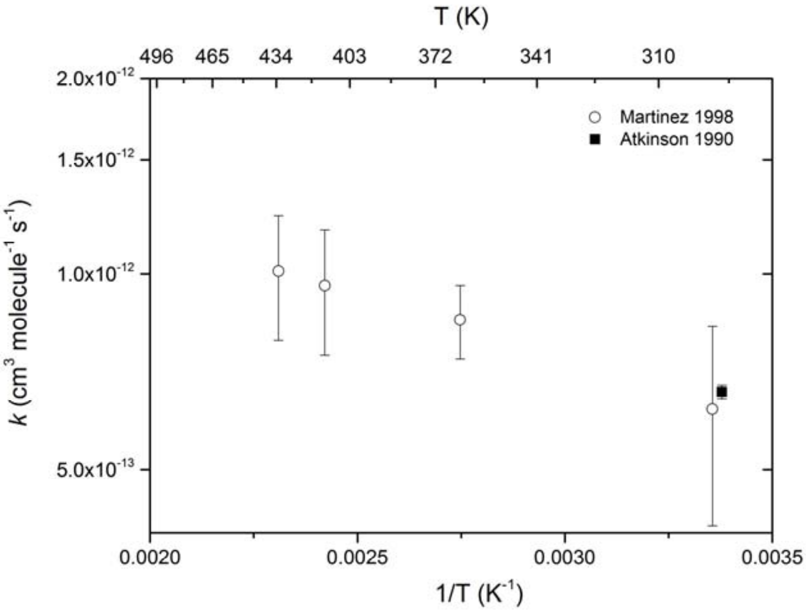
*Comments on Preferred Values*

The preferred value at 298 K is based on the relative rate study of Atkinson et al. 1990, which agrees with the absolute study of Martínez et al. (1999). The significant, positive dependence of $k$ on temperature observed by Martínez et al. (1999) requires validation.

There are no product studies of this reaction, though by analogy to other $NO_3$ + terpene reactions, the reaction will proceed mainly via addition of $NO_3$ across a double bond to form a chemically activated nitrooxyalkyl radical. At pressures found in the troposphere this adduct will undergo collisional stabilization prior to reaction with $O_2$ to form a nitrooxyalkyl peroxy radical.

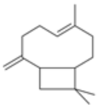
## References

Atkinson, R., Aschmann, S. M., and Arey, J., Atmos. Env. A, 24, 2647-2654, 1990.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Martínez, E., Cabañas, B., Aranda, A. and Martín, P., Env. Sci. Tech., 32, 3730-3734, 1998.



Rate coefficients for the reaction $NO_3$ + camphene

## Datasheet NO3_VOC47

**$NO_3$ +**  **(β-caryophyllene) → products**

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(1.92 \pm 0.35) \times 10^{-11}$ | 296 | Shu and Atkinson, 1995 | RR (a) |

β-caryophyllene is: *trans*-(1*R*,9*S*)-8-Methylene-4,11,11-trimethylbicyclo[7.2.0]undec-4-ene.

### Comments

(a) Relative rate of loss of β-caryophyllene and 2-methyl-2-butene (reference reactant) in a 6700 L Teflon chamber at 987 mbar (740 Torr) of air were monitored by GC-FID. $NO_3$ was generated by the thermal decomposition of $N_2O_5$. A correction was applied to take into account loss of β-caryophyllene by reaction with $NO_2$. The rate constant ratio, $k(NO_3 + \beta\text{-caryophyllene}) / k(NO_3 + \text{2-methyl-2-butene}) = 2.05 \pm 0.37$ is placed on an absolute basis using $k(NO_3 + \text{2-methyl-2-butene}) = 9.37 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (Atkinson and Arey, 2003).

### Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $1.9 \times 10^{-11}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.25 | 298 |

*Comments on Preferred Values*

The preferred value at 298 K is based on the relative rate study of Shu and Atkinson (1995). The error limits have been expanded to reflect the fact that this is the only study available. The rate coefficient is consistent with estimates based on the number of double bonds and the number and position of the alkyl substituents (Atkinson 1991).

There are no studies of the gas-phase products of this reaction, though it is expected to proceed predominantly via addition of $NO_3$ across a double bond to form a nitrooxyalkyl radical which can react with $O_2$ to form a nitrooxyalkyl peroxy radical.

Secondary aerosol is formed efficiently in chamber studies of the $NO_3$-radical initiated oxidation of β-caryophyllene with yields (defined as the mass of aerosol formed per mass of β-caryophyllene reacted) of close to 100 % (Jaoui et al., 2013; Fry et al., 2014) with compounds of molecular weight up to *m/z* 375 identified. Product organic nitrates have low vapour pressures and have been found to partition entirely to the aerosol phase (Fry et al., 2014).

## References

Atkinson, R., J. Phys. Chem. Ref. Data, 20, 459-507, 1991.

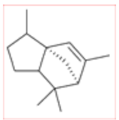
Atkinson, R., and Arey, J., Chem. Rev., 103, 4605-4638, 2003.

Fry, J. L., Draper, D. C., Barsanti, K. C., Smith, J. N., Ortega, J., Winkle, P. M., Lawler, M. J., Brown, S. S., Edwards, P. M., Cohen, R. C., and Lee, L., Env. Sci. Tech., 48, 11944-11953, 2014.

Jaoui, M., Kleindienst, T. E., Docherty, K. S., Lewandowski, M., and Offenberg, J. H., Environmental Chemistry, 10, 178-193, 2013.

Shu, Y. H., and Atkinson, R., J. Geophys. Res., 100, 7275-7281, 1995.

## Datasheet NO3_VOC48

**$NO_3$ +**  **(α-cedrene) → products**

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(8.16 \pm 0.72) \times 10^{-12}$ | 296 | Shu andAtkinson., 1995 | RR (a) |

α -cedrene is: (1*S*,2*R*,5*S*,7*R*)-2,6,6,8-tetramethyltricyclo[5.3.1.0$^{1,5}$]undec-8-ene

### Comments

(a) Relative rate of loss of α-cedrene and 2-methyl-2-butene (reference reactant) in a 6700 L Teflon chamber at 987 mbar (740 Torr) of air were monitored by GC-FID. $NO_3$ was generated by the thermal decomposition of $N_2O_5$. The rate constant ratio, $k(NO_3 + \alpha\text{-cedrene}) / k(NO_3 + \text{2-methyl-2-butene}) = 0.871 \pm 0.077$ is placed on an absolute basis using $k(NO_3 + \text{2-methyl-2-butene}) = 9.37 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (Atkinson and Arey, 2003).

### Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $8.2 \times 10^{-12}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.25 | 298 |

*Comments on Preferred Values*

The preferred value at 298 K is based on the relative rate study of Shu and Atkinson (1995). The error limits have been expanded to reflect the fact that this is the only study available. The rate coefficient is consistent with estimates based on the number of double bonds and the number and position of the alkyl substituents (Atkinson, 1991).

There are no studies of the gas-phase products of this reaction, though it is expected to proceed predominantly via addition of $NO_3$ across the double bond to form a nitrooxyalkyl radical which can react with $O_2$ to form a nitrooxyalkyl peroxy radical.

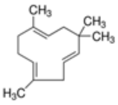
Secondary aerosol is formed efficiently in chamber studies of the $NO_3$-radical initiated oxidation of α-cedrene (Jaoui et al., 2013).

### References

Atkinson, R., J. Phys. Chem. Ref. Data, 20, 459-507, 1991.
Atkinson, R., and Arey, J., Chem. Rev., 103, 4605-4638, 2003.

Jaoui, M., Kleindienst, T. E., Docherty, K. S., Lewandowski, M., and Offenberg, J. H., Environ. Chem., 10, 178-193, 2013.
Shu, Y. H., and Atkinson, R., J. Geophys. Res., 100, 7275-7281, 1995.

## Datasheet NO3_VOC49

**$NO_3$ +**  **(α-humulene) → products**

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(3.53 \pm 0.26) \times 10^{-11}$ | 296 | Shu and Atkinson, 1995 | RR (a) |

α-humulene is: (1E,4E,8E)-2,6,6,9-tetramethylcycloundeca-1,4,8-triene

### Comments

(a) Loss of α-humulene and 2-methyl-2-butene (reference reactant) in a 6700 L Teflon chamber at 987 mbar (740 Torr) of air were monitored by GC-FID. $NO_3$ was generated by the thermal decomposition of $N_2O_5$. The rate constant ratio, $k$(α-humulene) / $k$($NO_3$ + 2-methyl-2-butene) = 3.77 ± 0.28 is placed on an absolute basis using $k$($NO_3$ + 2-methyl-2-butene) = $9.37 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (Atkinson and Arey, 2003).

### Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $3.5 \times 10^{-11}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.25 | 298 |

*Comments on Preferred Values*

The preferred value at 298 K is based on the relative rate study of Shu and Atkinson (1995). The error limits have been expanded to reflect the fact that this is the only study available. The rate coefficient is consistent with estimates based on the number of double bonds and the number and position of the alkyl substituents (Atkinson, 1991).

There are no studies of the gas-phase products of this reaction, though it is expected to proceed predominantly via addition of $NO_3$ across the double bond to form a nitrooxyalkyl radical which can react with $O_2$ to form a nitrooxyalkyl peroxy radical.

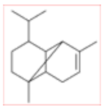
Secondary aerosol is formed efficiently in chamber studies of the $NO_3$-radical initiated oxidation of α-humulene (Jaoui et al., 2013).

### References

Atkinson, R., J. Phys. Chem. Ref. Data, 20, 459-507, 1991.
Atkinson, R., and Arey, J., Chem. Rev., 103, 4605-4638, 2003.

Jaoui, M., Kleindienst, T. E., Docherty, K. S., Lewandowski, M., and Offenberg, J. H., Environ. Chem., 10, 178-193, 2013.
Shu, Y. H., and Atkinson, R., J. Geophys. Res. -Atmos., 100, 7275-7281, 1995.

## Datasheet NO3_VOC50

**$NO_3$ +**  **(α-copaene) → products**

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(1.61 \pm 0.07) \times 10^{-11}$ | 296 | Shu and Atkinson, 1995 | RR (a) |

α -copaene is: (1*R*,2*S*,6*S*,7*S*,8*S*)-8-isopropyl-1,3-dimethyltricyclo[4.4.0.0$^{2,7}$]dec-3-ene.

### Comments

(a) Loss of α-copaene and 2-methyl-2-butene (reference reactant) in a 6700 L Teflon chamber at 987 mbar (740 Torr) of air were monitored by GC-FID on exposure to $NO_3$ radicals. $NO_3$ was generated by the thermal decomposition of $N_2O_5$. The rate constant ratio, $k(NO_3 + \alpha$-copaene) / $k(NO_3$ + 2-methyl-2-butene) = $1.72 \pm 0.08$ is placed on an absolute basis using $k(NO_3$ + 2-methyl-2-butene) = $9.37 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (Atkinson and Arey, 2003).

### Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $1.6 \times 10^{-11}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | $\pm 0.25$ | 298 |

*Comments on Preferred Values*

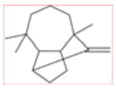
The preferred value at 298 K is based on the relative rate study of Shu and Atkinson (1995). The error limits have been expanded to reflect the fact that this is the only study available. The rate coefficient is consistent with estimates based on the number of double bonds and the number and position of the alkyl substituents (Atkinson 1991).

There are no studies of the gas-phase products of this reaction, though it is expected to proceed predominantly via addition of $NO_3$ across the double bond to form a nitrooxyalkyl radical which can react with $O_2$ to form a nitrooxyalkyl peroxy radical.

### References

Atkinson, R., J. Phys. Chem. Ref. Data, 20, 459-507, 1991.
Atkinson, R., and Arey, J., Chem. Rev., 103, 4605-4638, 2003.
Shu, Y. H., and Atkinson, R., J. Geophys. Res., 100, 7275-7281, 1995.

## Datasheet NO3_VOC51

### $NO_3$ +  (longifolene) → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(6.79 \pm 0.47) \times 10^{-13}$ | 296 | Shu and Atkinson, 1995 | RR (a) |

longifolene is: (1*R*,2*S*,7*S*,9*S*)- 3,3,7-trimethyl- 8-methylenetricyclo- [5.4.0.0$^{2,9}$]undecane.

## Comments

(a) Loss of longifolene and trans-2-butene (reference reactant) in a 6700 L Teflon chamber at 987 mbar (740 Torr) of air were monitored by GC-FID on exposure to $NO_3$ radicals. $NO_3$ was generated by the thermal decomposition of $N_2O_5$. The rate constant ratio, $k(NO_3$ + longifolene) / $k(NO_3$ + trans-2-butene) = 1.74 ± 0.12 is placed on an absolute basis using $k(NO_3$ + trans-2-butene) = $3.9 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (IUPAC, 2019).

## Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.8 \times 10^{-13}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.25 | 298 |

*Comments on Preferred Values*

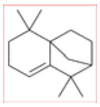
The preferred value at 298 K is based on the relative rate study of Shu and Atkinson (1995). The error limits have been expanded to reflect the fact that this is the only study available. The rate coefficient is consistent with estimates based on the number of double bonds and the number and position of the alkyl substituents (Atkinson 1991).

There are no studies of the gas-phase products of this reaction, though it is expected to proceed predominantly via addition of $NO_3$ across the double bond to form a nitrooxyalkyl radical which can react with $O_2$ to form a nitrooxyalkyl peroxy radical.

## References

Atkinson, R., J. Phys. Chem. Ref. Data, 20, 459-507, 1991.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Shu, Y. H., and Atkinson, R., J. Geophys. Res., 100, 7275-7281, 1995.

## Datasheet NO3_VOC52

**$NO_3$ +**  **(isolongifolene) → products**

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(3.89 \pm 0.41) \times 10^{-12}$ | 298 ± 2 | Canosa-Mas et al., 1999 | RR (a) |

isolongifolene is: 2,2,7,7-Tetramethyltricyclo[6.2.1.0$^{1,6}$]undec-5-ene.

### Comments

(a) Loss of isolongifolene and α-pinene (reference reactant) in a 56 L Teflon bag at 1013 mbar (760 Torr) of $N_2$ were monitored by GC-FID following exposure to $NO_3$ radicals generated by the thermal decomposition of $N_2O_5$. The rate constant ratio, $k(NO_3 + \text{isolongifolene}) / k(NO_3 + \alpha\text{-pinene}) = 0.627 \pm 0.066$ is placed on an absolute basis using $k(NO_3 + \alpha\text{-pinene}) = 6.2 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (IUPAC, 2019).

### Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $3.9 \times 10^{-12}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.25 | 298 |

*Comments on Preferred Values*

The preferred value at 298 K is based on the relative rate study of Canosa-Mas et al. (1999). The error limits have been expanded to reflect the fact that this is the only study available.

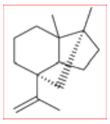
There are no studies of the gas-phase products of this reaction, though it is expected to proceed predominantly via addition of $NO_3$ across the double bond to form a nitrooxyalkyl radical which can react with $O_2$ to form a nitrooxyalkyl peroxy radical.

### References

Canosa-Mas, C. E., King, M. D., Scarr, P. J., Thompson, K. C., and Wayne, R. P., Phys. Chem. Chem. Phys., 1, 2929-2933, 1999.

IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

## Datasheet NO3_VOC53

**$NO_3$ +**  **(alloisolongifolene) → products**

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(1.41 \pm 0.24) \times 10^{-12}$ | 298 ± 2 | Canosa-Mas et al., 1999 | RR (a) |

alloisolongifolene is: (4R,7aS)-1,7a-Dimethyl-4-(prop-1-en-2-yl)octahydro-1H-1,4-methanoindene.

### Comments

(a) Loss of alloisolongifolene and cyclohexa-1,4-diene (reference reactant) in a 56 L Teflon bag at 1013 mbar (760 Torr) of $N_2$ were monitored by GC-FID following exposure to $NO_3$ radicals generated by the thermal decomposition of $N_2O_5$. The rate constant ratio, $k(NO_3$ + alloisolongifolene) / $k(NO_3$ + cyclohexa-1,4-diene) = 2.14 ± 0.37 is placed on an absolute basis using $k(NO_3$ + cyclohexa-1,4-diene) = $6.6 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (Atkinson and Arey, 2003).

### Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $1.4 \times 10^{-12}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.25 | 298 |

*Comments on Preferred Values*

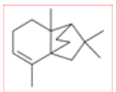
The preferred value at 298 K is based on the relative rate study of Canosa-Mas et al. (1999). The error limits have been expanded to reflect the fact that this is the only study available.

There are no studies of the gas-phase products of this reaction, though it is expected to proceed predominantly via addition of $NO_3$ across the double bond to form a nitrooxyalkyl radical which can react with $O_2$ to form a nitrooxyalkyl peroxy radical.

### References

Atkinson, R., and Arey, J., Chem. Rev., 103, 4605-4638, 2003.
Canosa-Mas, C. E., King, M. D., Scarr, P. J., Thompson, K. C., and Wayne, R. P., Phys. Chem. Chem. Phys., 1, 2929-2933, 1999.

## Datasheet NO3_VOC54

**$NO_3$ +**  **(α-neoclovene) → products**

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(8.25 \pm 2.1) \times 10^{-12}$ | 298 ± 2 | Canosa-Mas et al., 1999 | RR (a) |

α-neoclovene is: (1S,7aS)-1,2,3,6,7,7a-Hexahydro-2,2,4,7a-tetramethyl-1,3a-ethano-3aH-indene.

### Comments

(a) Loss of α-neoclovene and α-pinene (reference reactant) in a 56 L Teflon bag at 1013 mbar (760 Torr) of $N_2$ were monitored by GC-FID following exposure to $NO_3$ radicals generated by the thermal decomposition of $N_2O_5$. Significant loss of α-neoclovene was observed in the absence of $NO_3$ and correction was applied. The resulting rate constant ratio, $k(NO_3 + \alpha\text{-neoclovene}) / k(NO_3 + \alpha\text{-pinene}) = 1.33 \pm 0.34$ is placed on an absolute basis using $k(NO_3 + \alpha\text{-pinene}) = 6.2 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (IUPAC, 2019).

### Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $8.25 \times 10^{-12}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.25 | 298 |

*Comments on Preferred Values*

The preferred value at 298 K is based on the relative rate study of Canosa-Mas et al. (1999). The error limits have been expanded to reflect the fact that this is the only study available.

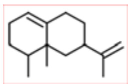
There are no studies of the gas-phase products of this reaction, though it is expected to proceed predominantly via addition of $NO_3$ across the double bond to form a nitrooxyalkyl radical which can react with $O_2$ to form a nitrooxyalkyl peroxy radical.

### References

Canosa-Mas, C. E., King, M. D., Scarr, P. J., Thompson, K. C., and Wayne, R. P., Phys. Chem. Chem. Phys., 1, 2929-2933, 1999.

IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

## Datasheet NO3_VOC55

**$NO_3$ +**  **(valencene) → products**

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(7.9 \pm 0.2) \times 10^{-12}$ | 298 ± 2 | Ham, 2013. | RR (a) |

valencene is: (2*R*)-8,8, 8a-trimethyl-2-prop-1-en-2-yl- 1,2,3,4,6,7-hexahydronaphthalene.

### Comments

(a) Loss of valencene and 3-carene or limonene (reference reactants) in a ≈ 100 L Teflon bag at atmospheric pressure of air were monitored by GC-MS following exposure to $NO_3$ radicals generated by the thermal decomposition of $N_2O_5$. The measured rate coefficient ratios were not reported. Ham (2013) used reference rate coefficients for $NO_3$ + 3-carene ($9.1\times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) and $NO_3$ + limonene ($1.22 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) that agree with present IUPAC recommendations (IUPAC, 2019).

### Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $7.9 \times 10^{-12}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.25 | 298 |

*Comments on Preferred Values*

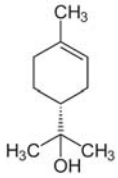
The preferred value at 298 K is based on the relative rate study of Ham, (2013). The error limits have been expanded to reflect the fact that this is the only study available.

There are no studies of the gas-phase products of this reaction, though it is expected to proceed predominantly via addition of $NO_3$ across the double bond to form a nitrooxyalkyl radical which can react with $O_2$ to form a nitrooxyalkyl peroxy radical.

### References

Ham, J. E., Int. J. Chem. Kinet., 45, 508-514, 2013.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

## Datasheet NO3_VOC56

$NO_3$ +  (α-terpineol) → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(1.9 \pm 0.2) \times 10^{-11}$ | 297 ± 3 | Jones and Ham, 2008. | RR (a) |
| $(1.6 \pm 0.2) \times 10^{-11}$ | | | RR (b) |

(α-terpineol is: (2-(4-methyl-1-cyclohex-3-enyl)propan-2-ol).

### Comments

(a) Loss of α-terpineol and either 2-carene or 3-carene (reference reactants) in a ≈ 65 L Teflon bag at atmospheric pressure of air were monitored by GC-MS following exposure to $NO_3$ radicals generated by the thermal decomposition of $N_2O_5$. The rate coefficient ratio $k$(α-terpineol) / $k$(2-carene) = 0.95 ± 0.02 was put on an absolute basis using $k$(2-carene) = $2.0 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019).

(b) See note (a). $k$(α-terpineol)/$k$(3-carene) = 1.76 ± 0.02 was put on an absolute basis using $k$(3-carene) = $9.1 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019).

### Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $1.7 \times 10^{-11}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.25 | 298 |

*Comments on Preferred Values*

The preferred value at 298 K is an averge of the relative rate studies of Jones and Ham, (2008). The error limits have been expanded to reflect the fact that this is the only study available.

Jones and Ham (2008) identified carbonyls, dicarbonyls and hydroxy-nitrates as the products of the reaction between $NO_3$ and terpineol, concluding that both addition of $NO_3$ to the double bond as well as abstraction of the tertiary H-atom take place. Yields were not reported.

## References

Jones, B.T., and Ham, J. E., Atmos. Env., 42, 6689-6698, 2008.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

## Datasheet NO3_AROM1

### $NO_3 + C_6H_6$ (Benzene) → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $\leq 5 \times 10^{-17}$ | 300 | Japar and Niki, 1975 | RR-FTIR (a) |
| $\leq 2.7 \times 10^{-17}$ | 298 ± 1 | Atkinson et al., 1984a | RR-FTIR (b) |
| $< 6 \times 10^{-17}$ | 298 ± 1 | Atkinson et al., 1984b | RR-FTIR (c) |

### Comments

(a) $NO_3$ radicals were generated from the thermal decomposition of $N_2O_5$. The experimental data were relative to the equilibrium coefficient $K$ for the $NO_3 + NO_2 \leftrightarrow N_2O_5$ reactions, and are placed on an absolute basis using $K = 2.15 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ at 300 K (IUPAC, 2019).

(b) $NO_3$ radicals were generated from the thermal decomposition of $N_2O_5$. The concentrations of benzene and ethene (the reference compound) were measured by GC, and a rate coefficient ratio of $k(NO_3$ + benzene$)/k(NO_3$ + ethene$) \leq 0.13$ obtained. This rate coefficient ratio is placed on an absolute basis using $k(NO_3$ + ethene$) = 2.1 \times 10^{-16}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (IUPAC, 2019).

(c) $NO_3$ radicals were generated from the thermal decomposition of $N_2O_5$. The concentrations of toluene and *n*-heptane (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(NO_3$ + benzene$)/k(NO_3$ + *n*-heptane$) < 0.4$ is placed on an absolute basis using $k(NO_3$ + *n*-heptane$) = 1.5 \times 10^{-16}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (Atkinson and Arey, 2003).

### Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $< 3 \times 10^{-17}$ | 298 |

*Comments on Preferred Values*

All three room temperature relative rate measurements (Japar and Niki, 1975; Atkinson et al., 1984a,b) obtained only upper limits to the rate coefficient. These studies are the basis for the preferred value.

### References

Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.

Atkinson, R., Plum, C. N., Carter, W. P. L., Winer, A. M. and Pitts Jr., J. N.: J. Phys. Chem., 88, 1210, 1984a.

Atkinson, R., Carter, W. P. L., Plum, C. N., Winer, A. M. and Pitts Jr., J. N.: Int. J. Chem. Kinet., 16, 887, 1984b.

IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

Japar, S. M. and Niki, H.: J. Phys. Chem., 79, 1629, 1975.

## Datasheet NO3_AROM2

### $NO_3 + C_6H_5CH_3$ (toluene) → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $\leq 5 \times 10^{-17}$ | 300 | Japar and Niki, 1975 | RR-FTIR (a) |
| $\leq 3.8 \times 10^{-15}$ | 300 ± 1 | Carter et al., 1981 | RR-GC (b) |
| $(6.7 \pm 2.6) \times 10^{-17}$ | 298 ± 1 | Atkinson et al., 1984a | RR-GC (c) |
| $(6.75 \pm 1.65) \times 10^{-17}$ | 298 ± 1 | Atkinson et al., 1984b | RR-GC (d) |
| $(7.81 \pm 0.83) \times 10^{-17}$ | 296 ± 2 | Atkinson and Aschmann, 1988 | RR-GC (d) |

## Comments

(a) $NO_3$ radicals were generated from the thermal decomposition of $N_2O_5$. The experimental data were relative to the equilibrium coefficient $K$ for the $NO_3 + NO_2 \leftrightarrow N_2O_5$ reactions, and are placed on an absolute basis by use of $K = 2.15 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ at 300 K (IUPAC, 2019).

(b) $NO_3$ radicals were generated from the reaction of $O_3$ with $NO_2$ in the presence of toluene and propene (the reference compound). The contribution of the $O_3$ reaction was taken into account in estimating the amount of propene reacted with $NO_3$ radicals. The concentrations of toluene and propene were monitored by GC, and the derived rate coefficient ratio is placed on an absolute basis using a rate coefficient of $k(NO_3 + \text{propene}) = 9.79 \times 10^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 300 K (IUPAC, 2019).

(c) $NO_3$ radicals were generated from the thermal decomposition of $N_2O_5$. The concentrations of toluene and ethene (the reference compound) were measured by GC, and a rate coefficient ratio of $k(NO_3 + \text{toluene})/k(NO_3 + \text{ethene}) = 0.32 \pm 0.12$ obtained. This rate coefficient ratio is placed on an absolute basis using $k(NO_3 + \text{ethene}) = 2.1 \times 10^{-16}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (IUPAC, 2019).

(d) $NO_3$ radicals were generated from the thermal decomposition of $N_2O_5$. The concentrations of toluene and *n*-heptane (the reference compound) were measured by GC. Rate coefficient ratios of $k(NO_3 + \text{toluene})/k(NO_3 + n\text{-heptane}) = 0.45 \pm 0.11$ (Atkinson et al., 1984b) and $0.57 \pm 0.06$ (Atkinson and Aschmann, 1988) were obtained. These rate coefficient ratios are placed on an absolute basis by use of rate coefficients of $k(NO_3 + n\text{-heptane}) = 1.37 \times 10^{-16}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 296 K (Atkinson, 1991) and $1.5 \times 10^{-16}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (Atkinson and Arey, 2003). Rate coefficient ratios of $k(NO_3 + C_6H_5CD_3)/k(NO_3 + n\text{-heptane}) = 0.28 \pm 0.05$ and $k(NO_3 + C_6D_5CD_3)/k(NO_3 + n\text{-heptane}) = 0.25 \pm 0.13$ at 296 ± 2 K were also determined by Atkinson and Aschmann (1988).

## Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $7.8 \times 10^{-17}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.25 | 298 |

*Comments on Preferred Values*

The room temperature relative rate measurements of Atkinson et al. (1984a, 1984b) and Atkinson and Aschmann (1988) are in good agreement, and are consistent with the upper limit of Carter et al. (1981). While the upper limit to the rate coefficient obtained by Japar and Niki (1975) relative to the equilibrium constant for the $NO_3 + NO_2 \leftrightarrow N_2O_5$ reactions is somewhat lower than the rate coefficients of Atkinson et al. (1984a,b) and Atkinson and Aschmann (1988), there are significant uncertainties in the equilibrium constant used for the $NO_3 + NO_2 \leftrightarrow N_2O_5$ reactions. The preferred 298 K value is based on the most recent study of Atkinson and Aschmann (1988). In that study, rate coefficients were also measured for the reactions of $NO_3$ radicals with $C_6H_5CD_3$ and $C_6D_5CD_3$, and the significant deuterium isotope effect for the $C_6H_5CD_3$ reaction indicates that the reaction proceeds by H- (or D-) atom abstraction from the $CH_3$ (or $CD_3$) substituent group.

$$NO_3 + C_6H_5CH_3 \rightarrow HNO_3 + C_6H_5CH_2$$

This conclusion is consistent with the trend in reaction rate coefficients for the reactions of $NO_3$ radicals with toluene, the xylenes and the trimethylbenzenes (Atkinson, 1991).

**References**

Atkinson, R.: J. Phys. Chem. Ref. Data, 20, 459, 1991.
Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
Atkinson, R., Plum, C. N., Carter, W. P. L., Winer, A. M. and Pitts Jr., J. N.: J. Phys. Chem., 88, 1210, 1984a.
Atkinson, R., Carter, W. P. L., Plum, C. N., Winer, A. M. and Pitts Jr., J. N.: Int. J. Chem. Kinet., 16, 887, 1984b.
Atkinson, R. and Aschmann, S. M.: Int. J. Chem. Kinet., 20, 513, 1988.
Carter, W. P. L., Winer, A. M. and Pitts Jr., J. N.: Environ. Sci. Technol., 15, 829, 1981.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Japar, S. M. and Niki, H.: J. Phys. Chem., 79, 1629, 1975.

## Datasheet NO3_AROM3

$$NO_3 + m\text{-}CH_3C_6H_4OH\ (m\text{-cresol}) \rightarrow CH_3C_6H_4O + HNO_3 \quad (1)$$
$$\rightarrow \text{other products} \quad (2)$$

### Rate coefficient data ($k = k_1 + k_2$)

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(8.10 \pm 1.16) \times 10^{-12}$ | 300 ± 1 | Carter et al., 1981 | RRGC (a) |
| $(1.66 \pm 0.18) \times 10^{-11}$ | 298 ± 1 | Atkinson et al., 1984 | RR-FTIR (b) |
| $\sim 1.33 \times 10^{-11}$ | 298 ± 1 | Atkinson et al., 1984 | RR-FTIR (c) |
| $(9.74 \pm 0.47) \times 10^{-12}$ | 296 ± 2 | Atkinson et al., 1992 | RR-GC (d) |

## Comments

(a) $NO_3$ radicals were generated from the reaction of $O_3$ with $NO_2$ in the presence of *m*-cresol and 2-methyl-2-butene (the reference compound) at atmospheric pressure of air. The contribution of the $O_3$ reaction was taken into account in estimating the amount of 2-methyl-2-butene reacted with $NO_3$ radicals. The concentrations of *m*-cresol and 2-methyl-2-butene were monitored by GC. The derived rate coefficient ratio is placed on an absolute basis using a rate coefficient of $k(NO_3 + \text{2-methyl-2-butene}) = 9.37 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson and Arey, 2003).

(b) $NO_3$ radicals were generated from the thermal decomposition of $N_2O_5$ in the presence of *m*-cresol and phenol (the reference compound) at atmospheric pressure of air. The concentrations of *m*-cresol and phenol were monitored by FTIR spectroscopy. The measured rate coefficient ratio of $k(NO_3 + m\text{-cresol})/k(NO_3 + \text{phenol}) = 4.36 \pm 0.46$ is placed on an absolute basis using a rate coefficient of $k(NO_3 + \text{phenol}) = 3.8 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019).

(c) $NO_3$ radicals were generated from the thermal decomposition of $N_2O_5$ at atmospheric pressure of air. The concentrations of *m*-cresol, $N_2O_5$ and $NO_2$ were monitored by FTIR spectroscopy. The rate coefficient for $NO_3$ + *m*-cresol was measured relative to the equilibrium coefficient $K$ for the reactions $NO_2 + NO_3 \leftrightarrow N_2O_5$. The experimental data are placed on an absolute basis by use of an equilibrium coefficient of $K = 2.75 \text{ x } 10^{-11}$ cm$^3$ molecule$^{-1}$ at 298 K (IUPAC, 2019). Evidence for secondary reactions removing *m*-cresol observed.

(d) $NO_3$ radicals were generated from the thermal decomposition of $N_2O_5$ in the presence of *m*-cresol and 2-methyl-2-butene (the reference compound) at atmospheric pressure of air. The concentrations of *m*-cresol and 2-methyl-2-butene were monitored by GC. The measured rate coefficient ratio of $k(NO_3 + m\text{-cresol})/k(NO_3 + \text{2-methyl-2-butene}) = 1.04 \pm 0.05$ is placed on an absolute basis using a rate coefficient of $k(NO_3 + \text{2-methyl-2-butene}) = 9.37 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson and Arey, 2003).

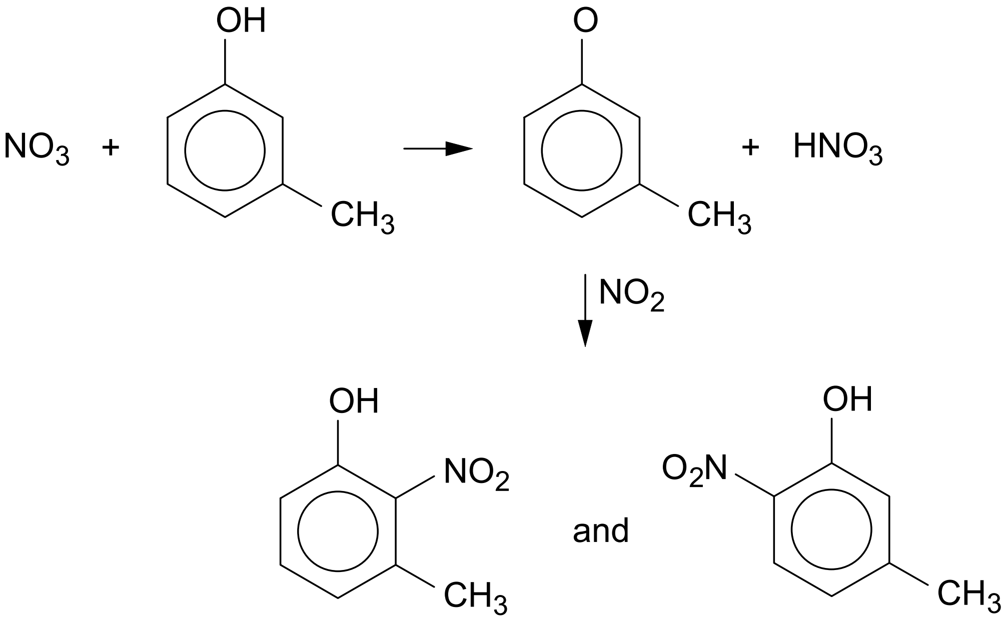
**Preferred Values**

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $1.0 \times 10^{-11}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | $\pm 0.15$ | 298 |

*Comments on Preferred Values*

The reported rate coefficients are all from relative rate studies conducted at room temperature, and range over a factor of 2. The rate coefficient of Carter et al. (1981) and that of Atkinson et al. (1984) relative to the equilibrium constant for the $NO_3 + NO_2 \leftrightarrow N_2O_5$ reactions are subject to significant uncertainties because of the concurrent reaction of $O_3$ with 2-methyl-2-butene in the Carter et al. (1981) study and the uncertainties in the equilibrium constant for the $NO_3 + NO_2 \leftrightarrow N_2O_5$ reactions in the Atkinson et al. (1984) study. The rate coefficient measured by Atkinson et al. (1984) relative to $NO_3$ + phenol is a factor of 1.7 higher than that of Atkinson et al. (1992), possibly due to difficulties in determining the small amounts of phenol reacted (Atkinson et al., 1984). The preferred value is based on the study of Atkinson et al. (1992) in which the rate coefficient was measured relative to that for $NO_3$ + 2-methyl-2-butene . The approximate (and potentially upper limit) rate coefficient of Atkinson et al. (1984) measured relative to the equilibrium constant for the $NO_3 + NO_2 \leftrightarrow N_2O_5$ reactions is in reasonable agreement with the preferred value, as is that of Carter et al. (1981).

Atkinson et al. (1992) observed the formation of 3-methyl-2-nitrophenol and 5-methyl-2-nitrophenol in 16.8 ± 2.9% and 19.6 ± 3.6% yields, respectively. 3- and 5-Methyl-2-nitrophenol formation is believed to arise from methylphenoxy + $NO_2$, and the measured 3- and 5-methyl-2-nitrophenol yields of Atkinson et al. (1992) therefore suggest that channel (1) accounts for at least 36 ± 5% of the overall reaction.



## References

Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
Atkinson, R., Aschmann, S. M., Arey, J.: Environ. Sci. Technol., 26, 1397, 1992.
Atkinson, R., Carter, W. P. L., Plum, C. N., Winer, A. M. and Pitts Jr., J. N.: Int. J. Chem. Kinet., 16, 887, 1984.
Carter, W. P. L., Winer, A. M. and Pitts Jr., J. N.: Environ. Sci. Technol., 15, 829, 1981.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

## Datasheet NO3_AROM4

$$NO_3 + o\text{-}CH_3C_6H_4OH\ (o\text{-cresol}) \rightarrow CH_3C_6H_4O + HNO_3 \quad (1)$$
$$\rightarrow \text{other products} \quad (2)$$

### Rate coefficient data ($k = k_1 + k_2$)

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(1.39 \pm 0.24) \times 10^{-11}$ | $300 \pm 1$ | Carter et al., 1981 | RR-GC (a) |
| $(1.30 \pm 0.14) \times 10^{-11}$ | $298 \pm 1$ | Atkinson et al., 1984 | RR-GC (b) |
| $(1.37 \pm 0.09) \times 10^{-11}$ | $296 \pm 2$ | Atkinson et al., 1992 | RR-GC (c) |

### Comments

(a) $NO_3$ radicals were generated from the reaction of $O_3$ with $NO_2$ in the presence of *o*-cresol and 2-methyl-2-butene (the reference compound) at atmospheric pressure of air. The contribution of the $O_3$ reaction was taken into account in estimating the amount of 2-methyl-2-butene reacted with $NO_3$ radicals. The concentrations of *o*-cresol and 2-methyl-2-butene were monitored by GC. The derived rate coefficient ratio is placed on an absolute basis using a rate coefficient of $k(NO_3 + \text{2-methyl-2-butene}) = 9.37 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson and Arey, 2003).

(b) $NO_3$ radicals were generated from the thermal decomposition of $N_2O_5$ in the presence of *o*-cresol and *m*-cresol (the reference compound) at atmospheric pressure of air. The concentrations of *o*- and *m*-cresol were monitored by GC. The measured rate coefficient ratio of $k(NO_3 + o\text{-cresol})/k(NO_3 + m\text{-cresol}) = 1.30 \pm 0.14$ is placed on an absolute basis using a rate coefficient of $k(NO_3 + m\text{-cresol}) = 1.0 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019).

(c) $NO_3$ radicals were generated from the thermal decomposition of $N_2O_5$ in the presence of *o*-cresol and 2-methyl-2-butene (the reference compound) at atmospheric pressure of air. The concentrations of *o*-cresol and 2-methyl-2-butene were monitored by GC. The measured rate coefficient ratio of $k(NO_3 + o\text{-cresol})/k(NO_3 + \text{2-methyl-2-butene}) = 1.46 \pm 0.09$ is placed on an absolute basis using a rate coefficient of $k(NO_3 + \text{2-methyl-2-butene}) = 9.37 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson and Arey, 2003).

### Preferred Values

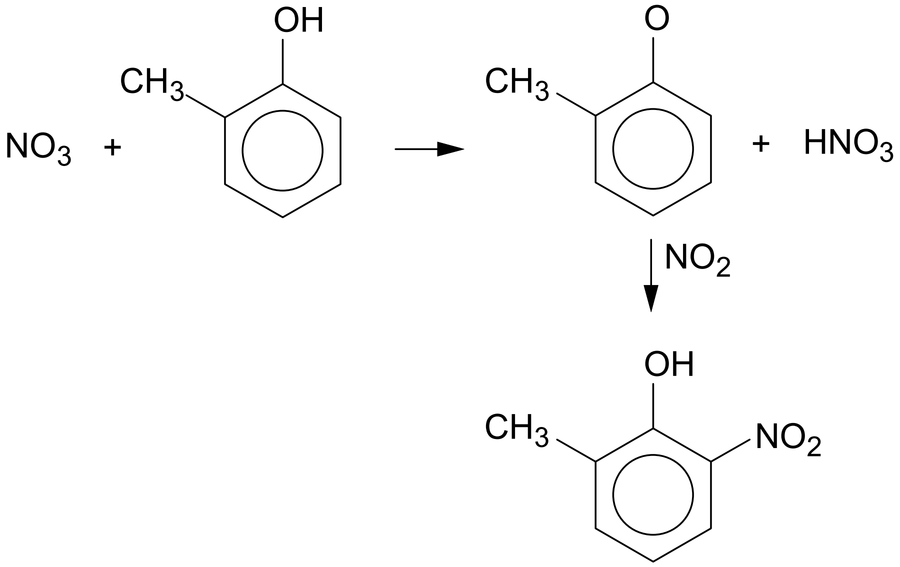
| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $1.4 \times 10^{-11}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | $\pm 0.15$ | 298 |

*Comments on Preferred Values*

The reported rate coefficients are all from relative rate studies conducted at room temperature, and are in very good agreement. The preferred value is based on the study of Atkinson et al. (1992) in which the rate coefficient was measured relative to that for $NO_3$ + 2-

methyl-2-butene . The good agreement of the rate coefficient of Atkinson et al. (1984) relative to that for $NO_3$ + *m*-cresol with the preferred value is gratifying, showing good self-consistency between the recommended rate coefficients for the reactions of $NO_3$ radicals with *o*- and *m*-cresol.

Atkinson et al. (1992) observed the formation of 6-methyl-2-nitrophenol in 12.8 ± 2.8% yield. 6-Methyl-2-nitrophenol formation is believed to arise from methylphenoxy + $NO_2$, and the measured 6-methyl-2-nitrophenol yield of Atkinson et al. (1992) therefore suggests that channel (1) accounts for at least 13 ± 3% of the overall reaction.



## References

Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
Atkinson, R., Aschmann, S. M., Arey, J.: Environ. Sci. Technol., 26, 1397, 1992.
Atkinson, R., Carter, W. P. L., Plum, C. N., Winer, A. M. and Pitts Jr., J. N.: Int. J. Chem. Kinet., 16, 887, 1984.
Carter, W. P. L., Winer, A. M. and Pitts Jr., J. N.: Environ. Sci. Technol., 15, 829, 1981.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

## Datasheet NO3_AROM5

$$\mathbf{NO_3 + \textit{p}\text{-}CH_3C_6H_4OH\ (\textit{p}\text{-}cresol) \rightarrow CH_3C_6H_4O + HNO_3} \quad \mathbf{(1)}$$
$$\mathbf{\rightarrow other\ products} \quad \mathbf{(2)}$$

### Rate coefficient data ($k = k_1 + k_2$)

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(1.50 \pm 0.24) \times 10^{-11}$ | 300 ± 1 | Carter et al., 1981 | RR-GC (a) |
| $(1.38 \pm 0.15) \times 10^{-11}$ | 298 ± 1 | Atkinson et al., 1984 | RR-GC (b) |
| $(1.07 \pm 0.10) \times 10^{-11}$ | 296 ± 2 | Atkinson et al., 1992 | RR-GC (c) |

### Comments

(a) $NO_3$ radicals were generated from the reaction of $O_3$ with $NO_2$ in the presence of *p*-cresol and 2-methyl-2-butene (the reference compound) at atmospheric pressure of air. The contribution of the $O_3$ reaction was taken into account in estimating the amount of 2-methyl-2-butene reacted with $NO_3$ radicals. The concentrations of *p*-cresol and 2-methyl-2-butene were monitored by GC. The derived rate coefficient ratio is placed on an absolute basis using a rate coefficient of $k(NO_3 + \text{2-methyl-2-butene}) = 9.37 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson and Arey, 2003).

(b) $NO_3$ radicals were generated from the thermal decomposition of $N_2O_5$ in the presence of *p*-cresol and *m*-cresol (the reference compound) at atmospheric pressure of air. The concentrations of *p*- and *m*-cresol were monitored by GC. The measured rate coefficient ratio of $k(NO_3 + p\text{-cresol})/k(NO_3 + m\text{-cresol}) = 1.38 \pm 0.15$ is placed on an absolute basis using a rate coefficient of $k(NO_3 + m\text{-cresol}) = 1.0 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IUPAC, 2019).

(c) $NO_3$ radicals were generated from the thermal decomposition of $N_2O_5$ in the presence of *p*-cresol and 2-methyl-2-butene (the reference compound) at atmospheric pressure of air. The concentrations of *p*-cresol and 2-methyl-2-butene were monitored by GC. The measured rate coefficient ratio of $k(NO_3 + p\text{-cresol})/k(NO_3 + \text{2-methyl-2-butene}) = 1.14 \pm 0.10$ is placed on an absolute basis using a rate coefficient of $k(NO_3 + \text{2-methyl-2-butene}) = 9.37 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson and Arey, 2003).

### Preferred Values

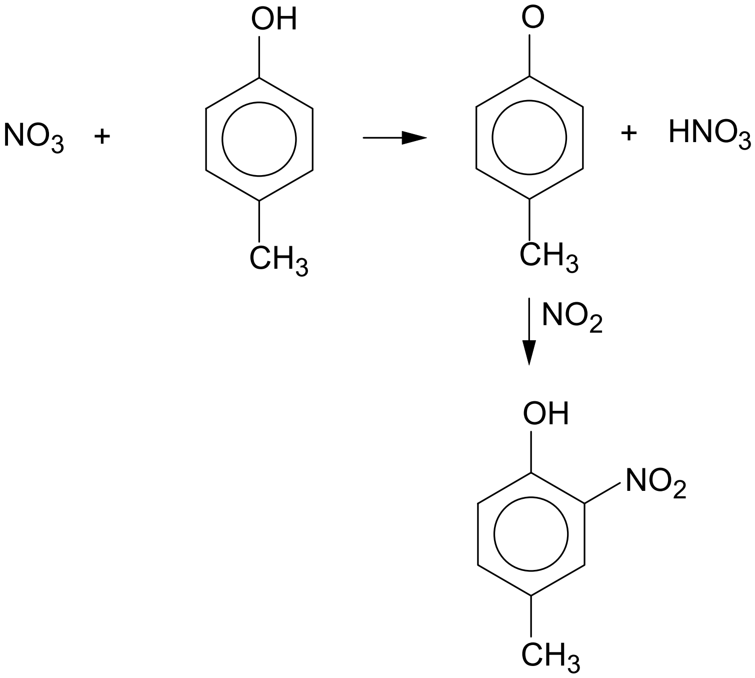
| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $1.1 \times 10^{-11}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.15 | 298 |

*Comments on Preferred Values*

The reported rate coefficients are all from relative rate studies conducted at room temperature, and are in reasonable agreement. The rate coefficient of Carter et al. (1981) is subject to some uncertainties because of the concurrent reaction of $O_3$ with 2-methyl-2-butene.

The preferred value is based on the study of Atkinson et al. (1992) in which the rate coefficient was measured relative to that for $NO_3$ + 2-methyl-2-butene.

Atkinson et al. (1992) observed the formation of 4-methyl-2-nitrophenol in 74 ± 16% yield. 4-Methyl-2-nitrophenol formation is believed to arise from methylphenoxy + $NO_2$, and the measured 4-methyl-2-nitrophenol yield of Atkinson et al. (1992) therefore suggests that channel (1) accounts for at least 76 ± 16% of the overall reaction.



## References

Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
Atkinson, R., Aschmann, S. M., Arey, J.: Environ. Sci. Technol., 26, 1397, 1992.
Atkinson, R., Carter, W. P. L., Plum, C. N., Winer, A. M. and Pitts Jr., J. N.: Int. J. Chem. Kinet., 16, 887, 1984.
Carter, W. P. L., Winer, A. M. and Pitts Jr., J. N.: Environ. Sci. Technol., 15, 829, 1981.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

## Datasheet NO3_AROM6

$$NO_3 + C_6H_5OH \text{ (Phenol)} \rightarrow C_6H_5O + HNO_3 \quad (1)$$

$$\rightarrow \text{other products} \quad (2)$$

### Rate coefficient data ($k = k_1 + k_2$)

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(2.61 \pm 0.53) \times 10^{-12}$ | $300 \pm 1$ | Carter et al., 1981 | RR-GC (a) |
| $(3.64 \pm 0.14) \times 10^{-12}$ | 294 | Atkinson et al., 1984 | RR-GC (b) |
| $(4.78 \pm 0.52) \times 10^{-12}$ | $298 \pm 1$ | Atkinson et al., 1984 | RR-FTIR (c) |
| $(3.92 \pm 0.25) \times 10^{-12}$ | $296 \pm 2$ | Atkinson et al., 1992 | RR-GC (b) |
| $(5.81 \pm 1.13) \times 10^{-12}$ | $295 \pm 2$ | Bolzacchini et al., 2001 | RR-GC (b) |

## Comments

(a) $NO_3$ radicals were generated from the reaction of $O_3$ with $NO_2$ in the presence of phenol and *cis*-2-butene (the reference compound) at atmospheric pressure of air. The contribution of the $O_3$ reaction was taken into account in estimating the amount of *cis*-2-butene reacted with $NO_3$ radicals. The concentrations of phenol and *cis*-2-butene were monitored by GC. The derived rate coefficient ratio is placed on an absolute basis using $k(NO_3 + cis\text{-2-butene}) = 3.52 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson and Arey, 2003).

(b) $NO_3$ radicals were generated from the thermal decomposition of $N_2O_5$ in the presence of phenol and 2-methyl-2-butene (the reference compound) at atmospheric pressure of air. The concentrations of phenol and 2-methyl-2-butene were monitored by GC. The measured rate coefficient ratios of $k(NO_3 + \text{phenol})/k(NO_3 + \text{2-methyl-2-butene}) = 0.389 \pm 0.014$ (Atkinson et al., 1984), $0.418 \pm 0.026$ (Atkinson et al., 1992) and $0.62 \pm 0.12$ (Bolzacchini et al., 2001) are placed on an absolute basis using $k(NO_3 + \text{2-methyl-2-butene}) = 9.37 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson and Arey, 2003).

(c) $NO_3$ radicals were generated from the thermal decomposition of $N_2O_5$ at atmospheric pressure of air. The concentrations of phenol, $N_2O_5$ and $NO_2$ were monitored by FTIR spectroscopy. The rate coefficient for $NO_3$ + phenol was measured relative to the equilibrium coefficient $K$ for the reactions $NO_2 + NO_3 \leftrightarrow N_2O_5$. The experimental data are placed on an absolute basis using $K = 2.75 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ at 298 K (IUPAC, 2019).

## Preferred Values

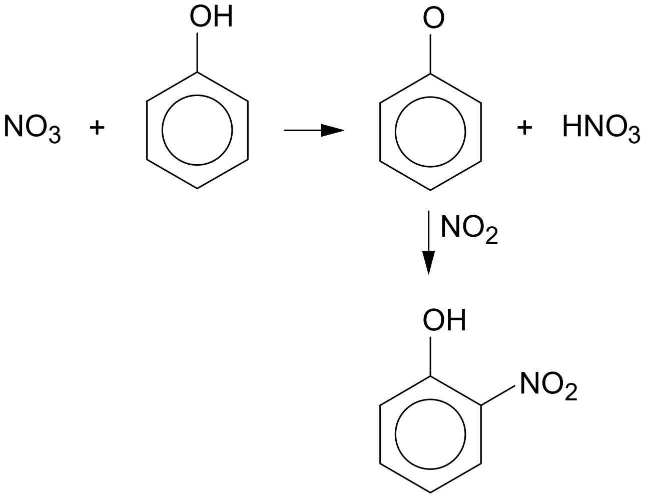
| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $3.8 \times 10^{-12}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | $\pm 0.15$ | 298 |

*Comments on Preferred Values*

The reported rate coefficients are all from relative rate studies conducted at room temperature. The rate coefficient of Carter et al. (1981) and that of Atkinson et al. (1984)

relative to the equilibrium constant for the $NO_3$ + $NO_2$ ↔ $N_2O_5$ reactions are subject to significant uncertainties because of the concurrent reaction of $O_3$ with 2-methyl-2-butene in the Carter et al. (1981) study and the uncertainties in the equilibrium constant for the $NO_3$ + $NO_2$ ↔ $N_2O_5$ reactions in the Atkinson et al. (1984) study. The preferred value is based on the studies of Atkinson et al. (1984; 1992) in which the rate coefficients were measured relative to those for $NO_3$ + alkene (2-methyl-2-butene in both studies) and used the thermal decomposition of $N_2O_5$ to generate $NO_3$ radicals.

Atkinson et al. (1992) observed the formation of 2-nitrophenol in 25.1 ± 5.1% yield. 2-Nitrophenol formation is believed to arise from phenoxy + $NO_2$, and the measured 2-nitrophenol yield of Atkinson et al. (1992) therefore suggests that channel (1) accounts for at least 25 ± 5% of the overall reaction.



**References**

Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
Atkinson, R., Aschmann, S. M., Arey, J.: Environ. Sci. Technol., 26, 1397, 1992.
Atkinson, R., Carter, W. P. L., Plum, C. N., Winer, A. M. and Pitts Jr., J. N.: Int. J. Chem. Kinet., 16, 887, 1984.
Bolzacchini, E., Bruschi, M., Hjorth, J., Meinardi, S., Orlandi, M., Rindone, B. and Rosenbohm, E.: Environ. Sci. Technol., 35, 1791, 2001.
Carter, W. P. L., Winer, A. M. and Pitts Jr., J. N.: Environ. Sci. Technol., 15, 829, 1981.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

## Datasheet NO3_AROM7

### $NO_3$ + 1,2-dihydroxybenzene ($1,2-C_6H_4(OH)_2$) → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(9.03 \pm 0.41) \times 10^{-11}$ | 298 ± 2 | Olariu et al., 2004 | RR-FTIR (a) |
| $(1.08 \pm 0.07) \times 10^{-10}$ | 296 ± 2 | Olariu et al., 2004 | RR-FTIR (b) |

## Comments

(a) $NO_3$ radicals generated by the thermal decomposition of $N_2O_5$. Experiments were carried out in a 1080 L chamber at 1 bar of air. The concentrations of 1,2-dihydroxybenzene and 2,3-dimethyl-2-butene (the reference compounds) were measured by FTIR spectroscopy. Wall losses of 1,2-dihydroxybenzene were measured and taken into account in the data analysis, and these contributed ~40% of the 1,2-dihydroxybenzene loss rate due to $NO_3$ radical reaction during the experiments. The measured rate coefficient ratio of $k(NO_3$ + 1,2-dihydroxybenzene$)/k(NO_3$ + 2,3-dimethyl-2-butene$) = 1.58 \pm 0.07$ is placed on an absolute basis using $k(NO_3$ + 2,3-dimethyl-2-butene$) = 5.72 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson and Arey, 2003).

(b) $NO_3$ radicals generated by the thermal decomposition of $N_2O_5$. Experiments were carried out in the ~200 m$^3$ EUPHORE chamber at atmospheric pressure of air. The concentrations of 1,2-dihydroxybenzene and 2,3-dimethyl-2-butene (the reference compounds) were measured by FTIR spectroscopy. Wall losses of 1,2-dihydroxybenzene were measured and taken into account in the data analysis, and these contributed ~40% of the 1,2-dihydroxybenzene loss rate due to $NO_3$ radical reaction during the experiments. The measured rate coefficient ratio of $k(NO_3$ + 1,2-dihydroxybenzene$)/k(NO_3$ + 2,3-dimethyl-2-butene$) = 1.88 \pm 0.11$ is placed on an absolute basis using $k(NO_3$ + 2,3-dimethyl-2-butene$) = 5.72 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson and Arey, 2003).

## Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $9.9 \times 10^{-11}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.15 | 298 |

### *Comments on Preferred Values*

The rate coefficients measured by Olariu et al. (2004) at 296-298 K in two reaction chambers differing in volume by a factor of ~200 using a relative rate method agree to within 20%. The 298 K preferred value is an average of the two values of Olariu et al. (2004). The assigned uncertainty reflects the fact that all of the data are from a single study.

## References

Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
Olariu, R. I., Bejan, I., Barnes, I., Klotz, B., Becker, K. H. and Wirtz, K: Int. J. Chem. Kinet., 36, 577, 2004.

## Datasheet NO3_AROM8

### $NO_3$ + 1,2-dihydroxy-3-methylbenzene → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(1.72 \pm 0.06) \times 10^{-10}$ | 298 ± 2 | Olariu et al., 2004 | RR-FTIR (a) |
| $(1.68 \pm 0.04) \times 10^{-10}$ | 296 ± 2 | Olariu et al., 2004 | RR-FTIR (b) |

## Comments

(a) $NO_3$ radicals generated by the thermal decomposition of $N_2O_5$. Experiments were carried out in a 1080 L chamber at 1 bar of air. The concentrations of 1,2-dihydroxy-3-methylbenzene and 2,3-dimethyl-2-butene (the reference compounds) were measured by FTIR spectroscopy. Wall losses of 1,2-dihydroxy-3-methylbenzene were measured and taken into account in the data analysis, and these contributed ~40% of the 1,2-dihydroxy-3-methylbenzene loss rate due to $NO_3$ radical reaction during the experiments. The measured rate coefficient ratio of $k(NO_3$ + 1,2-dihydroxy-3-methylbenzene$)/k(NO_3$ + 2,3-dimethyl-2-butene$) = 3.01 \pm 0.10$ is placed on an absolute basis using $k(NO_3$ + 2,3-dimethyl-2-butene$) = 5.72 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson and Arey, 2003).

(b) $NO_3$ radicals generated by the thermal decomposition of $N_2O_5$. Experiments were carried out in the ~200 m$^3$ EUPHORE chamber at atmospheric pressure of air. The concentrations of 1,2-dihydroxy-3-methylbenzene and 2,3-dimethyl-2-butene (the reference compounds) were measured by FTIR spectroscopy. Wall losses of 1,2-dihydroxy-3-methylbenzene were measured and taken into account in the data analysis, and these contributed ~40% of the 1,2-dihydroxy-3-methylbenzene loss rate during the experiments. The measured rate coefficient ratio of $k(NO_3$ + 1,2-dihydroxy-3-methylbenzene$)/k(NO_3$ + 2,3-dimethyl-2-butene$) = 2.93 \pm 0.06$ is placed on an absolute basis using $k(NO_3$ + 2,3-dimethyl-2-butene$) = 5.72 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson and Arey, 2003).

## Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $1.7 \times 10^{-10}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.15 | 298 |

*Comments on Preferred Values*

The two rate coefficients measured by Olariu et al. (2004) at 296-298 K in two reaction chambers differing in volume by a factor of ~200 using a relative rate method are in good agreement. The 298 K preferred value is an average of the two values of Olariu et al. (2004). The assigned uncertainty reflects the fact that all of the data are from a single study.

## References

Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
Olariu, R. I., Bejan, I., Barnes, I., Klotz, B., Becker, K. H. and Wirtz, K: Int. J. Chem. Kinet., 36, 577, 2004.

## Datasheet NO3_AROM9

### $NO_3$ + 1,2-dihydroxy-4-methylbenzene → products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Relative Rate Coefficients* | | | |
| $(1.60 \pm 0.06) \times 10^{-10}$ | 298 ± 2 | Olariu et al., 2004 | RR-FTIR (a) |
| $(1.35 \pm 0.04) \times 10^{-10}$ | 296 ± 2 | Olariu et al., 2004 | RR-FTIR (b) |

### Comments

(a) $NO_3$ radicals generated by the thermal decomposition of $N_2O_5$. Experiments were carried out in a 1080 L chamber at 1 bar of air. The concentrations of 1,2-dihydroxy-4-methylbenzene and 2,3-dimethyl-2-butene (the reference compounds) were measured by FTIR spectroscopy. Wall losses of 1,2-dihydroxy-4-methylbenzene were measured and taken into account in the data analysis, and these contributed ~40% of the 1,2-dihydroxy-4-methylbenzene loss rate due to $NO_3$ radical reaction during the experiments. The measured rate coefficient ratio of $k$($NO_3$ + 1,2-dihydroxy-4-methylbenzene)/$k$($NO_3$ + 2,3-dimethyl-2-butene) = 2.80 ± 0.10 is placed on an absolute basis using $k$($NO_3$ + 2,3-dimethyl-2-butene) = $5.72 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson and Arey, 2003).

(b) $NO_3$ radicals generated by the thermal decomposition of $N_2O_5$. Experiments were carried out in the ~200 m$^3$ EUPHORE chamber at atmospheric pressure of air. The concentrations of 1,2-dihydroxy-4-methylbenzene and 2,3-dimethyl-2-butene (the reference compounds) were measured by FTIR spectroscopy. Wall losses of 1,2-dihydroxy-4-methylbenzene were measured and taken into account in the data analysis, and these contributed ~40% of the 1,2-dihydroxy-4-methylbenzene loss rate during the experiments. The measured rate coefficient ratio of $k$($NO_3$ + 1,2-dihydroxy-4-methylbenzene)/$k$($NO_3$ + 2,3-dimethyl-2-butene) = 2.36 ± 0.06 is placed on an absolute basis using $k$($NO_3$ + 2,3-dimethyl-2-butene) = $5.72 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson and Arey, 2003).

### Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $1.5 \times 10^{-10}$ | 298 |
| *Reliability* | | |
| $\Delta \log k$ | ± 0.15 | 298 |

*Comments on Preferred Values*

The rate coefficients measured by Olariu et al. (2004) at 296-298 K in two reaction chambers differing in volume by a factor of ~200 using a relative rate method agree to within 20%. The 298 K preferred value is an average of the two values of Olariu et al. (2004). The assigned uncertainty reflects the fact that all of the data are from a single study.

## References

Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
Olariu, R. I., Bejan, I., Barnes, I., Klotz, B., Becker, K. H. and Wirtz, K: Int. J. Chem. Kinet., 36, 577, 2004.

# Photolysis
# VOCs ($\geq C_4$)

| ID | Reactants | | Products |
|---|---|---|---|
| P23 | **$CH_3C(O)C(O)CH_3$ + h*v*** | → | **$CH_3C(O) + CH_3C(O)$** |
| P24 | **i-$C_3H_7CHO$ + h*v*** | → | ***i*-$C_3H_7$ + HCO** |
| P26 | **cis/trans-but-2-enedial + h*v*** | → | **HCOCH=CHCHO** |
| P27 | **4-oxopent-2-enedial + h*v*** | → | **5-methyl-3*H*-furan-2-one** |
| P28 | **2-nitrophenol + h*v*** | → | **$C_6H_4(OH) + NO_2$** |
| P30 | **benzaldehyde + h*v*** | → | **$C_6H_5$ + HC(O)** |
| P31 | **3-methyl-2-nitrophenol + h*v*** | → | **$CH_3C_6H_3(OH) + NO_2$** |
| P32 | **4-methyl-2-nitrophenol + h*v*** | → | **$CH_3C_6H_3(OH) + NO_2$** |

# Datasheet P23

## $CH_3C(O)C(O)CH_3 + h\upsilon \rightarrow$ products

### Primary photochemical transitions

| Reaction | $\Delta H^{o}_{298}$/kJ·mol$^{-1}$ | $\lambda_{threshold}$/nm |
|---|---|---|
| $CH_3C(O)C(O)CH_3 \rightarrow CH_3C(O) + CH_3C(O)$ (1) | | 390 |
| $\rightarrow CH_3C(O) + CH_3 + CO$ (2) | | 338 |
| $\rightarrow 2CH_3 + 2CO$ (3) | | 300 |

### Absorption cross-section data

| Wavelength range/nm | Reference | Comments |
|---|---|---|
| 208-476 | McMillan, 1966 | |
| 230-470 | Plum *et al.*, 1983 | (a) |
| 206-493 | Horowitz *et al.*, 2001 | (b) |
| 184.9 | Rajakumar *et al.*, 2008 | (c) |

### Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3$)

| Measurement | Wavelength range/nm | Reference | Comments |
|---|---|---|---|
| $\phi = 0.16$ | 290-390 | Plum *et al.*, 1983 | (d) |
| $\phi(CH_3CO) = 0.76(61\ Torr)$<br>$= 0.79(101\ Torr)$<br>$= 0.79(207\ Torr)$<br>$= 0.86(302\ Torr)$<br>$= 0.92(419\ Torr)$<br>$= 0.90(509\ Torr)$<br>$= 0.96(643\ Torr)$ | 248 | Rajakumar *et al.*, 2008 | (e) |

### Comments

(a) Spectrophotometric study (Cary 17-D) using biacetyl pressures of ~4 mbar to 17 mbar. Data taken from Spectral Atlas: (http://www.atmosphere.mpg.de/enid/2295) which gives absorption cross sections read at 1- and 2-nm intervals from Fig. 1 of Plum et al (1983).

(b) Absorption measurements as a function of biacetyl pressure using a diode array spectrometer. Biacetyl pressure range of 0.5–10 Torr in which no deviations from Beer–Lambert law were observed. Cross sections averaged over 1 nm intervals are listed. Reported accuracy of the biacetyl data in this work was ±4% or $\pm 1 \times 10^{-21}$ cm$^2$molecule$^{-1}$, whichever was the larger.

(c) UV absorption measurements were made using a Hg pen-ray lamp light source at 184.9 nm combined with narrow bandpass filters and a photodiode detector. The cross section determined for this wavelength was $1.46 \times 10^{-18}$ cm$^2$molecule$^{-1}$. The concentration of biacetyl was determined by UV absorption at 248 nm, using the cross section of Horowitz et al. (2001).

(d) Rate of photolysis of biacetyl in air mixtures at atmospheric pressure measured in an environmental chamber. The quantum yield for the photodissociation of biacetyl was obtained by comparison of the measured rate of removal of glyoxal with the rate of photolysis of $NO_2$ under similar experimental conditions.

(e) Quantum yields determined from $CH_3CO$ production measured in its visible absorption band (490 - 660 nm) by CRDS following photolysis of biacetyl at 248 nm in a crossed beam pulsed laser photolysis cell. $CH_3CO$ yields were determined relative to those from a reference reaction; HO + $CH_3CHO$, with HO produced by co-photolysis of $H_2O_2$. Cited data for $\phi(CH_3CO)$ were for $N_2$ bath gas, a weaker pressure dependence was found for He.

## Preferred Values

### Absorption cross-sections at 298 K

| $\lambda$/nm | $10^{20}$ $\sigma$/cm$^2$ | $\lambda$/nm | $10^{20}$ $\sigma$/cm$^2$ | $\lambda$/nm | $10^{20}$ $\sigma$/cm$^2$ |
|---|---|---|---|---|---|
| 206 | 10.30 | 303 | 1.46 | 400 | 5.12 |
| 207 | 9.86 | 304 | 1.38 | 401 | 5.19 |
| 208 | 9.14 | 305 | 1.32 | 402 | 5.26 |
| 209 | 7.97 | 306 | 1.27 | 403 | 5.38 |
| 210 | 6.74 | 307 | 1.21 | 404 | 5.54 |
| 211 | 5.82 | 308 | 1.10 | 405 | 5.75 |
| 212 | 5.18 | 309 | 0.95 | 406 | 6.00 |
| 213 | 4.70 | 310 | 0.82 | 407 | 6.26 |
| 214 | 4.29 | 311 | 0.71 | 408 | 6.47 |
| 215 | 3.90 | 312 | 0.62 | 409 | 6.59 |
| 216 | 3.55 | 313 | 0.54 | 410 | 6.69 |
| 217 | 3.21 | 314 | 0.48 | 411 | 6.82 |
| 218 | 2.90 | 315 | 0.44 | 412 | 6.97 |
| 219 | 2.58 | 316 | 0.41 | 413 | 7.11 |
| 220 | 2.26 | 317 | 0.38 | 414 | 7.31 |
| 221 | 1.96 | 318 | 0.36 | 415 | 7.47 |
| 222 | 1.70 | 319 | 0.34 | 416 | 7.57 |
| 223 | 1.50 | 320 | 0.33 | 417 | 7.62 |
| 224 | 1.35 | 321 | 0.33 | 418 | 7.51 |
| 225 | 1.27 | 322 | 0.32 | 419 | 7.39 |
| 226 | 1.23 | 323 | 0.30 | 420 | 7.37 |
| 227 | 1.24 | 324 | 0.26 | 421 | 7.32 |
| 228 | 1.28 | 325 | 0.23 | 422 | 7.25 |
| 229 | 1.34 | 326 | 0.21 | 423 | 7.24 |
| 230 | 1.41 | 327 | 0.20 | 424 | 7.13 |
| 231 | 1.47 | 328 | 0.19 | 425 | 6.98 |
| 232 | 1.53 | 329 | 0.19 | 426 | 6.81 |
| 233 | 1.59 | 330 | 0.20 | 427 | 6.57 |
| 234 | 1.68 | 331 | 0.20 | 428 | 6.43 |
| 235 | 1.80 | 332 | 0.21 | 429 | 6.34 |
| 236 | 1.92 | 333 | 0.20 | 430 | 6.31 |
| 237 | 2.09 | 334 | 0.22 | 431 | 6.40 |
| 238 | 2.15 | 335 | 0.23 | 432 | 6.63 |
| 239 | 2.21 | 336 | 0.25 | 433 | 6.78 |
| 240 | 2.29 | 337 | 0.26 | 434 | 6.78 |
| 241 | 2.39 | 338 | 0.28 | 435 | 6.72 |

|  |  |  |  |  |  |
|---|---|---|---|---|---|
| 242 | 2.54 | 339 | 0.30 | 436 | 6.56 |
| 243 | 2.69 | 340 | 0.30 | 437 | 6.40 |
| 244 | 2.80 | 341 | 0.32 | 438 | 6.42 |
| 245 | 2.89 | 342 | 0.35 | 439 | 6.28 |
| 246 | 2.94 | 343 | 0.37 | 440 | 6.51 |
| 247 | 2.99 | 344 | 0.39 | 441 | 6.67 |
| 248 | 3.05 | 345 | 0.41 | 442 | 6.99 |
| 249 | 3.15 | 346 | 0.44 | 443 | 7.23 |
| 250 | 3.31 | 347 | 0.47 | 444 | 6.85 |
| 251 | 3.48 | 348 | 0.50 | 445 | 6.49 |
| 252 | 3.60 | 349 | 0.53 | 446 | 5.90 |
| 253 | 3.68 | 350 | 0.57 | 447 | 5.43 |
| 254 | 3.73 | 351 | 0.61 | 448 | 5.01 |
| 255 | 3.75 | 352 | 0.65 | 449 | 4.33 |
| 256 | 3.78 | 353 | 0.68 | 450 | 4.06 |
| 257 | 3.84 | 354 | 0.73 | 451 | 3.44 |
| 258 | 3.94 | 355 | 0.77 | 452 | 3.20 |
| 259 | 4.09 | 356 | 0.82 | 453 | 2.65 |
| 260 | 4.27 | 357 | 0.86 | 454 | 2.16 |
| 261 | 4.41 | 358 | 0.92 | 455 | 1.72 |
| 262 | 4.46 | 359 | 0.97 | 456 | 1.39 |
| 263 | 4.49 | 360 | 1.02 | 457 | 1.14 |
| 264 | 4.49 | 361 | 1.08 | 458 | 0.85 |
| 265 | 4.48 | 362 | 1.19 | 459 | 0.73 |
| 266 | 4.49 | 363 | 1.26 | 460 | 0.55 |
| 267 | 4.54 | 364 | 1.33 | 461 | 0.45 |
| 268 | 4.63 | 365 | 1.41 | 462 | 0.36 |
| 269 | 4.81 | 366 | 1.49 | 463 | 0.28 |
| 270 | 4.95 | 367 | 1.57 | 464 | 0.22 |
| 271 | 5.00 | 368 | 1.66 | 465 | 0.18 |
| 272 | 4.98 | 369 | 1.76 | 466 | 0.14 |
| 273 | 4.92 | 370 | 1.85 | 467 | 0.12 |
| 274 | 4.85 | 371 | 1.94 | 468 | 0.10 |
| 275 | 4.76 | 372 | 2.02 | 469 | 0.08 |
| 276 | 4.70 | 373 | 2.10 | 470 | 0.07 |
| 277 | 4.68 | 374 | 2.17 | 471 | 0.06 |
| 278 | 4.67 | 375 | 2.25 | 472 | 0.05 |
| 279 | 4.68 | 376 | 2.33 | 473 | 0.04 |
| 280 | 4.71 | 377 | 2.41 | 474 | 0.04 |
| 281 | 4.73 | 378 | 2.50 | 475 | 0.03 |
| 282 | 4.65 | 379 | 2.58 | 476 | 0.03 |
| 283 | 4.50 | 380 | 2.68 | 477 | 0.03 |
| 284 | 4.32 | 381 | 2.79 | 478 | 0.02 |
| 285 | 4.14 | 382 | 2.92 | 479 | 0.02 |
| 286 | 3.94 | 383 | 3.07 | 480 | 0.02 |
| 287 | 3.77 | 384 | 3.22 | 481 | 0.02 |
| 288 | 3.62 | 385 | 3.39 | 482 | 0.02 |
| 289 | 3.50 | 386 | 3.53 | 483 | 0.02 |
| 290 | 3.38 | 387 | 3.67 | 484 | 0.02 |
| 291 | 3.28 | 388 | 3.82 | 485 | 0.02 |
| 292 | 3.20 | 389 | 4.00 | 486 | 0.01 |
| 293 | 3.11 | 390 | 4.17 | 487 | 0.01 |
| 294 | 2.96 | 391 | 4.34 | 488 | 0.02 |

| | | | | | |
|---|---|---|---|---|---|
| 295 | 2.73 | 392 | 4.47 | 489 | 0.02 |
| 296 | 2.50 | 393 | 4.56 | 490 | 0.02 |
| 297 | 2.29 | 394 | 4.62 | 491 | 0.02 |
| 298 | 2.10 | 395 | 4.67 | 492 | 0.02 |
| 299 | 1.93 | 396 | 4.73 | 493 | 0.02 |
| 300 | 1.77 | 397 | 4.82 | | |
| 301 | 1.64 | 398 | 4.92 | | |
| 302 | 1.54 | 399 | 5.02 | | |

## Quantum Yields

At 248 nm: $\phi_1 + \phi_2 = 0.76$ for $p < 80$ mbar;
$\phi_1 = 2$; $\phi_2 = 0$ for $p = \infty$;
290 – 380 nm: $\phi_1 + \phi_2 + \phi_3 = 0.16$ (average for atmospheric photolysis at surface).

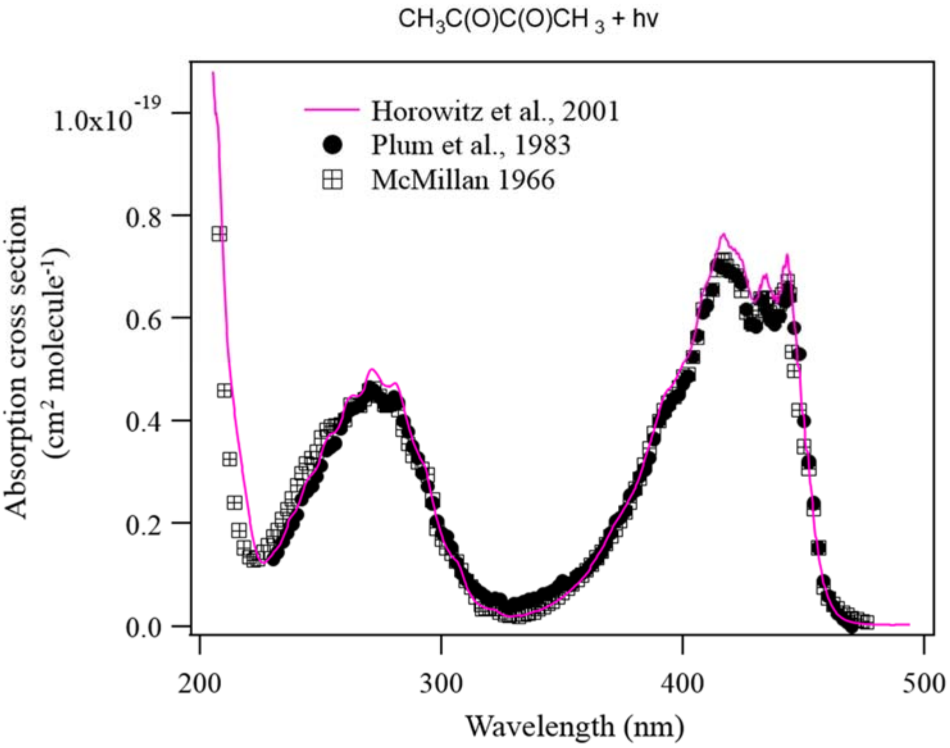
*Comments on Preferred Values*

Biacetyl exhibits two distinct absorption regions relevant for atmospheric photolysis. The first region consists of a broad band between 340 – 480 nm, on which three distinct peaks are superimposed at 417.2, 433.0 and 442.8 nm. The second region shows a broad band with some structure with a maximum absorption near 272 nm. The preferred values for the absorption cross-sections are based on those determined by Horowitz et al. (2001), which, are in satisfactory agreement with the earlier data of Plum et al. (1983) and McMillan et al., 1966 (e.g. $\sigma_{max} = 4.65 \times 10^{-20}$ cm$^2$molecule$^{-1}$ at 270 nm for the second band). The values given above are averaged over 1 nm and are taken from the compilation in http://www.atmosphere.mpg.de/enid/, which also contains data at other resolution. The overall accuracy for both bands is estimated at ±5%. The single wavelength determination of Rajakumar et al. (2008) at 184.9 nm is consistent with a third strong absorption band below 200 nm indicated by the data of Horowitz, (2001).

The recommended quantum yields for $\phi_1 + \phi_2$ are based on the data of Rajakumar *et al.* (2008), which are the only wavelength-resolved quantum yield data that have appeared. The observed pressure dependence of $\phi(CH_3CO)$ is due to dissociation of initially formed excited $CH_3CO^*$ and is reproduced reasonably well, over the range of pressures covered in this study, by a Stern–Volmer relationship for the quenching of $CH_3CO^*$. This analysis using an assumed high pressure limiting yield of $\phi^{\infty}(CH_3CO) = 2$, gave a zero pressure quantum yield of $\phi^{0}(CH_3CO) = 0.76 \pm 0.05$. The authors estimate the overall uncertainty in experimental values of $\phi(CH_3CO)$ from biacetyl photolysis at 248 nm to be 15% at the $2\sigma$ (95% confidence) level.

## References

Horowitz, A., Meller, R. and Moortgat, G. K., J Photochem.Photobiol., A: Chem., 146, 19, 2001.
Klotz, B. , Graedler, F., Sorensen, S., Barnes, I, and Becker, K.H., Int. J. Chem. Kinet., 33, 9–20, 2001.
McMillan, V. personal communication to J.G. Calvert, J.N.Pitts, Jr., Photochemistry, London, 1966, p. 422.
Plum, C. N., Sanhueza, E., Atkinson, R., Carter, W. P. L. and Pitts, Jr., J. N., Environ. Sci. Technol., 17, 479, 1983.
Rajakumar, B., Gierczak, T., Flad, J., Ravishankara, A.R., and Burkholder, J.B., J. Photochem Photobiol. A: Chem., 199, 336-344, 2008.



Absorption Spectrum of Biacetyl

# Datasheet P24

## *i*-$C_3H_7CHO$ + hυ → products

## Primary photochemical transitions

| Reaction | | $\Delta H^{\circ}_{298}$/kJ·mol$^{-1}$ | $\lambda_{threshold}$/nm |
|---|---|---|---|
| *i*-$C_3H_7CHO$ → *i*-$C_3H_7$ + HCO | (1) | | 349 |
| → $C_3H_8$ + CO | (2) | | |
| → *i*-$C_3H_7CO$ + H | (3) | | 327 |
| → $CH_3$ + $CH_3CHCHO$ | (4) | | |
| → $C_3H_6$ + HCHO | (5) | | |

## Absorption cross-section data

| Wavelength range/nm | Reference | Comments |
|---|---|---|
| 265.2-334.0 | Borkowski and Ausloos, 1962 | (a) |
| 206-444 | McMillan, 1966 | (b) |
| 202-365 | Martinez et al., 1992 | (c) |
| 280-330 | Chen et al, 2002 | (d) |

## Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5$)

| Measurement | Wavelength range/nm | Reference | Comments |
|---|---|---|---|
| $\phi$(HCO) = 0.20 | 253.7 | Desai et al, 1986 | (e) |
| $\phi$(HCO) = 0.45 | 280.3 | | |
| $\phi$(HCO) = 0.55 | 302.2 | | |
| $\phi$(HCO) = 0.88 | 312.8 | | |
| $\phi$(HCO) = 0.88 | 326.1 | | |
| $\phi$(HCO) = 0.69 | 334.1 | | |
| $\phi^0$(HCO) = 0.31±0.004 | 280 | Chen et al, 2002 | (d) |
| $\phi^0$ (HCO) = 1.10±0.10 | 320 | | |
| $\phi^0$(HCO) = 0.94±0.06 | 330 | | |

## Comments

(a) UV absorption measurements yielding molar extinction coefficients given in tabular form.

(b) Spectrophotometric study (Cary 17-D) using biacetyl pressures of ~4 mbar to 17 mbar. Cross-sections taken from Spectral Atlas (http://www.atmosphere.mpg.de/enid/2295) which gives absorption cross sections read at 1- and 2-nm intervals from figure in Calvert and Pitts,1966.

(c) Cross-sections determined from absorption measurements as a function of i-$C_3H_7CHO$ pressure using a diode array spectrometer, with resolution of 0.25 nm.

(d) Photolysis of *n*-butyraldehyde and *i*-butyraldehyde at 5-nm intervals in the 280-330 nm region using dye laser photolysis combined with CRDS. Absorption cross sections of *n*-butyraldehyde and *i*-butyraldehyde were obtained at each wavelength that was studied. The quantum yields of HCO and their dependences on photolysis wavelength, aldehyde pressure, and total pressure (10-525 mbar $N_2$) were determined, from measurement of this photoproduct by CRDS, using a probe laser at 613 - 617 nm. The time dependence of [HCO] photofragment was analysed using a model of the post flash radical chemistry and Stern-Volmer self-quenching to determine the initial, zero pressure quantum yields, $\phi^0$. Absolute absorption cross section of HCO at the probe laser wavelength was determined using HCO from the formaldehyde photolysis reaction $H_2CO + h\nu \rightarrow HCO + H$, for which the HCO quantum yield is known, or from the $Cl + H_2CO \rightarrow HCl + HCO$ reaction. Quantum yields decreased with wavelength at both the longer and shorter end of the range. $\phi^0$ between 280 – 330 nm was independent of $N_2$ pressure. At 285 nm, $\phi^0$ was independent of $p$(i-$C_3H_7CHO$) (1.3-13 mbar range). At 325 nm (closer to the dissociation limit), $\phi$(HCO) decreased with $p$(i-$C_3H_7CHO$), due to self quenching.

(e) Steady state photolysis of i-$C_3H_7CHO$ was studied in the presence of $O_2$ at 263 and 294 K at several incident wavelengths. The quantum yields of CO and $C_3H_6$ were measured using GC. The primary quantum yields $\phi_1$ (free radical channel) and $\phi_2$ (molecular channel) were deduced from the difference in CO and $C_3H_6$ yields. The pulsed flash photolysis of *i*-$C_3H_7CHO$ was also studied in the presence of air at 298 K. The transient UV absorption of peroxy radicals, formed by reaction of the photo-fragments with $O_2$, was monitored and relative quantum yields were obtained with 284.0, 302.5, 311.7, 325.0 and 330.5 nm incident radiation. The quantum yields were not pressure quenched, except for very slightly at 330.5 nm.

## Preferred Values

### Absorption cross-sections at 298 K

| $\lambda$/nm | $10^{20}\sigma$/cm$^2$ | $\lambda$/nm | $10^{20}\sigma$/cm$^2$ | $\lambda$/nm | $10^{20}\sigma$/cm$^2$ |
|---|---|---|---|---|---|
| 202 | 0.93 | 273 | 4.05 | 321 | 2.280 |
| 206 | 0.40 | 274 | 4.14 | 322 | 2.175 |
| 208 | 0.28 | 275 | 4.35 | 323 | 2.076 |
| 210 | 0.23 | 276 | 4.69 | 324 | 1.951 |
| 212 | 0.20 | 277 | 4.91 | 325 | 1.842 |
| 214 | 0.17 | 278 | 4.81 | 326 | 1.710 |
| 216 | 0.15 | 279 | 5.03 | 327 | 1.584 |
| 218 | 0.12 | 287 | 5.73 | 328 | 1.397 |
| 220 | 0.12 | 288 | 5.79 | 329 | 1.195 |
| 222 | 0.09 | 289 | 5.85 | 330 | 0.950 |
| 224 | 0.11 | 290 | 5.87 | 331 | 0.785 |
| 226 | 0.09 | 291 | 5.84 | 332 | 0.672 |
| 228 | 0.12 | 292 | 5.84 | 333 | 0.567 |
| 230 | 0.12 | 293 | 5.88 | 334 | 0.490 |
| 232 | 0.16 | 294 | 5.92 | 335 | 0.425 |
| 234 | 0.18 | 295 | 5.94 | 336 | 0.357 |
| 236 | 0.24 | 296 | 5.86 | 337 | 0.297 |
| 238 | 0.27 | 297 | 5.78 | 338 | 0.257 |
| 240 | 0.34 | 298 | 5.73 | 339 | 0.215 |
| 242 | 0.41 | 299 | 5.69 | 340 | 0.173 |
| 244 | 0.51 | 300 | 5.59 | 341 | 0.147 |
| 246 | 0.61 | 301 | 5.48 | 342 | 0.123 |
| 248 | 0.77 | 302 | 5.43 | 343 | 0.081 |

| | | | | | |
|---|---|---|---|---|---|
| 250 | 0.91 | 303 | 5.36 | 344 | 0.059 |
| 252 | 1.11 | 304 | 5.29 | 345 | 0.034 |
| 254 | 1.27 | 305 | 5.15 | 346 | 0.025 |
| 256 | 1.51 | 306 | 4.98 | 347 | 0.019 |
| 258 | 1.71 | 307 | 4.73 | 348 | 0.015 |
| 260 | 1.96 | 308 | 4.57 | 349 | 0.013 |
| 261 | 2.11 | 309 | 4.41 | 350 | 0.011 |
| 262 | 2.13 | 310 | 4.27 | 351 | 0.010 |
| 263 | 2.43 | 311 | 4.13 | 352 | 0.009 |
| 264 | 2.60 | 312 | 3.99 | 353 | 0.008 |
| 265 | 2.79 | 313 | 3.86 | 354 | 0.005 |
| 266 | 2.88 | 314 | 3.73 | 355 | 0.004 |
| 267 | 3.16 | 315 | 3.61 | 356 | 0.003 |
| 268 | 3.33 | 316 | 3.48 | 357 | 0.001 |
| 269 | 3.45 | 317 | 3.26 | 358 | 0.001 |
| 270 | 3.49 | 318 | 2.82 | 359 | 0.001 |
| 271 | 3.75 | 319 | 2.60 | | |
| 272 | 3.84 | 320 | 2.41 | | |

## Quantum Yields

| λ/nm | $\phi_1$ |
|---|---|
| 280 | 0.31 ± 0.04 |
| 285 | 0.50 ± 0.07 |
| 290 | 0.71 ± 0.04 |
| 295 | 0.91 ± 0.04 |
| 300 | 1.00 ± 0.14 |
| 305 | 0.92 ± 0.08 |
| 310 | 1.06 ± 0.07 |
| 315 | 1.06 ± 0.13 |
| 320 | 1.10 ± 0.10 |
| 325 | 1.10 ± 0.10 |
| 330 | 0.94 ± 0.06 |

### *Comments on Preferred Values*

The absorption spectrum of i-butyraldehyde shows a single broad band between 230 and 350 nm, with a maximum at 294 nm. The cross-sections from earlier scanning UV spectrometer measurements of McMillan (1966) agree well with the diode array measurements of Martinez et al.(1992), although there are small differences in the details of the weak structure near the maximum and on the long wavelength side of the band. The less well $\lambda$-resolved measurements of Chen et al. (2002) suggest a systematic red-shift of the band compared to these data. The preferred absorption cross-sections are a simple average of the measurements of Martinez et al. (1992) and McMillan (1966) at each corresponding wavelength. The uncertainty on the cross-sections near the band centre are better than 4%.

The two studies cited reporting quantum yields both show wavelength dependence of the HCO radical channel, with $\phi$(HCO) near unity around 310 nm, declining at both ends of the range 280 – 330 nm. The absolute values of the quantum yield of HCO at zero pressure measured directly by Chen et al. (2002) was generally slightly higher than the indirect determinations reported by Desai et al. (1986), but overall the agreement is good. Chen et al estimate and overall uncertainty of ~50%, comprising ±10% experimental error and 38% systematic error arising mostly from the cross sections for HCO (±20%) and i-$C_3H_7$CHO (10%;

note that the σ values of Chen differ from the above IUPAC preferred values near the maximim). Both studies concluded that pressure quenching by $N_2$ or $O_2$ was negligible except near the photodissociation threshold, but efficient quenching of excited i-butyraldehyde by ground state i-butyraldehyde occurs at $\lambda < 310$ nm. The reduced $\phi$(HCO) at $\lambda < 295$ nm is accounted for by the opening up of an additional photodissociation pathway (2) forming $C_3H_8$ + CO at higher photon energy. The Norrish Type II dissociation channel involving α-H transfer to give $C_2H_4$ + $CH_2CHOH$ products is not available for i-butyraldehyde and it can be concluded that the overall quantum yield $\phi$ ( = $\phi_1$ + $\phi_2$) = 1.0. The slight fall off in $\phi$ at the longest wavelengths near the photodissociation threshold could result from quenching by $N_2$

The preferred values of $\phi_1$ are the direct measurements of Chen et al. for $\phi$(HCO). For atmospheric photolysis of i-butyraldehyde the overall photolysis can be calculated with $\phi$ = 1.0, with the second contributing channel $\phi_2 = (1- \phi_1)$.

## References

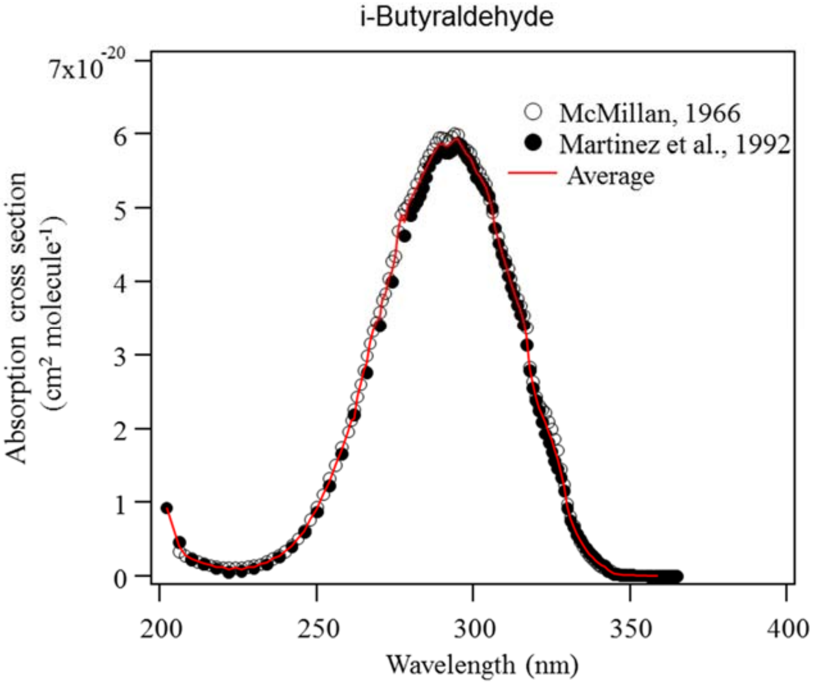
Borkowski, R. P. and Ausloos, P. , J. Am. Chem. Soc. 84, 4044-4048, 1962.

Chen, Y., Zhu, Lei and Francisco, J.S., J. Phys.Chem. A, 106, 7755-7763, 2002

Desai, J.; Heicklen, J.; Bahta, A.; Simonaitis, R. J. Photochem., *34*, 117-135, 1986.

McMillan, V. (1966), personal communication to J.G. Calvert, J.N.Pitts, Jr., Photochemistry, London, 1966, p. 369.

Martinez, R. D., Buitrago, A. A., Howell, N. W. , Hearn, C. H. and Joens, J. A., Atmos. Environ., 26A, 785, 1992.



Absorption Spectrum of i-Butyraldehyde

# Datasheet P26

## *cis*-HC(O)CH=CHC(O)H + hυ → products
## *trans*-HC(O)CH=CHC(O)H + hυ → products

### Primary photochemical transitions

| Reaction | | | $\lambda_{threshold}$/nm |
|---|---|---|---|
| HCOCH=CHCHO→ *trans/cis* | | HCOCH=CHCHO *cis/trans* (1) | |
| | → | HCOCH=CH + HCO (2) | ~290 |
| | → | HCOCH=CHCO + H (3) | |
| | → | 2HCO + $C_2H_2$ (4) | ~351 |
| | → | $CH_3COCH=CH_2$ + CO (5) | <346 |
| | → | 3H-furan-2-one (6) | <346 |

### Absorption cross-section data

| Wavelength range/nm | Reference | Comments |
|---|---|---|
| 193, 248, 308, 351 | Tang and Zhu, 2005 | (a) |
| 220 - 460 | Hufford et al , 1952 | (b) |

### Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5$)

| Measurement | Wavelength range/nm | Reference | Comments |
|---|---|---|---|
| *absolute quantum yields* | | | |
| $\phi$((HCO) )= 0.55 ± 0.07 | 193 | Tang and Zhu, 2005 | (c) |
| $\phi$((HCO)) = 0.12 ± 0.07 | 248 | | |
| *relative quantum yields* ($\varphi$ %) | | | |
| $\varphi$(1) = ~45 (cis-trans & trans-cis) | 320 – 480 | Bierbach et al., 1994 | (d) |
| $\varphi$(1) = ≤30 (cis-trans & trans-cis) | 254 | | |
| $\varphi$(2)= ≥1.1 | 193 | Tang and Zhu, 2005 | (e) |
| $\varphi$(2)= ≥3.7 | 248 | | |
| $\varphi$(2)= ≥15 | 308 | | |
| $\varphi$(2)= ≥23 | 351 | | |
| $\varphi$(6)= 0 | 193 | | |
| $\varphi$(6)= ≥2.8 | 248 | | |
| $\varphi$(6)= ≥1.2 | 308 | | |
| $\varphi$(6)= ≥1.1 | 351 | | |

## Comments

(a) Cross section data at 193 and 248 nm were determined by monitoring transmitted laser photolysis fluence as a function of butenendial pressure in the cell. The absolute cross-sections thus obtained were $(6.88 \pm 0.39) \times 10^{-18}$ and $(3.62 \pm 0.69) \times 10^{-19}$ $cm^2$ at 193 and 248 nm, respectively. The cited ($1\sigma$) error bars give estimated precision of the determination of the cross sections. At 308 and 351 nm upper limits of $< 6 \times 10^{-21}$ $cm^2$ were given.

(b) UV absorption spectrum of purified (crystalline fumaric dialdehyde) dissolved in iso-octane was reported. The sample was mainly the *trans*- isomer. The spectrum showed two absorption bands, one peaked at 225 nm ($\varepsilon$ =17 000 $cm^{-1}$) and the other peaked at 354 nm ($\varepsilon$ = 70 $cm^{-1}$).

(c) Quantum yield of HCO production determined from CRDS measurement of HCO concentration at 613.80 nm., using an absorption cross section of ~ $2.0 \times 10^{-18}$ $cm^2$/molecule at this wavelength. The system was calibrated at 248 nm relative to formaldehyde photolysis at this wavelength, for which the recommended $\phi((HCO))$= 0.29; at 193 nm HCO produced by the Cl + HCHO reaction was used for calibration, with Cl produced by $CCl_4$ photolysis at this wavelength. Estimated overall uncertainty in was 52% at 193 nm and 60% at 248 nm.

(c) Photo-oxidation studies in 1080 L quartz glass chamber surrounded by actinic fluorescent or low pressure mercury lamps. Total pressure 1000 mbar synthetic air and 296 ± 2 K. Loss of butenendial (*cis*- & *trans*- isomers) and formation of products, was measured from time-dependence of FTIR absorption. The main products formed included maleic anhydride, HCHO, $CH_3OH$ and $CH_3OOH$, with minor amounts of 3H-furan-2-one.

(d) Relative yields based on measurements, using FTIR, of end products (3H-furan-2-one and acrolein) of laser photolysis of butenendial in a closed cell at 193, 248, 308 and 351 nm. The two products are assumed to result directly from channels (2) and (6). CO was observed at all wavelengths but could not be asigned to a specific channel due to complex secondary chemistry. Acetylene was also observed but only at 193 nm. If the *trans/cis* isomerisation yields of Bierbach et al. are included, the total photolysis yield of butenendial is probably close to unity.

## Preferred Values

### Absorption cross-sections at 294 K

| $\lambda$/nm | $10^{20}$ $\sigma/cm^2$ | $\lambda$/nm | $10^{20}$ $\sigma/cm^2$ |
|---|---|---|---|
| 193 | 688 | 310 | 1.40 |
| 200 | 732 | 320 | 1.92 |
| 210 | 758 | 330 | 2.29 |
| 220 | 841 | 340 | 2.38 |
| 225 | 966 | 350 | 2.06 |
| 230 | 933 | 360 | 1.57 |
| 235 | 395 | 370 | 1.34 |
| 240 | 149 | 380 | 1.07 |
| 248 | 36.2 | 390 | 0.73 |
| 250 | 17.3 | 400 | 0.45 |
| 260 | 0.80 | 410 | 0.26 |
| 265 | 0.22 | 420 | 0.13 |
| 270 | 0.07 | 430 | 0.05 |

| | | | |
|---|---|---|---|
| 272 | 0.04 | 440 | 0.03 |
| 280 | 0.27 | 450 | 0.02 |
| 290 | 0.54 | 460 | 0.01 |
| 300 | 1.00 | | |

## Quantum Yields

| $\lambda$/nm | 350-460 | 193 | 248 | 308 | 351 |
|---|---|---|---|---|---|
| $\phi_1$ | 0.45 | | <0.4 | | |
| $\phi_2$ | 0 | 0.55± 0.29 | 0.12±0.07 | 0 | 0 |
| $\phi_6$ | | 0 | 0.028 | 0.012 | 0.012 |

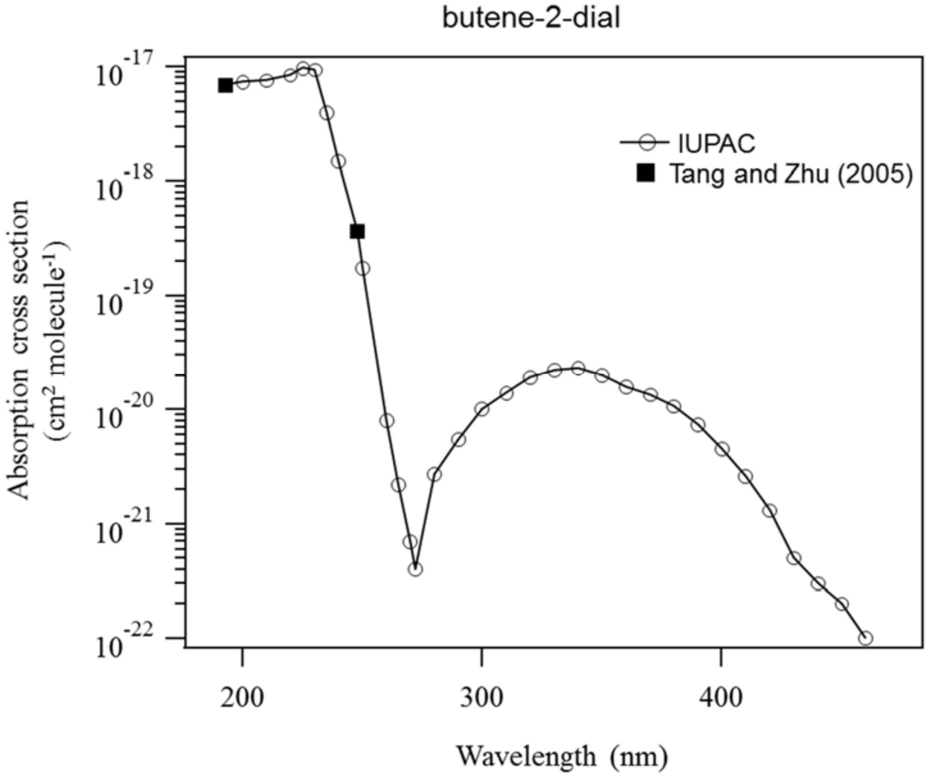
*Comments on Preferred Values*

There appear to be no measurements of the gas-phase UV/visible absorption spectrum of butene-2-dial but the absorption spectrum recorded by Hufford et al. (1952) in iso-octane solution resembles the gas phase spectrum of the related compound: 4-oxo-pentene-2-dial. The relative absorption coefficients extracted from Fig 1 of this work were scaled to the absolute gas phase cross-section $\sigma$(248 nm) determined by Tang and Zhu (2005) to provide the recommended values of $\sigma$ over the range 193 - 460 nm.

The only direct determination of primary quantum yields are those for HCO production reported by Tang and Zhu (2005). These results show that channel (2) only occurs at $\lambda$ <308 nm and is a major channel at 193 nm. The relative yields of the photolysis co-products by Tang and Zhu (2005) are only lower limits as secondary photolysis of these products occurs. Nevertheless it appears that channel (2) is not the only source of acrolein as it is observed at $\lambda$ > 308 nm. 3H-furan-2-one was a minor product compared with acrolein. The *cis/trans* isomerisation yields reported by Bierbach et al. (1994) are consistent with these results for channels (2) and (6), which are tentativly recommended. The major products observed from the photo-oxidation in synthetic air, reported by Bierbach et al., can be rationalised from secondary reactions of the primary photofragments.

## References

Bierbach, A., Barnes, Ian, Becker, K.H., and Wiesen, E., Environ.Sci.Technol., 28, 715 - 729, 1994.
Tang. Y. and Zhu, L., Chem Phys. Lett., 409, 151 - 156, 2005.
Hufford, D.L., Tarbell, D.S., Koszalka, T.R., J. Am. Chem. Soc., 74, 3014 - 3018, 1952.



Absorption Spectrum of butene-2-dial

# Datasheet P27

## 4-oxo-pent-2-enal ($CH_3C(O)CH=CHC(O)H$) + hυ → products

### Primary photochemical transitions

| Reaction | | | $\Delta H^\circ_{298}$/kJ·mol$^{-1}$ | $\lambda_{threshold}$/nm |
|---|---|---|---|---|
| *trans-/cis-* $CH_3$COCH=CHCHO | → | *cis-/trans-* $CH_3$COCH=CHCHO (1) | | |
| | → | 5-methyl-3*H*-furan-2-one (2) | | |
| | → | $CH_3$ + COCH=CHCHO (3) | | ~351 |
| | → | $CH_3$CO + CH=CHCHO (4) | | <346 |
| | → | $CH_3$COCH=CH + HCO (5) | | <346 |
| | → | $CH_3$COCH=CH2 + CO (6) | | |

### Absorption cross-section data

| Wavelength range/nm | Reference | Comments |
|---|---|---|
| 190-460 | Xiang et al., 2007 | (a) |

### Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6$)

| Measurement | Wavelength range/nm | Reference | Comments |
|---|---|---|---|
| *absolute quantum yields* | | | |
| $\phi$((HCO))= 0.13±0.02 (*trans*-) | 193 | Xiang et al., 2007 | (b) |
| $\phi$((HCO))= 0.078±0.012 (*cis*-) | | | |
| $\phi$((HCO)= 0.014±0.003(*trans*-) | 248 | | (b) |
| $\phi$((HCO))= 0.018±0.007(*cis*-) | | | |
| *relative quantum yields* ($\varphi$ %) | | | |
| $\varphi(1)$ = ~20 - 30 (cis-trans & trans-cis) | 320 - 480 | Bierbach et al., 1994 | (c) |
| $\varphi(1)$ = ≤20 (cis-trans & trans-cis) | 254 | | |
| $\varphi(CH_3CO)$= 11±3 | 193 | Xiang et al., 2007 | (d) |
| $\varphi(CH_3CO)$= 17±9 | 248 | | |
| $\varphi(2)$= 1.2±0.1 | 193 | | |
| $\varphi(2)$= 2.1±1.5 | 248 | | |
| $\varphi(2)$= 5.3±1.3 | 308 | | |
| $\varphi(2)$= 5.5±1.7 | 351 | | |
| $\varphi(3)$= 25±8 | 193 | | |
| $\varphi(3)$= 33±10 | 248 | | |
| $\varphi(3)$= 31±12 | 308 | | |
| $\varphi(3)$= 23±9 | 351 | | |

| | |
|---|---|
| $\varphi(6) = 25\pm10$ | 193 |
| $\varphi(6) = 23\pm8$ | 248 |
| $\varphi(6) = 40\pm10$ | 308 |
| $\varphi(6) = 33\pm9$ | 351 |

## Comments

(a) Three techniques - conventional UV-Vis absorption spectrometry, laser fluence attenuation, and cavity ringdown spectroscopy were used to determine absorption cross sections of purified samples of 4-oxo-pent-2-enal containing known amounts of *cis*- and *trans*- isomers defined by NMR. Cross section data at 1 nm intervals in the 190-250 nm region were determined by absorption in a 10 cm cell placed in a UV/visible spectrometer, with variation of the 4-oxo-2-pentenal pressure (mainly the *trans*- isomer) in the cell. The absolute uncertainty in these cross section data is about 40-70%. Cross section data at 193 and 248 nm were determined by monitoring transmitted laser photolysis fluence as a function of 4-oxo-2-pentenal pressure in the cell. The absolute cross section for 4-oxo-2-pentenal with a *trans/cis* ratio of 0.082:1 was: $4.79 \times 10^{-19}$ cm$^2$/molecule at 248 nm. The overall uncertainties in the determination of *cis*-4-oxo-2-pentenal cross sections were ±10% at 193 and 248 nm, and for *trans*-4-oxo-2-pentenal were ±15% at 193 nm and ±25% at 248 nm. Cross section data at 10 nm intervals in the 280-460 nm region were determined by cavity ring-down spectroscopy (CRDS). The method was calibrated using measurements of the cross section for acetone at 298 K and 300 nm which was within 14% of the preferred value. Some differences were obtained in the CRDS absorbances of samples containing either mainly cis-isomer and containing mainly trans-isomer, especially at $\lambda > 400$ nm. The relative amounts of *cis*- and *trans*-isomer in the mixtures was determined, which allowed the isomer-specific cross sections for 4-oxo-2-pentenal to be extracted.

(b) Quantum yield of HCO production determined from CRDS measurement of HCO concentration at 613.80 nm, using an absorption cross section of $\sim 2.0 \times 10^{-18}$ cm$^2$/molecule at this wavelength, calibrated relative to formaldehyde photolysis at 248 nm, for which the recommended $\phi((\mathrm{HCO})) = 0.29$.

(c) Photo-oxidation studies in 1080 L quartz glass chamber surrounded by actinic fluorescent or low pressure mercury lamps. Total pressure 1000 mbar synthetic air and 296 ± 2 K. Loss of 4-oxo-pent-2-enal (*cis*- & *trans*- isomers) and formation of products, from time-dependence of FTIR absorption. The main products formed included maleic anhydride, HCHO, $CH_3OH$ and $CH_3OOH$, with minor amounts of 5-Methyl-3H-furan-2-one.

(d) Relative yields based on measurements, using FTIR, of photolysis of 4-oxo-2-pentenal and amounts of it's end products: 5-Methyl-3H-furan-2-one, methyl vinyl ketone and ethane. The former two products are assumed to result directly from channels (2) and (6); ethane indicates $CH_3$ production in channel (3) or by dissociation of 'hot' $CH_3CO$ in channel (4). Significantly increased CO yields were observed at 193 and 248 nm. If the *trans/cis* isomerisation yields of Bierbach et al. are included, the total photolysis yield of 4-oxo-2-pentenal is close to unity, based on these results.

## Preferred Values

### Absorption cross-sections at 294 K

| λ/nm | $10^{20}$ σ/cm$^2$<br>*cis*- isomer | $10^{20}$ σ/cm$^2$<br>*trans*- isomer | $10^{20}$ σ/cm$^2$<br>50/50 *cis/trans* |
|---|---|---|---|
| 193 | 849 | 444 | 644 |
| 248 | 66.2 | 37.8 | 52 |
| 280 | 3.72 | 1.39 | 2.56 |
| 290 | 1.33 | 2.09 | 1.71 |
| 300 | 1.18 | 2.74 | 1.96 |
| 310 | 1.51 | 4.76 | 3.14 |
| 320 | 2.37 | 2.42 | 2.40 |
| 330 | 3.99 | 4.37 | 4.18 |
| 340 | 4.36 | 4.63 | 4.50 |
| 350 | 5.08 | 3.69 | 4.39 |
| 360 | 4.47 | 3.69 | 4.08 |
| 370 | 4.07 | 2.67 | 3.37 |
| 380 | 2.47 | 3.26 | 2.87 |
| 390 | 2.53 | 2.54 | 2.54 |
| 400 | 2.22 | 1.94 | 2.08 |
| 410 | 1.82 | 0.75 | 1.29 |
| 420 | 1.22 | 0.59 | 0.91 |
| 430 | 1.14 | 0.29 | 0.72 |
| 440 | 0.73 | 0.29 | 0.51 |
| 450 | 0.6 | 0.13 | 0.36 |
| 460 | 0.38 | 0.11 | 0.24 |

### Quantum Yields

| λ/nm | 350-460 | 193 | 248 | 308 | 351 |
|---|---|---|---|---|---|
| $\phi_1$ | 0.3 | - | <0.2 | - | - |
| $\phi_2$ | 0.05 | 0.01 | 0.02 | 0.05 | 0.05 |
| $\phi_3$ | - | 0.25 | 0.33 | 0.30 | 0.23 |
| $\phi_4$ | 0 | 0.11 | 0.17 | - | - |
| $\phi_5$ | - | 0.13 | 0.02 | 0 | 0 |
| $\phi_6$ | 0.33 | 0.25 | 0.25 | 0.40 | 0.33 |

*Comments on Preferred Values*

The cited data is the only reported quantitative study of gas-phase UV/visible absorption spectrum of 4-oxo-2-pentenal. It is composed of an absorption band in the shorter wavelength region ($\lambda_{max}$ = 215 nm; $\pi \rightarrow \pi^*$ transition) and broad absorption bands in the longer wavelength region ($\lambda_{max}$ = ~350 nm; most likely composed of two partially overlapping $n \rightarrow \pi^*$ transitions).

The absolute cross-sections for the wavelengths: 193nm, 248 nm and 280 – 460 nm (10 nm intervals) are listed in the paper of Xiang et al. (2007), together with the cross sections determined at 1 nm intervals by UV absorption on the 190 – 250 nm region for the mainly *trans*- isomer of 4-oxo-2-pentenal. Results using the different methods in the different spectral regimes were in reasonable agreement. A detailed account of the uncertainties in the experimental data was also given.

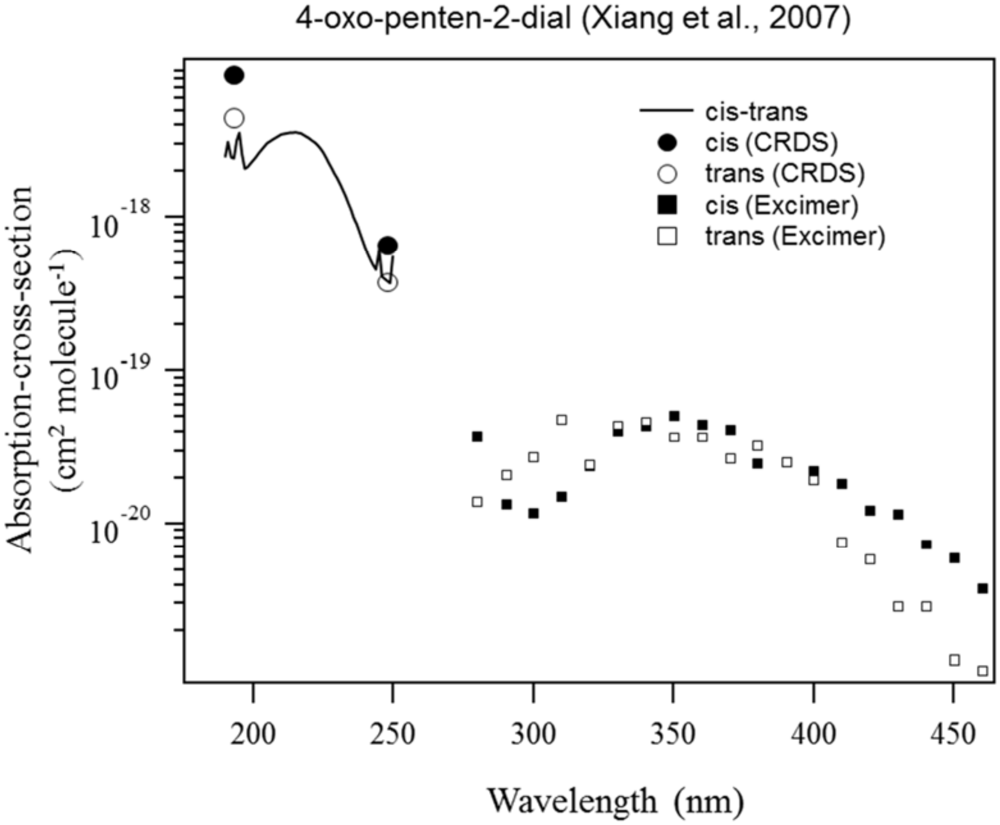
The preferred cross-sections are the isomer specific values reported by Xiang et al. (2007), based on their measurements using CRDS and LAS. A simple average of these recommended values applies to a 50:50 mixture of *cis/trans* isomers, which corresponds approximately to an equilibrium mixture for ambient conditions.

The only direct determination of primary quantum yields are those for HCO production reported by Xiang et al. (2007), and these results show that this channel only occurs at $\lambda$ <308 nm and remains a minor channel even at 193 nm. However the analysis of the relative yields of the photolysis products by Xiang et al. (2007), together with the *cis/trans* isomerisation yields reported by Bierbach et al (1994), give a consistent picture of the photolysis channels in the absence of $O_2$; the preferred quantum yields are based on the assumption that the overall photolysis quantum yield of *cis* and *trans* 4-oxo-2-pentenal is unity. The major products observed from the photo-oxidation in synthetic air, reported by Bierbach et al., can be rationalised from secondary reactions of the primary photofragments.

**References**

Bierbach, A., Barnes, I., Becker, K.H., and Wiesen, E.: Environ. Sci. Technol., 28, 715, 1994.

Xiang, B., Zhu, L., and Tang, Y.: J Phys. Chem. A, 111, 9025, 2007.



Absorption Spectrum of 4-oxo-penten-2-dial

# Datasheet P28

## 2-nitrophenol ($C_6H_4(OH)NO_2$) + hυ → products

### Primary photochemical transitions

| Reaction | | $\Delta H^\circ_{298}$/kJ·mol$^{-1}$ | $\lambda_{threshold}$/nm |
|---|---|---|---|
| $C_6H_4(OH)NO_2 \rightarrow C_6H_4(OH) + NO_2$ | (1) | | |
| $C_6H_4(OH)NO_2 \rightarrow C_6H_4(O) + HONO$ | (2) | | |

### Absorption cross-section data

| Wavelength range/nm | Reference | Comments |
|---|---|---|
| 320 - 450 | Chen et al., 2011 | (a) |

### Quantum yield data ($\phi = \phi_1 + \phi_2$)

| Measurement | Wavelength range/nm | Reference | Comments |
|---|---|---|---|
| $\phi$ (HONO) = 1.15 x $10^{-2}$ | 320 – 480 ($\lambda_{max}$ = 370) | Chen et al., 2011 | (b) |

### Comments

(a) Absorption cross sections of 2-nitrophenol were measured using incoherent broad-band cavity-enhanced absorption spectroscopy (IBBCEAS) with a Xe arc light source, giving a spectral range from 320 to 450 nm. The optical cavity was coupled into a 3.9 $m^3$ FEP chamber which contained the nitrophenols (99% purity) diluted to < 100 ppbv in purified air. The optical system was calibrated using methyl vinyl ketone absorption at 360 nm. Cross sections given at 1 nm intervals; overall error limits were estimated from standard deviations in the precision of the measurements, and other sources, to be 14% (1 s).

(b) Chen et al (2011) recalculated the quantum yield based on photolysis rates observed by Bardini (2006) under defined conditions in the EUPHORE chamber facility (Valencia, Spain), using their new gas phase cross-sections.

### Preferred Values

### Absorption cross-sections for 2-nitrophenol at 298 K

| λ/nm | $10^{20}\sigma$/cm$^2$ | λ/nm | $10^{20}\sigma$/cm$^2$ | λ/nm | $10^{20}\sigma$/cm$^2$ |
|---|---|---|---|---|---|
| 320 | 0.926 | 363 | 0.731 | 407 | 0.010 |
| 321 | 1.084 | 364 | 0.680 | 408 | 0.009 |
| 322 | 1.219 | 365 | 0.635 | 409 | 0.008 |
| 323 | 1.353 | 366 | 0.592 | 410 | 0.008 |
| 324 | 1.437 | 367 | 0.555 | 411 | 0.007 |
| 325 | 1.522 | 368 | 0.522 | 412 | 0.007 |
| 326 | 1.578 | 369 | 0.492 | 413 | 0.007 |
| 327 | 1.600 | 370 | 0.465 | 414 | 0.006 |

| | | | | | |
|---|---|---|---|---|---|
| 328 | 1.602 | 371 | 0.439 | 415 | 0.006 |
| 329 | 1.596 | 372 | 0.412 | 416 | 0.006 |
| 330 | 1.604 | 373 | 0.387 | 417 | 0.006 |
| 331 | 1.606 | 374 | 0.363 | 418 | 0.005 |
| 332 | 1.628 | 375 | 0.340 | 419 | 0.005 |
| 333 | 1.641 | 376 | 0.312 | 420 | 0.005 |
| 334 | 1.650 | 377 | 0.282 | 421 | 0.005 |
| 335 | 1.662 | 378 | 0.250 | 422 | 0.005 |
| 336 | 1.681 | 379 | 0.225 | 423 | 0.004 |
| 337 | 1.675 | 380 | 0.203 | 424 | 0.004 |
| 338 | 1.680 | 381 | 0.183 | 425 | 0.004 |
| 339 | 1.675 | 382 | 0.163 | 426 | 0.003 |
| 340 | 1.656 | 383 | 0.144 | 427 | 0.003 |
| 341 | 1.630 | 384 | 0.128 | 428 | 0.003 |
| 342 | 1.593 | 385 | 0.113 | 429 | 0.003 |
| 343 | 1.552 | 386 | 0.101 | 430 | 0.003 |
| 344 | 1.518 | 387 | 0.091 | 431 | 0.003 |
| 345 | 1.483 | 388 | 0.081 | 432 | 0.003 |
| 346 | 1.454 | 389 | 0.072 | 433 | 0.003 |
| 347 | 1.425 | 390 | 0.063 | 434 | 0.003 |
| 348 | 1.395 | 391 | 0.056 | 435 | 0.003 |
| 349 | 1.361 | 392 | 0.050 | 436 | 0.003 |
| 350 | 1.327 | 393 | 0.043 | 437 | 0.003 |
| 351 | 1.300 | 394 | 0.038 | 438 | 0.003 |
| 352 | 1.273 | 395 | 0.034 | 439 | 0.003 |
| 353 | 1.248 | 396 | 0.031 | 440 | 0.003 |
| 354 | 1.221 | 397 | 0.028 | 441 | 0.003 |
| 355 | 1.182 | 398 | 0.025 | 442 | 0.003 |
| 356 | 1.132 | 399 | 0.022 | 443 | 0.003 |
| 357 | 1.072 | 400 | 0.020 | 444 | 0.003 |
| 358 | 1.006 | 401 | 0.018 | 445 | 0.003 |
| 359 | 0.942 | 402 | 0.016 | 446 | 0.003 |
| 360 | 0.883 | 403 | 0.014 | 447 | 0.003 |
| 361 | 0.830 | 404 | 0.013 | 448 | 0.003 |
| 362 | 0.779 | 405 | 0.011 | 449 | 0.003 |
| | | 406 | 0.011 | 450 | 0.003 |

## Quantum Yields

No recommendation

*Comments on Preferred Values*

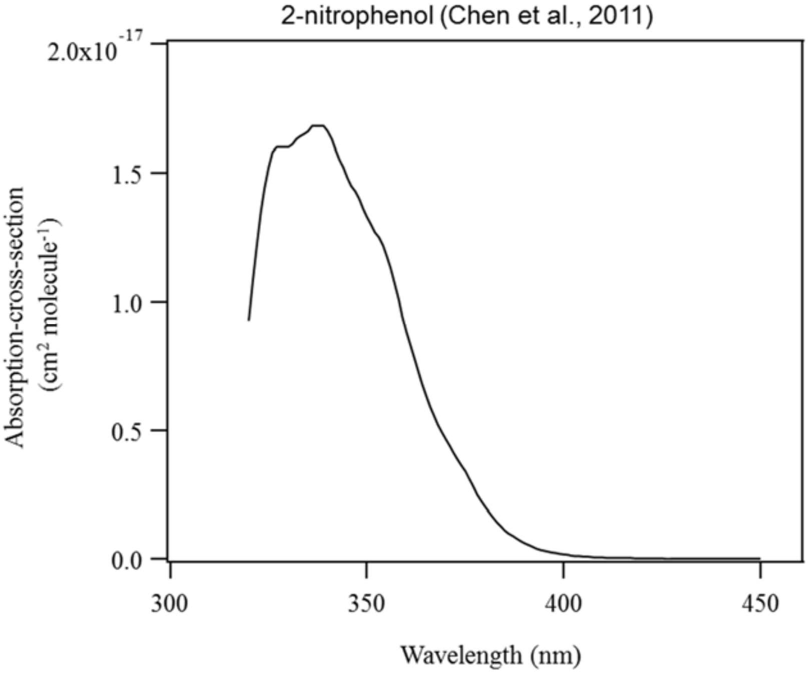
The recommended cross sections for 2-nitrophenol are those reported by Chen et al. (2011) These appear to be the only gas-phase spectra of this compound in the literature, although solution spectra of the nitrophenols have been measured. The absorption band of 2-nitrophenol peaks around 336 - 339 nm (absorption cross-section of $1.76 \times 10^{-17}$ cm$^2$ molecule$^{--1}$), which is blue-shifted by ~ 20 nm from the solution spectra recorded in acetonitryl (Bardini, PhD thesis, University of Cork, Ireland, 2006). The near-UV absorption of nitrophenols arises from the π(benzene ring) → π*(nitro group) transition.

The value of ϕ(HONO) recalculated by Chen et al (2011) from the measurements of Bardini (2006) in the EUPHORE chamber facility (Valencia, Spain), is substantially higher than earlier estimates e.g by Bejan et al. (2006), which were based on absorbed light intensity calculated from the solution phase spectrum of 2-nitrophenol, which is redshifted compared to the gas phase. the quantum yield based on photolysis rates observed by under defined conditions.

The value of ϕ(HONO) = $1.15 \times 10^{-2}$ could be used in atmospheric modelling, but experimental uncertainties preclude a safe recommendation.

**References**

Bejan, I., El Aal, Y.A., Barnes, I., Benter, T., Bohn, B., Wiesen, P. and J Kleffmann, J., Phys. Chem. Chem. Phys., 8, 2028–2035, 2006.
Bejan, I., Barnes, I., Olariu, R., Zhou, S., Wiesen, P., and Benter, Th., Phys. Chem. Chem. Phys., 9, 5686-5692, 2007.
Bardini, PhD thesis, University of Cork, Ireland, 2006.
Chen, J., Wenger, J.C., and Venables, D.S., J. Phys. Chem. *A*, 115, 12235-12242, 2011.



Absorption spectrum of 2-nitrophenol.

# Datasheet P30

## $C_6H_5C(O)H + h\upsilon \rightarrow$ products

### Primary photochemical transitions

| Reaction | | $\Delta H^\circ_{298}$/kJ·mol$^{-1}$ | $\lambda_{threshold}$/nm |
|---|---|---|---|
| $C_6H_5C(O)H \rightarrow C_6H_5 + HC(O)$ | (1) | 408.6 | 292 |
| $C_6H_5C(O)H \rightarrow C_6H_5CO + H$ | (2) | 363.9 | 328 |
| $C_6H_5C(O)H \rightarrow C_6H_6 + CO$ | (3) | 9.1 | 13.1 (μm) |

### Absorption cross-section data

| Wavelength range/nm | Reference | Comments |
|---|---|---|
| 220 - 300 | Nozière et al., 1994 | (a) |
| 245 - 300 | Caralp et al., 1999 | (b) |
| 255 - 296 | Etzkorn et al., 1999 | (c) |
| 280 - 308 | Zhu and Cronin, 2000 | (d) |
| 252 - 368 | Thiault et al., 2004 | (e) |
| 220 - 280 | El Dib et al., 2006 | (f) |
| 280 - 400 | Xiang et al., 2009 | (g) |
| 320 - 450 | Chen et al., 2011 | (h) |

### Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3$)

| Measurement | Wavelength range/nm | Reference | Comments |
|---|---|---|---|
| $\phi_1$(HCO) = 0.32±0.05 | 280 | Zhu and Cronin, 2000 | (d) |
| $\phi_1$ (HCO) = 0.45±0.05 | 285 | | |
| $\phi_1$ (HCO) = 0.29±0.05 | 308 | | |

### Comments

(a) The absorption cross sections were determined by flowing nitrogen containing a calibrated concentration of benzaldehyde through a 70 cm reaction cell. UV light from a $D_2$ lamp passed twice through the cell into a monochromator/photomultiplier unit for conventional absorption measurements. Resolution not given.

(b) Same set up as (a); no experimental details given.

(c) UV absorption cross sections were determined using a 1080 l quartz cell with a 0.5 m Czerny-Turner spectrometer coupled with a photodiode array detector (spectral resolution 0.15 nm). The maximum absolute absorption cross section for benzaldehyde at the 284.1 nm peak was $\sigma = (4.40 \pm 1.82) \times 10^{-18}$) cm$^2$molecule$^{-1}$.

(d) The UV photodissociation of benzaldehyde was investigated wavelengths of 280, 285 and 308 nm by employing excimer or dye laser photolysis in combination with CRDS. Absorption cross-sections of benzaldehyde were obtained from attenuation of the photolysis light. The HCO radical photofragmentation product was detected by CRDS at 614 nm and amounts formed after 10 μs were determined using the absorption cross-section of HCO at the probe laser wavelength, determined relative to the photolysis reaction: $H_2CO + h\nu \rightarrow HCO + H$, for which the HCO quantum yield is known. The uncertainty on the quantum yields reflects experimental scatter.

(e) Absorption cross-sections for benzaldehyde were measured in the wavelength region 252–368 nm using two different systems ($D_2$ lamp-diode array and $D_2$ lamp-monochromator). In addition, cross sections at 253.7 ($(8.5 \pm 1.3) \times 10^{-19}$), 312.2 ($(6.6 \pm 0.1) \times 10^{-20}$) and 365 nm ($(2.2 \pm 0.4)\times 10^{20}$) were measured using a Hg pen ray lamp and were found in good agreement with those obtained using the $D_2$ lamp-diode array system. The absorption spectra of aromatic aldehydes have been found to exhibit fine structures similarly to aromatic hydrocarbons.

(f) Photolysis of a slow flowing mixture of $Cl_2$, $N_2$, $O_2$, and $C_6H_5CH_3$. Absorption cross sections were determined by the "factor analysis method". Using factor analysis, the spectrum obtained is refined and the concentrations of the main absorbing species in a omplex mixture are extracted.

(g) Absorption measurements by CRDS. Cross sections and error limits (standard deviations in the precision of the measurements) given at 5 nm intervals in the range.

(h) Absorption cross sections of benzaldehyde were measured using incoherent broad-band cavity-enhanced absorption spectroscopy (IBBCEAS) with a Xe arc light source, giving a spectral range from 320 to 450 nm. The optical cavity was coupled into a 3.9 m$^3$ FEP chamber which contained the benzaldehyde (>99% purity) diluted to < 100 ppbv in purified air. The optical system was calibrated using methyl vinyl ketone absorption at 360 nm. Cross sections given at 1 nm intervals; overall error limits were estimated from standard deviations in the precision of the measurements, and other sources, to be 14% ($1\sigma$).

### Preferred Values

### Absorption cross-sections at 298 K

| $\lambda$/nm | $10^{20}\sigma$/cm$^2$ | $\lambda$/nm | $10^{20}\sigma$/cm$^2$ |
|---|---|---|---|
| 220 | 21.000 | 310 | 0.0480 |
| 225 | 32.000 | 315 | 0.0658 |
| 230 | 39.000 | 320 | 0.0576 |
| 235 | 32.000 | 325 | 0.0649 |
| 240 | 24.000 | 330 | 0.0667 |
| 245 | 2.080 | 335 | 0.0677 |
| 250 | 1.300 | 340 | 0.0627 |
| 255 | 0.920 | 345 | 0.0471 |
| 260 | 1.300 | 350 | 0.0508 |
| 265 | 1.640 | 355 | 0.0385 |
| 270 | 1.990 | 360 | 0.0468 |
| 275 | 2.270 | 365 | 0.0418 |
| 280 | 1.720 | 370 | 0.0130 |
| 285 | 1.830 | 375 | 0.0043 |
| 290 | 0.120 | 380 | 0.0007 |
| 295 | 0.053 | 385 | 0.0002 |
| 300 | 0.043 | 390 | 0.0001 |
| 305 | 0.056 | 395 | 0.0002 |

## Quantum Yields

| Wavelength /nm | $\phi_1$(HCO) |
|---|---|
| 308 | 0.29±0.05 |

*Comments on Preferred Values*

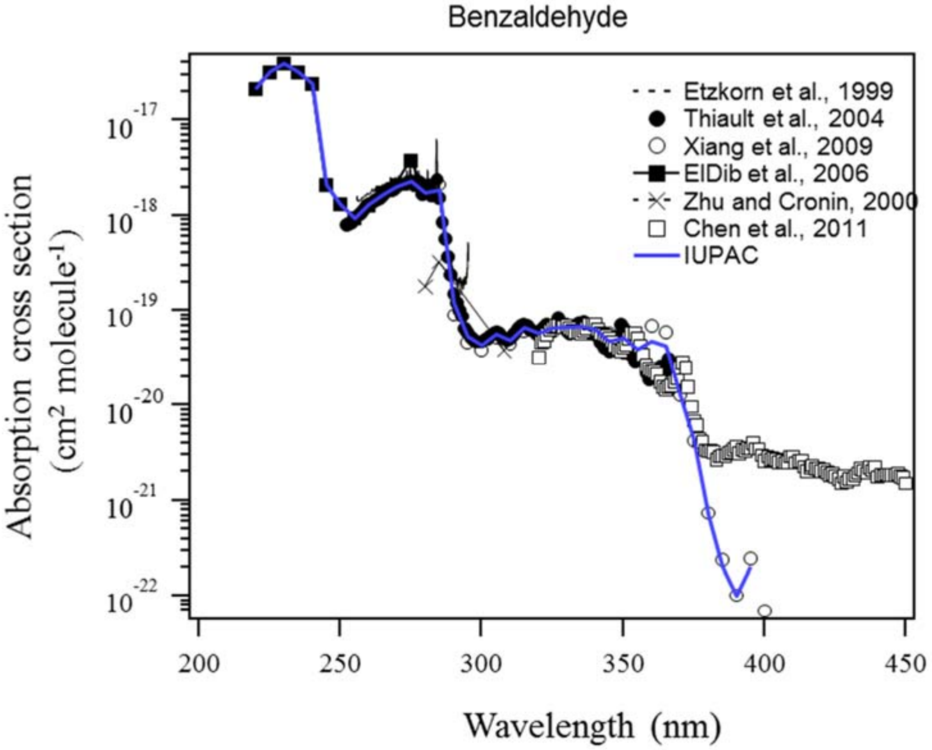
The absorption spectrum of benzaldehyde consists of three distinct regions; an intense band between 200 - 250 nm ($\sigma_{max}$ = 3.9 x $10^{-17}$ cm$^2$ at 230 nm); a second band between approx. 250 - 290 nm ($\sigma_{max}$ = 3.9 x $10^{-17}$ cm$^2$ at 230 nm); and a weaker absorbing plateau region with superimposed structure between 300 - 370 nm. The cross-section data of most of the studies are in reasonable agreement except for those of Noziere et al. (1999) which are systematically higher, and those of Zhu and Cronin which are significantly lower except at 318 nm where they are slightly higher, than other measurements. Part of the differences arise from different resolution of the measurements using narrow band (laser) and broad-band techniques, especially in regions with discrete absorption features. The most recent CEAS measurements of Chen at al. (2011) confirm the detailed structure in the near UV observed by Thiault et al. (2004), but the authors note a blue-shift in the wavelength calibration in the Thiault et al. results at $\lambda$ >335 nm, and an offset in their absorption at $\lambda$ >380 nm resulting from a baseline shift.

The preferred absorption cross-sections at $\lambda$ > 295 nm are averaged values from the measurements of Thiault et al.(2004) (blue shifted by 4nm between 335 – 375 nm), Xiang et al. (2009) and Chen et al.(2011) in the regions of data overlap. Between 255 nm < $\lambda$ < 295 nm the preferred values are average values of the data from Etzkorn et al. (1999), Thiault et al. (2004), and El Dib et al. (2006). The data of El Dib et al. (2006) are recommended for $\lambda$ < 255 nm.

The recommended quantum yield $\phi$(HCO) at 308 nm is the wavelength resolved value reported by Zhu and Cronin (2000). This gives a lower limit to the overall $\phi$. The values at at shorter wavelength may be in unrepresentative due to fine structure effects in this structured part of the spectrum. Nevertheless these results indicate that photolysis is a potentially important removal process for aromatic aldehydes in the troposphere.

## References

Chen, J., Wenger, J.C., and Venables, D.S., J. Phys. Chem. A, 115, 12235-12242, 2011.
Caralp, F., Focher, V., Lesclaux, R., Wallington, T.J., and Hurley, M.D., Phys. Chem. Chem. Phys., 1, 3509-3517, 1999.
El Dib, G., Chakir, A., Roth, E., Brion, J. and Daumont, D., J. Phys. Chem. A: 110, 7848-7857, 2006.
Etzkorn, T., Klotz, B., Sørensen S., Patroescu, I.V., Barnes, I., Becker, K.H., and Platt, U. Atmos. Environ., 33, 525-540, 1999.
B. Nozière, R. Lesclaux, M.D. Hurley, M.A. Dearth, and T.J. Wallington, J. Phys. Chem., 98, 2864-2873, 1994.
Thiault, G., Mellouki, A., Le Bras, G., Chakir, A., Sokolowski-Gomez, N. and Daumont, D., J. Photochem. Photobiol. A: Chem., 162, 273-281, 2004.
Xiang, B., Zhu, C. and Zhu, L., Chem. Phys. Lett., 474, 74-78, 2009.
Zhu, L. and Cronin, T.J., Chem. Phys. Lett., 317, 227-231, 2000.



Absorption spectrum of benzaldehyde

## Datasheet P31

### 3-methyl-2-nitrophenol ($CH_3C_6H_3(OH)NO_2$) + hυ → products

### Primary photochemical transitions

| Reaction | |
|---|---|
| $CH_3C_6H_3(OH)NO_2 \rightarrow CH_3C_6H_3(OH) + NO_2$ | (1) |
| $CH_3C_6H_3(OH)NO_2 \rightarrow CH_3C_6H_3(O) + HONO$ | (2) |

### Absorption cross-section data

| Wavelength range/nm | Reference | Comments |
|---|---|---|
| 320 – 450 | Chen et al., 2011 | (a) |

### Quantum yield data ($\phi = \phi_1 + \phi_2$)

| Measurement | Wavelength range/nm | Reference | Comments |
|---|---|---|---|
| $\phi$(HONO) = 1.5 x $10^{-4}$ | 320 – 480 ($\lambda_{max}$ = 370) | Bejan et al., 2006 | (b) |

### Comments

(a) Absorption cross sections of 3-methyl-2-nitrophenol were measured using incoherent broad-band cavity-enhanced absorption spectroscopy (IBBCEAS) with a Xe arc light source, giving a spectral range from 320 to 450 nm. The optical cavity was coupled into a 3.9 $m^3$ FEP chamber which contained the nitrophenols (99% purity) diluted to < 100 ppbv in purified air. The optical system was calibrated using methyl vinyl ketone absorption at 360 nm. Cross sections given at 1 nm intervals; overall error limits were estimated from standard deviations in the precision of the measurements, and other sources, to be 14% (1σ).

(b) The photolysis of nitrophenols was studied in a glass flow reactor, irradiated by fluorescent lamps emitting 300-500 nm. Concentration of 3-methy-2-nitrophenol measured by FTIR and of the HONO product by derivativisation on-line followed by LPAS. Value of $\phi$(HONO) was estimated from photolysis rate and absorbed intensity calculated from the solution phase spectrum of 3-methyl-2-nitrophenol.

### Preferred Values

### Absorption cross-sections for 3-methyl-2-nitrophenol at 298 K

| λ/nm | $10^{20}\sigma/cm^2$ | λ/nm | $10^{20}\sigma/cm^2$ | λ/nm | $10^{20}\sigma/cm^2$ |
|---|---|---|---|---|---|
| 320 | 0.454 | 363 | 0.553 | 407 | 0.035 |
| 321 | 0.544 | 364 | 0.533 | 408 | 0.033 |
| 322 | 0.615 | 365 | 0.512 | 409 | 0.030 |

| | | | | | |
|---|---|---|---|---|---|
| 323 | 0.637 | 366 | 0.494 | 410 | 0.028 |
| 324 | 0.690 | 367 | 0.476 | 411 | 0.025 |
| 325 | 0.717 | 368 | 0.455 | 412 | 0.022 |
| 326 | 0.734 | 369 | 0.439 | 413 | 0.021 |
| 327 | 0.756 | 370 | 0.425 | 414 | 0.019 |
| 328 | 0.753 | 371 | 0.407 | 415 | 0.019 |
| 329 | 0.770 | 372 | 0.388 | 416 | 0.016 |
| 330 | 0.779 | 373 | 0.379 | 417 | 0.015 |
| 331 | 0.795 | 374 | 0.370 | 418 | 0.013 |
| 332 | 0.797 | 375 | 0.356 | 419 | 0.013 |
| 333 | 0.812 | 376 | 0.345 | 420 | 0.012 |
| 334 | 0.829 | 377 | 0.333 | 421 | 0.012 |
| 335 | 0.828 | 378 | 0.323 | 422 | 0.012 |
| 336 | 0.841 | 379 | 0.313 | 423 | 0.010 |
| 337 | 0.847 | 380 | 0.296 | 424 | 0.001 |
| 338 | 0.849 | 381 | 0.280 | 425 | 0.009 |
| 339 | 0.847 | 382 | 0.264 | 426 | 0.008 |
| 340 | 0.843 | 383 | 0.248 | 427 | 0.008 |
| 341 | 0.842 | 384 | 0.231 | 428 | 0.007 |
| 342 | 0.842 | 385 | 0.215 | 429 | 0.008 |
| 343 | 0.832 | 386 | 0.196 | 430 | 0.008 |
| 344 | 0.823 | 387 | 0.181 | 431 | 0.009 |
| 345 | 0.812 | 388 | 0.166 | 432 | 0.008 |
| 346 | 0.803 | 389 | 0.148 | 433 | 0.009 |
| 347 | 0.797 | 390 | 0.135 | 434 | 0.010 |
| 348 | 0.786 | 391 | 0.122 | 435 | 0.008 |
| 349 | 0.778 | 392 | 0.109 | 436 | 0.009 |
| 350 | 0.768 | 393 | 0.099 | 437 | 0.009 |
| 351 | 0.763 | 394 | 0.089 | 438 | 0.010 |
| 352 | 0.750 | 395 | 0.081 | 439 | 0.010 |
| 353 | 0.739 | 396 | 0.073 | 440 | 0.010 |
| 354 | 0.729 | 397 | 0.068 | 441 | 0.008 |
| 355 | 0.720 | 398 | 0.063 | 442 | 0.007 |
| 356 | 0.708 | 399 | 0.059 | 443 | 0.008 |
| 357 | 0.686 | 400 | 0.056 | 444 | 0.009 |
| 358 | 0.663 | 401 | 0.052 | 445 | 0.008 |
| 359 | 0.640 | 402 | 0.049 | 446 | 0.008 |
| 360 | 0.618 | 403 | 0.045 | 447 | 0.008 |
| 361 | 0.594 | 404 | 0.043 | 448 | 0.007 |
| 362 | 0.572 | 405 | 0.040 | 449 | 0.006 |
| | | 406 | 0.037 | 450 | 0.006 |

## Quantum Yields

No recommendation

*Comments on Preferred Values*

The recommended cross sections for 3-methyl-2-nitrophenol are those reported by Chen et al. (2011) These appear to be the only gas-phase spectra of this compound in the literature, although solution spectra of the nitrophenols have been measured. The absorption band of 3-methy-2-nitrophenol peaks around 336 - 339 nm (absorption cross-section of 1.76 × 10$^{-17}$ cm$^2$molecule$^{--1}$), which is blue-shifted by ~ 20 nm from the solution spectra recorded in acetonitryl (Bardini, PhD thesis, University of Cork, Ireland, 2006). The near-UV absorption of nitrophenols arises from the π(benzene ring) → π*(nitro group) transition.

Bejan et al (2006) showed that HONO was a direct product of photolysis. However the value of ϕ(HONO) reported by Bejan et al (2006) is likely to be underestimated since it was based on absorbed light intensity calculated from the solution phase spectrum of 3-methy-2-nitrophenol, which Chen et al. (2011) show is redshifted compared to the gas phase.

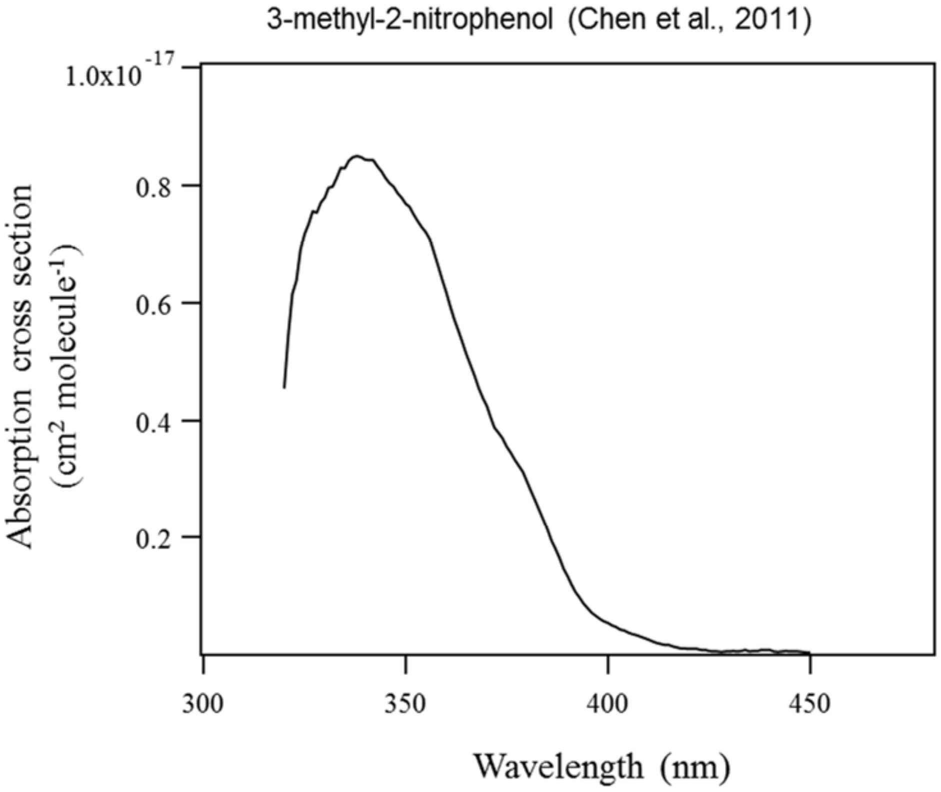
## References

Bejan, I., El Aal, Y.A., Barnes, I., Benter, T., Bohn, B., Wiesen, P. and J Kleffmann, J., Phys. Chem. Chem. Phys., 8, 2028–2035, 2006.

Bejan, I., Barnes, I., Olariu, R., Zhou, S., Wiesen, P., and Benter, Th., Phys. Chem. Chem. Phys., 9, 5686-5692, 2007.

Bardini, PhD thesis, University of Cork, Ireland, 2006.

Chen, J., Wenger, J.C., and Venables, D.S., J. Phys. Chem. A, 115, 12235-12242, 2011.



Absorption spectrum of 3-methyl-2-nitrophenol.

# Datasheet P32

## 4-methyl-2-nitrophenol ($CH_3C_6H_3(OH)NO_2$) + hυ → products

### Primary photochemical transitions

| Reaction | |
|---|---|
| $CH_3C_6H_3(OH)NO_2 \rightarrow CH_3C_6H_3(OH) + NO_2$ | (1) |
| $CH_3C_6H_3(OH)NO_2 \rightarrow CH_3C_6H_3(O) + HONO$ | (2) |

### Absorption cross-section data

| Wavelength range/nm | Reference | Comments |
|---|---|---|
| 320 – 450 | Chen et al., 2011 | (a) |

### Quantum yield data ($\phi = \phi_1 + \phi_2$)

| Measurement | Wavelength range/nm | Reference | Comments |
|---|---|---|---|
| $\phi$ (HONO) = ~$10^{-4}$ | 320 – 480 ($\lambda_{max}$ = 370) | Bejan et al., 2006 | (b) |

### Comments

(a) Absorption cross sections of 4-methyl-2-nitrophenol were measured using incoherent broad-band cavity-enhanced absorption spectroscopy (IBBCEAS) with a Xe arc light source, giving a spectral range from 320 to 450 nm. The optical cavity was coupled into a 3.9 $m^3$ FEP chamber which contained the nitrophenols (99% purity) diluted to < 100 ppbv in purified air. The optical system was calibrated using methyl vinyl ketone absorption at 360 nm. Cross sections given at 1 nm intervals; overall error limits were estimated from standard deviations in the precision of the measurements, and other sources, to be 14% (1 $\sigma$).

(b) The photolysis of nitrophenols was studied in a glass flow reactor, irradiated by fluorescent lamps emitting 300-500 nm. Concentration of 4-methy-2-nitrophenol measured by FTIR and of the HONO product by derivativisation on-line followed by LPAS. HONO formed but $\phi$(HONO) was not determined.

### Preferred Values

### Absorption cross-sections for 4-methyl-2-nitrophenol at 298 K

| λ/nm | $10^{20}\sigma$/cm$^2$ | λ/nm | $10^{20}\sigma$/cm$^2$ | λ/nm | $10^{20}\sigma$/cm$^2$ |
|---|---|---|---|---|---|
| 320 | 0.352 | 363 | 0.829 | 407 | 0.022 |
| 321 | 0.403 | 364 | 0.798 | 408 | 0.018 |
| 322 | 0.458 | 365 | 0.775 | 409 | 0.014 |
| 323 | 0.559 | 366 | 0.744 | 410 | 0.011 |
| 324 | 0.653 | 367 | 0.713 | 411 | 0.008 |

| | | | | | |
|---|---|---|---|---|---|
| 325 | 0.666 | 368 | 0.688 | 412 | 0.007 |
| 326 | 0.725 | 369 | 0.662 | 413 | 0.004 |
| 327 | 0.735 | 370 | 0.640 | 414 | 0.003 |
| 328 | 0.763 | 371 | 0.623 | 415 | 0.001 |
| 329 | 0.782 | 372 | 0.598 | 416 | 0.002 |
| 330 | 0.782 | 373 | 0.581 | 417 | 0.001 |
| 331 | 0.818 | 374 | 0.564 | 418 | |
| 332 | 0.831 | 375 | 0.543 | 419 | |
| 333 | 0.860 | 376 | 0.525 | 420 | |
| 334 | 0.866 | 377 | 0.505 | 421 | |
| 335 | 0.899 | 378 | 0.487 | 422 | |
| 336 | 0.912 | 379 | 0.470 | 423 | |
| 337 | 0.946 | 380 | 0.451 | 424 | |
| 338 | 0.964 | 381 | 0.425 | 425 | |
| 339 | 0.995 | 382 | 0.402 | 426 | |
| 340 | 1.022 | 383 | 0.374 | 427 | |
| 341 | 1.010 | 384 | 0.351 | 428 | |
| 342 | 1.006 | 385 | 0.319 | 429 | |
| 343 | 1.015 | 386 | 0.288 | 430 | |
| 344 | 1.005 | 387 | 0.259 | 431 | |
| 345 | 1.001 | 388 | 0.231 | 432 | |
| 346 | 1.012 | 389 | 0.204 | 433 | |
| 347 | 1.017 | 390 | 0.177 | 434 | |
| 348 | 1.005 | 391 | 0.153 | 435 | |
| 349 | 1.015 | 392 | 0.134 | 436 | |
| 350 | 1.022 | 393 | 0.116 | 437 | |
| 351 | 1.011 | 394 | 0.102 | 438 | |
| 352 | 1.021 | 395 | 0.089 | 439 | |
| 353 | 1.026 | 396 | 0.081 | 440 | |
| 354 | 1.011 | 397 | 0.073 | 441 | |
| 355 | 1.007 | 398 | 0.065 | 442 | |
| 356 | 0.995 | 399 | 0.059 | 443 | |
| 357 | 0.977 | 400 | 0.054 | 444 | |
| 358 | 0.952 | 401 | 0.048 | 445 | |
| 359 | 0.927 | 402 | 0.045 | 446 | |
| 360 | 0.901 | 403 | 0.041 | 447 | |
| 361 | 0.877 | 404 | 0.035 | 448 | |
| 362 | 0.850 | 405 | 0.031 | 449 | |
| | | 406 | 0.027 | 450 | |

## Quantum Yields

No recommendation

*Comments on Preferred Values*

The recommended cross sections for 4-methyl-2-nitrophenol are those reported by Chen et al. (2011). These appear to be the only gas-phase spectra of this compound in the literature, although solution spectra of the nitrophenols have been measured. The absorption of 4-methyl-2-nitrophenol varied linearly with concentration and the resulting spectra are shown in Figure 1. The absorption band of 4-methyl-2-nitrophenol peaks around 340-353 nm (absorption cross-section of 1.76 × $10^{-17}$ $cm^2$molecule$^{--1}$), which is blue-shifted by ~30 nm from the solution spectra recorded in acetonitryl (Bardini, PhD thesis, University of Cork, Ireland, 2006). The near-UV absorption of nitrophenols arises from the π(benzene ring) → π*(nitro group) transition.

The photolysis frequency reported by Bejan et al (2007) was approximately a factor of 2 slower than for 3-methy-2-nitrophenol. Values of ϕ(HONO) were not given.

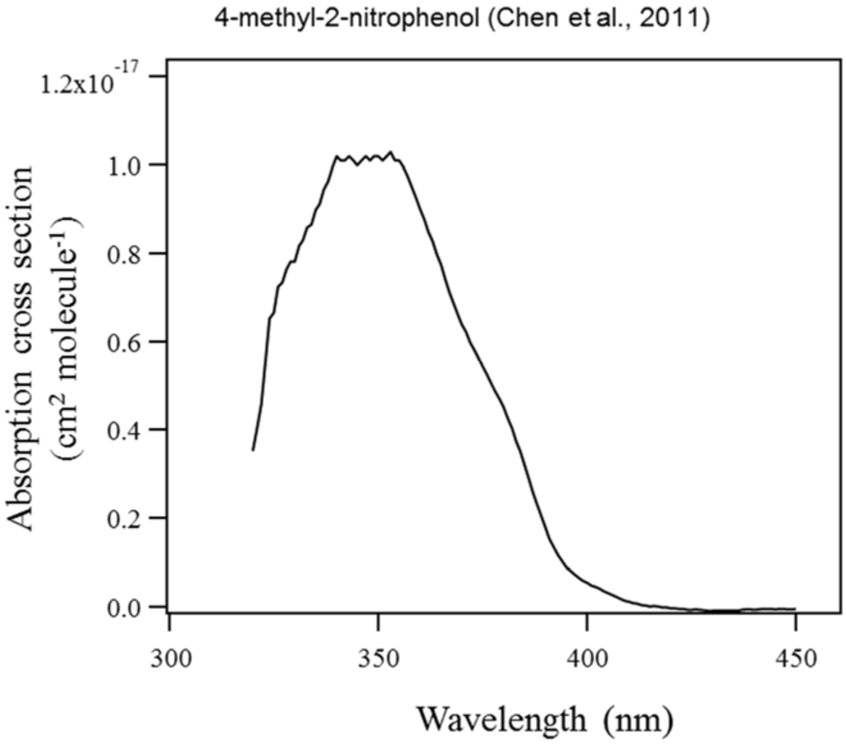
## References

Bejan, I., El Aal, Y.A., Barnes, I., Benter, T., Bohn, B., Wiesen, P. and J Kleffmann, J., Phys. Chem. Chem. Phys., 8, 2028–2035, 2006.

Bejan, I., Barnes, I., Olariu, R., Zhou, S., Wiesen, P., and Benter, Th., Phys. Chem. Chem. Phys., 9, 5686-5692, 2007.

Bardini, PhD thesis, University of Cork, Ireland, 2006.

Chen, J., Wenger, J.C., and Venables, D.S., J. Phys. Chem. A, 115, 12235-12242, 2011.



Absorption spectrum of 4-methy-2-nitrophenol.