

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HO_x_VOC51

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This data sheet last evaluated: January 2009; last change in preferred values: August 2008.



$$\Delta H^\circ(1) = -155 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -374 \text{ kJ}\cdot\text{mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$7.7 \times 10^{-14} \exp[(1296 \pm 364)/T]$	274-338	Cox and Tyndall, 1980	MM-AS (a)
$(6.5 \pm 1.0) \times 10^{-12}$	298		
$(5.4 \pm 1.1) \times 10^{-12}$	300	Jenkin et al., 1988	MM-IR-AS (b)
$3.0 \times 10^{-13} \exp[(720 \pm 100)/T]$	228-380	Dagaut et al., 1988	FP-AS (c)
$(2.9 \pm 0.4) \times 10^{-12}$	298		
$(4.8 \pm 0.2) \times 10^{-12}$	300	Moortgat et al., 1989	MM-IR-AS (d)
$4.4 \times 10^{-13} \exp[(780 \pm 55)/T]$	248-573	Lightfoot et al., 1990	FP-AS (e)
$(6.2 \pm 1.0) \times 10^{-12}$	298		
$2.9 \times 10^{-13} \exp(862 \pm 44)/T]$	248-700	Lightfoot et al., 1991	FP-AS (f)
$(5.13 \pm 0.55) \times 10^{-12}$	298	Boyd et al., 2003	PLP-AS (g)
$3.82 \times 10^{-13} \exp(781 \pm 127)/T]$	205-298	Raventos-Duran et al., 2007	DF-CIMS (h)
$(5.5 \pm 0.6) \times 10^{-12}$	298		
<i>Branching Ratios</i>			
$k_1/k = 0.92 \pm 0.05$	295	Wallington and Japar, 1990; Wallington, 1991	P-FTIR (i)
$k_2/k = 1/[1+498 \exp(-1160/T)]$	218-298	Elrod et al., 2001	DF-CIMS (j)
$k_2/k = 0.11 \pm 0.02$	298		

Comments

- (a) MM study of photolysis of Cl₂ in the presence of CH₄-H₂-O₂ mixtures at 1013 mbar (760 Torr) pressure. CH₃O₂ and HO₂ radicals were monitored by absorption at 250 nm and 210 nm, respectively.
- (b) MM study of photolysis of Cl₂ in the presence of CH₄-H₂O₂-O₂ mixtures. HO₂ radicals were monitored by IR absorption with a tunable diode laser and CH₃O₂ monitored by UV absorption at 260 nm. $\sigma(\text{CH}_3\text{O}_2) = 3.53 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ was determined at 260 nm. k determined from observed perturbation of the second-order kinetics of the HO₂ radical self-reaction by the presence of CH₃O₂ in large excess. Experiments were carried out at a total pressure of 13 mbar (10 Torr). Similar experiments on mixtures of Cl₂-H₂-CH₄-O₂ were performed at 1013 mbar (760 Torr) total pressure and 303 K and yielded $k = (6.8 \pm 0.9) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which was taken as confirmation of the value obtained at 13 mbar (10 Torr).
- (c) FP-UV absorption study involving Cl₂-CH₃OH-CH₄-O₂-N₂ mixtures at total pressures of 133 mbar (100 Torr); $\sigma(\text{HO}_2)$ and $\sigma(\text{CH}_3\text{O}_2)$ were determined over the wavelength range 215 nm to 280 nm. At 250 nm $\sigma(\text{CH}_3\text{O}_2) = 3.3 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ was determined. First- or second-order kinetics conditions were not obtainable for either HO₂ or CH₃O₂ and k was determined from numerical

simulation of the absorption decay curves.

- (d) Study of the photooxidation of CH₃CHO at 933 mbar (700 Torr), with double multipath spectrometer, combining both IR and UV absorption spectrometry for monitoring reactants and products, together with modulated photolysis for transient detection. Transient absorptions were assigned to peroxy radicals and the rate coefficient was obtained from kinetic analysis by numerical simulation.
- (e) FP-UV absorption study of Cl₂-CH₃OH-CH₄-O₂-N₂ mixtures at pressures of 160 mbar or 1013 mbar (120 Torr or 760 Torr). Revised cross-section data were used, $\sigma(\text{HO}_2) = 5.3 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ at 210 nm and $\sigma(\text{CH}_3\text{O}_2) = 3.6 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ at 260 nm.
- (f) FP-UV absorption study of Cl₂-CH₃OH-CH₄-O₂-N₂ mixtures at 1013 mbar (760 Torr) and over the temperature range 600 K to 719 K. The temperature-dependent rate coefficient listed above was derived by the authors from a re-analysis of all of their data, including previous studies from flash photolysis experiments.
- (g) PLP-UV absorption study of H₂O₂-CH₄-O₂-N₂ mixtures at 1013 mbar (760 Torr) and 298 K. Conditions were chosen such that HO₂ was in excess, with initial concentration ratios [HO₂]/[CH₃O₂] in the range 4 - 10. *k* was determined from simulation of transient decay traces recorded at 270 nm and either 210 nm or 220 nm. The signal at 270 nm was dominated by CH₃O₂ absorption, with its decay being almost entirely due to the reaction with HO₂. The signal at 210 nm or 220 nm was mainly due to HO₂ absorption, with its self-reaction making the major contribution to its removal.
- (h) Turbulent fast-flow system operating at total pressures over the range 100 to 267 mbar. CH₃O₂ was produced by reaction of CH₄ with F atoms and subsequent addition of O₂. The CH₃O₂ was mixed with excess HO₂ produced by the H+O₂+M reaction. Concentrations of CH₃O₂ and HO₂ were monitored following chemical ionization using SF₆⁻ as the reagent ion. *k* obtained from simulation of the system. Upper limit branching ratios reported for channels forming CH₃OH + O₃ and CH₃O + HO + O₂, based on failure to detect O₃ and HO as products.
- (i) Photolysis of F₂ in the presence of CH₄ and H₂ in synthetic air or O₂ at total pressures in the range 20 mbar (15 Torr) to 933 mbar (700 Torr). CH₃OOH, CH₄, and a number of minor products were monitored by FTIR.
- (j) Turbulent fast-flow system operating at total pressures of 133 mbar (100 Torr). CH₃O₂ was produced by reaction of CH₄ with F atoms and subsequent addition of O₂. The CH₃O₂ was mixed with HO₂ produced by the H+O₂+M reaction. Concentrations of CH₃O₂, CH₃OOH, CH₂O, and HO₂ were monitored by time-resolved CIMS. Values of *k*₂ were derived by detailed modelling of the [CH₂O] profile. Values of the branching ratio are based on an overall value of $k = 3.8 \times 10^{-13} \exp(800/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Preferred Values

Parameter	Value	T/K
<i>k</i>	$5.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	298
<i>k</i>	$3.8 \times 10^{-13} \exp(780/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	205-580
<i>k</i> ₁ / <i>k</i>	0.9	298
<i>k</i> ₂ / <i>k</i>	0.1	298
<i>k</i> ₁ / <i>k</i>	1-(<i>k</i> ₂ / <i>k</i>)	220-298
<i>k</i> ₂ / <i>k</i>	$1/[1+ 498 \exp(-1160/T)]$	220-298
<i>Reliability</i>		
Δ log <i>k</i>	± 0.2	298
Δ <i>E/R</i>	± 200 K	

$\Delta k_1/k$	± 0.1	298
$\Delta k_2/k$	± 0.1	298
$\Delta(E_2/R - E/R)$	± 500 K	

Comments on Preferred Values

The reported values of k are in generally good agreement, although some systematic differences are apparent in studies using UV absorption spectroscopy, due in part to the use of different values of UV absorption cross sections for HO₂ and CH₃O₂ in the analyses. The preferred rate coefficient at 298 K is the mean of the reported room temperature values. The recommended temperature coefficient remains based on that reported by Lightfoot et al. (1990), which was selected on the basis of the wider range of temperatures studied, compared with the earlier investigations of Cox and Tyndall (1980) and Dagaut et al. (1988). The temperature dependence reported more recently by Raventos-Duran et al. (2007) agrees with this recommendation and allows the temperature range of the preferred values to be extended.

The studies of Kurylo et al. (1987), Jenkin et al. (1988) and Lightfoot et al. (1990) show that the room temperature rate coefficient is independent of pressure over the range 13 mbar to 1013 mbar. Raventos-Duran et al. (2007) have also found k to be independent of pressure over the range 100 mbar to 200 mbar for the temperature range 205 K to 298 K. English et al. (2008) have investigated the influence of water vapour at concentrations up to ca. 3×10^{17} molecule cm⁻³, over the range 263-303 K. No significant effect was observed.

The direct experimental studies of the branching ratio show that formation of CH₃OOH and O₂ via reaction channel (1) dominates at room temperature (Wallington and Japar, 1990; Wallington, 1991; Elrod et al., 2001), and this is also consistent with a number of theoretical appraisals of the reaction (Hou and Wang, 2005; Zhou et al., 2006; Anglada et al., 2006). The study of Elrod et al. (2001) provides direct evidence for a small contribution from channel (2) at 298 K ($k_2/k \approx 0.1$), increasing at lower temperatures to a value of $k_2/k \approx 0.3$ at 218 K. Provisionally, the expression for k_2/k derived by Elrod et al. (2001) is accepted with substantial error limits, until confirmatory studies on both the temperature and pressure dependence are available. The (major) balance of the reaction is assigned to channel (1). Raventos-Duran et al. (2007) have confirmed that reaction channels forming CH₃OH + O₃ and CH₃O + HO + O₂ are not significant, assigning respective upper limit ratios of about 0.02 and 0.04 at 298 K, decreasing to about 0.01 and 0.02 at 205 K.

References

- Anglada, J. M., Olivella, S. and Sol, A.: *J. Phys. Chem. A*, 110, 6073, 2006.
 Boyd, A. A., Flaud, P.-M., Daugey, M. and Lesclaux, R.: *J. Phys. Chem. A*, 107, 818, 2003.
 Cox, R. A. and Tyndall, G. S.: *J. Chem. Soc. Faraday Trans.*, 2, 76, 153, 1980.
 Dagaut, P., Wallington, T. J. and Kurylo, M. J.: *J. Phys. Chem.*, 92, 3833, 1988.
 Elrod, M. J., Ranschaert, D. L. and Schneider, N. J.: *Int. J. Chem. Kinet.*, 33, 363, 2001.
 English, A. M., Hansen, J. C., Szente, J. J. and Maricq, M. M.: *J. Phys. Chem. A*, 112, 9220, 2008.
 Hou, H. and Wang, B.: *J. Phys. Chem. A*, 109, 451, 2005.
 Jenkin, M. E., Cox, R. A., Hayman, G. D. and Whyte, L. J.: *J. Chem. Soc. Faraday Trans. 2*, 84, 913 1988.
 Kurylo, M. J., Dagaut, P., Wallington, T. J. and Neuman, D. M.: *Chem. Phys. Lett.*, 139, 513, 1987.
 Lightfoot, P. D., Roussel, P., Caralp, F. and Lesclaux, R.: *J. Chem. Soc. Faraday Trans.* 87, 3213, 1991.
 Lightfoot, P. D., Veyret, B. and Lesclaux, R.: *J. Phys. Chem.* 94, 708, 1990.
 Moortgat, G. K., Cox, R. A., Schuster, G., Burrows, J. P. and Tyndall, G. S.: *J. Chem. Soc. Faraday Trans. 2*, 85, 809, 1989.
 Raventos-Duran, M. T., McGillen, M., Percival, C. J., Hamer, P. D. and Shallcross, D. E.: *Int. J. Chem. Kinet.*, 39, 571, 2007.
 Wallington, T. J. and Japar, S. M.: *Chem. Phys. Lett.*, 167, 513, 1990.

Wallington, T. J.: J. Chem. Soc. Faraday Trans., 87, 2379, 1991.

Zhou, X-M., Zhou, Z-Y., Wu, Q-Y, Jalbout, A. F. and Zhang, N.: Int. J. Quant. Chem., 106, 514, 2006.

