IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HOx_VOC23

$$HO + CH_3OH \rightarrow H_2O + CH_2OH \qquad (1)$$
$$\rightarrow H_2O + CH_3O \qquad (2)$$

$\Delta H°(1) = -95.2 \text{ kJ·mol}^{-1}$

$\Delta H°(2) = -60.2 \text{ kJ·mol}^{-1}$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.06 \pm 0.10) \times 10^{-12}$	296 ± 2	Overend and Paraskevopoulos, 1978	FP-RA
$(1.00 \pm 0.10) \times 10^{-12}$	298	Ravishankara and Davis, 1978	FP-RF
$4.8 \times 10^{-12} \exp[-(480 \pm 70)/T]$	240-440	Wallington and Kurylo, 1987	FP-RF
$(8.61 \pm 0.47) \times 10^{-13}$	296		
$(1.01 \pm 0.10) \times 10^{-12}$	298 ± 2	McCaulley et al., 1989	DF-LIF
$5.89 \times 10^{-20} T^{2.65} \exp(444/T)$	294-866	Hess and Tully, 1989	PLP-LIF
$(9.34 \pm 0.41) \times 10^{-13}$	294		
$(9.0 \pm 0.9) \times 10^{-13}$	298 ± 2	Nelson et al., 1990	PR-RA
$(8.64 \pm 1.30) \times 10^{-12}$	1205 ± 16	Bott and Cohen, 1991	SH-RA
$3.6 \times 10^{-12} \exp[-(415 \pm 70)/T]$	235-360	Jiménez et al., 2003	PLP-LIF
$(9.3 \pm 1.1) \times 10^{-13}$	298		
$6.67 \times 10^{-18} T^2 \exp[(140 \pm 14)/T]$	210-351	Dillon et al., 2005	PLP-LIF
$(9.3 \pm 0.7) \times 10^{-13}$	298 ± 1		
Relative Rate Coefficients			
$(9.0 \pm 0.7) \times 10^{-13}$	300 ± 3	Tuazon et al., 1983	RR (a)
$(9.3 \pm 2.2) \times 10^{-13}$	298 ± 2	Nelson et al., 1990	RR (b)
$(8.6 \pm 0.8) \times 10^{-13}$	298 ± 4	Picquet et al., 1998	RR (c)
$(9.6 \pm 1.0) \times 10^{-13}$	298 ± 2	Oh and Andino, 2001	RR (d)
$(8.4 \pm 0.7) \times 10^{-13}$	298 ± 2	Oh and Andino, 2001	RR (b)
$(7.88 \pm 0.47) \times 10^{-13}$	296 ± 2	Sørensen et al., 2002	RR (e,f)
$(8.18 \pm 0.52) \times 10^{-13}$	296 ± 2	Sørensen et al., 2002	RR (e,g)
Branching Ratios			
$k_2/k = 0.15 \pm 0.08$	298 ± 2	McCaulley et al., 1989	(h)

Comments

(a) HO radicals were generated by the dark reaction of hydrazine with O_3 in air. The concentrations of methanol and dimethyl ether (the reference compound) were measured by FTIR spectroscopy. The measured rate coefficient ratio of k(HO + methanol)/k(HO + dimethyl ether) = 0.314 ± 0.024 is placed on an absolute basis using the rate coefficient k(HO + dimethyl ether) = 2.86×10^{-12} cm^3 molecule^{-1} s^{-1} at 300 K (IUPAC, current recommendation).

(b) HO radicals were generated by the photolysis of CH_3ONO in air at >300 nm. The concentrations of methanol and cyclohexane (the reference compound) were measured by GC. The measured rate coefficient ratio of k(HO + methanol)/k(HO + cyclohexane) is placed on an absolute basis using a rate coefficient of k(HO + cyclohexane) = 6.97 x 10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson, 2003).

(c) HO radicals were generated by the photolysis of H_2O_2 in air at 254 and 310 nm. The concentrations of methanol and n-pentane (the reference compound) were measured by GC. The measured rate coefficient ratio, k(HO + methanol)/k(HO + n-pentane), is placed on an absolute basis using a rate coefficient of k(HO + n-pentane) = 3.80 x 10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson, 2003).

(d) HO radicals were generated by the photolysis of CH_3ONO in air at >300 nm. The concentrations of methanol and ethanol (the reference compound) were measured by GC. The measured rate coefficient ratio of k(HO + methanol)/k(HO + ethanol) = 0.30 ± 0.03 is placed on an absolute basis using a rate coefficient of k(HO + ethanol) = 3.2 x 10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, current recommendation).

(e) HO radicals were generated by the photolysis of CH_3ONO in air at 1.0 bar (750 Torr). The concentrations of methanol and acetylene or ethene (the reference compounds) were measured by in situ FTIR spectroscopy. The measured rate coefficient ratios of k(HO + methanol)/k(HO + acetylene) = 1.01 ± 0.06 and k(HO + methanol)/k(HO + ethene) = 0.095 ± 0.006 are placed on an absolute basis using rate coefficients of k(HO + acetylene) = 7.8 x 10^{-13} cm^3 molecule^{-1} s^{-1} at 750 Torr pressure of air or O_2 and 296 ± 2 K (Sørensen et al., 2003) and k(HO + ethene) = 8.61 x 10^{-12} cm^3 molecule^{-1} s^{-1} at 296 K and atmospheric pressure of air (Atkinson, 1997). No effect of the presence of NaCl or NH_4NO_3 aerosol was observed.

(f) Relative to acetylene.

(g) Relative to ethene.

(h) Derived from measurements of the rate coefficients for the reactions of the HO radical with CH_3OH, CD_3OH and CD_3OD and of the DO radical with CH_3OH, CH_3OD, CD_3OH and CD_3OD, assuming that secondary kinetic isotope effects are negligible.

Preferred Values

k = 9.0 x 10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K.
k = 2.85 x 10^{-12} exp(-345/T) cm^3 molecule^{-1} s^{-1} over the temperature range 210-300 K.
k_2/k = 0.15 at 298 K.

Reliability
Δlog k = ± 0.08 at 298 K.
$\Delta(E/R)$ = ± 150 K.
$\Delta k_2/k$ = ± 0.10 at 298 K.

Comments on Preferred Values

The preferred rate coefficient is obtained by fitting the absolute rate coefficients of Wallington and Kurylo (1987), Hess and Tully (1989), Jiménez et al. (2003) and Dillon et al. (2005) to the three parameter expression $k = CT^2$ exp(-D/T). This results in k = 6.38 x 10^{-18} T^2 exp(144/T) cm^3 molecule^{-1} s^{-1} over the temperature range 210-866 K. The preferred Arrhenius expression, $k = A$ exp(-B/T), is centered at 245 K, and is derived from the three parameter equation with $A = C e^2 T^2$ and $B = D + 2T$. Note that the Arrhenius expression should not be used outside of the stated temperature range (210-300 K); rather the three-parameter expression k = 6.38 x 10^{-18} T^2 exp(144/T) cm^3 molecule^{-1} s^{-1} should be employed. The absolute room temperature rate coefficients of Overend and Paraskevopoulos (1978), Ravishankara et al. (1978), McCaulley et al. (1989) and Nelson et al. (1990) are in good

agreement with the preferred values, as are the room temperature relative rate coefficients of Tuazon et al. (1983), Nelson et al. (1990), Picquet et al. (1998), Oh and Andino (2001) and Sørensen et al. (2002).

The kinetic (McCaulley et al., 1989) and product (Hägele et al., 1983; Meier et al., 1984) studies show that the reaction proceeds mainly by channel (1) at room temperature, as expected from the thermochemistry of the reaction pathways (1) and (2).

References

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

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

Bott, J. F. and Cohen, N.: Int. J. Chem. Kinet. 23, 1075, 1991.

Dillon, T. J., Hölscher, D., Sivakumaran, V., Horowitz, A. and Crowley, J. N.: Phys. Chem. Chem. Phys. 7, 349, 2005.

Hägele, J., Lorenz, K., Rhäsa, D. and Zellner, R.: Ber. Bunsenges. Phys. Chem. 87, 1023, 1983.

Hess, W. P. and Tully, F. P.: J. Phys. Chem. 93, 1944, 1989.

IUPAC,: http://iupac.pole-ether.fr, 2013.

Jiménez, E., Gilles, M. K. and Ravishankara, A. R.: J. Photochem. Photobiol. A: Chem. 157, 237, 2003.

McCaulley, J. A., Kelly, N., Golde, M. F. and Kaufman, F.: J. Phys. Chem. 93, 1014, 1989.

Meier, U., Grotheer, H. H. and Just, Th.: Chem. Phys. Lett. 106, 97, 1984.

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.

Overend, R. and Paraskevopoulos, G.: J. Phys. Chem. 82, 1329, 1978.

Picquet, B., Heroux, S., Chebbi, A., Doussin, J.-F., Durand-Jolibois, R., Monod, A., Loirat, H. and Carlier, P.: Int. J. Chem. Kinet. 30, 839, 1998.

Ravishankara, A. R. and Davis, D. D.: J. Phys. Chem. 82, 2852, 1978.

Sørensen, M., Hurley, M. D., Wallington, T. J., Dibble, T. S. and Nielsen, O. J.: Atmos. Environ. 36, 5947, 2002.

Sørensen, M., Kaiser, E. W., Hurley, M. D., Wallington, T. J. and Nielsen, O. J.: Int. J. Chem. Kinet. 35, 191, 2003.

Tuazon, E. C., Carter, W. P. L., Atkinson, R. and Pitts Jr., J. N.: Int. J. Chem. Kinet. 15, 619, 1983.

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