IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet II.A2.5 HOx_VOC3

This data sheet last evaluated: December 2005.

$HO + C_2H_4 + M \rightarrow C_2H_4OH + M$

$\Delta H° = -23$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	*Reference*	Technique/ Comments
Absolute Rate Coefficients			
5.5×10^{-29} [Ar]	296	Zellner and Lorenz, 1984	PLP-RF (a)
$(6.1 \pm 1.2) \times 10^{-29}$ [N_2]	300	Kuo and Lee, 1991	DF-RF (b)
$(5.2 \pm 1.1) \times 10^{-29}$ [O_2]	300		
4.1×10^{-29} $(T/300)^{-3.4}$ [He]	300-800	Fulle et al., 1997	PLP-LIF (c)
$(2.8 \pm 0.1) \times 10^{-29}$ $(T/300)^{-3.5}$ [He]	300-423	Chuong and Stevens, 2000	DF-LIF (d)
$(11.6 \pm 1.8) \times 10^{-29}$ [N_2]	296	Vakhtin et al., 2003	PLP-LIF (e)
Relative Rate Coefficients			
$(9.5^{+3.2}_{-2.4}) \times 10^{-29}$ [air]	295	Klein et al., 1984	RR (f)
$(5.9^{+3.0}_{-1.0}) \times 10^{-29}$ [Ar]	295		

Comments

(a) Pressure range 4 mbar to 130 mbar, temperature range 296-524 K. Falloff extrapolation using $F_c = 0.8$.

(b) Pressure range 0.4 mbar to 66 mbar. HO radicals were generated by reaction of H atoms with excess NO_2. Data extrapolated using $F_c = 0.7$.

(c) The pressure was varied between 1 mbar and 150 bar. Falloff curves were also constructed using earlier rate data with a calculated $F_c = 0.21 \exp(-220/T) + \exp(-T/305)$ and $F_c(300) = 0.47$. The value $\Delta H°(0\ K) = -(123 \pm 6)$ kJ mol^{-1} was derived from a third-law analysis of the equilibrium constant K_c for which $K_c = 2.1 \times 10^{-2}\ T^{-0.95} \exp(14780/T)$ bar^{-1} was obtained from measurements performed at 646-803 K and He pressures up to 140 bar.

(d) Pressure range 2.6 mbar to 8 mbar. Falloff extrapolation using $F_c = 0.6$ and $k_\infty = 1.96 \times 10^{-12} \exp(438/T)$ cm^3 molecule^{-1} s^{-1} from ref. 5. Difference to the results from ref. 3 due to the use of a larger F_c.

(e) Experiments with pulsed Laval nozzle supersonic expansion over the range $2 \times 10^{16} \leq [N_2] \leq 3 \times 10^{18}$ molecule cm^{-3} at 296 K. Single experiments at (2-3) x 10^{16} molecule cm^{-3} also at 96, 110, and 165 K. Falloff extrapolation with $F_c = 0.65$ and k_∞ (296 K) = 7.5×10^{-12} cm^3 molecule^{-1} s^{-1}.

(f) HO_2NO_2-NO system used as source of HO radicals. Reaction of HO radicals with C_2H_4 was studied in 420 L glass reactor relative to HO + *n*-hexane where the latter reaction was calibrated against absolute measurements of the reaction HO + *n*-butane [k(295 K) = 2.53 x 10^{-12} cm^3 $molecule^{-1}$ s^{-1}]. Pressure range 1.3-1000 mbar, falloff curves constructed with F_c = 0.7.

Preferred Values

$k_0 = 8.6 \times 10^{-29} (T/300)^{-3.1}$ $[N_2]$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 200-300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.

$\Delta n = \pm 2$.

Comments on Preferred Values

Preferred values based on an average of the data from Zellner and Lorenz (1984), Kuo and Lee (1991), Fulle et al. (1997), Chuong and Stevens (2000), Klein et al. (1984), Atkinson (1994), Tully (1983), Davis et al. (1975), Howard (1976), Greiner (1970), Morris et al. (1971), Overend and Paraskevopoulos (1977), Atkinson et al (1977), Lloyd et al. (1976), Cox (1975), and Vakhtin et al. (2003) where the latter work showed the lowest scatter and, therefore, is given the highest weight. Falloff curves are constructed with the calculated F_c = 0.48 from Fulle et al. (1997).

High-pressure rate coefficients
Rate coefficient data

k_0/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	*Reference*	Technique/ Comments
Absolute Rate Coefficients			
$(8.47 \pm 0.24) \times 10^{-12}$	291	Tully, 1993	PLP-LIF (a)
$3.3 \times 10^{-12} \exp[(320 \pm 150)/T]$	296-524	Zellner and Lorenz, 1984	PLP-RF (b)
9.7×10^{-12}	298		
$(9.4 \pm 1.6) \times 10^{-12}$	298	Nielsen et al., 1990	(c)
$(7.7 \pm 1.0) \times 10^{-12}$	298	Becker, Geiger and Wiesen, 1991	PLP-LIF (d)
1.0×10^{-11}	300-800	Fulle et al., 1997	PLP-LIF (e)
$(8.7 \pm 0.7) \times 10^{-12} (T/300)^{-0.85}$	96-296	Vakhtin et al., 2003	PLP-LIF (f)
Relative Rate Coefficients			
$(8.11 \pm 0.37) \times 10^{-12}$	299 ± 2	Atkinson et al., 1982	RR (g)
$(8.5 \pm 0.6) \times 10^{-12}$	295	Klein et al., 1984	RR (h)

Comments

(a) Higher end of falloff curve at 66 mbar to 790 mbar; temperature range 291 K to 591 K.

(b) See comment (a) for k_0.
(c) Pulse radiolysis of H_2O-Ar mixtures. HO monitored by UV absorption at 309 nm. Rate coefficient determined at a total pressure of 1 bar.
(d) Experiments were carried out at a total pressure of 1 bar of synthetic air. Numerical simulation with a mechanism of 12 reactions.
(e) See comment (c) for k_0.
(f) See comment (e) for k_0.
(g) HO radicals were generated by photolysis of CH_3ONO in presence of air containing NO. Concentrations of ethene and cyclohexane (the reference compound) were measured by GC. The rate coefficient ratio of k(HO + ethene)/k(HO + cyclohexane) = 1.12 ± 0.05 is placed on an absolute basis by use of a rate coefficient of k(HO + cyclohexane) = 7.24 x 10^{-12} cm^3 $molecule^{-1}$ s^{-1} (Atkinson, 1997).
(h) See comment (f) for k_0.

Preferred Values

k = 7.8 x 10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 298 K and 1 bar of air.
k_∞ = 9.0 x 10^{-12} $(T/300)^{-0.85}$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 100-500 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.
$\Delta n = \pm 0.3$.

Comments on Preferred Values

The preferred value is from Vakhtin et al. (2003), being similar to those selected in Fulle et al. (1997), Lloyd et al. (1976) and Nielsen et al. (1990). Falloff curves should be calculated with the theoretical expression for F_c = 0.48 which probably applies to M = He as well as N_2 and is practically constant over the indicated temperature range.

The following text-line combines the preferred values for the high and low pressure limiting rate coefficients to generate a single, cut-and-paste expression for calculation of k:

=((8.6e-29*(T/300)^-3.1)*M*(9.0e-12*(T/300)^-0.85))/((8.6e-29*(T/300)^-3.1)*M+(9.0e-12*(T/300)^-0.85))*10^(log10(0.48)/(1+(log10((8.6e-29*(T/300)^-3.1)*M/(9.0e-12*(T/300)^-0.85))/(0.75-1.27*log10(0.48)))^2))

The molecular density, M = 7.243×10^{21}P(bar)/T(K)

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