

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet II.A2.4 HO_x_VOC2

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$$\Delta H^\circ = -145 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(3 \pm 1) \times 10^{-30} (T/300)^{1.0}$ [Ar]	297-429	Perry and Williamson, 1982	FP-RF (a)
$(6 \pm 3) \times 10^{-30}$ [He]	298	Hack et al., 1983	DF-EPR (b)
$(2.5 \pm 0.3) \times 10^{-30}$ [Ar]	295	Schmidt et al., 1985	PLP-LIF (c)
5×10^{-30} [N ₂]	298	Wahner and Zetzsch, 1985	PLP-A (d)
$(4.1 \pm 1.6) \times 10^{-30}$ [N ₂]	298	Bohn et al., 1996	PLP-A (e)
$4.3 \times 10^{-29} (T/300)^{-3.1} \exp(-910/T)$ [He]	300-814	Fulle et al., 1997	PLP-LIF (f)
2.1×10^{-30} [He]	298		
<i>Relative Rate Coefficients</i>			
$(2.92 \pm 0.55) \times 10^{-30}$ [air]	296	Sørensen et al., 2003	RR (g)

Comments

- Photolysis of H₂O-C₂H₂ mixtures at 26-530 mbar of Ar diluent. Pressure dependence observed in agreement with the earlier work of Perry et al. (1977) and Michael et al. (1980). Evaluation of the falloff curve with $F_c = 0.5$.
- Pressures of 2.0-2.6 mbar of He diluent were used. By the use of data from Perry and Williamson (1982) and $F_c = 0.5$, a falloff analysis of the measured k leads to the given k_0 value.
- Experiments were conducted in He, Ar and N₂ at pressures between 1 mbar and 1000 mbar. Construction of falloff curve with $F_c = 0.6$ leads to $k_\infty = (8.3 \pm 0.8) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- Experiments in N₂ over the range 20 mbar to 1000 mbar. Falloff curve constructed with $F_c = 0.6$, leading to $k_\infty = 9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- Experiments with M = N₂, O₂, and synthetic air at pressures from 15 mbar to 1 bar. Falloff extrapolation with $F_c = 0.6$. Effective rate coefficients for HO radical removal in O₂ and synthetic air were markedly lower than in N₂ due to HO radical regeneration by the reaction $\text{C}_2\text{H}_2\text{OH} + \text{O}_2 \rightarrow \text{HO} + \text{products}$, which shows evidence for an influence of the extent of vibrational de-excitation of C₂H₂OH.
- Pressure range 2 mbar to 130 bar of He diluent. Combined with the data of Schmidt et al. (1985), falloff curves were constructed using a calculated $F_c = \{0.17 \exp(-51/T) + \exp(-$

$T/204$ }, i.e., $F_c(298\text{ K}) = 0.37$. From a third-law analysis of the equilibrium constant, the value $\Delta H^\circ(0\text{ K}) = -(146 \pm 10)\text{ kJ mol}^{-1}$ was derived. The equilibrium constant obtained at temperatures above 700 K is given by $K_c = 5.4 \times 10^{-2} T^{-1.7} \exp(17560/T)\text{ bar}^{-1}$.

- (g) HO radicals were generated by the photolysis of CH_3ONO in air. The concentrations of C_2H_2 and dimethyl ether or propane (the reference compounds) were monitored by in situ FTIR spectroscopy or GC-FID, respectively. The measured rate coefficient ratios $k(\text{HO} + \text{C}_2\text{H}_2)/k(\text{HO} + \text{dimethyl ether})$ and $k(\text{HO} + \text{C}_2\text{H}_2)/k(\text{HO} + \text{propane})$ were placed on an absolute basis using rate coefficients of $k(\text{HO} + \text{dimethyl ether}) = 2.98 \times 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ and $k(\text{HO} + \text{propane}) = 1.11 \times 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ (Sørensen et al., 2003). Experiments were carried out over the pressure range 25-750 Torr (33-1000 mbar) of air or O_2 with analysis by FTIR spectroscopy and dimethyl ether as the reference compound, and over the pressure range 25-7905 Torr (33 mbar to 10.5 bar) of $\text{O}_2\text{-N}_2$ diluent, with propane as the reference organic. Falloff curve was constructed with $F_c = 0.6$. Use of $F_c = 0.4$ led to $k_0[\text{air}] = (7.00 \pm 1.30) \times 10^{-30}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ and $k_\infty = (1.06 \pm 0.034) \times 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$.

Preferred Values

$k_0 = 5 \times 10^{-30} (T/300)^{-1.5} [\text{N}_2]\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ over the temperature range 300-800 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ at 298 K.

$\Delta n = \pm 1.5$.

Comments on Preferred Values

The preferred rate coefficient at 298 K is based on the experimental data of Schmidt et al. (1985), Wahner and Zetzsch (1985) and Bohn et al. (1996) and the theoretical analysis of Smith et al. (1984). The temperature dependence is based on the data of Perry et al. (1977), Michael et al. (1980) and Perry and Williamson (1982) as discussed and evaluated by Atkinson (1989). At temperatures above ~ 500 K another component of the rate coefficient with a much stronger temperature dependence also has to be taken into account (Atkinson, 1989). The preferred values should be used in connection with the calculated F_c values from Fulle et al. (1997) such as given in comment (f) of k_0 ($F_c = 0.37$ at 298 K). The temperature dependence is based on the data of Perry et al. (1977), Michael et al. (1980) and Perry and Williamson (1982).

A comparison of the data of Perry et al. (1977), Michael et al. (1980), Perry and Williamson (1982), Hack et al. (1983), Atkinson and Aschmann (1984), Schmidt et al. (1985), Wahner and Zetzsch (1985), Hatakeyama et al. (1986), Liu et al. (1988), Arnts et al. (1989) and Bohn et al. (1996) at pressures between 0.01-1 bar with the results from Fulle et al. (1997) at 2-80 bar shows considerable discrepancies, with the data of Fulle et al. (1997) leading to k_∞ considerably higher than the lower pressure data. This influences the construction of falloff curves and the extrapolation to k_0 . The recent study of Sørensen et al. (2003) confirms the earlier data of Perry et al. (1977), Michael et al. (1980), Perry and Williamson (1982), Hack et al. (1983), Atkinson and Aschmann (1984), Schmidt et al. (1985), Wahner and Zetzsch

(1985), Hatakeyama et al. (1986), Liu et al. (1988), Arnts et al. (1989) and Bohn et al. (1996) [see below].

High-pressure rate coefficients Rate coefficient data

$k_{\infty}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(6.91 \pm 0.90) \times 10^{-13}$	297	Perry and Williamson, 1982	FP-RF (a)
$(8.3 \pm 0.8) \times 10^{-13}$	295	Schmidt et al., 1985	PLP-LIF (b)
9×10^{-13}	298	Wahner and Zetzsch, 1985	PLP-A (c)
$(8.5 \pm 0.6) \times 10^{-13}$	298	Bohn et al., 1996	PLP-A (d)
$8.5 \times 10^{-12} \exp(-705/T)$	333-1273	Liu et al., 1988	PR-RA (e)
8.0×10^{-13}	298*		
$3.8 \times 10^{-11} \exp(-910/T)$	300-814	Fulle et al., 1997	PLP-LIF (f)
1.8×10^{-12}	298*		
<i>Relative Rate Coefficients</i>			
$(8.1 \pm 1.3) \times 10^{-13}$ (1 bar air)	298	Atkinson and Aschmann, 1984	RR (g)
$(8.1 \pm 1.8) \times 10^{-13}$ (1 bar air)	297 \pm 2	Hatakeyama et al., 1986	RR (h)
$(7.0 \pm 0.7) \times 10^{-13}$ (1 bar air)	297 \pm 2	Arnts et al., 1989	RR (i)
$(9.69 \pm 0.30) \times 10^{-13}$	296	Sørensen et al., 2003	RR (j)
$(7.67 \pm 0.06) \times 10^{-13}$ (1 bar air)	296	Sørensen et al., 2003	RR (k,l)
$(8.2 \pm 1.0) \times 10^{-13}$ (1 bar N ₂ -O ₂)	296	Sørensen et al., 2003	RR (k,m)

Comments

- (a) See comment (a) for k_0 .
- (b) See comment (c) for k_0 .
- (c) See comment (d) for k_0 .
- (d) See comment (e) for k_0 .
- (e) Measurements were conducted at 1 bar of Ar.
- (f) See comment (f) for k_0 .
- (g) HO radicals were generated by the photolysis of CH₃ONO in CH₃ONO-NO-C₂H₂-cyclohexane-air mixtures at 1 bar total pressure. The concentrations of acetylene and cyclohexane (the reference compound) were measured by GC. The measured rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{cyclohexane}) = 6.97 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 2003).
- (h) HO radicals were generated by photolysis of H₂O₂ in air at 254 nm. The concentrations of acetylene and cyclohexane (the reference compound) were monitored by FTIR spectrometry. Measurements were carried out at 1 bar pressure in air. The measured rate coefficient ratio $k(\text{HO} + \text{C}_2\text{H}_2)/k(\text{HO} + \text{cyclohexane}) = 0.116 \pm 0.025$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{cyclohexane}) = 6.95 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 2003).
- (i) HO radicals were generated by the photolysis of CH₃ONO in air at 1 bar pressure. The concentrations of acetylene and ethane (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{HO} + \text{C}_2\text{H}_2)/k(\text{HO} + \text{ethane}) = 2.84 \pm 0.26$ (two standard deviations) is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{ethane}) = 2.45 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2005).

- (j) See comment (g) for k_0 .
- (k) HO radicals were generated by the photolysis of CH₃ONO in air at 928-1013 mbar of O₂-N₂ diluent. The concentrations of C₂H₂ and dimethyl ether or propane (the reference compounds) were monitored by in situ FTIR spectroscopy or GC-FID, respectively. The measured rate coefficient ratios $k(\text{HO} + \text{C}_2\text{H}_2)/k(\text{HO} + \text{dimethyl ether}) = 0.276 \pm 0.021$ and $k(\text{HO} + \text{C}_2\text{H}_2)/k(\text{HO} + \text{propane}) = 0.761 \pm 0.09$ were placed on an absolute basis using rate coefficients of $k(\text{HO} + \text{dimethyl ether}) = 2.78 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2005) and $k(\text{HO} + \text{propane}) = 1.08 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2005).
- (l) Relative to dimethyl ether.
- (m) Relative to propane.

Preferred Values

$k = 7.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 1 bar of air.

$k_\infty = 1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 1 bar air and 298 K.

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

Comments on Preferred Values

The recent study of Sørensen et al. (2003) confirms the earlier data of Perry et al. (1977), Michael et al. (1980), Perry and Williamson (1982), Atkinson and Aschmann (1984), Schmidt et al. (1985), Wahner and Zetzsch (1985), Hatakeyama et al. (1986), Liu et al. (1988), Arnts et al. (1989) and Bohn et al. (1996), all of which indicate a rate coefficient at room temperature and 1 bar of air or N₂ of $\sim 8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and a value of $k_\infty \sim 1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. These data are, however, inconsistent with those from the study of Fulle et al. (1997), for reasons which are presently not understood (at 298 K and 1 bar of He, the data of Fulle et al. (1997) lead to $k = 1.12 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, with $k_\infty = 1.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K).

The preferred values are based on the data of Perry and Williamson (1982), Atkinson and Aschmann (1984), Schmidt et al. (1985), Wahner and Zetzsch (1985), Hatakeyama et al. (1986), Liu et al. (1988), Arnts et al. (1989), Bohn et al. (1996) and Sørensen et al. (2003) and are applicable to room temperature only.

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 $k(298 \text{ K})$:

$$=((5e-30*(T/300)^{-1.5}*M*(1.0e-12))/((5e-30*(T/300)^{-1.5}*M+(1.0e-12))*10^{(\log_{10}(0.37)/(1+(\log_{10}((5e-30*(T/300)^{-1.5}*M/(1.0e-12))/(0.75-1.27*\log_{10}(0.37)))^2))})$$

The molecular density, $M = 7.243 \times 10^{21} P(\text{bar})/T(\text{K})$

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