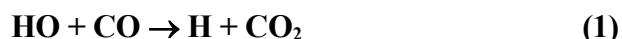


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HO_x_VOC10

Website: <http://iupac.pole-ether.fr>. See website for latest evaluated data. Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission.

This data sheet updated: 12th January 2005.



$$\Delta H^\circ(1) = -102.3 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ(2) = -114.6 \text{ kJ mol}^{-1}$$

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</i>	<i>Rate</i>		
<i>Coefficients</i>			
$k(P \rightarrow 0)$			
1.37×10^{-13}	300	Greiner, 1969	FP-RA (a,c)
1.35×10^{-13}	300	Stuhl and Niki, 1972	FP-RF
1.66×10^{-13}	300	Mulcahy and Smith, 1971	DF-MS
1.33×10^{-13}	298	Westenberg and de Haas, 1973	DF-EPR
1.39×10^{-13}	298	Smith and Zellner, 1973	FP-RA (a,c)
1.58×10^{-13}	298	Davis et al., 1974	FP-RF
1.56×10^{-13}	296	Howard and Evenson, 1974	DF-LMR
1.20×10^{-13}	298	Trainor and von Rosenberg, 1974	FP-RA (a,c)
0.90×10^{-13}	298	Gordon and Mulac, 1975	PR-RA (b,d)
1.54×10^{-13}	299	Atkinson et al., 1977	FP-RF (e)
1.63×10^{-13}	296	Overend and Paraskevopoulos, 1977	FP-RA (d,f)
1.41×10^{-13}	299	Perry et al., 1977	FP-RF (g)
1.46×10^{-13}	300	Biermann et al., 1978	FP-RA (h)
1.50×10^{-13}	298	Dreier and Wolfrum, 1981	DF (i)
1.46×10^{-13}	298	Husain et al., 1982	FP-RF
1.28×10^{-13}	298	Ravishankara and Thompson, 1983	FP-RF (j)
1.50×10^{-13}	298	Paraskevopoulos and Irwin, 1984	FP-RA
1.58×10^{-13}	298	Hofzumahaus and Stuhl, 1984	FP-RA (k)
1.23×10^{-13}	298	Jonah et al., 1984	PR-RA (l)
0.88×10^{-13}	298	Beno et al., 1985	PR-RA (l)
1.47×10^{-13}	299	Hynes et al., 1986	PLP-LIF
1.50×10^{-13}	298	Stachnik and Molina, 1988	PLP-RA
1.26×10^{-13}	298	Wahner and Zetsch, 1988	PLP-A (m)
1.49×10^{-13}	298	Brunning et al., 1988	FP-LIF (n)
1.30×10^{-13}	298	Forster et al., 1995	PLP-LIF
1.53×10^{-13}	298	Golden et al., 1998	PLP-LIF
1.57×10^{-13}	220-400	McCabe et al., 2001	PLP-LIF
$k/k(P \rightarrow 0)$ with $[\text{N}_2]$ in molecule cm^{-3}			
$1 + [\text{N}_2]/5.4 \times 10^{19}$	298	Paraskevopoulos and Irwin, 1984	FP-RA
$1 + [\text{N}_2]/4.1 \times 10^{19}$	298	Hofzumahaus and Stuhl, 1984	FP-RA (o)
$1 + [\text{N}_2]/4.8 \times 10^{19}$	298	Hynes et al., 1986	PLP-LIF
$1 + [\text{N}_2]/4.6 \times 10^{19}$	298	Wahner and Zetsch, 1988	PLP-A (o)

$1 + [\text{N}_2]/4.4 \times 10^{19}$	220-400	McCabe et al., 2001	PLP-LIF
$1 + [\text{N}_2]/4.0 \times 10^{19}$	200-300	Fulle et al., 1996	PLP-LIF (p)

Comments

- (a) Extrapolation for $P \rightarrow 0$ with pressure dependence from Golden et al. (1998).
 (b) Extrapolation for $P \rightarrow 0$ with pressure dependence from Paraskevopoulos and Irwin (1984).
 (c) Measurements at 100 Torr of He giving $k = 1.43 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
 (d) Measurements at 760 Torr of Ar giving $k = 1.54 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
 (e) No pressure dependence detected between 25 and 650 Torr of Ar. Value taken as indicated.
 (f) Measurements at 50 Torr of He giving $k = 1.66 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
 (g) Measurements at 25 Torr of SF_6 giving $k = 1.53 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
 (h) Measurements at 25 Torr of N_2 giving $k = 1.51 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
 (i) Measurements of CO_2 yields accounting for loss of HO by other reactions.
 (j) Measurements at 100 Torr of Ar giving $k = 1.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
 (k) Measurements at 760 Torr of N_2 giving $k = 2.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
 (l) Measurements at 760 Torr of Ar giving $k = 2.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
 (m) Measurements at 760 Torr of N_2 giving $k = 2.15 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
 (n) Measurements at 25 Torr of Ar giving $k = 1.53 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
 (o) Referred to $k_0 = 1.44 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
 (p) Measurements up to 700 bar of He with data representation between 90 and 3000 K. Conversion to the bath gas N_2 with efficiency relative to He at 298 K, see comments on preferred values. Temperature dependence from theoretical modelling of the experimental results, see Troe (1998).

Preferred Values

$k = 1.44 \times 10^{-13} (1 + [\text{N}_2]/4.2 \times 10^{19} \text{ molecule cm}^{-3}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200-300 K and the pressure range 0-1 bar of N_2 .

Reliability

$\Delta \log k = \pm 0.05$ at 298 K.

$\Delta \log k = \pm 0.1$ over the temperature range 200-300 K and the pressure range 0-1 bar.

Comments on Preferred Values

The preferred values at $P \rightarrow 0$ represent a weighted average of all low pressure data excluding pulse radiolysis results which show larger scatter. The preferred values at $P = 1$ bar of N_2 correspond to an average over those results for which $k/k(P \rightarrow 0)$ is given in the table (except the results from Fulle et al. (1996) which were obtained in the bath gas He).

The preferred values for k cannot be used over larger pressure and temperature ranges where more complicated expressions have to be employed. One may, e.g. take the representation

$k_1 = k_{1,0} \left\{ 1 - \left[\frac{x}{(x+1)} \right] F_c^{1/[1+(\log x)^2]} \right\}$, $k_2 = k_{2,0} \left[\frac{(1+y)}{(1+x)} \right] F_c^{1/[1+(\log x)^2]}$ with $x = k_{2,0}/(k_{2,\infty} - k_{1,0})$ and $y = k_{1,0}/(k_{2,\infty} - k_{1,0})$, $F_c \approx 0.7$, $k_{1,0} = 1.8 \times 10^{-12} \exp(-2720/T) + 1.6 \times 10^{-13} \exp(-60/T)$, $k_{2,0} = [\text{He}] 2.0 \times 10^{-32} (T/300)^{-2.7} \exp(-490/T)$ and $k_{2,\infty} = 1.8 \times 10^{-11} \exp(-1850/T) + 1.5 \times 10^{-12} \exp(-130/T)$, see Fulle et al. (1996) and Troe (1998). For N_2 instead of He, $k_{2,0}$ should be increased by a factor of 1.6. These expressions also give the partitioning of k into k_1 and k_2 . For the limited temperature and pressure range of the present evaluation, the simplified model from the introduction for complex-forming bimolecular reactions can be used. At low pressures this gives a relative HOCO yield of approximately $[k - k(P \rightarrow 0)]/[k(P \rightarrow \infty) - k(P \rightarrow 0)]$ which at 298 K and 1 bar of N_2 corresponds to about 12 % (Troe, 1998). As HOCO under excess of O_2 rapidly reacts to $\text{HO}_2 + \text{CO}_2$ (Miyoshi et al., 1994) and as other

reactions of HOCO presumably proceed similarly as reactions of H, k probably in effect can be used as if it would correspond to reaction (1) alone. At higher temperatures, thermal decomposition of HOCO would occur which would lead to more complex kinetic rate laws, see Forster et al. (1996). This can be neglected at temperatures below 300 K.

The present evaluation was based on absolute rate coefficients only, neglecting relative rate measurements and measurements in other bath gases such as H₂O. Reference to this work is found in the given literature. Since the reaction has been studied very extensively, the present evaluation also cannot be exhaustive. The thermochemistry of HOCO is based on the new determination by Feller et al. (2003). There is extensive modelling of the reaction, see Golden et al. (1998) and Troe (1998), which provide excellent representations of the experimental data with empirically fitted potential parameters. Increasingly reliable quantum-chemical determinations of the HOCO potential (see e.g. Yu et al. (2001) and Lakin et al. (2003)) allows also for more basic treatments of the dynamics, see e.g. Medvedev et al., (2004), He et al. (2004), Valero and Kroes (2002), Valero et al. (2004). However, this work does not yet replace the experiments on which this evaluation is based.

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