IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iClOx22

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This data sheet last evaluated: 28th June 2007; no revision of preferred values.

$HO + HCl \rightarrow H_2O + Cl$

$\Delta H° = -65.4$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
(6.4 ± 0.7) x 10^{-13}	295	Takacs and Glass, 1973	DF-EPR
4.1 x 10^{-12} exp[-(529 ± 24)/T]	220-480	Smith and Zellner, 1974	FP-RA
(6.9 ± 1) x 10^{-13}	298		
2.0 x 10^{-12} exp[-(312 ± 10)/T]	224-440	Zahniser et al., 1974	DF-RF
(6.7 ± 0.4) x 10^{-13}	297		
(6.6 ± 1.7) x 10^{-13}	293	Hack et al., 1977	DF-EPR (a)
3.3 x 10^{-12} exp[-(472 ± 40)/T]	250-402	Ravishankara et al., 1977	FP-RF
(6.6 ± 0.4) x 10^{-13}	298		
(6.66 ± 0.52) x 10^{-13}	300	Husain et al., 1981	FP-RF
(6.8 ± 0.25) x 10^{-13}	298 ± 4	Cannon et al., 1984; Smith and Williams, 1986	FP-LIF
2.1 x 10^{-12} exp[-(285 ± 40)/T]	258-334	Keyser, 1984	DF-RF
(7.9 ± 0.4) x 10^{-13}	295 ± 2		
4.6 x 10^{-12} exp[-(500 ± 60)/T]	240-295	Molina et al., 1984	PLP/FP-RF
(8.5 ± 1.5) x 10^{-13}	295		
2.94 x 10^{-12} exp[-(446 ± 32)/T]	300-700	Husain et al., 1984	FP-RF
(6.7 ± 0.46) x 10^{-13}	300		
2.4 x 10^{-12} exp[-(327 ± 28)/T]	240-363	Ravishankara et al., 1985	FP-RF/PLP-RF/
(8.01 ± 0.44) x 10^{-13}	298		PLP-LIF (b)
(7.8 ± 0.3) x 10^{-13}	298	Sharkey and Smith, 1993	PLP-LIF
(5.4 ± 0.25) x 10^{-13}	216		
(5.6 ± 0.45) x 10^{-13}	178		
(5.2 ± 0.3) x 10^{-13}	138		
3.28 x 10^{-17} $T^{1.66}$ exp(184/T)	200-400	Battin-Leclerc et al., 1999	PLP-LIF (c)
(7.96 ± 0.60) x 10^{-13}	298		
3.2 x 10^{-15} $T^{0.99}$ exp(-62/T)	298-1015	Bryukov et al., 2006	PLP-LIF (d)
(7.39 ± 0.11) x 10^{-13}	298		

Comments

(a) Rate coefficients also measured at 435 K and 567 K of 8.1 x 10^{-13} cm^3 molecule^{-1} s^{-1} and 1.25 x 10^{-12} cm^3 molecule^{-1} s^{-1}, respectively.

(b) Rate coefficients measured over the temperature range 240-1055 K. The Arrhenius plot of the rate coefficients measured over this extended temperature range is curved, with k = 4.5 x 10^{-17} $T^{1.65}$ exp(112/T) cm^3 molecule^{-1} s^{-1} (Ravishankara et al., 1985).

(c) Over the limited temperature range 200-298 K, the data were also fit to the Arrhenius expression, with k = 1.7 x 10^{-12} exp[-(225 ± 20)/T] cm^3 molecule^{-1} s^{-1} (note that the

publication of Battin-Leclerc et al (1999) gives a pre-exponential factor in the Arrhenius expression of 1.7 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1}). Rate coefficients were also measured for the reactions of the HO radical with DCl (252-387 K) and for the reactions of the DO radical with HCl (213-372 K) and DCl (213-401 K).

(d) The cited 298 K rate coefficient is the weighted average of the two measurements at 298 K. Combining their data with those of Battin-Leclerc et al. (1999), Bryukov et al. (2006) derived the expression $k = 6.64 \times 10^{-16}\ T^{1.20} \exp(72/T)$ cm^3 $molecule^{-1}$ s^{-1} for the temperature range 200-1015 K.

Preferred Values

$k = 7.8 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.
$k = 1.7 \times 10^{-12} \exp(-230/T)$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 200-300 K.

Reliability

$\Delta \log k = \pm 0.06$ at 298 K.
$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

The studies of Keyser (1984), Molina et al. (1984), Ravishankara et al. (1985), Battin-Leclerc et al. (1999) and Bryukov et al. (2006), in which careful attention was paid to the HCl present in the experiments, all show room temperature values somewhat higher than most other studies (Takacs and Glass, 1973; Smith and Zellner, 1974; Zahniser et al., 1974; Hack et al., 1977; Ravishankara et al., 1977; Husain et al., 1981, 1984; Cannon et al., 1984; Smith and Williams, 1986). Ravishankara et al. (1985) showed that HCl losses can be a problem, leading to erroneously low measured rate coefficients, and this is a plausible cause of these discrepancies. The rate coefficients obtained in the studies of Keyser (1984), Molina et al. (1984), Ravishankara et al. (1985), Battin-Leclerc et al. (1999) and Bryukov et al. (2006) are in good agreement. An Arrhenius plot of the rate coefficients from these five studies exhibits curvature (Battin-Leclerc et al., 1999; Bryukov et al., 2006). The preferred temperature-dependent expression for the range 200-300 K is obtained by a linear least-squares fit to the ≤299 K data from the studies of Keyser (1984), Molina et al. (1984), Ravishankara et al. (1985), Battin-Leclerc et al. (1999) and Bryukov et al. (2006). Over more extended temperature ranges the three parameter expression obtained by Bryukov et al. (2006), of $k = 6.64 \times 10^{-16}\ T^{1.20} \exp(72/T)$ cm^3 $molecule^{-1}$ s^{-1} (200-1015 K), should be used. Results of the low temperature study of Sharkey and Smith (1993) are in good agreement with the recommended Arrhenius expression down to 216 K, but are (as expected due to the non-Arrhenius behaviour) significantly higher at 178 K and 138 K.

References

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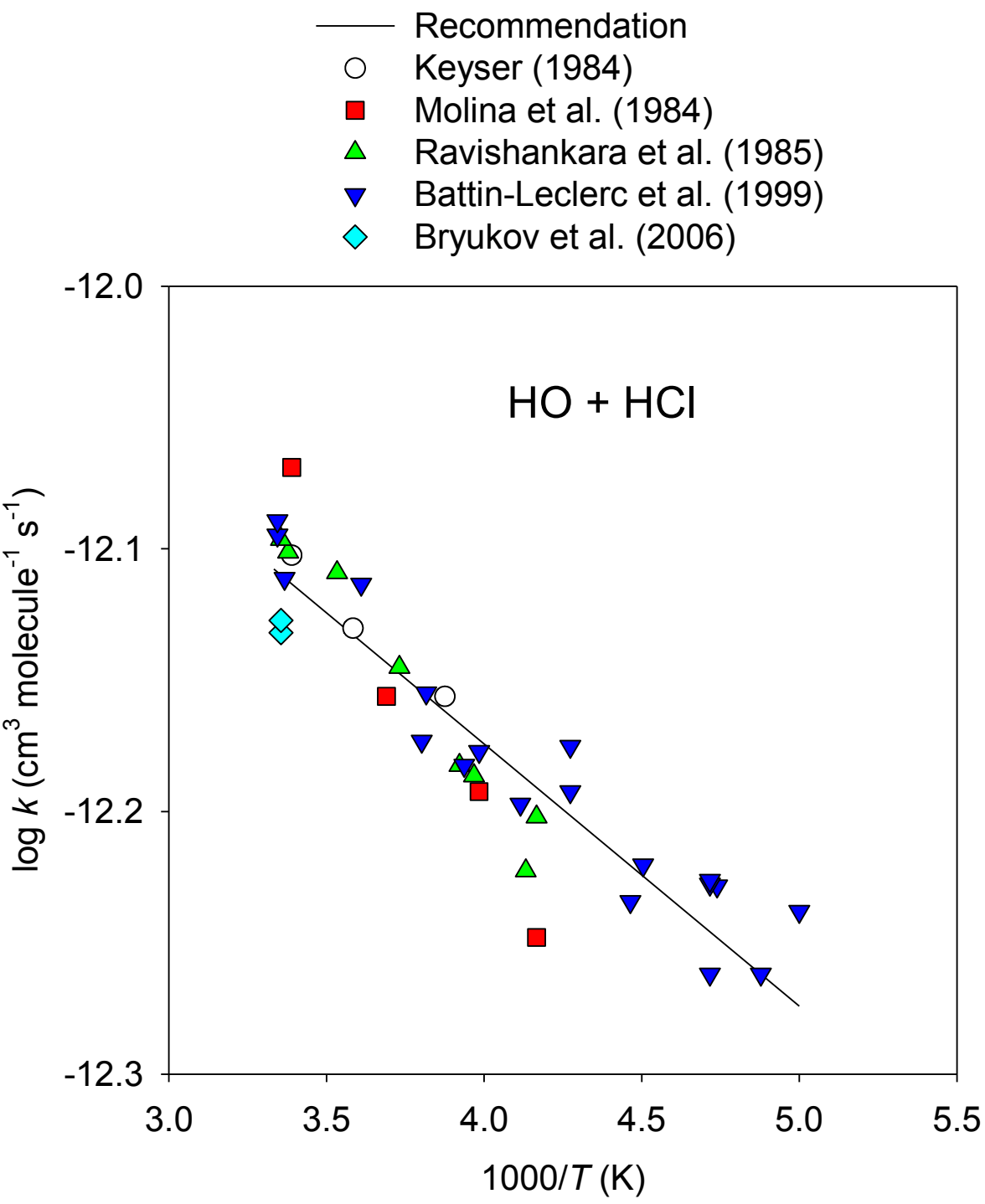
Recommendation
Keyser (1984)
Molina et al. (1984)
Ravishankara et al. (1985)
Battin-Leclerc et al. (1999)
Bryukov et al. (2006)
HO + HCl
log k (cm3 molecule-1 s-1)
-12.0
-12.1
-12.2
-12.3
3.0
3.5
4.0
4.5
5.0
5.5
1000/T (K)