IUPAC Task Group on Atmospheric chemical Kinetic Data Evaluation – Data Sheet iClOx29

This data sheet updated: 25th September 2003.

$$ClO + HO_2 \rightarrow HOCl + O_2 \qquad (1)$$
$$\rightarrow HCl + O_3 \qquad (2)$$
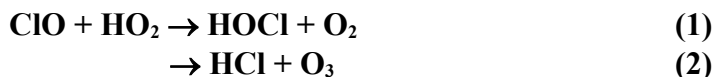
$\Delta H°(1) = -194 \text{ kJ·mol}^{-1}$

$\Delta H°(2) = -65.8 \text{ kJ·mol}^{-1}$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
(3.8 ± 0.7) x 10^{-12}	298	Reimann and Kaufman, 1978[1]	DF-RF
3.3 x 10^{-11} exp$(-850/T)$ + 4.5 x 10^{-12} $(T/300)^{-3.7}$	235-393	Stimpfle, Perry and Howard, 1979[2]	DF-LMR
(6.43 ± 0.96) x 10^{-12}	298		
(4.5 ± 0.9) x 10^{-12}	298	Leck, Cook and Birks, 1980[3]	DF-MS
(5.4^{+4}_{-2}) x 10^{-12}	300	Burrows and Cox, 1981[4]	MM-UVA
(6.2 ± 1.5) x 10^{-12}	308	Cattell and Cox, 1986[5]	MM-UVA (a)
2.84 x 10^{-12} exp$[(312 \pm 60)/T]$	203-364	Nickolaisen *et al.*, 2000[6]	FP-UVA (b)
(7.79 ± 0.83) x 10^{-12}	299		(c)
(8.26 ± 1.38) x 10^{-12}	299		(d)
7.1 x 10^{-12} exp$[(-16 \pm 17)/T]$	215-298	Knight *et al.*, 2000[7]	DF-MS (e)
(7.1 ± 1.8) x 10^{-12}	294		
Branching Ratios			
$k_2/k \leq 0.02$	298	Leck, Cook and Birks, 1980[3]	(f)
$k_2/k \leq 0.015$	298	Leu, 1980[6]	(f)
$k_2/k \leq 0.03$	248		
$k_2/k \leq 0.003$	298	Burrows and Cox, 1981[4]	(g)
$k_1/k > 0.95$	210-300	Finkbeiner *et al.*, 1995[8]	(h)
$k_2/k = 0.05 \pm 0.02$	210		
$k_2/k = 0.02 \pm 0.01$	240		
$k_2/k \leq 0.01$	215-298	Knight *et al.*, 2000[7]	(f)

Comments

(a) k independent of pressure over the range 65-1000 mbar.

(b) k independent of pressure over the range 65-930 mbar. Two chemical systems employed to generate ClO and HO$_2$: (i) the photolysis of Cl$_2$-Cl$_2$O-CH$_3$OH-O$_2$-N$_2$ mixtures, and (ii) the photolysis of Fl$_2$-H$_2$-O$_2$-Cl$_2$O-N$_2$ mixtures. The latter system consistently yielded slightly higher values of k, although differences are well within error limits of each system. Unpublished results[9] from the same laboratory using DF-MS at 1 Torr are also cited. The results give a near-zero temperature dependence over the range 233-380 K ($E/R = 72 \pm 42$

K), and a value of k about a factor of 2 lower at 298 K compared with the FP-UVA measurement.

(c) Cl_2-Cl_2O-CH_3OH-O_2-N_2 system.

(d) Fl_2-H_2-O_2-Cl_2O-N_2 system.

(e) k measured in 1.4-2.2 mbar He. ClO and HO_2 generated from five combinations of precursor reagents: (i) CH_3OH-Cl_2O, (ii) CH_3OH-$OClO$, (iii) $HCHO$-Cl_2O, (iv) $HCHO$-$OClO$, and (v) H_2O_2-$OClO$. Systems yielded consistent results. Additional experiments performed with related chemical systems involving presence of O_3, generated higher values of k, described by the expression $(6.6 \pm 0.8) \times 10^{-12} \exp[(85 \pm 18)/T]$ over the temperature range 223-333 K. This was attributed to inefficient quenching at 1.3 mbar of the vibrationally excited ClO generated from the $Cl + O_3$ reaction.

(f) DF-MS detection of O_3.

(g) MM-CL detection of O_3.

(h) Flow system with steady-state photolysis (310 nm to 400 nm) of Cl_2-H_2-Cl_2O-O_2-Ar mixtures at a total pressure of 910 mbar. HOCl and O_3 products were monitored by matrix-isolation FTIR spectroscopy.

Preferred Values

$k = 6.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.2 \times 10^{-12} \exp(340/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230 K to 300 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = \pm 350$ K.

Comments on Preferred Values

The reported studies have been carried out over a range of temperatures and pressures, using a variety of techniques. The room temperature values of k cover a range of more than a factor of two. Systematic studies of the pressure dependence[5,6] show no significant variation above 65 mbar, although the average of the published low pressure discharge flow measurements is slightly lower than the average of the higher pressure measurements. The recent studies of the temperature dependence[6,7] disagree with the previously reported[2] strong negative temperature dependence at temperatures below 298 K, and the associated non-linear Arrhenius behaviour. However, there is also substantial disagreement between the recent studies, which yield values of E/R of -312 K[6] and 16 K.[7]

The preferred value at 298 K is based on the average of the room temperature data of Stimpfle *et al.*,[2] Cattell and Cox,[5] Nickolaisen *et al.*[6] and Knight and Crowley.[7] The preferred value of E/R is based on the average of the three temperature dependence studies, using Stimpfle *et al.*[2] data for T $\leq$ 298 K (for which E/R = -709 K). The uncertainties in k at 298 K and E/R reflect the range of reported values.

All of the available data suggest that channel (1) is the dominant, if not sole, pathway over the temperature range of the preferred values With the exception of the matrix-isolation results of Finkbeiner *et al.*,[8] no evidence for channel (2) has been reported. Recent theoretical studies[6,10] conclude that the contribution of channel (2) is essentially zero.

References

[1] B. Reimann and F. Kaufman, J. Chem. Phys. **69**, 2925 (1978).

[2] R. M. Stimpfle, R. A. Perry, and C. J. Howard, J. Chem. Phys. **71**, 5183 (1979).

[3] T. J. Leck, J.-E. L. Cook, and J. W. Birks, J. Chem. Phys. **72**, 2364 (1980).

[4] J. P. Burrows and R. A. Cox, J. Chem. Soc. Faraday Trans. 1, **77**, 2465 (1981).

[5] F. C. Cattell and R. A. Cox, J. Chem. Soc. Faraday Trans. 2, **82**, 1413 (1986).

[6] S. L. Nickolaisen, C. M. Roehl, L. K. Blakeley, R. R. Friedl, J. S. Francisco, R. Liu and S. P. Sander, J. Phys. Chem. A, **104**, 308 (2000).

[7] G. P. Knight, T. Beiderhase, F. Helleis, G. K. Moortgat and J. N. Crowley, J. Phys. Chem. A, **104**, 1674 (2000).

[8] M. Finkbeiner, J. N. Crowley, O. Horie, R. Müller, G. K. Moortgat, and P. J. Crutzen, J. Phys. Chem. **99**, 16264 (1995).

[9] B. Laszlo, R. R. Friedl and S. P. Sander, unpublished results.

[10] N. Kaltsoyannis and D. M. Rowley, Phys. Chem. Chem. Phys. **4**, 419 (2002).