IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iClOx10

This data sheet updated: 9th March 2005.

$Cl + O_2 + M \rightarrow ClOO + M$

$\Delta H° = -23.8 \text{ kJ·mol}^{-1}$

Low-pressure rate coefficients
Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
5.6×10^{-34} [Ar]	200-300	Clyne and Coxon, 1968	DF (a)
1.7×10^{-33} [N$_2$ + O$_2$]	300	Nicholas and Norrish, 1968	FP-UVA (b)
$(8.9 \pm 2.9) \times 10^{-33}$ [O$_2$]	186.5	Nicovich et al., 1991	PLP-RF (c)
1.6×10^{-33} (T/300)$^{-2.9}$ [O$_2$]	160-260	Baer et al., 1991	PLP-UVA
$(6.3 \pm 1.2) \times 10^{-33}$ [O$_2$]	186.5		(d)
1.4×10^{-33} (T/300)$^{-3.9}$ [N$_2$]	160-260	Baer et al., 1991	PLP-UVA (d)

Comments

(a) Measurements attributed to D. H. Stedman. Cl atoms were monitored by chlorine afterglow emission.

(b) Rate coefficients were determined by a complex analysis of the time-resolved production of ClO radicals in the photolysis of Cl$_2$-O$_2$ mixtures. ClO radicals were measured by photographic recording of their absorption.

(c) Photolysis of Cl$_2$-O$_2$ mixtures at 181-200 K and with O$_2$ pressures of 20-53 mbar. Detection of Cl(^{2}P$_{3/2}$) atoms. An equilibrium constant for the reaction of $K_p = 18.9$ bar^{-1} was determined at 185.4 K.

(d) Photolysis of Cl$_2$-O$_2$-M mixtures with M = He, Ar, O$_2$ and N$_2$, with detection of ClOO radicals. Redetermination of the ClOO radical absorption cross-sections gave ε(248 nm) = 3.4 $\times$ 10^{-17} cm^2 molecule^{-1}. Measurements over the temperature range 160-260 K and the pressure range 1-1000 bar were in agreement with the data of Mauldin et al. (1992). Negligible deviations from third-order behavior were observed at pressures below 10 bar. At higher pressures, an anomalous transition to a high pressure plateau was observed. This and the anomalously strong temperature dependence suggest that the reaction proceeds on a radical-complex instead of the usual energy transfer mechanism. An equilibrium constant of $K_p = 5.3 \times 10^{-6}$ exp(23.4 kJ mol^{-1}/RT) bar^{-1} was determined over the temperature range 180 K to 300 K.

Preferred Values

$k_0 = 1.4$ x 10^{-33} $(T/300)^{-3.9}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 160-300 K.
$k_0 = 1.6$ x 10^{-33} $(T/300)^{-2.9}$ [O_2] cm^3 molecule^{-1} s^{-1} over the temperature range 160-300 K.

Reliability

Δlog $k_0 = \pm 0.2$ at 200 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

The two recent studies of Nicovich et al. (1991) and Baer et al. (1991) are in good agreement and are also consistent with the older data of Nicholas and Norrish (1968), if one takes into account the strong temperature dependence of k_0. The most extensive measurements of Baer et al. (1991) are the basis for the preferred values. No falloff expressions are reported here, because deviations from third-order behavior become apparent only at pressures higher than 10 bar and because the falloff formalism does not apply to the radical-complex mechanism which is probably operating in this case.

References

Baer, S., Hippler, H., Rahn, R., Siefke, M., Seitzinger, N. and Troe, J.: J. Chem. Phys., 95, 6463, 1991.
Clyne, M. A. A. and Coxon, J. A.: Proc. Roy. Soc. London, A303, 207, 1968.
Mauldin III, R. L., Burkholder, J. B. and Ravishankara, A. R.: J. Phys. Chem., 96, 2582, 1992.
Nicholas, J. E. and Norrish, R. G. W.: Proc. Roy. Soc. London, A307, 391, 1968.
Nicovich, J. M., Kreutter, K. D., Shackelford, C. J. and Wine, P. H.: Chem. Phys. Lett., 179, 367, 1991.