

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iClOx25

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This data sheet updated: 12th July 2006.



$$\Delta H^\circ(1) = -210 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ(2) = -15.6 \text{ kJ mol}^{-1}$$

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 Rate Coefficients</i>			
$4.50 \times 10^{-13} \exp[(804 \pm 114)/T]$	293-473	Poulet et al., 1986	DF-LIF/EPR (a)
$(7.2 \pm 0.5) \times 10^{-12}$	293		
$1.43 \times 10^{-12} \exp[(597 \pm 36)/T]$	242-392	Gierczak et al., 2006	PLP-LIF (b)
$(1.06 \pm 0.20) \times 10^{-11}$	296		

Comments

- (a) k was determined from pseudo-first order decay of HO; pressure range 0.7 – 1.9 mbar. [OCIO] determined from measured flow rates. HOCl was observed as a reaction product, using MS, and its concentration determined using the $\text{HO} + \text{Cl}_2 \rightarrow \text{HOCl} + \text{Cl}$ reaction as a calibration source of HOCl. Computer simulation of the reaction system indicated that HOCl is formed primarily in the $\text{HO} + \text{OCIO}$ reaction [channel (1)] and not as a result of secondary reactions of the HO_2 radical with ClO, with $k_1/k \geq 0.80$ at room temperature.
- (b) k was determined from pseudo-first order decay of HO, and was independent of pressure over the range 33 – 133 mbar (helium). [OCIO] determined from *in-situ* measurements using FTIR and UV diode array spectroscopy.

Preferred Values

$$k = 1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 1.4 \times 10^{-12} \exp(600/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 240 - 400 \text{ K.}$$

$$k_1/k = 1.0.$$

Reliability

$$\Delta \log k_1 = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 200 \text{ K.}$$

$$\Delta \log (k_1/k) = \pm 0.2 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred values of k are based on the study of Gierczak et al. (2006), in which concentrations of the excess reagent, OCIO, were determined by *in-situ* spectroscopic measurements, and which considered temperatures below room temperature. The earlier results of Poulet et al. (1986) are in reasonable agreement with the recommendation, and are

encompassed by the assigned reliability limits. The preferred value of k_1/k is based on the observation and interpretation of HOCl formation at room temperature, reported by Poulet et al. (1986).

Xu et al. (2003) have reported *ab initio* molecular orbital and variational RRKM theory calculations of the rate coefficient and product channels. The results yield rate coefficients of a similar magnitude to those obtained in the experimental studies, and also provide support for the dominance of channel (1), as reported by Poulet et al. (1986) at 1.3 mbar. Channel (2) is predicted to gain importance at elevated temperatures, and a pressure-dependent association channel to form HOClO₂ is predicted to account for ca. 20% of the reaction at 130 mbar and 300 K, and to be the major channel at atmospheric pressure. However, no pressure dependence of k was reported by Gierczak et al. (2006) for the range 33-133 mbar of helium, although experimental studies at higher pressures are ideally required to investigate the possible contribution of the association channel.

References

- Gierczak, T, Burkholder, J. B. and Ravishankara, A.R.: Int. J. Chem. Kinet., 38, 234, 2006.
Poulet, G., Zagogianni, H. and Le Bras, G.: Int. J. Chem. Kinet., 18, 847, 1986.
Xu, Z-F., Xu, R. and Lin, M.C.: J. Phys. Chem. A., 107, 1040, 2003.