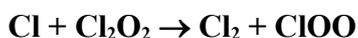


IUPAC Task Group on Atmospheric chemical Kinetic Data Evaluation – Data Sheet iClOx19

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 re-transmitted or disseminated either electronically or in hard copy without explicit written permission.

This data sheet updated: 12th July 2006.



$$\Delta H^\circ = -151.4 \text{ kJ mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$7.6 \times 10^{-11} \exp[(65.4 \pm 17.9)/T]$	217-298	Ingham et al., 2005	DF-MS (a)
$(9.30 \pm 0.95) \times 10^{-11}$	298		
$(9.51 \pm 1.17) \times 10^{-11}$	298		
<i>Relative Rate Coefficients</i>			
$(1.00 \pm 0.02) \times 10^{-10}$	233	Cox and Hayman, 1988	P-UVA (b)

Comments

- (a) k was determined from pseudo-first order decay of Cl_2O_2 in the presence of an excess of Cl atoms. $[\text{Cl}]$ was determined after titration to either BrCl or vinyl chloride, following reaction with Br_2 or vinyl bromide (the two presented values of k at 298 K were reported for these respective titration reactions). The temperature dependence expression was obtained from fitting an Arrhenius expression to all the data.
- (b) Static photolysis of $\text{Cl}_2\text{-Cl}_2\text{O-N}_2$ mixtures at 350 nm. The time dependence of $[\text{Cl}_2\text{O}_2]$ and $[\text{Cl}_2\text{O}]$ were monitored by photodiode array UV spectroscopy, yielding $k(\text{Cl} + \text{Cl}_2\text{O})/2k = 0.54 \pm 0.01$ at 233 K. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(\text{Cl} + \text{Cl}_2\text{O}) = 1.08 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 233 K (this evaluation).

Preferred Values

$$k = 9.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 7.6 \times 10^{-11} \exp(65/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range } 220 - 300 \text{ K.}$$

Reliability

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

$$\Delta(E/R) = \pm 150 \text{ K.}$$

Comments on Preferred Values

The preferred values are based on the direct study of Ingham et al. (2005), who report a very weak negative temperature dependence for the reaction. The rate coefficient at 233 K from the Ingham et al. (2005) rate expression is in excellent agreement with that derived from the earlier relative rate determination of Cox and Hayman (1988). Although there is no reported confirmation of the likely reaction products ($\text{Cl}_2 + \text{ClOO}$), Ingham et al. (2005) were able to rule out the alternative formation of Cl_2O and ClO from a failure to detect ClO as a product under any of the conditions employed in their study.

References

Cox, R. A. and Hayman, G. D.: *Nature*, 332, 796, 1988.

Ingham, T., Sander, S. P. and Friedl, R. R., *Faraday Discuss.*, 130, 89, 2005.