IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iClOx17

This data sheet updated: 25th September 2003.

$Cl + OClO \rightarrow ClO + ClO$

$\Delta H° = -12.6$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$>8.3 \times 10^{-13}$	298	Clyne and Coxon, 1968[1]	DF-UVA
$(8.5 \pm 1.2) \times 10^{-12}$	~298	Basco and Dogra, 1971[2]	FP-UVA
$(5.9 \pm 0.9) \times 10^{-11}$	298-588	Bemand, Clyne, and Watson, 1973[3]	DF-RF/MS (a)
$3.0 \times 10^{-11} \exp(174/T)$	229-428	Toohey, 1988[4]	DF-RF (b)
$(5.44 \pm 0.09) \times 10^{-11}$	298		
Relative Rate Coefficients			
$3.7 \times 10^{-10} \exp[-(3020 \pm 101)/T]$	338-365	Gritsan, Panfilov, and Sukhanow, 1975[5]	(c)

Comments

(a) Discharge flow system with resonance fluorescence detection of Cl atom decay in excess OClO and MS measurement of OClO decay in excess Cl.

(b) The measured rate coefficients (cm^3 molecule^{-1} s^{-1}) were: 229 K, $(6.28 \pm 0.21) \times 10^{-11}$; 247 K, $(6.12 \pm 0.20) \times 10^{-11}$; 268 K, $(5.6 \pm 0.30) \times 10^{-11}$; 298 K, $(5.44 \pm 0.09) \times 10^{-11}$; 367 K, $(4.84 \pm 0.24) \times 10^{-11}$; and 428 K, $(4.40 \pm 0.17) \times 10^{-11}$. A unit-weighted least-squares analysis of these data, using the Arrhenius expression, leads to $k = 3.0 \times 10^{-11} \exp(174/T)$ cm^3 molecule^{-1} s^{-1}.

(c) Thermal decomposition of OClO. Complex chemical system.

Preferred Values

$k = 5.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 3.2 \times 10^{-11} \exp(170/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220 K to 430 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

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

Comments on Preferred Values

The data of Toohey[4] agree well with the earlier study of Bemand *et al.*[3] at 298 K, but show a small negative temperature dependence over a similar temperature range to that over which Bemand *et al.*[3] saw little change in k. The preferred value is the average of the 298 K values from the two studies of Bemand *et al.*[3] and Toohey,[4] and the temperature dependence of

Toohey[4] is accepted but with error limits covering the possibility that k is independent of temperature. The earlier data of Clyne and Coxon[1] and Basco and Dogra[2] are rejected following the recommendation of Bemand *et al*.[3]

References

1 M. A. A. Clyne and J. A. Coxon, Proc. Roy. Soc. (London) **A303**, 207 (1968).

2 N. Basco and S. K. Dogra, Proc. Roy. Soc. (London) **A323**, 417 (1971).

3 P. P. Bemand, M. A. A. Clyne, and R. T. Watson, J. Chem. Soc. Faraday Trans. 1, **69**, 1356 (1973).

4 D. W. Toohey, "Kinetic and Mechanistic Studies of Reactions of Bromine and Chlorine Species Important in the Earth's Stratosphere," Ph.D. Thesis, Harvard University, Cambridge, MA (1988).

5 V. I. Gritsan, V. N. Panfilov, and I. L. Sukhanov, Reaction Kinetics and Catalysis Letters **2**, 265 (1975).