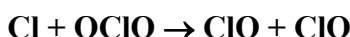


# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iClOx17

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This data sheet updated: 25<sup>th</sup> September 2003.



$$\Delta H^\circ = -12.6 \text{ kJ}\cdot\text{mol}^{-1}$$

## Rate coefficient data

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

## Comments

- Discharge flow system with resonance fluorescence detection of Cl atom decay in excess OCIO and MS measurement of OCIO decay in excess Cl.
- The measured rate coefficients ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) 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  $k = 3.0 \times 10^{-11} \exp(174/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- Thermal decomposition of OCIO. Complex chemical system.

## Preferred Values

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

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

### Reliability

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

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

### Comments on Preferred Values

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

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

### References

- <sup>1</sup> M. A. A. Clyne and J. A. Coxon, Proc. Roy. Soc. (London) **A303**, 207 (1968).
- <sup>2</sup> N. Basco and S. K. Dogra, Proc. Roy. Soc. (London) **A323**, 417 (1971).
- <sup>3</sup> P. P. Bemand, M. A. A. Clyne, and R. T. Watson, J. Chem. Soc. Faraday Trans. 1, **69**, 1356 (1973).
- <sup>4</sup> 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).
- <sup>5</sup> V. I. Gritsan, V. N. Panfilov, and I. L. Sukhanov, Reaction Kinetics and Catalysis Letters **2**, 265 (1975).