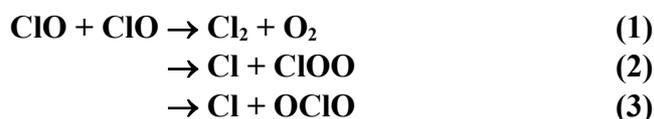


## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iClOx34

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: 25<sup>th</sup> September 2003.



$$\Delta H^\circ(1) = -203.2 \text{ kJ}\cdot\text{mol}^{-1}$$

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

$$\Delta H^\circ(3) = 12.7 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data ( $k = k_1 + k_2 + k_3$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$k_1 = 1.01 \times 10^{-12} \exp[-(1590 \pm 100)/T]$	260-390	Nickolaisen, Friedl, and Sander, 1994 <sup>1</sup>	(a)
$k_2 = 2.98 \times 10^{-11} \exp[-(2450 \pm 330)/T]$	260-390		
$k_3 = 3.50 \times 10^{-13} \exp[-(1370 \pm 150)/T]$	260-390		
<i>Branching Ratios</i>			
$k_1/k = 0.39 \pm 0.06$	298	Horowitz, Crowley, and Moortgat, 1994 <sup>2</sup>	(b)
$k_2/k = 0.41 \pm 0.06$	298		
$k_3/k = 0.20 \pm 0.03$	298		
$k_3/k_2 = 0.27 \exp[(220 \pm 100)/T]$	285-331		

### Comments

- (a) Flash photolysis-long pathlength UV absorption technique.  $\text{Cl}_2$ - $\text{Cl}_2\text{O}$  mixtures were photolyzed at wavelengths longer than 300 nm. The UV absorption of ClO and OCIO were monitored with an optical multichannel analyzer. The reaction was studied over a wide range of temperature, pressure, and initial reactant stoichiometry.
- (b)  $\text{Cl}_2$ -sensitized continuous photolysis of  $\text{Cl}_2$ - $\text{O}_3$  mixtures in excess  $\text{O}_2$ . Decay of  $\text{O}_3$  and formation of OCIO monitored by UV absorption.

### Preferred Values

$$k_1 = 4.8 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_2 = 8.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_3 = 3.5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_1 = 1.0 \times 10^{-12} \exp(-1590/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 260 \text{ K to } 390 \text{ K.}$$

$$k_2 = 3.0 \times 10^{-11} \exp(-2450/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 260 \text{ K to } 390 \text{ K.}$$

$k_3 = 3.5 \times 10^{-13} \exp(-1370/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 260 K to 390 K.

### Reliability

$\Delta \log k_1 = \Delta \log k_2 = \Delta \log k_3 = \pm 0.2$  at 298 K.

$\Delta(E_1/R) = \Delta(E_3/R) = \pm 300$  K.

$\Delta(E_2/R) = \pm 500$  K.

### Comments on Preferred Values

The ClO + ClO reaction exhibits both bimolecular and termolecular reaction channels. The termolecular reaction, which leads to the formation of the ClOCl dimer, dominates at high pressure ( $> 0.013$  bar at 298 K), but is not kinetically important at temperatures above  $\sim 283$  K because of the instability of the dimer with respect to the reverse decomposition.

The recommended values for the individual reaction channels are those from the study of Nickolaisen *et al.*<sup>1</sup> This study, using a flash photolysis-long pathlength UV absorption technique, is the most comprehensive study of this system, covering a wide range of temperature, initial reactant stoichiometry and pressure. These results<sup>1</sup> are preferred over the results of earlier studies of the total bimolecular rate coefficient at low pressures by Clyne and co-workers,<sup>3</sup> as discussed in the reviews of Watson,<sup>4,5</sup> and those of other studies reported by Cox and Derwent,<sup>6</sup> Hayman *et al.*,<sup>7</sup> Simon *et al.*<sup>8</sup> and Horowitz *et al.*<sup>9</sup>

The room temperature branching ratios from the study of Nickolaisen *et al.*<sup>1</sup> are  $k_1:k_2:k_3 = 0.29:0.50:0.21$ . Horowitz *et al.*<sup>2</sup> in their study of the temperature dependence of the channel branching ratios report slightly different values of  $k_1:k_2:k_3 = 0.39:0.41:0.20$  at 298 K and observed distinctly non-Arrhenius behavior for  $k$  over the temperature range 285 K to 331 K. Their study<sup>2</sup> was carried out in excess O<sub>2</sub>, where the quantum yield for O<sub>3</sub>-photosensitized decomposition (which reflects Cl atom generation in this reaction) was consistently lower than in excess N<sub>2</sub>. The mechanistic explanation for this observation and for the apparent non-Arrhenius behavior remains obscure. The bath gas effect on  $\Phi(-\text{O}_3)$  can be accounted for by the observed difference in the branching ratios in the presence of O<sub>2</sub> and N<sub>2</sub>, suggesting that O<sub>2</sub> is not involved in the ClO + ClO reaction simply as a third-body quencher.

### References

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- <sup>4</sup> R. T. Watson, *J. Phys. Chem. Ref. Data* **6**, 871 (1977).
- <sup>5</sup> R. T. Watson, Proceedings of the NATO Advanced Study Institute on Atmospheric Ozone, Report FAA-EE-80-20, FAA, Washington, DC (1980).
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- <sup>7</sup> G. D. Hayman, J. M. Davies, and R. A. Cox, *Geophys. Res. Lett.* **13**, 1347 (1986).
- <sup>8</sup> F. G. Simon, W. Schneider, G. K. Moortgat, and J. P. Burrows, *J. Photochem. Photobiol. A* **55**, 1 (1990).
- <sup>9</sup> A. Horowitz, D. Bauer, J. N. Crowley, and G. K. Moortgat, *Geophys. Res. Lett.* **20**, 1423 (1993).