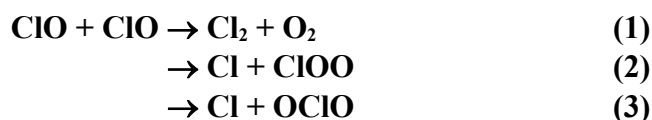


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iClOx34

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: 25th 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 ¹	(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 ²	(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. Cl_2 - Cl_2O 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) Cl_2 -sensitized continuous photolysis of Cl_2 - O_3 mixtures in excess O_2 . Decay of 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 ~ 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.*¹ 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 results¹ are preferred over the results of earlier studies of the total bimolecular rate coefficient at low pressures by Clyne and co-workers,³ as discussed in the reviews of Watson,^{4,5} and those of other studies reported by Cox and Derwent,⁶ Hayman *et al.*,⁷ Simon *et al.*⁸ and Horowitz *et al.*⁹

The room temperature branching ratios from the study of Nickolaisen *et al.*¹ are $k_1:k_2:k_3 = 0.29:0.50:0.21$. Horowitz *et al.*² 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 study² was carried out in excess O₂, where the quantum yield for O₃-photosensitized decomposition (which reflects Cl atom generation in this reaction) was consistently lower than in excess N₂. 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 O₂ and N₂, suggesting that O₂ is not involved in the ClO + ClO reaction simply as a third-body quencher.

References

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