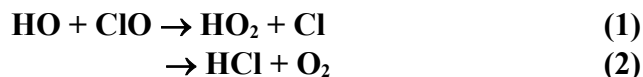


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iClOx24

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This data sheet updated: 23th July 2003.



$$\Delta H^\circ(1) = -2.9 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -231 \text{ kJ}\cdot\text{mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(9.1 \pm 1.3) \times 10^{-12}$	298	Leu and Lin, 1979 ¹	DF-RF
$(1.17 \pm 0.33) \times 10^{-11}$	248-335	Ravishankara, Eisele and Wine, 1983 ²	DF-RF
$(1.19 \pm 0.09) \times 10^{-11}$	243-298	Burrows, Wallington and Wayne, 1984 ³	DF-RF (a)
$8.0 \times 10^{-12} \exp[(235 \pm 46)/T]$	219-373	Hills and Howard, 1984 ⁴	DF-LMR (b)
$(1.75 \pm 0.31) \times 10^{-11}$	298		
$(1.94 \pm 0.38) \times 10^{-11}$	298	Poulet, Laverdet and Le Bras, 1986 ⁵	DF-LIF (c)
$5.5 \times 10^{-12} \exp[(292 \pm 72)/T]$	205-298	Lipson <i>et al.</i> , 1997 ⁶	DF-CIMS
$(1.46 \pm 0.23) \times 10^{-11}$	298		
$k_2 = 1.7 \times 10^{-13} \exp[(363 \pm 50)/T]$	210-298	Lipson <i>et al.</i> , 1997 ⁶	DF-CIMS (d)
$k_2 = 5.7 \times 10^{-13}$	298		
$8.9 \times 10^{-12} \exp[(295 \pm 95)/T]$	234-356	Kegley-Owen <i>et al.</i> , 1999 ⁷	DF (e)
$(2.44 \pm 0.63) \times 10^{-11}$	298		
$k_2 = 3.2 \times 10^{-13} \exp[(325 \pm 60)/T]$	207-298	Lipson <i>et al.</i> , 1999 ⁸	F-CIMS (f)
$k_2 = (9.5 \pm 1.6) \times 10^{-13}$	298		
$6.7 \times 10^{-12} \exp[(360 \pm 90)/T]$	230-360	Bedjanian, Riffault and Le Bras, 2001 ⁹	DF-MS (g)
$(2.2 \pm 0.4) \times 10^{-11}$	298		
$k_2 = 9.7 \times 10^{-14} \exp[(600 \pm 120)/T]$	230-320		
$k_2 = (7.3 \pm 2.2) \times 10^{-13}$	298		
$7.2 \times 10^{-12} \exp[(333 \pm 70)/T]$	218-298	Wang and Keyser, 2001 ¹⁰	DF-RF/UVA (h)
$(2.22 \pm 0.33) \times 10^{-11}$	298		
$k_2 = (1.25 \pm 0.45) \times 10^{-12}$	298	Tyndall <i>et al.</i> , 2002 ¹¹	FP-IR (i)
<i>Branching Ratios</i>			
$k_2/k = 0.05 \pm 0.02$	298	Lipson <i>et al.</i> , 1997 ⁶	DF-CIMS (j)
$k_2/k = 0.06 \pm 0.02$	210		
$k_2/k = 0.090 \pm 0.048$	218-298	Wang and Keyser, 2001 ¹²	DF-RF/IR/UVA(h, k)

Comments

- (a) Rate coefficient ratio of $k_1/k = 0.85 \pm 0.07$, independent of temperature over the range 243-298 K, was determined from measurement of HO₂ radical concentrations (after conversion to HO radicals by reaction with NO).
- (b) The rate coefficient ratio, k_1/k , was measured to be $k_1/k = 0.86 \pm 0.14$ at 293 K from measurement of the HO₂ radical concentrations by LMR.

- (c) The rate coefficient ratio, k_1/k , was measured to be 0.98 ± 0.12 at 298 K from MS detection of HCl.
- (d) Measurements of the DCl product by CIMS in experiments using DO radicals. The overall rate coefficient measured for reaction of DO radicals with ClO radicals was $k = 4.2 \times 10^{-12} \exp[(280 \pm 114)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200 K to 298 K, a factor of 1.35-1.4 lower than the rate coefficient for the HO radical reaction.
- (e) HO radicals were generated by pulsed laser photolysis of O₃ (or ClO) at 248 nm and monitored by LIF. ClO radicals were generated by reaction of Cl atoms (produced by a microwave discharge in Cl₂-He mixtures) with O₃, and monitored by UV/visible absorption.
- (f) Turbulent flow reactor operated at total pressures of 125 mbar to 270 mbar. The measurements of the rate coefficients k_2 were combined with the overall rate coefficient $k = 5.5 \times 10^{-12} \exp(292/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ previously determined by the same research group⁶ to derive the branching ratio $k_2/k = 0.07 \pm 0.03$, independent of temperature (207-298 K) and total pressure (125-270 mbar).
- (g) ClO generated from Cl + O₃ (following discharge of Cl₂ or F + Cl₂). HO was generated from H + NO₂ (following discharge of H₂). ClO concentrations were measured directly at the parent peak. HO measured as HOBr⁺, following titration with Br₂. Experiments carried out at 1 Torr under pseudo-first order conditions with ClO in excess. Direct measurement of k_2 from observed HCl formation is consistent with $k_2/k = 0.035 \pm 0.010$ over the temperature range 230-320 K.
- (h) ClO generated from Cl + O₃ (following discharge of Cl₂). HO was generated either from F + H₂O (following discharge of F₂) or from H + NO₂ (following discharge of H₂). ClO and HO concentrations measured by UV absorption and RF, respectively. Experiments carried out at 1.3 mbar under pseudo-first order conditions with ClO in excess.
- (i) ClO and HO generated from the 308 nm laser photolysis of Cl₂-O₃-H₂O-He mixtures at *ca.* 40-55 mbar. Initial concentrations of ClO and HO calculated from laser fluence and precursor concentrations. HCl production determined using time-resolved tunable diode laser spectroscopy. k_2 determined from simulation of the results of experiments performed with a range of starting conditions.
- (j) From the rate coefficients k_2 and k for the DO radical reaction.
- (k) HCl measured using long-path tunable diode laser spectroscopy.

Preferred Values

$k = 2.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 7.3 \times 10^{-12} \exp(300/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200 K to 380 K.

$k_2/k = 0.06$, independent of temperature over the range 200 K to 300 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

$\Delta(E/R) = \pm 100 \text{ K}$.

$\Delta(k_2/k) = \pm 0.04$ over the temperature range 200 K to 300 K.

Comments on Preferred Values

The preferred value of k at 298 K is an average of the values reported by Hills and Howard,⁴ Poulet *et al.*,⁵ Lipson *et al.*,⁶ Kegley-Owen *et al.*,⁷ Bedjanian *et al.*⁹ and Wang and Keyser.¹¹ The preferred Arrhenius expression is based on the mean of the E/R values from the temperature dependence studies of Hills and Howard,⁴ Lipson *et al.*,⁶ Kegley-Owen *et al.*,⁷ Bedjanian *et al.*⁹ and Wang and Keyser,¹¹ combined with a pre-exponential factor adjusted to give the preferred value of k at 298 K. These studies are generally in good agreement, as

reflected in the uncertainties assigned to k and E/R . Values of the branching ratio, k_2/k , derived from both direct measurements of k_2 and $k^{6,9}$ and from measurements of the branching ratio itself¹², yield values lying in the range 0.035-0.09. The temperature independent preferred value of k_2/k is based on the mean of these values, with the assigned uncertainty encompassing the extremes of the reported measurements.

References

- ¹ M. T. Leu and C. L. Lin, *Geophys. Res. Lett.* **6**, 425 (1979).
- ² A. R. Ravishankara, F. L. Eisele, and P. H. Wine, *J. Chem. Phys.* **78**, 1140 (1983).
- ³ J. P. Burrows, T. J. Wallington, and R. P. Wayne, *J. Chem. Soc. Faraday 2*, **80**, 957 (1984).
- ⁴ A. J. Hills and C. J. Howard, *J. Chem. Phys.* **81**, 4458 (1984).
- ⁵ G. Poulet, G. Laverdet, and G. Le Bras, *J. Phys. Chem.* **90**, 159 (1986).
- ⁶ J. B. Lipson, M. J. Elrod, T. W. Beiderhase, L. T. Molina, and M. J. Molina, *J. Chem. Soc. Faraday Trans.* **93**, 2665 (1997).
- ⁷ C. S. Kegley-Owen, M. K. Gilles, J. B. Burkholder, and A. R. Ravishankara, *J. Phys. Chem. A* **103**, 5040 (1999).
- ⁸ J. B. Lipson, T. W. Beiderhase, L. T. Molina, M. J. Molina, and M. Olzmann, *J. Phys. Chem. A* **103**, 6540 (1999).
- ⁹ Y. Bedjanian, V. Riffault and G. Le Bras, *Int. J. Chem. Kinet.* **33**, 587 (2001).
- ¹⁰ J. J. Wang and L. F. Keyser, *J. Phys. Chem. A* **105**, 10544 (2001).
- ¹¹ G. S. Tyndall, C. S. Kegley-Owen, J. J. Orlando and A. Fried, *J. Phys. Chem. A* **106**, 1567 (2002).
- ¹² J. J. Wang and L. F. Keyser, *J. Phys. Chem. A* **105**, 6479 (2001).