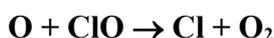


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iClOx2

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: 23th July 2003.



$$\Delta H^\circ = -229.5 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(5.3 \pm 0.8) \times 10^{-11}$	298	Bemand et al., 1973	DF-RF
$(5.7 \pm 2.3) \times 10^{-11}$	298	Bemand et al., 1973	DF-MS
$1.07 \times 10^{-10} \exp[-(224 \pm 76)/T]$	220-426	Clyne and Nip, 1976	DF-RF
$(5.2 \pm 1.6) \times 10^{-11}$	298		
$5.2 \times 10^{-11} \exp[-(96 \pm 20)/T]$	236-422	Leu, 1984	DF-RF
$(3.6 \pm 0.7) \times 10^{-11}$	296		
$(4.2 \pm 0.8) \times 10^{-11}$	241-298	Margitan, 1984	PLP-RF
$(3.5 \pm 0.5) \times 10^{-11}$	252-347	Schwab et al., 1984	DF-RF/RA/LMR (a)
$1.55 \times 10^{-11} \exp[(263 \pm 60)/T]$	231-367	Nicovich et al., 1988	PLP-RF (b)
$(3.8 \pm 0.6) \times 10^{-11}$	298		
$3.0 \times 10^{-11} \exp[(75 \pm 40)/T]$	227-362	Goldfarb et al., 2001	PLP-RF (c)
$(3.9 \pm 0.6) \times 10^{-11}$	298		
<i>Relative Rate Coefficients</i>			
$4.5 \times 10^{-11} \exp[-(14 \pm 120)/T]$	218-295	Zahniser and Kaufman, 1977	RR (d)
$(4.3 \pm 0.7) \times 10^{-11}$	295		
$2.6 \times 10^{-11} \exp[(97 \pm 64)/T]$	220-387	Ongstad and Birks, 1986	RR (e)
$(3.8 \pm 0.6) \times 10^{-11}$	298		

Comments

- (a) Discharge flow system with LMR detection of ClO radicals and resonance fluorescence detection of O(³P) and Cl atoms. Pseudo-first order decay of O(³P) atoms in the presence of excess ClO and decay of ClO in the presence of excess O(³P) gave good agreement for the rate coefficient k . There was no discernable temperature dependence over the range studied. The total pressure was in the range 1.1 mbar to 2.7 mbar.
- (b) Dual pulsed laser photolysis system with resonance fluorescence detection in slow flow reactor. ClO radicals were produced by reaction of excess Cl, produced by 351 nm excimer laser photolysis of Cl₂, with known concentrations of O₃. O(³P) atoms were produced by 266 nm laser photolysis of ClO after appropriate delay time, and were monitored by resonance fluorescence. The measured O(³P) atom decay rate was corrected for losses due to reaction with Cl₂ and other routes. The total pressure was in the range 33 mbar to 667 mbar, and no effect of pressure on the rate coefficient k was observed.

- (c) Discharge flow tube coupled to a pulsed laser photolysis-resonance fluorescence apparatus. O atoms were produced by PLP of ClO at 308 nm, and their pseudo-first-order decay in excess ClO was monitored by RF. ClO radicals were produced by reaction of excess Cl atoms with O₃ or Cl₂O. Cl atoms were produced in the microwave discharge of a Cl₂-He mixture. The total pressure was in the range 7-29 mbar. In this paper the authors, on the basis of a careful analysis of their data and the existing literature data on this reaction (see Comments on Preferred Values), proposed a temperature-dependent expression to be used for atmospheric calculations.
- (d) The rate coefficient k was measured relative to $k(\text{Cl} + \text{O}_3)$ using the discharge flow technique in conjunction with resonance fluorescence monitoring of Cl atom concentrations and resonance absorption monitoring of O(³P) atom concentrations in a system where O(³P), Cl, ClO and O₃ had reached a steady-state condition. The tabulated Arrhenius expression was obtained by combining the experimentally determined ratio of $k(\text{O} + \text{ClO})/k(\text{Cl} + \text{O}_3) = 1.55 \exp[(246 \pm 30)/T]$ with the rate coefficient of $k(\text{Cl} + \text{O}_3) = 2.9 \times 10^{-11} \exp(-260/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2003).
- (e) Discharge flow system with detection of O(³P) atoms by O + NO + M chemiluminescence in the presence of excess ClO. The ClO radical concentrations were determined indirectly by *in situ* conversion to NO₂ by addition of NO and k measured relative to $k(\text{O} + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2) = 6.58 \times 10^{-12} \exp[-(142 \pm 23)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, determined concurrently in the same system. The total pressure was 3.1 mbar. No effect of O₂ was observed at 230 K.

Preferred Values

$k = 3.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 2.5 \times 10^{-11} \exp(110/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 220 K to 390 K.

Reliability

$\Delta \log k = \pm 0.06$ at 298 K.

$\Delta(E/R) = \pm 50 \text{ K}$.

Comments on Preferred Values

The preferred value accepts the recommendation of Goldfarb et al. (2001) based on a careful analysis of their data and data published in previous studies. The data used in the analysis were those published in Zahniser and Kaufman (1977), Margitan (1984), Schwab et al. (1984), Ongstad and Birks (1986), Nicovich et al. (1988) and Goldfarb et al. (2001). On the basis of newer information, the rate coefficients reported by Zahniser and Kaufman (1977), Margitan (1984) and Ongstad and Birks (1986) were adjusted (Goldfarb et al., 2001). Leu and Yung (1987) have shown that the yields of O₂(¹Δ) and O₂(¹Σ) in the reaction are $<2 \times 10^{-2}$ and $(4.4 \pm 1.1) \times 10^{-4}$ respectively.

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