

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet III.A2.50 iClOx35

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$$\Delta H^\circ = -75.7 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$5.0 \times 10^{-32} [\text{O}_2]$	298	Johnston et al., 1969	MM (a)
$2.0 \times 10^{-32} [\text{Ar}]$	298	Walker, 1972	DF-UVA (b)
$1.1 \times 10^{-32} [\text{O}_2]$	300	Basco and Hunt, 1979	FP-UVA (c)
$3.0 \times 10^{-32} [\text{N}_2]$	298	Cox et al., 1979	MM (d)
$6.0 \times 10^{-32} (T/300)^{-2.1} [\text{O}_2]$	268-338	Hayman et al., 1986	MM (e)
$(1.8 \pm 0.5) \times 10^{-32} (T/300)^{-3.6} [\text{N}_2]$	194-247	Sander, Friedl and Yung, 1989	FP-UVA (f)
$(1.64 \pm 0.09) \times 10^{-32} (T/300)^{-4.4} [\text{N}_2]$	200-263	Trolier, Mauldin and Ravishankara, 1990	FP-UVA (g)
$(1.32 \pm 0.08) \times 10^{-32} (T/300)^{-4.4} [\text{O}_2]$	200-263		
$1.22 \times 10^{-33} \exp[(833 \pm 34)/T] [\text{N}_2]$	195-390	Nickolaisen, Friedl and Sander, 1994	FP-UVA (h)
$(1.96 \pm 0.24) \times 10^{-32} [\text{N}_2]$	300		
$(1.24 \pm 0.09) \times 10^{-32} [\text{O}_2]$	300		
$(2.5 \pm 0.4) \times 10^{-32} [\text{N}_2]$	300	Bloss, 1999	FP-UVA (i)
$1.7 \times 10^{-32} [\text{N}_2]$	300	Stark, 1999	PLP-UVA (j)
$1.1 \times 10^{-31} [\text{N}_2]$	200		
$(1.59 \pm 0.60) \times 10^{-32} (T/300)^{-4.5} [\text{N}_2]$	183-245	Bloss et al., 2001	FP-UVA (k)

Comments

- (a) Photolysis of $\text{Cl}_2\text{-O}_2$ mixtures in the pressure range 0.07-1 bar.
- (b) Pressure range 1.3-10 mbar.
- (c) Pressure range 70-930 mbar.
- (d) Photolysis of $\text{Cl}_2\text{-O}_2$ mixtures at 50-400 mbar.
- (e) Measurements in $\text{Cl}_2\text{-O}_2$ mixtures in the ratio 2:3, pressure range 7-30 mbar.
- (f) ClO radicals generated from $\text{Cl}_2\text{-Cl}_2\text{O}$ or $\text{Cl}_2\text{-O}_3$ mixtures with concentrations of bath gases N_2 , Ar or O_2 in the range of 10^{18} molecule cm^{-3} to 3×10^{19} molecule cm^{-3} . Falloff extrapolations to k_0 and k_∞ used a value of $F_c = 0.6$.

- (g) ClO radicals generated from Cl₂-O₃ mixtures in the presence of 33 mbar to 800 mbar of He, N₂, O₂ or SF₆, ClO radicals and Cl₂O₂ monitored by long-path UV absorption. Falloff curves extrapolated with $F_c = 0.6$.
- (h) Pulsed laser photolysis of Cl₂ at $\lambda > 300$ nm in the presence of Cl₂O. ClO radicals generated by the reaction $\text{Cl} + \text{Cl}_2\text{O} \rightarrow \text{ClO} + \text{Cl}_2$ and monitored by UV absorption spectroscopy using either a photomultiplier for detection at 275.5 nm or an optical multichannel analyzer for detection over the wavelength range 270 nm to 280 nm. Measurements at 20-600 mbar. From a third-law analysis, a value of $\Delta H^\circ = -(75.7 \pm 0.9)$ kJ mol⁻¹ was derived. Third-body efficiencies for the bath gases He, Ar, CF₄, SF₆ and Cl₂ were also determined.
- (i) ClO radicals generated by flash photolysis of Cl₂-Cl₂O-N₂ mixtures and detected by UV absorption. The bath gas pressure was varied between 0.25 bar and 1 bar. Falloff extrapolation used $F_c = 0.6$. Small discrepancies between the various studies were attributed to the slightly different absorption cross-sections used.
- (j) ClO radicals generated by pulsed laser photolysis of Cl₂O between 0.1 bar and 1000 bar pressure of He and N₂. The observed pressure dependences differ from conventional falloff expressions, suggesting overlapping contributions from the energy transfer and radical-complex mechanism, as well as diffusion control at the highest pressures. The cited rate coefficients correspond to a representation of the falloff curve at pressures below 1 bar using $F_c = 0.6$.
- (k) See comment (i). Pressure range 30-930 mbar. Falloff extrapolation with $F_c = 0.6$ and $k_\infty = (1.36 \pm 0.2) \times 10^{-12} (T/300)^{-3.09}$ cm³ molecule⁻¹ s⁻¹.

Preferred Values

$$k_0 = 2.0 \times 10^{-32} (T/300)^{-4} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range 190-300 K.}$$

Reliability

$$\Delta \log k_0 = \pm 0.1 \text{ at 298 K.}$$

$$\Delta n = \pm 1.5.$$

Comments on Preferred Values

The preferred values are based on the studies of Trolier et al. (1999) and Bloss et al. (2001) accounting for some falloff, see comments on high-pressure rate coefficients.

High-pressure rate coefficients Rate coefficient data

$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(6 \pm 2) \times 10^{-12}$	194-247	Sander, Friedl and Yung, 1989	FP-UVA (a)
$(4.8 \pm 1.3) \times 10^{-12}$	200-263	Trolier, Mauldin and Ravishankara, 1990	FP-UVA (b)
$(6 \pm 2) \times 10^{-12}$	195-390	Nickolaisen, Friedl and Sander, 1994	FP-UVA(c)
$(5 \pm 3) \times 10^{-12}$	300	Bloss, 1999	FP-UVA (d)
4.5×10^{-12}	300	Stark, 1999	PLP-UVA (e)
7×10^{-12}	200		
$(1.36 \pm 0.22) \times 10^{-12} (T/300)^{-3.09}$	183-245	Bloss et al., 2001	FP-UVA (f)

Comments

- (a) See comment (a) for k_0 .
- (b) See comment (b) for k_0 .
- (c) See comment (c) for k_0 . The k_∞ value was obtained from falloff data measured below 250 K.
- (d) See comment (d) for k_0 .
- (e) See comment (e) for k_0 . The cited rate coefficients are given for the energy-transfer mechanism only, such that the falloff curves below 1 bar are fitted. Above 1 bar pressure additional contributions from the radical-complex mechanism become increasingly important such that maximum values of k of $4.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K and $8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 200 K are reached near 200 bar, before they decrease because of diffusional control.
- (f) See comment (i) and (k) for k_0 .

Preferred Values

$k_\infty = 1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 190-300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over the temperature range 190 K to 300 K.

Comments on Preferred Values

It is difficult to provide a reasonable representation of k_0 , k_∞ , and F_c , because there is ample evidence that this reaction is governed by a superposition of the energy transfer and the radical-complex mechanism. The pressure dependence at $P > 1$ bar looks anomalous (Stark, 1999). Likewise, the absolute value and the temperature coefficient of k_0 appear unusual. Neglecting these aspects, one may use the representation given by Bloss et al. (2001) with $F_c = 0.6$ and k_0 and k_∞ as given in the table. We here choose a different representation with $F_c = 0.45$ and the preferred values given above which represent the data equally well at $P < 1$ bar. However, we keep in mind that the mechanistic complications of this system ask for different treatments. Difficulties in the theoretical analysis of the rate coefficients were also encountered by Bloss et al. (2001), Golden (2003) and Zhu and Lin (2003).

The following text-line combines the preferred values for the high and low pressure limiting rate coefficients to generate a single, cut-and-paste expression for calculation of k :

$$=((2.0\text{e-}32*(T/300)^{-4}) * M * (1.0\text{e-}11)) / ((2.0\text{e-}32*(T/300)^{-4}) * M + (1.0\text{e-}11)) * 10^{(\log_{10}(0.45) / (1 + (\log_{10}((2.0\text{e-}32*(T/300)^{-4}) * M / (1.0\text{e-}11)) / (0.75 - 1.27 * \log_{10}(0.45))))^2)}$$

The molecular density, $M = 7.243 \times 10^{21} P(\text{bar}) / T(\text{K})$

References

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