IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet III.A2.47 iClOx32

This data sheet last evaluated: March 2005.

$ClO + NO_2 + M \rightarrow ClONO_2 + M$

$\Delta H° = -111.9$ kJ·mol^{-1}

Low-pressure rate coefficients
Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(4.4 \pm 0.66) \times 10^{-33} \exp(1087/T)$ [N_2]	250-356	Birks et al., 1977	DF-MS (a)
$(1.52 \pm 0.23) \times 10^{-31}$ (T/300)$^{-3.15}$ [N_2]	251-365	Zahniser et al., 1977	DF-RF (b)
$(3.69 \pm 0.24) \times 10^{-23} \exp(1150/T)$ [N_2]		Leu et al., 1977	DF-MS (c)
$4.3 \times 10^{-33} \exp[(1085 \pm 86)/T]$ [N_2]	274-339	Cox and Lewis, 1979	(d)
$(1.5 \pm 0.12) \times 10^{-31}$ [N_2]	298	Molina, Molina and Ishiwata, 1980	PLP-UVA (e)
$(1.5 \pm 0.2) \times 10^{-31}$ [N_2]	298	Dasch, Sternberg and Schindler, 1981	PLP-UVA (f)
$2.8 \times 10^{-33} \exp(1090/T)$ [He]	250-387	Lee et al., 1982	DF-LMR
$3.5 \times 10^{-33} \exp(1180/T)$ [O_2]	250-416		(g)
2.09×10^{-31} [N_2]	297		
$(1.8 \pm 0.4) \times 10^{-31}$ [N_2]	270-295	Cox, Burrows and Coker, 1984	(h)
$(1.6 \pm 0.2) \times 10^{-31} (T/300)^{-3.0}$ [N_2]	264-343	Handwerk and Zellner, 1984	FP-UVA (i)
$(1.40 \pm 0.07) \times 10^{-31}$ [N_2]	298	Wallington and Cox, 1986	(j)
$(1.8 \pm 0.3) \times 10^{-31} (T/300)^{-3.4}$ [air]	213-298	Percival et al., 1997	(k)

Comments

(a) Pressure range 1.3-7 mbar.

(b) Resonance fluorescence of Cl after conversion of ClO into Cl. Pressure range 1.4-9 mbar. Measurement in N_2 only at 300 K, temperature coefficient taken from measurements in He.

(c) Pressure range 1.3-8 mbar.

(d) Modulated photolysis with UV absorption detection of ClO radicals. The pressure range studied was 33-815 mbar. Small deviations from third-order kinetics were observed near 1 bar.

(e) The ClO radical decay was monitored. FTIR spectroscopy was also used to monitor the reaction products.

(f) ClO radicals were generated from Cl_2O and monitored at 258.2 nm. The pressure range was 27-800 mbar.

(g) Detection of ClO($X^2\Pi_{3/2}$, v = 0) with an optically pumped spectrometer. Measurements were carried out at pressures over the range 0.8-8.8 mbar.

(h) Modulated photolysis of Cl_2-Cl_2O-NO_2-N_2 mixtures. $ClONO_2$ formation was followed by diode laser spectroscopy. This study ruled out the formation of isomers other than $ClONO_2$.
(i) The pressure range was 23-1052 mbar, with experiments being conducted at 264 K, 298 K and 343 K.
(j) Modulated photolysis of $OClO$-NO_2-N_2 mixtures with detection of ClO radicals by UV absorption.
(k) Turbulent flow measurements at 213 K and 298 K with high pressure chemical ionization mass spectrometry over the pressure range 200-790 mbar. The falloff extrapolation used $F_c = 0.6$, in agreement with earlier data.

Preferred Values

$k_0 = 1.6 \times 10^{-31} (T/300)^{-3.4}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 250-350 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ at 298 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

There is excellent agreement between the various studies of this reaction in the falloff region close to the low pressure limit (Birks et al., 1977; Zahniser et al., 1977; Leu et al., 1977; Cox and Lewis, 1979; Molina et al., 1980; Dasch et al., 1981; Lee et al., 1982; Cox et al., 1984; Handwerk and Zellner, 1984; Wallington and Cox, 1986; Percival et al., 1997).

High-pressure rate coefficients
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
(3-6) x 10^{-12}	298	Dasch, Sternberg and Schindler, 1981	PLP-UVA (a)
$(1.2\ ^{+1.2}_{-0.6})$ x 10^{-11}	264-343	Handwerk and Zellner, 1984	FP-UVA (b)
(1.5 ± 0.7) x 10^{-11} $(T/300)^{-1.9}$	213-298	Percival et al., 1997	(c)

Comments

(a) See comment (c) for k_0. The extrapolation to k_∞ is very uncertain, and the value of F_c was unspecified.
(b) See comment (f) for k_0. The extrapolation to k_∞ is very uncertain. The reported value of k_∞ was based on theoretical predictions. Using the reported values of k_0 and k_∞, and $F_c = 0.55$, 0.50 and 0.45 at 264 K, 298 K and 343 K, respectively, falloff curves were obtained which are in good agreement with the majority of the available data.
(c) See comment (h) for k_0. The falloff extrapolation was carried out with $F_c = 0.6$, independent of temperature.

Preferred Values

$k_\infty = 7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 250-350 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over the temperature range 250-350K.

Comments on Preferred Values

Because there are no direct measurements of k at pressures much above 1 bar, k_∞ cannot be established with certainty. There are two alternatives for a representation of the rate data at pressures up to 1 bar. One may use the values chosen by Percival et al. (1997) with $F_c = 0.6$ and a temperature dependent k_∞ such as given in the table. Alternatively, one may follow our policy of choosing a more reasonable F_c such as recommended by Cobos and Troe (2003) and then fit k_∞. Using $F_c = 0.4$ such as recommended also for $HO + NO_2 (+ M) \rightarrow HONO_2 (+ M)$, the rate data in the falloff range below 1 bar from Percival et al. (1997) are well reproduced with a temperature independent $k_\infty = (7 \pm 2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. Because a value for F_c smaller than 0.6 appears theoretically much more justified, we here adopt the second alternative. However, we emphasize that the two alternatives work equally well for the representation of data below 1 bar.

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:

=((1.6e-31*(T/300)^-3.4)*M*(7e-11))/((1.6e-31*(T/300)^-3.4)*M+(7e-11))*10^(log10(0.4)/(1+(log10((1.6e-31*(T/300)^-3.4)*M/(7e-11))/(0.75-1.27*log10(0.4)))^2))

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

References

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