IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet III.A4.97 iIOx19

The citation for this data sheet is: IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, (http://iupac.pole-ether.fr).

This datasheet last evaluated: 9th March 2005.

$IO + NO_2 + M \rightarrow$ products

$\Delta H° = -79$ 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			
$(4.3 \pm 2.0) \times 10^{-31}$ [N_2]	277	Jenkin and Cox, 1985	MM-A (a)
7.7×10^{-31} $(T/300)^{-5.0}$ [N_2]	254-354	Daykin and Wine, 1990	PLP-A (b)
$(3.6 \pm 1.0) \times 10^{-31}$ [He]	298	Maguin et al., 1992	DF-MS (c)
$(7.9 \pm 2.2) \times 10^{-31}$ [N_2]	298		
$(1.80 \pm 0.07) \times 10^{-31} \times (T/300)^{-2.6}$ [O_2]	290-350	Larin et al., 1998	FR-F (d)
4.1×10^{-31} $(T/298)^{-6.3}$ [N_2]	238-298	Hölscher and Zellner, 2002	PLP-LIF (e)
1.3×10^{-30} $(T/300)^{-4.5}$ [N_2]	216-474	Allan and Plane, 2002	PLP-LIF (f)

Comments

(a) Photolysis of I_2 in the presence of O_3 producing IO radicals monitored by absorption at 427 nm in the presence of an excess of NO_2. The total pressure was varied over the range 47-537 mbar of N_2. The falloff curve was analyzed using $F_c = 0.4$ by analogy to the BrO + NO_2 + M reaction. A small correction was made for a second-order component to the IO radical kinetics at higher pressures.

(b) IO radicals generated by pulsed laser photolysis of I_2-NO_2-N_2 mixtures at 351 nm; IO radicals monitored by absorption at 427 nm. Pressure range 53-1000 mbar. The data were extrapolated to the low- and high-pressure rate coefficients using $F_c = 0.4$.

(c) IO radicals and $IONO_2$ detected by MS. IO radicals were generated by the reaction O + $I_2 \rightarrow$ IO + I. The pressure range was 1.6-2.8 mbar of He. Using a relative third-body efficiency of N_2 and He for the analogous BrO + NO_2 + M (ratio $k_0(N_2)/k_0(He) = 2.2$) from Sander et al. (1981), the value reported above was derived.

(d) I atoms generated by photolysis of a flow of CH_3I at 254 nm; IO radicals formed by the reaction I + $O_3 \rightarrow$ IO + O_2. Pressure range 1.3-8 mbar of O_2. Assuming a ratio of $\beta_c(N_2)/\beta_c(O_2) = 1.4$, the expression $k_0 = 2.50 \times 10^{-31} \times (T/300)^{-2.6}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 290 K to 350 K was derived.

(e) Laser flash photolysis of mixtures of O_3, CF_3I and NO_2 in air with pulsed LIF detection of IO. Pressure range 50-400 mbar. Evaluation of the falloff curve with $F_c = 0.6$. Rate coefficients about 20% below those from Daykin and Wine (1990).

(f) Laser flash photolysis of NO_2 in the presence of CF_3I and N_2 with LIF detection of IO. Falloff extrapolation with $F_c = 0.57$ obtained from RRKM theory. Rate coefficients about 20% above

data from Daykin and Wine (1990). Preliminary results by Blitz et al. (2000) are cited which are close to the present results.

Preferred Values

$k_0 = 7.7 \times 10^{-31} (T/300)^{-5}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 250-360 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.

$\Delta n = \pm 2$.

Comments on Preferred Values

The preferred values for k_0 are an average of the data of Daykin and Wine (1990), the value of Maguin et al. (1992) derived with the given ratio of efficiencies for N_2 and He, the data from Hölscher and Zellner (2002), extrapolated with $F_c = 0.4$ instead of 0.6, and the data from Allan and Plane (2002). The measurements of Larin et al. (1998) are a factor of 4 lower than the preferred values and need to be confirmed.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.6 \pm 0.6) \times 10^{-11}$	277	Jenkin and Cox, 1985	MM-A (a)
1.55×10^{-11}	254-354	Daykin and Wine, 1990	PLP-A (b)
1.0×10^{-11}	238-298	Hölscher and Zellner, 2002	PLP-LIF (c)
$6.5 \times 10^{-12} (T/300)^{-1.3}$	216-474	Allan and Plane, 2002	PLP-LIF (d)

Comments

(a) See comment (a) for k_0. The rate coefficient k_∞ was obtained from a fit of the falloff curve using $F_c = 0.4$.
(b) See comment (b) for k_0.
(c) See comment (e) for k_0.
(d) See comment (f) for k_0.

Preferred Values

$k_\infty = 1.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 250-360 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over the temperature range 250-360 K.

Comments on Preferred Values

The preferred values for k_∞ are based on the data of Daykin and Wine (1990). Falloff extrapolations are made with $F_c = 0.4$, independent of temperature over the range 250 to 360 K. If

extrapolated with this F_c instead of $F_c \approx 0.6$, the measurements by Hölscher and Zellner (2002) and Allan and Plane (2002) are consistent with the preferred k_∞.

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:

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=((7.7e-31*(T/300)^-5)*M*(1.6e-11))/((7.7e-31*(T/300)^-5)*M+(1.6e-11))*10^(log10(0.4)/(1+(log10((7.7e-31* (T/300)^-5)*M/(1.6e-11))/(0.75-1.27*log10(0.4)))^2))
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The molecular density, $M = 7.243\times10^{21}$P(bar)/T(K)

References

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