IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iIOx12

$$IO + NO_3 \rightarrow OIO + NO_2 \qquad (1)$$
$$\rightarrow I + NO_2 + O_2 \qquad (2)$$
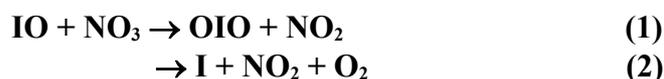
$\Delta H°(1) = -78.9 \text{ kJ mol}^{-1}$
$\Delta H°(2) = -48.8 \text{ kJ mol}^{-1}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$k_1 = (9 \pm 4) \times 10^{-12}$	298	Dillon et al., 2008	PLP-LIF (a)

Comments

(a) Experiments at 33-93 mbar N_2. IO was generated in the reaction of I ($\approx 3 \times 10^{11}$ molecule cm^{-3} made from CF_3I photolysis at 248 nm) with NO_3. NO_3 (3-30 $\times 10^{12}$ molecule cm^{-3}) was generated in the reaction of HO atoms with HNO_3, the HO being formed by HNO_3 photolysis at 248 nm. The kinetics of the title reaction were derived by monitoring IO by LIF (445 nm excitation). The concentration of the excess reagent (NO_3) was determined by monitoring NO_2 (LIF) formed in the photolysis of HNO_3 and equating this to initial HO generated. The rapid reaction of I with NO_3 to form IO (IUPAC, 2008) means that this study was blind to channel (2). Non exponential behaviour of IO could be assigned to diffusive effects and was corrected by numerical modelling using an assumed reaction scheme.

Preferred Values

$k_1 = 9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability
 $\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The single study of this reaction (Dillon et al., 2008) was blind to reaction channels that regenerate I atoms thus applies to k_1 only. The reaction scheme was complex and required numerical simulation to correct (by a factor 1.4) results obtained in a simple analysis based on the rise and decay of IO. We adopt the value of k_1 reported by Dillon et al. (2008) but expand

the uncertainty to reflect the complex analysis and the fact that there has been only a single study. Further studies would be useful to confirm this result and identify the products.

References

Dillon, T. J., Tucceri, M. E., Sander, R., and Crowley, J. N.: Phys. Chem. Chem. Phys., 10, 1540, 2008.