IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iIOx23

This data sheet last evaluated: 29th March 2006 (with no revision of preferred values).

$OIO + NO \rightarrow IO + NO_2$

$\Delta H^o = -17.9$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$7.6 \times 10^{-13} \exp((607 \pm 128)/T)$	235-320	Plane et al., 2006	PLP-CRDS (a)
$(6.0 \pm 1.1) \times 10^{-12}$	298		

Comments

(a) OIO formed in self-reaction of IO, produced by 193 nm photolysis of N_2O in the presence of CF_3I. The rate coefficient k was determined from the decay of OIO in the presence of excess NO. [OIO] measured by time resolved cavity ring-down spectroscopy (CRDS) at 567.808 nm. k was independent of pressure in the range 27 – 96 mbar at 300 K.

Preferred Values

$k = 6.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.1 \times 10^{-12} \exp(542/T)$ cm^3 molecule^{-1} s^{-1} over range 240 – 320 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 250$

Comments on Preferred Values

The single experimental study provides well defined rate constants over the given pressure and temperature range, despite the complex source chemistry for the OIO radical. The observed rate constants and their temperature and pressure dependence were well reproduced by quantum chemical and RRKM calculations using a potential surface with a weakly bound OIONO intermediate which dissociates into IO + NO_2 products. Even at 1 bar pressure significant formation of OIONO is not predicted to occur. The authors recommend the expression: $(1.1 \pm 0.4) \times 10^{-12} \exp((542 \pm 130)/T)$ for k (cm^3 molecule^{-1} s^{-1}) at 1 bar, taking account of experimental uncertainties and the theoretical analysis, which is adopted for the preferred value for formation of IO + NO_2 all pressures.

References

Plane, J. M. C., Joseph, D. M., Allan, B. J., Ashworth, S. H., and Francisco, J. S.: Phys.Chem.A., 110, 93, 2006.