IUPAC Task Group on Atmospheric chemical Kinetic Data Evaluation – Data Sheet iIOx8

This data sheet updated: 31st July 2006.

$I_2 + NO_3 \rightarrow I + IONO_2$
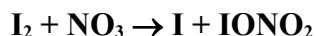
Rate coefficient data

$\Delta H \approx -10$ kJmol^{-1}

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
(1.5 ± 0.5) x 10^{-12}	292-423	Chambers et al., 1992	DF (a)

Comments

(a) Laser induced fluorescence detection of I_2 and visible absorption spectroscopic measurement of NO_3. NO_3 radicals were produced by the $F + HNO_3$ reaction. Pseudo first-order conditions were used, with NO_3 concentrations in excess over I_2. Experiments were performed to substantiate that I_2 loss was due to reaction with NO_3 radicals, and small corrections were made to compensate for diffusion effects; the overall error takes into account the uncertainties in the NO_3 radical concentrations ($\pm26\%$).

Preferred Values

$k = 1.5$ x 10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K

Reliability

$\Delta \log k = \pm0.5$ at 298 K.

Comments on Preferred Values

There is only one reported measurement of this rate constant and the products of the reaction were not determined. Chambers et al. (1992) argue that product channels giving $I + IO + NO_2$, $I + O_2 + INO$ or $IO + INO_2$ are endothermic, and propose formation of $I + IONO_2$.

Several values of the bond dissociation energy, $D_0(IO-NO_2)$ have been reported: Rayez and Destriau (1993) calculated 132 kJmol^{-1}, somewhat higher than the value reported by Allan and Plane (2002) of 95 kJmol^{-1}. Recent calculations of Papayannis and Kosmas (2004, 2005) return values of close to 130 kJmol^{-1}, whereas an analysis of rate data for $IO + NO_2$ has led to a best value of ≈ 150 kJmol^{-1} (Golden, 2006). Based on formation enthalpies (IUPAC, 2006) of IO (116 kJmol^{-1}), NO_2 (33 kJmol^{-1}), I_2 (62 kJmol^{-1}) and I (107 kJmol^{-1}) the title reaction becomes exothermic for values of $D_0(IO-NO_2)$ which are greater than ≈ 120 kJmol^{-1} as most of the calculations above indicate is the case. The value for the reaction enthalpy quoted above is estimated using $D_0(IO-NO_2) = 130$ kJmol^{-1} yielding an enthalpy of formation of

IONO$_2$ of 29 kJmol^{-1}. The error limits for k have been expanded to take into account that only one data set is available, and products were not observed.

References

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Chambers, R. M., Heard, A. C. and Wayne, R. P.: J. Phys. Chem. 96, 3321, 1992.

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Papayannis, D. and Kosmas, A.: Chem. Phys. Lett. 398, 75, 2004.

Papayannis, D. and Kosmas, A.: Chem. Phys. 315, 251, 2005.

Rayez, M. T. and Destriau, M.: Chem. Phys. Lett., 206, 278, 1993.