IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iBrOx4

This data sheet updated: 25th September 2003.

$Br + HO_2 \rightarrow HBr + O_2$

$\Delta H° = -162.8$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$1.4 \times 10^{-11} \exp[-(590 \pm 140)/T]$	260-390	Toohey, Brune and Anderson, 1987[1]	DF-LMR/RF (a)
$(2.0 \pm 0.3) \times 10^{-12}$	298		
$(1.5 \pm 0.2) \times 10^{-12}$	298	Laverdet *et al*., 1990[2]	DF-EPR (b)
$4.9 \times 10^{-12} \exp[-(310 \pm 40)/T]$	230-355	Bedjanian *et al*., 2001[3]	DF-MS (c)
$(1.71 \pm 0.20) \times 10^{-12}$	297		

Comments

(a) Br atoms generated either directly by discharge of Br_2, or from the addition of diluted Br_2 to an excess of $O(^3P)$ atoms. HO_2 radicals were generated by the $F + H_2O_2$ reaction. HO_2 radicals and Br atoms were monitored by laser magnetic resonance and resonance fluorescence, respectively. k was determined from pseudo-first order decay of HO_2 in the presence of excess Br.

(b) Br atoms generated either directly by discharge of Br_2, or from the $Cl + CH_2{=}CHBr$ reaction. HO_2 radicals were generated from the reaction of Cl with CH_3OH in the presence of O_2. k was determined from pseudo-first order decay of HO_2 in the presence of excess Br. A reinterpretation of previous indirect measurements conducted in the same laboratory (Poulet *et al*.[4]) is also given. This yielded revised values of k in the range (1.0-2.2) x 10^{-11} cm^3 molecule^{-1} s^{-1}.

(c) Br atoms generated either directly by discharge of Br_2, or from the $H + Br_2$ or $Cl + Br_2$ reactions. HO_2 radicals were generated by the $F + H_2O_2$ reaction. k was determined from pseudo-first order decay of HO_2 in the presence of excess Br.

Preferred Values

$k = 1.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 7.7 \times 10^{-12} \exp(-450/T)$ molecule^{-1} s^{-1} over the temperature range 230 K to 390 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The preferred value at 298K is the mean of the results of Toohey *et al*.,[1] Laverdet *et al.*[2] and Bedjanian *et al.*,[3] which are all in acceptable agreement. The preferred Arrhenius expression is based on the mean of the *E/R* values from the temperature dependence studies of Toohey *et al*.[1] and Bedjanian *et al.*,[3] combined with a pre-exponential factor adjusted to give the preferred value of *k* at 298 K. The uncertainty in the preferred value of *E/R* reflects the fact that the values reported by Toohey *et al*.[1] and Bedjanian *et al.*[3] differ by almost a factor of two. The observed kinetics are consistent with the mechanism proceeding via direct hydrogen atom abstraction to yield HBr, as also indicated by theoretical studies of the reaction.[5]

References

1 D. W. Toohey, Wm. H. Brune, and J. G. Anderson, J. Phys. Chem. **91**, 1215 (1987).

2 G. Laverdet, G. Le Bras, A. Mellouki, and G. Poulet, Chem. Phys. Lett. **172**, 430 (1990).

3 Y. Bedjanian, V. Riffault, G. Le Bras and G. Poulet, J. Phys. Chem. A **105**, 573 (2001).

4 G. Poulet, G. Laverdet, and G. Le Bras, J. Chem. Phys. **80**, 1922 (1984).

5 R. Sumathi and S. D. Peyerimhoff, Phys. Chem. Chem. Phys. **1**, 3973 (1999).