IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iBrOx17

$$BrO + HO_2 \rightarrow HOBr + O_2 \qquad (1)$$
$$\rightarrow HBr + O_3 \qquad (2)$$
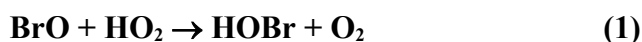
$\Delta H°(1) \geq -190 \text{ kJ·mol}^{-1}$
$\Delta H°(2) = -28 \text{ kJ·mol}^{-1}$

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(3.4 \pm 1.0) \times 10^{-11}$	298	Bridier, Veyret and Lesclaux, 1993[1]	FP-UVA (a)
$4.77 \times 10^{-12} \exp[(580 \pm 100)/T]$	233-344	Larichev *et al.*, 1995[2]	DF-MS (b)
$(3.4 \pm 0.6) \times 10^{-11}$	303		
$2.5 \times 10^{-12} \exp[(520 \pm 80)/T]$	210-298	Elrod *et al.*, 1996[3]	DF-MS (c)
$(1.4 \pm 0.3) \times 10^{-11}$	298		
$3.13 \times 10^{-12} \exp[(536 \pm 206)/T]$	233-348	Li, Friedl and Sander, 1997[4]	DF-MS (d)
$(1.73 \pm 0.61) \times 10^{-11}$	298		(e)
$(2.05 \pm 0.64) \times 10^{-11}$	298		(f)
$(2.0 \pm 0.6) \times 10^{-11}$	298	Cronkhite *et al.*, 1998[5]	PLP-IR/UVA (g)
$9.4 \times 10^{-12} \exp[(345 \pm 60)/T]$	230-360	Bedjanian, Riffault and Poulet, 2001[6]	DF-MS (h)
$(3.1 \pm 0.8) \times 10^{-11}$	298		
$(2.35 \pm 0.82) \times 10^{-11}$	298	Bloss *et al.*, 2002[7]	FP-UVA (a)

Comments

(a) Photolysis of Br_2-O_3-Cl_2-CH_3OH-O_2-He mixtures. HO_2 and BrO radical concentrations were monitored by UV absorption spectroscopy under conditions where the HO_2 radical and BrO radical concentrations were of a similar magnitude.

(b) BrO radicals were generated by the $O(^3P)$ + Br_2 reaction, and their concentrations were monitored by MS in an excess of HO_2 radicals. A preliminary report of this study was noted in Poulet *et al.*[8]

(c) Turbulent flow system at 130 mbar total pressure. Reactant and product species were monitored by CIMS. BrO radicals were produced by the $O(^3P)$ + Br_2 reaction and HO_2 radicals by the H + O_2 + M reaction. k was determined by monitoring the BrO radical concentrations in an excess of HO_2.

(d) BrO and HO_2 were monitored by MS. BrO radicals were produced by the Br + O_3 or $O(^3P)$ + Br_2 reactions and HO_2 radicals by the F + H_2O_2 or Cl + CH_3OH reactions. Experiments were carried out under conditions of both [BrO] >> [HO_2] and [HO_2] >> [BrO]. A similar temperature dependence of k was observed in each case, but values of k determined with excess BrO were systematically ~20% to 25% higher than those in excess HO_2.

(e) HO_2 in excess.

(f) BrO in excess.
(g) Photolysis of Cl_2-CH_3OH-O_2-Br_2-O_3-N_2 mixtures. HO_2 and BrO radical concentrations were monitored simultaneously by infrared tunable diode laser absorption spectroscopy and UV absorption spectroscopy, respectively. Rate coefficients k were determined with $[HO_2] \gg [BrO]$.
(h) BrO radicals were produced by the Br + O_3 or $O(^3P)$ + Br_2 reactions and HO_2 radicals by the F + H_2O_2 reaction. Experiments were carried out under conditions of both $[BrO] \gg [HO_2]$ and $[HO_2] \gg [BrO]$. No systematic difference in the determined values of k was observed. Consistent values of k, measured relative to $k(Br+HO_2)$, were also reported.

Preferred Values

$k = 2.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 4.5 \times 10^{-12}$ exp(500/T) cm^3 molecule^{-1} s^{-1} over the temperature range 210 K to 360 K.

Reliability
   Δlog $k = \pm 0.3$ at 298 K.
   $\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values
   Disregarding the early study of Cox and Sheppard,[9] which gave a very low value for k, the reported rate coefficients at 298 K cover a range of just over a factor of two. This is despite the use of very similar techniques in some of the studies. The temperature dependence of k has generally provided values of E/R which are in good agreement, although that from the most recent temperature dependence study[6] is substantially lower than three previous determinations.
   The preferred value at 298 K is the mean of the rate coefficients of Bridier *et al.*,[1] Larichev *et al.*,[2] Elrod *et al.*,[3] Li *et al.*,[4] Cronkhite *et al.*,[5] Bedjanian *et al.*,[6] and Bloss *et al.*,[7] with substantial uncertainty limits. The preferred Arrhenius expression for k is obtained by taking the mean of the E/R values from the studies of Larichev *et al.*,[2] Elrod *et al.*,[3] Li *et al.*,[4] and Bedjanian *et al.*,[6] and combining it with a pre-exponential factor adjusted to give the preferred value of k at 298 K. The uncertainty in the preferred E/R value has been increased to encompass the recent result of Bedjanian *et al.*.[6]
   Several studies[2-4,6] have shown that the major product is HOBr. Larichev *et al.*[2] and Bedjanian *et al.*[6] were unable to obtain evidence for O_3 formation in their mass spectrometric studies of the reaction and set upper limits for the branching ratio of k_2/k <0.015 and <0.004, respectively. From a study of the reverse reaction at above room temperature, Mellouki *et al.*[10] have determined, by extrapolation, that the yield of HBr + O_3 is negligible (<0.01%) down to 200 K. Furthermore, k appears to be independent of pressure over the range covered by the studies to date of 1 mbar to 1 bar,[1-5] and there is no evidence for stable adduct formation. Thus all of the available data suggests that channel (1) is the sole pathway over the temperature range of the preferred values. This is supported by two recent theoretical studies[11,12] which conclude that the contribution of channel (2) is essentially zero.

References

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