IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iBrOx18

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$$\mathbf{BrO + O_3 \rightarrow Br + 2O_2} \quad \mathbf{(1)}$$
$$\mathbf{\rightarrow OBrO + O_2} \quad \mathbf{(2)}$$

$\Delta H°(1) = -151$ kJ·mol^{-1}
$\Delta H°(2) = -99$ 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			
$\sim 10^{-17}$	318-343	Rattigan, et al., 1995	P-AS (a)
$k_2 = 7 \times 10^{-14} \exp[-(3100 \pm 350)/T]$	318-343		
$k_2 = 2.1 \times 10^{-18}$	298*		
$<(2.1 \pm 0.7) \times 10^{-17}$	298	Rowley et al., 1996	FP-AS (b)
$k_2 = (1.66 \pm 0.11) \times 10^{-18}$	298		

Comments

(a) Photolysis of Br_2-O_3 mixtures at 380 nm to 480 nm in N_2 or O_2 bath gas at total pressures in the range 16 mbar to 1000 mbar. Time-resolved UV absorption spectroscopy was used to monitor the concentrations of O_3, Br_2 and BrO radicals before, during, and after irradiation. OBrO was also detected in absorption in the wavelength range 400 nm to 600 nm.

(b) Flash photolysis-long-path UV absorption technique. BrO radicals were produced by photolysis at ~400 nm of Br_2 in an excess of O_3. Time-resolved UV/visible absorption spectra of BrO were recorded over the range 234 nm to 367 nm and of OBrO over the range 425 nm to 558 nm. The BrO decay was largely due to the BrO + BrO reaction but deviations from second-order behavior were observed at high O_3 concentrations, and attributed to the BrO + O_3 reaction. The upper limit was derived from an analysis of the [BrO] temporal profiles at high O_3 concentrations.

Preferred Values

$k < 2 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The two most recent studies of Rattigan et al. (1995) and Rowley et al. (1996) are in good agreement and set a lower upper limit to the rate coefficient for this reaction than did previous studies (Sander and Watson, 1981; Mauldin III et al., 1993). The preferred upper limit to k at 298 K is therefore based on the results reported by Rattigan et al. (1995) and Rowley et al. (1996). Previously, the reaction of BrO with O_3 had been assumed to occur exclusively by

channel (1), but the positive identification of OBrO as a reaction product indicates that channel (2) is likely to be significant. The existing determinations of k_2 are in good agreement (Rattigan et al., 1995; Rowley et al., 1996) but involve significant uncertainties. Further studies are necessary before a branching ratio can be recommended.

References

Mauldin III, R. L., Wahner, A. and Ravishankara, A. R.: J. Phys. Chem. 97, 7585, 1993.
Rattigan. O. V., Cox, R. A. and Jones, R. L.: J. Chem. Soc. Faraday Trans. 91, 4189, 1995.
Rowley, D. M., Harwood, M. H., Freshwater, R. A. and Jones, R. L.: J. Phys. Chem. 100, 3020,1996.
Sander, S. P. and Watson, R. T.: J. Phys. Chem. 85, 4000, 1981.