IUPAC Task Group on Atmospheric Chemicl Kinetic Data Evaluation – Data Sheet oBrOx11

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$$HO_2 + CH_2BrO_2 \rightarrow O_2 + CH_2BrO_2H \quad (1)$$
$$\rightarrow O_2 + HC(O)Br + H_2O \quad (2)$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(6.7 \pm 3.8) \times 10^{-12}$	298	Villenave and Lesclaux, 1995	FP-UVA (a)
Branching Ratios			
$k_1/k \geq 0.85$ $k_2/k \leq 0.15$	297	Chen et al., 1995	UVP-FTIR (b)

Comments

(a) Flash photolysis of Cl_2 in the presence of CH_3Br-CH_3OH-O_2-N_2 mixtures at a pressure of 1013 mbar. Decays in transient absorptions (with contributions from CH_2BrO_2 and HO_2) were recorded in the wavelength range 250 nm to 280 nm. k derived from simulations of the decay traces using an explicit reaction mechanism.

(b) CH_2BrO_2 and HO_2 radicals were generated from the steady-state photolysis of Cl_2 in the presence of CH_3Br-H_2-air mixtures at 933 mbar. FTIR spectroscopic analysis identified CH_2BrO_2H and HC(O)Br as carbon-containing primary products. The cited branching ratios were derived by taking account of secondary reactions in the system, and the possibility that HCOBr is formed from the in-situ oxidation of CH_2BrO_2H.

Preferred Values

$k = 6.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1/k = 1.0$ at 298 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.
$\Delta(k_1/k) = {}^{+0.0}_{-0.15}$ at 298 K.

Comments on Preferred Values

While the above value of the rate coefficient seems reasonable, it has been derived from the analysis of a comparatively complex chemical system and requires independent verification to reduce the recommended error limits. Within the uncertainty of the determination (Villenave and Lesclaux, 1995), k is indistinguishable from that recommended for the reactions of HO_2 with CH_3O_2 and CH_2ClO_2 suggesting that, like Cl, the presence of the Br group has only a minor influence on the rate coefficient. However, the reported dominance of channel (1) (Chen et al., 1995) contrasts with that observed for CH_2ClO_2, for which formation of HC(O)Cl, H_2O and O_2 is the major pathway. Confirmatory product studies are also required.

References

Chen, J., Catoire, V. and Niki, H.: Chem. Phys. Lett. 245, 519, 1995.
Villenave, E. and Lesclaux, R.: Chem. Phys. Lett. 236, 376, 1995.