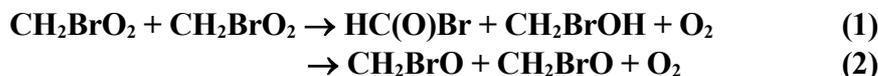


# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oBrOx13

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This data sheet updated: 29<sup>th</sup> March 2005.



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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$k_{\text{obs}} = (3.26 \pm 0.31) \times 10^{-11}$	298	Nielsen et al., 1991	PR-UVA (a,b)
$(1.05 \pm 0.40) \times 10^{-12}$	298	Villenave and Lesclaux, 1995	FP-UVA (c)
<i>Branching Ratios</i>			
$k_2/k \approx 1.0$	298	Nielsen et al., 1991	UVP-FTIR (d)
$k_2/k \approx 1.0$	297	Chen et al., 1995	UVP-FTIR (e)

## Comments

- (a)  $k_{\text{obs}}$  is based on the measured overall second-order decay of  $\text{CH}_2\text{BrO}_2$ , defined by  $-\text{d}[\text{CH}_2\text{BrO}_2]/\text{dt} = 2k_{\text{obs}}[\text{CH}_2\text{BrO}_2]^2$ . Br atoms and  $\text{HO}_2$  radicals formed from the subsequent chemistry of  $\text{CH}_2\text{BrO}$  (formed from channel (2)) are expected to lead to secondary removal of  $\text{CH}_2\text{BrO}_2$ , such that  $k_{\text{obs}}$  represents an upper limit for the true value of  $k$ .
- (b) Pulse radiolysis study of  $\text{CH}_3\text{Br-O}_2\text{-SF}_6$  mixtures with  $\text{CH}_2\text{BrO}_2$  radicals being monitored by UV absorption, with  $\sigma_{250 \text{ nm}} = (7.20 \pm 0.83) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ . The derived value of  $k_{\text{obs}}$  was found to be independent of wavelength over the range 250-310 nm and of pressure over the range 150-1000 mbar of  $\text{SF}_6$ .
- (c) Flash photolysis of  $\text{Cl}_2$  in the presence of  $\text{CH}_3\text{Br-O}_2\text{-N}_2$  mixtures at a pressure of 1013 mbar, with  $\text{CH}_2\text{BrO}_2$  radicals being monitored by UV absorption, with  $\sigma_{250 \text{ nm}} = (3.35 \pm 0.10) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ . Decays in transient absorption signals were recorded in the wavelength range 240 nm to 280 nm.  $k$  derived from simulations of the decay traces using an explicit reaction mechanism.
- (d)  $\text{CH}_2\text{BrO}_2$  radicals were generated from the steady-state photolysis of  $\text{Cl}_2$  in the presence of  $\text{CH}_3\text{Br-air}$  mixtures. Two major carbon-containing products, CO and  $\text{HC(O)Br}$ , were observed by FTIR spectroscopic analysis.  $\text{HC(O)Br}$  was believed to arise from the reaction of  $\text{CH}_2\text{BrO}$  with  $\text{O}_2$ .
- (e)  $\text{CH}_2\text{BrO}_2$  radicals were generated from the steady-state photolysis of  $\text{Cl}_2$  in the presence of  $\text{CH}_3\text{Br-air}$  mixtures at 930 mbar. FTIR spectroscopic analysis identified  $\text{CH}_2\text{O}$  as the major carbon-containing primary product, suggesting  $\text{CH}_2\text{BrO}$  (formed from channel (2)) predominantly decomposes by Br atom elimination. Lower yields of  $\text{HC(O)Br}$  were observed, but  $\text{CH}_2\text{BrOH}$  was not identified as a product. CO formation also observed from secondary reactions of primary products with Cl and Br.

## Preferred Values

$k_2/k = 1.0$  at 298 K.

### Reliability

$\Delta(k_2/k) = {}^{+0.0}_{-0.1}$  at 298 K.

### Comments on Preferred Values

The preferred unity value of  $k_2/k$  is based on the results of the product study of Chen et al. (1995), in which no evidence for formation of  $\text{CH}_2\text{BrOH}$  (which would be formed by channel (1)) was obtained. Observation of  $\text{CH}_2\text{O}$  as the major primary product was also consistent with the dominance of channel (2), followed by decomposition of  $\text{CH}_2\text{BrO}$  by Br atom elimination. The two kinetics studies (Nielsen et al., 1991; Villenave and Lesclaux, 1995) are in significant disagreement, yielding rate coefficients which differ by more than an order of magnitude, and UV absorption spectra for  $\text{CH}_2\text{BrO}_2$  which differ in both shape and magnitude. The spectrum reported by Villenave and Lesclaux (1995) is similar to that typically observed for peroxy radicals, with a single maximum at 240 nm. The spectrum reported by Nielsen et al. (1991) displays a second intense maximum at 280 nm, and thus appears to be subject to interference. Although the value of  $k$  reported by Villenave and Lesclaux (1995) is likely to be indicative of the magnitude of the self-reaction rate coefficient for  $\text{CH}_2\text{BrO}_2$ , the mechanism used to extract  $k$  from the observed decay profiles assumed secondary removal of  $\text{CH}_2\text{BrO}_2$  by reaction with  $\text{HO}_2$  generated from the exclusive reaction of  $\text{CH}_2\text{BrO}$  with  $\text{O}_2$ . It is possible that the actual formation of Br atoms leads to a similar degree of secondary removal of  $\text{CH}_2\text{BrO}_2$ , but Villenave and Lesclaux (1995) did not observe formation of BrO (the likely product) in the system. More information is therefore needed on the kinetics and mechanism of the secondary reactions, in addition to further kinetics studies of the title reaction, to allow  $k$  to be defined more accurately.

### References

- Chen, J., Catoire, V. and Niki, H.: Chem. Phys. Lett. 245, 519, 1995.  
Nielsen, O. J., Munk, J., Locke, G. and Wallington, T. J.: J. Phys. Chem. 95, 8714, 1991.  
Villenave, E. and Lesclaux, R.: Chem. Phys. Lett. 236, 376, 1995.