

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oBrOx14

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This data sheet updated: 29th 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>			
$k_{\text{obs}} = (6.2 \pm 1.2) \times 10^{-12}$	298	Crowley and Moortgat, 1992	MM-UVA (a,b)
$6.15 \times 10^{-14} \exp[(1247 \pm 203)/T]$	275-373	Villeneuve et al., 2003	FP-UVA (c)
$(4.49 \pm 0.22) \times 10^{-12}$	298		
<i>Branching Ratios</i>			
$k_1/k = 0.43$	296	Yarwood et al., 1992	UV-P-FTIR(d)
$k_2/k = 0.57$			

Comments

- k_{obs} is based on the measured overall second-order decay of $\text{CH}_2\text{BrCH}_2\text{O}_2$, defined by $-\text{d}[\text{CH}_2\text{BrCH}_2\text{O}_2]/\text{dt} = 2k_{\text{obs}}[\text{CH}_2\text{BrCH}_2\text{O}_2]^2$. As described in detail by Lesclaux (1997), HO_2 radicals formed from the subsequent chemistry of $\text{CH}_2\text{BrCH}_2\text{O}$ (formed from channel (2)) are expected to lead to secondary removal of $\text{CH}_2\text{BrCH}_2\text{O}_2$. The true value of k is expected to fall in the range $k_{\text{obs}}/(1+\alpha) < k < k_{\text{obs}}$, where $\alpha = k_2/k$.
- Molecular modulation study of the photolysis of Br_2 in the presence of $\text{C}_2\text{H}_4\text{-O}_2\text{-N}_2$ mixtures at total pressures up to 800 mbar. Modulated waveforms for the formation and removal of $\text{CH}_2\text{BrCH}_2\text{O}_2$ radicals were monitored by absorption at 270 nm, i.e. where HO_2 does not absorb.
- Flash photolysis of Br_2 in the presence of $\text{C}_2\text{H}_4\text{-O}_2\text{-N}_2$ mixtures at a pressure of 1013 mbar. Decays in transient absorption signals (with contributions from $\text{CH}_2\text{BrCH}_2\text{O}_2$ and HO_2) were recorded in the wavelength range 210 nm to 290 nm. k derived from simulations of the decay traces using an explicit reaction mechanism.
- Steady-state photolysis of Br_2 in the presence of $\text{C}_2\text{H}_4\text{-O}_2\text{-N}_2$ mixtures at 933 mbar total pressure, with FTIR spectroscopic determination of products. The major products observed were BrCH_2CHO , $\text{BrCH}_2\text{CH}_2\text{OH}$, and $\text{BrCH}_2\text{CH}_2\text{OOH}$. The branching ratio, $k_2/k_1 = 1.35 \pm 0.07$, was determined from the yields of BrCH_2CHO and $\text{BrCH}_2\text{CH}_2\text{OH}$ relative to the loss of C_2H_4 .

Preferred Values

$k = 4.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 6.0 \times 10^{-14} \exp(1250/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 270-380 K.

$k_2/k = 0.57$ at 298 K.

Reliability

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

$\Delta(E/R) = \pm 500 \text{ K}$.

$$\Delta(k_1/k) = \Delta(k_2/k) = \pm 0.1 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred values of k are based on the temperature dependence expression of Villenave et al. (2003), with which the earlier 298 K k_{obs} determination of Crowley and Moortgat (1992) is entirely consistent. The preferred values of the branching ratios are based on the data of Yarwood et al. (1992), which require confirmation.

The above value of k is similar to that for the self-reaction of $\text{CH}_2\text{ClCH}_2\text{O}_2$, both showing an enhancement of a factor of ca. 50 compared with the self-reaction rate coefficient for the unsubstituted analogue, $\text{C}_2\text{H}_5\text{O}_2$.

References

- Crowley, J. N. and Moortgat, G. K.: J. Chem. Soc. Faraday Trans. 88, 2437, 1992.
Lesclaux, R.: Combination of peroxy radicals in the gas phase. In 'Peroxy Radicals', edited by Z.B. Alfassi. John Wiley and Sons, 1997.
Villenave, E., Moisan, S. and Lesclaux, R.: J. Phys. Chem. A 107, 2470, 2003.
Yarwood, G., Peng, N. and Niki, H.: Int. J. Chem. Kinet. 24, 369, 1992.