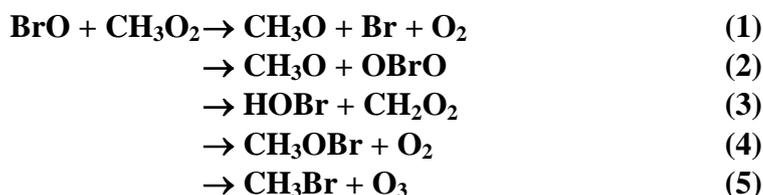


## Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oBrOx15

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### Rate coefficient data ( $k = k_1 + k_2 + k_3 + k_4 + k_5$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(5.7 \pm 0.6) \times 10^{-12}$	298	Aranda et al., 1997	DF-MS/LIF (a)
$4.6 \times 10^{-13} \exp[(798 \pm 76)/T]$	233-333	Enami et al., 2007	FP-CRD (b)
$(6.2 \pm 2.5) \times 10^{-12}$	298		
$2.42 \times 10^{-14} [(1617 \pm 94)/T]$	243-296	Shallcross et al., 2015	DF-CIMS (c)
$(5.7 \pm 0.26) \times 10^{-12}$	296		
<i>Branching ratios</i>			
$k_3/k = 0.8 \pm 0.2$	298	Aranda et al., 1997	DF-MS/LIF (a)
$(k_1 + k_2)/k = 0.3 \pm 0.1$	298		
$k_3/k = 0.8 \pm 0.1$	246-296	Shallcross et al., 2015	DF-CIMS (c)

### Comments

- (a) Flow tube operated at 1.3 mbar of He. BrO and CH<sub>3</sub>O<sub>2</sub> were formed in the reactions Br + O<sub>3</sub>, and F + CH<sub>4</sub> in the presence of O<sub>2</sub>, respectively, and monitored by MS as their parent ions. The experiments were conducted under pseudo first-order conditions, with BrO in excess of CH<sub>3</sub>O<sub>2</sub>. The products observed were HOBr (MS) and CH<sub>3</sub>O (LIF). The CH<sub>3</sub>O profile was modeled by taking into account its presence as impurity in the CH<sub>3</sub>O<sub>2</sub> source, and its reaction with BrO.
- (b) CH<sub>3</sub>O<sub>2</sub> and BrO generated in the 213 nm photolysis of CH<sub>3</sub>Br in the presence of O<sub>2</sub> ( $3\text{-}60 \times 10^{17} \text{ molecule cm}^{-3}$ ) and O<sub>3</sub> ( $1\text{-}10 \times 10^{15} \text{ molecule cm}^{-3}$ ) so that BrO and CH<sub>3</sub>O<sub>2</sub> were initially present in similar concentration. Alternatively, N<sub>2</sub>O / acetone were photolysed at 193 nm in the presence of Br<sub>2</sub> / O<sub>2</sub>. BrO, at initial concentrations of  $\approx (2\text{-}8) \times 10^{12} \text{ molecule cm}^{-3}$ , was monitored at 329.53 nm, CH<sub>3</sub>O<sub>2</sub> was not detected. The rate coefficients were derived from numerical modeling of complex reaction schemes for both radical generation systems, with the title reaction suggested to contribute between 33 and

74 % of the BrO decay. No pressure dependence of  $k$  observed between 133 and 266 mbar. Lack of BrO regeneration via  $\text{Br} + \text{O}_3$  was taken to indicate that channel (1) contributes less than 40 % as BrOO would decompose rapidly to  $\text{Br} + \text{O}_2$ . OBrO was not detected and an upper limit of 0.1 estimated for branching to channel (2).

- (c) Turbulent flow reactor (133-200 mbar  $\text{N}_2$ ) with  $[\text{CH}_3\text{O}_2] \gg [\text{BrO}]$ . BrO was generated in the reaction of  $\text{O}(^3\text{P})$  with  $\text{Br}_2$ ,  $\text{CH}_3\text{O}_2$  was generated in the reaction of  $\text{CH}_3$  radicals (made from  $\text{F} + \text{CH}_4$ ) with  $\text{O}_2$ .  $\text{CH}_3\text{O}_2$  ( $1\text{-}20 \times 10^{11}$  molecule  $\text{cm}^{-3}$ ) and BrO ( $1\text{-}6 \times 10^{10}$  molecule  $\text{cm}^{-3}$ ) were detected subsequent to ionization by  $\text{SF}_6^-$ .

### Preferred Values

Parameter	Value	T/K
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$5.7 \times 10^{-12}$	298 K
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$2.65 \times 10^{-14} \exp(1600/T)$	240-300
$k_1/k$	0.2	240-300
$k_3/k$	0.8	240-300
<i>Reliability</i>		
$\Delta \log k$	$\pm 0.3$	298
$\Delta(E/R)$	$\pm 200$	240-300
$\Delta(k_1/k)$	$\pm 0.03$	
$\Delta(k_3/k)$	$\pm 0.1$	

### Comments on Preferred Values

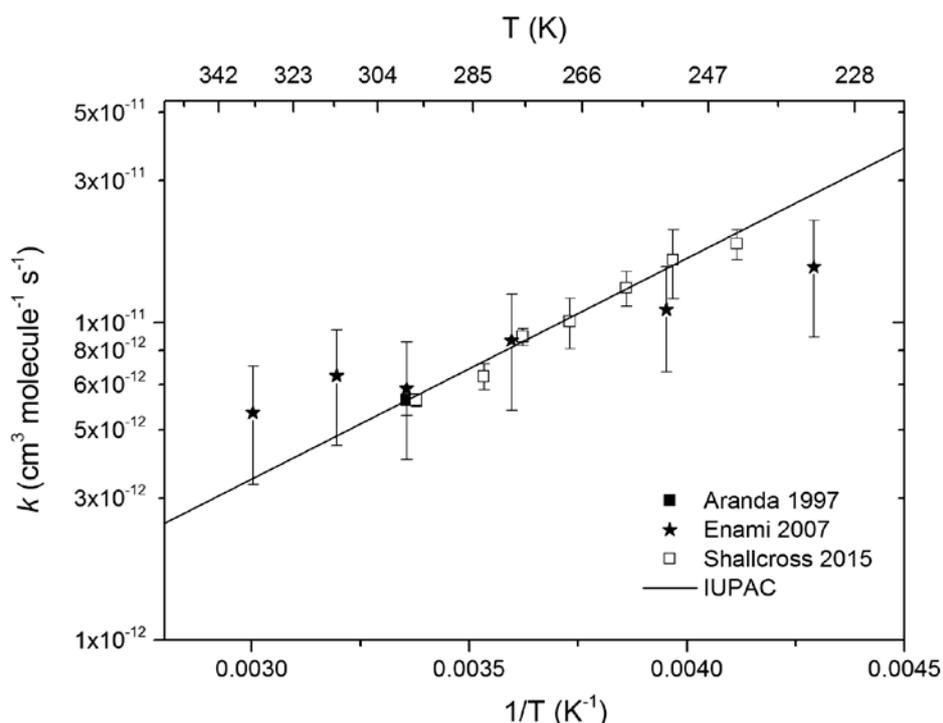
The preferred value of  $k$ (298 K) is an average of the more direct, flow tube studies of Aranda et al. (1997) and Shallcross et al., (2015). The good agreement between all three studies at room temperature indicates that there is no significant pressure dependence between a few Torr of He and 200 Torr  $\text{N}_2$  or  $\text{O}_2$ . The preferred temperature dependence is taken from Shallcross et al. (2015) with expanded errors to reflect the difference in activation energy compared to Enami et al (2007) and the fact that, although pseudo-first order conditions were fulfilled, the relative change in concentration of BrO was insufficient to prove exponential behaviour.

Aranda et al. (1997) derived a branching ratio to HOBr formation (channel (3)) of  $(0.8 \pm 0.2)$ , and that to  $\text{CH}_3\text{O}$  formation (channels (1) and (2)) as  $(0.3 \pm 0.1)$ . Shallcross et al., (2015) report HOBr yields of  $0.86 \pm 0.1$ ,  $0.8 \pm 0.1$  and  $0.73 \pm 0.1$  at 296, 261 and 246 K, respectively, which are thus in very good agreement. OBrO and  $\text{CH}_3\text{OBr}$  were not detected by either Aranda et al. (1997) or Enami et al. (2007), ruling out a significant contribution from channels (2) and (4). The kinetics of BrO decay in the presence of excess  $\text{O}_3$  (Enami et al., 2007) confirms that channel (1) contributes less than 40 %. The fact that both Aranda et al. (1997) (BrO in excess) and Shallcross et al (2015) ( $\text{CH}_3\text{O}_2$  in excess) derive the same yield of HOBr helps rule out that its formation is due to reactions of  $\text{CH}_3\text{O}$  (formed in channel (1)) with BrO. Assuming that the reaction proceeds almost entirely via (1) and (3) we thus prefer  $k_1/k = 0.2$  and  $k_3/k = 0.8$ , independent of temperature. We add expanded error limits to reflect the fact that calibration of the HOBr and  $\text{CH}_3\text{O}$  signals is not straightforward and that the fate of the Criegee intermediate ( $\text{CH}_2\text{O}_2$ ) in these reaction systems is largely unknown.

The theoretical studies of Guha and Francisco, (2003) were unable to reproduce the experimentally derived reaction mechanism and they suggested that HOObBr and HCHO are formed via rearrangement of a CH<sub>3</sub>OOObBr association complex. The more recent theoretical work (Shallcross et al., 2015) concludes, however that formation of HOBr + CH<sub>2</sub>O<sub>2</sub> dominates.

## References

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Experimental rate coefficients for reaction between CH<sub>3</sub>O<sub>2</sub> and BrO. The solid line is the IUPAC preferred value calculated from  $k = 2.65 \times 10^{-14} \exp(1600/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .