

## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation - Data Sheet oBrOx19; VII.A3.4

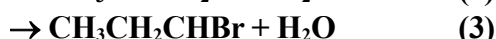
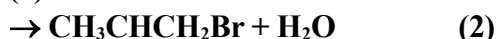
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This datasheet last evaluated: June 2015; last change in preferred values: June 2009.



(1)



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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(5.29 \pm 0.29) \times 10^{-12} \exp[-(456 \pm 31)/T]$	233-372	Téton et al. (1996)	PLP-LIF (a)
$1.17 \times 10^{-12}$	298		
$(5.75 \pm 0.90) \times 10^{-12} \exp[-(504 \pm 50)/T]$	294-365	Nelson et al. (1997)	DF-LIF (b)
$(1.01 \pm 0.10) \times 10^{-12}$	295		
$9.1 \times 10^{-14} T^{0.5} \exp(-157/T)$	230-386	Herndon et al. (2001)	PLP-LIF (c)
$(8.8 \pm 0.4) \times 10^{-13}$	298		
$(6.6 \pm 0.52) \times 10^{-18} T^2 \exp(154 \pm 24)$	230-360	Gilles et al. (2002)	PLP-LIF (d)
$(9.72 \pm 0.32) \times 10^{-13}$	297		
$2.99 \times 10^{-13} (T/298)^{2.79} \exp(369/T)$	210-480	Kozlov et al. (2003)	FP-RF (e)
$(1.01 \pm 0.15) \times 10^{-12}$	298		
$1.32 \times 10^{-17} T^{1.95} \exp(25/T)$	297-725	Brykov et al. (2007)	PLP-LIF (f)
$9.51 \times 10^{-13}$	297		
<i>Relative Rate Coefficients</i>			
$(1.10 \pm 0.06) \times 10^{-12}$	300	Donaghy et al. (1993)	RR (g)

### Comments

- (a) HO radicals were generated by the photolysis of  $\text{H}_2\text{O}_2$  at 248 nm in approximately 100 Torr (133 mbar) of helium diluent.
- (b) HO radicals were generated by the reaction of H atoms with  $\text{NO}_2$  in 1.1-2.3 Torr (1.5-3.1 kPa) of helium diluent.
- (c) HO radicals were produced by the photolysis of HONO at 355 nm (third harmonic Nd:YAG laser) in approximately 100 Torr (133 mbar) of helium diluent.
- (d) HO radicals were generated by the photolysis of HONO at 351 nm in 50 Torr (67 kPa) of helium diluent.
- (e) HO radicals were generated by the photolysis of  $\text{H}_2\text{O}$  using a xenon flash lamp. Experiments were performed in 30 Torr (4 mbar) of argon diluent.
- (f) HO radicals were generated by either the photolysis of  $\text{N}_2\text{O}$  at 193 nm (ArF excimer laser) to make  $\text{O}(^1\text{D})$  atoms in the presence of  $\text{H}_2\text{O}$  vapor, or the photolysis of  $\text{HNO}_3$  at 248 nm (KrF excimer laser) in 6.69-26.73 kPa of helium diluent.
- (g) The rate coefficient ratio  $k(\text{HO} + \text{C}_3\text{H}_5\text{Br})/k(\text{HO} + \text{cyclohexane}) = 0.156 \pm 0.008$  was placed on an absolute basis using  $k(\text{HO} + \text{cyclohexane}) = 3.26 \times 10^{-17} T^2 \exp(-262/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Atkinson, 2003).

### Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$1.0 \times 10^{-12}$	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$3.91 \times 10^{-12} \exp(-399/T)$	210-300
$k_1/k$	0.32	
$k_2/k$	0.56	
$k_3/k$	0.12	
<i>Reliability</i>		
$\Delta \log k$	0.1	298
$\Delta \log E/R$	$\pm 200$	
$\Delta k_1/k$	0.10	
$\Delta k_2/k$	0.05	
$\Delta k_3/k$	0.10	

### Comments on Preferred Values

The rate coefficients obtained in the absolute rate studies by Téton et al. (1996), Nelson et al. (1997), Gilles et al. (2002), Kozlov et al. (2003), and Brykov et al. (2003) and in the relative rate study by Donaghy et al. (1993) are in good agreement. The results from the absolute rate study by Herndon et al. (2001) at ambient temperature and above lie approximately 20-30% below those from the other studies. Excluding the data from Herndon et al. (2001) and fitting the three parameter equation  $k = CT^2 \exp(-D/T)$  to the remaining composite data set gives  $k = 8.14 \times 10^{-18} T^2 \exp(111/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Centering this expression at 255 K with  $A = C e^2 T^2$  and  $B = D + 2T$  gives  $k = 3.91 \times 10^{-12} \exp(-399/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  which is recommended over the range 210-300 K.

From an analysis of kinetic data for the reaction of HO radicals with  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ ,  $\text{CD}_3\text{CH}_2\text{CH}_2\text{Br}$ ,  $\text{CD}_3\text{CH}_2\text{CD}_2\text{Br}$ ,  $\text{CH}_3\text{CD}_2\text{CD}_2\text{Br}$ , and  $\text{CD}_3\text{CD}_2\text{CD}_2\text{Br}$ , Gilles et al. (2002) deduced branching ratios at 298 K for abstraction at the 1-, 2-, and 3- positions in  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$  of  $0.32 \pm 0.08$ ,  $0.56 \pm 0.04$ , and  $0.12 \pm 0.08$ , respectively. As discussed by Calvert et al. (2008), Gilles et al. (2002) conducted a study of the products of the OH radical initiated oxidation of  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$  in 620 Torr of air in the presence of  $\text{NO}_x$  at room temperature. Propanal and bromoacetone were identified in molar yields of  $30 \pm 15$  and  $50 \pm 20\%$ , respectively. The propanal and bromoacetone yields were indistinguishable from the branching ratios for hydrogen abstraction by OH radicals at the 1- and 2- positions deduced from the experiments with the deuterated n-propyl bromide samples. At low  $[\text{O}_2]$  propene was observed as a product indicating that reaction with  $\text{O}_2$  and dissociation via Br atom elimination are competing loss mechanisms for  $\text{CH}_3\text{CHCH}_2\text{Br}$  radicals. Gilles et al. (2002) derived  $k_{\text{O}_2}/k_{\text{diss}} = (4.0 \pm 0.6) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1}$ . In one atmosphere of air  $k_{\text{O}_2}[\text{O}_2]/k_{\text{diss}} = 21$ , and reaction with  $\text{O}_2$  dominates the atmospheric fate of  $\text{CH}_3\text{CHCH}_2\text{Br}$  radicals. Reaction of HO radicals with  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$  at the 3- position is expected to be of minor ( $< 20\%$ ) importance. The major products of the HO radical initiated oxidation of  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$  are propanal and bromoacetone.

### References

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