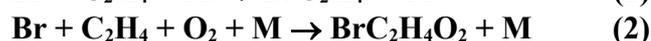


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet X_VOC30

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This data sheet updated: 3rd July 2005.



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients (k_1)</i>			
$3.0 \times 10^{-33} \exp [(730 \pm 220/T)] [\text{He}]$ $(1.2 \pm 0.3) \times 10^{-15} (1.3 \text{ mbar He})$	233 - 320 298	Bedjanian et al., 1999	DF-MS (a)
<i>Relative Rate Coefficients (k_2)</i>			
$< 2.5 \times 10^{-13}$	295	Wallington et al., 1989	RR (b)
$1.69 \times 10^{-13} (1013 \text{ mbar air})$	298	Barnes et al., 1989	RR (c)
$(1.05 \pm 0.37) \times 10^{-14} (67 \text{ mbar air})$	298		RR (d)
$(1.10 \pm 0.37) \times 10^{-13} (1013 \text{ mbar air})$	313		
$(5.71 \pm 0.38) \times 10^{-14} (1013 \text{ mbar air})$	333		
$(2.98 \pm 0.15) \times 10^{-14} (1013 \text{ mbar air})$	353		
$(1.32 \pm 0.11) \times 10^{-13} (933 \text{ mbar air})$	296	Yarwood et al., 1992	RR (e)
$(4.06 \pm 0.36) \times 10^{-13} (933 \text{ mbar air})$	261	Ramacher et al., 2001	RR (f)
$(2.40 \pm 0.36) \times 10^{-13} (933 \text{ mbar air})$	280		
$(1.22 \pm 0.18) \times 10^{-13} (933 \text{ mbar air})$	296		
$(6.62 \pm 0.46) \times 10^{-13} (933 \text{ mbar air})$	228	Ramacher et al., 2001	RR (g)
$(5.71 \pm 0.40) \times 10^{-13} (933 \text{ mbar air})$	239		
$(4.54 \pm 0.32) \times 10^{-13} (933 \text{ mbar air})$	249		
$(3.68 \pm 0.26) \times 10^{-13} (933 \text{ mbar air})$	261		
$(4.15 \pm 0.41) \times 10^{-14} (920-970 \text{ mbar air})$	298	Anthony and Roscoe, 2004	RR (h)

Comments

- (a) Experiments conducted at pressures of 0.7 – 2.7 mbar He. Rate coefficient cited is at the low pressure limit, $k_1 = k_{1,0}$. Br was detected as BrCl after titration with NOCl, and Br₂ was added to partly convert the BrC₂H₄ radical to BrC₂H₄Br, which was also detected. The kinetics of the title reaction were derived from fitting to an analytical expression that took loss of BrC₂H₄ by reaction with both Br₂ and Br into account.
- (b) CW photolysis of Br₂ in the presence of C₂H₄ in 986 mbar (740 Torr) air and CH₃CHO as reference reactant. The depletion of reactants was followed by GC to derive $k(\text{Br} + \text{C}_2\text{H}_4) / k(\text{Br} + \text{CH}_3\text{CHO}) < 0.067$. An absolute upper limit was calculated using $k(\text{Br} + \text{CH}_3\text{CHO}) = 3.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K (IUPAC, 2005).
- (c) CW photolysis of Br₂ (300 – 500 nm) in the presence of C₂H₄ in 1013 mbar (760 Torr) N₂/O₂ bath gas and CH₃CHO as reference compound. Depletion of reactants monitored by GC. The tabulated rate coefficient in air was obtained by extrapolation of data obtained with O₂ partial pressures between 6.7 and 133 mbar (5 to 100 Torr) to 210 mbar O₂, and put on absolute basis using $k(\text{Br} + \text{CH}_3\text{CHO}) = 3.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2005).

- (d) CW photolysis of Br₂ (300 – 500 nm) in the presence of C₂H₄ in 33 – 1013 mbar (25 – 760 Torr) N₂/O₂ bath gas and 2,2,4-trimethylpentane (TMP) as reference compound. Depletion of reactants monitored by GC or FTIR spectroscopy. Data put on absolute basis using $k(\text{Br} + \text{TMP}) = (3.66 \pm 0.29) \times 10^{-12} (\exp(-1832/T))$, which in turn was measured relative to $k(\text{Br} + 2\text{-methylpropane}) = 1.61 \times 10^{-10} \exp(-3464/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Seakins et al., 1992).
- (e) CW photolysis ($\lambda > 400 \text{ nm}$) of Br₂ in presence of C₂H₄ and HCHO (reference reactant) in 933 mbar (700 Torr) air or N₂/O₂ bath gas. The depletion of reactants was monitored by FTIR spectroscopy. A rate coefficient ratio of $k(\text{Br} + \text{C}_2\text{H}_4) / k(\text{Br} + \text{HCHO}) = (0.12 \pm 0.01)$ was determined for 296 K and 933 mbar (700 Torr) air, and $k(\text{Br} + \text{C}_2\text{H}_4)$ was converted to an absolute value by use of $k(\text{Br} + \text{HCHO}) = 1.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2005).
- (f) CW photolysis ($\lambda > 420 \text{ nm}$) of Br₂ in the presence of C₂H₄ and HCHO as reference reactant at total pressures of 933 – 946 (700 – 710 Torr) air. Depletion of reactants was monitored by FTIR spectroscopy. The following rate coefficient ratios were obtained: $k(\text{Br} + \text{C}_2\text{H}_4) / k(\text{Br} + \text{HCHO}) = (0.487 \pm 0.073)$ at 261 K, (0.247 ± 0.037) at 280 K and (0.112 ± 0.017) at 296 K. The tabulated absolute rate coefficients were derived using $k(\text{Br} + \text{HCHO}) = 7.7 \times 10^{-12} \exp(-580/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2005).
- (g) As (f) but using CH₃CHO as reference reactant. The following rate coefficient ratios were obtained: $k(\text{Br} + \text{C}_2\text{H}_4) / k(\text{Br} + \text{CH}_3\text{CHO}) = (0.277 \pm 0.019)$ at 228 K, (0.217 ± 0.015) at 239 K, (0.160 ± 0.011) at 249 K, and (0.119 ± 0.008) at 261 K. The absolute rate coefficients listed in the table were derived using $k(\text{Br} + \text{CH}_3\text{CHO}) = 1.8 \times 10^{-11} \exp(-460/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2005).
- (h) Broad band photolysis of Br₂ in presence of ethene and di-ethyl ether as reference reactant. Rate coefficient ratio measured as a function of O₂ pressure in a total pressure of ≈ 1 atmosphere. Trace gas analysis by GC. Rate coefficient ratio $k(\text{Br} + \text{C}_2\text{H}_4)/k(\text{Br} + \text{di-ethyl ether})$ placed on an absolute basis by use of $k(\text{Br} + \text{di-ethyl ether}) = 2.34 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This value was derived from measurements of $k(\text{Br} + \text{di-ethyl ether})/k(\text{Br} + 2\text{-methyl propane})$ and an absolute value of $k(\text{Br} + 2\text{-methyl propane}) = 1.44 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Seakins et al., 1992). Value listed above was obtained by interpolation of O₂ pressure dependent rate coefficients at one atmosphere pressure.

Preferred Values

$k_2 = 1.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 1 atmosphere air.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K and one atmosphere air.

Comments on Preferred Values

The measured rate coefficients reveal a strong dependence on total pressure, temperature and the O₂ partial pressure (Barnes et al., 1989; Ramacher et al., 2001; Anthony and Roscoe, 2004). This has been taken to indicate that the mechanism involves formation of a Br-C₂H₄ adduct, which can dissociate to reactants or react with O₂ to form a peroxy radical. For this reason, the effective rate coefficient is significantly higher in air than in an oxygen free bath gas at total pressures of up to an atmosphere, which is in the middle of the fall off region. The 298 K recommendation is based on the average of the results of Yarwood et al. (1992) and Ramacher et al. (2001), which were both obtained relative to HCHO and which are in excellent agreement. As noted by both Barnes et al. (1989) and Ramacher et al. (2001), there is an inconsistency between the data sets of Barnes et al. (1989) obtained using CH₃CHO and 2,2,4-trimethylpentane / 2-methylpropane as reference reactants, and the higher value of

$k(298\text{ K}) = 1.69 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ obtained in that study is considered less reliable. Similarly, the use by Anthony and Roscoe (2004) of di-ethyl ether / 2-methylpropane as primary and secondary reference reactants is considered less reliable. These authors also indicate that the O_2 pressure effect may be influenced by high pressures of Br_2 as this can compete with O_2 for reaction with the BrC_2H_4 adduct.

The expression: $k(T) = 2.80 \times 10^{-13} \exp(224/T) \times B / \{B + 8.5 \times 10^{12} \exp(-3200/T)\} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ where $B = 7.5 \times 10^{-12} [\text{O}_2] \text{ s}^{-1}$ and $[\text{O}_2]$ is in molecules cm^{-3} was given by Ramacher et al. (2001) to describe the temperature dependence of the effective rate coefficient in one atmosphere of air. Further studies of the rate coefficient in air at low pressures and temperatures would be useful to aid modelling of the role of this reaction at high altitudes.

Identification of brominated aldehydes, alcohols and acids in product studies provides evidence for the formation and subsequent reaction of the $\text{BrC}_2\text{H}_4\text{O}_2$ peroxy radical in air (Barnes et al. 1989; Yarwood et al. 1992).

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