IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation - Data Sheet oBrOx16; VII.A3.1

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$HO + CHBr_3 \rightarrow CBr_3 + H_2O$

Rate coefficient data (k)

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
9.94×10^{-13} exp[(-387±22)/T]	230-370	Orkin et al. (2013)	FP-RF (a)
$(2.69 \pm 0.04) \times 10^{-13}$	298		
Relative Rate Coefficients			
1.31×10^{-12} exp(-584/T)	298-366	DeMore (1996)	RR (b)
1.86×10^{-13}	298		

Comments

(a) HO radicals generated by the VUV pulsed photolysis of H_2O in 30 Torr (40 mbar) of argon diluent. HO radicals were monitored by resonance fluorescence near 308 nm. The purity of the $CHBr_3$ sample was checked using GC-MS. Results measured using an older version of the FP-RF system with a different gas handling system and higher flash energies were consistent with those using a newer version of the experimental apparatus.
(b) HO radicals produced by photolysis of O_3 at 254 nm in the presence of H_2O vapor in argon diluent (total pressure was not specified). CH_2Cl_2 was used as the reference compound. The loss of $CHBr_3$ and CH_2Cl_2 was measured using FTIR spectroscopy. A rate coefficient ratio $k(HO+CHBr_3)/k(HO+CH_2Cl_2) = (0.73 \pm 0.16) \exp[(276 \pm 71)/T]$ was reported. Using $k(HO+CH_2Cl_2) = 1.8 \times 10^{-12} \exp(-860/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2008) gives $k(HO+CHBr_3) = 1.31 \times 10^{-12} \exp(-584/T)$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	2.7×10^{-13}	298
k /cm^3 molecule^{-1} s^{-1}	$1.00 \times 10^{-12} \exp(-388/T)$	290-370
Reliability		
$\Delta \log k$	0.15	298
Δ E/R	± 300	

Comments on Preferred Values

There is a substantial disagreement between the results from the relative rate study by DeMore (1996) and the absolute rate study by Orkin et al. (2013). Considerable efforts were made by Orkin et al. (2013) to assure the purity of the $CHBr_3$ sample and it is unlikely that

the discrepancy reflects the presence of a reactive impurity in the work of Orkin et al. (2013). Orkin et al. (2013) obtained consistent results using two different versions of their experimental system over a period of several years. DeMore (1996) used CH_2Cl_2 as a reference compound. In the presence of O_2 the degradation of CH_2Cl_2 produces chlorine atoms (Niki et al., 1980). At 298 K, the rate coefficient ratio $k(Cl+CHBr_3)/k(Cl+CH_2Cl_2)$ = 0.65 (IUPAC, 2014) is substantially smaller than the rate coefficient ratio $k(HO+CHBr_3)/k(HO+CH_2Cl_2)$ = 2.7 (IUPAC, 2014). Additional loss of CH_2Cl_2 via reaction with chlorine atoms is a plausible explanation of the discrepancy between the results from DeMore (1996) and the absolute rate study by Orkin et al. (2013). The recommended Arrhenius expression is derived from a fit to the data from Orkin et al. (2013).

References

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