IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet X_VOC33

This data sheet updated: 1st June 2005.

$Br + CH_3CHO \rightarrow HBr + CH_3CO$

$\Delta H° = 7.6$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(3.5 \pm 0.5) \times 10^{-12}$	300	Islam et al., 1984	(a)
$1.51 \times 10^{-11} \exp[-(364 \pm 41)/T]$	255-400	Nicovich et al., 1990	LP-RF
4.45×10^{-12}	298		
$(3.5 \pm 0.3) \times 10^{-12}$	298	Szilagyi et al., 1998	F-RF
Relative Rate Coefficients			
$(3.7 \pm 0.1) \times 10^{-12}$	298	Niki et al., 1985	RR (b)
$2.6 \times 10^{-11} \exp[-(580 \pm 200)/T]$	250-296	Ramacher et al., 2000	RR(c)
4.0×10^{-12}	296		

Comments

(a) Very low pressure reactor study. Br atoms were generated by microwave discharge of Br_2 in helium, with mass spectrometric detection of reactants and products.

(b) Br atoms were generated by photolysis of Br_2 at 350 nm to 600 nm in 930 mbar (700 Torr) total pressure of N_2. The rate coefficient was determined relative to that for the reaction of Br atoms with HCHO, with $k(Br + CH_3CHO)/k(Br + HCHO) = 3.39 \pm 0.10$. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(Br + HCHO) = 1.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(c) Br atoms were generated by photolysis of Br_2 in the presence of HCHO and CH_3CHO in 1 bar N_2. Relative rates of decay of the two aldehydes were determined by an FTIR spectrometer system. The relative rates of decay were found to be independent of temperature over the range 250-296 K with the value $k(Br + CH_3CHO)/k(Br + HCHO) = 3.60 \pm 0.29$. This temperature-independent rate coefficient ratio is placed on an absolute basis using $k(Br + HCHO) = 7.7 \times 10^{-12} \exp(-580/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k = 3.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.8 \times 10^{-11} \exp(-460/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250 K to 400 K.

Reliability

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

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The room temperature value is the average of the rate coefficients reported by Islam et al. (1984), Nicovich et al. (1990), Szilagyi et al. (1998) and Niki et al. (1985), and is in excellent agreement with the relative data of Ramacher et al. (2000). The temperature dependence is derived from the results of Nicovich et al. (1990), and is consistent with the relative rate data of Ramacher et al. (2000). The *A*-factor is adjusted to yield the 298 K preferred value. The preferred room temperature rate coefficient is consistent with the relative rate studies of Barnes et al. (1989) and Wallington et al. (1989) [which do not provide definitive data concerning the rate constant for the reaction of Br atoms with CH_3CHO].

References

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