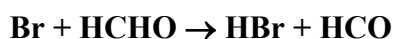


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet X_VOC32

Website: <http://iupac.pole-ether.fr>. See website for latest evaluated data. Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission.

This data sheet updated: 1st June 2005.



$$\Delta H^\circ = 3.5 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$1.44 \times 10^{-11} \exp[-(750 \pm 112)/T]$	223-480	Nava et al., 1981	FP-RF (a)
$(1.08 \pm 0.10) \times 10^{-12}$	298		
$2.97 \times 10^{-11} \exp[-(1015 \pm 70)/T]$	295-480	Poulet et al., 1981	DF-MS
$(9.4 \pm 0.8) \times 10^{-13}$	295		
<i>Relative Rate Coefficients</i>			
$5.0 \times 10^{-12} \exp[-(460 \pm 200)/T]$	250-296	Ramacher et al., 2000	RR(b)
1.08×10^{-12}	296		

Comments

- (a) There appears to be curvature in the Arrhenius plot above room temperature; using the low-temperature values at 223, 254, and 298 K gives $E/R = 584 \text{ K}$.
- (b) 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 $k(\text{Br} + \text{CH}_3\text{CHO})/k(\text{Br} + \text{HCHO}) = 3.60 \pm 0.29$. This temperature-independent rate coefficient ratio is placed on an absolute basis by use of $k(\text{Br} + \text{CH}_3\text{CHO}) = 1.8 \times 10^{-11} \exp(-460/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).

Preferred Values

$$k = 1.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 7.7 \times 10^{-12} \exp(-580/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 220\text{-}300 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.15 \text{ at } 298 \text{ K.}$$

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

Comments on Preferred Values

In the derivation of the preferred rate expression only data at and below room temperature were used. The room temperature value is the average of the absolute rate coefficients reported by Nava et al. (1981) and Poulet et al. (1981), and is in excellent agreement with the value derived from the relative rate data of Ramacher et al. (2000). The temperature dependence is derived from the low temperature results of Nava et al. (1981) ($E/R = 584$ K; see comment (a)), 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.

References

IUPAC: <http://iupac.pole-ether.fr>, 2013.

Nava, D. F., Michael, J. V. and Stief, L. J.: J. Phys. Chem. 85, 1896, 1981.

Poulet, G., Laverdet, G. and Le Bras, G.: J. Phys. Chem. 85, 1892, 1981.

Ramacher, B., Orlando, J. J. and Tyndall, G. S.: Int. J. Chem. Kinet. 32, 460, 2000.