IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oBrOx1

This data sheet updated: 4th July 2005.

HO + CH_3Br → H_2O + CH_2Br

ΔH^o = -71.9 kJ mol^{-1}

Rate coefficient data

k/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
(3.5 ± 0.8) x 10^{-14}	296 ± 2	Howard and Evenson, 1976	DF-LMR
7.93 x 10^{-13} exp[-(889 ± 59)/T	244-350	Davis et al., 1976	FP-RF
(4.14 ± 0.43) x 10^{-14}	298		
2.35 x 10^{-12} exp[-(1300 ± 150)/T	233-379	Mellouki et al., 1992	PLP-LIF
(2.96 ± 0.36) x 10^{-14}	298		
5.79 x 10^{-12} exp[-(1560 ± 150)/T	250-400	Zhang et al., 1992	FP-RF
(3.08 ± 0.47) x 10^{-14}	298		
1.86 x 10^{-12} exp[-(1230 ± 150)/T]	248-390	Chichinin et al., 1994	DF-EPR
(3.03 ± 0.45) x 10^{-14}	298		
Relative Rate Coefficients			
5.43 x 10^{-18} T^2exp[-(812 ± 46)/T]	298-360	Hsu and DeMore, 1994	RR (a)
3.16 x 10^{-14}	298		

Comments

(a) HO radicals were generated from the UV photolysis of O_3 in the presence of water vapor, in O_3-H_2O-CH_3Br-CH_3CHF_2-O_2-N_2 mixtures. The concentrations of CH_3Br and CH_3CHF_2 were measured by FTIR spectroscopy. The measured rate coefficient ratio of k(HO + CH_3Br)/k(HO + CH_3CHF_2) = (1.94 ± 0.28) exp[-(232 ± 46)/T] is placed on an absolute basis by use of a rate coefficient of k(HO + CH_3CHF_2) = 2.80 x 10^{-18} T^2 exp(-580/T) cm^3 $molecule^{-1}$ s^{-1} (IUPAC, 2005).

Preferred Values

k = 2.9 x 10^{-14} cm^3 $molecule^{-1}$ s^{-1} at 298 K.
k = 1.7 x 10^{-12} exp(-1215/T) cm^3 $molecule^{-1}$ s^{-1} over the temperature range 240-300 K.

Reliability

$\Delta \log k = \pm 0.08$ at 298 K.
$\Delta(E/R) = \pm 150$ K.

Comments on Preferred Values

The recent absolute rate coefficient measurements of Mellouki et al. (1992), Zhang et al. (1992) and Chichinin et al. (1994), which are in excellent agreement, are significantly lower than those previously determined by Howard and Evenson (1976) and Davis et al. (1976). The relative

rate coefficients of Hsu and DeMore (1994) are also in excellent agreement with the absolute rate coefficients of Mellouki et al. (1992), Zhang et al. (1992) and Chichinin et al. (1994). A unit-weighted least-squares analysis of the rate coefficients of Mellouki et al. (1992), Zhang et al. (1992) and Chichinin et al. (1992), using the three parameter expression $k = CT^2 \exp(-D/T)$, leads to $k = 3.44 \times 10^{-18} T^2 \exp(-687/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230-400 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is derived from three parameter expression with $A = C e^2 T^2$ and $B = D + 2T$.

References

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Hsu, K.-J. and DeMore, W. B.: Geophys. Res. Lett., 21, 805, 1994.

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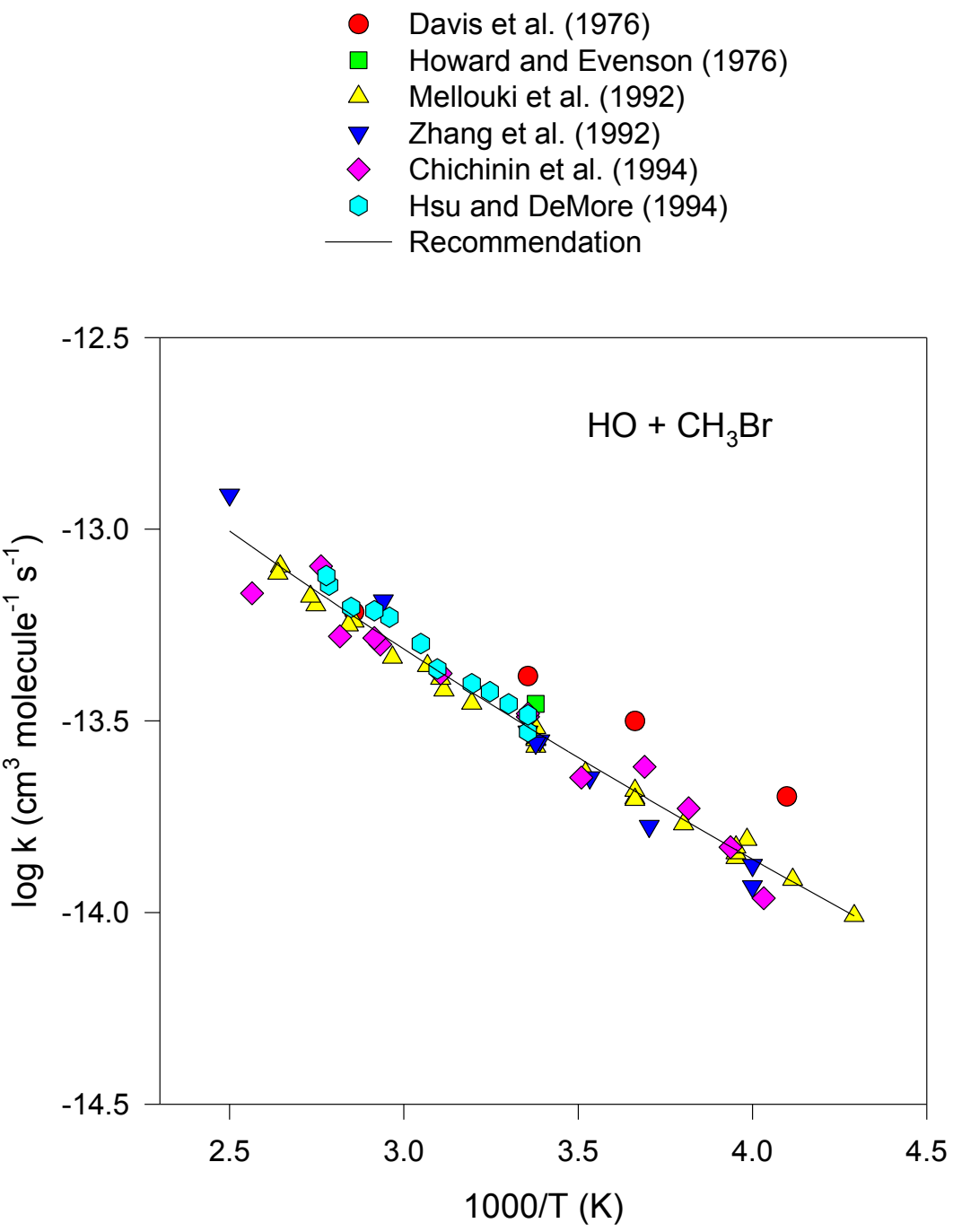
Zhang, Z., Saini, R. D., Kurylo, M. J. and Huie, R. E.: Geophys. Res. Lett., 19, 2413, 1992.


Davis et al. (1976)
Howard and Evenson (1976)
Mellouki et al. (1992)
Zhang et al. (1992)
Chichinin et al. (1994)
Hsu and DeMore (1994)
Recommendation
HO + CH3Br
log k (cm3 molecule-1 s-1)
-12.5
-13.0
-13.5
-14.0
-14.5
2.5
3.0
3.5
4.0
4.5
1000/T (K)