IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oBrOx2

This data sheet updated: 29th March 2005.

$HO + CH_2Br_2 \rightarrow H_2O + CHBr_2$

$\Delta H^o = -79.6$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$1.91 \times 10^{-12} \exp[-(840 \pm 100)/T]$	243-380	Mellouki et al., 1992	PLP-LIF
$(1.13 \pm 0.15) \times 10^{-13}$	298		
$1.51 \times 10^{-12} \exp[-(720 \pm 60)/T]$	288-368	Zhang et al., 1997	DF-RF
$(1.33 \pm 0.14) \times 10^{-13}$			
Relative Rate Coefficients			
$(9.2 \pm 0.6) \times 10^{-14}$	298	Orlando et al., 1996	RR (a)
$1.51 \times 10^{-12} \exp[-(715 \pm 39)/T]$	293-375	DeMore, 1996	RR (b)
1.37×10^{-13}	298		

Comments

(a) HO radicals were generated by the photolysis of O_3 in the presence of H_2O, and acetone was used as the reference compound. CH_2Br_2 and acetone were monitored by FTIR spectroscopy, and a rate coefficient ratio of $k(HO + CH_2Br_2)/k(HO + \text{acetone}) = 0.54 \pm 0.03$ was determined. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(HO + \text{acetone}) = 1.7 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, current recommendation).

(b) HO radicals were generated by the photolysis of O_3 at 254 nm in the presence of H_2O, and CH_2Cl_2 was used as the reference compound. CH_2Br_2 and CH_2Cl_2 were monitored by FTIR spectroscopy, and a rate coefficient ratio of $k(HO + CH_2Br_2)/k(HO + CH_2Cl_2) = 0.84 \exp[(145 \pm 39)/T]$ was determined. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(HO + CH_2Cl_2) = 1.8 \times 10^{-12} \exp(-860/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

$k = 1.1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.5 \times 10^{-12} \exp(-775/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240-300 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The room temperature rate coefficients of Mellouki et al. (1992), Orlando et al. (1996), DeMore (1996) and Zhang et al. (1997) range from 9.2 x 10^{-14} cm^3 $molecule^{-1}$ s^{-1} to 1.43 x 10^{-13} cm^3 $molecule^{-1}$ s^{-1}. The relative rate coefficients of DeMore (1996) and the absolute rate coefficients of Zhang et al. (1997), obtained over the temperature range ~290-370 K, are systematically higher than the absolute rate data of Mellouki et al. (1992), by ~20% at 290 K and ~10% at 370 K. Because the Mellouki et al. (1992) study included measurements down to significantly lower temperatures than did the other studies, and their room temperature rate coefficient is in between those of Orlando et al. (1996), DeMore (1996) and Zhang et al. (1997), the Mellouki et al. (1992) study is used as the basis for the preferred values. While an Arrhenius plot of the Mellouki et al. (1992) data shows little evidence for curvature, the absolute rate coefficients of Mellouki et al. (1992) have been fitted to the three-parameter expression $k = CT^2 \exp(-D/T)$, resulting in $k = 2.86 \times 10^{-18} T^2 \exp(-246/T)$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 243-380 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is derived from the three-parameter expression with $A = C e^2 T^2$ and $B = D + 2T$..

References

DeMore, W. B.: J. Phys. Chem., 100, 5813, 1996

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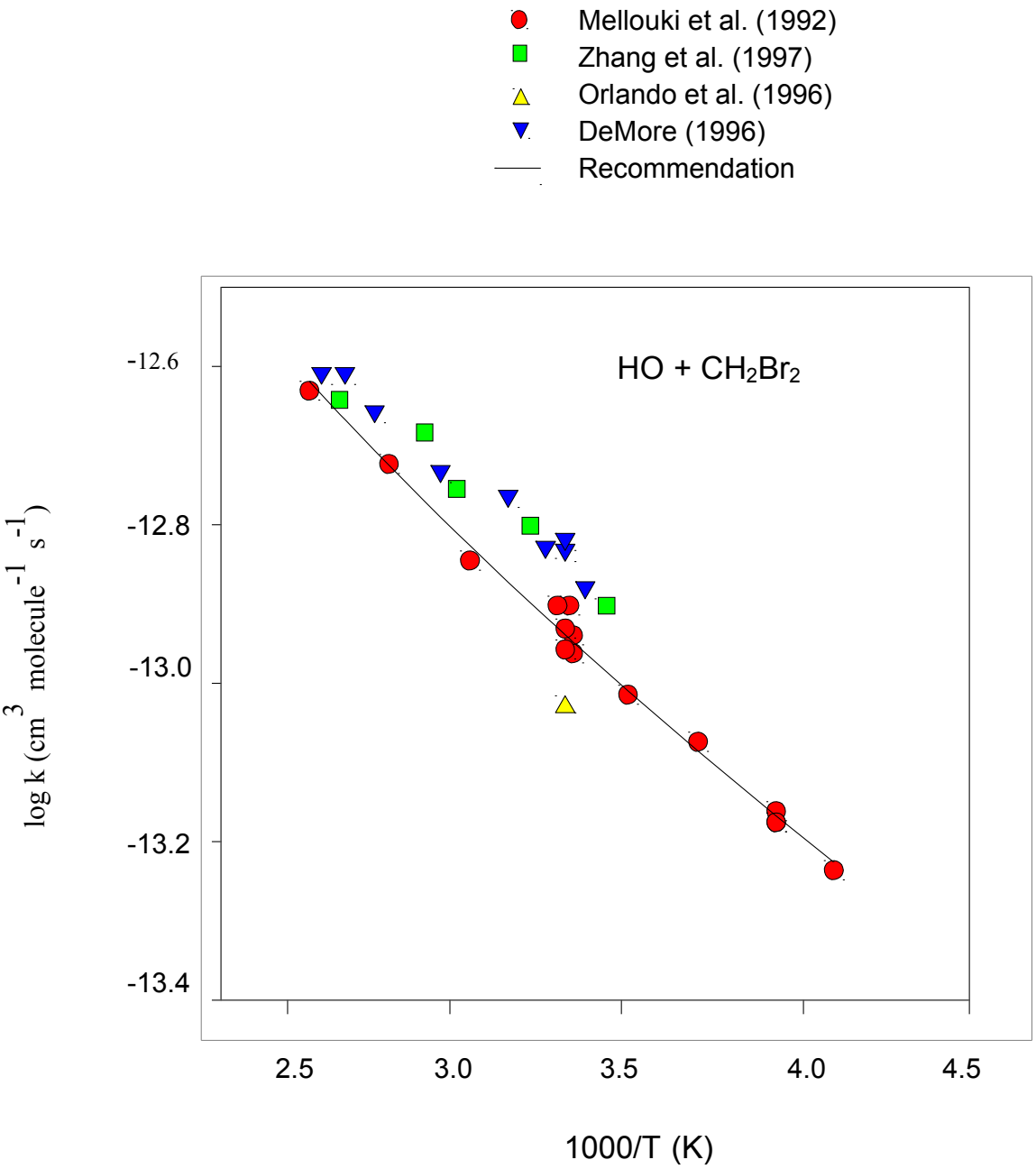
Orlando, J. J., Tyndall, G. S., Wallington, T. J. and Dill, M.: Int. J. Chem. Kinet., 28, 433, 1996.

Zhang, Z., Zhong, J. and Qiu, L.: J. Atmos. Chem., 27, 209, 1997.


Mellouki et al. (1992)
Zhang et al. (1997)
Orlando et al. (1996)
DeMore (1996)
Recommendation
HO + CH2Br2
-12.6
-12.8
-13.0
-13.2
-13.4
log k (cm3 molecule-1 s-1)
2.5
3.0
3.5
4.0
4.5
1000/T (K)