IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HOx_VOC35

This data sheet updated: 12th December 2007 (with no revision of the preferred values).

HO + HC(O)OH → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
(4.62 ± 0.78) x 10^{-13}	298-430	Wine et al., 1985	FP/PLP-RF (a)
(4.90 ± 0.12) x 10^{-13}	296	Jolly et al., 1986	PLP-RA (b)
2.91 x 10^{-13} exp[(102 ± 194)/T]	297-445	Singleton et al., 1988	PLP-RA
(4.47 ± 0.28) x 10^{-13}	297		
(3.7 ± 0.4) x 10^{-13}	298	Dagaut et al., 1988	FP-RF

Comments

(a) H atom formation was also measured by resonance fluorescence, and an H-atom formation yield of 0.75 ± 0.25 measured. At 298 K, the measured rate coefficient for the reaction of the HO radical with DC(O)OH was identical to that for HO radical reaction with HC(O)OH.

(b) Experiments with added O_2 led to non-exponential and slower HO radical decays, indicating the formation of H atoms from the HO radical reaction with HC(O)OH.

Preferred Values

k = 4.5 x 10^{-13} cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 290-450 K.

Reliability

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

$\Delta(E/R) = \pm 250$ K.

Comments on Preferred Values

A major problem with the determination of the rate coefficient for this reaction concerns the ready dimerization of HC(O)OH. The studies of Wine et al. (1985), Jolly et al. (1986) and Singleton et al. (1988) monitored formic acid in the experimental systems used by UV absorption spectroscopy. The data from these studies (Wine et al., 1985; Jolly et al., 1986; Singleton et al., 1988) agree well, and are in reasonable agreement with the room temperature rate coefficient of Dagaut et al. (1988). The data of Wine et al. (1985) and Singleton et al. (1988) show that the temperature dependence of the rate coefficient is zero within the experimental uncertainties. The average of the rate coefficients of Wine et al. (1985), Jolly et al. (1986) and Singleton et al. (1988) has been used to derive the preferred rate coefficient.

The studies of Wine et al. (1985) and Jolly et al. (1986) showed that H atoms are produced in this reaction, with a yield of 0.75 ± 0.25 (Wine et al., 1985). Furthermore, Wine et al. (1985) and Singleton et al. (1988) showed that within the experimental uncertainties the rate coefficient for the

reaction of the HO radical with DC(O)OH is identical to that for HC(O)OH at 298 K. Also, the room temperature rate coefficients for the reactions of the DO radical with HC(O)OD and DC(O)OD are significantly lower than those for the reactions of the HO radical with HC(O)OH and DC(O)OH (Singleton et al., 1988). The reaction then appears to proceed by,

$$\begin{array}{l} OH + HC(O)OH \rightarrow H_2O + HC(O)O \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad H + CO_2 \end{array}$$

with overall abstraction of the H (or D) atom from the -OH (or -OD) group being the major pathway at room temperature.

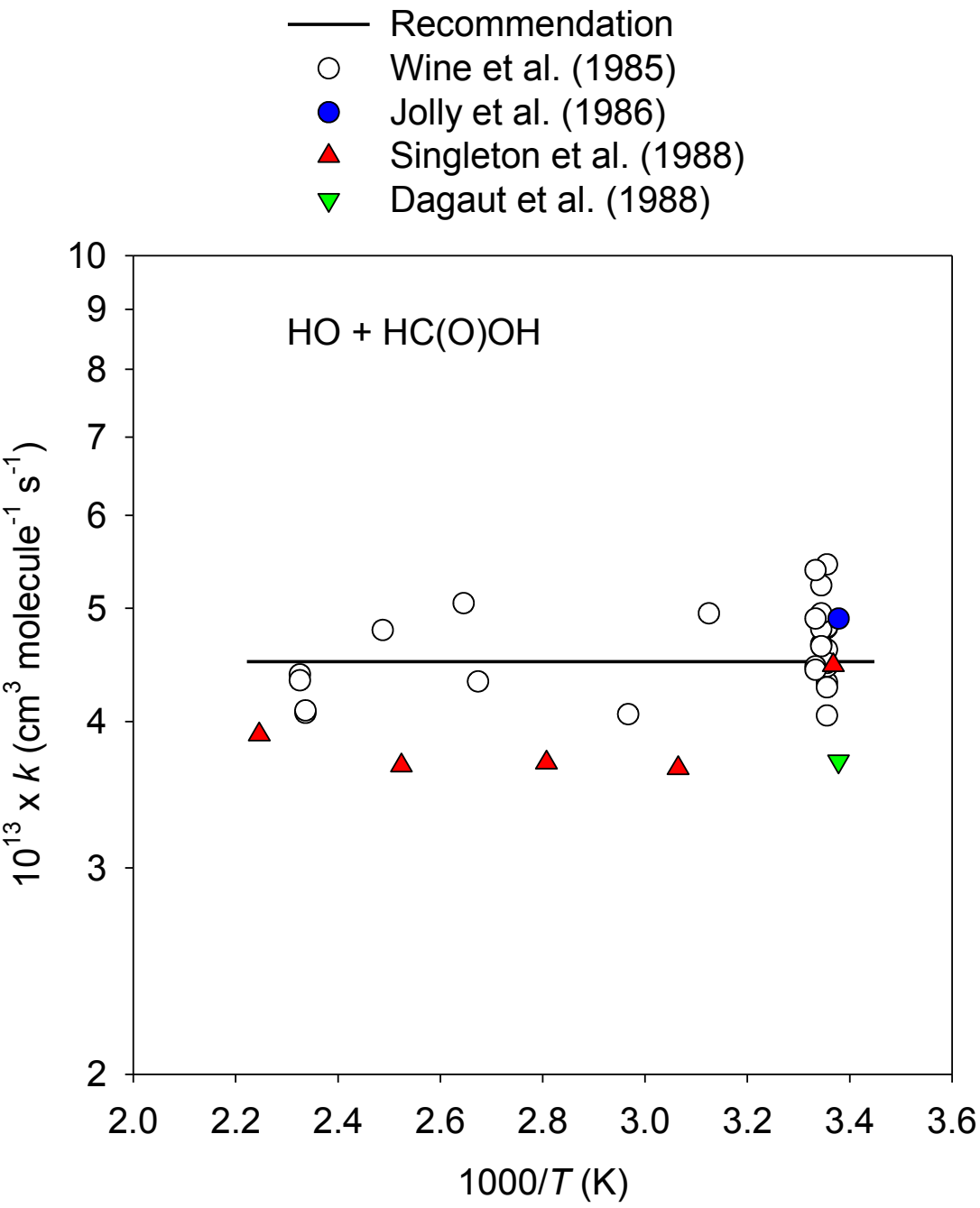
References

Dagaut, P., Wallington, T. J., Liu, R. and Kurylo, M. J.: Int. J. Chem. Kinet., 20, 331, 1988.

Jolly, G. S., McKenney, D. J., Singleton, D. L., Paraskevopoulos, G. and Bossard, A. R.: J. Phys. Chem., 90, 6557, 1986.

Singleton, D. L., Paraskevopoulos, G., Irwin, R. S., Jolly, G. S. and McKenney, D. J.: J. Am. Chem. Soc., 110, 7786, 1988.

Wine, P. H., Astalos, R. J. and Mauldin III, R. L.: J. Phys. Chem., 89, 2620, 1985.


Recommendation
Wine et al. (1985)
Jolly et al. (1986)
Singleton et al. (1988)
Dagaut et al. (1988)
HO + HC(O)OH
10
9
8
7
6
5
4
3
2
10^{13} x k (cm^3 $molecule^{-1}$ s^{-1})
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
1000/T (K)