IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet SOx4

This data sheet updated: 19th November 2001.

$O + CH_3SSCH_3 \rightarrow CH_3SO + CH_3S$

$\Delta H^\circ = -167$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(2.12 \pm 0.22) \times 10^{-10}$	270-329	Lee and Tang, 1980[1]	DF-RF
$4.35 \times 10^{-11} \exp[(251 \pm 61)/T]$	298-571	Nip, Singleton and Cvetanovic, 1981[2]	(a)
$(1.0 \pm 0.3) \times 10^{-10}$	298		

Comments

(a) $O(^3P)$ atoms were generated by the mercury-photosensitized photolysis of N_2O using a sinusoidally-modulated mercury lamp, and monitored by NO_2 chemiluminescence using a phase-shift technique.

Preferred Values

$k = 1.5 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 6.5 \times 10^{-11} \exp(250/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290-570 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

The data of Nip *et al.*,[2] obtained using a modulated photolysis technique, are about a factor of 2 lower than the data from the earlier discharge flow-resonance fluorescence study of Lee and Tang,[1] who reported no temperature dependence over the rather limited range 270-329 K. The cause of the

discrepancy between the two measurements is not clear. The preferred value at 298 K is an average of the values from the two studies.[1,2] The temperature dependence is that from Nip *et al*.[2] with the *A* factor adjusted to yield the preferred value at 298 K.

The product study of Cvetanovic *et al*.[3] suggests that at high pressures, 0.39-1.58 bar, the reaction proceeds mainly by addition followed by rapid fragmentation to CH_3S + CH_3SO. A broad chemiluminescence spectrum in the range 240-460 nm from this reaction at 1.3 mbar (1 Torr) pressure has been reported by Pavanaja *et al*.[4] They identified the emitting species as electronically excited HO and SO_2, and showed from a computer simulation that production of these excited species is consistent with secondary chemistry following the initial reaction to give the products shown above.

References

1 J. H. Lee and I. N. Tang, J. Chem. Phys. **72**, 5718 (1980).

2 W. S. Nip, D. L. Singleton, and R. J. Cvetanovic, J. Am. Chem. Soc. **103**, 3526 (1981).

3 R. J. Cvetanovic, D. L. Singleton, and R. S. Irwin, J. Am. Chem. Soc. **103**, 3530 (1981).

4 U. B. Pavanaja, H. P. Upadhyaya, A. V. Sapre, K. V. S. Rama Rao, and J. P. Mittal, J. Chem. Soc. Faraday Trans. **90**, 825 (1994).