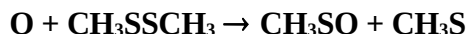


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet SOx4

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: 19th November 2001.



$$\Delta H^\circ = -167 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Temp./K | Reference | Technique/ Comments |
|--|---------|---|------------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $(2.12 \pm 0.22) \times 10^{-10}$ | 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 N₂O using a sinusoidally-modulated mercury lamp, and monitored by NO₂ chemiluminescence using a phase-shift technique.

Preferred Values

$$k = 1.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

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

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 100 \text{ K.}$$

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 CH₃S + CH₃SO. 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 SO₂, 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).