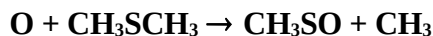


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet SO_x2

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.



$$\Delta H^\circ = -133 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$1.42 \times 10^{-11} \exp[(366 \pm 15)/T]$	268-424	Lee, Timmons and Stief, 1976 ¹	FP-RF
$(4.84 \pm 0.52) \times 10^{-11}$	298		
$1.28 \times 10^{-11} \exp[(404 \pm 30)/T]$	272-472	Lee, Tang and Klemm, 1980 ²	DF-RF
$(4.83 \pm 0.46) \times 10^{-11}$	296		
$1.11 \times 10^{-11} \exp[(460 \pm 41)/T]$	296-557	Nip, Singleton and Cvetanovic, 1981 ³	(a)
5.11×10^{-11}	297		

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

$k = 5.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.3 \times 10^{-11} \exp(409/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 270-560 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

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

Comments on Preferred Values

The data of Nip *et al.*³ are in excellent agreement, over the entire temperature range studied, with both of the studies of Lee *et al.*^{1,2} The preferred values of k at 298 K and (E/R) are obtained from a least-squares fit of the data from those three studies¹⁻³. The product study of Cvetanovic *et al.*⁴ suggests that at high pressures (0.39-1.58 bar) the reaction proceeds almost entirely by addition followed by rapid fragmentation to $\text{CH}_3 + \text{CH}_3\text{SO}$. 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.*⁵ They identified the emitting species as electronically excited HO and SO_2 , and by numerical integration they showed 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, R. B. Timmons, and L. J. Stief, *J. Chem. Phys.* **64**, 300 (1976).
- ² J. H. Lee, I. N. Tang, and R. B. Klemm, *J. Chem. Phys.* **72**, 1793 (1980).
- ³ W. S. Nip, D. L. Singleton, and R. J. Cvetanovic, *J. Am. Chem. Soc.* **103**, 3526 (1981).
- ⁴ R. J. Cvetanovic, D. L. Singleton, and R. S. Irwin, *J. Am. Chem. Soc.* **103**, 3530 (1981).
- ⁵ 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).