# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet SOx2


This data sheet updated: 19th November 2001.

---

**$O + CH_3SCH_3 \rightarrow CH_3SO + CH_3$**

$\Delta H^\circ = -133$ kJ·mol$^{-1}$

## Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | **Reference** | Technique/ Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $1.42 \times 10^{-11} \exp[(366 \pm 15)/T]$ | 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) |
| $5.11 \times 10^{-11}$ | 297 | | |

## Comments

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

## Preferred Values

$k = 5.0 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K.
$k = 1.3 \times 10^{-11} \exp(409/T)$ cm$^3$ molecule$^{-1}$ 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 studies[1-3]. 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 $CH_3$ + $CH_3SO$. 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*.[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).