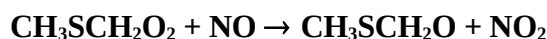


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet SOx68

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 last evaluated: 28th June 2007; no revision of preferred values.



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(1.9 \pm 0.6) \times 10^{-11}$	298	Wallington et al., 1993	(a)
$(8.0 \pm 3.1) \times 10^{-12}$	298	Turnipseed et al., 1996	(b)
$4.9 \times 10^{-12} \exp[(263 \pm 132)/T]$	261-400	Urbanski et al., 1997	(c)
$(1.14 \pm 0.05) \times 10^{-11}$	298		

Comments

- (a) Pulse radiolysis of $\text{CH}_3\text{SCH}_3\text{-SF}_6\text{-O}_2\text{-NO}$ mixtures. Generation of $\text{CH}_3\text{SCH}_2\text{O}_2$ radicals occurred by $\text{F} + \text{CH}_3\text{SCH}_3 \rightarrow \text{CH}_3\text{SCH}_2 + \text{HF}$, followed by $\text{CH}_3\text{SCH}_2 + \text{O}_2 \rightarrow \text{CH}_3\text{SCH}_2\text{O}_2$. $[\text{NO}_2]$ was monitored at 400 nm. Yield of NO_2 compared with yield of F atoms suggested that 80% of the reaction leads to NO_2 production.
- (b) Derived from pulsed laser photolysis of $\text{H}_2\text{O}_2\text{-NO-CH}_3\text{SCH}_3\text{-O}_2$ mixtures at 29 mbar total pressure, with monitoring of the temporal profiles of HO and CH_3S radicals by LIF. The cited rate coefficient was obtained from numerical modeling using a 34 step mechanism and assuming that $\text{CH}_3\text{SCH}_2\text{O}_2 + \text{CH}_3\text{SCH}_2\text{O}_2 \rightarrow \text{CH}_3\text{SCH}_2\text{O} + \text{CH}_3\text{SCH}_2\text{O} + \text{O}_2$ followed by decomposition of the $\text{CH}_3\text{SCH}_2\text{O}$ radical to $\text{HCHO} + \text{CH}_3\text{S}$.
- (c) $\text{CH}_3\text{SCH}_2\text{O}_2$ radicals were generated by the 248 nm pulsed laser photolysis of $\text{C(O)Cl}_2\text{-CH}_3\text{SCH}_3\text{-O}_2\text{-N}_2$ mixtures at 13 mbar total pressure, and the rate of formation of the product HCl was monitored in the presence of varying concentrations of NO by TDLAS. Secondary reactions were shown to be unimportant, and a HCHO yield of 1.04 ± 0.13 was measured, with the HCHO arising from decomposition of $\text{CH}_3\text{SCH}_2\text{O}$ radicals..

Preferred Values

$k = 4.9 \times 10^{-12} \exp(260/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 260-400 K.

$k = 1.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

The three studies carried out to date (Wallington et al., 1993; Turnipseed et al., 1996; Urbanski et al., 1997) result in room temperature rate coefficients varying by a factor of 2.4. In the study of Wallington et al. (1993), the formation rate of $\text{CH}_3\text{SCH}_2\text{O}_2$ radicals was not much faster than the loss rate by reaction with NO (Urbanski et al., 1997). The Turnipseed et al. (1996) study was more indirect and subject to significant uncertainties. Accordingly, the preferred value of the rate coefficient is based on the most direct study of Urbanski et al. (1997). The $\text{CH}_3\text{SCH}_2\text{O}$ radical decomposes rapidly to form $\text{HCHO} + \text{CH}_3\text{S}$ (Urbanski et al., 1997).

References

- Turnipseed, A. A., Barone, S. B. and Ravishankara, A. R.: J. Phys. Chem. 100, 14703, 1996.
Urbanski, S. P., Stickel, R. E., Zhao, Z. and Wine, P. H.: J. Chem. Soc. Faraday Trans. 93, 2813, 1997.
Wallington, T. J., Ellermann, T. and Nielsen, O. J.: J. Phys. Chem. 97, 8442, 1993.