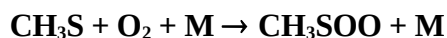


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet SOx56

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.



$$\Delta H^\circ = -48.9 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$<2 \times 10^{-17}$	298	Balla, Nelson and McDonald, 1986 ¹	PLP-LIF
$<1 \times 10^{-16}$	298	Black and Jusinski, 1986 ²	PLP-LIF
$<2.5 \times 10^{-18}$	298	Tyndall and Ravishankara, 1989 ³	PLP-LIF
$(1.81 \pm 0.28) \times 10^{-13}$ 107 mbar (He)	216	Turnipseed, Barone and Ravishankara, 1992 ⁴	(a)
$(1.55 \pm 0.23) \times 10^{-13}$ 107 mbar (He)	222		
$(1.05 \pm 0.20) \times 10^{-13}$ 107 mbar (He)	233		
$(9.0 \pm 1.6) \times 10^{-14}$ 107 mbar (He)	237		
$(8.62 \pm 0.84) \times 10^{-14}$ 107 mbar (He)	242		
$(7.0 \pm 2.0) \times 10^{-14}$ 107 mbar (He)	250		
<i>Relative Rate Coefficients</i>			
2×10^{-14}	298	Hatakeyama and Akimoto, 1983 ⁵	RR (b)
2.9×10^{-17}	298	Grosjean, 1984 ⁶	RR (c)
$>2.3 \times 10^{-16}$	296	Balla and Heicklen, 1985 ⁷	RR (d)

Comments

- (a) Pulsed laser photolysis system with LIF detection of CH_3S radicals. The measured rate coefficients were observed to vary with the total pressure and the diluent gas. An upper limit to the rate coefficient for the reaction of the CH_3SOO radical with O_2 of $4 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 258 K was also derived. The $\text{CH}_3\text{S-OO}$ bond energy was determined to be 49 kJ mol^{-1} at 298 K from measurements of the equilibrium constant over the temperature range 216-258 K, with $\Delta H_f(\text{CH}_3\text{SOO}) = 75.7 \pm 4.2 \text{ kJ mol}^{-1}$ at 298 K.
- (b) Photolysis of $\text{CH}_3\text{SSCH}_3\text{-RONO-NO}$ -air mixtures. The products were analyzed by FTIR and GC-MS and the yields of SO_2 and CH_3SNO measured. From an assumed mechanism, the rate coefficient ratio $k(\text{CH}_3\text{S} + \text{NO})/k = 2 \times 10^3$ was derived. A rate coefficient of $k(\text{CH}_3\text{S} + \text{NO}) = 4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was used to obtain the rate coefficient given in the table.
- (c) Environmental chamber study using the oxidation of organo-sulfur compounds in air by natural sunlight. Major products were SO_2 , $\text{CH}_3\text{SO}_3\text{H}$ and HCHO . Production of SO_2 and sulphur were

related to an unidentified compound (assumed to be CH₃SNO₂) formed from CH₃S + NO₂. A rate coefficient ratio of $k(\text{CH}_3\text{S} + \text{NO}_2)/k = 2 \times 10^6$ was derived, and placed on an absolute basis by use of $k(\text{CH}_3\text{S} + \text{NO}_2) = 5.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).

- (d) From the photolysis of (CH₃S)₂-O₂-N₂ mixtures at 253.7 nm, with product analysis by GC and MS. The SO₂ yield was measured as a function of [(CH₃S)₂], [O₂] and light intensity. From an assumed mechanism, a value of $k^2/2k(\text{CH}_3\text{S} + \text{CH}_3\text{S}) > 6 \times 10^{-22} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was derived. A rate coefficient of $k(\text{CH}_3\text{S} + \text{CH}_3\text{S}) = 4.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (from Graham *et al.*⁸) was used to obtain the rate coefficient given in the table.

Preferred Values

Data of Turnipseed *et al.*,⁴ given in above Table. These data at 107 mbar He are described by $k(210 - 250 \text{ K}) = 1.2 \times 10^{-16} \exp(1580/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Reliability

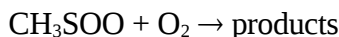
$\Delta \log k = \pm 0.3$ over the temperature range 216-250 K at 107 mbar He.

Comments on Preferred Values

The study of Turnipseed *et al.*⁴ was the first to observe addition of O₂ to the CH₃S radical to form CH₃SOO [and not CH₃S(O)O], because the reaction was observed to be reversible leading to equilibrium between CH₃S radicals, O₂ and CH₃SOO radicals.⁴ Previous studies¹⁻³ of the reaction of CH₃S radicals with O₂ at 298 K did not observe the equilibrium addition of O₂ to CH₃S radicals, and the rate coefficients measured correspond to upper limits to the rate coefficients for the reactions



and/or



The reaction of CH₃S radicals with O₂ to form the CH₃SOO radical, and the reverse reaction, result in ~33% of CH₃S radicals being present as the CH₃SOO adduct at 298 K and ground level,⁴ with the [CH₃SOO]/[CH₃S] ratio being strongly temperature dependent.⁴

References

- ¹ R. J. Balla, H. H. Nelson, and J. R. McDonald, *Chem. Phys.* **109**, 101 (1986).
- ² G. Black and L. E. Jusinski, *J. Chem. Soc. Faraday Trans. 2*, **82**, 2143 (1986).
- ³ G. S. Tyndall and A. R. Ravishankara, *J. Phys. Chem.* **93**, 2426 (1989).
- ⁴ A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, *J. Phys. Chem.* **96**, 7502 (1992).
- ⁵ S. Hatakeyama and H. Akimoto, *J. Phys. Chem.* **87**, 2387 (1983).
- ⁶ D. Grosjean, *Environ. Sci. Technol.* **18**, 460 (1984).
- ⁷ R. J. Balla and J. Heicklen, *J. Photochem.* **29**, 297 (1985).
- ⁸ D. M. Graham, R. L. Mieville, R. H. Pallen, and C. Sivertz, *Can. J. Chem.* **42**, 2250 (1964).