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

This data sheet last evaluated: November 2017; last change in preferred values: November 2001.

$CH_3S + O_2 + M \rightarrow CH_3SOO + M$
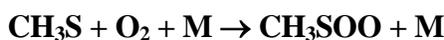
$\Delta H° = -48.9 \text{ kJ·mol}^{-1}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$<2 \times 10^{-17}$	298	Balla et al., 1986	PLP-LIF
$<1 \times 10^{-16}$	298	Black and Jusinski, 1986	PLP-LIF
$<2.5 \times 10^{-18}$	298	Tyndall and Ravishankara, 1989	PLP-LIF
$(1.81\pm0.28) \times 10^{-13}$ 107 mbar (He)	216	Turnipseed et al., 1992	(a)
$(1.55\pm0.23) \times 10^{-13}$ 107 mbar (He)	222		
$(1.05\pm0.20) \times 10^{-13}$ 107 mbar (He)	233		
$(9.0 \pm 1.6) \times 10^{-14}$ 107 mbar (He)	237		
$(8.62\pm0.84) \times 10^{-14}$ 107 mbar (He)	242		
$(7.0\pm2.0) \times 10^{-14}$ 107 mbar (He)	250		
Relative Rate Coefficients			
2×10^{-14}	298	Hatakeyama and Akimoto, 1983	RR (b)
2.9×10^{-17}	298	Grosjean, 1984	RR (c)
$>2.3 \times 10^{-16}$	296	Balla and Heicklen, 1985	RR (d)

Comments

(a) Pulsed laser photolysis system with LIF detection of CH$_3$S 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$_3$SOO radical with O$_2$ of 4 x 10^{-17} cm^3 molecule^{-1} s^{-1} at 258 K was also derived. The CH$_3$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 $\Delta H_f(CH_3SOO) = 75.7 \pm 4.2$ kJ mol^{-1} at 298 K.

(b) Photolysis of CH_3SSCH_3-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 $k(CH_3S + NO)/k = 2 \times 10^3$ was derived. A rate coefficient of $k(CH_3S + NO) = 4 \times 10^{-11}$ cm^3 molecule^{-1} 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, CH_3SO_3H and HCHO. Production of SO_2 and sulphur were related to an unidentified compound (assumed to be CH_3SNO_2) formed from $CH_3S + NO_2$. A rate coefficient ratio of $k(CH_3S + NO_2)/k = 2 \times 10^6$ was derived, and placed on an absolute basis by use of $k(CH_3S + NO_2) = 5.8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(d) From the photolysis of $(CH_3S)_2$-O_2-N_2 mixtures at 253.7 nm, with product analysis by GC and MS. The SO_2 yield was measured as a function of $[(CH_3S)_2]$, $[O_2]$ and light intensity. From an assumed mechanism, a value of $k^2/2k(CH_3S + CH_3S) > 6 \times 10^{-22}$ cm^3 molecule^{-1} s^{-1} was derived. A rate coefficient of $k(CH_3S + CH_3S) = 4.1 \times 10^{-11}$ cm^3 molecule^{-1} 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. (1992) are preferred. These data at 107 mbar He are described by $k(210 - 250 \text{ K}) = 1.2 \times 10^{-16} \exp (1580/T)$ cm^3 molecule^{-1} 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. (1992) was the first to observe addition of O_2 to the CH_3S radical to form CH_3SOO [and not $CH_3S(O)O$], because the reaction was observed to be reversible leading to equilibrium between CH_3S radicals, O_2 and CH_3SOO radicals. The earlier studies by Balla et al. (1986), Black et al. (1986) and Tyndall et al. (1989) of the reaction of CH_3S radicals with O_2 at 298 K did not observe the equilibrium addition of O_2 to CH_3S radicals, and the rate coefficients measured correspond to upper limits to the rate coefficients for the reactions $CH_3S + O_2 \rightarrow$ products other than CH_3SOO and/or $CH_3SOO + O_2 \rightarrow$ products.

The reaction of CH_3S radicals with O_2 to form the CH_3SOO radical, and the reverse reaction, result in ~33% of CH_3S radicals being present as the CH_3SOO adduct at 298 K and ground level, with the $[CH_3SOO]/[CH_3S]$ ratio being strongly temperature dependent (Turnipseed et al., 1992).

References

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