IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet SOx59

This data sheet updated: 19th November 2001.

$CH_3S + NO + M \rightarrow CH_3SNO + M$

Low-pressure rate coefficients

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./ K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(3.24 \pm 0.36) \times 10^{-29}$ [N_2]	295	Balla, Nelson and McDonald, 1986[1]	(a)
$(1.43 \pm 0.36) \times 10^{-29}$ [N_2]	351		
$(1.13 \pm 0.20) \times 10^{-29}$ [N_2]	397		
$(5.84 \pm 0.66) \times 10^{-30}$ [N_2]	453		

Comments

(a) Pulsed laser photolysis of $(CH_3S)_2$-NO-N_2 (or SF_6) mixtures at 266 nm, with CH_3S being monitored by LIF. Lower part of the falloff curves were measured over the pressure range 2-400 mbar (1.5-300 Torr) of N_2. Falloff extrapolations were carried out with fitted values of F_c of 0.6, 0.86, 0.77, and 0.94 at 295, 351, 397, and 453 K, respectively.

Preferred Values

$k_0 = 3.3 \times 10^{-29} (T/300)^{-4}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 290-450 K. This value was obtained by fitting to the pressure and temperature dependent data in N_2 using a temperature independent values of Fc = 0.54 and k_∞ derived from data in SF_6 (see below).

Reliability

$\Delta \log k_0 = 0.3$ at 298 K.

$\Delta n = \pm 2$.

Comments on Preferred Values

The preferred values are based on the data of Balla *et al.*[1] A further determination in N_2 at a single temperature and pressure (298 K and 25 Torr) by Turnipseed *et al.*[2] is in good agreement. Although the

falloff extrapolations in ref. 1 were made with a theoretically improbable temperature coefficient of F_c, the low-pressure rate coefficients are much less influenced by this extrapolation than the high-pressure rate coefficients.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./ K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$1.81 \times 10^{-12} \exp(900/T)$	295-453	Balla, Nelson and McDonald, 1986[1]	(a)
$(3.97 \pm 0.44) \times 10^{-11}$ in 300 Torr SF_6	295		

Comments

(a) See comment (a) for k_0. High-pressure limit was obtained from measurements at 267 and 400 mbar (200 and 300 Torr) of SF_6.
(b) Based on the data of Balla *et al*.[1]
(c) See Comments on Preferred Values.

Preferred Values

$k_\infty = 4.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 290-450 K.

Reliability

$\Delta \log k_\infty = \pm 0.5$ over the temperature range 290-450 K.

Comments on Preferred Values

The negative temperature coefficient of k_∞ reported in ref. 1 is most probably due to an increasing underestimate of the falloff corrections with increasing temperature. We recommend the use of the extrapolated k_∞ value at 298 K over large temperature ranges together with $F_c = 0.54$. Along with the values recommended for k_0 above, this parameterisation accurately reproduces all the data in N_2.

Intermediate Falloff Range

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	P/mbar	M	Temp./K	Reference	Comments
$(1.69 \pm 0.04) \times 10^{-11}$	28	He	227	Turnipseed, Barone and Ravishankara, 1993[3]	(a)
$(1.30 \pm 0.09) \times 10^{-11}$	25	He	242		
$(1.89 \pm 0.08) \times 10^{11}$	25	He	242		

Comments

(a) CH_3S radicals were generated by either photolysis of dimethyl sulfide at 193 nm or photolysis of dimethyl disulfide at 248 nm. The decay of CH_3S radical concentrations was followed by LIF. Experiments were performed under slow gas flow conditions.

References

1 R. J. Balla, H. H. Nelson, and J. R. McDonald, Chem. Phys. **109**, 101 (1986).
2 A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem. **100**, 14703 (1996).
3 A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem. **97**, 5926 (1993).