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

 The citation for this data sheet is: Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Atmos. Chem. Phys. 4, 1461, 2004; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, (http://iupac.pole-ether.fr).
This data sheet last evaluated: November 2017; last change in preferred values: 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 et al., 1986	(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.(1986). A further determination in N_2 at a single temperature and pressure (298 K and 25 Torr) by Turnipseed et al. (1986) is in good agreement. Although the falloff extrapolations of Balla et al. (1986) 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 et al., 1986	(a)
$(3.97 \pm 0.44) \times 10^{-11}$ in 300 Torr SF_6	295		

Comments

(a) See comment (a) for k_0. The high-pressure limit was obtained from measurements at 267 and 400 mbar (200 and 300 Torr) of SF_6.

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 by Balla et al. (1986) 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 et al., 1993	
$(1.30 \pm 0.09) \times 10^{-11}$	25	He	242		(a)
$(1.89 \pm 0.08) \times 10^{11}$	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

Balla, R. J., Nelson, H. H., and McDonald, J. R.:Chem. Phys. 109, 101, 1986.
Turnipseed, A. A., Barone, S. B., and Ravishankara, A. R.: J. Phys. Chem. 97, 5926, 1993.
Turnipseed, A. A., Barone, S. B., and Ravishankara, A. R.: J. Phys. Chem. 100, 14703, 1996.