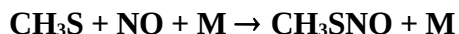


## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet SOx59

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: 19<sup>th</sup> November 2001.



### Low-pressure rate coefficients

#### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./ K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(3.24 \pm 0.36) \times 10^{-29} [\text{N}_2]$	295	Balla, Nelson and McDonald, 1986 <sup>1</sup>	(a)
$(1.43 \pm 0.36) \times 10^{-29} [\text{N}_2]$	351		
$(1.13 \pm 0.20) \times 10^{-29} [\text{N}_2]$	397		
$(5.84 \pm 0.66) \times 10^{-30} [\text{N}_2]$	453		

#### Comments

- (a) Pulsed laser photolysis of  $(\text{CH}_3\text{S})_2\text{-NO-N}_2$  (or  $\text{SF}_6$ ) mixtures at 266 nm, with  $\text{CH}_3\text{S}$  being monitored by LIF. Lower part of the falloff curves were measured over the pressure range 2-400 mbar (1.5-300 Torr) of  $\text{N}_2$ . 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

$k_0 = 3.3 \times 10^{-29} (T/300)^{-4} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 290-450 K. This value was obtained by fitting to the pressure and temperature dependent data in  $\text{N}_2$  using a temperature independent values of  $F_c = 0.54$  and  $k_\infty$  derived from data in  $\text{SF}_6$  (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.*<sup>1</sup> A further determination in  $\text{N}_2$  at a single temperature and pressure (298 K and 25 Torr) by Turnipseed *et al.*<sup>2</sup> 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

$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./ K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$1.81 \times 10^{-12} \exp(900/T)$	295-453	Balla, Nelson and McDonald, 1986 <sup>1</sup>	(a)
$(3.97 \pm 0.44) \times 10^{-11}$ in 300 Torr SF <sub>6</sub>	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<sub>6</sub>.
- (b) Based on the data of Balla *et al.*<sup>1</sup>
- (c) See Comments on Preferred Values.

#### Preferred Values

$k_\infty = 4.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , 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  $k_\infty$  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  $k_\infty$  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<sub>2</sub>.

## Intermediate Falloff Range

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	P/mbar	M	Temp./K	Reference	Comments
$(1.69 \pm 0.04) \times 10^{-11}$	28	He	227	Turnipseed, Barone and Ravishankara, 1993 <sup>3</sup>	(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)  $\text{CH}_3\text{S}$  radicals were generated by either photolysis of dimethyl sulfide at 193 nm or photolysis of dimethyl disulfide at 248 nm. The decay of  $\text{CH}_3\text{S}$  radical concentrations was followed by LIF. Experiments were performed under slow gas flow conditions.

### References

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