

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet SOx34

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 last evaluated: 28th June 2007; no revision of preferred values.

NO₃ + CH₃SSCH₃ → products

Rate coefficient data

<i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
1.9 × 10 ⁻¹³ exp[(290 ± 50)/T]	280-350	Wallington et al., 1986	FP-A
(4.9 ± 0.8) × 10 ⁻¹³	298 ± 2		
7.4 × 10 ⁻¹³ exp[(0 ± 200)/T]	334-382	Dlugokencky and Howard, 1988	F-LIF
(7.4 ± 1.5) × 10 ⁻¹³	298		
<i>Relative Rate Coefficients</i>			
(see comment)	297 ± 2	Mac Leod et al., 1986	RR (a)

Comments

- (a) NO₃ radicals were generated by the thermal decomposition of N₂O₅ in N₂O₅-NO₂-air mixtures at atmospheric pressure. The relative decay rates of CH₃SSCH₃ and *trans*-2-butene were monitored by FTIR spectroscopy and GC, respectively. However, the more recent study of Atkinson et al. (1988) has shown that reliable rate coefficient data cannot be obtained from the chemical system used by Mac Leod et al. (1986).

Preferred Values

$k = 7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range ~300-380 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The two absolute studies (Wallington et al., 1986; Dlugokencky and Howard, 1988) are in reasonable agreement with respect to the room temperature rate coefficient. While the reported rate coefficient from the relative rate study (Mac Leod et al., 1986) was an order of magnitude lower than the absolute data, the recent study of Atkinson et al. (1988) shows that this was due to complexities in the experimental system used. Accordingly, the preferred values are based upon the absolute rate studies, and mainly on the data of Dlugokencky and Howard (1988), with the error limits being sufficient to encompass the data of Wallington et al. (1986).

As for the NO₃ radical reactions with CH₃SH and CH₃SCH₃, the NO₃ radical reaction with CH₃SSCH₃ is expected to proceed by initial addition, followed by decomposition of the addition adduct (Mac Leod et al., 1986; Jensen et al., 1992)



References

- Atkinson, R., Aschmann, S. M. and Pitts Jr., J. N.: J. Geophys. Res. 93, 7125, 1988.
Dlugokencky, E. J. and Howard, C. J.: J. Phys. Chem. 92, 1188, 1988.
Jensen, N. R., Hjorth, J., Lohse, C., Skov, H. and Restelli, G.: J. Atmos. Chem. 14, 95, 1992.
Mac Leod, H., Aschmann, S. M., Atkinson, R., Tuazon, E. C., Sweetman, J. A., Winer, A. M. and Pitts Jr., J. N.: J. Geophys. Res. 91, 5338, 1986.
Wallington, T. J., Atkinson, R., Winer, A. M. and Pitts Jr., J. N.: J. Phys. Chem. 90, 5393, 1986.