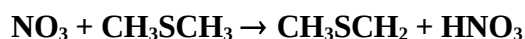


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet SO_x33

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: 20th November 2001.



$$\Delta H^\circ = -35 \text{ kJ mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(1.0 \pm 0.2) \times 10^{-12}$	278-318	Tyndall <i>et al.</i> , 1986 ¹	MM-A
$(9.9 \pm 3.5) \times 10^{-13}$	298		
$(7.5 \pm 0.5) \times 10^{-13}$	298 ± 2	Wallington <i>et al.</i> , 1986 ²	FP-A
$4.7 \times 10^{-13} \exp[(170 \pm 130)/T]$	280-350	Wallington <i>et al.</i> , 1986 ³	FP-A
$(8.1 \pm 1.3) \times 10^{-13}$	298 ± 2		
$1.79 \times 10^{-13} \exp[(530 \pm 40)/T]$	256-376	Dlugokencky and Howard, 1988 ⁴	F-LIF
$(1.06 \pm 0.13) \times 10^{-12}$	298		
$(1.3 \pm 0.3) \times 10^{-12}$	298 ± 1	Daykin and Wine, 1990 ⁵	PLP-A
<i>Relative Rate Coefficients</i>			
$(9.92 \pm 0.20) \times 10^{-13}$	296 ± 2	Atkinson <i>et al.</i> , 1984 ⁶	RR (a)

Comments

- (a) NO₃ radicals were generated by the thermal decomposition of N₂O₅ in air at 1 atmosphere total pressure. The concentrations of CH₃SCH₃ and *trans*-2-butene were measured by GC, and the measured rate coefficient ratio of $k(\text{NO}_3 + \text{CH}_3\text{SCH}_3)/k(\text{NO}_3 + \textit{trans}\text{-2-butene}) = 2.55 \pm 0.05$ is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + \textit{trans}\text{-2-butene}) = 3.89 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K.⁷

Preferred Values

$$k = 1.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 1.9 \times 10^{-13} \exp(520/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 250\text{-}380 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.15 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 200 \text{ K.}$$

Comments on Preferred Values

The absolute¹⁻⁵ and relative⁶ rate coefficient studies are in reasonable agreement, although the data of Wallington *et al.*^{2,3} are ~20% lower than the other data.^{1,4-6} The absolute rate coefficients measured by Tyndall *et al.*,¹ Dlugokencky and Howard⁴ and Daykin and Wine⁵ and the relative rate coefficient of Atkinson *et al.*⁶ have been fitted to an Arrhenius expression to obtain the preferred values. The experimental data show that the rate coefficient is independent of total pressure over the range ~0.0013-1 bar.

The magnitude of the rate constant and the negative temperature dependence indicates that this reaction proceeds by initial addition of the NO₃ radical to the S atom. The kinetic data of Daykin and Wine⁵ and Jensen *et al.*⁸ for CH₃SCH₃ and CD₃SCD₃ show that the rate determining step involves H- (or D-) atom abstraction, indicating that the reaction is



This conclusion is consistent with the product studies of Jensen *et al.*^{8,9} and Butkovskaya and Le Bras.¹⁰ Butkovskaya and Le Bras¹⁰ used a DF-MS technique to show that the alternative reaction pathway yielding CH₃SONO₂ + CH₃ accounts for <2% of the overall reaction at 298 K and 1.3 mbar total pressure.

References

- ¹ G. S. Tyndall, J. P. Burrows, W. Schneider, and G. K. Moortgat, *Chem. Phys. Lett.* **130**, 463 (1986).
- ² T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., *J. Phys. Chem.* **90**, 4640 (1986).
- ³ T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., *J. Phys. Chem.* **90**, 5393 (1986).
- ⁴ E. J. Dlugokencky and C. J. Howard, *J. Phys. Chem.* **92**, 1188 (1988).
- ⁵ E. P. Daykin and P. H. Wine, *Int. J. Chem. Kinet.* **22**, 1083 (1990).
- ⁶ R. Atkinson, J. N. Pitts, Jr., and S. M. Aschmann, *J. Phys. Chem.* **88**, 1584 (1984).
- ⁷ R. Atkinson, *J. Phys. Chem. Ref. Data* **26**, 215 (1997).
- ⁸ N. R. Jensen, J. Hjorth, C. Lohse, H. Skov, and G. Restelli, *J. Atmos. Chem.* **14**, 95 (1992).
- ⁹ N. R. Jensen, J. Hjorth, C. Lohse, H. Skov, and G. Restelli, *Atmos. Environ.* **25A**, 1897 (1991).
- ¹⁰ N. I. Butkovskaya and G. Le Bras, *J. Phys. Chem.* **98**, 2582 (1994).