

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet SOx61

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CH₃SO + O₃ → products

Rate coefficient data

<i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
1 × 10 ⁻¹²	298	Tyndall and Ravishankara, 1989	PLP-LIF
(6.0 ± 3.0) × 10 ⁻¹³	300	Dominé et al., 1992	(a)
<i>Relative Rate Coefficients</i>			
(3.2 ± 1.6) × 10 ⁻¹³	300	Borissenko et al., 2003	(b)

Comments

- (a) Discharge flow study. Photoionization mass spectrometry was used to monitor CH₃SO radicals. The reaction of O(³P) + C₂H₅SCH₃ was used as a source of CH₃SO radicals. The reaction system is complex owing to chain branching processes and HO formation from unknown sources, the latter of which has been quenched by addition of 1.3 × 10¹⁴ molecule cm⁻³ of C₂F₃Cl. The rate coefficient obtained was considered preliminary in view of the small number of experiments.
- (b) PLP/LIF study using LIF detection of the product SO₂ excited at 220.6 nm into the short-lived C(*tilde*)(¹B₂) electronic state. CH₃SO was generated in the reaction O(³P) + CH₃SCH₃ (DMS) with O(³P) from O₃ photolysis at 248 nm. Relative SO₂ yields from photolyzed mixtures of DMS/NO₂/O₃ were measured as a function of [O₃]/[NO₂] and resulted in the ratio $k/k_{ref}(\text{CH}_3\text{SO} + \text{NO}_2 \rightarrow \text{products}) = (2.13 \pm 0.9) \times 10^{-2}$. This ratio was converted to k using $k_{ref}(\text{CH}_3\text{SO} + \text{NO}_2 \rightarrow \text{products}) = (1.5 \pm 0.4) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. The absolute SO₂ product yield was measured relative to the one from the photolysis of CH₃SSCH₃ (DMDS)/NO₂ and CS₂/NO₂ mixtures resulting in SO₂. The SO₂ yield of the CS₂/NO₂ photolysis system was assumed to be unity which allowed the measurement of absolute SO₂ yields. The study was performed over the pressure range 187-880 mbar of N₂ and the SO₂ yield, thus the branching ratio, was (1.0 ± 0.12) in the pressure range 667-933 mbar.

Preferred Values

$k = 4.1 \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ at 298 K.

Reliability

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

Comments on Preferred Values

The measurement of k by Dominé et al. (1992) is more direct than the original study of Tyndall and Ravishankara (1989) in which the rate coefficient was derived by a complex analysis of the reaction system. However, there are still a number of uncertainties in the study by Dominé et al. (1992), who consider their quoted value of k to be preliminary. The study by Borissenko et al. (2003) is a relative rate study based on $\text{CH}_3\text{SO} + \text{NO}_2$ that was also investigated by Kukui et al. (2000). The branching ratio for the SO_2 -forming reaction channel as well as the relative rate constant have been obtained relative to the reference reaction $\text{CH}_3\text{SO} + \text{NO}_2$ over a comparable pressure range. The branching ratio for SO_2 formation in $\text{CH}_3\text{SO} + \text{NO}_2$ obtained by Borissenko et al. (2003) is a factor of two larger across the studied pressure range compared to the earlier study by Kukui et al. (2000) which, however, does not directly affect k . Owing to the fact that the value of k by Borissenko et al. (2003) is within the uncertainty limit obtained by Dominé et al. (1992) the upper limiting k value of the latter is recommended because the pressure range extends to 880 mbar.

References

- Borissenko, D., Kukui, A., Laverdet, G. and Le Bras, G.: J. Phys. Chem. 107A, 1155, 2003.
Dominé, F., Ravishankara, A. R. and Howard, C. J.: J. Phys. Chem. 96, 2171, 1992.
Kukui, A., Bossoutrot, V., Laverdet, G. and Le Bras, G.: J. Phys. Chem. A 104, 935, 2000.
Tyndall, G. S. and Ravishankara, A. R.: J. Phys. Chem. 93, 2426, 1989.