

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet SO_x23

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

HO + CH₃SSCH₃ → products

Rate coefficient data

<i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
5.9 × 10 ⁻¹¹ exp[(380 ± 160)/ <i>T</i>] (1.98 ± 0.18) × 10 ⁻¹⁰	249-367 298	Wine et al., 1981	FP-RF
6.2 × 10 ⁻¹¹ exp[(410 ± 210)/ <i>T</i>] (2.39 ± 0.30) × 10 ⁻¹⁰ (2.4 ± 0.9) × 10 ⁻¹⁰	297-366 297 298	Abbatt et al., 1992 Dominé and Ravishankara, 1992	DF-LIF (a)
<i>Relative Rate Coefficients</i>			
(2.40 ± 0.86) × 10 ⁻¹⁰	297 ± 2	Cox and Sheppard, 1980	RR (b)

Comments

- (a) Discharge-flow system with photoionization-MS detection of CH₃SOH and CH₃S product species. The temporal profiles of these product species yielded the cited rate coefficient. The CH₃S radical formation yield from the HO radical reaction with CH₃SSCH₃ was measured to be 0.28 ± 0.20 using a pulsed laser photolysis system with LIF detection of CH₃S. The photolysis of CH₃SSCH₃ at 266 nm was used to normalize the CH₃S radical signal, with the CH₃S radical formation yield from the photolysis of CH₃SSCH₃ being 1.8 ± 0.2 at 248 nm (Turnipseed et al., 1993).
- (b) A rate coefficient ratio of $k(\text{HO} + \text{CH}_3\text{SSCH}_3)/k(\text{HO} + \text{ethene}) = 28 \pm 10$ was measured by GC analyses of CH₃SSCH₃ and ethene in irradiated HONO-CH₃SSCH₃-ethene-air mixtures at atmospheric pressure. The measured rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{ethene}) = 8.57 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 297 K and atmospheric pressure of air (Atkinson, 1997).

Preferred Values

$k = 2.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 7.0 \times 10^{-11} \exp(350/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250-370 K.

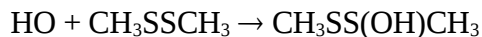
Reliability

$\Delta \log k = \pm 0.10$ at 298 K.

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

Comments on Preferred Values

The absolute rate coefficients of Wine et al. (1981), Abbatt et al. (1992) and Dominé and Ravishankara (1992) are in excellent agreement. The preferred values are derived from a least-squares analysis of the absolute rate coefficients of Wine et al. (1981) and Abbatt et al. (1992). The magnitude of the rate coefficient and the negative temperature dependence indicates that the reaction proceeds by initial HO radical addition to the S atoms:



Dominé and Ravishankara (1992) measured a CH₃S yield of 0.28 ± 0.20, independent of pressure (73-640 mbar) and diluent gas (N₂ and SF₆) at 298 K, indicating that products other than CH₃S and CH₃SOH are formed in this reaction. Butkovskaya and Setser (1999), from a study of the IR chemiluminescence from the reactions of HO and DO radicals with CH₃SSCH₃, concluded that the major reaction pathway is that to form CH₃SH (or CH₃SD) + CH₃SO, with these products dominating by a factor of ≥3 over formation of CH₃S + CH₃SOH (1999). Hence the studies of Dominé and Ravishankara (1992) and Butkovskaya and Setser (1999) are not inconsistent.

References

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Butkovskaya, N. I. and Setser, D. W.: Chem. Phys. Lett. 312, 37, 1999.
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Turnipseed, A. A., Barone, S. B. and Ravishankara, A. R.: J. Phys. Chem. 97, 5926, 1993.
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