

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet SO_x21

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

HO + CH₃SH → products

Rate coefficient data

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Temp./K | Reference | Technique/ Comments |
|--|-------------|------------------------|------------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $8.89 \times 10^{-12} \exp[(398 \pm 151)/T]$ | 300-423 | Atkinson et al., 1977 | FP-RF |
| $(3.39 \pm 0.34) \times 10^{-11}$ | 300 | | |
| $1.15 \times 10^{-11} \exp[(338 \pm 100)/T]$ | 244-366 | Wine et al., 1981 | FP-RF |
| $(3.37 \pm 0.41) \times 10^{-11}$ | 298 | | |
| $1.01 \times 10^{-11} \exp[(347 \pm 59)/T]$ | 254-430 | Wine et al., 1984 | FP-RF |
| 3.24×10^{-11} | 298 | | |
| 3.69×10^{-11} | 270 | Hynes and Wine, 1987 | PLP-LIF (a) |
| 3.17×10^{-11} | 300 | | |
| <i>Relative Rate Coefficients</i> | | | |
| $(9.68 \pm 0.97) \times 10^{-11}$ | 297 ± 2 | Cox and Sheppard, 1980 | RR (b) |
| $(3.72 \pm 0.37) \times 10^{-11}$ | 300 | Barnes et al., 1986 | RR (c) |
| $(3.50 \pm 0.49) \times 10^{-11}$ | 313 | | |

Comments

- The rate coefficients were observed to be independent of total pressure and of the presence or absence of O₂, up to 196 mbar O₂ at 270 K or 933 mbar O₂ at 300 K.
- HO radicals were generated by the photolysis of HONO-NO-air mixtures at atmospheric pressure. The decay of CH₃SH was measured relative to that of C₂H₄ by GC, and the relative rate coefficient placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{C}_2\text{H}_4) = 8.57 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 297 K and atmospheric pressure of air (Atkinson, 1997).
- HO radicals were generated by the photolysis of H₂O₂ in N₂ at atmospheric pressure. The decay of CH₃SH was measured relative to that for propene by GC, and the relative rate coefficients placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{propene}) = 4.85 \times 10^{-12} \exp(504/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at atmospheric pressure of air (Atkinson, 1997).

Preferred Values

$k = 3.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 9.9 \times 10^{-12} \exp(356/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240-430 K.

Reliability

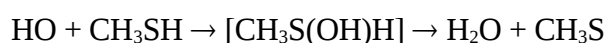
$\Delta \log k = \pm 0.10$ at 298 K.

$\Delta(E/R) = \pm 100 \text{ K}$.

Comments on Preferred Values

The preferred values are based upon a least-squares analysis of the absolute rate coefficients of Atkinson et al. (1977), Wine et al. (1981; 1984) and Hynes and Wine (1987), which are in excellent agreement. The relative rate study of Barnes et al. (1986) shows that erroneous rate coefficient data are obtained in the presence of O₂ and NO, thus accounting for the much higher value of Cox and Sheppard (1980).

The study of Hynes and Wine (1987) shows that there is no observable effect of O₂ on the measured rate coefficient, and the rate coefficients at 298 K for the reactions of the HO radical with CD₃SH⁴ and CH₃SD³ are within 15% of that for HO + CH₃SH. These data indicate (Wine et al., 1984; Hynes and Wine, 1987) that the reaction proceeds via initial addition of HO to form the adduct CH₃S(OH)H (Wine et al., 1984). Tyndall and Ravishankara (1989) have determined, by monitoring the CH₃S radical by LIF, a CH₃S radical yield from the reaction of the HO radical with CH₃SH of 1.1 ± 0.2. The reaction then proceeds by



Butkovskaya and Setser (1999) concluded, from observations of the IR chemiluminescent spectra of reactions of HO and DO radicals with CH₃SH and CH₃SD, that direct H-atom abstraction from the CH₃ group accounts for 11 ± 4% of the total of the DO radical reactions and 24 ± 8% of the total of the HO radical reactions.

References

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