$CH_3S + O_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$<8 \times 10^{-14}$	298	Black and Jusinski, 1986	PLP-LIF
$(4.1 \pm 2.0) \times 10^{-12}$	298	Tyndall and Ravishankara, 1989	PLP-LIF
$(5.7 \pm 1.4) \times 10^{-12}$	300	Dominé et al., 1992	(a)
$1.98 \times 10^{-12} \exp[(290 \pm 40)/T]$	295-359	Turnipseed et al., 1993	(b)
5.16×10^{-12}	298		
$(1.02 \pm 0.30) \times 10^{-12} \exp[(432 \pm 77)/T]$	259-381	Martinez et al., 2000	(c)
$(4.6 \pm 0.6) \times 10^{-12}$	298		

Comments

(a) Discharge flow study. CH_3S radicals were generated by reaction of Cl with CH_3SH. Photoionization mass spectrometry was used to monitor CH_3S radicals. C_2F_3Cl was added to scavenge OH radicals and hence suppress OH radical-initiated chain reaction which regenerates CH_3S. Some curvature was observed on [CH_3S] logarithmic decay plots in excess O_3. The initial slope was used to calculate k.

(b) Pulsed laser photolysis of $(CH_3)_2S$-O_3-O_2-He (193 nm) mixtures. [CH_3S] was monitored by LIF. Pressure range 27-267 mbar (20-200 Torr).

(c) Pulsed laser photolysis of CH_3SCH_3/O_3 mixtures at 193 nm in the range 33-400 mbar He and 259-381 K. [CH_3S] was monitored by LIF leading to the pressure-independent k with a slight negative activation energy. No regeneration of CH_3S was observed under the chosen experimental conditions (5-15% O_2 impurity relative to [O_3], observation of CH_3S over up to 7-10 lifetimes).

Preferred Values

$k = 4.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = (1.15 \pm 0.30) \times 10^{-12} \exp[(432 \pm 77)/T]$ cm^3 molecule^{-1} s^{-1} over the temperature range 259-381 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

It is difficult to study this reaction because in some conditions rapid chain processes involving the reaction products occur to regenerate CH_3S radicals (Tyndall and Ravishankara, 1989; Dominé et al., 1992; Tunipseed et al., 1993). This complication appears to be absent in the most recent studies of Turnipseed et al. (1993) and Martinez et al. (2000) under the conditions used for rate coefficient determinations. Their value of *k* at 298 K is in good agreement with other studies in which care was taken to allow for this complication (Tyndall and Ravishankara, 1989; Dominé et al., 1992). The mean of the values from the two most recent studies (Turnipseed et al., 1993; Martinez et al., 2000) is taken as our recommended value at 298 K.

There are two studies of the temperature dependence of *k* (Turnipseed et al., 1993; Martinez et al., 2000). The rate parameters resulting from the most recent study covering the widest temperature range are accepted once the pre-exponential factor is adjusted to yield the recommended value of *k* at 298 K.

References

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