IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet SOx70

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

$CH_3SCH_2O_2 + CH_3SCH_2O_2 \rightarrow CH_3SCH_2OH + CH_3SCHO + O_2$ (1)
$\rightarrow 2CH_3SCH_2O + O_2$ (2)

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leq 7.9 \times 10^{-12}$	298	Wallington et al., 1993	(a)
$(1.2 \pm 0.5) \times 10^{-11}$	298	Urbanski et al., 1997	(b)

Comments

(a) k is defined by $-d[CH_3SCH_2O_2]/dt = 2k[CH_3SCH_2O_2]^2$. Pulse radiolysis study of CH_3SCH_3-O_2-SF_6 mixtures with monitoring of $CH_3SCH_2O_2$ radical concentrations by UV absorption with $\sigma_{250} = (4.3 \pm 0.7) \times 10^{-18}$ cm^2 molecule^{-1}. The observed value of $k_{obs} = (7.9 \pm 1.4) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} is an upper limit to k because of the possibility of secondary reactions giving rise to an increasing decay rate of $CH_3SCH_2O_2$ radicals.

(b) $CH_3SCH_2O_2$ radicals were generated by the 248 nm pulsed laser photolysis of $C(O)Cl_2$-CH_3SCH_3-O_2-N_2 mixtures at 27 mbar total pressure, and the products HCl and HCHO were monitored by TDLAS. The importance of secondary reactions (including from photolysis products of CH_3SCH_3) was investigated experimentally and by computer modeling, and a yield of HCHO from the self-reaction of $CH_3SCH_2O_2$ radicals of 0.97 ± 0.08 was obtained by extrapolation to zero CH_3SCH_3 concentration. The cited value of the rate coefficient was obtained from numerical modeling. It was concluded that the reaction leads to formation of CH_3SCH_2O radicals via pathway (2), with the CH_3SCH_2O radical rapidly decomposing to form HCHO (and CH_3S).

Preferred Values

$k = 1.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2/k = 1.0$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K
$\Delta(k_2/k) = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred value is an average of the measured overall rate coefficients of Wallington et al. (1993) and Urbanski et al. (1997). The product data of Urbanski et al. (1997) show that the reaction proceeds by channel (2), and that the alkoxy radical CH_3SCH_2O decomposes: $CH_3SCH_2O \rightarrow CH_3S + HCHO$. Reaction of the CH_3S radical with the $CH_3SCH_2O_2$ radical could lead to an enhanced decay rate of the $CH_3SCH_2O_2$ radicals, and hence the preferred value of the rate coefficient is rigorously an upper limit.

References

Urbanski, S. P., Stickel, R. E., Zhao, Z. and Wine, P. H.: J. Chem. Soc. Faraday Trans. 93, 2813, 1997.
Wallington, T. J., Ellermann, T. and Nielsen, O. J.: J. Phys. Chem. 97, 8442, 1993.