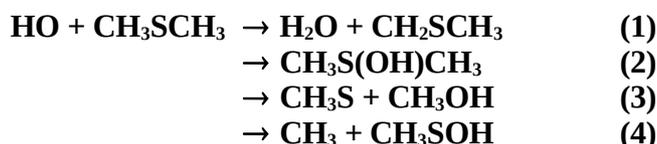


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet Sox22

Website: <http://iupac.pole-ether.fr>. See website for latest evaluated data. Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission.

This data sheet updated: 1st August 2006.



$$\Delta H^\circ(1) = -105 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) \approx -43 \text{ kJ}\cdot\text{mol}^{-1} \text{ (uses } \Delta H_f \text{ CH}_3\text{S(OH)CH}_3 = 43 \text{ kJ}\cdot\text{mol}^{-1} \text{ from Turnipseed et al., 1996)}$$

$$\Delta H^\circ(3) = -77 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(4) \approx 0 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data ($k = k_1 + k_2 + k_3 + k_4$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$k_1 = 6.8 \times 10^{-11} \exp[-(138 \pm 46)/T]$	248-363	Wine et al., 1981	FP-RF
$k_1 = (4.26 \pm 0.56) \times 10^{-12}$	298		
$k_1 = (3.22 \pm 1.16) \times 10^{-12}$	293	Martin et al., 1985	DF-EPR
$k_1 = 2.5 \times 10^{-12} \exp[(130 \pm 102)/T]$	297-400	Wallington et al., 1986	FP-RF
$k_1 = 4.46 \times 10^{-12}$	297		
$k = (6.28 \pm 0.10) \times 10^{-12}$ (1 bar of air)	298	Hynes et al., 1986	PLP-LIF (a)
$k_1 = 1.36 \times 10^{-11} \exp[-(332 \pm 96)/T]$	276-397	Hynes et al., 1986	FP-RF
$k_1 = 4.46 \times 10^{-12}$	298		
$k_1 = 1.18 \times 10^{-11} \exp[-(236 \pm 150)/T]$	260-393	Hsu et al., 1987	DF-RF (b)
$k_1 = (5.54 \pm 0.15) \times 10^{-12}$	298		
$k_1 = (3.50 \pm 0.20) \times 10^{-12}$	295	Nielsen et al., 1989	PR-UV
$k_1 = 1.35 \times 10^{-11} \exp[-(285 \pm 135)/T]$	297-368	Abbatt et al., 1992	DF-LIF (c)
$k_1 = (4.98 \pm 0.46) \times 10^{-12}$	297 ± 2		
$k_1 = (4.95 \pm 0.35) \times 10^{-12}$	298	Barone et al., 1996	PLP-LIF
<i>Relative Rate Coefficients</i>			
$k_1 = (5.00 \pm 0.50) \times 10^{-12}$	296	Wallington et al., 1986	RR-FTIR (d)
$k = (8.0 \pm 0.20) \times 10^{-12}$ (1 bar air)	296		
$k_1 = (4.40 \pm 0.40) \times 10^{-12}$	298	Barnes et al., 1988	RR-GC (e)
$k = (8.00 \pm 0.50) \times 10^{-12}$ (1 bar air)	298		
$k_1 = 1.56 \times 10^{-12} \exp[(369 \pm 27)/T]$	250-299	Albu et al., 2006	RR-FTIR (f)
[O ₂] = 0 mbar			
$k = 1.31 \times 10^{-14} \exp[(1910 \pm 69)/T]$			
[O ₂] = 207 mbar			
$k = 1.56 \times 10^{-12} \exp[(1587 \pm 24)/T]$			
[O ₂] = 380 mbar			
$k = (7.80 \pm 1.80) \times 10^{-12}$ (1 bar air)	298		
<i>Branching Ratios</i>			
$k_1/k = 0.84 \pm 0.15$	298	Stickel et al., 1993	(g)
$k_1/k = 0.84 \pm 0.26$	298	Turnipseed et al., 1996	(h)
$k_3/k < 0.04$	298	Turnipseed et al., 1996	(i)
$k_4/k < 0.07$	298	Zhao et al., 1996	(j)

Comments

- (a) The effect of O₂ was investigated over the temperature range 261-321 K. The measured rate coefficient was observed to depend on the O₂ concentration, and the rate coefficient given in the table is that measured at 1 bar (750 Torr) total pressure of air. The rate coefficient measured in the absence of O₂ is ascribed to reaction (1).
- (b) Rate coefficient not affected by the addition of up to 1.3 mbar (1 Torr) of O₂.
- (c) HO generated from the H + NO₂ reaction. The total pressure was varied over the range 14.1-130 mbar (10.6-97.5 Torr) of N₂. The measured rate coefficient was invariant to the total pressure over this range.
- (d) Reference reactant was cyclohexane. The measured ratio $k(\text{HO} + \text{CH}_3\text{SCH}_3) / k(\text{HO} + \text{cyclohexane})$ was converted to an absolute rate coefficient using $k(\text{HO} + \text{cyclohexane}) = 6.92 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 2003).
- (e) Reference reactant was ethene. Rate coefficient ratios, $k(\text{HO} + \text{CH}_3\text{SCH}_3) / k(\text{HO} + \text{ethene})$ at various partial pressures of O₂ in a total pressure of 1 bar were converted to an absolute rate coefficient using $k(\text{HO} + \text{ethene}) = 8.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- (f) Mainly C₂H₄ but also C₃H₆ and 2-methylpropene were used as reference reactants with $k(\text{HO} + \text{C}_2\text{H}_4) = 1.96 \times 10^{-12} \exp(438/T)$, $k(\text{HO} + \text{C}_3\text{H}_6) = 4.85 \times 10^{-12} \exp(504/T)$, $k(\text{HO} + \text{C}_2\text{H}_4) = 9.47 \times 10^{-12} \exp(504/T)$ (Atkinson, 1997).
- (g) For the reaction DO + CH₃SCH₃, HDO was monitored by tuneable diode laser absorption spectroscopy, and the branching ratio obtained by assuming a unit HDO yield from the DO radical reaction with *n*-hexane and cyclohexane. The branching ratio was independent of total pressure of N₂ [13-40 mbar (10-30 Torr)], temperature (298-348 K) and replacement of 13 mbar (10 Torr) total pressure of N₂ by 13 mbar total pressure of O₂. From the temporal profiles of the HDO signals, rate coefficients k_1 for the reaction of the DO radical with CH₃SCH₃ of $(5.4 \pm 0.4) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 13 mbar (10 Torr) N₂, $(5.8 \pm 1.9) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 40 mbar (30 Torr) N₂, and $(4.4 \pm 1.0) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 348 K and 13 mbar (10 Torr) N₂ were also obtained, in agreement with the rate coefficients for the HO radical reaction.
- (h) Indirect measurement of CH₃SCH₂ by addition of O₂ and NO and measuring CH₃S formation by LIF.
- (i) Direct detection of CH₃S by LIF.
- (j) Direct detection of CH₃ using TDLAS.

Preferred Values

$$k_1 (298 \text{ K}) = 4.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_2 (298 \text{ K}, 1 \text{ bar air}) = 2.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_1 = 1.12 \times 10^{-11} \exp(-250/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range 240-400 K.}$$

$$k_2 = 9.5 \times 10^{-39} [\text{O}_2] \exp(5270/T) / \{1 + 7.5 \times 10^{-29} [\text{O}_2] \exp(5610/T)\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range 240-360 K at pressures close to 1 bar.}$$

Reliability

$$\Delta \log k_1 = \pm 0.10 \text{ at 298 K.}$$

$$\Delta(E/R) = \pm 150 \text{ K.}$$

$$\Delta \log k_2 = \pm 0.2 \text{ K at 1 bar of air.}$$

Comments on Preferred Values

It is now recognised (Hynes et al., 1986; Barone et al., 1996; Atkinson, 1994; Wallington et al., 1986; Barnes et al., 1988; Albu et al., 2006) that this reaction proceeds via the two reaction pathways (1) and (2). The CH₃S(OH)CH₃ adduct radical decomposes sufficiently rapidly such that in the absence of O₂ only the rate coefficient k_1 is measured. In the presence of O₂ the CH₃S(OH)CH₃ radical reacts by CH₃S(OH)CH₃ + O₂ → products. Hence only in the presence of O₂ is the addition channel (2) observed, with the rate coefficient being dependent on the O₂ concentration but, to at least a first approximation, not

on the concentration of other third bodies such as N₂, Ar or SF₆ (Hynes et al., 1985; Abbatt et al., 1992). HO₂ is formed at ≈ 50 % yield in the reaction of CH₃S(OH)CH₃ with O₂.

The most recent absolute rate coefficients measured in the absence of O₂ (Wine et al., 1981; Hynes et al., 1986; Hsu et al., 1987; Abbatt et al., 1992; Barone et al., 1996) confirm that the earlier absolute rate coefficients of Atkinson et al. (1978) and Kurylo (1978) are erroneously high, and those of Mac Leod et al. (1984) were in error because of wall reactions. Wine et al., (1981), Hynes et al. (1986), Hsu et al. (1987) and Abbatt et al. (1992) all determined a positive dependence on temperature for the abstraction process. In contrast, Wallington et al. (1986) and Albu et al. (2006) found slight negative temperature dependences. Albu et al. (2006) could not rule out that this is due to the presence of O₂ impurity in their relative rate experiments at atmospheric pressure. The relative rate study of Wallington et al. (1986) showed that previous relative studies carried out in the presence of NO were dubious. The preferred rate coefficients k_1 for the abstraction channel (1) are therefore based on the studies of Wine et al. (1981), Hynes et al. (1986), Hsu et al. (1987), Abbatt et al. (1992) and Barone et al. (1996).

The dependence of k on [O₂] has been investigated by Wallington et al. (1986), Barnes et al. (1988), Hynes et al. (1986), Williams et al. (2001) and Albu et al. (2006). Hynes et al. (1986), Williams et al. (2001) and Albu et al. (2006) show that the degree of enhancement of the overall rate coefficient due to O₂ is strongly temperature dependent.

The rate coefficient given for the HO radical addition channel (2) utilises the data of Hynes et al. (1986), Williams et al. (2001) and Albu et al. (2006). The expression for k_2 reproduces the [O₂] and temperature dependence of k_{obs} ($k_{\text{obs}} = k_1 + k_2 + k_3 + k_4 \equiv k_1 + k_2$) of Hynes et al. (1986), Williams et al. (2001) and Albu et al. (2006) at pressures close to one atmosphere (where the rate coefficients for HO addition to CH₃SCH₃ and the reverse dissociation step may be in the falloff region). The recommended parameterisation returns a room temperature overall rate coefficient ($k_1 + k_2$) for 1 bar of air of $k = 7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which lies between values of ≈ $8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ obtained in relative rate measurements in one atmosphere of air (Wallington et al., 1986; Barnes et al., 1988; Albu et al., 2006) and the Hynes et al. (1986) absolute value of $6.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The agreement at lower temperatures is even better than this.

References

- Abbatt, J. P. D., Fenter, F. F., Anderson, J. G.: *J. Phys. Chem.*, 96, 1780-1785, 1992.
- Albu, M., Barnes, I., Becker, K. H., Patroescu-Klotz, I., Mocanu, R and Benter, T.: *Phys. Chem. Chem. Phys.*, 8, 728-736, 2006.
- Atkinson, R., Perry, R. A. and Pitts, Jr. J. N.: *Chem. Phys. Lett.*, 54, 14-18, 1978.
- Atkinson, R.: *J. Phys. Chem. Ref. Data, Monograph 2*, 1, 1994.
- Atkinson, R.: *J. Phys. Chem. Ref. Data*, 26, 215-290, 1997.
- Atkinson, R.: *Atmos. Chem. Phys.*, 3, 2233, 2003
- Barnes, I., Bastian, V., and Becker, K. H.: *Int. J. Chem. Kinet.*, 20, 415-431, 1988.
- Barone, S. B., Turnipseed, A. A., and Ravishankara, A. R.: *J. Phys. Chem.*, 100, 14694-14702, 1996.
- Hsu, Y.-C., Chen, D.-S., and Lee, Y.-P.: *Int. J. Chem. Kinet.*, 19, 1073-1082, 1987.
- Hynes, A. J., Wine, P. H., and Semmes, D. H.: *J. Phys. Chem.*, 90, 4148-4156, 1986.
- Kurylo, M. J.: *Chem. Phys. Lett.*, 58, 233-237, 1978.
- Mac Leod, H., Jourdain, J. L., Poulet, G., and Le Bras, G.: *Atmos. Environ.*, 18, 2621-2626, 1984.
- Martin, D., Jourdain, J. L., and Le Bras, G.: *Int. J. Chem. Kinet.*, 17, 1247-1261, 1985.
- Nielsen, O. J., Sidebottom, H. W., Nelson, L., Treacy, J. J., and O'Farrell, D. F.: *Int. J. Chem. Kinet.*, 21, 1101-1112, 1989.
- Stickel, R. E., Zhao, Z., and Wine, P. H.: *Chem. Phys. Lett.*, 212, 312-318, 1993.
- Turnipseed, A. A., Barone, S. B., and Ravishankara, A. R., *J. Phys. Chem.*, 100, 14703-14713, 1996.
- Wallington, T. J., Atkinson, R., Tuazon, E. C., and Aschmann, S. M.: *Int. J. Chem. Kinet.*, 18, 837-846, 1986.
- Williams, M. B., Campuzano-Jost, P., Bauer, D., and Hynes, A. J.: *Chem. Phys. Lett.*, 344, 61-67, 2001.

Wine, P. H., Kreutter, N. M., Gump, C. A., and Ravishankara, A. R.: J. Phys. Chem., 85, 2660- 2665, 1981.
Zhao, Z., Stickel, R. E., and Wine, P. H.: Chem. Phys. Lett., 251, 59-66, 1996.