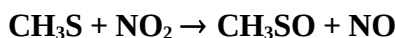


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet SOx60

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: 3rd July 2005.



$$\Delta H^\circ = -138 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$8.3 \times 10^{-11} \exp[(80 \pm 60)/T]$	295-511	Balla et al., 1986	PLP-LIF
9.8×10^{-11}	295		
$(6.10 \pm 0.90) \times 10^{-11}$	298	Tyndall and Ravishankara, 1989	PLP-LIF
$(5.1 \pm 0.9) \times 10^{-11}$	297	Dominé et al., 1990	DF-MS
$2.1 \times 10^{-11} \exp[(320 \pm 40)/T]$	242-350	Turnipseed et al., 1993	(a)
$(6.28 \pm 0.28) \times 10^{-11}$	298		
$(3.8 \pm 0.3) \times 10^{-11} \exp [(160 \pm 22)/T]$	263-381	Martínez et al., 1999	PLP-LIF(b)
$(6.52 \pm 0.65) \times 10^{-11}$	298		
$(4.3 \pm 1.0) \times 10^{-11} \exp [(241 \pm 62)/T]$	222-420	Chang et al., 2000	PLP-LIF(c)
$(10.1 \pm 0.5) \times 10^{-11}$	297		

Comments

- Pulsed laser photolysis at 193 nm or 248 nm of $(\text{CH}_3)_2\text{S}-\text{NO}_2$ or $(\text{CH}_3)_2\text{S}_2-\text{NO}_2$ mixtures in bath gas of He, N_2 or SF_6 . $[\text{CH}_3\text{S}]$ was monitored by LIF. Pressure varied over the range of 27-267 mbar (20-200 Torr) He.
- Pulsed laser photolysis of CH_3SCH_3 (193 nm) or CH_3SSCH_3 (248 nm) mixed with NO_2 in 40-400 Torr He bath gas, detection of CH_3S by LIF. Addition of up to 5 Torr O_2 (as scavenger of CH_3 formed in photolysis of CH_3SCH_3) had no influence on the rate coefficient.
- Pulsed laser photolysis of CH_3SSCH_3 (248 nm) mixed with NO_2 in 73-269 Torr He bath gas, detection of CH_3S by LIF.

Preferred Values

$$k = 6.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 3.0 \times 10^{-11} \exp(210/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 240\text{-}350 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.15 \text{ at } 298 \text{ K.}$$

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

Comments on Preferred Values

The recommended value at 298 K is the mean of the studies of Tyndall and Ravishankara (1989), Dominé et al. (1990), Turnipseed et al. (1993) and Martínez et al. (1999), which are in good agreement. There are four studies of the temperature dependence of k , all giving a negative value of E/R but differing significantly in magnitude. Two studies, Balla et al. (1986) and Chang et al. (2000) obtained values of k nearly twice as large as those found in the other studies. It has been suggested (Tyndall et al., 1989) that this could result from secondary chemistry arising from the higher radical concentrations used in the work of Balla et al. (1986) though this argument does not apply to Chang et al. (2000). The temperature dependent expression for k is derived by fitting to the data of Turnipseed et al. (1993) and Martínez et al. (1999) and adjusting for the recommended value of k at 298 K.

The CH_3SO yield has been determined by Dominé et al. (1990) to be 1.07 ± 0.15 ; the yield of NO was determined by Tyndall and Ravishankara (1989) to be 0.8 ± 0.2 . End product studies (Barnes et al. 1987) are in agreement with this conclusion. Theoretical calculations suggest the intermediacy of a CH_3SNO_2 association complex (Wang et al., 2002).

References

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