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

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$CH_3S + NO_2 \rightarrow CH_3SO + NO$

ΔH° = -138 kJ·mol^{-1}

Rate coefficient data

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

Comments

(a) Pulsed laser photolysis at 193 nm or 248 nm of $(CH_3)_2S$-NO_2 or $(CH_3)_2S_2$-NO_2 mixtures in bath gas of He, N_2 or SF_6. [CH_3S] was monitored by LIF. Pressure varied over the range of 27-267 mbar (20-200 Torr) He.

(b) 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.

(c) 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 x 10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K.
k = 3.0 x 10^{-11} exp(210/T) cm^3 molecule^{-1} s^{-1} over the temperature range 240-350 K.

Reliability

$\Delta \log k$ = ± 0.15 at 298 K.
$\Delta(E/R)$ = ± 200 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 Martìnez 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 Martìnez 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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