IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet SOx33

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$NO_3 + CH_3SCH_3 \rightarrow CH_3SCH_2 + HNO_3$

ΔH° = -35 kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
(1.0 ± 0.2) x 10^{-12}	278-318	Tyndall *et al*., 1986[1]	MM-A
(9.9 ± 3.5) x 10^{-13}	298		
(7.5 ± 0.5) x 10^{-13}	298 ± 2	Wallington *et al*., 1986[2]	FP-A
4.7 x 10^{-13} exp[(170 ± 130)/T]	280-350	Wallington *et al*., 1986[3]	FP-A
(8.1 ± 1.3) x 10^{-13}	298 ± 2		
1.79 x 10^{-13} exp[(530 ± 40)/T]	256-376	Dlugokencky and Howard, 1988[4]	F-LIF
(1.06 ± 0.13) x 10^{-12}	298		
(1.3 ± 0.3) x 10^{-12}	298 ± 1	Daykin and Wine, 1990[5]	PLP-A
Relative Rate Coefficients			
(9.92 ± 0.20) x 10^{-13}	296 ± 2	Atkinson *et al*., 1984[6]	RR (a)

Comments

(a) NO_3 radicals were generated by the thermal decomposition of N_2O_5 in air at 1 atmosphere total pressure. The concentrations of CH_3SCH_3 and *trans*-2-butene were measured by GC, and the measured rate coefficient ratio of $k(NO_3 + CH_3SCH_3)/k(NO_3 + trans\text{-2-butene}) = 2.55 \pm 0.05$ is placed on an absolute basis by use of a rate coefficient of $k(NO_3 + trans\text{-2-butene}) = 3.89 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 296 K.[7]

Preferred Values

k = 1.1 x 10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K.
k = 1.9 x 10^{-13} exp(520/T) cm^3 molecule^{-1} s^{-1} over the temperature range 250-380 K.

Reliability

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

Comments on Preferred Values

The absolute[1-5] and relative[6] rate coefficient studies are in reasonable agreement, although the data of Wallington *et al*.[2,3] are ~20% lower than the other data.[1,4-6] The absolute rate coefficients measured by Tyndall *et al*.,[1] Dlugokencky and Howard[4] and Daykin and Wine[5] and the relative rate coefficient of Atkinson *et al*.[6] have been fitted to an Arrhenius expression to obtain the preferred values. The experimental data show that the rate coefficient is independent of total pressure over the range ~0.0013-1 bar.

The magnitude of the rate constant and the negative temperature dependence indicates that this reaction proceeds by initial addition of the NO_3 radical to the S atom. The kinetic data of Daykin and Wine[5] and Jensen *et al*.[8] for CH_3SCH_3 and CD_3SCD_3 show that the rate determining step involves H- (or D-) atom abstraction, indicating that the reaction is

$$NO_3 + CH_3SCH_3 \leftrightarrow [CH_3S(ONO_2)CH_3]^{\ddagger} \rightarrow CH_3SCH_2 + HNO_3$$

This conclusion is consistent with the product studies of Jensen *et al*.[8,9] and Butkovskaya and Le Bras.[10] Butkovskaya and Le Bras[10] used a DF-MS technique to show that the alternative reaction pathway yielding $CH_3SONO_2 + CH_3$ accounts for <2% of the overall reaction at 298 K and 1.3 mbar total pressure.

References

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