IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet SOx48

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$SO_3 + NH_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
(6.9 ± 1.5) x 10^{-11}	298	Shen, Suto and Lee, 1990	(a)
(2.0 ± 0.6) x 10^{-11}	295	Lovejoy and Hanson, 1996	(b)
(1.8 ± 0.5) x 10^{-11}	300	Lovejoy, 1997	(c)

Comments

(a) Flow system with NH_3 in large excess. [SO_3] monitored by observation of SO_2 fluorescence in range 280-390 nm from photofragmentation of SO_3 by 147 nm radiation. He carrier gas at 1.3-2.7 mbar (1-2 Torr) total pressure.

(b) Laminar flow reactor study with N_2 as the carrier gas in the pressure range 13-533 mbar (10-400 Torr), using CIMS detection. Both the decrease of SO_3 as well as the formation of $SO_3 \cdot NH_3$ were monitored. The rate constant was pressure dependent with $k_o = (3.9 \pm 0.8)$ x 10^{-30} cm^6 molecule^{-2} s^{-1} and $k_\infty = (4.7 \pm 1.4)$ x 10^{-11} cm^3 molecule^{-1} s^{-1} at 295 K.

(c) Experimental details in (b) except for a reduced pressure range of 27-106 mbar (20-80 Torr) of N_2 and a temperature range of 280-340 K. The rate constant is pressure dependent with $k_o^{300} = (3.6 \pm 0.4)$ x 10^{-30} cm^6 molecule^{-2} s^{-1} and $k_\infty^{300} = (4.3 \pm 1.2)$ x 10^{-11} cm^3 molecule^{-1} s^{-1}. A third law determination of the reaction enthalpy for $SO_3 + NH_3 \leftrightarrow H_3NSO_3$ resulted in $\Delta H^o_{298} = -100.4 \pm 4.2$ kJ mol^{-1}.

Preferred Values

$k = 2.0$ x 10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K and 1 Atm.

Reliability
     $\Delta \log k = \pm 0.2$ at 298 K.

Comments on Preferred Values
     The preferred value is given for one atmosphere from the work of Lovejoy and Hanson (1996) in view of the extended pressure range used. The extrapolation of k to 1 atm has been performed following the Troe formalism. The more recent work Lovejoy and Hanson, 1996; Lovejoy, 1997) showed the product of the reaction to be the association complex $NH_3 \cdot SO_3$, sulfamic acid.

References

Shen, G., Suto, M. and Lee, L. C.: J. Geophys. Res. 95, 13981, 1990.
Lovejoy, E. R.: J. Phys. Chem. A 101, 4950, 1997.
Lovejoy, E. and Hanson, D. R.: J. Phys. Chem. 100, 4459, 1996.