IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet SOx47

This data sheet updated: 20th November 2001.

$SO_3 + H_2O \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	**Reference**	Technique/ Comments
Absolute Rate Coefficients			
9×10^{-13}	300	Castleman et al., 1974	F-MS
$\leq(5.7 \pm 0.9) \times 10^{-15}$	298	Wang et al., 1989	(a)
$\leq 2.4 \times 10^{-15}$	~298	Reiner and Arnold, 1993	(b)
$(1.2 \pm 0.2) \times 10^{-15}$	298	Reiner and Arnold, 1994	(b)
Complex mechanism	295	Kolb et al., 1994	(c)
Complex mechanism	250-360	Lovejoy et al., 1996	(d)
Complex mechanism	283-370	Jayne et al., 1997	(e)

Comments

(a) Flow system with He and N_2 as carrier gases and H_2O in large excess over SO_3. SO_3 was monitored by the photodissociation of SO_3 at 147 nm and detection of SO_2 fluorescence at 300-390 nm. A halocarbon wall coating of the flow tube was used.

(b) Fast flow system at pressures of 31 to 260 mbar of synthetic air, using CIMS to detect SO_3, H_2O and H_2SO_4. Small corrections for wall reactions were applied.

(c) Atmospheric pressure turbulent flow reactor using N_2 as a carrier gas in the pressure range 133-1013 mbar (100-760 Torr) and CIMS detection. Both the decrease in SO_3 as well as the increase in H_2SO_4 were monitored. The rate law was found to be first-order in $[SO_3]$ and second-order in $[H_2O]$. Rate constants ranging from 2×10^{-10} to 1.4×10^{-12} cm^3 molecule $^{-1}$ s^{-1} were estimated based on H_2O dimers and the $SO_3 \cdot H_2O$ adduct, respectively.

(d) Laminar flow reactor with detection by CIMS. The observations were consistent with rapid association of SO_3 with H_2O to form the adduct $H_2O \cdot SO_3$, which then reacts with water to form H_2SO_4.

(e) Details at (c). The pressure-independent first-order loss rate coefficient for SO_3 may be expressed as $k = (3.9 \pm 0.8) \times 10^{-41} \exp(6830/T)[H_2O]^2 s^{-1}$ over the range 283 to 370 K. The onset of H_2SO_4 homogeneous nucleation was observed at $[SO_3] > 10^{12}$ molecule cm^{-3}.

Preferred Values

$k = 5.7 \times 10^4$ s^{-1} at 298 K and 50% relative humidity.

Comments on Preferred Values

No recommendation was made on the basis of the work of Castleman et al. (1975), due to the likely interference of wall reactions in their work. The studies of Wang et al. (1989), Reiner and Arnold (1993, 1994) and Kolb et al. (1994) have now confirmed that suspicion. Wang et al. (1989) obtained an upper limit to the rate coefficient which is more than two orders of magnitude lower than the value of Castleman et al. (1975), by treatment of the flow tube walls to reduce wall effects, and the studies of Reiner and Arnold (1993, 1994) using the laminar flow tube method, obtain the lowest values for the rate constant (Reiner and Arnold, 1993; 1994). The flow studies of Kolb et al. (1994), Lovejoy et al. (1996) and Jayne et al. (1997) arrive at a rate law first order in SO_3 and second order in H_2O.

References

Castleman, Jr., A. W., Davis, R. E., Munkelwitz, H. R., Tang, I. N. and Wood, W. P.: Int. J. Chem. Kinet., Symp. 1, 629, 1975.

Jayne, J. T., Pöschl, U., Chen, Y., Dai, D., Molina, L. T., Worsnop, D. R., Kolb, C. E. and Molina, M. J.: J. Phys. Chem. A 101, 10000, 1997.

Kolb, C. E., Jayne, J. T., Worsnop, D. R., Molina, M. J., Meads, R. F. and Viggiano, A. A.: J. Am. Chem. Soc. 116, 10314, 1994.

Lovejoy, E. R., Hanson, D. R. and Huey, L. G.: J. Phys. Chem. 100, 19911, 1996.

Reiner, T. and Arnold, F.: Geophys. Res. Lett. 20, 2659, 1993.

Reiner, T. and Arnold, F.: J. Chem. Phys. 101, 7399, 1994.

Wang, X., Yin, Y. G., Suto, M., Lee, L. C. and O'Neal, H. E.: J. Chem. Phys. 89, 4853, 1989.