IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet SOx35

This data sheet updated: 19th November 2001.

HS + O_2 → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$<4 \times 10^{-17}$	298	Black, 1984[1]	PLP-LIF
$\leq 1 \times 10^{-17}$	298	Friedl, Brune and Anderson, 1985[2]	DF-LIF
$<1 \times 10^{-14}$	298	Schoenle, Rahman and Schindler, 1987[3]	DF-MS
$<4 \times 10^{-19}$	298	Stachnik and Molina, 1987[4]	PLP-UVA
$<1.5 \times 10^{-17}$	295	Wang, Lovejoy and Howard, 1987[5]	DF-LMR

Preferred Values

$k < 4 \times 10^{-19}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The reaction of HS with O_2 is so slow that attempts to measure the rate coefficient have yielded only upper limits that fall in the range 4×10^{-19} to 4×10^{-17} cm^3 molecule^{-1} s^{-1} at 298 K. The preferred value is from the study of Stachnik and Molina,[4] which gives the lowest upper limit and appears reliable.

In a theoretical study by Goumri *et al.*[6], the kinetics of the reaction HS + O_2 → HSOO were analyzed using RRKM theory with Gaussian-2 (G2) theory being used to calculate the thermochemistry. Under atmospheric conditions the rate constant is close to the low-pressure limit $k_0 = 9.2 \times 10^{-34}$ (T/298)$^{-1.69}$ cm^6 molecule^{-2} s^{-1} for T = 200-400 K. The low value of the S-O bond dissociation energy (91.5 kJ · mol^{-1}) implies that HSOO formation is unimportant in the atmosphere.

References

[1] G. Black, J. Chem. Phys. **80**, 1103 (1984).
[2] R. R. Friedl, W. H. Brune, and J. G. Anderson, J. Phys. Chem. **89**, 5505 (1985).
[3] G. Schoenle, M. M. Rahman, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **91**, 66 (1987).
[4] R. A. Stachnik and M. J. Molina, J. Phys. Chem. **91**, 4603 (1987).
[5] N. S. Wang, E. R. Lovejoy, and C. J. Howard, J. Phys. Chem. **91**, 5743 (1987).
[6] A. Goumri, J-D. R. Rocha, and P. Marshall, J. Phys. Chem. **99**, 10834 (1995).