IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet I.A4.109 SOx37

This data sheet evaluated: November 2001.

HS + NO + M → HSNO + M

ΔH° = -139 kJ·mol^{-1}

Low-pressure rate coefficients
Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
2.7 x 10^{-31} (T/300)$^{-2.48}$ [N_2]	250-445	Black *et al*., 1984[1]	PLP-LIF (a)
(1.4 ± 0.13) x 10^{-30} [Ar]	293	Bulatov, Kozliner and Sarkisov, 1985[2]	PLP (b)

Comments

(a) HS formed by photolysis of H_2S at 193 nm and detected at 354.5 nm. The pressure dependence was studied over the range 40-1013 mbar (50–750 Torr). The falloff curve was represented with F_c = 0.6 and k_∞ = 2.7 x 10^{-11} cm^3 molecule^{-1} s^{-1}. Theoretical modeling with the given ΔH°.

(b) Intracavity laser spectroscopic detection of HSO radicals at 583 nm in photolyzed H_2S-NO-NO_2-Ar mixtures, with HSO radicals being formed from the reaction HS + NO_2. Measurements were carried out at 16 mbar (12 Torr) total pressure.

Preferred Values

k_0 = 2.4 x 10^{-31} (T/300)$^{-2.5}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 250-300 K.

Reliability

$\Delta \log k_0$ = ±0.3 at 298 K.

Δn = ±1.

Comments on Preferred Values

The temperature-dependent measurements from ref. 1 give a consistent picture for the association reaction. Previous work[3] at low pressures did not identify the termolecular nature of the reaction and yielded significantly higher rate coefficients (5.6×10^{-13} cm^3 molecules^{-1} s^{-1} at 10 Torr Ar and 298 K).

High-pressure rate coefficients
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(2.7 \pm 0.5) \times 10^{-11}$	250-300	Black *et al*., 1984[1]	PLP-LIF (a)

Comments

(a) See comment (a) for k_0.

Preferred Values

$k_\infty = 2.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 250-300 K.

Reliability

$\Delta \log k_\infty = 0.5$ over the temperature range 250-300 K.

Comments on Preferred Values

The falloff extrapolation with $F_c = 0.6$ of ref. 1 towards k_∞ appears less certain than to k_0. The preferred values are based on the data of Black *et al*.[1]

The following text-line combines the preferred values for the high and low pressure limiting rate coefficients to generate a single, cut-and-paste expression for calculation of k:

=((2.4e-31*(*T*/300)^-2.5)*M*(2.7e-11))/((2.4e-31*(*T*/300)^-2.5)*M+(2.7e-11))*10^(log10(0.6)/(1+(log10((2.4e-31*(*T*/300)^-2.5)*M/(2.7e-11))/(0.75-1.27*log10(0.6)))^2))

The molecular density, $M = 7.243 \times 10^{21} P(\text{bar})/T(\text{K})$

References

1 G. Black, R. Patrick, L. E. Jusinski, and T. G. Slanger, J. Chem. Phys. **80**, 4065 (1984).
2 V. P. Bulatov, M. Z. Kozliner, and O. M. Sarkisov, Khim Fiz. **4**, 1353 (1985).
3 J.J. Tiee, F.B. Wampler, R.C. Oldenburg and W.W. Rice, Chem. Phys. Lett. **82**, 80 (1981).