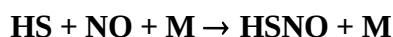


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet I.A4.109 SO_x37

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$$\Delta H^\circ = -139 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$2.7 \times 10^{-31} (T/300)^{-2.48} [\text{N}_2]$	250-445	Black <i>et al.</i> , 1984 ¹	PLP-LIF (a)
$(1.4 \pm 0.13) \times 10^{-30} [\text{Ar}]$	293	Bulatov, Kozliner and Sarkisov, 1985 ²	PLP (b)

Comments

- (a) HS formed by photolysis of H₂S 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 $k_\infty = 2.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Theoretical modeling with the given ΔH° .
- (b) Intracavity laser spectroscopic detection of HSO radicals at 583 nm in photolyzed H₂S-NO-NO₂-Ar mixtures, with HSO radicals being formed from the reaction HS + NO₂. Measurements were carried out at 16 mbar (12 Torr) total pressure.

Preferred Values

$k_0 = 2.4 \times 10^{-31} (T/300)^{-2.5} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250-300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

The temperature-dependent measurements from ref. 1 give a consistent picture for the association reaction. Previous work³ at low pressures did not identify the termolecular nature of the reaction and yielded significantly higher rate coefficients ($5.6 \times 10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ at 10 Torr Ar and 298 K).

High-pressure rate coefficients Rate coefficient data

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

Comments

(a) See comment (a) for k_0 .

Preferred Values

$k_{\infty} = 2.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, 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).