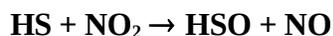


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet SO_x38

Website: <http://iupac.pole-ether.fr>. See website for latest evaluated data. Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission.

This data sheet updated: 19th November 2001.



$$\Delta H^\circ = -90 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(3.5 \pm 0.4) \times 10^{-11}$	298	Black, 1984 ¹	PLP-LIF
$(2.4 \pm 0.2) \times 10^{-11}$	293	Bulatov, Kozliner, and Sarkisov, 1984 ²	PLP-A (a)
$(3.0 \pm 0.8) \times 10^{-11}$	298	Friedl, Brune and Anderson, 1985 ³	DF-LIF
$(8.6 \pm 0.9) \times 10^{-11}$	298	Schoenle, Rahman and Schindler, 1987 ⁴	DF-MS (b)
$4.8 \pm 1.0) \times 10^{-11}$	298	Stachnik and Molina, 1987 ⁵	PLP-UVA
$2.9 \times 10^{-11} \exp(237/T)$	221-415	Wang, Lovejoy and Howard, 1987 ⁶	DF-LMR
$(6.7 \pm 1.0) \times 10^{-11}$	298		

Comments

- (a) HSO radical product was monitored by intracavity laser absorption at 583 nm.
(b) Measured both HS decay and HSO formation by MS. If the HS decay data are taken alone the rate coefficient (once corrected according to erratum paper) increases to $1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Preferred Values

$k = 6.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 2.9 \times 10^{-11} \exp(240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 220-420 K.

Reliability

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

$\Delta(E/R) = \pm 100 \text{ K}$.

Comments on Preferred Values

There is considerable scatter in the measured values of k^{1-6} with no obvious correlation with the conditions used or the technique. The presence of H atoms in the system is known to lead to complicating secondary chemistry, and some of the differences may be due to this, particularly where HS has been generated by photolysis of H₂S. In more recent studies,^{5,6} care has been taken to eliminate or model such effects, but significant differences still persist. The study of Wang *et al.*⁶ represents the only data set in which different source of HS have been employed to get the same result, and the only study in which data was obtained in the absence of H₂S. Wang *et al.*⁶ also showed that the reaction DS + NO₂ has the same rate coefficient as HS + NO₂. In a further study, using C₂H₄S as DS source, Fenter and Anderson⁷ obtained $k(273-373\text{ K}) = (3.4 \pm 0.8) \times 10^{-11} \exp \{210 \pm 70/T\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the reaction of DS with NO₂. This is in good agreement with the result of Wang *et al.*⁶. The preferred value at 298 K and the temperature coefficient are taken from the study of Wang *et al.*⁶. The absence of any pressure effect on the rate constant at pressures up to 0.96 bar^{1,5} indicates that any addition channel is unimportant up to these pressures.

References

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- ⁵ R. A. Stachnik and M. J. Molina, *J. Phys. Chem.* **91**, 4603 (1987).
- ⁶ N. S. Wang, E. R. Lovejoy, and C. J. Howard, *J. Phys. Chem.* **91**, 5743 (1987).
- ⁷ F.F. Fenter and J.G. Anderson, *Int. J. Chem. Kin.* **26**, 801, (1994).