

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet I.A4.89 SO_x18

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This data sheet last evaluated: November 2017; last change in preferred values: Jan 2008.



$$\Delta H^\circ(1) = -44 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -154 \text{ kJ}\cdot\text{mol}^{-1}$$

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>			
1×10^{-12} at 70 Torr [N ₂]	247-299	Hynes et al., 1988	PLP-LIF (a)
6×10^{-13} at 30 Torr [N ₂]	259-318	Murrells et al., 1990	PLP-LIF (b)
5.0×10^{-32} [He]	298	Diau and Lee, 1991	PLP-LIF (c)
8.9×10^{-32} [He]	269		
14.7×10^{-32} [He]	249		

Comments

- Photolysis of H₂O₂ at 248 nm in mixtures of CS₂ and He, N₂, air, or O₂. Pressure range 87-920 mbar.
- Photolysis of H₂O₂ at 248 nm or 266 nm in mixtures of CS₂ and He-N₂ or He-SF₆ mixtures. Pressure range 12-80 mbar. The effect of O₂ (0.7 - 20 mbar) on the rate coefficient was studied.
- Photolysis of H₂O₂ at 248 nm in mixtures of CS₂ and added He or Ar (limited data set). Pressure range 12-360 mbar of Ar or He. Effect of CS₂ on the rate coefficient was studied.

Preferred Values

$$k_{1,0} = 1 \times 10^{-30} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \text{ independent of temperature over the range 250-320 K.}$$

Reliability

$$\Delta \log k_{1,0} = \pm 0.5.$$

Comments on Preferred Values

Because of the low thermal stability of HOCS₂, experimental studies have to account for the re-dissociation of the adduct, in which the HO is thought to be bound to sulphur (McKee and Wine, 2001). The preferred values are based on a combination of the data for M = N₂ from Hynes et al. (1988) and Murrels et al. (1990), with a falloff representation (see below). The data and a falloff representation indicates that the low pressure limit is approached within 10% only at pressures below about 27 mbar (20 Torr). The strong temperature dependence ($E/R = -1610$ K) of k_{01} for M = He derived in Diau and Lee (1991) is not consistent with the results from Hynes et al. (1998) in He, or Murrels et al. (1990) in N₂. Hynes et al. (1998) do however report a strong temperature dependence at 680 ± 20 Torr N₂ or O₂ or air ($k = 6.9 \times 10^{-14} \exp(1150/T)$ cm³ molecule⁻¹s⁻¹). It appears that reaction (2) is slow, with a rate coefficient of $k_2 < 2 \times 10^{-15}$ cm³ molecule⁻¹ s⁻¹ at 298 K (see below).

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>			
5.8×10^{-12} at 0.91 bar [N ₂]	250-270	Hynes et al., 1988	PLP-LIF (a)
3.1×10^{-12} at 0.88 bar [N ₂]	297		
1.9×10^{-12} at 150 Torr [Ar]	209	Bulatov et al., 1988	PLP-LIF (b)
1.3×10^{-12} at 1.01 bar [air]	295	Becker et al., 1990	PLP-LIF (c)

Comments

- (a) See comment (a) for $k_{1,0}$.
- (b) Mixtures of O₂-H₂O-CS₂-Ar. The rates of HOCS₂ formation and decomposition were measured, with an equilibrium constant of $K_c = 2.6 \times 10^{-17}$ cm³ molecule⁻¹.
- (c) H₂O₂ was photolysed at 248 nm in mixtures of CS₂ and N₂-O₂ or Ar-O₂. The partial pressure of O₂ was in the range 0.32-1013 mbar, at a total pressure of 1.01 bar. The rate coefficient was found to increase further when more O₂ was added, with a value of 2.79×10^{-12} cm³ molecule⁻¹ s⁻¹ obtained at 996 mbar O₂.

Preferred Values

$k_{1,\infty} = 2.5 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, independent of temperature over the range 250-300 K.

Reliability

$\Delta \log k_{1,\infty} = \pm 0.5$ over the temperature range 250-300 K.

Comments on Preferred Values

The preferred rate coefficient $k_{1,\infty}$ is based on a falloff representation of the data from Hynes et al. (1988) and Murrells et al. (1990). The largest weight is given to the measurements near 250-260 K where decomposition of the adduct and the subsequent kinetics are of comparably minor influence in contrast to the room temperature experiments. A falloff curve with an estimated value of $F_c = 0.44$ was employed for extrapolation (Cobos and Troe, 2003). Experiments at 1 bar

total pressure are apparently still far below the high pressure limit. An extensive discussion of the complicated mechanism is given in Hynes et al. (1988), Murrells et al. (1990), Lovejoy et al. (1990) and McKee and Wine (2001). Rate expressions combining adduct formation, dissociation, and subsequent reaction with O₂ have been proposed which are not reproduced here (see also data sheets on HOCS₂ + M and HOCS₂ + O₂). More experiments separating the individual steps are required, as are temperature dependent studies at low pressures.

The adduct HOCS₂ was detected mass-spectrometrically by de Petris et al. (2006). It can be of SC(OH)S or SCS(OH) structure, such as suggested from different products in the reaction with NO (Bil et al., 2016).

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*:

$$=((1e-30)*M*(2.5e-11))/((1e-30)*M+(2.5e-11))*10^{(\log10(0.44)/(1+(\log10((1e-30)*M/(2.5e-11))/(0.75-1.27*\log10(0.44)))^2))}$$

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

Rate coefficient data *k*₂

<i>k</i> ₂ /cm ³ molecule ⁻¹ s ⁻¹	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
<9.9 x 10 ⁻¹⁵	251	Wine et al., 1980	FP-RF
<1.5 x 10 ⁻¹⁵	297		
<1.6 x 10 ⁻¹⁵	363		
≤2 x 10 ⁻¹⁵	299	Murrells et al., 1990	PLP-LIF
<3 x 10 ⁻¹⁵	330	Lovejoy et al., 1990	DF-LMR (a)

Comments

- (a) Based on the observed HS radical yield of <50% of the HO radicals consumed and a total HO radical loss rate coefficient of 6 x 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹.

Preferred Values

*k*₂ < 2 x 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹ at 298 K.

Comments on Preferred Values

The upper limit to the preferred value for *k*₂ is based on the absolute rate coefficient studies of Wine et al. (1980) and Murrells et al. (1990), and is consistent with the study of Lovejoy et al. (1990) in which HS radical formation and HO radical decays were measured.

References

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