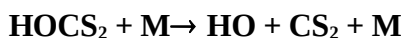


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet SOx19

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This data sheet updated: 19th November 2001.



$$\Delta H^\circ = 44.0 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients Rate coefficient data

$k_0[\text{M}]/\text{s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
1.3×10^4 at 0.100 bar [N ₂]	255	Hynes, Wine and Nicovich, 1988 ¹	PLP-LIF (a)
2.6×10^4 at 0.108 bar [N ₂]	280		
4.3×10^3 at 0.020 bar [N ₂]	277	Murrells, Lovejoy and Ravishankara, 1990 ²	PLP-LIF (b)
3.0×10^4 at 0.032 bar [N ₂]	298		
7.36×10^{-15} [He]	298	Diau and Lee, 1991 ³	PLP-LIF (c)
2.14×10^{-15} [He]	269		
0.46×10^{-15} [He]	249		

Comments

- Photolysis at 298 K in mixtures of CS₂ and He, N₂, air or O₂. Pressure range 87-920 mbar (65-690 Torr). A value of K_c (297 K) = $1.39 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1}$ was obtained for the equilibrium between HO + CS₂ and HOCS₂ as well as K_c (247 K) = $3.5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1}$.
- Photolysis of H₂O₂ at 248 nm and 266 nm in He-N₂-CS₂ or He-SF₆-CS₂ mixtures. Pressure range = 12-80 mbar (9-60 Torr). The effect of O₂ [0.7-20 mbar (0.5-15 Torr)] on the rate was studied. K_c (299 K) = $1.7 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1}$, K_c (274 K) = $7.5 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1}$ and K_c (249 K) = $5.1 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1}$ were obtained for the equilibrium between HO + CS₂ and HOCS₂.
- Photolysis of H₂O₂ at 248 nm in mixtures of CS₂ and He or Ar. Pressure range 12-360 mbar (9-270 Torr) of He. The effect of CS₂ on the rate was studied. K_c (298 K) = $0.87 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1}$, K_c (273 K) = $4.2 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1}$ and K_c (249 K) = $2.6 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1}$ were obtained for the equilibrium between HO + CS₂ and HOCS₂.

Preferred Values

$k_0 = 4.8 \times 10^{-14} [\text{N}_2] \text{ s}^{-1}$ at 298 K.

$k_0 = 1.6 \times 10^{-6} \exp(-5160/T) [\text{N}_2] \text{ s}^{-1}$ over the temperature range 250-300 K.

Reliability

$\Delta \log k_0 = \pm 0.5$ at 298 K.

$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The preferred values are based on a falloff representation from refs. 1 and 2 of the data for the reverse process $\text{HO} + \text{CS}_2 + \text{M} \rightarrow \text{HOCS}_2 + \text{M}$ and the determination of the equilibrium constant from the same work. The data from ref. 3 are not consistent with this evaluation (with differences of about a factor of 2). HOCS_2 formation and dissociation are characterized by an equilibrium constant of $K_c = 5.16 \times 10^{-25} \exp(5160/T) \text{ cm}^3 \text{ molecule}^{-1}$, such as derived from the data of ref. 2.

High-pressure rate coefficients Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
3.1×10^4 at 0.907 bar $[\text{N}_2]$	252	Hynes, Wine and Nicovich, 1988 ¹	PLP-LIF (a)
6.5×10^4 at 0.913 bar $[\text{N}_2]$	270		
2.2×10^5 at 0.880 bar $[\text{N}_2]$	297		
7.4×10^4	298	Bulatov <i>et al.</i> , 1988 ⁴	PLP-LIF (b)

Comments

- (a) See comment (a) for k_0 .
- (b) Photolysis of O_3 in the presence of H_2O , CS_2 and Ar. Rate of HOCS_2 formation and decomposition measured and evaluated with an equilibrium constant of $K_c = 2.6 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1}$.

Preferred Values

$k_\infty = 4.8 \times 10^5 \text{ s}^{-1}$ at 298 K.

$k_\infty = 1.6 \times 10^{13} \exp(-5160/T) \text{ s}^{-1}$ over the temperature range 250-300 K.

Reliability

$\Delta \log k_\infty = \pm 0.5$ at 298 K.

$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The preferred values are based on the falloff extrapolation of the data for the reverse reaction and the equilibrium constant $K_c = 5.16 \times 10^{-25} \exp(5160/T) \text{ cm}^3 \text{ molecule}^{-1}$ from ref. 2. Falloff curves are constructed with an estimated value of $F_c = 0.8$. The small preexponential factor of k_∞ can be explained theoretically as being due to the low bond energy of HOCS₂. For discussion of the mechanism see refs. 1, 2 and 5.

References

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