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

This data sheet updated: 19th November 2001.

$HOCS_2 + M \rightarrow HO + CS_2 + M$

$\Delta H^\circ = 44.0$ kJ·mol^{-1}

Low-pressure rate coefficients
Rate coefficient data

k_0[M]/ s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
1.3 x 10^4 at 0.100 bar [N_2]	255	Hynes, Wine and Nicovich, 1988[1]	PLP-LIF (a)
2.6 x 10^4 at 0.108 bar [N_2]	280		
4.3 x 10^3 at 0.020 bar [N_2]	277	Murrells, Lovejoy and Ravishankara, 1990[2]	PLP-LIF (b)
3.0 x 10^4 at 0.032 bar [N_2]	298		
7.36 x 10^{-15} [He]	298	Diau and Lee, 1991[3]	PLP-LIF (c)
2.14 x 10^{-15} [He]	269		
0.46 x 10^{-15} [He]	249		

Comments

(a) Photolysis at 298 K in mixtures of CS_2 and He, N_2, air or O_2. Pressure range 87-920 mbar (65-690 Torr). A value of K_c (297 K) = 1.39 x 10^{-17} cm^3 molecule^{-1} was obtained for the equilibrium between HO + CS_2 and $HOCS_2$ as well as K_c (247 K) = 3.5 x 10^{-16} cm^3 molecule^{-1}.

(b) Photolysis of H_2O_2 at 248 nm and 266 nm in He-N_2-CS_2 or He-SF_6-CS_2 mixtures. Pressure range = 12-80 mbar (9-60 Torr). The effect of O_2 [0.7-20 mbar (0.5-15 Torr)] on the rate was studied. K_c (299 K) = 1.7 x 10^{-17} cm^3 molecule^{-1}, K_c (274 K) = 7.5 x 10^{-17} cm^3 molecule^{-1} and K_c (249 K) = 5.1 x 10^{-16} cm^3 molecule^{-1} were obtained for the equilibrium between HO + CS_2 and $HOCS_2$.

(c) Photolysis of H_2O_2 at 248 nm in mixtures of CS_2 and He or Ar. Pressure range 12-360 mbar (9-270) Torr of He. The effect of CS_2 on the rate was studied. K_c (298 K) = 0.87 x 10^{-17} cm^3 molecule^{-1}, K_c (273 K) = 4.2 x 10^{-17} cm^3 molecule^{-1} and K_c (249 K) = 2.6 x 10^{-16} cm^3 molecule^{-1} were obtained for the equilibrium between HO + CS_2 and $HOCS_2$.

Preferred Values

$k_0 = 4.8 \times 10^{-14}$ [N_2] s^{-1} at 298 K.
$k_0 = 1.6 \times 10^{-6} \exp(-5160/T)$ [N_2] 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 HO + CS_2 + M → $HOCS_2$ + 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 $K_c = 5.16 \times 10^{-25} \exp(5160/T)$ cm^3 $molecule^{-1}$, such as derived from the data of ref. 2.

High-pressure rate coefficients
Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
3.1×10^4 at 0.907 bar [N_2]	252	Hynes, Wine and Nicovich, 1988[1]	PLP-LIF (a)
6.5×10^4 at 0.913 bar [N_2]	270		
2.2×10^5 at 0.880 bar [N_2]	297		
7.4×10^4	298	Bulatov *et al*., 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 $K_c = 2.6 \times 10^{-17}$ cm^3 $molecule^{-1}$.

Preferred Values

$k_\infty = 4.8 \times 10^5$ s^{-1} at 298 K.
$k_\infty = 1.6 \times 10^{13} \exp(-5160/T)$ 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 x 10^{-25} exp(5160/T) cm^3 $molecule^{-1}$ 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 $HOCS_2$. For discussion of the mechanism see refs. 1, 2 and 5.

References

1 A. J. Hynes, P. H. Wine, and J. M. Nicovich, J. Phys. Chem. **92**, 3846 (1988).
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4 V. P. Bulatov, S. G. Cheskis, A. A. Iogansen, P. V. Kulatov, O. M. Sarkisov, and E. Hassinen, Chem. Phys. Lett. **153**, 258 (1988).
5 E. R. Lovejoy, T. P. Murrells, A. R. Ravishankara, and C. J. Howard, J. Phys. Chem. **94**, 2386 (1990).