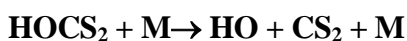


## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet SOx19

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. The citation for this data sheet is: Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Atmos. Chem. Phys. 4, 1461, 2004; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, (<http://iupac.pole-ether.fr>).

This data sheet last evaluated: November 2017; last change in preferred values: 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>			
$1.3 \times 10^4$ at 0.100 bar [N <sub>2</sub> ]	255	Hynes et al., 1988	PLP-LIF (a)
$2.6 \times 10^4$ at 0.108 bar [N <sub>2</sub> ]	280		
$4.3 \times 10^3$ at 0.020 bar [N <sub>2</sub> ]	277	Murrells et al., 1990	PLP-LIF (b)
$7.36 \times 10^{-15}$ [He]	298	Diau and Lee, 1991	PLP-LIF (c)
$2.14 \times 10^{-15}$ [He]	269		
$0.46 \times 10^{-15}$ [He]	249		

### Comments

- Photolysis at 298 K in mixtures of CS<sub>2</sub> and He, N<sub>2</sub>, air or O<sub>2</sub>. 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 + CS<sub>2</sub> and HOCS<sub>2</sub> as well as  $K_c$  (247 K) =  $3.5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1}$ .
- Photolysis of H<sub>2</sub>O<sub>2</sub> at 248 nm and 266 nm in He-N<sub>2</sub>-CS<sub>2</sub> or He-SF<sub>6</sub>-CS<sub>2</sub> mixtures. Pressure range = 12-80 mbar (9-60 Torr). The effect of O<sub>2</sub> [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 + CS<sub>2</sub> and HOCS<sub>2</sub>.
- Photolysis of H<sub>2</sub>O<sub>2</sub> at 248 nm in mixtures of CS<sub>2</sub> and He or Ar. Pressure range 12-360 mbar (9-270 Torr) of He. The effect of CS<sub>2</sub> 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 + CS<sub>2</sub> and HOCS<sub>2</sub>.

### Preferred Values

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

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

#### Reliability

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

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

#### Comments on Preferred Values

The preferred values are based on a falloff representation from Hynes et al. (1988) and Murells et al. (1990) 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 Diau and Lee (1991) are not consistent with this evaluation (with differences of about a factor of 2).  $\text{HOCS}_2$  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 Murrells et al. (1988).

### High-pressure rate coefficients Rate coefficient data

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

### Comments

- (a) See comment (a) for  $k_0$ .  
(b) Photolysis of  $\text{O}_3$  in the presence of  $\text{H}_2\text{O}$ ,  $\text{CS}_2$  and Ar. Rate of  $\text{HOCS}_2$  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

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

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

#### 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 Murrels et al. (1990). Falloff curves are constructed with an estimated value of  $F_c = 0.8$ . The small preexponential factor of  $k_{\infty}$  can be explained theoretically as being due to the low bond energy of HOCS<sub>2</sub>. Theoretical studies by McKee (1993), Nagy et al. (2011), and Zeng (2017) confirm the existence of two isomers of the adduct.

**References**

- Bulatov, V. P., Cheskis, S. G., Iogansen, A. A., Kulatov, P. V., Sarkisov, O. M. and Hassinen, E.: Chem. Phys. Lett., 153, 258, 1988.  
Diau, E. W.-G., and Lee, Y.-P.: J. Phys. Chem., 95, 379, 1991.  
Hynes, A. J., Wine, P. H., and Nicovich, J. M.: J. Phys. Chem., 92, 3846, 1988.  
McKee, M. L.: Chem. Phys. Lett. 201, 41, 1993.  
McKee, M. L., and Wine, P. H.: J. Am. Chem. Soc., 123, 2344, 2001.  
Murrells, T. P., Lovejoy, E. R., and Ravishankara, A. R.: J. Phys. Chem., 94, 2381, 1990.  
Nagy, B., Szakacs, P., Csontos, J., Rolik, Z., and Kallay, M.: J. Phys. Chem. A 115, 7823, 2011.  
Wine, P. H., Shah, R. C., and Ravishankara, A. R.: J. Phys. Chem., 84, 2499, 1980.  
Zeng, Z., Altarawneh, M., and Dlugogorski, B. Z.: Chem. Phys. Lett. 669, 43, 2017.