

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet SOx49

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$$\Delta H^\circ(1) = -378 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -165 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data ($k = k_1 + k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$k_2 = (4.5 \pm 1.7) \times 10^{-19}$	293	Richardson, 1975	(a)
$k_2 = (5.9 \pm 1.3) \times 10^{-18}$	495		
$(2.9 \pm 0.4) \times 10^{-19}$	298	Black et al, 1983	(b)
<i>Branching Ratios</i>			
$k_2/k_1 = 1.2$	298	Wood and Heicklen, 1971a, 1973/74	(c)
$k_2/k_1 = 1.2$	341-415	Wood and Heicklen, 1971b	(d)

Comments

- Discharge flow system used. CS radicals were produced by a discharge through CS₂. CS, SO₂, CO and OCS were measured by MS. A very slow liner flow rate ($\sim 100 \text{ cm s}^{-1}$) was necessary to observe reaction. SO₂, a product formed via channel (1), was at least one order of magnitude lower in concentration than CO and OCS.
- CS radicals were produced by pulsed laser photolysis of CS₂ in He bath gas [32 mbar (24 Torr)], and were monitored by LIF at 257.7 nm.
- Photolysis of CS₂-O₂ mixtures, with analysis of CO, OCS, SO₂ and S₂O products by GC. Light of wavelength 313 nm was used in Wood and Heicklen (1971a), which has insufficient energy to dissociate the CS₂, but CS was postulated to have been formed by reaction of electronically excited CS₂ with O₂. In the later study (Wood and Heicklen, 1973/74), $\lambda = 213.9 \text{ nm}$ was used which can photodissociate CS₂.
- Explosion limits of CS₂-O₂ mixtures were determined by GC. The [CO]/[OCS] ratio was relatively unaffected by pressure and temperature changes, and the value of 0.84 found for this ratio is the same as that observed in photochemical studies (Wood and Heicklen, 1971a; 1973/74). The explosion limits were modeled on the basis of an assumed mechanism of eight reactions, and a computer fit to the data yielded the value for k_2/k_1 .

Preferred Values

$k = 2.9 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.6$ at 298 K.

Comments on Preferred Values

The reaction of CS with O₂ is slow at 298 K and difficult to study. The technique used by Black et al. (1983) seems the most suitable for avoiding the difficulties associated with the slowness of the reaction, and their rate coefficient at 298 K is preferred.

The relative importance of the two possible reaction channels is in dispute. Evidence from the photochemical and explosion limit studies (Wood and Heicklen, 1971a,b; 1973/74) indicate a comparable importance of channels (1) and (2), but in the more direct flow system study (Richardson, 1975) k_1 was found to be at least an order of magnitude less than k_2 . However, the value of k_2 obtained in the fast flow study (Richardson, 1975) appears to be unacceptably high. We make no recommendation for the branching ratio.

The one available measurement of k at higher temperatures (Richardson, 1975), when combined with the 298 K values, leads to an Arrhenius expression with an extremely low pre-exponential factor. No recommendation is hence made for the temperature dependence.

References

- Black, G., Jusinski, L. E. and Slinger, T. G.: Chem. Phys. Lett. 102, 64, 1983.
Richardson, R. J.: J. Phys. Chem. 79, 1153, 1975.
Wood, W. P. and Heicklen, J.: J. Photochem. 2, 173, 1973/74.
Wood, W. P. and Heicklen, J.: J. Phys. Chem. 75, 854, 1971.
Wood, W. P. and Heicklen, J.: J. Phys. Chem. 75, 861, 1971.