

# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet SOx17

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This data sheet last evaluated: 28<sup>th</sup> June 2007; no revision of preferred values.

## HO + OCS → products

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$1.3 \times 10^{-12} \exp[-(2300 \pm 100)/T]$ $(6 \pm 4) \times 10^{-16}$	300-517 300	Leu and Smith, 1981	DF-RF (a)
$1.13 \times 10^{-13} \exp[-(1200 \pm 400)/T]$ $(2.0^{+0.4}_{-0.8}) \times 10^{-15}$	255-483 300	Cheng and Lee, 1986	DF-RF (b)
$(1.92 \pm 0.25) \times 10^{-15}$	298	Wahner and Ravishankara, 1987	FP/PLP-LIF (c)

### Comments

- The measured HO radical decay rates were corrected for the presence of H<sub>2</sub>S in the OCS sample used ( $0.01 \pm 0.003\%$  H<sub>2</sub>S for the experiments at 300-421 K and  $0.04 \pm 0.01\%$  H<sub>2</sub>S for the experiments at 517 K). At 300 K the measured rate coefficient, uncorrected for the presence of H<sub>2</sub>S, was  $1.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- The purity of OCS was checked by FTIR spectroscopy, showing that H<sub>2</sub>S was present at less than 0.005%. The measured rate coefficient  $k$  was independent of pressure (1.2-7.9 mbar) and the addition of O<sub>2</sub> (up to 18% or 0.36 mbar of O<sub>2</sub>).
- The rate coefficient  $k$  was independent of pressure (120-400 mbar), the nature of buffer gas, and the addition of O<sub>2</sub> (up to 48 mbar).

### Preferred Values

$k = 2.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 1.1 \times 10^{-13} \exp(-1200/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 250-500 K.

#### Reliability

$\Delta \log k = \pm 0.3$  at 298 K.

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

#### Comments on Preferred Values

The rate coefficients measured by Cheng and Lee (1986) and Wahner and Ravishankara (1987) are approximately a factor of 3 higher at 298 K than the earlier value of Leu and Smith (1981). This may be due to the corrections applied by Leu and Smith (1981) to account for the presence of traces of H<sub>2</sub>S in their system, because in the absence of any correction to the measured rate coefficient of Leu and Smith<sup>1</sup> there is reasonable agreement between the studies (Leu and Smith, 1981; Cheng and Lee, 1986; Wahner and Ravishankara, 1987). Cheng and Lee (1986) took care to keep the H<sub>2</sub>S level in their OCS very low and this, together with the confirmatory measurements of Wahner and Ravishankara (1987), leads us to

recommend their values. These recommendations are compatible with the earlier upper limits given by Atkinson et al. (1978) and Ravishankara et al. (1980), but not with the higher value obtained by Kurylo (1978), which may have been due to the occurrence of interfering secondary chemistry and/or excited state reactions.

Kurylo and Laufer (1979) have suggested that the reaction proceeds through adduct formation, as found for the reaction of HO with CS<sub>2</sub>, followed by decomposition of the adduct to yield mainly HS + CO<sub>2</sub>. This is supported by the product study of Leu and Smith (1981) at 517 K. However, in contrast to the HO + CS<sub>2</sub> reaction, there is no marked effect of O<sub>2</sub> on the rate coefficient. Furthermore, very little oxygen atom exchange between H<sup>18</sup>O and OCS is found (Greenblatt and Howard, 1989), which may suggest that any adduct formed is weakly bound and short-lived.

### References

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