

## Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet SOx11

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### Cl + CS<sub>2</sub> + O<sub>2</sub> → products

#### Rate coefficient data

<i>k</i> /cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
<5 x 10 <sup>-15</sup> (air, 400 mbar)	293	Nicovich et al., 1990	(a)
<i>Relative Rate Coefficients</i>			
(0.83 ± 0.17) x 10 <sup>-13</sup> (air, 1013 mbar)	298	Martin et al., 1987	RR (b)
<4 x 10 <sup>-15</sup> (air, 933 mbar)	298	Wallington et al., 1991	RR (c)

#### Comments

- Pulsed laser photolysis of Cl<sub>2</sub> in CS<sub>2</sub>-N<sub>2</sub>-O<sub>2</sub> mixtures over the pressure range of 40-400 mbar and the temperature range of 193-258 K. [Cl] was monitored by resonance fluorescence. Experiments in absence of O<sub>2</sub> reveal reversible adduct formation and establishment of equilibrium between Cl, CS<sub>2</sub> and CS<sub>2</sub>Cl. Thermodynamic parameters for equilibrium derived. The upper limit tabulated for overall removal of CS<sub>2</sub> in presence of O<sub>2</sub> is for all channels of CS<sub>2</sub>Cl + O<sub>2</sub> reaction which do not lead to Cl atom formation.
- Steady state photolysis of Cl<sub>2</sub> in presence of CS<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, and reference compound (CH<sub>4</sub> or CH<sub>3</sub>Cl) at 1013 mbar total pressure. [CS<sub>2</sub>] and [CH<sub>4</sub>] or [CH<sub>3</sub>Cl] were monitored by mass spectrometry.  $k(\text{Cl} + \text{CH}_3\text{Cl}) = 4.9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  were used to put  $k$  on an absolute basis (IUPAC, current recommendation).
- Steady state photolysis of Cl<sub>2</sub> in the presence of CS<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub> and the reference compound (CH<sub>4</sub>, CH<sub>3</sub>Cl or CHF<sub>2</sub>Cl). [CS<sub>2</sub>] and the concentration of the reference compound was monitored by FTIR. CH<sub>4</sub> and CH<sub>3</sub>Cl were shown to be unsuitable as reference compounds. Value of  $k(\text{Cl} + \text{CHF}_2\text{Cl})/k(\text{Cl} + \text{CH}_4) < 0.04$  measured in same study and combined with  $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and measured  $k(\text{Cl} + \text{CS}_2)/k(\text{Cl} + \text{CHF}_2\text{Cl})$  in presence of O<sub>2</sub> to give tabulated upper limit to  $k$ .

#### Preferred Values

$k = 4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K in air at 1 bar.

#### Comments on Preferred Values

The overall reaction of Cl with CS<sub>2</sub> is slow. Nicovich et al. (1990) have shown that it proceeds initially by rapid formation of the ClCS<sub>2</sub> adduct, as suggested earlier by Martin et al., (1987), but the

subsequent reaction of the adduct with O<sub>2</sub> appears to be slow. The Cl atom is most likely weakly bound to a S atom in the initially formed adduct, which can then isomerise to form an SC(Cl)S adduct (see Wang and Phillips, 2002 and references to other theoretical studies therein).

The recommended upper limit is that of Wallington et al. (1991) which agrees with the work of Nicovich et al. (1990). Wallington et al. (1991) have suggested that the value obtained by Martin et al. (1987) was erroneously high due to complexities in their system arising from HO radical production from the reference compounds that were chosen.

### References

IUPAC, <http://iupac.pole-ether.fr>

Martin, D., Barnes, I. and Becker, K. H.: Chem. Phys. Lett., 140, 195, 1987.

Nicovich, J. M., Shackelford, C. J. and Wine, P. H.: J. Phys. Chem., 94, 2896, 1990.

Wallington, T. J., Andino, J. M. and Potts, A. R.: Chem. Phys. Lett., 176, 103, 1991.

Wang, D. and Phillips, D. L.: Chem. Phys. Lett., 362, 205, 2002.