

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

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Cl + CS₂ + O₂ → products

Rate coefficient data

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

Comments

- Pulsed laser photolysis of Cl₂ in CS₂-N₂-O₂ 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 O₂ reveal reversible adduct formation and establishment of equilibrium between Cl, CS₂ and CS₂Cl. Thermodynamic parameters for equilibrium derived. The upper limit tabulated for overall removal of CS₂ in presence of O₂ is for all channels of CS₂Cl + O₂ reaction which do not lead to Cl atom formation.
- Steady state photolysis of Cl₂ in presence of CS₂, N₂, O₂, and reference compound (CH₄ or CH₃Cl) at 1013 mbar total pressure. [CS₂] and [CH₄] or [CH₃Cl] 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 Cl₂ in the presence of CS₂, N₂, O₂ and the reference compound (CH₄, CH₃Cl or CHF₂Cl). [CS₂] and the concentration of the reference compound was monitored by FTIR. CH₄ and CH₃Cl 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 O₂ 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 CS₂ is slow. Nicovich et al. (1990) have shown that it proceeds initially by rapid formation of the ClCS₂ adduct, as suggested earlier by Martin et al., (1987), but the

subsequent reaction of the adduct with O₂ 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>

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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.