# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet SOx12


This data sheet updated: 19th November 2001.

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$$\mathbf{Cl + CH_3SH \rightarrow HCl + CH_3S} \quad \mathbf{(1)}$$
$$\mathbf{\rightarrow HCl + CH_2SH} \quad \mathbf{(2)}$$

$\Delta H^{\circ}(1) = -66.1$ kJ·mol$^{-1}$

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

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | **Reference** | Technique/ Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $(1.8 \pm 0.4) \times 10^{-10}$ | 298 | Nesbitt and Leone, 1980[1] | PLP-CL |
| $k_2 = (4.3 \pm 1) \times 10^{-12}$ | 298 | Nesbitt and Leone, 1981[2] | PLP-CL |
| $(1.1 \pm 0.4) \times 10^{-10}$ | 298 | Mellouki, Jourdain and Le Bras, 1988[3] | DF-EPR/MS |
| $1.19 \times 10^{-10} \exp[(151 \pm 38)/T]$ | 193-430 | Nicovich, Wang and Wine, 1995[4] | PLP-RF |
| $(2.0 \pm 0.3) \times 10^{-10}$ | 298 | | |

## Preferred Values

$k = 2.0 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K.
$k = 1.2 \times 10^{-10} \exp(150/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ over the temperature range 190-430 K.

*Reliability*

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 100$ K.

*Comments on Preferred Values*

The preferred value accepts the results of the study of Nicovich *et al*.,[4] which was an extensive study conducted over a wide range of experimental conditions. In that study the value of $k$ at room temperature was found to be independent of pressure over the range studied [33-200 mbar (25-150 Torr)]. The room temperature value of $k$ reported by Nesbitt and Leone[1] is in good agreement with the preferred value, but the Mellouki *et al*.[3] reported value is lower by a factor of two. The results of Nesbitt and Leone[2] show that only about 2% of the total reaction occurs by channel (2), via abstraction from the methyl group. An ab initio study of reactions of chlorine atoms with several reduced sulfur compounds has been reported by Wilson and Hirst.[5] For this reaction these results indicate that formation of the adduct is rate-limiting, but that H-atom abstraction is expected to be important.

## References


[1] D. J. Nesbitt and S. R. Leone, J. Chem. Phys. **72**, 1722 (1980).
[2] D. J. Nesbitt and S. R. Leone, J. Chem. Phys. **75**, 4949 (1981).
[3] A. Mellouki, J. L. Jourdain, and G. Le Bras, Chem. Phys. Lett. **148**, 231 (1988).
[4] J. M. Nicovich, S. Wang, and P. H. Wine, Int. J Chem. Kinet. **27**, 359 (1995).
[5] C. Wilson and D. M. Hirst, J. Chem. Soc. Faraday Trans. **93**, 2831 (1997).