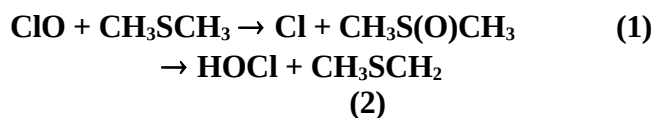


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet SO_x75

Website: <http://iupac.pole-ether.fr>. See website for latest evaluated data. Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission.

This data sheet updated: 31st May 2007.



$$\Delta H^\circ(1) = -25.3 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(3.9 \pm 0.5) \times 10^{-14}$	298	Barnes et al., 1989	DF-MS
$(9.5 \pm 2.0) \times 10^{-15}$	298 ± 1	Barnes et al., 1991	DF-MS
$1.2 \times 10^{-15} \exp[(354 \pm 163)/T]$	259-335	Díaz-de-Mera et al., 2002	DF-MS (a)
$(3.9 \pm 1.2) \times 10^{-15}$	298		

Comments

- (a) At 298 K no effect of pressure on the rate coefficients was observed over the range 0.5-2 Torr (0.67-2.7 mbar) of He diluent. The measured rate coefficients were: at 259 K, $(4.5 \pm 2.4) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 1.3 mbar pressure; at 298 K, $(4.0 \pm 1.6) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 0.67 mbar, $(3.9 \pm 1.2) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 1.3 mbar and $(4.5 \pm 1.6) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 2.7 mbar pressure; and at 335 K, $(3.3 \pm 1.7) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 1.3 mbar pressure.

Preferred Values

$$k = 5.3 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 1.7 \times 10^{-15} \exp(340/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 250\text{-}340 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.5 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 400 \text{ K.}$$

Comments on Preferred Values

The three measurements of Barnes et al. (1989; 1991) and Díaz-de-Mera et al. (2002) of this rate coefficient used basically the same technique, yet vary by a factor of 10 at 298 K. In the first study of Barnes et al. (1989), wall effects were evident and it was recognized that the rate coefficient k obtained was likely to be an upper limit. Better control of wall effects was obtained in the second study of Barnes et al. (1991), and the rate coefficient obtained was preferred (Barnes et al., 1991). The rate coefficients

determined by Díaz-de-Mera et al. (2002) [see comment (a)] at the three temperatures studied are identical within the cited uncertainties and a simple average of $4.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature, may be just as appropriate as the temperature-dependent expression cited by Díaz-de-Mera et al. (2002) and listed in the table. The preferred value at 298 K is a weighted average of the rate coefficients of Barnes et al. (1991) and Díaz-de-Mera et al. (2002). The temperature dependence is based on a unit-weighted least-squares analysis of the rate coefficients of Díaz-de-Mera et al. (2002), with the *A*-factor being adjusted to fit the preferred 298 K rate coefficient. The uncertainty in the value of (*E*/*R*) is sufficient to encompass a temperature-independent rate coefficient. Clearly, further studies of this reaction as a function of temperature and pressure are required.

The reaction is usually assumed to produce $\text{CH}_2\text{S(O)CH}_3 + \text{Cl}$ [channel (1)], but although the sulfoxide has been detected (Barnes et al., 1989), no yields have been measured. Theoretical calculations suggest that both reaction channels (1) and (2) occur, and that they account for 73% and 27% of the overall reaction, respectively, at 298 K (Sayin and McKee, 2004), with the computed rate coefficient being in good agreement with the preferred 298 K value (note, however, that this is not the case for the $\text{IO} + \text{CH}_3\text{SCH}_3$ reaction where the calculations of Sayin and McKee (2004) lead to a 298 K rate coefficient higher than the experimental values by a factor of 10^3).

References

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