IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet SOx13

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$$\mathbf{Cl + CH_3SCH_3 \rightarrow HCl + CH_3SCH_2} \qquad \mathbf{(1)}$$
$$\mathbf{Cl + CH_3SCH_3 \rightarrow CH_3 + ClSCH_3} \qquad \mathbf{(2)}$$
$$\mathbf{Cl + CH_3SCH_3 \rightarrow CH_3Cl + CH_3S} \qquad \mathbf{(3)}$$
$$\mathbf{Cl + CH_3SCH_3 + M \rightarrow ClS(CH_3)_2 + M} \qquad \mathbf{(4)}$$

$\Delta H^\circ(1) = -39.6$ kJ mol^{-1}
$\Delta H^\circ(3) = -41.5$ kJ mol^{-1}

Rate coefficient data ($k = k_1 + k_2 + k_3 + k_4$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1.8×10^{-10} (4 mbar N_2)	297	Stickel et al., 1992	PLP-RF (a)
$(3.3 \pm 0.5) \times 10^{-10}$ (933 mbar N_2)			
$2.0 \times 10^{-10} \exp[-(332 \pm 173)/T]$ (0.66-1.3 mbar He)	259-364	Diaz-de-Mera et al., 2002	DF-MS (b)
$(6.9 \pm 1.3) \times 10^{-11}$ (0.66-1.3 mbar He)	298		
Relative Rate Coefficients			
$(3.2 \pm 0.3) \times 10^{-10}$ (986 mbar N_2)	295	Nielsen et al., 1990	RR (c)
$(3.81 \pm 0.23) \times 10^{-10}$ (1 bar N_2)	298	Kinnison et al., 1996	RR (d)
$(4.43 \pm 0.17) \times 10^{-10}$ (1bar air)	298		
Branching ratios			
$k_1/k = 0.45$ (1 bar N_2)	298	Stickel et al., (1992)	(e)
$k_3/k < 0.02$ (13-39 mbar N_2)	298	Zhao et al., 1996	(f)
$k_1/k > 0.97$ (1.33 mbar He)	298	Butkovskaya et al., 1995	(g)
$k_3/k = (1.34 \pm 0.07) \times 10^{-3}$ (1 bar N_2)	298	Langer et al., (1996)	(h)

Comments

(a) Pulsed laser photolysis of $C(O)Cl_2$-CH_3SCH_3-N_2 mixtures at 266 nm. [Cl] was monitored by resonance fluorescence. Some experiments were carried out with CD_3SCD_3 and $C_2H_5SC_2H_5$. Reaction studied over the temperature range 240-421 K.

(b) Discharge flow-mass spectrometer experiment at 0.66 to 1.33 mbar of He. Experiments were conducted under pseudo-first order conditions with Cl atoms in excess. At these low pressures of He the association channel is not important and k can be equated to k_1 with an estimated upper limit to the yield of $ClS(CH_3)_2$ of 0.05.

(c) Photolysis of mixtures of $C(O)Cl_2$-CH_3SCH_3-cyclohexane-N_2 in a Teflon chamber. [Cyclohexane] and [CH_3SCH_3] measured at intervals by GC. k(Cl + cyclohexane) = 3.1 x 10^{-10} cm^3 $molecule^{-1}$ s^{-1} used (Atkinson and Aschmann, 1985).

(d) Photolysis of $C(O)Cl_2$ in presence of CH_3SCH_3 and n-butane as reference reactant at 1bar total pressure of N_2 or air. Depletion of CH_3SCH_3 and n-butane were monitored by GC-FID. The relative rate constant, k(Cl + CH_3SCH_3)/k(Cl + n-butane) = (1.86 $\pm$ 0.11) in N_2 and k(Cl + CH_3SCH_3)/k(Cl + n-butane) = (2.16 $\pm$ 0.08) in air and were put on an absolute basis using k(Cl + n-butane) = 2.05 x 10^{-10} cm^3 $molecule^{-1}$ s^{-1} (IUPAC, current recommendation).

(e) Yield of HCl studied by 248 nm pulsed laser photolysis of $C(O)Cl_2$-CH_3SCH_3-CO_2-N_2 mixtures over the pressure range 0.6-203 Torr and at 297 K. HCl formation was monitored by tunable diode laser spectroscopy, and an absolute yield obtained relative to Cl + C_2H_6.

(f) Yield of CH_3 studied by 248 nm pulsed laser photolysis of $C(O)Cl_2$-CH_3SCH_3-CO_2-N_2 mixtures over the pressure range 13.3-40 mbar and at 297 K. [HCl] monitored by tunable diode laser spectroscopy, and an absolute yield obtained relative to Cl + CH_4.

(g) Discharge flow-mass spectrometer set up. CH_3SCH_2 radicals formed in (1) were titrated with Cl_2 to form the stable product CH_3SCH_2Cl. In a similar manner, observation of CH_3Cl and CH_3SCl was used to infer yields of CH_3 (2) or CH_3S radicals (3).

(h) Reaction between Cl and CH_3SCH_3 initiated by photolysis of $C(O)Cl_2$ or $SOCl_2$ at 254 nm in 1 bar air. Branching ratio derived from observation of CH_3Cl formation and CH_3SCH_3 loss by GC.

Preferred Values

k = 3.4 x 10^{-10} cm^3 $molecule^{-1}$ s^{-1} at 298 K and 1 bar total pressure.
k_1/k = 0.45 at 298 K and 1bar total pressure
k_4/k = 0.55 at 298 K and 1bar total pressure

Reliability

$\Delta \log k = \pm 0.2$ at 298 K and 1 bar N_2.

Comments on Preferred Values

The preferred value of k at 1 bar total pressure is an average of the data of Stickel et al. (1992), Nielsen et al. (1990) and Kinnison et al. (1996), which are in good agreement.

The study of this reaction by Stickel et al. (1992) shows the reaction kinetics to have a complex dependency on temperature and pressure. The overall reaction rate is close to collisional and increases with decreasing temperature and with increasing pressure, with the high pressure limit approached between 150 and 700 Torr. The HCl yield approaches unity as the pressure tends to zero (Stickel et al. 1992; Butkovskaya et al. 1995) and decreases to a value of ~0.5 at 203 Torr N_2 and 297 K. The contribution of reactions (2) and (3) appear to be insignificant (Butkovskaya et al. 1995; Langer et al. 1996; Zhao et al. 1996).

These findings are interpreted in terms of the occurrence of two reaction channels, Cl abstraction (1) and adduct formation (4). At low pressures the abstraction channel is dominant but with increasing pressure the adduct can be stabilized leading to an increase in the total k as pressure increases and temperature decreases. Urbanski and Wine (1999) have characterised the adduct both in terms of its spectroscopy (UV absorption spectrum with σ max of 3.48 x 10^{-17} cm^2 $molecule^{-1}$ at 340 nm) and kinetically (reaction with O_2, NO and NO_2). Thermal decomposition of the adduct to reform Cl atoms was not observed on the ms time scale of the experiments of Stickel et al. (1992).

The results of Stickel et al. (1992) and Díaz-de-Mera et al. (2002) disagree at low pressures, with Stickel et al. deriving a negative temperature dependence at 4mbar N_2, and Díaz-de-Mera et al. (2002) a positive temperature dependence at 1.3 mbar He. For this reason, our recommendations are limited to high pressures and 298 K where the results of Stickel et al. (1992), Nielsen et al. (1990) and Kinnison et al. (1996) are in reasonable agreement. The results of Kinnison et al. (1996) yielded a rate coefficient which is larger in air than in N_2, perhaps indicating that the $ClS(CH_3)_2$ adduct can react with O_2. Urbanski and Wine (1999) place an upper limit of 4 x 10^{-18} cm^3 $molecule^{-1}$ s^{-1} on this reaction.

As discussed by Urbanski and Wine (1999), the effective overall rate coefficient and products under atmospheric conditions will depend on the fate of the $ClS(CH_3)_2$ adduct. Should thermal decomposition to Cl and CH_3SCH_3 dominate, this would reduce the effective rate coefficient to that of k_1. The similar rate coefficients obtained by observation of CH_3SCH_3 decay over time scales of minutes in the relative rate studies and those obtained by observation of Cl decay over ms in the absolute studies may indicate that the adduct has a lifetime of several minutes with respect to thermal decomposition. This leaves open the possibility that its photolysis is important. Urbanski and Wine (1999) estimated lifetimes with respect to atmospheric photolysis of about 10s. In the absence of other loss processes, photolysis of the adduct on this time scale would also reduce the effective rate coefficient to k_1 if the products were Cl atoms and CH_3SCH_3. Other thermodynamically feasible photolysis channels result in formation of e.g. CH_3Cl (Urbanski and Wine, 1999) and do not reduce k. Lifetimes for the reactive removal of $ClS(CH_3)_2$ via reaction with NO or NO_2 can be calculated from the rate coefficients presented by Urbanski and Wine of $k(ClS(CH_3)_2+NO)$ = 1.19 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1} and $k(ClS(CH_3)_2+NO)$ = 2.70 x10^{-11} cm^3 $molecule^{-1}$ s^{-1}. However, until the lifetime of the adduct with respect to thermal decomposition and reaction with O_2 are known, the recommended overall rate coefficient appears to be most the suitable for modelling the lifetime of CH_3SCH_3 with respect to Cl atom reaction in the boundary layer.

References

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