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


Cl + CH3SCH3 → HCl + CH3SCH2 (1)
Cl + CH3SCH3 → CH3 + ClSCH3 (2)
Cl + CH3SCH3 → CH3Cl + CH3S (3)
Cl + CH3SCH3 + M → ClS(CH3)2 + M (4)

ΔH°(1) = -39.6 kJ mol⁻¹
ΔH°(3) = -41.5 kJ mol⁻¹

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

<table>
<thead>
<tr>
<th>( k/\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} )</th>
<th>Temp./K</th>
<th>Reference</th>
<th>Technique/Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absolute Rate Coefficients</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.8 x 10⁻¹⁰ (4 mbar N₂)</td>
<td>297</td>
<td>Stickel et al., 1992</td>
<td>PLP-RF (a)</td>
</tr>
<tr>
<td>(3.3 ± 0.5) x 10⁻¹⁰ (933 mbar N₂)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>2.0 x 10⁻¹⁰ ( \exp\left[-(332 ± 173)/T\right] )</td>
<td>259-364</td>
<td>Diaz-de-Mera et al., 2002</td>
<td>DF-MS (b)</td>
</tr>
<tr>
<td>(0.66-1.3 mbar He)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(6.9 ± 1.3) x 10⁻¹¹ (0.66-1.3 mbar He)</td>
<td>298</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(3.6± 0.2) x 10⁻¹⁰ (1bar air)</td>
<td>298</td>
<td>Enami et al., 2004</td>
<td>CRDS (c)</td>
</tr>
<tr>
<td>Relative Rate Coefficients</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(3.2 ± 0.3) x 10⁻¹⁰ (986 mbar N₂)</td>
<td>295</td>
<td>Nielsen et al., 1990</td>
<td>RR (d)</td>
</tr>
<tr>
<td>(3.81 ± 0.23) x 10⁻¹⁰ (1 bar N₂)</td>
<td>298</td>
<td>Kinnison et al., 1996</td>
<td>RR (e)</td>
</tr>
<tr>
<td>(4.43 ± 0.17) x 10⁻¹⁰ (1bar air)</td>
<td>298</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(5.42 ± 1.85) x 10⁻¹³ ( \exp(1946/T) )</td>
<td>283-308</td>
<td>Arsene et al., 2005</td>
<td>P-FTIR (f)</td>
</tr>
<tr>
<td>3.7 x 10⁻¹⁰ (1bar air)</td>
<td>298</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Branching ratios</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_1/k = 0.45 ) (1 bar N₂)</td>
<td>298</td>
<td>Stickel et al., 1992</td>
<td>(g)</td>
</tr>
<tr>
<td>( k_3/k &lt; 0.02 ) (13-39 mbar N₂)</td>
<td>298</td>
<td>Zhao et al., 1996</td>
<td>(h)</td>
</tr>
<tr>
<td>( k_1/k &gt; 0.97 ) (1.33 mbar He)</td>
<td>298</td>
<td>Butkovskaya et al., 1995</td>
<td>(i)</td>
</tr>
<tr>
<td>( k_1/k = 0.50 ) (1 bar N₂)</td>
<td>298</td>
<td>Enami et al., 2004</td>
<td>(c)</td>
</tr>
</tbody>
</table>

Comments
Pulsed laser photolysis of C(O)Cl₂-CH₃SCH₃-N₂ mixtures at 266 nm. [Cl] was monitored by resonance fluorescence. Some experiments were carried out with CD₂SCD₃ and C₂H₅SC₂H₅. Reaction studied over the temperature range 240-421 K.

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 k₁ with an estimated upper limit to the yield of ClS(CH₃)₂ of 0.05.

Rise and decay time profiles of the ClS(CH₃)₂ adduct were followed by CRDS after laser photodissociation of Cl₂SO. The falloff curve for adduct formation was derived from measurements between 20 and 300 Torr of N₂ and over the range 278-318 K of this work and results from earlier work, leading to 

\[ k_{4,0} = (2.2 \pm 0.7) \times 10^{-28} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \] and 

\[ k_{4,\infty} = (2.2 \pm 0.2) \times 10^{-10} \text{ s}^{-1} \] (evaluated with \( F_c = 0.6 \)).

Photolysis of mixtures of C(O)Cl₂-CH₃SCH₃-cyclohexane-N₂ in a Teflon chamber. [Cyclohexane and [CH₃SCH₃] measured at intervals by GC. \( k(\text{Cl + cyclohexane}) = 3.1 \times 10^{10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) used (Atkinson and Aschmann, 1985).

Photolysis of C(O)Cl₂ in presence of CH₃SCH₃ and n-butane as reference reactant at 1 bar total pressure of N₂ or air. Depletion of CH₃SCH₃ and n-butane were monitored by GC-FID. The relative rate constant, 

\[ k(\text{Cl + CH₃SCH₃})/k(\text{Cl + n-butane}) = (1.86 \pm 0.11) \text{ in N₂ and } k(\text{Cl + CH₃SCH₃})/k(\text{Cl + n-butane}) = (2.16 \pm 0.08) \text{ in air} \]

and were put on an absolute basis using 

\[ k(\text{Cl + n-butane}) = 2.05 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \] (IUPAC, current recommendation).

Photolysis of mixtures of trichloroacetyl chloride, as source for Cl atoms, with CH₃SCH₃, N₂, and O₂ in a 1080 l reactor. Reactions of chlorine atoms with cyclohexane, n-butane, or propene were used as references (IUPAC, current recommendation). Reactant concentrations were followed by FTIR absorption spectroscopy.

Yield of HCl studied by 248 nm pulsed laser photolysis of C(O)Cl₂-CH₃SCH₃-CO₂-N₂ 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 + C₂H₆.

Yield of CH₃ studied by 248 nm pulsed laser photolysis of C(O)Cl₂-CH₃SCH₃-CO₂-N₂ 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 + CH₄.

Discharge flow-mass spectrometer set up. CH₃SCH₂ radicals formed in (1) were titrated with Cl₂ to form the stable product CH₃SCH₂Cl. In a similar manner, observation of CH₃Cl and CH₃SCl was used to infer yields of CH₃ (2) or CH₃S radicals (3).

Reaction between Cl and CH₃SCH₃ initiated by photolysis of C(O)Cl₂ or SOCl₂ at 254 nm in 1 bar air. Branching ratio derived from observation of CH₃Cl formation and CH₃SCH₃ loss by GC.

Preferred Values
\[ k = 3.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K and 1 bar of air.} \]

\[ k_1/k = 0.50 \text{ at 298 K and 1 bar} \]

\[ k_4/k = 0.50 \text{ at 298 K and 1 bar} \]

**Reliability**

\[ \Delta \log k = \pm 0.2 \text{ at 298 K and 1 bar N}_2. \]

**Comments on Preferred Values**

The preferred value of \( k \) at 1 bar total pressure is from Enami et al. (2004) in good agreement with the data of Stickel et al. (1992), Nielsen et al. (1990), and Kinnison et al. (1996).

The study of this reaction by Stickel et al. (1992) shows the reaction kinetics to have a complex dependence 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 \( \sigma_{\text{max}} = 3.48 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1} \) 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). Theoretical studies of the reaction by Enami et al. (2004) confirm this interpretation.

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 4 mbar 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 \( 4 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) 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\(_3\)SCH\(_3\) dominate, this would reduce the effective rate coefficient to that of \( k_1 \). The similar rate coefficients obtained by observation of CH\(_3\)SCH\(_3\) 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\(_3\)SCH\(_3\). Other thermodynamically feasible photolysis channels result in formation of e.g. CH\(_3\)Cl (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 \( k(\text{ClS(CH}_3)_2+\text{NO}) = 1.19 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) and \( k(\text{ClS(CH}_3)_2+\text{NO}_2) = 2.70 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \). 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\(_3\)SCH\(_3\) with respect to Cl atom reaction in the boundary layer.
References