Kinetic Study of the Reactions CH₂ClCH₂Cl + OH, CH₃C(O)CH₃ + Cl and HC(O)OCH₂CH₃ + Cl by the Relative Rate Method

STIG RUNE SELLEVÅG AND CLAUS JØRGEN NIELSEN*

Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo, Norway

The kinetics of the OH reaction with 1,2-dichloroethane and of the Cl reactions with acetone and ethyl formate was studied by the relative rate method at 298 K and 1013 hPa using long path Fourier transform infrared detection. The results, with 3σ errors, are \( k_{OH-CH₂ClCH₂Cl} = 2.16(13) \times 10^{-12} \), \( k_{Cl-CH₃C(O)CH₃} = 2.00(9) \times 10^{-12} \), and \( k_{Cl-HC(O)OCH₂CH₃} = 1.10(7) \times 10^{-12} \) cm² molecule⁻¹ s⁻¹.

© Anita Publications. All rights reserved.

1 Introduction

During ongoing work in our laboratory concerning the atmospheric chemistry of fluorinated alcohols and ethers, we have used 1,2-dichloroethane, acetone and ethyl formate as reference compounds in relative rate measurements, and we have noticed that there were some inconsistencies in the OH and Cl rate coefficients used in the literature for these compounds. In the present work we report our findings for the following reactions:

\[
\begin{align*}
CH₂ClCH₂Cl + OH & \rightarrow \text{Products} \\
CH₃C(O)CH₃ + Cl & \rightarrow \text{Products} \\
HC(O)OCH₂CH₃ + Cl & \rightarrow \text{Products}
\end{align*}
\]

The rate coefficient of the OH reaction with 1,2-dichloroethane has previously been measured by Aarns et al.,¹ Howard and Evenson,² Taylor et al.,³ and Qiu et al.⁴ Chiorboli et al.⁵ have modelled the reaction rate coefficient in terms of eleven qualitative descriptors drawn from the chemical structures of 76 halogenated methanes and ethanes.

A critical evaluation of the rate coefficient for the reaction between acetone and chlorine atoms was presented by Atkinson et al.⁶ Their recommended value has a 60% uncertainty, and is primarily based on a relative rate study by Wallington et al.⁷ However, Atkinson et al.⁸ adjusted the value of the reaction rate coefficient of the reference compound used by Wallington et al.⁷ The Cl + CH₃C(O)CH₃ reaction rate coefficient has since then been measured by Olsson et al.⁹ and by Notario et al.¹⁰

To our knowledge there has only been one previous kinetic study of the chlorine reaction with ethyl formate, a laser photolysis – resonance fluorescence study by Notario et al.¹⁰

2 Experimental

The OH and Cl reaction rate coefficients were determined by the relative rate method

\[
\begin{align*}
A + X & \xrightarrow{k₁} \text{Prod} \\
R + X & \xrightarrow{k₂} \text{Prod}
\end{align*}
\]

where A is the reactant of interest, R is the reference compound, X is the radical, and \( k₁ \) and \( k₂ \) are the

* Author to whom correspondence should be addressed. E-mail: claus.nielsen@kjemi.uio.no
reaction rate coefficients. Assuming that the reactant and reference compounds are lost solely via reaction with the radical species of interest and that they are not reformed in any process, the relative rate coefficient, \( k_{\text{rel}} \), can be obtained by the following relation:

\[
\ln \left( \frac{[A]_0}{[A]_t} \right) = k_{\text{rel}} \cdot \ln \left( \frac{[R]_0}{[R]_t} \right) \quad k_{\text{rel}} = \frac{k_1}{k_{11}}
\]

(1)

in which \([A]_0\), \([R]_0\), \([A]_t\), and \([R]_t\) denote the concentrations of A and R at time zero and \(t\), respectively. A plot of \(\ln([A]_0/[A]_t)\) vs. \(\ln([R]_0/[R]_t)\) will give \(k_{\text{rel}}\) as the slope.

The measurements were performed at 1013 ± 15 hPa and 298 ± 2 K in synthetic air in a 250 L smog chamber of electropolished stainless steel with \textit{in situ} FTIR detection. The smog chamber is equipped with White-type multiple reflection mirrors and with an optical path length of 120 m. The FTIR spectra were recorded in the wavelength region 4000–400 cm\(^{-1}\) using a Bruker IFS 88 spectrometer employing a nominal resolution of 0.5 cm\(^{-1}\), Happ-Genzel apodization and adding 100 scans. The recording time for 100 scans was ca. 75 s.

Hydroxyl radicals were generated by photolysis of ozone/water mixtures. Typical volume fractions of water and ozone were 1000 and 500 ppm, respectively. Ozone was produced from oxygen by using a TRI-OX Ozone Generator model T-200 that converts approximately 2% of the oxygen gas flow to ozone. The photodissociation of ozone was accomplished by two Philips TL 20W/12 fluorescence lamps (\(\lambda_{\text{max}} \approx 310\) nm) mounted in a quartz tube in the smog chamber. The photolysis was done in intervals of 3–10 minutes length. Chlorine atoms were produced by photolysis of molecular chlorine by using two Philips TLD 18W/08 fluorescence lamps (\(\lambda_{\text{max}} \approx 370\) nm). Typical volume fractions of Cl\(_2\) were 20–30 ppm. The photolysis was carried out in intervals of 1–5 minutes length.

Synthetic air (CO + NO\(_2\) < 100 ppb, C\(_6\)H\(_{14}\) < 1 ppm), ethane (99.0 %), chlorine gas (99.8 %) and oxygen gas (99.95 %) were delivered from AGA. Acetone, 1,2-dichloroethane and ethyl formate were standard commercial chemicals with purity better than 98 %. All organic compounds except ethane were degassed by doing three freeze-pump-thaw cycles.

The volume fractions of the organic compounds were typically 3–10 ppm. The rate coefficient of the \(\text{OH}\) reaction with 1,2-dichloroethane was determined relatively to that of ethane, while the rate coefficients of the Cl reactions with acetone and ethyl formate were determined relative to those of 1,2-dichloroethane and ethane, respectively. The organic compounds were photostable under our experimental conditions and all reaction mixtures were stable in the reaction chamber when the photolysis lamps were turned off.

3 Results

Spectral subtraction was used to determine the relative concentrations of the reactants at different points of time during the reactions. Reference spectra of the reactants and identified products were included in the subtraction procedure along with a sloping baseline. The data from the spectral subtraction procedure was plotted according to Eq. 1, and the relative rate coefficients were determined by using a least-squares method that takes into account the uncertainty in both the ordinate and the abscissa. Each relative rate coefficient was determined from three independent measurements.
Kinetic Study of the Reactions \( CH_2ClCH_2Cl + OH, \ CH_3C(\text{O})CH_3 + Cl \ldots \)

\( CH_2ClCH_2Cl + OH \). In the study of the OH reaction with 1,2-dichloroethane and ethane, the relative concentration of 1,2-dichloroethane was determined by analysing the 1250–1220 cm\(^{-1}\) spectral region while the ethane concentration was determined from the 2910–2845 cm\(^{-1}\) region. The products from the OH initiated oxidation of \( CH_2ClCH_2Cl \) were HCl, CO\(_2\), HCOCl, and \( CH_2ClCOCl \). Bands belonging to

![Figure 1. FTIR spectra of the reaction mixture 1,2-dichloroethane/ethane/water/ozone. (A) Spectra of the \( CH_2 \) twisting mode region of 1,2-dichloroethane where (a) is reference spectrum, (c) is before reaction with OH, (d) is after reaction with OH, and (e) is residual after subtraction. (B) Spectra of the symmetric \( CH_3 \) stretching mode region of ethane where (b) is reference spectrum, (c) is before reaction with OH, (d) is after reaction with OH, and (e) is residual after subtraction.](image)

\( CH_3COOH, HCOOH, O_3 \) and \( H_2O \) overlapped the \( CH_2 \) twisting mode of 1,2-dichloroethane, while HCHO \( CH_2ClCH_2Cl, HCOCl, HCl \) and \( H_2O \) bands overlapped the symmetric \( CH_3 \) stretching mode of ethane around 2895 cm\(^{-1}\). Spectra of the reaction mixture before and after the reaction with OH along with the residuals after the spectral subtraction are shown in Fig. 1, and a plot of \( ln[[CH_2ClCH_2Cl]/[CH_2ClCH_2Cl]] \) vs. \( ln[[CH_3CH_3]/[CH_3CH_3]] \) is shown in Fig. 2A.

An analysis of the data gave a relative rate coefficient of 0.86(5) and an intercept of 0.005(5); errors quoted represent 3\( \sigma \) from the statistical analysis. That is, there is apparently very little systematic error arising from competing reactions, see below, and in the spectral determination of the relative reactant concentration. The recommended OH reaction rate coefficient of ethane is \( 2.5 \times 10^{-13} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), which places the absolute rate coefficient of the OH + 1,2-dichloroethane reaction at \( 2.16(13) \times 10^{-13} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\). Uncertainty in the rate coefficient of the reference compound is not included.

There is a clear downward curvature in the relative rate plot of the OH + 1,2-dichloroethane/ethane data when more than 20% of the reactants have reacted. Thus, the data points beyond 20% reaction were excluded from the analysis. The fact that chlorine atoms react ca. 45 times faster with ethane than with 1,2-dichloroethane, suggest that significant amounts of chlorine atoms were released and contributed in

![Figure 2. (A) \( ln[[1,2-dichloroethane]/[1,2-dichloroethane]] \) vs. \( ln[[\text{ethane}]/[\text{ethane}]] \) during the reaction with OH radicals. (B) \( ln[[\text{acetone}]/[\text{acetone}]] \) vs. \( ln[[1,2-dichloroethane]/[1,2-dichloroethane]] \) during the reaction with Cl atoms. (C) \( ln[[\text{ethyl formate}]/[\text{ethyl formate}]] \) vs. \( ln[[\text{ethane}]/[\text{ethane}]] \) during the reaction with chlorine atoms. The uncertainty in each data point is based on an estimated uncertainty of 0.01 in the relative concentrations.](image)
\( CH_2C(O)CH_3 + Cl \). The rate coefficient for the Cl atom reaction with acetone was measured relatively to that of 1,2-dichloroethane. The relative concentrations of acetone were determined by analysing the antisymmetric CH\(_2\) stretching mode in the 3050–3000 cm\(^{-1}\) region and reference spectra of CH\(_2\)ClCH\(_2\)Cl, HCOOH, HCOCl, HCl and H\(_2\)O were included in the spectral subtraction. Analysis of the 1305–1270 cm\(^{-1}\) region, see above, gave the relative concentrations of 1,2-dichloroethane. The spectral range contained overlapping bands from CH\(_2\)C(O)CH\(_3\), CH\(_3\)COOH, HCOCl and H\(_2\)O. The residuals after the spectral subtractions were similar in magnitude to those shown in Fig. 1A. Analysis of the relative rate plot (Fig. 2B) gave \( k_{rel} = 1.54 \pm 0.64 \) and an insignificant intercept of \(-0.037(27) (3\sigma)\). Using a rate coefficient of \(1.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) for the Cl reaction with 1,2-dichloroethane,\(^{13}\) gives an absolute rate coefficient of \(2.00(9) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) for the reaction between acetone and chlorine atoms. Uncertainty in the rate constant of the reference compound is not included.

The major products of the reaction between chlorine atoms and acetone were CO, CO\(_2\), and HCOOC. Acetyl chloride, CH\(_3\)COCl, was a minor product (< 5 %) and traces of CH\(_3\)COOH were also seen.

\( HC(O)OCH_2CH_3 + Cl \). Figure 2C shows a plot of ln\(\{[HC(O)OCH_2CH_3]/[HC(O)OCH_2CH_3]_0\}\) versus ln\(\{[\text{CH}_3\text{CH}_3]/[\text{CH}_3\text{CH}_3]_0\}\) during their reaction with Cl atoms. The relative concentrations of ethyl formate and ethane were determined by spectral subtraction in the 1250–1150 and 2920–2850 cm\(^{-1}\) regions, respectively. Reference spectra of HCOOH, CH\(_3\)COOH and H\(_2\)O were included in the subtraction procedure in the 1250–1150 cm\(^{-1}\) region, while additional spectra of HC(O)OCH\(_2\)CH\(_3\), HCl, HCHO and HCOOH were included in the analysis of the 2920–2850 cm\(^{-1}\) CH\(_3\) stretching mode region of ethane. The residuals after the subtractions were similar in magnitude to those shown in Fig. 1. Analysis of the data, Fig. 2C, gave a relative rate coefficient of 0.186(12) and an insignificant intercept of \(-0.011(9) (3\sigma)\). The preferred rate constant for the Cl reaction with ethane is \(5.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\),\(^{12}\) which gives an absolute rate coefficient of \(1.10(7) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) for the Cl reaction with ethyl formate when the uncertainty in the rate constant of ethane is not taken into consideration.

The main products of the Cl initiated oxidation of ethyl formate are HCOOH, CO and CO\(_2\), and only traces of CH\(_3\)COOH were found in the spectra.

4 Discussion

Table 1 gives a comparison of the results from the different studies of the OH reaction with 1,2-dichloroethane. The reaction rate coefficient measured in this work is in very good agreement with the previous experimental studies.

The primary products observed in the OH initiated oxidation of 1,2-dichloroethane in our system (ca. 500 ppm O\(_3\)) were HCl, CO\(_2\), CH\(_2\)CICOCl, and HCOCl (the other compounds observed during the reaction stem from the oxidation of ethane). Our results therefore confirm the proposed reaction mechanism of Wallington et al.,\(^{13}\) in which the eventually formed oxy radical primarily eliminates HCl:

\[
\text{CH}_2\text{ClCH}_2\text{Cl} \xrightarrow{\text{OH}} \text{O}_2 \xrightarrow{\text{HO}_2\text{RO}_2\text{O}_1} \text{CH}_2\text{ClC(O)HCl} \rightarrow \text{CH}_2\text{ClCO} + \text{HCl} \quad (V)
\]

The chloroacetyl radical, formed in reaction (V), will add O\(_2\), react with HO\(_2\), RO\(_2\) or O\(_3\) and eliminate CO\(_2\) to give the CH\(_2\)Cl radical, which in turn gives formyl chloride. The Cl atoms liberated in the later stages of the reaction most likely stem from either photolysis of or from the slow OH initiated oxidation of formyl chloride.\(^{12}\)
Table 1 also includes a comparison of the available measurements of the rate coefficient for the reaction between acetone and chlorine atoms. As seen, the reaction rate coefficient measured in this work falls between the values reported by Olsson et al. and Wallington et al., but it disagrees with the preferred reaction rate coefficient of Atkinson et al. and the results of Notario et al. As mentioned in the introduction, the evaluation of Atkinson and co-workers is based on a study by Wallington et al. The preferred value of $3.5 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ was obtained by combining a measurement of $k(\text{Cl} + \text{CH}_3\text{Cl})/k(\text{Cl} + \text{CH}_3\text{CH}_2\text{Cl}) = 0.201(27)$ and $k(\text{Cl} + \text{CH}_3\text{CH}_3) = 5.9 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. Wallington and co-workers used $8.04 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ as rate constant for the reaction between chlorine atoms and chloroethane. Wallington and co-workers remeasured the Cl rate constant of chloroethane and obtained a new value of $8.7(1.0) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, with the conclusion that the new value should supersede the previous values. Recently, Dobis and Benson measured a rate coefficient equal to $8.07(36) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for the reaction between chlorine atoms and chloroethane. We conclude that a re-evaluation of the Cl + CH$_3$CICH$_2$Cl reaction rate coefficient is needed and that the preferred value should be adjusted from $3.5 \times 10^{-12}$ to $2 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

Acetyl chloride was one of the observed products in the reaction between chlorine atoms and acetone. The compound is only a minor product of the reaction (< 5%), but a mechanism solely based on hydrogen abstraction cannot explain this production. We suggest that addition of Cl atoms to the carbonyl bond constitute a minor channel in the reaction. A similar mechanism has been proposed by Wollenhaupt et al. and by Wollenhaupt and Crowley for the reaction between acetone and OH radicals where the product formed is acetic acid. Recently, Vasári et al. characterised by ab initio calculations two different pathways for the reaction between OH and acetone. An activation energy of 33.9 kJ mol$^{-1}$ was found for the addition of OH to the carbonyl bonding. This is, however, not consistent with the experimental activation energy (3.5 kJ mol$^{-1}$) determined by Wollenhaupt and co-workers.

As mentioned, there has only been one previous measurement of the rate coefficient for Cl reaction with ethyl formate. Our value of 1.10(7) x 10$^{-11}$ is in good agreement with the results from previous study, 1.34(15) x 10$^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The observed product distribution, with HCOOH being the main product, indicates that the major site of attack by the chlorine atoms is on the methyl group. A recent structure activity relationship for esters also point to this site of attack. Through a series of fast elementary steps this will result in the thermally unstable formic acid anhydride, which converts to formic acid and CO through intermolecular hydrogen transfer.

$$
\text{HC(O)OCH}_2\text{CH}_2 + \text{Cl} \rightarrow \text{HC(O)OCH}_2\text{CH}_2 + \text{HCl} \\
\text{HC(O)OCH}_2\text{CH}_2 + \text{O}_2 \rightarrow \text{HO}_2\text{.RO}_2 \rightarrow \Delta \rightarrow \text{HC(O)OCH}_2 + \text{HCHO} \quad \text{(IV)} \\
\text{HC(O)OCH}_2 + \text{O}_2 \rightarrow \text{HO}_2\text{.RO}_2 \rightarrow \text{HC(O)OC(O)H} \rightarrow \text{HCOOH + CO}
$$

Table 1. Comparison of measured rate coefficients for the OH reaction with 1,2-dichloroethane and for the Cl reaction with acetone.

<table>
<thead>
<tr>
<th>OH + CH$_3$CICH$_2$Cl</th>
<th>Method$^a$</th>
<th>Reference</th>
<th>Cl + CH$_3$C(O)CH$_3$</th>
<th>Method$^a$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{\text{OH}} / 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$</td>
<td>RR-FTIR</td>
<td>This work</td>
<td>$k_{\text{Cl}} / 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$</td>
<td>RR-FTIR</td>
<td>This work</td>
</tr>
<tr>
<td>2.16 ± 0.13$^b$</td>
<td>RR-GC</td>
<td>Ref. 1</td>
<td>2.00 ± 0.09$^e$</td>
<td>RR-FTIR</td>
<td>Ref. 7</td>
</tr>
<tr>
<td>2.8 ± 0.6</td>
<td>DF-LMR</td>
<td>Ref. 2</td>
<td>2.37 ± 0.12$^c$</td>
<td>RR-LP</td>
<td>Ref. 8</td>
</tr>
<tr>
<td>2.2 ± 0.5$^c$</td>
<td>LP-LIF</td>
<td>Ref. 3</td>
<td>1.69 ± 0.32$^k$</td>
<td>Evaluated</td>
<td>Ref. 6</td>
</tr>
<tr>
<td>2.48 ± 0.38$^d$</td>
<td>DF-RF</td>
<td>Ref. 4</td>
<td>3.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.22 ± 0.44$^e$</td>
<td></td>
<td></td>
<td>3.06 ± 0.38</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$RR = relative rate; FTIR = Fourier transform infrared spectroscopy; GC = gas chromatography; DF = discharge flow; LMR = laser magnetic resonance; LP = laser photolysis; LIF = laser induced fluorescence; RF = resonance laser fluorescence; PLF = pulsed laser photolysis. $^b$Relative to ethane, $k = 2.5 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. $^c$Measured at 296 K. $^d$Relative to CH$_3$Cl, $k = 1.3 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. $^e$Relative to CH$_3$CH$_2$Cl, $k = 8.04 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. $^f$Measured at 295 K. $^g$Relative to CINO$_2$, $k = 1.0 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. $^h$Measured at 294 K.
Acknowledgements

This work is part of the project “Impact of Fluorinated Alcohols and Ethers on the Environment” (IAFAEE) and has received support from the CEC Environment and Climate program through contract ENVK2-1999-00099.

References

[Received: 26.6.2002]