Studies by the Electron Cyclotron Resonance (ECR)-Technique IX: Interactions of Low-Energy Electrons with the Molecules CH$_2$Cl$_2$ and CHCl$_3$ in the Gas Phase

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The capture of thermal electrons by the molecules CH$_2$Cl$_2$ and CHCl$_3$ is reinvestigated and discussed. An attempt is presented to describe the reaction path in terms of potential energy diagrams.

Introduction

Interactions of low-energy electrons with potential electron scavengers can conveniently be followed using the ECR-technique. Absolute rate constants for capture processes together with Arrhenius parameters were determined at thermal electron energies. Also, changes of relative attachment cross sections may be followed as function of the electron energy with only slight modifications of the experimental procedure.

In this paper results are given on the interactions of low-energy electrons with the molecules CH$_2$Cl$_2$ and CHCl$_3$. The results presented here are supplementary to the results obtained on Cl$_2$ and CCl$_4$. Potential energy diagrams are constructed using the experimental data reported in this study and a model suggested by Wentworth et al. 5-7.

All experiments were carried out in a quartz flow tube equipped with five mixing chambers located at various distances from the resonance cavity. Argon was used as a carrier gas and, at the same time, as the electron source. Experimental details are given elsewhere 2-4.

Results and Discussion

a) Rate constants: In Figs. 1 and 2 the measured rates for the electron disappearance in the presence of dichloromethane and chloroform are plotted as a function of [CH$_2$Cl$_2$] and [CHCl$_3$], respectively. Each point given was determined from the time-dependence of the capture process at constant scavenger concentration [RCI]. The increase of the $k_{exp}$-values at low [CHCl$_3$] (Fig. 2) is due, in part at least, to heterogeneous electron losses at the wall.
of the flow tube\textsuperscript{4}. The $k$-values of $4.6 \times 10^{-12}$ cm$^3$ sec$^{-1}$ for CH$_2$Cl$_2$ and $1.3 \times 10^{-9}$ cm$^3$ sec$^{-1}$ for CHCl$_3$ were obtained from the concentration-independent values for the disappearance of electrons in the presence of the halides. These rate constants are in good agreement with other data reported previously\textsuperscript{8}. In microwave conductivity measurements\textsuperscript{9} the rate constant for electron capture by CHCl$_3$ in n-C$_6$H$_{14}$ decreased from $2.65 \times 10^{-9}$ cm$^3$ sec$^{-1}$ in going from 80 to 33 torr of total pressure. From an Arrhenius plot (see Fig. 6 of Ref.\textsuperscript{9}), a $k$-value of $1.8 \times 10^{-9}$ cm$^3$ sec$^{-1}$ for the electron capture by CHCl$_3$ could be determined for 20° C and 17 torr. If the pressure of n-hexane was further lowered, the above $k$-value would come even closer to the rate constant of $1.3 \times 10^{-9}$ cm$^3$ sec$^{-1}$ obtained in this work.

An activation energy of $AE = 2.3$ kcal \cdot mole$^{-1}$ was obtained for electron attachment to CHCl$_3$ from measurements in the temperature range 20 - 180° C and [CHCl$_3$] $\geq 1.5 \times 10^{14}$ cm$^{-3}$. This $AE$-value is also in good agreement with previous findings\textsuperscript{3, 9, 10}.

\textit{b) The reaction path:} It is most likely that thermal electron capture by the molecules CH$_2$Cl$_2$ and CHCl$_3$ proceeds dissociatively via the formation of a temporary compound negative ion RC1$^-$ (R = CH$_2$Cl or CHCl$_2$), i.e.

$$e_{th} + RCl \rightarrow RC1^- \rightarrow R + Cl^-.$$  \hfill (1)

For both CH$_2$Cl$_2$ and CHCl$_3$ molecules, the dissociative electron attachment process is exothermic with $\Delta H^0 = -9$ and $-15$ kcal \cdot mole$^{-1}$ respectively, as calculated from the respective heats of formation $\Delta H^0$ for Cl$^-$, CH$_2$Cl, CHCl$_2$, CH$_2$Cl$_2$ and CHCl$_3$ (see Table 1). Other probable reactions are highly endothermic and thus can be excluded. On the other hand, the dissociation asymptote of CH$_2$Cl$_2^-$ and CHCl$_3^-$ lies around 0.29 and $0.43$ eV, respectively, below the ground state of the neutral molecules, as determined from the dissociation energies for CH$_2$Cl$-$Cl and CHCl$_2$-Cl (see Table 1) and the electron affinity $EA(\text{Cl}) = 3.613$ eV\textsuperscript{11} of the chlorine atom.

The values of 76.6 and 73.3 kcal \cdot mole$^{-1}$ for $D(\text{CH}_2\text{Cl}^-\text{-Cl})$ and $D(\text{CHCl}_2^-\text{-Cl})$, respectively, used in this work were taken as average values (Table 1) of the data found in the literature for the halogenated methanes of the form CH$_{1-n}$Cl$_n$ ($n = 1, 2, 3, 4$). It is noted here that the average values for the dissociation energies of CH$_3$-Cl and CH$_2$Cl-Cl were calculated from the experimental electron attachment cross section, $\sigma_{rel}$, by reflection\textsuperscript{13} on the probability density distribution function $\Psi_0^2$ for the neutral molecule RCl.

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta H^0_t$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$^-$</td>
<td>$-55.9$ a, $-58.8$ b, $-58.9$ c</td>
</tr>
<tr>
<td>CH$_2$Cl</td>
<td>25.8 d$^1$, 25.5 d$^2$, 30.0 b</td>
</tr>
<tr>
<td>CHCl$_2$</td>
<td>$-21$ e, $-21.5$ f, $-22.1$ b, $-22.5$ d$^1$, $-22.8$ d$^2$, $-22.83$ a</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>18.8 d$^1$, 18.6 d$^2$</td>
</tr>
<tr>
<td>CH$_2$Cl-Cl</td>
<td>73.3 k, 76 e, 77.2 b, 78 l</td>
</tr>
<tr>
<td>CHCl$_2$-Cl</td>
<td>71.9 b, 73 l, 73.5 k, 75 e</td>
</tr>
</tbody>
</table>

References to Table 1

\begin{itemize}
  \item a) "JANAF Thermochemical Tables", by D. R. Stull and H. Prophet, National Bureau of Standards, NSRDS-NBS 37, June 1971.
  \item b) J. J. De Corpo, D. A. Bafus, and J. L. Franklin, J. Chem. Phys. 54, 1592 [1971].
  \item d) Yu. Papulov, Zh. Obsch. Khim. 37, 1183, 1191 [1967]; $^1 = $ experimental value, $^2 = $ calculated value.
  \item f) H. J. Bernstein, J. Phys. Chem. 69, 1550 [1965].
  \item g) R. I. Reed and W. Snedden, Trans. Faraday Soc. 55, 876 [1959].
  \item h) Yu. Papulov, Zh. Obsch. Khim. 34, 1252 [1964].
\end{itemize}
Table 2. Parameters used for the calculation of the potential energy diagrams for the molecules CH₂Cl₂ and CHCl₃.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value †</th>
<th>Ref.</th>
<th>Parameter</th>
<th>Value †</th>
<th>Ref.</th>
</tr>
</thead>
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<tr>
<td>D(CH₂Cl—Cl)</td>
<td>3.32 *</td>
<td>11</td>
<td>D(CHCl₂—Cl)</td>
<td>3.18 *</td>
<td>11</td>
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<tr>
<td>EA (Cl)</td>
<td>3.613</td>
<td></td>
<td>EA (Cl)</td>
<td>3.613</td>
<td>11</td>
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<td>Uₘₕ</td>
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<td>AE</td>
<td>0.10</td>
<td>c</td>
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<tr>
<td>AE</td>
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<td>ω₀</td>
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<td>a</td>
<td>ω₀</td>
<td>680 cm⁻¹</td>
<td>d</td>
</tr>
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<td>r₀</td>
<td>1.77 Å</td>
<td>b</td>
<td>r₀</td>
<td>1.77 Å</td>
<td>b</td>
</tr>
</tbody>
</table>

† All values are given in eV ( = 23.063 kcal·mole⁻¹), except as noted.
* Average value (see Table 1).
c This work.

CH₃Cl₂: As in the case of CH₂Cl₂, a similar approach was followed to determine the potential energy diagrams for CHCl₂ (Figure 4). Curve (a) corresponds again to I = 0.663 eV ⁵, ⁶. For curves (b) and (c), the activation energies of 3.1 kcal·mole⁻¹ (see ⁶) and 2.3 kcal·mole⁻¹ obtained in this work were used, respectively. Curve (d) was calculated using the energy dependence of σᵣₑ₁ for CHCl₂ ¹⁴.

CHCl₃: The potential energy diagrams for the neutral and the negatively charged CH₂Cl−Cl, shown in Fig. 3, were constructed with the aid of the data compiled in Table 2. Curve (a) was obtained using the fixed value of 0.663 eV for the intercept I of the plot AE vs [D (R−Cl) − EA (Cl)] ⁵, ⁶. In view, however, of the spread in D (R−Cl) data (see Table 1), the value for I was calculated in this work separately for each molecule using the average D (R−Cl) values, the well-accepted EA (Cl) = 3.613 eV ¹¹ and the experimentally determined activation energies AE. Curves (b) and (c) in Fig. 3 were obtained using the activation energy AE = 7.5 kcal·mole⁻¹ (see ⁶) and 4.1 kcal·mole⁻¹ (see ⁸), respectively. The energy-dependence of the cross section σᵣₑ₁ (in relative units) for the electron capture by CH₂Cl₂ ¹⁴ is shown in Fig. 3 with ordinates representing the energy of the free electrons (points *). Reflection of σᵣₑ₁ on Ψ₀² results in curve (d) shown as (++) in Figure 3.

The potential energy curves obtained from the experimental capture cross sections and those calculated from the empirical modified Morse function seem to be reasonably close to each other (Figs. 3 and 4). Better agreement between the two potential energy representations resulted when the smaller activation energies, measured by the ECR-technique, were used [curve (c) in Figs. 3 and 4]. The existence of a shallow minimum in the RC1−* potential energy curve should not affect the electron capture...
process since it lies much below the potential energy curve for the neutral molecule RCl\(^{15}\).

At this point it is fair to say that the overall picture of this potential energy representation can be considered as satisfactory for diatomic-like R–Cl molecules, despite the many assumptions and simplifications made in the approach by Wentworth and coworkers\(^{5−7}\).

Acknowledgement

The financial support of one of us (A.A.C.) by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.


8 E. Schultes, A. A. Christodoulides, and R. N. Schindler, Chem. Phys., accepted for publication (1975) see compilation of data Tables 2 and 3.


12 P. M. Morse, Phys. Rev. 34, 57 [1929].

13 H. D. Hagstrum and J. T. Tate, Phys. Rev. 59, 354 [1941].


15 The separation time \(r_s\) which is required for R and Cl\(^-\) to separate from the equilibrium distance \(r_0\) to the crossing point \(r_c\) of the RCl and RCl\(^-\) potential energy curves may be estimated\(^{16}\) through the expression

\[
\tau_s = \frac{\int_{r_s}^{r_c} \frac{dr}{v(r)}}{\frac{d}{dt} \left( \frac{\left[ U(r)/M_f \right]^{1/2}}{a} \right)},
\]

Assuming portion (d) in Figs. 3 and 4 to be straight lines, Eq. (a) becomes

\[
\tau_s = \left[ \frac{M_f}{2} \right]^{1/4} \left[ r_0/\left( \frac{1}{2} + r_0/U_{\max} \right) \right].
\]

Substituting the respective values, the separation times for CH\(_2\)Cl-Cl and CHCl\(_3\)-Cl are found to be \(1.2\times10^{-13}\) and \(1.9\times10^{-13}\) sec, respectively.