Studies by the Electron Cyclotron Resonance(ECR)-Technique IX: Interactions of Low-Energy Electrons with the Molecules CH_2Cl_2 and $CHCl_3$ in the Gas Phase

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The capture of thermal electrons by the molecules CH_2Cl_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[1]. Absolute rate constants for capture processes together with Arrhenius parameters were determined at thermal electron energies[2]. Also, changes of relative attachment cross sections may be followed as function of the electron energy with only slight modifications of the experimental procedure[3].

In this paper results are given on the interactions of low-energy electrons with the molecules CH_2CL_2 and $CHCl_3$. The results presented here are supplementary to the results obtained on Cl_2 and CCl_4[4]. Potential energy diagrams are constructed using the experimental data reported in this study and a model suggested by Wentworth et alias[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 $[CH_2Cl_2]$ and $[CHCl_3]$, respectively. Each point given was determined from the time dependence of the capture process at a constant scavenger concentration [RCl]. 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

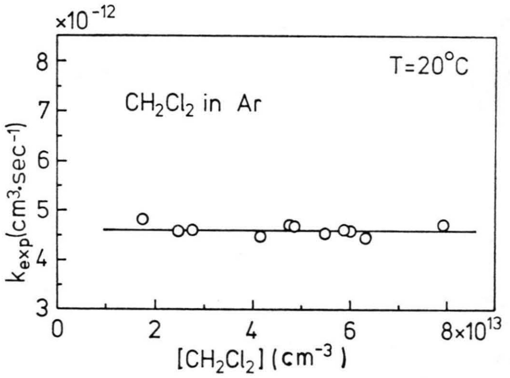

Fig. 1. Concentration-dependence of the rate of electron loss, k_{exp}, in the presence of CH_2Cl_2 in Ar at 20 °C. Each point was determined from the time-dependence of the capture process at constant $[CH_2Cl_2]$.

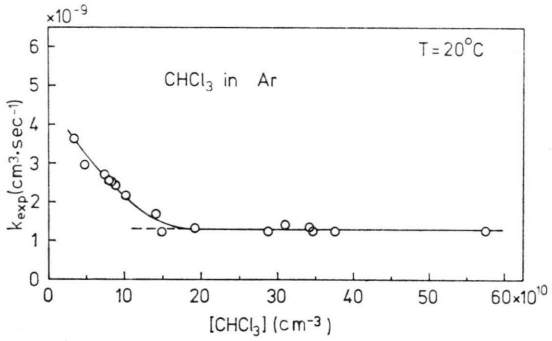

Fig. 2. Concentration-dependence of the rate of electron loss, k_{exp}, in the presence of $CHCl_3$ in Ar at 20 °C. Each point was determined from the time-dependence of the capture process at constant $[CHCl_3]$.

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of the flow tube[4]. The *k*-values of 4.6×10^{-12} $cm^3\ sec^{-1}$ for CH_2Cl_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[8]. In microwave conductivity measurements[9] the rate constant for electron capture by $CHCl_3$ in n-C_6H_{14} decreased from 2.65 to $2.2 \times 10^{-9}\ cm^3\ sec^{-1}$ in going from 80 to 33 torr of total pressure. From an Arrhenius plot (see Fig. 6 of Ref. [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 · $mole^{-1}$ was obtained for electron attachment to $CHCl_3$ from measurements in the temperature range 20 – 180° C and $[CHCl_3] \geqq 1.5 \times 10^{11}\ cm^{-3}$. This AE-value is also in good agreement with previous findings[3, 9, 10].

b) The reaction path: It is most likely that thermal electron capture by the molecules CH_2Cl_2 and $CHCl_3$ proceeds dissociatively via the formation of a temporary compound negative ion RCl^{-*} ($R = CH_2Cl$ or $CHCl_2$), i.e.

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

For both CH_2Cl_2 and $CHCl_3$ molecules, the dissociative electron attachment process is exothermic with $\Delta H_r^0 = -9$ and -15 kcal · $mole^{-1}$ respectively, as calculated from the respective heats of formation ΔH_f^0 for Cl^-, CH_2Cl, $CHCl_2$, CH_2Cl_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 $CH_2Cl_2^{-*}$ and $CHCl_3^{-*}$ lies ~0.29 and ~0.43 eV, respectively, below the ground state of the neutral molecules, as determined from the dissociation energies for $CH_2Cl - Cl$ and $CHCl_2 - Cl$ (see Table 1) and the electron affinity EA(Cl) = 3.613 eV[11] of the chlorine atom.

The values of 76.6 and 73.3 kcal · $mole^{-1}$ for $D(CH_2Cl - Cl)$ and $D(CHCl_2 - Cl)$, 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 $CH_{4-n}Cl_n$ ($n = 1, 2, 3, 4$). It is noted here that the average values for the dissociation energies of $CH_3 - Cl$ and $CCl_3 - Cl$ are 81.4 and 68.4 kcal · $mole^{-1}$, as obtained from eleven and seven indepentend determinations, respectively.

Table 1. Heats of formation, $\Delta H^0{}_f$, and dissociation energies D(R – Cl), in kcal · $mole^{-1}$.
* In the last column are average values used in the present work.

Species	$\Delta H^0{}_f$	
Cl^-	-55.9^{a}, -58.8^{b}, -58.9^{c}	-57.9 *
CH_2Cl	25.8^{d1}, 25.5^{d2}, 30.0^{b}	27.1
CH_2Cl_2	-21^{e}, -21.5^{f}, $=22.1^{b}$, -22.5^{d1}, -22.8^{d2}, -22.83^{a}	-22.1
$CHCl_2$	18.8^{d1}, 18.6^{d2}	18.7
$CHCl_3$	-23.4^{f}, -24^{e}, -24.3^{d2}, -24.4^{g}, -24.66^{a}, -24.9^{d1}	-24.3
	D(R – Cl)	
$CH_2Cl - Cl$	73.3^{g}, 76^{e}, 77.2^{h}, 78^{i}, 78.5^{k}	76.6
$CHCl_2 - Cl$	71.9^{h}, 73^{i}, 73.5^{k}, 75^{e}	73.3

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c) Potential energy diagrams: An attempt is presented to describe the reaction path for the dissociative capture process in terms of the potential energy diagrams for the neutral molecule RCl ($R = CH_2Cl$ or $CHCl_2$) and the temporary compound negative ion RCl^{-*}. The semiempirical Morse function[12] was selected to represent the potential energy curve for the molecule RCl in its ground state as a function of the C – Cl bond distance. The ionic state RCl^{-*} leading to the dissociation fragments R and Cl^- was approximated through a modified Morse function suggested by Wentworth and his coworkers[5–7]. In addition, a small part of this ionic state was calculated from the experimental electron attachment cross section, σ_{rel}, by reflection[13] on the probability density distribution function $\Psi_0{}^2$ for the neutral molecule RCl.

Table 2. Parameters used for the calculation of the potential energy diagrams for the molecules CH_2Cl_2 and $CHCl_3$.

Parameter	Value †	Ref.	Parameter	Value †	Ref.
$D(CH_2Cl-Cl)$	3.32 *		$D(CHCl_2-Cl)$	3.18 *	
EA (Cl)	3.613	11	EA (Cl)	3.613	11
U_{max}	0.75	14	U_{max}	0.37	14
AE	0.18	8	AE	0.10	c
AE	0.325	6	AE	0.134	6
ω_0	670 cm^{-1}	a	ω_0	680 cm^{-1}	d
r_0	1.77 Å	b	r_0	1.77 Å	b

† All values are given in eV (= 23.063 kcal·mole^{-1}), except as noted.

* Average value (see Table 1).

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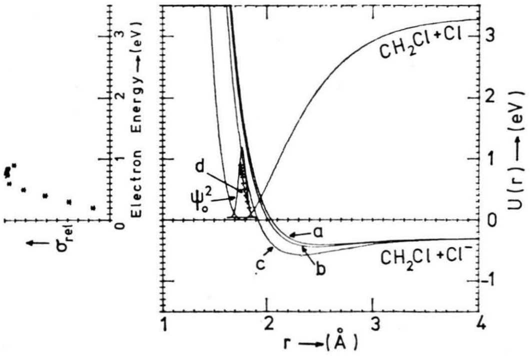

Fig. 3. Potential energy curves for CH_2Cl_2 and $CH_2Cl_2^{-*}$. The experimental energy-dependence for electron capture by CH_2Cl_2 is given along the ordinate. For other curves, see text.

CH_2Cl_2: The potential energy diagrams for the neutral and the negatively charged CH_2Cl-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 σ_{rel} (in relative units) for the electron capture by CH_2Cl_2 [14] is shown in Fig. 3 with ordinates representing the energy of the free electrons (points *). Reflection of σ_{rel} on Ψ_0^2 results in curve (d) shown as (+) in Figure 3.

$CHCl_3$: As in the case of CH_2Cl_2, a similar approach was followed to determine the potential energy diagrams for $CHCl_3$ (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 σ_{rel} for $CHCl_3$ [14].

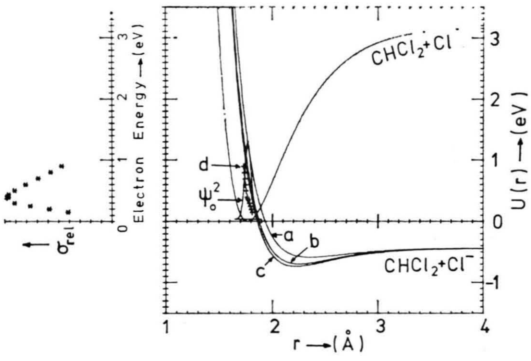

Fig. 4. Potential energy curves for $CHCl_3$ and $CHCl_3^{-*}$. The experimental energy-dependence for electron capture by $CHCl_3$ is given along the ordinate. For other curves, see text.

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 RCl^{-*} 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

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[15] The separation time τ_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

$$\tau_S = \int_{r_0}^{r_C} \frac{dr}{v(r)} = \int_{r_0}^{r_C} \frac{dr}{[2\,U(r)/M_r]^{1/2}} \,. \qquad \text{(a)}$$

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

$$\tau_S = [M_r/2]^{1/2}\,[r_C/U_C{}^{1/2} - r_0/U_{\max}^{1/2}] \,. \qquad \text{(b)}$$

Substituting the respective values, the seperation times for CH_2Cl-Cl and $CHCl_2$-Cl are found to be 1.2×10^{-13} and 1.9×10^{-13} sec, respectively.

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