Low-Energy Electron Attachment by Chloroalkanes

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Thermal electron attachment rate constants for 1,1,2-trichloroethane, 1,1,2,2-tetrachloroethane, 1- and 2-chloropropanes, and 1,1-, 1,2-, 2,2-, and 1,3-dichloropropanes have been measured using an electron swarm method. It has been found that all the investigated compounds attach electrons only in a two-body process. Corresponding rate constants are equal to 1.4×10^{-10}, 3.2×10^{-8}, 2.7×10^{-13}, 3.8×10^{-12}, 5.7×10^{-11}, 8.1×10^{-12}, 6.3×10^{-12}, and 1.2×10^{-11} cm^3 molecule^{-1} s^{-1}, respectively. The dependence of the electron capture rate constants on the electronic polarizability of the accepting center of the molecule and the vertical attachment energy has been demonstrated.

Introduction

Thermal electron capture processes in the gas phase constitute an important class of chemical reactions. If electron energies are in thermal equilibrium with the surrounding molecules, the rate constant for the electron capture strongly depends on the shape and position of the resonance and its overlap with the Maxwell−Boltzman distribution of the electron and molecule energies.[1−3] Hence, the measured rate constants differ by six orders of magnitude (from 10^{-7} down to $<10^{-13}$ cm^3 molecule^{-1} s^{-1}). Despite a large effort in this field, there is still a lack of systematic data which could serve as an experimental basis for verifying theoretical considerations. Moreover, because of various experimental problems and the different methods applied, the data from various laboratories differ quite often by more than an order of magnitude. The largest group of compounds for which the rate constants have already been measured consists of haloalkanes, and we believe that further effort should concentrate on this group.

For now, there exist two approaches to systematize the available rate constants. Christophorou has demonstrated that the experimental thermal rate constants for a large number of halocarbons depend on the energy of the electron-attaching state, as measured by electron transmission spectroscopy.[4,5] We, in turn, have concentrated on the link between the structure of the molecule and its ability to accept thermal electrons. For this purpose one can consider such characteristics as the dipole moment of the molecule or the bond, μ, electronic polarizability, α, total molecular polarizability, $\alpha + \mu^2/3kT$, and electron affinity of the molecule or of the electronegative atom.

As was pointed out recently by Hotop et al.,[6] the long-range electron nonpolar molecule interaction is described by the polarization potential depending on the electronic polarizability, $V(r) = -\alpha e^2/2r$.[4] This leads to the threshold cross-section for s-wave capture at low energies, $\sigma(E \rightarrow 0)$, proposed by Vogt and Wannier:[7]

$$\sigma(E \rightarrow 0) = 4\pi a_0^2 (\alpha/2E)^{1/2} \qquad (1)$$

where a_0 is the Bohr radius, α the polarizability, and E the electron energy. Thus, the polarizability of the molecule is the essential factor determining the thermal electron capture rate constant. The presence of a permanent dipole moment causes some additional interaction, which should increase the electron capture cross-section to some extent. Accordingly to their estimation this effect can be neglected at α around 9×10^{-24} cm^3 and μ around 0.5 D. This led them to eq 2 for the thermal electron capture rate constant, where α values are expressed in 10^{-24} cm^3 units.

$$k_{th} = (4 \times 10^{-8})\alpha^{1/2} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \qquad (2)$$

Using literature values for α (9.45×10^{-24} and 10.7×10^{-24} cm^3 for CFCl$_3$ and 1,1,1-C$_2$Cl$_3$F$_3$), they obtained $k = 6.2 \times 10^{-7}$ and 6.6×10^{-7} cm^3 molecule^{-1} s^{-1}, respectively. These are essentially in good agreement with the experimental values (cf. the data in Table 1). However, eq 2 can only be applied to the highly halogenated alkanes, for which the thermal s-wave electron cross-section approaches its limiting value, $\pi\lambda^2$, where λ is the reduced de Broglie wavelength. This corresponds to $k_{th} \approx 4 \times 10^{-7}$ cm^3 molecule^{-1} s^{-1}. For other compounds the dependence of the experimental thermal rate constants on polarizability is also observed, but it is much stronger than that following from eq 2. In fact, it is rather exponential. The second observation is that k_{th} actually does not depend on the polarizability of the molecule as a whole, but on the summary polarizability of the halogen atoms at the carbon atom where the capture occurs. This term has been defined in ref 10. The influence of halogens at neighboring carbons is appreciably less and should be taken with a coefficient <1.[3,8−10]

This work is a continuation of our effort to measure systematically the rate constants for thermal electron capture by haloalkanes using the electron swarm method. To date, the measurements concentrated exclusively on halomethanes and haloethanes. Here we also present the rate constants for 1- and 2-chloropropanes and all four isomers of dichloropropane.

Using the semiempirical AM1 method, we have calculated the changes in molecular structure on going from a neutral to a transient negative ion. The results have been compared with the molecular characteristics and thermal electron capture rate constants.

Experimental Section

An electron swarm method employing a pulse ionization chamber with two parallel electrodes has been applied. The

TABLE 1: Rate Constants for Electron Capture by Chlorine-Containing Halocarbons Together with Corresponding Values of α_{center}

compd	α_{center}, 10^{-24} cm^3	N_{Cl}	N_F	k, cm^3 molecule^{-1} s^{-1} [ref]	k_{av}, cm^3 molecule^{-1} s^{-1}
CH$_3$Cl	2.14	1	0	2×10^{-13} [16]	
CHF$_2$Cl	3.26	1	2	1.1×10^{-13} [47]	
CF$_3$Cl	3.82	1	3	4.2×10^{-13} [13], 1.3×10^{-13} [46], 2×10^{-13} [34, 35], 5.2×10^{-14} [15], 7×10^{-14} [32]	2.1×10^{-13}
CH$_2$Cl$_2$	4.28	2	0	6.5×10^{-13} [17], 2.6×10^{-13} [50], 4.7×10^{-12} [15], 4.6×10^{-12} [18], 4.8×10^{-12} [19]	4.7×10^{-12}
CHFCl$_2$	4.84	2	1	6.1×10^{-12} [13], 5×10^{-12} [49], 1.5×10^{-12} [28]	5.5×10^{-12}
CF$_2$Cl$_2$	5.40	2	2	1.9×10^{-9} [13], 9.6×10^{-10} [49], 3.2×10^{-9} [20, 21], 1.2×10^{-9} [35], 7×10^{-10} [32], 8×10^{-10} [31], 1.8×10^{-9} [25], 1.3×10^{-9} [44], 2.2×10^{-9} [45]	1.6×10^{-9}
CHCl$_3$	6.42	3	0	4.4×10^{-9} [21], 1.3×10^{-9} [18], 3.8×10^{-9} [17, 30], 2×10^{-9} [14, 44], 2.7×10^{-9} [17], 2.6×10^{-9} [31], 2.3×10^{-9} [17], 2.2×10^{-9} [19]	2.7×10^{-9}
CFCl$_3$	6.98	3	1	2.4×10^{-7} [1, 23, 41], 1×10^{-7} [32], 3.1×10^{-7} [25, 41], 1.8×10^{-7} [14]	2.1×10^{-7}
CCl$_4$	8.56	4	0	4×10^{-7} [14, 21], 3.6×10^{-7} [13], 4.1×10^{-7} [31], 4.2×10^{-7} [17, 29], 3.8×10^{-7} [41], 4.4×10^{-7} [17, 30]	4×10^{-7}
CH$_3$CH$_2$Cl	2.14	1	0	3.4×10^{-14} [39], 5×10^{-13} [16]	
CH$_3$CF$_2$Cl	3.26	1	2	6×10^{-13} [9, 48]	
CF$_3$CF$_2$Cl	4.10	1	3.5	3.3×10^{-12} [9, 48]	
CF$_3$CFCl$_2$	5.68	2	2.5	4.8×10^{-9} [29, 36, 37]	
CH$_3$CHCl$_2$	4.28	2	0	2.1×10^{-11} [36]	
CH$_2$ClCH$_2$Cl	3.21	1.5	0	2.6×10^{-11} [39], 3.2×10^{-11} [36]	2.9×10^{-11}
CF$_2$ClCF$_2$Cl	4.89	1.5	3	7×10^{-10} [29, 37]	
CH$_3$CCl$_3$	6.42	3	0	1.1×10^{-8} [14], 1.6×10^{-8} [23], 1.5×10^{-8} [20, 36–38]	1.4×10^{-8}
CF$_3$CCl$_3$	7.26	3	1.5	2.5×10^{-7} [9, 48], 1.4×10^{-7} [14], 2.8×10^{-7} [37], 2.4×10^{-7} [38, 39], 2.25×10^{-7} [37]	2.2×10^{-7}
CH$_2$ClCHCl$_2$	5.35	2.5	0	1.4×10^{-10} [present data], 3.1×10^{-10} [20, 38], 1.8×10^{-10} [36–38], 1.5×10^{-10} [23]	2×10^{-10}
CF$_2$ClCFCl$_2$	6.47	2.5	2	5.4×10^{-9} [9, 48], 1.2×10^{-8} [25], 1.1×10^{-8} [36], 1.15×10^{-8} [37], 1.1×10^{-8} [38]	1.1×10^{-8}
CHCl$_2$CHCl$_2$	6.42	3	0	3.5×10^{-8} [present data], 3.2×10^{-8} [39]	3.3×10^{-8}
CH$_3$CH$_2$CH$_2$Cl	2.14	1	0	3.6×10^{-13} [present data]	
CH$_3$CHClCH$_3$	2.14	1	0	3.8×10^{-12} [present data]	
CH$_3$CH$_2$CHCl$_2$	4.28	2	0	5.7×10^{-11} [present data]	
CH$_3$CCl$_2$CH$_3$	4.28	2	0	6.3×10^{-12} [present data]	
CH$_3$CHClCH$_2$Cl	3.21	1.5	0	8.1×10^{-12} [present data]	
CH$_2$ClCH$_2$CH$_2$Cl	2.57	1.2	0	2×10^{-12} [present data]	

experimental procedure has been described in detail previously.[10] In brief, the experimental setup used for the investigation consisted of an ionization chamber with two parallel electrodes, a preamplifier, a fast (2 ns) oscilloscope with digital memory connected with a computer, and a computer-controlled power supply.

The electron acceptor was introduced into the ionization chamber in an excess of carbon dioxide as a carrier gas. The electron swarm was produced in the process of the ionization of the carrier gas by an α-particle in the plane of a ^{238}Pu α-particle source placed parallel to the electrodes. The electron swarm moved to the collecting electrode under the influence of a uniform electric field, E, and the rate of its disappearance due to the electron capture was measured.

Carrier gas concentrations, N, from 9×10^{18} to 3.3×10^{19} molecule cm^{-3} were used. The measurements were carried out at the density-reduced electric field, E/N, in the range of 6×10^{-18} to 9×10^{-17} V cm^2 molecule^{-1} where electrons in carbon dioxide are in thermal equilibrium with gas molecules.[11] Each chloropropane–carbon dioxide mixture was introduced into a chamber at the highest applied total pressure (ca. 1000 Torr). The 500 pulses were registered for a given E/N and averaged. The procedure was usually repeated for five E/N values. Next, the mixture was pumped out to a lower pressure, and the measurement was repeated for ca. 15 consecutive pressures in the range 300–1000 Torr. The whole experiment was carried out for a few different initial concentrations of chloropropane in carbon dioxide.

We used technical carbon dioxide and applied a special procedure for its purification. The other gases were from Aldrich (CH$_2$ClCHCl$_2$, CHCl$_2$CHCl$_2$, CH$_3$CH$_2$CHCl$_2$, CH$_3$CCl$_2$CH$_3$, and CH$_3$CHClCH$_2$Cl) and from Merck-Schuchardt (CH$_2$ClCH$_2$CH$_2$-Cl) with stated purity >97%. All the compounds were purified

by the vacuum freeze–pump–thaw technique. The measurements were carried out at room temperature (293 $\pm$ 3 K).

Results and Discussion

The rate constants obtained for CH$_2$ClCHCl$_2$, CHCl$_2$CHCl$_2$, CH$_3$CH$_2$CH$_2$Cl, CH$_3$CHClCH$_3$, CH$_3$CH$_2$CHCl$_2$, CH$_3$CCl$_2$CH$_3$, CH$_3$CHClCH$_2$Cl, and CH$_2$ClCH$_2$CH$_2$Cl are presented in Table 1 together with available literature data for chloroalkanes and chlorofluoroalkanes.

An inspection of Table 1 allows one to observe the following features: (1) There is a strong increase in the rate constant with the number of chlorine atoms, by an order of magnitude or more with each chlorine. (2) Increasing the number of fluorine atoms also increases the rate constant, but to much less extent. (3) The increase of the carbon chain does not seem to have an appreciable influence on the rate constant. (4) Most of the rate constants were measured only one or two times. However, in some cases, mostly for multichlorides, there exist enough compatible data to average them and recommend these averages as well established. They are shown in Table 1 and agree well with those recommended by Christophorou.[4]

As we have demonstrated previously,[3,8–10] one can expect a linear dependence of log(k) on the electronic polarizability of the attaching center, α_{center}. As an attaching center we consider that part of the molecule which is immediately connected with the attachment process; e.g., in the case of C$_n$H$_{2n-m+2}$Hal$_m$ α_{center} is a sum of polarizabilities of halogen atoms calculated using an additivity rule, while carbon and hydrogen atoms are eliminated from consideration. If halogens are placed at neighboring carbon atoms, the best correlation is obtained if one first calculates the sum of polarizabilities at each carbon and then takes the higher value with coefficient 1 and the other one with coefficient 0.5. In the case of CH$_2$ClCH$_2$CH$_2$Cl in

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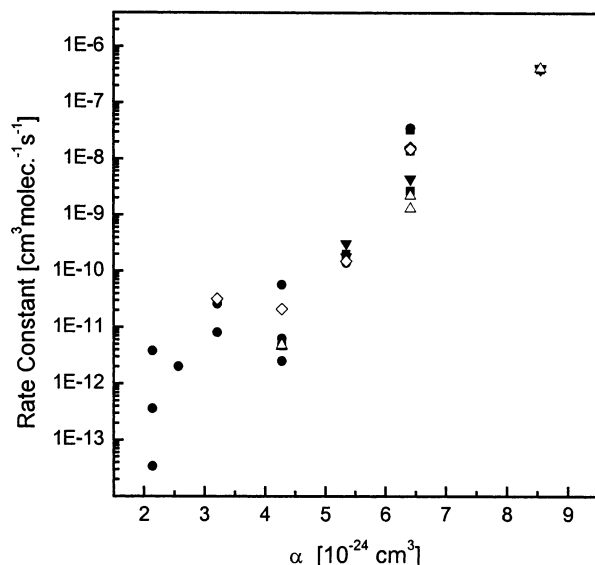
Figure 1. Dependence of the electron capture rate constant on α_{center} for chloroalkanes: (■) average, (●) this work, (▼) Smith et al., (△) Schultes et al., (◇) Christophorou et al. (see Table 1).
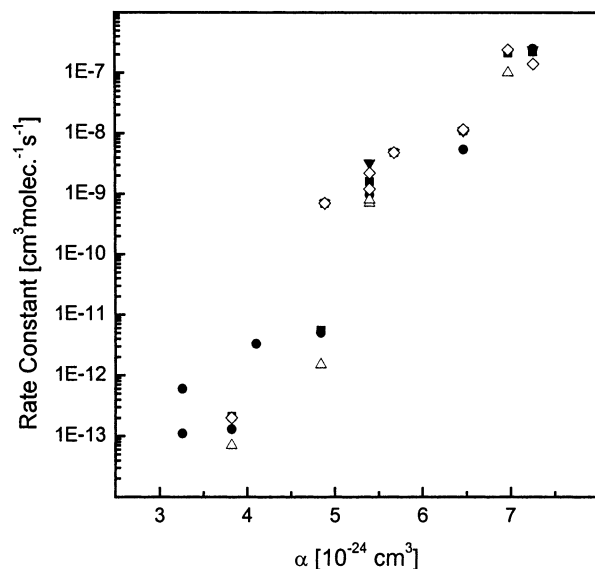
Figure 2. Dependence of the electron capture rate constant on α_{center} for chlorofluoroalkanes: (■) average, (●) this work, (▼) Smith et al., (◇) Schultes et al., (◇) Christophorou et al. (see Table 1).

which halogen atoms are separated by CH_2 groups, we have chosen the coefficient 0.2. The α_{center} values calculated using $\alpha_{Cl} = 2.18 \times 10^{-24} \text{ cm}^3$ and $\alpha_F = 0.56 \times 10^{-24} \text{ cm}^{3\ 12}$ are shown in Table 1. To confirm the above statements, to date we could only use the data for halomethanes and haloethanes as the data for higher haloalkanes were not available. This is the first opportunity to consider the influence of the position of the attaching center as well as the length of the alkane chain on the rate constant.

The plot of the rate constant vs α_{center} is shown in log scale in Figure 1 for chloroalkanes and in Figure 2 for chlorofluoroalkanes.

When available, the average rate constant, k_{av}, was plotted, as well as the values from the four independent laboratories in which rate constants for more than 10 compounds have been measured. Despite large scattering, which is not necessarily due to experimental error, in both figures the exponential dependence of the thermal electron capture on α_{center} is visible. Also, there is no systematic difference between the data obtained in different
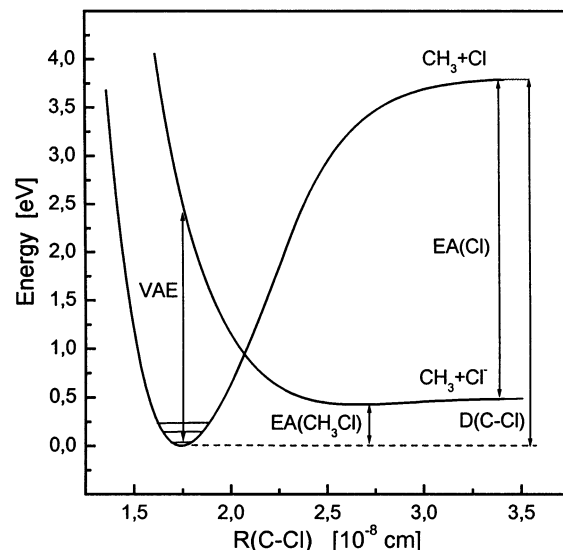
**Figure 3.** Potential curves for a methyl chloride molecule and its negative ion.

laboratories, with different techniques and at different times. Thus, it seems that α_{center} is the crucial characteristic of the molecule determining its ability to accept an electron.

To rationalize this statement, we have performed calculations of the structure of the molecules and corresponding molecular negative ions using a semiempirical SCF AM1 method. We have analyzed the influence of chlorine and fluorine atoms placed in different numbers at different carbon atoms of halomethanes, haloethanes, and halopropanes. This method allows one to calculate the energetically optimized structure (angles, bond lengths) and total energy and/or binding electronic energy of both the molecule and its negative ion. Applying a potential function, one can also build a whole potential energy curve for a particular bond with the residual structure frozen. The example set of curves for methyl chloride is shown in Figure 3.

The dependence of a capture cross-section on energy has a resonant form which is a result of a Franck−Condon transition from the ground vibrational level of the neutral to the transient negative ion. The energy of this transition is the vertical attachment energy, VAE, in Figure 3. Using electron transmission spectroscopy, Burrow et al.[49−51] have measured VAE for a set of chloroalkanes and chlorofluoroalkanes. These are collected in Table 2. Figure 4 shows the data as a function of α_{center}. Again, as expected VAE depends on α_{center} with some difference between the two sets.

Figure 5 shows the correlation between VAE and rate constants for thermal electron capture where both were available. One can see again the exponential dependence of the thermal rate constant on VAE.

For electrons with thermal energy distribution, as in all cases presented in Table 2, this transition can be probable if VAE is low enough (curve crossing occurs near the lowest vibrational level of the neutral). If however the resonance lies high above the thermal region, then the probability of such a transition at the thermal electron energy distribution is rather low and another mechanism should be involved. This is based on the fact that even at room temperature the higher vibrational levels of the molecule are partly populated. The F−C transition from these levels requires a much smaller electron contribution from the thermal energy distribution. In this case the rate constant or, in fact, activation energy depends on the level of the crossing of the potential energy curves for the neutral and transient negative ion.
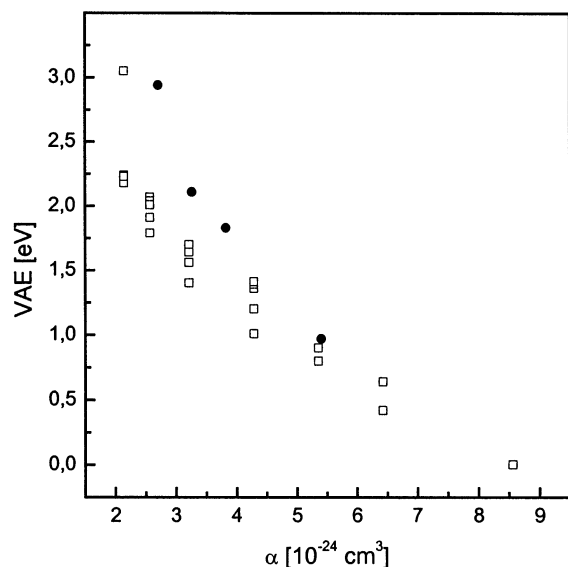
**Figure 4.** Dependence of VAE on α_{center} for (□) chloroalkanes and (●) chlorofluoroalkanes.

TABLE 2: Relative Changes in the Bond Length for a Negative Ion and Its Neutral, $\Delta R/R$, Charge Located on the Corresponding Cl Atom in the Anion, Ch, and Adiabatic Electron Affinity, AEA, Calculated Using the AM1 Method for α_{center} as in Table 1 and Vertical Attachment Energy, VAE (from Aflatooni et al.[49−51]), for Chlorine-Substituted Halocarbons

compd	α_{center}, 10^{-24} cm^3	VAE, eV	$\Delta R/R$	Ch$_{Cl}$	AEA, eV
CH$_3$Cl	2.14		0.52	0.94	**−0.43**
CH$_2$FCl	2.7	2.94	0.48	0.94	0.33
CHF$_2$Cl	3.26	2.11	0.2	0.68	0.95
CF$_3$Cl	3.82	2.11	0.15	0.56	1.85
CH$_2$Cl$_2$	4.28	1.01	0.08	0.48	0.27
CHFCl$_2$	4.84	0.94	0.08	0.48	1.13
CHCl$_3$	6.42		0.04	0.37	1.12
CF$_2$Cl$_2$	5.4	0.97	0.08	0.45	2.06
CFCl$_3$	6.98	0.47	0.05	0.37	2.02
CCl$_4$	8.56	0	0.04	0.31	1.88
CH$_3$CH$_2$Cl	2.14		0.59	0.96	**−0.19**
CH$_3$CF$_2$Cl	3.26		0.2	0.68	1.03
CF$_3$CF$_2$Cl	4.1		0.14	0.52	2.04
CF$_3$CFCl$_2$	5.68		0.07	0.383	2.03
CH$_3$CHCl$_2$	4.28	1.36	0.08	0.48	0.33
CH$_2$ClCH$_2$Cl	3.21	1.7	0.15	0.55	0.37
CF$_2$ClCF$_2$Cl	4.89		0.118	0.487	2.03
CF$_2$ClCFCl$_2$	6.47		0.08	0.4	2.1
CH$_3$CCl$_3$	6.42		0.05	0.37	1.1
CF$_3$CCl$_3$	7.26		0.04	0.3	1.89
CH$_2$ClCHCl$_2$	5.35	0.8	0.21	0.62	0.86
CHCl$_2$CHCl$_2$	6.42		0.12	0.46	1.04
CH$_3$CH$_2$CH$_2$Cl	2.14		0.62	0.97	**−0.18**
CH$_3$CHClCH$_3$	2.14		0.76	0.94	0.33
CH$_3$CH$_2$CHCl$_2$	4.28	1.39	0.17	0.61	0.35
CH$_3$CCl$_2$CH$_3$	4.28	1.41	0.08	0.48	0.39
CH$_3$CHClCH$_2$Cl	3.21	1.64	0.31	0.77	**−0.05**
CH$_2$ClCH$_2$CH$_2$Cl	2.568	1.91	0.35	0.81	0.02

Figure 6 shows the potential curves for methyl chlorides. As expected, the equilibrium internuclear distance for the C−Cl bond in the molecule, R(C−Cl), does not change appreciably, while the well depth diminishes slightly from CH$_3$Cl to CCl$_4$. The main changes occur when the ion is formed: R(C−Cl$^-$) shortens strongly with the number of Cl atoms, and the adiabatic electron affinity, EA, increases. Our calculations (not presented in Table 2) show that the additional charge distributes symmetrically between all Cl atoms.
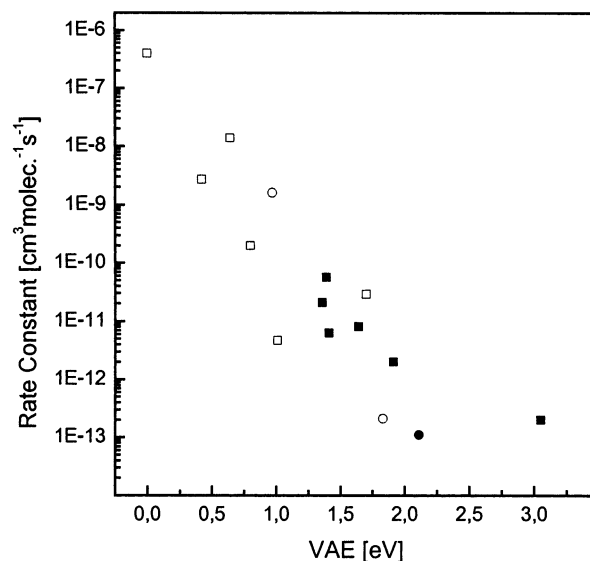
Figure 5. Dependence of the thermal electron capture rate constant on VAE for (■) chloroalkanes, single, (●) chlorofluoroalkanes, single, (□) chloroalkanes, average, and (○) chlorofluoroalkanes, average.
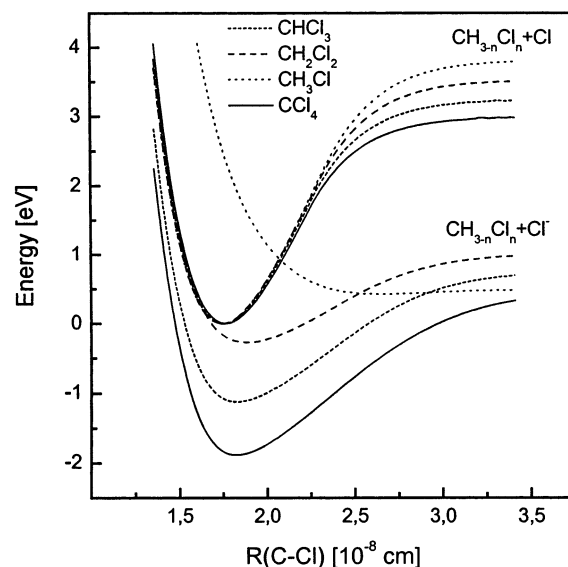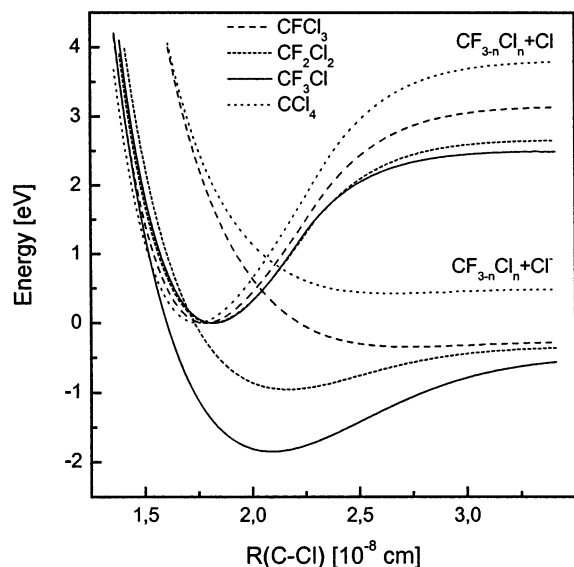

Figure 6. Potential curves for chloromethane molecules and their negative ions.

Figure 7 shows the influence of the number of fluorine atoms in F-substituted methyl chloride. The addition of the fluorine atom also shortens R(C−Cl$^-$) and increases EA, but the charge remains mostly on the chlorine atom (see Table 2).

Figure 8 shows the potential curves for 1-Cl-substituted alkanes. It is seen that the length of the chain beyond C$_2$ does not influence the ion parameters.

Figure 9 shows the relative elongation of the C−Cl bond, $\Delta R/R = [R($C−Cl$^-) − R($C−Cl$)]/R($C−Cl$)$, charge on the single Cl atom, Ch$_{Cl}$, and adiabatic electron affinity for methyl chlorides as a function of a summary polarizability of chlorine atoms (α_{center}). Figure 10 shows a plot of $\Delta R/R$ and Ch$_{Cl}$ versus α_{center} for all chloro- and chlorofluoroalkanes shown in Table 1. Despite a rather appreciable scattering of the results, it is seen that both Cl and F atoms influence these parameters in the same way and according to the value of α_{center}. However, this is not true in the case of EA, as shown in Figure 11. The EA value depends linearly on the number of halogen atoms in the accepting center (calculated the same way as α_{center}; i.e., halogens on neighboring C atoms are counted with an adequate
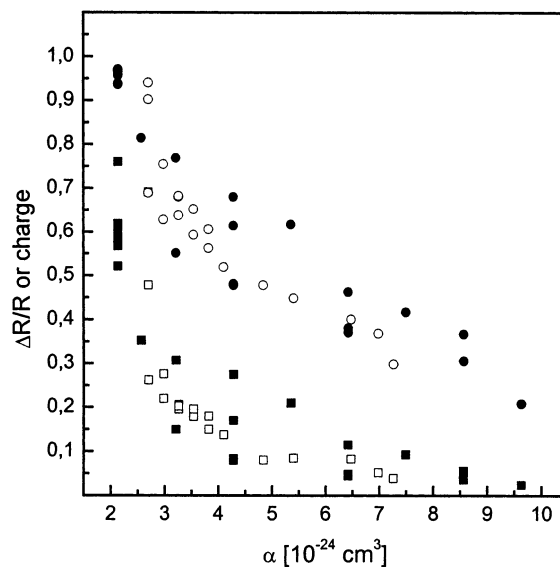
Figure 7. Potential curves for chlorofluoromethane molecules and their negative ions.
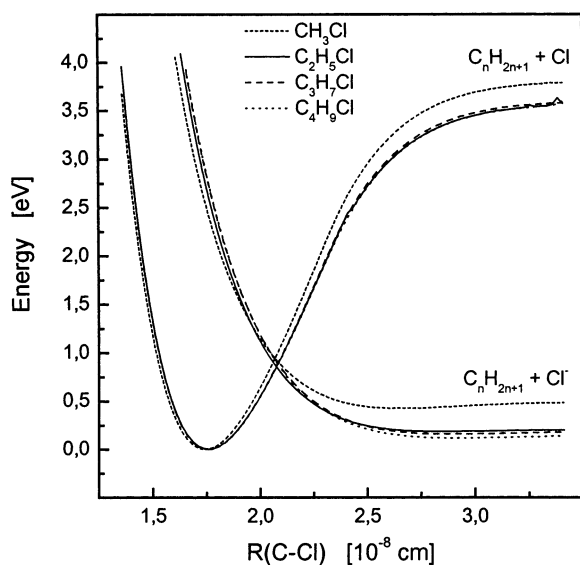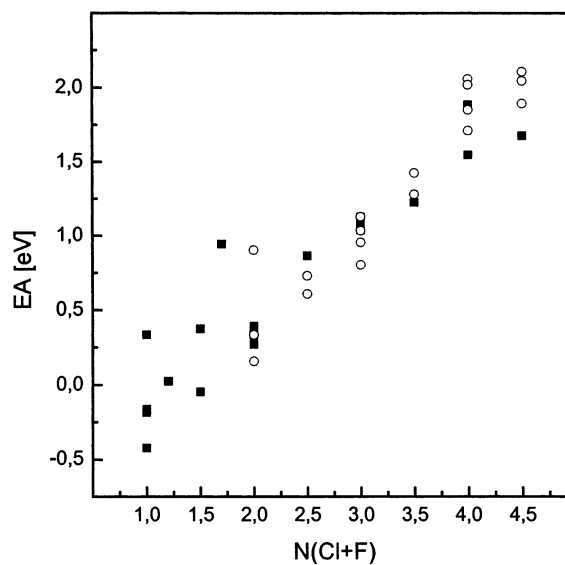

Figure 8. Potential curves for 1-chloroalkane molecules and their negative ions.
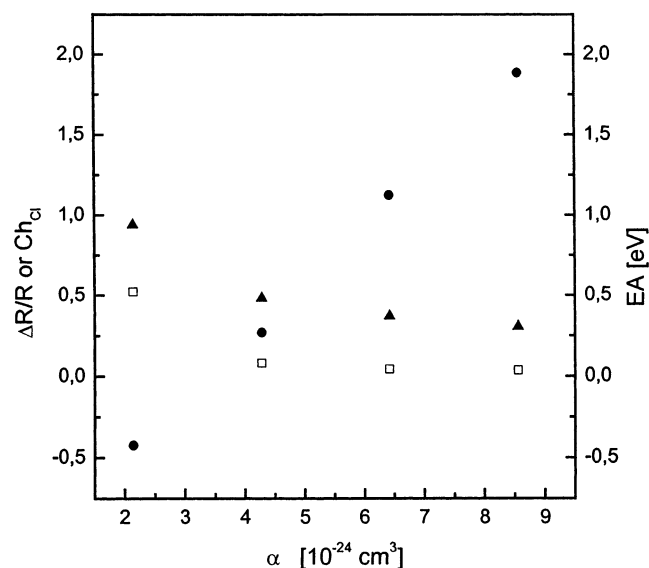
Figure 9. $\Delta R/R$ ($\square$), Ch_{Cl} ($\blacktriangle$), and EA ($\bullet$) vs α_{center} for chloromethanes.

Figure 10. $\Delta R/R$ ($\blacksquare$) and Ch_{Cl} ($\bullet$) (chloroalkanes) and $\Delta R/R$ ($\square$) and Ch_{Cl} ($\circ$) (chlorofluoroalkanes) vs α_{center}.

Figure 11. EA vs the number of halogen atoms in the accepting center, $N(Cl + F)$, calculated as for α_{center}: ($\blacksquare$) chloroalkanes, ($\circ$) chlorofluoroalkanes.

coefficient) independently of their polarizability. As a matter of fact the only parameter which is almost the same for both halogen atoms is again their electron affinity (EA(Cl) = 3.6 eV and EA(F) = 3.4 eV[13]). One is tempted to suppose that this joint characteristic rules the electron affinity of the molecule.

In summary, one can state the following: (1) The additional electron in the transient negative ion of chloroalkanes or chlorofluoroalkanes occupies the LUMO of the chlorine atom. (2) This causes elongation of the C−Cl bond and formation of the negative ion above the dissociation limit as the electron affinity of the chlorine atom is higher than the C−Cl bond energy. (3) Consecutive addition of chlorine atoms at the same carbon causes distribution of the additional charge over all chlorine atoms. The consequent lowering of the charge on the individual chlorines diminishes the bond elongation and increases the adiabatic electron affinity. (4) All this increases the degree of overlap of the potential curves of the C−Cl and C−Cl⁻ bonds, which in turn decreases the vertical attachment energy and increases the thermal electron capture rate constant. (5) The length of the carbon chain has a minor effect on the

electron capture process. (6) Addition of the fluorine atom to chloride also decreases the elongation of the C−Cl bond in an ion and increases the adiabatic electron affinity of the molecule. (7) The changes in the bond length depend on the polarizability of the accepting center and those of electron affinity on the number of halogen atoms in this center. (8) The dependence of the thermal electron capture rate constant and vertical attachment energy on α_{center} for chloroalkanes and chlorofluoroalkanes shows that the polarizability of the halogen atoms is the main factor (with some influence of their electron affinity) determining the electron capture process. (9) The influence of a given halogen atom on the electron capture process diminishes with its distance from the accepting halogen. (10) The preliminary results on propyl chlorides with chlorine in positions 1 and 2 indicate that also the chlorine position has some effect on the electron capture rate constant. (11) Finally, one can observe some change in the equilibrium angle as a result of the ion formation, which can cause an additional energetic barrier for this process. Also this effect diminishes with α_{center}.

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