Thermal Electron Attachment to Chloroalkanes and Herschbach Ionic Morse Potentials for Carbon Tetrachloride (CCl_4)

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New rate constants for thermal electron attachment to chloroalkanes were measured in a recent swarm ionization cell study (Barszczewska, W.; Kopyra, J.; Wnorowska, J; Szamrej, I *J. Phys. Chem. A* **2003**, *107,* 11427). Electron affinities of haloakanes were calculated and used to construct one ionic potential energy curve to model the electron attachment process. Six of the 11 summary items presented should be revisited based on the following results and published complementary studies. The adiabatic electron affinity of CCl_4 is calculated using the MNDO CURES-EC approach to be 2.2 eV in agreement with experiment. The Feynman, Lesk, Herschbach, Wentworth hypotheses place a lower limit of zero on the long-range electron affinity, the adiabatic electron affinity, and the anion dissociation energy in a given bond dimension. Eight ionic Morse potential energy curves for $CCl_4(-)$ are calculated using the Herschbach classifications and experimental or predicted metrics. The antibonding, a, and bonding, b, curves are a two-dimensional cut through the multidimensional surface in which the geometry of the leaving groups are fixed. The X curve allows for rearrangement while the "c" curves are in a third electron−molecule dimension.

Introduction

In a recent swarm ionization cell study, designated BKWS, new rate constants for thermal electron attachment, k_1, to 1,1,2-$C_2H_3Cl_3$, 1,1,2,2-$C_2H_2Cl_4$, and 1,1-, 1,2-, 2,2-, and 1,3- $C_3H_6Cl_2$ were presented. The above values at 293(3) K and literature k_1 were correlated to the de Broglie wavelength of the electron, total molecular polarizability, vertical electron affinities, VE_a, and adiabatic electron affinities, AE_a. For the same molecules, semiempirical AM1 electron affinities, E_a, and anionic bond distances were predicted. One undefined anion potential energy curve for many of these compounds was used to model the thermal electron attachment process.[1]

The E_a is the difference in energy between the most stable state of the neutral and the lowest energy of a specific state of a negative ion. The VE_a (VAE in BKWS) is the difference in energy between the neutral and the negative ion in the geometry of the ground state of the neutral. The VDE is the energy difference between one state of a negative ion and the neutral in the geometry of that particular anion. The largest E_a is the ground state or adiabatic electron affinity, AE_a. The long-range electron affinities, LE_a are always positive due to polarization, dipole, quadrupole, and other attractive forces. When the valence orbitals are at least half-filled and the LUMO are positive, the AE_a will be the LE_a. The valence state or short-range electron affinities, SE_a and the VE_a, can be negative or positive.

From the Feynman/Lesk/Herschbach/Wentworth, FLHW, hypotheses, all LE_a, AE_a, and anion dissociation energies are greater than zero. The hypotheses are based on published work: (1) There is a long-range attraction between an electron and any atom, molecule, or radical (Feynman); (2) according to the variational principal, all AE_a are greater than zero (Lesk); (3) "pseudo-two-dimensional" Morse potentials can be used to describe ions (Herschbach); and (4) at sufficiently high *T* and *P*, the Fermi−Dirac statistics apply and the particle nature of thermal electrons predominates (Wentworth).[2−6]

Over the past 44 years the Wentworth/Chen/Lovelock groups have presented studies of the interactions of thermal electrons with molecules as a function of temperature using the electron capture detector, ECD, or negative ion mass spectrometry, NIMS. Many of the studies were published in ACS or AIP journals. The most recent deals with ECD, NIMS, and electron impact studies on C_2Cl_4.[2,6−22] From this body of work, E_a, partition function ratios for the equilibrium constants for electron molecule reactions, Q_{an}, k_1, rate constants for thermal electron detachment, k_{-1}, rate constants for negative ion dissociation, k_2, and solvation energy differences between anions and neutrals in aprotic solvents have been determined. Both activation energies and preexponential terms are obtained when the temperature dependence is measured. These studies assume the electron is in thermal equilibrium with the reactants. The E_a can be verified by reduction potentials in aprotic solvents. Theoretical semiempirical quantum mechanical calculations using the CURES-EC approach have been used to support the value of these fundamental properties. The experiments have been modeled using Herschbach ionic Morse potential energy curves, HIMPEC. Experimental E_a from this laboratory for many molecules are available in compilations such as those of Christodoulides, McCorkle, and Christophorou, and the NIST database.[24,25] Unfortunately, BKWS were apparently unaware of our published work. The first objective of this paper is to identify summary items in the BKWS that should be revisited.

The swarm ionization cell is a static, constant temperature, ECD. A similar device was used with ethylene as a carrier to determine electron affinities of pyrene, anthracene, and tetracene in 1968.[9] Unlike the ECD where on-line purification via the gas chromatographic column is attained, samples for static systems must be highly purified, especially those that react weakly with thermal electrons. The magnetron method is also a static system.[23] In the ECD, NIMS, and magnetron methods the E_a is determined from the equilibrium constant for the reaction with molecules.[2,6] Multiple electron affinities have been

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observed in ECD data. Over 300 AE$_a$ in NIST are confirmed by half-wave reduction potentials in aprotic solvents and CURES-EC calculations.[2,6−25]

A second purpose of this article is to illustrate the unique ability of the ECD to probe the kinetics and thermodynamics of the reactions of thermal electrons with molecules at atmospheric pressure. As noted by Wentworth and Becker in 1960, "From the statistical thermodynamic equilibrium constant for an ideal gas mixture (and the electron capture detector response), it should be possible to calculate the electron affinity."[6] Extant ECD data for acetophenone, CCl_4, methylene chloride, and chloroform will be used as examples of nondissociative and unimolecular dissociative thermal electron attachment reaction studies. No examples of consecutive dissociative electron attachment will be given. The AE$_a$ for CCl_4 will be calculated using the semiempirical CURES-EC approach. Eight Herschbach ionic Morse Potentials, HIMPEC, will be calculated for $CCl_4(-)$.[2,6−25]

Kinetic Model of the Electron Capture Detector

The ECD is used to study thermal electron reactions at different temperatures.The kinetic model of the ECD has been described extensively, but for convenience, a brief summary is presented.[2,6−11,18,19,21,22] Electrons rapidly reach a thermal distribution at atmospheric pressure. The electron current with and without AB, I_{e-} and I_b, are recorded as a sample elutes from the chromatographic column. The molar response K is calculated from the Wentworth equation: $K[AB] = \{I_b - I_{e-}\}/2I_e$ where [AB] is calculated from the amount of sample and the flow rate to give the concentration. The reactions are electron attachment, detachment, dissociation, and recombination with ions, P(+).

$$AB + e^- \underset{k_{-1}}{\overset{k_1}{=}} AB^- \xrightarrow{k_2} A + B^- \tag{1}$$

$$e^- \text{ or } AB^- + P(+) \xrightarrow{k_D \text{ or } k_N} \text{neutrals} \tag{2}$$

Assuming pseudo-unimolecular recombination, the steady-state treatment for a single state gives

$$K = k_1(k_N + k_2)/((k_D(k_{-1} + k_N + k_2)) \tag{3}$$

Assuming multiple states that do not interconvert, with $k_1 = A_1T^{-1/2}\exp(-E_1/RT)$; $k_{-1} = A_{-1}T\ \exp(-E_{-1}/RT)$

$$\begin{aligned} KT^{3/2} = \Sigma[(k_N + k_2)\, k_D]\underline{[(Q)_i \exp(E_{ai}/RT)]} \\ \{1 + (k_N + k_2)(\underline{T^{1/2}\ (Q)_i \exp(E_{ai}/RT)}\} \\ A_{1i} \exp(-E_{1i}/RT) \end{aligned} \tag{4}$$

When $k_{-1} \gg (k_N + k_2)$, the E_a and Q_{an} are determined since

$$\ln KT^{3/2} = \ln[Q_{an}] + \ln[k_N/k_D] + 11.73 + E_a/RT \tag{5}$$

The Q_{an} is the partition function ratio for the anion to the neutral excluding the spin multiplicity. The value of 11.73 is calculated from fundamental constants and the translational partition function of the electron.

When $k_{-1} \ll (k_N + k_2)$ or unimolecular dissociation takes place the A_1 and E_1 are determined since

$$\ln KT^{1/2} = \ln[A_1/k_D] - E_1/RT \tag{6}$$

The $A_{1(max)}$ ($E_1 = 0$) is the de Broglie A_1, DeBA. The value of ln(DeBA) calculated from fundamental constants at the nominal temperature of the ECD is about 36.

When consecutive dissociation takes place and $k_2 \gg k_N$ and $k_{-1} \gg k_2$, with $k_2 = A_2T\exp(-E_2/RT)$, the A_2 and E_2 are determined since

$$\ln KT^{3/2} = \ln(T/2A_D) + \ln(A_2A_1/A_{-1}) + (E_a - E_2)/RT \tag{7}$$

Thus the positive slope changes to a negative slope as the temperature is increased. Compounds that undergo this type of dissociation are acetates, anhydrides, nitromethane, and halogenated aromatic compounds. At higher temperatures, where $k_{-1} \ll k_2$, eq 6 is again obtained and A_1 and E_1 are obtained.[2]

If structure is observed in the ECD data, multiple states are indicated. If sufficient data are obtained, the fundamental properties of individual states can be determined. Alternatively, if the fundamental properties of one state are measured by a different technique, properties for other states can be obtained. Examples of these more complicated cases can be found in the literature.[2,6−22]

Herschbach Ionic Morse Potential Energy Curves

In 1966 Herschbach classified ionic potential energy curves based on molecular anion formation or dissociation in a vertical transition, the vertical electron affinity VE$_a$, the sign of E_{dea}, ($E_{dea} = E_a(B) - D(A-B)$), and the presence of a minimum in the potential energy curve.[5] The symbols have their conventional definitions. In 2002 Chen and Chen modified these classifications by including only Morse potentials which have a minimum and adding the sign of the E_a of the specific state as a fourth metric.[12−14,20] This led to $2^3 = 8$ primary Herschbach ionic Morse potential curves, HIMPEC, described by the symmetrical notation M(0,1,2,3) and D(0,1,2,3) where the integers refer to the number of positive metrics, E_a, VE$_a$, E_{dea}, and M stands for molecular ion formation and D dissociation. Eight subclasses Mc(m) and Dc(m) are defined based on the crossing of the long-range and ionic curves to give molecular ions or dissociation. The M curves are Mc but some of the D curves can also be Mc.

The Morse potentials are given by

$$\begin{aligned} U(AB) = -2D_e(AB)\exp(-\beta(r - r_e)) + \\ D_e(AB)\exp(-2\beta(r - r_e)) \end{aligned} \tag{8}$$

$$\begin{aligned} U(AB[-]) = -2k_AD_e(AB)\exp(-k_B\beta(r - r_e)) + \\ k_RD_e(AB)\exp(-2k_B\beta(r - r_e)) - E_a(\text{B or A}) \end{aligned} \tag{9}$$

$D_e(AB)$ is the spectroscopic dissociation energy, r is the internuclear separation, $r_e = r$ at the minimum of $U(AB)$, $\beta = \nu_e(2\pi^2\mu/D_e[AB])^{1/2}$, μ, is the reduced mass. The k_A, k_B, and k_R are dimensionless constants. The change in the mass of the neutral by the addition of an electron is included in the k_B term.

$$D_e(AB[-]) = [k_A{}^2/k_R]D_e(AB) \tag{10}$$

$$r_e(AB[-]) = [\ln(k_R/k_A)]/[k_B\beta(AB)] + r_e(AB) \tag{11}$$

$$\upsilon_e(AB[-]) = [k_Ak_B/k_R{}^{1/2}]\upsilon_e(AB) \tag{12}$$

$$VE_a = D_e(AB)(2k_A - k_R) - E_{dea} \tag{13}$$

The Herschbach metrics E_{dea}, E_a, and VE$_a$ give k_A and k_R using eqs 10 and 13. Any of the following can be used to

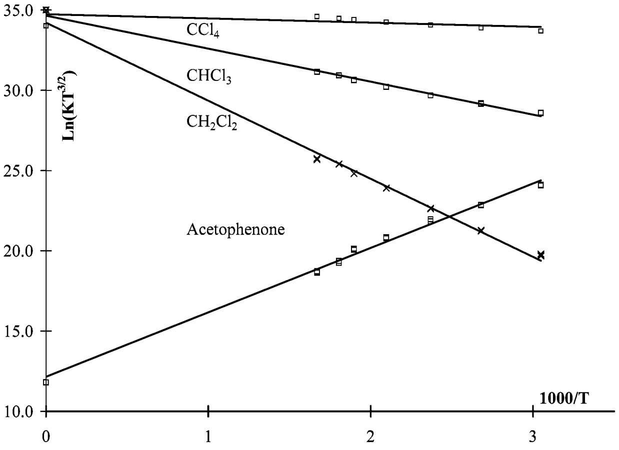

Figure 1. Electron capture detector data for acetophenone and chloromethanes from ref 2.

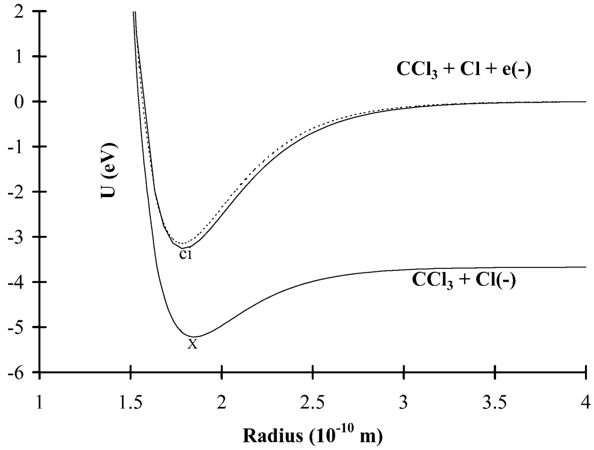

Figure 2. Morse potential energy curves for neutral and anionic CCl_4 which allow rearrangement.

determine k_B: ion distributions, activation energies, anion frequencies, and anion internuclear distance.

CURES-EC Semiempirical Calculations

The procedure is called "CURES-EC". This method has the acronym CURES-EC from "*C*onfiguration interaction or *U*nrestricted orbitals to *R*elate *E*xperimental quantities to *S*elf-consistent field values by estimating *E*lectron *C*orrelation".[2,19] The acronym is appropriate since it is a post self-consistent field approach to cure the electron correlation problem in a semiempirical calculation. It has been used to obtain ionization potentials, gas-phase acidities, and bond dissociation energies. With the general availability of modern desktop computers and software to carry out the theoretical calculations, it is possible for anyone to reproduce the calculations. The calculations are carried out on a pentium desktop computer with commercial software. The HYPERCHEM input files (HlN) files for the various species contain the charge densities and a complete description of the geometric and energy properties of the neutral molecule and the anion. These compact files are an efficient way to store and communicate this information.[2,19]

The first step in CURES-EC is to obtain the most appropriate electron affinity, either experimentally or by chemical logic. In the case of CCl_4, these are obtained from the magnetron and the alkali metal beam methods. The second step is to carry out geometry optimization quantum mechanical calculations for both the neutral and the negative ion. If large geometry changes are possible, the structure is annealed. The E_a is the difference in the electronic energies of the neutral and the negative ion at the global minimum. Then multiconfiguration configuration interaction, MCCI, is added to minimize the difference between the calculated and selected values. Starting from the geometry of the neutral and adding an electron without geometry optimization gives the VE_a.

Only a few MCCI combinations make large changes in the values. These are the UHF and RHF values *w* designated as UHF, RHF(0000), (0011), (1100), (0022), (2200), (3300), (0033). The numbers are the filled and unfilled orbitals used in the RHF configuration interaction for the ion and neutral, respectively. The designation RHF(3300) means that the energy of the neutral is obtained without additional electron correlation (00). For the anion, the original parameters did not include enough electron correlation so that three filled and three unfilled orbitals (33) were mixed in the MCCI calculation.

Results

From eq 6, a plot of $\ln(KT^{3/2})$ versus $1000/T$ will have a positive slope indicating molecular ion formation in the ECD. This is illustrated by the data for acetophenone, shown in Figure 1. The partition function ratio is obtained from the intercept. The absolute E_a is determined from the slope by multiplication by the gas constant. These can be confirmed by experimental half-wave reduction potentials and CURES-EC calculations.

For the chloroalkanes, dissociative thermal electron attachment takes place in the ECD as indicated by the negative slope. Molecular electron affinities cannot be obtained in this case. Two E_a for CCl_4 are listed in NIST, 0.8(3) eV and 2.1(1) eV. The values in parentheses are the random uncertainties in the last figure. The higher value is both accurate and precise since it was determined by two different experimental techniques, the magnetron method and the alkali metal beam method. The lower value, determined by one method, may be for an excited state. BKWS predicted AM1 E_a for 28 halocarbons, including the E_a of CCl_4, 1.88 eV, but did not compare the predicted value with experiment. The negative calculated AE_a disagree with the FLHW hypotheses. The MNDO(0034) CURES-EC value of 2.2 eV agrees with experiment. The MNDO(0000) value is 2.3 eV

Rate constants for dissociative thermal electron attachment to molecules, $k_1 = A_1T^{-1/2}\exp(-E_1/RT)$, are obtained from ECD data as shown for chloromethanes in Figure 1, using eq 7. The negative slope indicates unimolecular dissociative thermal electron attachment. As shown in Figure 1, the intercepts, A_1, are relatively constant so the relative rate constants at room temperature are related to the activation energies. In the swarm ionization experiments the rate constants were determined at only one temperature. For the strongly capturing species, it was noted that $k_1 = A_1(\text{thermal}) = 4 \times 10^{-8}(\alpha^{1/2})$, where α is the polarizability. However, the k_1 for low-capturing species were unexpectedly observed to be exponentially related to α. If the relationship, $k_1 = A_1T^{-1/2}\exp(-E_1/RT)$ is used, the dependence of A_1 and α could be examined. This would require the measurement of k_1 as a function of temperature.

In BKWS, only one undefined negative ion potential energy curve was drawn for each haloalkane. Similar curves were drawn for haloalkanes using the Morse function as early as 1968. In Figure 2 is an approximate HIMPEC for $CCl_4(-)$ drawn from the AE_a and VE_a from Figure 6 of BKWS and the approximate "backside" crossing. This is M(3) and Mc(3) since all three metrics are positive and molecular ion formation occurs in the Franck Condon region. The AM1 AE_a is equal to the experimental value. The negative ion and neutral curves cross above $U = 2$ eV, and the VE_a is positive, not zero. This curve does

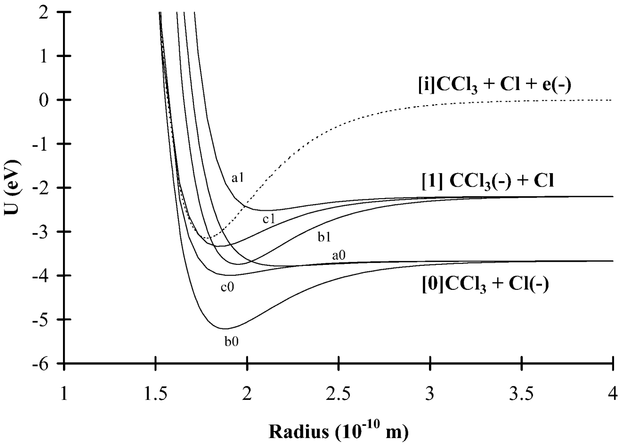

Figure 3. Morse potential energy curves for neutral and anionic CCl_4. The a and b curves assume two-dimensional cuts through the surface.

not agree with the experimental ECD activation energy or electron transmission VE_a, both of which are zero. It does agree with the alkali metal beam and magnetron value of the AE_a and is designated the X curve. In 1989 we presented three anion curves for $CCl_4(-)$ based on experimental data and in 2004 discussed more curves.[2,20]

Six anion curves were constructed for $C_2Cl_4(-)$ using experimental data and theoretically predicted values where data are not available for the Herschbach metrics.[20] Similarly, eight HIMPEC for $CCl_4(-)$ can be calculated. These are crossing, c1 and c0; "bonding" b0 and b1; "antibonding", a0 and a1; and X and ci. The 0 and 1 refer to the lowest dissociation limits in a single bond dissociation: 0—[$Cl(-) + CCl_3$] and 1—[$Cl + CCl_3(-)$]. In addition to the "X" ground state curve drawn to the "0" level, a long-range ci curve can be drawn to [$Cl + CCl_3 + e(-)$]. The X and ci curves are shown in Figure 2 and the others in Figure 3.

Two experimental E_a for CCl_4 were obtained from the NIST tables. The activation energy for thermal electron attachment was obtained from the ECD and electron transmission data. In addition, vertical electron affinities are obtained from electron impact and transmission data.[2,20] The bond energy in the a curves are estimated to be larger than polarization bonds.[7] The X, c0, and b0 curves are M(3) since all three metrics are positive. The c1 curve is M(2) with E_{dea} negative. The b1 curve is M(1) with only E_a positive. These curves could be involved with the alkali metal beam formation of the parent negative ion. The b1 and c1 curves are crossed by the a0 curve which could lead to dissociation. The a0 curve is D(2) and Mc(2) and with the c1 and b1 curves is responsible for the electron impact spectra and the ECD activation energy and the electron transmission spectra. The a1 curve is D(0) and Dc(0) and is least defined by experiment. This illustrates the use of the HIMPEC metrics and classifications to consolidate data.

Summary and Conclusions

The swarm ionization cell results are a welcomed independent confirmation of our experimental and theoretical studies, especially the experimental k_1(293K) and the AM1 calculations of the E_a. The majority of the summary items in BKWS state experimental and theoretical results. Item 1 refers to the LUMO of an atom when it should refer to the LUMO of the molecule. Item 7 does not specify which "electron affinity". Items 3, 4, and 11 refer to a single potential energy curve and should be revisited in the light of multiple curves, especially since the reported curve does not reflect the experimental E_1 or VE_a. Item 8 suggests the polarizability, not the activation energy, governs the thermal electron attachment. This must be reconsidered especially since only Cl- and F-substituted molecules are included. Finally, the AM1 E_a should be compared with experiment.

The new contributions of this article are the calculation and classification of eight HIMPEC for polyatomic molecules and the statement of the Feynman/Lesk/Herschbach/Wentworth hypotheses. These place a lower limit of zero on the LE_a, AE_a, and the D_e for dissociation in a given bond dimension. The a and b "pseudo-two-dimensional Morse potentials" are a cut through the multidimensional surface in which the geometry of the leaving groups are fixed in their neutral geometry. The X curves allow for rearrangement, while the "c" curves are in a third electron−molecule dimension. These curves are first approximations to the true potential energy curves. The use of the Morse potential is possibly not applicable in the long ranges, but since no data are available in that region, these will serve as hypothetical curves.

Dedication

This article is dedicated to the memory of Professor W. E. Wentworth who now like Lincoln belongs to the ages. Without him the authors and all of his students would not be scientists but above all would not be the persons that they are today. This manuscript was read to him after he suffered a massive stroke on February 22, 2004. He could not speak but nodded in agreement and shook his head when he wanted changes.

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