J. Phys. Chem. A **2006,** *110,* 4363−4368

Electron Capture Detector Response and Dissociative Electron Attachment Cross Sections in Chloroalkanes and Chloroalkenes

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Received: November 14, 2005

Electron capture detectors (ECDs) are widely used in gas chromatography to detect electronegative compounds. In this work, we examine the connections between the ECD response and the cross sections for dissociative electron attachment (DEA) determined from low energy electron beam studies in the chloroalkane family, stressing in particular the role of temporary anion state energies. We show that attachment rate coefficients computed from these cross sections are well correlated with ECD response, and that the latter decreases exponentially with increasing energies of the lowest anion states. ECD measurements are also carried out in monochloroalkanes substituted with unsaturated ethenyl and phenyl moieties, and the response is shown to depend strongly on the mixing between the unsaturated π^* and the C−Cl σ^* temporary anions as exhibited by the vertical attachment energies (VAEs) of these states. The results show good correlations between the chloroalkene and phenyl chloride ECD responses and the VAEs for the mixed states.

I. Introduction

The response of electron capture detectors (ECDs) to various molecular families is generally known empirically, but the connections between response and properties of the temporary anion states of these compounds are not well established. Because the primary electron loss mechanism arises from attachment and formation of temporary anions that subsequently dissociate or are collisionally stabilized, the energies, lifetimes, and potential surfaces of these transient intermediates are fundamental to a quantitative understanding of ECDs. In particular, it is important to explore the role of vertical attachment energies (VAEs), the energies required to attach an electron into normally unoccupied molecular orbitals with the molecules in their equilibrium geometries. The VAE associated with attachment into the lowest unoccupied molecular orbital (LUMO) is especially significant because it provides a measure of the ease of reduction of the molecule. Calculated LUMO energies have been widely used in quantitative structure/reactivity relationships (QSARs)[1] as key parameters in reductive processes. However, as shown elsewhere by direct comparison with measured VAEs, such calculated energies may not be internally consistent from one molecular family to another or between orbitals of different symmetries.[2]

Our objectives in the present work are 2-fold. We begin by illustrating experimentally the link between ECD response and the most fundamental measure of the process, namely, the electron attachment cross section. Data for the latter rarely include numerous members of a molecular family so that the trends can be observed. Thus, it is not surprising that such comparisons, to our knowledge, have not been previously reported. For this purpose, we use data derived from measured cross sections for the dissociative electron attachment (DEA) process, $e + AB \rightarrow AB^{-*} \rightarrow A + B^-$, in perhaps the simplest chemical family to interpret, the chloro-substituted alkanes. Specifically, we compare ECD response with attachment rate constants derived from Cl^- producing cross sections measured in an electron beam apparatus.[3] The results obtained above are readily interpretable in terms of electron attachment into the σ^* LUMOs of the compounds, which are derived from combinations of local C−Cl antibonding σ^* orbitals.

In the second part of our study, we extend our ECD measurements to a series of nonplanar mono-chloroalkenes and phenyl chlorides in which we vary the separation between the C−Cl and unsaturated moieties. In these compounds, the LUMO is comprised of a wave function mixture of the π^* orbital residing on the double bond or phenyl group with the C−Cl σ^* orbital. We show that the ECD response varies exponentially with the VAE for attachment into this hybrid temporary anion state.

II. Experimental Section

The attaching electrons in ECDs are generally assumed to have reached thermal equilibrium with the gases in the cell at the atmospheric pressure of the buffer gas. For our compounds, the loss of electrons owing to production of Cl^- is related to the integral of the total DEA cross section over the thermal distribution of electron energies. The family of chloroalkanes studied here allows a considerable, perhaps unique, simplification of the ECD processes that could occur in molecules with less favorable characteristics. At thermal energies, Cl^- is the only anion product, and the potential energy surfaces leading to this product are repulsive along the C−Cl coordinate, although weak minima arising from polarization may occur at large separations. As far as we are aware, none of the compounds form metastable anion states at thermal energies with lifetimes that would permit them to be stabilized or destabilized by collisions with the buffer gas. Finally, because of the large electron affinity of Cl (3.6 eV), thermal detachment at 300 °C from Cl^- is not significant. In any case, we report

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10.1021/jp058293b CCC: $33.50

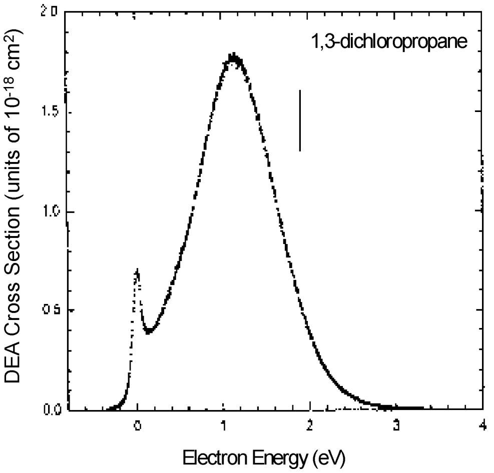

Figure 1. The cross section for dissociative electron attachment of 1,3-dichloropropane as a function of electron impact energy. The vertical line indicates the energy for vertical electron attachment into the lowest unoccupied molecular orbital. The data are from ref 1.

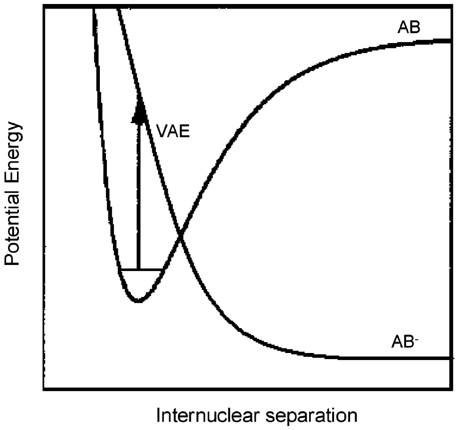

Figure 2. Morse potential curve for a hypothetical diatomic molecule AB and its anion AB$^-$. The vertical arrow indicates the VAE of the molecule.

only relative ECD responses, and in the following we assume these responses are proportional to the Cl$^-$ production. The measured DEA cross sections of chloroalkanes[3] typically display a double peaked structure at energies below approximately 4 eV (Figure 1). The origins of these peaks are best understood by considering the schematic potential curves (Figure 2). In Figure 2, the bound curve (AB) illustrates the potential energy of the neutral molecule (plus a zero energy electron at infinite distance) as a function of a C−Cl stretching coordinate. The repulsive curve (AB$^-$) shows the energy of the temporary anion state formed by attachment of an impinging electron into the LUMO, generally composed of one or more localized C−Cl σ^* orbitals, depending on the degree of chlorination. The electron energy required to occupy this orbital, with the molecule in its ground state geometry, is the VAE and is a fundamentally important property of the molecule, indicating the ease with which a compound may be reduced. VAEs may be determined experimentally in the gas phase by observing the energies at which resonance peaks occur in the total electron scattering cross section. Electron transmission spectroscopy (ETS)[4] is widely used for this purpose, and VAEs of numerous chloroalkanes have been reported elsewhere.[5,6] Because of the short lifetimes of such temporary anion states, it is useful to keep in mind that an electron may attach over a range of energies around VAE because of the spread in energy given by the Heisenberg uncertainty principle.

We next review the DEA process briefly.[7] Following electron attachment into a C−Cl antibonding orbital, the C−Cl bond begins to stretch. During this period, the electron may detach, returning the molecule to its ground or a vibrationally excited state. The temporary anions that survive to the crossing point between the two potential curves in Figure 2 give rise to the stable chloride anion. The peak lying at higher energy in Figure 1 indicates the electron energy dependence of this yield. The vertical line in this figure shows the VAE for this compound (1.91 eV) determined by ETS. The shift of the peak in the DEA cross section away from the VAE to a lower energy is a consequence of the short lifetime of the temporary anion state.[7] The magnitudes of the DEA cross sections have been measured for a large number of chloroalkanes[3] and correlate with VAE over about 6 orders of magnitude. The actual dependence is discussed in more detail elsewhere.[3]

The mechanism producing the peak near zero energy in Figure 1 is well understood in a qualitative sense. From studies of the temperature dependence of the electron attachment process in similar molecules, the existence of an activation energy was inferred[8] that was identified with the energy of the crossing point in Figure 2. The conventional view is that vibrationally excited levels of the neutral molecule lying above this energy can readily attach slow electrons and thus contribute to DEA at very low electron energies. Calculations presented elsewhere[9] show that the process is more complicated and that attachment to levels *just below* the crossing point can also contribute by quantum tunneling through the narrow barrier. Combining these effects gives rise to a DEA cross section that diverges as the electron energy approaches zero. The convolution of such a diverging cross section with the electron energy distribution limits the peak amplitude and produces the characteristic "zero energy" peak observed in electron beam experiments. The separation between this peak and the higher lying peak is a function of the degree of chlorination. Increasing chlorination reduces the VAE, tending to merge the two DEA peaks into a single large low energy feature.

The relative size of the two peaks in Figure 1 is sensitive to the vibrational temperature of the molecules, with the low energy peak growing rapidly with increasing temperature. Because excited vibrational levels lie closer to the anion potential curve, electron attachment can take place at larger C−Cl bond distances where the probability of survival to the crossing point is greater, and thus the upper peak shifts to lower energy and also grows in amplitude with increasing temperature.

Dissociative Electron Attachment at Thermal Energies. Because the electron energy distribution employed in the electron beam experiments we refer to here cannot resolve the zero energy peaks in the DEA cross sections, a straightforward numerical integration over the product of cross section and a thermal electron energy distribution cannot be carried out to derive a quantity to be tested against the ECD response. However, an equivalent approach[9] will permit this comparison. In brief, the electron beam data were fit to model cross sections having the appropriate low energy dependence given by theory and convoluted by the broadening due to the electron beam energy distribution. From these fits, the contribution arising solely from the "zero peak" in the DEA yield could be determined. As the actual computed parameter for comparison, we use the energy integrated cross section from its low energy side up to its maximum and label it as the "integrated half-peak cross section." This choice is somewhat arbitrary but we desired to emphasize the contribution arising primarily from vibrationally excited molecules for a comparison with the ECD response.

TABLE 1: Electron Capture Detector Area Ratio, Energy-Integrated Half-peak Cross Sections, Thermal Electron Attachment Rate Constants, and Vertical Attachment Energies of Selected Chloroalkanes

	compound	ECD area ratio with detector temperature 300 °C	ECD area ratio with detector temperature 150 °C	integrated half-peak cross sections (cm^{2}eV)^a	attachment rate constant (cm^3/s)^a	VAE (eV)^b
1	tetrachloromethane	80.155	77.785	2.281×10^{-15}	2.80×10^{-7}	-0.34 to -0.08
2	trichloromethane	8.078	-	4.915×10^{-17}	9.41×10^{-9}	0.42
3	1,1,1-trichloroethane	23.134	20.048	1.236×10^{-16}	5.88×10^{-9}	0.64
4	1,1,2-trichloroethane	3.173	1.268	8.231×10^{-18}	1.20×10^{-9}	0.80
5	1,1,2-trichloro-2-methylpropane	1.811	0.803	2.338×10^{-18}	2.90×10^{-10}	0.90
6	dichloromethane	0.160	-	8.020×10^{-20}	1.60×10^{-11}	1.01
7	1,2,3-trichloropropane	2.844	-	2.653×10^{-18}	6.31×10^{-10}	1.20
8	1,2-dichloro-2-methylpropane	0.159	0.037	3.949×10^{-19}	4.80×10^{-11}	1.40
9	2,2-dichloropropane	0.394	-	6.138×10^{-19}	5.73×10^{-11}	1.41
10	2,3-dichlorobutane	0.167	-	2.616×10^{-19}	3.11×10^{-11}	1.56
11	1,2-dichloropropane	0.170	0.04	1.907×10^{-19}	2.70×10^{-11}	1.64
12	1,2-dichloroethane	0.201	0.023	1.613×10^{-19}	4.72×10^{-11}	1.70
13	1,3-dichloropropane	0.114	nd^c	4.298×10^{-20}	4.94×10^{-12}	1.91
14	1,5-dichloropentane	0.010	nd	7.120×10^{-21}	9.00×10^{-13}	2.04
15	1,4-dichlorobutane	0.014	nd	1.474×10^{-20}	2.80×10^{-12}	2.07
16	1-chlorohexane	1.15×10^{-3}	nd	-	-	~2.20

[a] Reference 9. [b] Reference 3. [c] nd = not detectable.

The electron beam data of Aflatooni and Burrow[3] were also used to compute the actual thermal electron attachment rate constant that includes not only the contribution from the "zero peak" but the portion arising from the more energetic but less numerous electrons in the distribution that overlap the upper DEA peak as well.[9] The latter quantity should be a better match to the ECD response. We note here a significant difference between the gas-phase measurements[3] and those measured with the gas chromatography with electron capture detector (GC/ECD). The beam experiments were carried out at a gas temperature of approximately 65 °C, whereas those involving the ECD were taken at 300 °C. We discuss the implications of this temperature difference later.

Following a description of the ECD measurements, we explore how well the zero peak data and the attachment rate constant data derived from electron beam measurements correlate with the ECD response. Next, we examine how the ECD response varies with the measured VAEs of the compounds.

ECD Measurements. Briefly, the ECD detector consists of a cavity with two electrodes and a radiation source that emits β-radiation (e.g., ^{63}Ni). Collisions between electrons and the carrier gas (Ar/CH$_4$) produce a plasma containing electrons and positive ions. After rapidly thermalizing, the electrons are collected, establishing a steady background current. As electronegative compounds enter the detector, negative ions are formed by the capture of free electrons, resulting in decreases in the background current. The ECD response generally depends on several factors, including (a) the mode of signal processing used, (b) the electron capture rate constant of the analyte, (c) the stoichiometry of the reaction of electrons with the analyte,[10] and (d) the detector temperature.[11] Here, we explore the second and the fourth of these factors.

The ECD response was measured for a number of chloroalkanes and normalized to equal molar concentrations. To establish the standard curves, different concentrations of each compound were prepared in acetonitrile containing 0.65 μM CCl$_4$ as an internal standard and analyzed by GC/ECD (Hewlett-Packard, Wilmington, DE) using a 30 m × 0.53 mm DB-1 column (J&W Scientific, Folsom, CA) with H$_2$ as the carrier gas. Injector and detector temperatures were 220 and 300 °C, respectively. An anode-purged ^{63}Ni ECD detector was used with a flow rate of 20 mL min^{-1} using 5% CH$_4$ in Ar as the auxiliary gas. The oven program was 50 °C for 4 min then increased at 30 °C/min to 110 °C and held for 2 min. The area ratio of each compound to CCl$_4$ was normalized to 0.05 mM concentration.

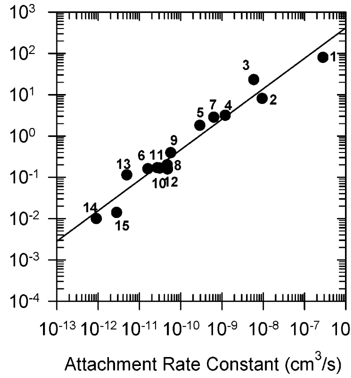

Figure 3. Correlation between ECD normalized-concentration area ratios of selected chloroalkanes and attachment rate constants computed from the electron beam cross sections.

III. Results and Discussion

Chloroalkanes. Table 1 summarizes the ECD response function (area ratio), the energy integrated cross sections for the half-peak, the attachment rate constant from electron beam data, and the VAEs. The 16 compounds are numbered and listed in order of increasing VAE.

In Figure 3 we plot the ECD area ratio, that is, the normalized-concentration GC/ECD area ratios of the selected chloroalkanes to the CCl$_4$ internal standard, as a function of the attachment rate constant computed from the electron beam data. The graph is presented as a log−log plot with the same range on both axes. The good correlation between ECD response and attachment rate indicates that the particular DEA reactions discussed here account for the major processes important for the ECD response in these compounds. The slope of the best fit line, however, is less than unity, with the ECD response covering 4 orders of magnitude whereas the attachment rate constants span more than five. This appears to be a consequence of the temperature differences at which the ECD and electron beam measurements were taken. Because the population of highly excited vibrational levels increases more rapidly than that for low lying levels, for a given increase of temperature, we anticipate that the electron beam data for compounds with low attachment rate constants will increase more rapidly with

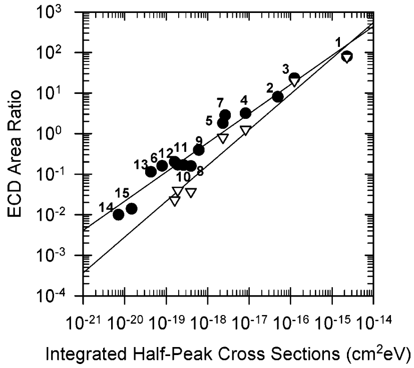

Figure 4. Correlation between ECD normalized-concentration area ratios of selected chloroalkanes and integrated half-peak cross sections at 300 °C (●) and 150 °C (▽).

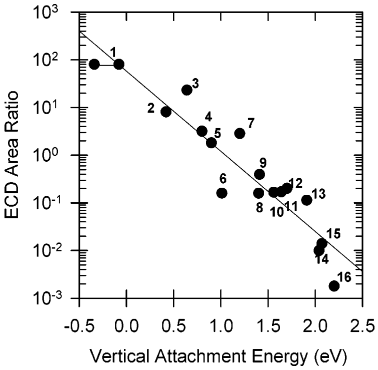

Figure 5. Correlation between ECD normalized-concentration area ratios of selected chloroalkanes and vertical attachment energies.

temperature than will that for compounds with high rate constants, thus shifting the slope of the curve toward unity. To support this, we refer to Figure 4 in which the ECD response is plotted as a function of the integrated half-peak cross section. Again a good correlation is observed (closed circles) indicating that the "zero peak" accounts for the major portion of the electron attachment. Area ratios for seven representative compounds were measured at an ECD cell temperature of 150 °C rather than 300 °C (open triangles in Figure 4). As anticipated, the slope increases towards unity. The sensitivity of the ECD decreases with decreasing temperature and at 150 °C was insufficient to detect 1,3-dichloropropane, 1,5-dichloropentane, 1,4-dichlorobutane, and 1-chlorohexane, which have the smallest attachment rate constants.

Differences in the relative positions of compounds in Figures 3 and 4, particularly compounds **2** and **3**, can be attributed to the large contribution from the upper resonance peak in the DEA cross section[3] of trichloromethane, which lies at relatively low energy and greatly enhances the attachment rate constant.

Because reduction of the chloroalkanes results in the loss of electron to form Cl^-, a connection between ECD response and VAE is anticipated and was observed (Figure 5). A related correlation was previously verified in the electron beam study[9] in which an exponential dependence of the integrated half-peak areas on VAE was found. It is interesting to note that dichloromethane (**6**), which was anomalous in the earlier electron beam studies,[3,9] is a consistent outlier in the ECD response vs VAE as well. We also note that the VAE of CCl_4, being < 0 eV, cannot be determined by ETS. The bracketed values for **1** in Figure 5 are estimates determined from semiempirical calculations described elsewhere.[6]

In contrast to the data in Figures 3 and 4 in which both axes reflect measured quantities that should be closely related, the dependence of ECD response on VAE is sensitive to individual molecular properties and more scatter in the graph is expected. From theoretical treatments of DEA,[7] we know that the cross section is an exponential function of the anion lifetime and the separation time required to reach the crossing point (Figure 2). Both of these parameters are functions of VAE, and the fact that there is a reasonable correlation at all testifies to a relatively smooth variation of the parameters with VAE, owing to the strong "family" resemblance of this set of molecules.[3] The DEA cross section at thermal energies is also likely to be very sensitive to the energy of the curve crossing and small differences here may account for a portion of the scatter.

TABLE 2: Electron Capture Detector Area Ratio and π^*/σ^* Vertical Attachment Energies of Selected Chloroalkenes and Phenyl Chlorides

	compound	ECD area ratio	π^*/σ^* VAE (eV)[a]
17	allyl chloride	2.89×10^{-2}	1.04
18	4-chloro-1-butene	9.46×10^{-3}	1.40
19	5-chloro-1-pentene	4.90×10^{-3}	1.58
20	6-chloro-1-hexene	1.80×10^{-3}	1.68
21	benzyl chloride	4.04×10^{-1}	0.63
22	(2-chloroethyl)benzene	7.80×10^{-3}	0.89
23	3-phenylpropyl chloride	3.10×10^{-4}	0.97
24	1-chloro-4-phenylbutane	1.30×10^{-3}	1.00

[a] For internal consistency, the values of ref 17 are used. Those for 21−24 from ref 16 agree within 0.02 eV.

Chloroalkenes and Phenyl Chlorides. In the previous section we focused on the more fundamental aspects of ECDs, showing that their responses are consistent with measured DEA cross sections in chloroalkanes. We now illustrate how ECD measurements can provide insight into the DEA process in compounds in which cross sections or thermal attachment rate coefficients are not available.

For this study, we consider two families of compounds in which a CH_2Cl moiety is attached to an ethenyl or phenyl group directly or through several intervening CH_2 spacers. The unsaturated groups introduce additional low-lying temporary anion states of π^* symmetry. As a function of the C−Cl bond distance, the energies of these π^* resonances remain roughly parallel to that of the ground state of the neutral molecule. The shapes of these potential surfaces might suggest that they play no role in DEA. However, in these nonplanar molecules, π^* and σ^* orbitals may mix, allowing each anion state to acquire some characteristics of the other. The mixing creates an avoided crossing between the nominally π^* and σ^* potential curves which allows the former to contribute to the DEA process. The coupling between these states, of course, will vary with the physical separation of the two groups.

The DEA cross sections in these and similar compounds have been studied by others.[12−16] In brief, the measurements show that the maximum DEA cross sections occur at the energies of the nominal π^* resonances, and that they increase in magnitude as the mixing between π^* and σ^* orbitals increases. None of the studies, however, addresses the effect of such mixing on the low energy DEA cross section or the thermal electron attachment rate coefficient.

With this background, we carried out ECD measurements on four chloroalkenes (**17**−**20**) and four phenyl chlorides (**21**−**24**) (Table 2). Because the VAEs for attachment into the π^* LUMOs in both benzene and ethene lie below that for the C−Cl σ^* orbital, the LUMOs in our compounds have primarily π^* character with a bonding admixture of the C−Cl σ^* which we will label as "π^*/σ^*". The VAEs for attachment into these LUMOs have been determined by ETS[17] (Table 2). The shortest

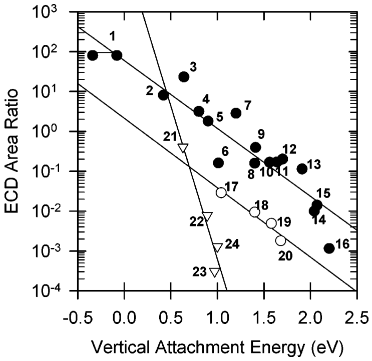

Figure 6. Correlation between ECD normalized-concentration area ratios of selected chloroalkanes (●), chloroalkenes (○), phenyl chlorides (▽) with their respective σ^* and π^*/σ^* vertical attachment energies.

compounds, allyl chloride and benzyl chloride, possess the lowest lying VAEs, reflecting the greatest mixing between π^* and σ^*. As the separation between C−Cl and the unsaturated group increases, the VAE increases, approaching that for the unmixed π^* in unsubstituted ethene or benzene.

In Figure 6, we plot the ECD response as a function of the π^*/σ^* VAEs for chloroalkenes (open circles) and phenyl chlorides (open triangles). ECD responses for chloroalkanes (closed circles) are also shown for reference. Over the relatively narrow range of VAEs explored here, the response is observed to vary in an approximately exponential manner. The slopes, however, are substantially different, with that for the phenyl-based compounds falling off much faster with increasing VAE than the ethenyl-based compounds or the chloroalkanes. We note here that relative responses of the two longest phenyl-based compounds are reversed from our expectation. As shown by Modelli et al.,[16] the DEA cross sections of **23** and **24** at their π^*/σ^* maxima fall in the anticipated order, with that of **24** smaller than that of **23** owing to the decreased π^* and σ^* mixing in the longer compound. Thus the reversal at thermal energies is puzzling. It is, however, confirmed by the electron beam measurements of Modelli et al.[16] which show a smaller zero peak in **23** than in **24**. Although conformational differences could play a role, the three most stable conformers in these compounds have been computed by Modelli et al.[16] They appear to be quite similar and thus unlikely to account for this behavior. At present we have no further explanation.

In the limit of large separation between C−Cl and the unsaturated group, it is reasonable to expect that the ECD response will approach that of a long normal monochloroalkane. Using 1-chlorohexane (**16**) as an example of the latter, its response is indeed observed to lie near those of the longest phenyl and ethenyl compounds. Consistently, the LUMO VAEs of these compounds are approaching the limiting values characteristic of the unsaturated groups, 1.1 eV for benzene[18] and 1.8 eV for ethylene.[19]

The relative VAEs of the separated groups allow a qualitative explanation of the large difference in slopes of the ECD response in these two series. The π^* VAE of ethylene lies relatively close to the σ^* VAEs of normal monochloroalkanes, which fall in the range of 2.2−2.4 eV.[20] This small energy enhances π^*/σ^* mixing in the ethenyl compounds relative to that in the phenyl-based compound in which the gap is much bigger. The large mixing is evident in the shift in VAE between **20** and **17**, compared to the smaller value in going from **24** to **21**. On the other hand, regarding the shortest members of each series, **21** and **17**, in which the mixing is largest, the ECD response of **21** is substantially larger. This is likely a consequence not only of the lower VAE of **21** but of the longer temporary anion lifetime of the phenyl group.

The trend line in the chloroalkene family appears to be parallel to that for the chloroalkanes but approximately 30 times smaller in magnitude. We offer no explanation for why the lines are parallel and it may well be fortuitous. The difference in magnitude appears to arise from differences in the degree of chlorination. We note that monochlorohexane (**16**) lies closer to the (mono)chloroalkene line than it does to the polychlorinated compounds (**1**−**15**).

These results indicate the difficulties of predicting ECD responses in molecules, even those featuring only two coupled temporary anion states and without the additional complications from collisional conversion in to and out of stable parent anion states. Indeed, to our knowledge, there are no first principles calculations for the DEA process in such compounds. Nevertheless, ECD responses plotted against VAEs obtained from gas-phase electron scattering measurements display trends within molecular families that give insight to the subtle interactions between such anion states and the role they play in the thermal energy attachment cross section. In this regard, we view the energies of these states as more fundamental than the polarizabilities of attaching centers put forth by others[21] to rationalize rate constants in halogenated compounds.

IV. Conclusions

In this work we have shown that ECD responses are consistent with attachment rate constants derived from electron beam experiments in a large family of chloroalkanes, and they decline exponentially with the VAEs for attachment into the LUMOs of these compounds. We stress the role played by vibrationally excited states of the neutral molecules in the thermal attachment process.

We applied ECD measurements to a study of attachment in two series of nonplanar unsaturated monochloro compounds and show that coupling between the nominal π^* and σ^* resonances affects the thermal attachment cross section significantly and that, again, the VAE for attachment into the LUMO allows the trends to be most evident. Given the ease with which such ECD measurements can be made, compared especially to the difficulties of obtaining cross sections from electron scattering at low energy, it is surprising that it has not been applied more often to study the properties of temporary anion states.

Acknowledgment. This research was supported by grants from EPA/EPSCoR and the National Research Initiative of the USDA Cooperative State Research, Education and Extension Service, grant number 2001-35107-11147. The authors are grateful to Professor Gordon Gallup for many useful conversations. This study was motivated in part by a suggestion from Professor Lynn Roberts. A contribution of Res. Div. Projects NEB-40-002 and NEB-40-019, Journal Ser. no. 14994.

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