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Temporary π* and σ* Anions and Dissociative Electron Attachment in Chlorobenzene and Related Molecules

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Coupled-cluster, Hartree−Fock, and B3LYP calculations are employed to study the gas-phase empty-level structures of chlorobenzene, benzyl chloride, and (2-chloroethyl)benzene. All three theoretical approaches reproduce accurately the energy trends of vertical electron attachment observed in the electron transmission spectra and predict the occurrence of the lowest σ* resonance about 2 eV higher in energy than the lowest π* resonance, in contrast with a recent suggestion by others. The relative cross sections for dissociative electron attachment are measured in the benzene derivatives and in saturated chlorohydrocarbons. The Cl^- currents and a comparison of the energies of maximum production in the dissociative attachment spectra with the resonance energies located in the electron transmission spectra clearly indicate, that in the benzene derivatives, dissociation follows electron trapping into a ring π* empty orbital and subsequent intramolecular transfer to the chlorine atom, in line with the conclusions of an earlier work.

Introduction

In gas-phase collisions, an isolated molecule can temporarily attach an electron of proper energy into a vacant orbital, the process being referred to as a shape resonance.[1] Electron transmission spectroscopy (ETS)[2] is one of the most suitable means for detecting the formation of these short-lived anions. Because electron attachment is rapid with respect to nuclear motion, temporary anions are formed in the equilibrium geometry of the neutral molecule. The (positive) impact electron energies at which attachment occurs are properly denoted as vertical attachment energies (VAEs) and are the negatives of the vertical electron affinities (VEAs). When suitable energetic and kinetic conditions are met, the decay of the unstable molecular anions can follow a dissociative channel (in competition with simple re-emission of the extra electron), which generates long-lived negative fragments. Dissociative electron attachment spectroscopy (DEAS) measures the yield of these fragments as a function of the incident electron energy.

The ability of halohydrocarbons to attach low-energy electrons, generally with subsequent production of halogen anions, plays an important role in chemistry and biochemistry. From an environmental point of view, analogies can be envisaged between DEA in halohydrocarbons and the reductive dehalogenation promoted by bacteria in anaerobic sediments, sewage sludge, and aquifer materials.[3]

In saturated chloro-, bromo-, and iodohydrocarbons, the production of negative halogen fragments follows electron attachment to the σ* lowest-unoccupied molecular orbital (LUMO), with mainly halogen character.[4−6] However, in halo derivatives of unsaturated hydrocarbons, such as benzene and ethene, numerous studies[7−14] demonstrate that the maximum yield of halogen anion fragments occurs close to the energies of the corresponding π* resonances observed in ETS.

Clarke and Coulson[15] noted that, in the dissociation of the chlorobenzene anion, the lowest potential surface must produce the Cl^- (^1S) anion and the C_6H_5 ($^2A_1$) radical in their electronic ground states. For reasons of symmetry, electron attachment to the empty π* MOs cannot lead to these products if the planar geometry of the neutral molecule is retained. On the other hand, at the observed energy of maximum Cl^- yield, the excited (π^7) phenyl radical is not accessible.

As pointed out in the literature,[11,12,16] mechanisms that couple σ* and π* potential surfaces (through out-of-plane vibrations or incipient out-of-plane distortions in the anion) can allow π* temporary anions to cross over to the lowest (repulsive) σ* potential surface, thus accounting for the observed enhancement of Cl^- production at the energy of the π* resonance.

A recent paper,[17] however, points out that such mechanisms need not to be invoked for chlorobenzene. According to the authors, the $^2A_1$ (σ*) anion state that leads to dissociation is the most stable not only at large C−Cl distances, but also at the geometry of the neutral molecule. Thus, the lowest vertical electron attachment process would be associated with the σ^*_{C-Cl} MO. In particular, final-state relaxation effects reverse the energy ordering of the anion with respect to that of the empty MOs in the neutral state, in line with the predictions of PM3 semiempirical calculations.[17]

In this work, we present the results of theoretical methods (including coupled-cluster calculations, which should account for correlation effects) that are more reliable than the semiempirical approach for evaluating the relative energies of the lowest π* and σ* anion states of chlorobenzene, benzyl chloride, and (2-chloroethyl)benzene. Independent indications are deduced from a comparison of the Cl^- peak energies in the DEA spectra of the benzene derivatives and of saturated chlorohydrocarbons with those of the corresponding resonances observed in the ET spectra and from measurements of the relative cross sections for the DEA processes.

Results and Discussion

ET Spectra and Calculations. Table 1 reports the VAEs measured in the 0−4 eV energy range in the ET spectra of

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TABLE 1: VAEs (eV) Measured in the ET Spectra and Peak Energies (eV) and Relative Anion Currents Measured in the DEA Spectra

	ETS		DEAS	
	AE (eV)			
	π^*	σ^*	peak energy (eV)	relative intensity
chlorobenzene	0.72	2.44[a]	0.72[a]	1
	0.75	2.42[b]	0.74[d]	
	0.75	2.46[c]	0.75[e]	
			0.75[f]	
benzyl chloride	0.63, 1.00	2.86[a]	0.54[a]	17.5[a]
	0.65, 1.05	2.8[g]	0.52[f]	17.7[f]
(2-chloroethyl)benzene	0.87	2.7[f]	0.76[f]	0.94[f]
tert-butyl chloride		1.80[h]	1.42[i]	0.093[f]
2-chlorobutane		2.05[i]	1.4[i]	0.051[j]
1-chlorobutane		2.39[i]	1.4[i]	≤0.006[j]

[a] From ref 12. [b] From ref 18. [c] From ref 19. [d] From ref 17. [e] From ref 11. [f] This work. [g] From ref 20. [h] From ref 21. [i] From ref 4. [j] From ref 22.

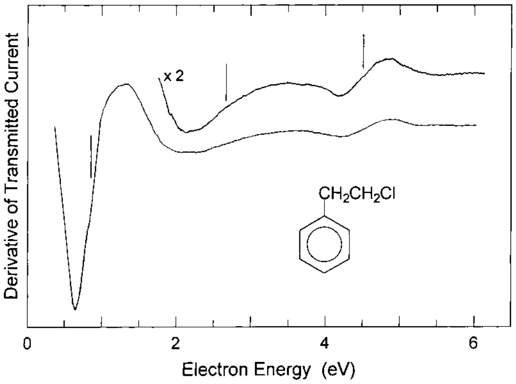

Figure 1. ET spectrum of (2-chloroethyl)benzene. Vertical lines indicate the VAEs.

monochloro derivatives of benzene, *tert*-butyl chloride, 2-chlorobutane, and 1-chlorobutane. The values are taken from the literature except for (2-chloroethyl)benzene, whose ET spectrum is reported here for the first time (see Figure 1). In chlorobenzene[12,18,19] and benzyl chloride,[12,20] the two resonances (not resolved in the former) in the 0.7−1.1 eV energy range and the broader resonance around 2.5 eV were assigned to electron capture into the two π^* MOs deriving from the benzene e_{2u} LUMO and into a σ^*_{Cl-C} MO, respectively. These assignments were based on comparisons with the spectra of reference molecules such as benzene and chloroalkanes and were later supported by Hückel and ab initio STO-3G calculations.[18]

In contrast, it has recently been suggested[17] that, because of different electron reorganization, the empty MO energy ordering of the neutral chlorobenzene molecule is reversed upon anion formation, the most stable anion being the $^2A_1$ (σ^*). This hypothesis was supported by the anion/neutral energy differences obtained with semiempirical PM3 calculations.

Adequate theoretical approaches for describing the energetics of temporary electron capture involve difficulties not encountered for cation states. In the Koopmans' theorem (KT) approximation,[23] the negatives of the energies of the filled and empty MOs are assumed to equal the ionization energies (IEs) and the EAs, respectively. This approximation neglects correlation and relaxation effects, which tend to cancel out when IEs, but not EAs, are evaluated. For this reason and because of deficiencies in the atomic basis sets, KT predictions generally underestimate the latter by several electronvolts, the discrepancy growing with increasing orbital energy. However, it has been shown that the experimental π^* VAEs can be closely reproduced by shifting and scaling the empty MO energies obtained with Hartree−Fock (HF) calculations.[24] In a better approximation, although the limit of neglecting correlation is not removed, HF calculations can be used for calculating the anion/neutral energy difference. In addition, extension of the atomic basis set, with inclusion of diffuse functions, improves the description of anion states but generates solutions (discretized continuum[25]) not associated with empty valence MOs and with anion formation. More sophisticated methods account for correlation using the coupled-cluster theory.[26]

TABLE 2: VAEs (eV), Obtained as Differences between the Total Energies of the Anion and the Neutral, for the Anion States Corresponding to a Temporary Occupation of the Lowest-Lying Empty MOs of Toluene and Chlorobenzene Supplied by CCSD Calculations Using the D95* Basis Set

compound (point group)	MO symmetry	VAE (eV)
toluene	a′ (π^*_S)	2.54
(C_s)	a″ (π^*_A)	2.46
chlorobenzene	a_1 (σ^*)	4.07
(C_{2v})	b_1 (π^*_S)	2.10
	a_2 (π^*_A)	2.02

Here are presented the results of coupled-cluster calculations with all single and double substitutions (CCSD),[27] using the D95* basis set,[28] for evaluating the energies (relative to the neutral state) of the $^2A_2$ and $^2B_1$ (π^*) and $^2A_1$ (σ^*) anion states of chlorobenzene (C_{2v} point group) at the optimized geometry of the neutral molecule, that is, the VAEs. The energies of the corresponding $^2A'$ and $^2A''$ (π^*) anion states of toluene (C_s point group) are also calculated for comparison. Geometry optimizations of the neutral molecules were performed at the B3LYP/D95* level. The C−Cl distance (1.76 Å) predicted in chlorobenzene is to be compared with the experimental (electron diffraction) value of 1.737 Å.[29]

The CCSD results are reported in Table 2. With respect to the values measured in the ET spectra (for C_6H_5Cl, 0.74 and 2.44 eV, see Table 1; for $C_6H_5CH_3$, 1.11 eV[30]), the calculated π^* and σ^* VAEs are 1.3 and 1.6 eV too high, respectively. This is likely to be attributed to the limits of the D95* basis set. More extended basis sets (not employed to limit the storage and time requirements of the coupled-cluster calculations and to avoid the need for distinguishing solutions associated with anion states from those belonging to the discretized continuum) would supply lower anion energies. Once this energy shift is accounted for, however, the calculated VAEs closely reproduce experimental values and support the previous assignments, in contrast with the prediction of PM3 calculations.[17]

For both chlorobenzene and toluene, the most stable anion state is predicted to be associated with electron capture into the antisymmetric component (π^*_A) of the benzene e_{2u} (π^*) LUMO, which has a node at the substituted carbon atom. The symmetric counterpart (π^*_S) is destabilized by mixing with the filled σ_π (CH_3) MOs (toluene) or with the chlorine electron lone pair of π symmetry (chlorobenzene). According to the calculations, however, the π^*_A/π^*_S energy gap is very small (<0.1 eV), in agreement with the ET spectra of both compounds, where the two π^* contributions to the first signal are not resolved. The CCSD results also accurately reproduce the VAE decrease (0.4 eV) observed on going from toluene to chlorobenzene, which is caused by the electron-withdrawing inductive effect of the chlorine atom. Finally, the $^2A_1$ (σ^*) anion state of chlorobenzene is calculated to lie 2.0 eV above the $^2A_2$ (π^*)

TABLE 3: Vertical and Adiabatic Attachment Energy (VAE and AAE) Values (eV) for Toluene, Chlorobenzene, Benzyl Chloride, and (2-Chloroethyl)benzene Calculated as the Anion/Neutral Energy Difference with the UHF/D95* and B3LYP/D95* Methods[a]

		UHF/D95*		B3LYP/D95*			
	MO symmetry	VAE	AAE	VAE	AAE	KT-HF/D95*	expt VAE
toluene	a′ (π^*_S)	2.75		2.00		3.63 (1.27)	
	a″ (π^*_A)	2.64		1.94		3.49 (1.17)	1.11[b]
chlorobenzene	a_1 (σ^*)	4.21	0.62	3.27	0.58	5.88	2.44
	b_1 (π^*_S)	2.22	2.05	1.55	1.30	3.13 (0.90)	
	a_2 (π^*_A)	2.15	1.95	1.49	1.20	3.06 (0.85)	0.74
benzyl chloride	a′ (σ^*)	4.3[c]		3.3[c]		5.60	2.83
	a″ (π^*_A)	2.24		1.53		3.16 (0.92)	1.02
	a′ (π^*_S)	1.93		1.02		2.79 (0.65)	0.64
(2-chloroethyl)benzene	a′ (σ^*)	4.5[c]		3.4[c]		5.78	2.7
	a″ (π^*_A)	2.24		1.54		3.18 (0.94)	
	a′ (π^*_S)	2.21		1.33		3.12 (0.89)	0.87

[a] The empty MO energies for the neutral molecules obtained with KT-HF/D95* calculations are also reported, together with the corresponding VAEs (in parentheses) obtained from the regression line given in ref 24. [b] From ref 30. [c] Evaluated from the planar conformer (see text).

anion state, in good agreement with the energy difference (1.7 eV) between the first two resonances displayed in the ET spectrum.

The VAEs, obtained as the differences in the total energies of the anions and the neutral molecules at the unrestricted HF (UHF) and density functional theory (DFT) B3LYP levels of theory, are given in Table 3 for toluene, chlorobenzene, benzyl chloride, and (2-chloroethyl)benzene. The VAEs supplied for the first two compounds closely match the CCSD results, being only slightly higher (≤ 0.2 eV). Probably, electronic relaxation is overestimated because of the neglect of correlation, thus attenuating the effects of the latter limitation. All of the DFT-B3LYP VAEs are somewhat lower but display exactly the same trends. In particular, they confirm the small (<0.1 eV) energy splitting between the two π^* anion states and the higher (1.8 eV) energy of the first σ^* anion state of chlorobenzene.

Both sets of calculations are also able to reproduce the experimental trend of the first VAE (albeit with a maximum VAE variation that is smaller than 0.25 eV) on going from chlorobenzene to benzyl chloride and (2-chloroethyl)benzene (where the chlorine atom is separated from the ring by one and two CH_2 groups, respectively). In the most stable conformer of benzyl chloride, the C−Cl bond is perpendicular to the ring, thus allowing for mixing between the σ^*_{Cl-C} and π^*_S MOs. As a consequence, the latter MO is stabilized with respect to the noninteracting π^*_A MO. Because of the large localization at the chlorine atom of the σ^* MO, the corresponding interaction is much smaller in (2-chloroethyl)benzene. Consistently, only in the ET spectrum of benzyl chloride are the two π^* resonances resolved. Their energy separation (0.4 eV) is well reproduced by both the UHF and B3LYP calculations.

The anion energy can be calculated only for the most stable anion of each symmetry. This prevented direct calculation of the σ^* VAE in the perpendicular conformers of benzyl chloride and (2-chloroethyl)benzene. For these compounds, the σ^* VAEs given in Table 3 were calculated in the planar conformation (where the π^* and σ^* anions have different symmetries) and then shifted 0.26 and 0.29 eV higher in energy, respectively, i.e., the destabilization predicted by KT-HF/D95* calculations for the σ^* MO on going from the planar to the perpendicular conformer in the neutral state.

The neutral-state MO energies supplied by HF/D95* calculations are reported in Table 3. Even the simpler KT approach supplies all of the significant indications described above. In addition, we used the linear correlation ($\mathrm{VAE} = -1.4100 + 0.73865E$, where E is the calculated energy) found by Staley and Strnad[24] between experimental π^* VAEs and the corresponding MO energies calculated at the KT-HF/D95V level. When the present MO energies are introduced in the regression, the resulting VAEs (given in parentheses in Table 3) are in excellent agreement (≤ 0.1 eV) with experiment.

Finally, for chlorobenzene the adiabatic AEs (AAEs, i.e., the energy difference between the anion and the neutral state each in its optimized geometry) were also calculated (see Table 3). Electron capture into the π^* MOs does not produce drastic changes in the equilibrium geometry, so the π^* AAEs are only 0.2−0.3 eV smaller than the VAEs. In contrast, as expected, electron addition to the σ^* MO leads to breakage of the C−Cl bond. However, the B3LYP calculations predict the presence of a minimum (although very shallow) in the optimized geometry of the σ^* anion (which remains planar) at a C−Cl distance of 2.67 Å. The dissociation limit (leading to the $C_6H_5^{\bullet}$ radical and the Cl^- anion in their ground states) is predicted to lie 0.5 eV (UHF) or 0.7 eV (B3LYP) higher in energy.

DEA Spectra. The DEA spectra of (2-chloroethyl)benzene, chlorobenzene, benzyl chloride, and *tert*-butyl chloride were recorded to obtain a self-consistent set of data for the peak energies and, mainly, for the relative intensities. We have previously measured[22] the intensity of the total anion current in the normal and secondary chlorobutanes relative to that of *tert*-butyl chloride.

Our apparatus can measure the total negative current at the walls of the collision chamber or, alternatively, the current of anions extracted from the collision chamber and mass-selected with a quadrupole filter. Although the total negative current at the walls of the collision chamber can, in principle, be affected by spurious trapped electrons, this intensity measurements should be more reliable with respect to the current detected through the mass filter because of kinetic energy discrimination in the anion extraction efficiency. The main discrepancy between the two sets of measurement was found in benzyl chloride, where the signal relative to chlorobenzene was 17.7 times larger in the total current (in close agreement with previous results[12]) and only 6.9 times in the Cl^- current recorded through the quadrupole mass filter. Consistently, the Cl^- anion was found to be produced with a larger kinetic energy excess in benzyl chloride than in chlorobenzene.[11]

The total yields of negative ions (essentially due only to the Cl^- fragment) as a function of the incident electron energy are displayed in Figure 2. The zero-energy signals (not observed or weak in the mass-selected Cl^- current) are likely affected by sample impurities. The peak energies and intensities (evaluated from the peak heights in the total anion current, with the same pressure for all compounds) relative to those of chloro-

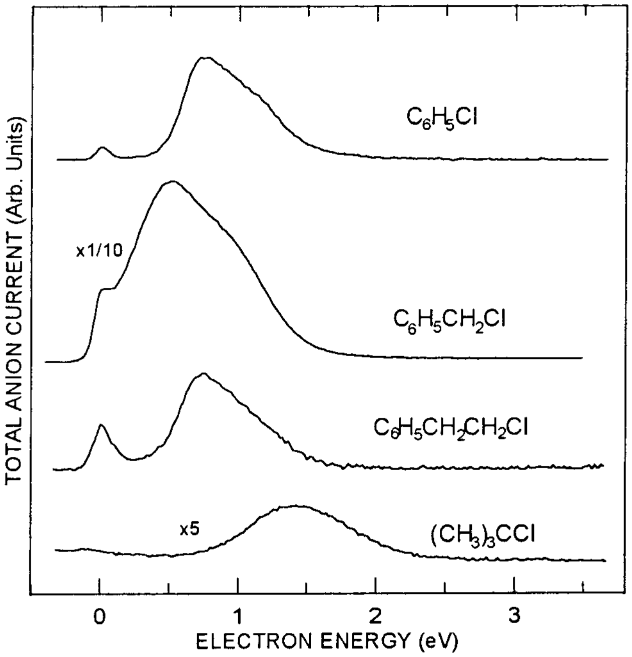

Figure 2. Total anion current, as a function of the incident electron energy, in chlorobenzene, benzyl chloride, (2-chloroethyl)benzene, and *tert*-butyl chloride.

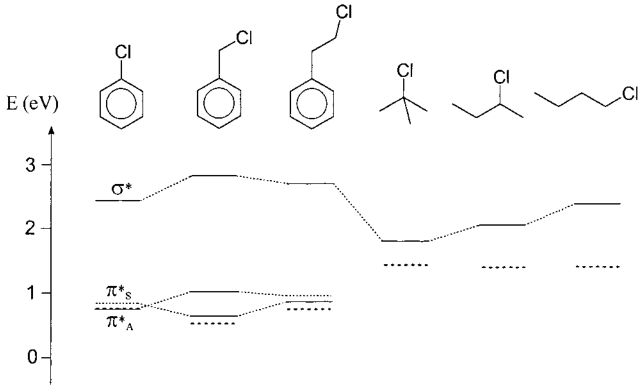

Figure 3. Diagram of the resonance energies measured in the ET spectra (full lines) and of the peak energies measured in the DEA spectra (dashed lines).

benzene are given in Table 1. The diagram of Figure 3 compares the energies of the resonances observed in the ET spectra (full lines) with the energies of the peaks displayed in the DEA spectra (dashed lines).

As noticed in a previous study of monochloroalkanes,[4] although the $\sigma^*_{\mathrm{Cl-C}}$ VAE gradually decreases with branching (2.39 eV in 1-chlorobutane, 2.05 eV in 2-chlorobutane, and 1.80 eV in *tert*-butyl chloride), the Cl^- current in the DEA spectra peaks at a nearly constant energy of 1.4 eV. This finding was interpreted[4] in terms of the inverse dependence of lifetime on energy. In these molecules, the temporary σ^* anions formed at energies >1.4 eV mainly decay by re-emission of the extra electron because dissociation requires a longer survival time. However, Table 1 shows that, whereas the DEA peak energy remains constant, the intensity of the Cl^- current decreases sizably with increasing VAE (relative to that of *tert*-butyl chloride, in 2-chloro- and 1-chlorobutane, the DEA peak heights are only 55% and $\leq 6\%$, respectively). This is consistent with the expectation that the electron capture cross section at 1.4 eV (where the lifetime is still sufficiently long to favor dissociation of the temporary molecular anions) is the highest in *tert*-butyl chloride (where the maximum cross section occurs only 0.4 eV higher in energy) and becomes gradually smaller as the center of the σ^* resonance moves further away to higher energy.

Figure 3 clearly shows that the DEA behavior of (2-chloroethyl)benzene (a phenyl-substituted 1-chloroalkane) is quite different from that of 1-chlorobutane: the Cl^- current peaks at much lower energy with an intensity more than 150 times higher (see Table 1). In this case, in fact, dissociation follows electron capture into the ring π^* LUMO. A possible contribution to the Cl^- signal (peaking at about 1.4 eV) from the σ^* resonance centered at 2.7 eV is expected to be even less intense than in 1-chlorobutane (where the σ^* VAE is smaller) and to be hidden by the high-energy wing of the main peak.

As mentioned above, σ^*/π^* mixing in (2-chloroethyl)benzene is small because of the large localization of the $\sigma^*_{\mathrm{Cl-C}}$ MO at the (remote from the ring) chlorine atom. In chlorobenzene, for symmetry reasons, σ^*/π^* mixing does not occur in the rigid structure of the neutral molecule and relies on vibronic coupling or geometrical distortion of the anion on the time scale of the π^* resonance. The Cl^- cross sections measured in these two compounds are similar and, in particular, larger by 1 and 2 orders of magnitude with respect to those of *tert*-butyl chloride and 1-chlorobutane (see Table 1). At variance with chlorobenzene and (2-chloroethyl)benzene, in benzyl chloride, the out-of-plane C−Cl bond adjacent to the ring permits large σ^*/π^* overlap, as indicated by the stabilization of the π^*_{S} resonance. The consequent localization of the π^*_{S} MO at the C−Cl bond determines an increase of the Cl^- production by an order of magnitude.

Cl^- detachment following π^* electron capture is an example of intramolecular electron transfer. The abundance of the negative fragment reflects the rate of transfer of the electron from the ring, where it is initially trapped, to the halogen atom. In chloroalkenes, a similar dependence of the Cl^- yield on the distance from the ethene double bond was observed.[31,32]

As a final comment, Figure 3 and Table 1 show that, whereas in benzyl chloride and (2-chloroethyl)benzene, the Cl^- current peaks at energy slightly lower (as normally found) than the first (π^*_{S}) resonance displayed in the ET spectrum, in chlorobenzene, the two energies are nearly coincident. Moreover, the calculations predict that only in chlorobenzene is the first resonance associated with the antisymmetric π^*_{A} MO, the π^*_{S} resonance being located about 0.1 eV higher in energy. This finding suggests that, also in chlorobenzene, Cl^- production could (mainly) come from electron capture into the π^*_{S} (b_1) MO. Consistently, whereas simple motion of the chlorine atom out of the ring plane is sufficient to cause $\sigma^*/\pi^*_{\mathrm{S}}$ mixing, involvement of the π^*_{A} MO (because of its node at the substituted carbon atom) requires distortion of the C−Cl bond with respect to both the ring plane and the plane perpendicular to it. On the other hand, it is also to be noticed that the C−Cl dissociation energy (4.07 eV) in chlorobenzene reported in the literature[33] leads to a thermodynamic threshold energy of 0.45 eV for the production of Cl^-, whereas in benzyl chloride, the C−Cl bond energy should be smaller than the EA (3.62 eV) of the chlorine atom.[11] In agreement with this finding, the rise of the Cl^- current is clearly steeper in chlorobenzene (see Figure 2), and the peak could be shifted to higher energy by the occurrence of a vertical onset well above zero energy.

Experimental Section

ET and DEA Spectra. Our electron transmission apparatus is in the format devised by Sanche and Schulz[34] and has been previously described.[35] To enhance the visibility of the sharp resonance structures, the impact energy of the electron beam is modulated with a small ac voltage, and the derivative of the electron current transmitted through the gas sample is measured directly by a synchronous lock-in amplifier. The present spectra were obtained by using the apparatus in the "high-rejection" mode[36] and are, therefore, related to the nearly total scattering cross section. The electron beam resolution was about 50 meV (fwhm). The energy scale was calibrated with reference to the $(1s^12s^2\ )^2S$ anion state of He. The estimated accuracy is ±0.05 or ±0.1 eV, depending on the number of decimal digits reported.

The collision chamber of the ETS apparatus was modified[13] to allow for ion extraction at 90° with respect to the electron beam direction. In this arrangement, ions are then accelerated and focused toward the entrance of a quadrupole mass filter. Alternatively, the total anion current can be collected and measured (with a Keithley 485 picoammeter) at the walls of the collision chamber (about 0.8 cm from the electron beam). The DEAS data reported here were obtained with an electron beam current about twice as large as that used for the ET experiment. The energy spread of the electron beam increased to about 120 meV, as evaluated from the width of the SF_6^- signal at zero energy used for calibration of the energy scales.

The relative total anion currents were evaluated from the peak heights with the same pressure reading for all compounds (2×10^{-5} mbar, measured in the main a vacuum chamber by means of a cold cathode ionization gauge). Preliminary measurements showed that the total anion current reading is proportional to the pressure, at least in the $10^{-5}-(4 \times 10^{-5})$ mbar range.

Computational Details. The calculations on the neutral and anion states were performed with the Gaussian 98 set of programs.[37] Geometry optimizations on the neutral molecules and relative anions were performed using the B3LYP density functional method[38] with the Dunning/Huzinaga full double-ζ D95* basis set (for Cl, 12s, 8p, 1d/6s, 4p, 1d; for C, 9s, 5p, 1d/4s, 2p, 1d; for H, 4s/2s)[28] that is more suitable for describing the diffuseness in space of anion states than the standard 6-31G* basis set.

Geometry optimization of the chlorobenzene $^2A_2$, $^2B_1$, and $^2A_1$ anions and of the toluene $^2A''$ and $^2A'$ anions were carried out with fixed orbital occupation numbers to constrain the electronic state of the anion. For the anion states, unrestricted orbitals were employed.

The vertical and adiabatic attachment energies were evaluated as the energy differences between the anion state (in the required geometry) and the neutral state with the HF and B3LYP methods using the D95* basis set.

The vertical attachment energies of chlorobenzene and toluene were also evaluated using the coupled-cluster method with single and double excitations and noniterative inclusion of triple excitations CCSD(T)[39] to account, at least to some extent, for correlation effects.

Conclusions

All of the theoretical methods employed (coupled-cluster, Hartree−Fock, and density functional theory B3LYP) accurately reproduce the trends of the VAEs measured in the ET spectra of chlorobenzene, benzyl chloride, and (2-chloroethyl)benzene, where the chlorine atom is attached to the ring or separated by one or two CH_2 groups. The calculations locate the lowest-lying σ^* anion state about 2 eV higher in energy than the lowest π^* anion state, in quantitative agreement with the ET experiment.

A comparison of the DEA peak energies for Cl^- production with the ET resonance energies in the chlorobenzenes and in chloroalkanes clearly indicates that, in the former compounds, dissociation follows electron attachment to a ring π^* MO and intramolecular transfer to the chlorine atom. Further support for the occurrence of this mechanism comes from the relative DEA cross sections (1 order of magnitude smaller in chlorobenzene and (2-chloroethyl)benzene than in benzyl chloride, but 2 orders of magnitude larger than in the saturated 1-chlorobutane), which can be explained in terms of the extent of σ^*/π^* mixing in the temporary molecular anion.

Both the theoretical and experimental results concordantly support the representation of the potential energy curves given by Clarke and Coulson[15] for the neutral state of chlorobenzene and its low-lying anion states, where, at the equilibrium geometry of the neutral molecule, the σ^* anion state is significantly higher in energy than the π^* anion states, in contrast to the recent hypothesis[17] of a reversed energy ordering.

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