Electron attachment by chloro and bromomethanes

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Electron transmission spectra and mass spectra of negative ions from dissociative electron attachment have been obtained for the series CCl₄, CBrCl, CBr₂Cl, and CBr₄. Systematic changes are observed in the attachment energies of the t₁ unoccupied orbitals in the end members and their split components in the mixed compounds. Cl⁻ and Br⁻ ion-production maxima are observed to correspond to attachment energies measured by ETS. Multiple scattering-X̅e continuum calculations give elastic-electron-scattering cross sections for CCl₄ and CBr₄ which are consistent with experiment in the low energy region, but fail to reproduce the maximum in total cross section observed at higher energy. Calculated and experimental valence orbital I.P.'s and UV excitation energies for CCl₄ and CBr₄ are shown to be consistent with our electron transmission results.

INTRODUCTION

Electron capture and subsequent dissociation of halogen-substituted methanes has received considerable attention recently. This is in part due to the significance of such processes to atmospheric chemistry and to the application of haloalkanes as gaseous dielectrics. The energetics of low-energy electron capture by molecules can be studied by electron transmission spectroscopy (ETS). The technique is well established in the study of substituted alkenes where the spectra display well-defined features due to shape resonances associated with electron capture into specific molecular orbitals. The analysis of such spectra employs the “composite molecule” or “molecules-in-molecules” approach. By this method each feature in the spectrum is assigned to an orbital associated with a molecular fragment, such as a substituent or a portion of the unsaturated backbone. This approach is not appropriate for substituted alkanes where the spectra of the parent hydrocarbons are featureless, and those of the haloalkanes show only weak and rather broad features. Perhaps the difficulties with interpretation and the rather uninteresting appearance of the spectra account for the paucity of ETS data on the haloalkanes.

The electron transmission spectra of some chloromethanes and chlorofluoromethanes have been reported by Burrow et al. Their assignment of the observed anion states, although plausible, was based upon virtual-orbital energies derived from small-basis-set-SCF calculations for the neutral molecules. This approach can at best yield relative electron affinities, and in fact, a discrepancy between calculation and experiment of about 3 eV was postulated and a number of unobserved states were predicted. Of course electron transmission spectroscopy involves a scattering process, so any such bound-state approach is suspect.

Unlike electron transmission data, there is a large amount of data on the dissociation of haloethanes. Most of these studies concentrate upon the chlorinated or fluorinated methanes because of their environmental importance. However, little effort has been made to correlate dissociative attachment data with electron transmission spectra, although such a connection is expected and is observed for unsaturated halocarbons previously studied.

In the present work we have investigated both electron transmission and dissociative attachment in the family of bromochloromethanes (CCl₃, CBrCl, CBr₂Cl, CBr₄). To aid in making orbital assignments, as well as in understanding the scattering process, we present appropriate bound-state and continuum quantum calculations. We also make quantitative comparison of our results with UV absorption and photoemission, as well as other ETS data, in an attempt to substantiate our assignments. Our data overlap that of Burrow et al. in the case of CCl₄, where our calculations as well as other data from the literature confirm their assignment of the first ETS feature to the ³T₂ anion, thus implying that the ³A₁ ground-state anion is stable.

EXPERIMENT

The apparatus used for the study of low-energy electron capture and dissociative attachment is an electron transmission spectrometer to which a time-of-flight mass spectrometer (TOFMS) has been appended. The electron transmission spectrometer has been described in detail elsewhere so only a brief explanation will be given here. A detailed summary of the mass spectrometer follows.

Electron transmission spectroscopy is a technique for measuring the energy of a temporary negative ion formed by electron capture into an unoccupied orbital of a molecule. The experiment involves the measurement of the transparency of a gas to an electron beam as a function of energy. The transparency depends in an inverse fashion upon the electron-scattering cross section. Temporary negative ion formation occurs with a large cross section only over a narrow energy range. The negative ion promptly decays by giving up the trapped electron or by dissociative attachment. The formation and decay process appears as a sharp fluctuation in the electron-scattering cross section. This process, as well as the corresponding feature in the transmission vs electron energy spectrum, is referred to as a “resonance.”

The electron spectrometer consists of an electron source followed by an electron monochromator, a gas cell,
and an electron collector. The electron beam is aligned by a homogenous magnetic field (B = 70 G) generated by a pair of Helmholtz coils mounted outside the vacuum system. The spectrometer is baked daily to 350 °C to ensure stable operation after exposure to molecular compounds. In practice the first derivative of the transmitted current as a function of energy is recorded since the derivative is sensitive to the abrupt change in transmitted current associated with a resonance.19 The energy associated with a resonance is known as an “attachment energy” (A.E.) and, with respect to the derivative spectrum, is taken to be the point vertically midway between the minimum and the maximum which characterize the resonance. The electron energy scale is calibrated with reference to features in the N2 spectrum near 2 eV.20 For the present purposes, an attachment energy may be identified with the negative of the corresponding vertical electron affinity (E.A.).21

Dissociation of a temporary negative anion into a stable negative ion and a stable neutral fragment may occur if the nuclei have sufficient time to move before the electron is reemitted and if sufficient energy is available to break the necessary bonds. The mass and kinetic energy of the resultant stable ion can be determined by measuring its velocity following acceleration through a known potential difference. In the present experiment the mass resolution of the TOFMS is better than 1 amu for ions with mass less than 150 amu, and the kinetic energy may be determined to within 0.1 eV.

The TOFMS is attached to the electron transmission spectrometer's gas cell, and consists of a deflection tube, followed by a gate, a drift tube, and an ion detector (Fig. 1). Ions drift out of the collision chamber and are accelerated by 20.00 eV as they enter the deflection tube. The deflection tube contains a pair of electrodes which create an electric field perpendicular to the magnetic field generated by the ETS Helmholtz coils. The Coulomb force opposes the Lorentz force, thus allowing the ions to reach the field-free region outside of the Helmholtz coils. Here the ions encounter a gate, consisting of a series of grids, at the entrance to a 40 cm drift tube. A 30 ns, 20 V pulse opens the gate. Ions which drift the length of the tube are detected by a copper–beryllium, focused mesh, electron multiplier. All of the units of the TOFMS (with the exception of the detector) are constructed of nonmagnetic stainless steel and are baked daily to 350 °C to ensure the same stable operation obtained from the electron transmission spectrometer.

The mass spectrometer is also used to produce a second type of spectrum. By applying a constant voltage to the TOFMS gate and drift tube, ions may arrive continuously at the detector. Then scanning the electron energy produces an ion production rate vs electron energy spectrum. The crossed electric and magnetic fields in the deflection tube act as a Wien filter which allows some mass selection. For compounds which produce only one species of ion, or for compounds which produce ions with large mass differences, an ion production rate vs electron energy spectrum for a single mass is obtained. The halogen ions, F−, Cl−, and Br−, all have sufficient mass differences to allow them to be separated by the Wien filter. This type of data has the same energy resolution as the electron transmission data.

RESULTS

The derivative electron transmission spectra of CCl4, CBrCl3, CBr2Cl2, and CBr4 are presented in Fig. 2. Two low-energy features are present for CBr2Cl2, and one for each of the remaining compounds. The single feature in CBrCl3 does however exhibit some indication of a second overlapping resonance. The number of resonances observed for each compound can be explained by a simple model in which one anion state is associated with each carbon–halogen bond. Thus as suggested by Burrow et al.,2 CCl4 and CBr4 (with $T_d^2$ symmetry) are expected to have an anion state with $A_1$ symmetry and a triply degenerate anion state of $T_2$ symmetry. However, there is evidence that the ground state anions of both CCl4 and CBr4 have positive vertical electron affinities22 and thus cannot be observed by electron transmission spectroscopy. Multiple-scattering $X\alpha$ (MS-$X\alpha$) calculations of the electron affinities of CCl4 and CBr4, using the bound transition state approach, give $-0.1$ and $+1.4$ eV, respectively, in reasonable agreement with the experimental values23 of $+0.15$ and $+1.17$ eV obtained from studies of the spectra of donor–acceptor complexes. Thus, a single anion state of $T_2$ symmetry is expected to be observed for both...
CCl₄ and CBr₄. For CBrCl₃ (C₃ᵥ symmetry) the triply degenerate T₂ state is split into a doubly degenerate anion state of E symmetry and a second anion of A₁ symmetry. Because bromine and chlorine have very similar electron properties, the bromine substitution is expected to only slightly perturb the molecular system from the CCl₄ electronic configuration in which case the splitting between the E and A₁ states may be small. This would account for the unusual shape of the CBrCl₃ electron transmission feature. For CBr₂Cl₂ the E anion state is split into two states of B₁ symmetry both of which should be observed. The second A₁ state is probably considerably higher in energy and the corresponding feature in the spectrum would be very broad.

Continuum MS-Xα calculations have been employed to obtain explicit scattering cross section for CCl₄ and CBr₄. For CBr₄, the experimental internuclear distance of 1.942 Å, standard α’s, and standard sphere sizes were used (Fig. 3). The calculations support the assignments made above for CCl₄ and CBr₄ in the low energy region. Beyond 4 eV the calculated cross section is monotonically decreasing for CBr₄, with no indication of the second broad feature seen near 5.5 eV in the electron transmission data. For CCl₄ the cross section shows a weak maximum at about 6 eV, perhaps consistent with the experimental feature at 6.3 eV. This 6.0 eV maximum arises from a competition between increasing cross sections in some channels and decreasing cross-sections in others, and does not appear to be a resonant effect. Thus, the CCl₄ and CBr₄ cross sections are qualitatively similar, but the t₂ resonance is more distinct for CBr₄, partly due to its larger cross section and partly due to weaker competition from a₁ scattering. Since the a₁ resonance is calculated to lie slightly above threshold, but experiment indicates it to be slightly below (i.e., a bound state with a barely positive E.A.), our calculations probably exaggerate the a₁ contribution near threshold in CCl₄. Comparison with measured absolute cross sections for CCl₄ indeed indicates that our calculated t₂ cross section has its maximum at about the right energy and has about the right magnitude but that it is too broad and the a₁ contribution adding to it near threshold is too high.

The yield of Cl⁻ and Br⁻ ions as a function of electron energy is presented in Fig. 4. Above 3 eV only very small numbers of ions were detected. The CCl₄ dissociation spectrum is very similar to those published previously. The most notable features of the ion spectra are the threshold peaks. The cross section for dissociative attachment near
threshold in these compounds is enormous as has been observed by Chutjian and co-workers for the case of attachment to CCl$_4$ by electrons of energy less than 50 meV and as is implied by our calculations above. These overwhelming attachment processes have a deleterious effect upon the performance of our apparatus at very low electron energies. The shape and location of the threshold peaks were found to be strongly dependent upon sample gas pressure. With increasing pressure the threshold peaks broaden and their apparent maxima move to higher energies. With decreasing pressure the threshold peaks become narrow and move toward lower energy. Apparently the residual sample background pressure outside the sample cell (<5×10$^{-6}$ Torr) attenuates the incident current near threshold. As a result our experiments cannot be expected to characterize the shape of the cross section vs energy function at energies below 0.15 eV.

Each of the dissociation spectra also exhibit one ion peak below 1 eV. In CBrCl$_3$, the Cl$^-$ and Br$^-$ ion peak locations coincide, but the Cl$^-$ production exceeds Br$^-$ production by 3 to 1. For CBr$_2$Cl$_2$ the ion peaks have different locations. Overall Br$^-$ is the more abundant ion, but at slightly higher energies Cl$^-$ production becomes more prominent. Time-of-flight measurements indicate that all the ions are created with less than 0.1 eV of initial kinetic energy. The attachment energies, ion peak energies, and possible anion state assignments are presented as a correlation diagram in Fig. 5.

Locations of the ion peaks near 1 eV correspond quite well to the positions of features in the electron transmission spectra. The tendency for the ion peaks to fall slightly below the resonance energies is expected since the lifetime of the resonant state and hence the probability of dissociation increases with decreasing electron energy. The correlation between electron transmission features and ion peaks suggests the bonding character of the unoccupied molecular orbitals responsible for the observed anion states. For CBr$_2$Cl$_2$ the electron transmission resonance near 1 eV must be due to electron capture in a $\sigma^*$ orbital with predominantly C-Cl character, and the lower energy resonance must be due primarily to electron capture into a $\pi^*$ orbital of C-Br character. Similarly, the single feature in CCl$_4$ and CBr$_4$ may be assigned to electron capture into orbitals with C-Cl and C-Br character, respectively. However, for CBrCl$_3$ it is still...
have suggested that a low-lying Franck-Condon region. Energy level just below zero will give rise to resonant scattering energies. The valence term energy for the ETS peaks at 1.0 eV in CCl₄ and 0.4 eV in CBr₄ to a I.P.'s and UV excitation energies of CBr₄ are also obtained attachment energies, within the transition state approach as relate the valence orbital I.P.'s and excitation energies for the ground vibrational level of the neutral molecule in the approach of the potential curve of the anion and that of the interpretation focuses more generally upon the close ap-

The mechanism giving rise to the threshold peaks in the ion production spectra may be similar to that observed for dissociative attachment to HCl which has its maximum at 0.8 eV, far below the ETS peak at 3.3 eV which corresponds to occupation of the orbital. Dornke and Cederbaum have suggested that a low-lying orbital anion state coupled to the continuum will produce resonance activity near threshold. The state in CCl₄ and CBr₄ may also be such a low energy orbital. Another possibility is that dissociation at low energies is caused by a resonant state created just above threshold by the bound orbital state of these compounds. It is well known that a potential well which possesses an energy level just below zero will give rise to resonant scattering of low energy electrons. MS-calculations support this second possibility since they predict a large increase in scattering cross section for both CCl₄ and CBr₄ at very low energies due to interaction with the orbital channel. However, small errors in the calculated energies of the states may significantly affect these calculated cross sections. Another interpretation focuses more generally upon the close approach of the potential curve of the anion and that of the ground vibrational level of the neutral molecule in the Franck-Condon region.

For the end members we can, as explained previously, relate the valence orbital I.P.'s and UV excitation energies, and attachment energies, within the transition state approach as shown in Fig. 6. The MS-calculations give reasonably accurate for all three quantities. As shown in Table I, the I.P.'s and UV excitation energies of CBr₄ are also obtained accurately. We can thus establish that our assignment of the ETS peaks at 1.0 eV in CCl₄ and 0.4 eV in CBr₄ to a orbital state is quantitatively consistent with experimental values for the orbital IP's and the orbital excitation energies. The valence term energy for the orbital (orbital - UV excitation) is considerably more positive in CBr₄ than in CCl₄ (5.7 vs 4.7 eV, experimentally). This is consistent with a positive value for the E.A. for the ion state of CBr₄ and supports our contention that the orbital lies below threshold in ETS.

**TABLE I. Ionization potentials and UV absorption energies (in eV) for CCl₄ and CBr₄ from MS-Xα calculations and experiment.**

<table>
<thead>
<tr>
<th></th>
<th>CCl₄</th>
<th>CBr₄</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calc</td>
<td>Exp'</td>
</tr>
<tr>
<td>1t₁ I.P.</td>
<td>11.4</td>
<td>11.7</td>
</tr>
<tr>
<td>Xnb₂, I.P.</td>
<td>12.2</td>
<td>12.5</td>
</tr>
<tr>
<td>1t₂→empty a₁</td>
<td>8.2</td>
<td>7.0'</td>
</tr>
<tr>
<td>1t₁→empty t₂</td>
<td>9.2</td>
<td>8.8 (8.4 sh)</td>
</tr>
<tr>
<td>Xnb₂→empty a₁</td>
<td>9.0</td>
<td>9.2</td>
</tr>
<tr>
<td>Xnb₂→empty t₂</td>
<td>10.0</td>
<td>9.5</td>
</tr>
</tbody>
</table>

* Reference 30.
* Reference 31.
* Reference 32.

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5. An error of a factor of 2 in previously reported cross sections [see: J. A. Tossell and J. W. Davenport, J. Chem. Phys. 83, 4824 (1985)] has been corrected in the results reported here.