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Empty Level Structure and Dissociative Electron Attachment Cross Sections in Bromo and Chloro Dihaloalkanes

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The energies of electron attachment associated with temporary occupation of the C−Br and/or C−Cl virtual σ^* orbitals of dichloro, bromochloro, and dibromo alkanes are measured in the gas phase with electron transmission spectroscopy (ETS). The corresponding orbital energies of the neutral molecules, supplied by HF/6-31G(d)//MP2/6-31G(d) calculations and scaled using an empirically calibrated linear equation, are compared with the experimental vertical attachment energies (VAEs). The largest energy splittings between the first two σ^* anion states are found in the methane derivatives, but two distinct resonances are also observed in the bromochloro and dibromo ethane derivatives. The temporary anions observed in ETS may dissociate, producing Br^- and Cl^- negative fragments with widely varying cross sections over the dihaloalkanes studied. The absolute total dissociative electron attachment (DEA) cross sections are evaluated, and their peak values are compared with the corresponding VAEs. In the mixed bromochloro alkanes, the relative intensities of the Br^- and Cl^- anion currents detected with a mass filter are also evaluated.

Introduction

Electron−molecule collisions play an important role in various scientific fields from both theoretical and technological points of view.[1] In particular, dissociative single-electron transfer reactions in solution is an extensively studied[2−4] process because of its great relevance in electrochemistry, biochemistry, and photochemistry. The counterpart of this process in the gas phase is referred to as dissociative electron attachment (DEA).[5] As a first step, an isolated molecule can temporarily capture an electron of proper energy in a vacant molecular orbital (MO) to form an RX^- anion, unstable with respect to both electron detachment and dissociation. When suitable energetic conditions occur, the decay of this temporary molecular anion can follow a dissociative channel that generates a long-lived negative fragment and a neutral radical, in kinetic competition[6] with simple re-emission of the extra electron

$$RX + e^- \rightarrow RX^- \rightarrow R^{\bullet} + X^-$$

where $R^{\bullet}$ is a neutral radical and X^- is a long-lived negative fragment.

An important improvement in the detection and characterization of unstable gas-phase anions was made with the electron transmission spectroscopy (ETS) technique devised by Sanche and Schulz,[7] which is still one of the most suitable means for observing the formation of temporary anions and measuring negative electron affinities (EAs). The ETS technique takes advantage of the sharp variations in the total electron−molecule scattering cross section caused by resonance processes, namely, temporary capture of electrons with appropriate energy and angular momentum into empty MOs.[5] Electron attachment is rapid with respect to nuclear motion so that temporary anions are formed in the equilibrium geometry of the neutral molecule. The measured vertical attachment energies (VAEs) are the negative vertical EAs.

Additional information on temporary negative ion states can be supplied by dissociative electron attachment spectroscopy (DEAS),[5,8] which measures the yield of negative fragments as a function of the incident electron energy, thus revealing possible dissociative decay channels of the molecular anions formed by resonance. The peaks in the DEA spectra are generally shifted to lower energy relative to the corresponding resonances observed in ETS; this process is well understood in terms of shorter lifetime and greater distance to the crossing between the anion and neutral potential curves for the anions formed on the high-energy side of the resonance.[6] This shift can be quite large (for instance, about 1 eV in the 1-Cl-alkanes[9]), depending in an inverse fashion upon the resonance lifetime. Aflatooni and Burrow[10] demonstrated that the DEA cross sections for Cl^- production in mono and polychloro alkanes correlate strongly with the corresponding VAEs for the formation of the lowest anion states measured in ETS.

Halohydrocarbons are pollutants of anthropological or natural origin, ubiquitous in all environmental compartments.[11] In particular, this class of compounds is responsible for ozone decomposition in the stratosphere,[12] and some of them (for instance, dibromopropanes[13]) can cause DNA damage. Because of their persistence and toxicity, halohydrocarbons have been the object of many studies to determine their reaction mechanisms in the environment. Reductive dehalogenation was found to be one of the most important pathways of transformation, where the initial rate-determining step consists of electron addition to form a radical anion.[14] The widespread use of haloalkanes for reactions at technologically important surfaces[15,16] requires a greater knowledge of their electronic structures and the nature of their halo-carbon bonding and the energies and

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mechanisms involved in the breaking of these bonds. In particular, dichloroalkanes have been used to create dipole-directed 1D assemblies on Si(100) surfaces.[17]

The energy of temporary electron attachment into the lowest-unoccupied molecular orbital (LUMO) in the gas phase supplied by ETS provides a fundamental measure of the susceptibility of a compound to electron reduction, whereas DEAS can provide the cross section for the successive rupture of the C-halogen bond as a function of the incident electron energy. We have previously employed ETS and DEAS to study resonance formation of temporary anions and DEA in monochloro- and monobromo-saturated and unsaturated hydrocarbons,[18−22] where the DEA cross section of the bromides was found to be sizeably larger than that of the corresponding chlorides.[21,22] Here we extend the ET study of the empty level structure and measurements of the DEA cross sections to dichloro, dibromo, and mixed bromochloro dihaloalkanes, where the low-lying anion states arise from electron occupation of normally empty σ^* MOs with mainly C-halogen character. An important aspect of DEA studies that is not always met in the literature is concerned with the quantitative determination of the observed fragment anion currents and thus the cross section for the process. In this work, the relative and absolute cross sections are evaluated.

Experimental Section

Our electron transmission apparatus is in the format devised by Sanche and Schulz[7] and has been previously described.[23] 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. Each resonance is characterized by a minimum and a maximum in the derivative signal. The energy of the midpoint between these features is assigned to the VAE. We obtained the present spectra by using the apparatus in the "high-rejection" mode,[24] and they 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 $(1s^1s^2)$ ^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 has been modified[25] to allow for ion extraction at 90° with respect to the electron beam direction. These 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 picoammeter) at the walls of the collision chamber (about 0.8 cm from the electron beam). Although the negative ion current at the walls of the collision chamber can, in principle, be affected by spurious trapped electrons, these measurements are more reliable with respect to the current detected through the mass filter because of kinetic energy discrimination in the anion extraction efficiency in the latter. In a previous test[26] with monochloro alkanes, our relative total anion currents reproduced to within 1% the ratios in the absolute cross sections reported by Pearl and Burrow.[27]

The DEAS data reported here were obtained with an electron beam current more than twice as large as that used for the ET experiment. The energy spread of the electron beam increased to about 110 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, normalized to the same electron beam current and sample pressure (measured in the main vacuum chamber by means of a cold cathode ionization gauge) for all compounds. Preliminary measurements showed that the total anion current reading is linearly proportional to the pressure, at least in the (1 to 3) × 10^{-5} mbar range.

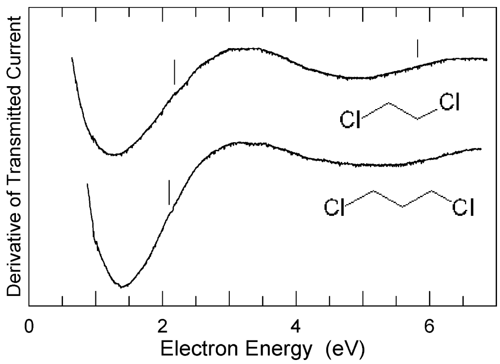

Figure 1. Derivative of transmitted current as a function of incident electron energy in 1,2-dichloroethane and 1,3-dichloropropane. Vertical lines locate the VAEs.

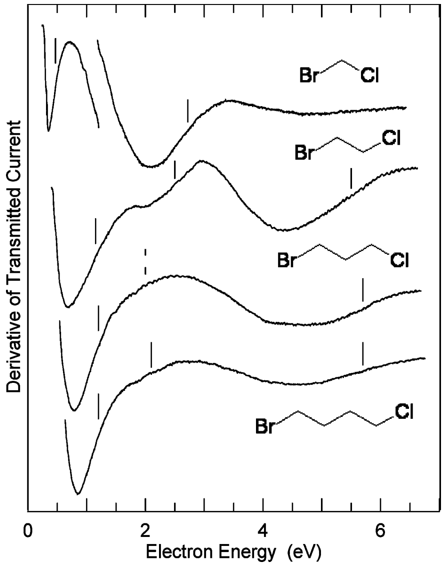

Figure 2. Derivative of transmitted current as a function of incident electron energy in bromochloromethane, 1-bromo-2-chloroethane, 1-bromo-3-chloropropane, and 1-bromo-4-chlorobutane. Vertical lines locate the VAEs.

The calculations were carried out with the Gaussian 03 set of programs.[28] The geometry optimizations and electronic structure calculations on the neutral molecules were performed using the MP2 and B3LYP methods with the standard 6-31G(d) basis set.

All compounds were commercially available.

Results and Discussion

Electron Transmission Spectra and Calculated Empty Molecular Orbital Energies. Figure 1 reports the ET spectra of 1,2-dichloroethane and 1,3-dichloropropane in the 0−7 eV energy range, Figure 2 reports the ET spectra of bromochloromethane, 1-bromo-2-chloro-ethane, 1-bromo-3-chloro-propane, and 1-bromo-4-chloro-butane, and Figure 3 reports the ET spectra of dibromomethane, 1,2-dibromoethane, 1,3-dibromopropane, and 1,4-dibromobutane. The VAEs measured in these compounds and in the related molecules dichloromethane,[29] 1-chloropropane,[9] and 1-bromopropane[21] are given in the diagram of Figure 4 and Table 1, together with the lowest HF/6-31G(d) virtual orbital energies (VOEs) of the neutral

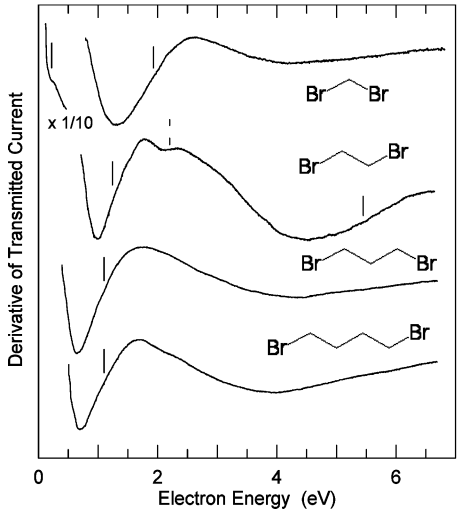

Figure 3. Derivative of transmitted current as a function of incident electron energy in dibromomethane, 1,2-dibromoethane, 1,3-dibromopropane, and 1,4-dibromobutane. Vertical lines locate the VAEs.

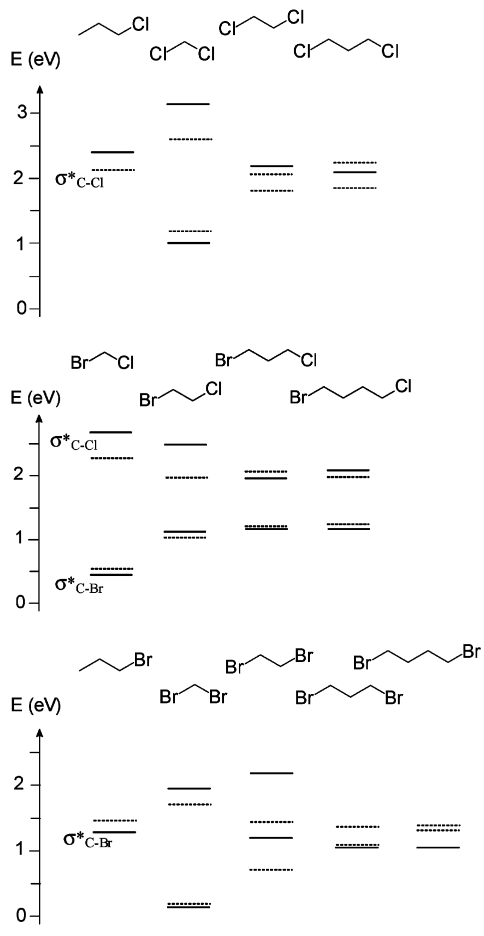

Figure 4. Diagrams of experimental VAEs (full lines) and scaled VOEs (dotted lines).

molecules obtained for the geometries optimized at the MP2/6-31G(d) level. In Table 1 (and as dotted lines in Figure 4) are also reported the VOEs scaled with the linear correlation ($VAE_{(eV)} = 0.901(VOE_{(eV)}) - 2.550$) empirically calibrated with the lowest σ^*_{C-Cl} VAE of 13 mono- and polychloroalkanes by Aflatooni et al.[29]

TABLE 1: HF/6-31G(d)//MP2/6-31G(d) VOEs, Scaled VOEs (See Text), And Measured VAEs

	orbital	VOE	scaled VOE	VAE
$CH_3CH_2CH_2Cl$[a]	σ^*_{C-Cl}	5.242	2.17	2.4
CH_2Cl_2[b]	σ^*_{C-Cl}	5.718	2.60	3.17
	σ^*_{C-Cl}	4.164	1.20	1.01
$ClCH_2CH_2Cl$	σ^*_{C-Cl}	5.140	2.08	
	σ^*_{C-Cl}	4.847	1.82	2.2
$ClCH_2CH_2CH_2Cl$	σ^*_{C-Cl}	5.366	2.28	
	σ^*_{C-Cl}	4.874	1.84	2.1
$BrCH_2Cl$	σ^*_{C-Cl}	5.367	2.29	2.72
	σ^*_{C-Br}	3.462	0.57	0.47
$BrCH_2CH_2Cl$	σ^*_{C-Cl}	5.017	1.97	2.5
	σ^*_{C-Br}	3.983	1.04	1.15
$BrCH_2CH_2CH_2Cl$	σ^*_{C-Cl}	5.180	2.12	2.0
	σ^*_{C-Br}	4.217	1.25	1.2
$BrCH_2CH_2CH_2CH_2Cl$	σ^*_{C-Cl}	5.060	2.01	2.1
	σ^*_{C-Br}	4.242	1.27	1.2
$C\ H_3CH_2CH_2Br$[c]	σ^*_{C-Br}	4.464	1.47	1.3
CH_2Br_2	σ^*_{C-Br}	4.750	1.73	1.93
	σ^*_{C-Br}	3.095	0.24	0.2
$BrCH_2CH_2Br$	σ^*_{C-Br}	4.436	1.45	<2.2
	σ^*_{C-Br}	3.615	0.71	1.2
$BrCH_2CH_2CH_2Br$	σ^*_{C-Br}	4.379	1.39	
	σ^*_{C-Br}	4.071	1.12	1.1
$BrCH_2CH_2CH_2CH_2Br$	σ^*_{C-Br}	4.404	1.42	
	σ^*_{C-Br}	4.305	1.33	1.1

[a] VAEs from ref 9. [b] VAEs from ref 29. [c] VAEs from ref 21. All values in electronvolts.

The ET spectra of 1,2-dichloroethane and 1,3-dichloropropane (Figure 1) display a single broad resonance centered at about 2.1 eV because of the unresolved contributions from the two lowest σ^* empty MOs, predicted by the calculations to be mainly localized on both of the C−Cl bonds. In agreement, the scaled VOEs of the two σ^*_{C-Cl} MOs are split by only 0.3 to 0.4 eV and satisfactorily reproduce the measured VAEs. (See Table 1 and Figure 4.) In addition, the spectra are an average over all populated conformational isomers. In particular, the first scaled VOE (1.82 eV) of 1,2-dichloroethane is perfectly consistent with the VAE of the first anion state estimated[10] by deconvolution of the very broad (fwhm ≥1.7 eV) ETS signal. The previously reported first VAEs of 1-chloropropane[9] and dichloromethane[29,30] are also well reproduced. Only the higher-lying σ^*_{C-Cl} VAE of dichloromethane is underestimated by the corresponding scaled VOE.

The ET spectrum of dichloroethane also shows a broad signal centered at about 5.5 to 6 eV. Analogous features are observed in some of the bromochloro and dibromo derivatives analyzed, whereas some others display only a less distinct signal starting at about 4.5 to 5 eV. Consistently, according to the calculations in all compounds, the scaled energy of the third empty MO with mainly σ^*_{C-H} character is about 4 eV, and several other MOs with mainly σ^*_{C-H} or σ^*_{C-C} character follow at higher energy.

In the series of the mixed bromochloro alkanes, the first anion state is sizeably more stable than that of the corresponding dichloro derivatives. According to the calculations, the first and second empty MOs possess mainly σ^*_{C-Br} and σ^*_{C-Cl} character, respectively, although in bromochloromethane, the two MOs are significantly mixed. Interestingly, it can be noted (Table 1 and Figure 4) that, despite the fact that the VOE/VAE linear correlation employed has been calibrated with only chloroalkanes and the first anion state has mainly σ^*_{C-Br} character, the first VAEs are closely reproduced by the corresponding scaled VOE. Also, the second (mainly σ^*_{C-Cl}) VAE is well reproduced, except for the ethane derivative. The second resonance displayed by the ET spectrum of 1-bromo-3-chloro propane is weak and barely resolved from the first one so that the uncertainty of the

TABLE 2: Peak Energies (electronvolts) and Total Anion Currents Measured in the DEA Spectra and Relative Intensities of the Halide Anions (Accounting for Isotope Abundance) Measured in the Bromochloro Derivatives[a]

		DEAS (total anion current)			
	ETS		cross sec./10^{-18} cm^2		mass filter
	VAE	peak energy	this work	lit.	Br^-/Cl^- ratio
$CH_3CH_2CH_2CH_2Cl$[b]	2.4	1.4	≤0.18	0.165[c]	
CH_2Cl_2	1.01	0.44	5.85	5.17[d]	
$ClCH_2CH_2Cl$	2.2	0.36	11.3	9.30[d]	
$ClCH_2CH_2CH_2Cl$	2.1	1.3	2.16	1.79[d]	
$CH_3CH_2CH_2Br$[e]	1.3	0.65	4.06		
$BrCH_2Cl$	0.47	≤0.1	586		30.0
$BrCH_2CH_2Cl$	1.1	≤0.1	271		1.3
$BrCH_2CH_2CH_2Cl$	1.2	0.3	37.0		9.0
$BrCH_2CH_2CH_2CH_2Cl$	1.2	0.3	22.3		7.5
CH_2Br_2	0.2	0.02	3660		
$BrCH_2CH_2Br$	1.2	0.04	2930		
$BrCH_2CH_2CH_2Br$	1.1	0.4	135		
$BrCH_2CH_2CH_2CH_2Br$	1.1	0.4	108		

[a] First VAEs (electronvolts) measured in the ET spectra are also reported for comparison. [b] Ref 20. [c] Ref 27. [d] Ref 10. [e] Ref 21.

corresponding VAE (2.0 eV) reported in Table 1 might be larger than ± 0.1 eV. Compared with their dichloro counterparts, where the two σ^* resonances are resolved only in the methane derivative, in the mixed derivatives, the C−Br and C−Cl σ^* resonances are also well resolved in the ethane derivative and still distinguishable in the longer-chain derivatives.

The ET spectra of the dibromoalkanes are displayed in Figure 3. Their electron acceptor properties are somewhat larger than those of the corresponding bromochloro derivatives. In particular, the first anion state of dibromomethane lies only slightly above zero energy. The corresponding signal in the ET spectrum (Figure 3) appears as a shoulder at 0.2 eV superimposed on the high-energy side of the intense electron beam source signal. The first two VAEs of dibromomethane determined here are in good agreement with those reported in previous work.[31] The first σ^*_{C-Br} VAE (1.1 to 1.2 eV) of the longer alkyl-chain derivatives is only slightly smaller than that (1.3 eV) of the 1-Br linear monoalkanes.[21] Again, the scaled VOEs satisfactorily match the measured VAEs, with the exception of the second VAE of 1,2-dibromoethane. It can be noticed, however, that the second narrow structure displayed by the ET spectrum of 1,2-dibromo ethane at 2.2 eV results from the overlap between the two unresolved σ^*_{C-Br} resonances so that 2.2 eV is an upper bound to the second VAE. A crude estimate can be made using the relation ($E_{max} = 1.4(VAE)$) between VAEs and energies of the corresponding maxima (E_{max}) in the derivative of the transmitted current found[29] in the ET spectra of a series of monochloroalkanes. This would lead to VAE = 1.6 eV, which is in good agreement with the scaled value (1.45 eV). In any case, in contrast with the dichloro analogue, in 1,2-dibromoethane, the two lower-lying σ^* anion states give rise to distinct signals, which is in agreement with the larger energy separation predicted by the calculations. The ET spectra of 1,3-dibromopropane and 1,4-dibromobutane display a single resonance centered at 1.1 eV. In agreement, the scaled VOEs of the in-phase and out-of-phase σ^*_{C-Br} MOs differ by only 0.3 eV in the former, whereas in the latter, where the overlap between the σ^*_{C-Br} MOs is very small, the two anion states are predicted to be virtually degenerate.

A final comment on the ET spectra concerns the resonance widths. The wave functions associated with the C−Cl and C−Br σ^* MOs are expected to possess a large component of p_σ character, so that according to the Wigner threshold law,[32] the widths should vary according to approximately $VAE^{1.5}$, as previously verified for chloro and bromo alkanes.[29,33] For the most resolved resonances observed here below 2 eV, the widths, evaluated as the dip-to-peak energy separations, correlate linearly (slope = 0.49) with $VAE^{1.5}$, although the squared correlation coefficient (0.80) is rather small.

Dissociative Electron Attachment Spectra. Most of the DEA studies reported in the literature are concerned with only the energy of the maxima observed in the cross section and the nature of the negative fragments produced but not with the quantitative aspects, that is, determination of the (absolute or relative) dissociative cross sections. These important measurements are delicate and, unfortunately, can sometimes be affected by the presence of traces of impurities, owing to very large variations in the DEA cross sections, especially near-zero energy.

The peak energies measured in the total anion currents of the dihaloalkanes studied here and their intensities (evaluated from the peak heights normalized to the same electron beam current and the same pressure reading for all the compounds) are given in Table 2. The fourth column reports the absolute cross sections as evaluated from comparison of the absolute cross sections found by Burrow and coworkers in monochloro alkanes[27] and alkylbenzenes[34] with our measurements on the same compounds. The average conversion factor (standard deviation = ±25%) between the two sets of values has been applied to the present dihaloalkanes.

Figure 5 displays the total yield of negative ions measured at the walls of the collision chamber in dichloromethane, 1,2-dichloroethane, and 1,3-dichloropropane as a function of the incident electron energy in the 0−3 eV energy range. Mass analysis revealed that the total anion current is essentially only due to the Cl^- fragment. The presence of Cl^- peaks at zero energy in the DEA spectra indicates that the C−Cl bond dissociation energy is smaller than the EA of the chlorine atom (3.61 eV[35]). The zero-energy signals may be associated with thermally excited vibrational levels of the neutral molecules and the inverse energy dependence of the electron attachment cross section for the *s* wave that causes the yield to climb at zero energy.[36] The spectra of dichloromethane, 1,2-dichloroethane, and 1,3-dichloropropane display maxima in the total anion current, respectively, at 0.44, 0.36, and 1.3 eV (Table 2), which is in good agreement with those previously reported,[10] although in the present spectra of the latter two compounds, the relative intensities of the zero-energy peaks are 2 to 3 times larger. This

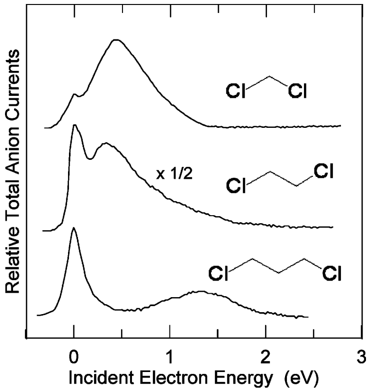

Figure 5. Total anion current as a function of incident electron energy in dichloromethane, 1,2-dichloroethane, and 1,3-dichloropropane.

is likely to be ascribed to contributions from traces of impurities with a large zero-energy cross section (CCl_4, for example).

Importantly, the cross sections measured here in these dichloroalkanes at the maxima above zero energy are compared with previously reported data and serve as a benchmark to test the reliability of our evaluations of the absolute DEA cross section. As shown in Table 2, the present determinations are in good agreement with those found by Aflatooni and Burrow,[10] being systematically about 12% larger. In particular, the present data confirm the anomalous cross section decrease on going from 1,2-dichloroethane to CH_2Cl_2, despite the significantly smaller VAE (about 1 eV) of the latter. In fact, it has been pointed out by the above-mentioned authors[10] that this compound is the only one (among a large number of mono-, di-, and trichloro alkanes) that does not fit the exponential relation between DEA cross sections and VAEs.

Another unexpected finding emerges from the comparison between the ethane and propane derivatives. Although their first VAEs (measured and calculated) are very close to each other (both about 2.1 eV), the DEA spectrum of 1,2-dichloroethane displays a maximum at only 0.4 eV, whereas in 1,3-dichloropropane, the corresponding peak is located at 1.3 eV. The behavior of the latter is in line with that of the linear monochloroalkanes (VAE about 2.4 eV, DEA peak at about 1.4 eV), although the DEA cross section of 1,2-dichloroethane is one order of magnitude larger. (See Table 2.) Such a large energy shift of the DEA peak upon going from the ethane to the propane derivative is not observed in the mixed bromochloro and dibromo alkanes. (See below.)

Replacement of a chlorine atom with a bromine atom in the 1,2-, 1,3-, and 1,4-dichloro derivatives of ethane, propane, and butane, respectively, to give the mixed bromochloro analogues causes a VAE decrease of about 1 eV. The DEA spectra (Figure 6) of the bromochloro derivatives of propane and butane show maxima of the total anion current at zero energy and distinct shoulders at about 0.3 eV. The two signals are not resolved in the DEA spectra of 1-bromo-2-chloroethane and bromochloromethane, which display a single peak at ≤ 0.1 eV. The measured total anion currents (Table 2) are about 20 times larger than those of the corresponding dichloro alkanes, except for the methane derivative, where the cross section is about 100 times larger. The absolute total DEA cross section (3.7×10^{-17} cm^2) measured here in 1-bromo-3-chloropropane at the 0.3 eV shoulder as well as the relative contributions from the mass-analyzed Br^- and Cl^- negative fragments (see below) are in good agreement with recent evaluations[37] of the Br^- (3×10^{-17} cm^2) and Cl^- (0.5×10^{-17} cm^2) partial cross sections.

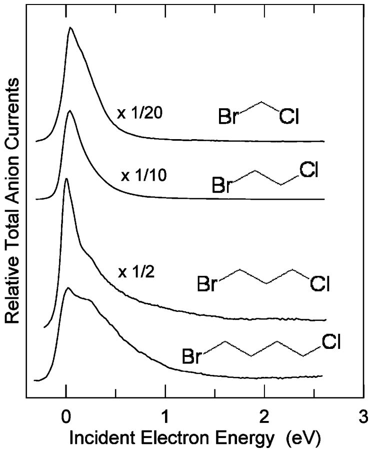

Figure 6. Total anion current as a function of incident electron energy in bromochloromethane, 1-bromo-2-chloroethane, 1-bromo-3-chloropropane, and 1-bromo-4-chlorobutane.

Moreover, although the first VAE (about 1.2 eV) measured in the ET spectra of these ethane, propane, and butane bromochloro derivatives is only slightly smaller than that (1.3 eV) of the corresponding 1-bromoalkanes,[21] the DEA cross sections are sizably larger (about 6, 9, and 60 times, respectively). In particular, in 1-bromo-3-chloropropane, even accounting for a contribution from Cl^- of about 10% (see below) to the total cross section, the Br^- current can be evaluated to be about 8 times larger than that of the 0.6 eV peak in 1-bromopropane.[21] This result is in contrast with previous literature data,[38] according to which the Br^- current of 1-bromo-3-chloropropane would be only slightly larger than that of 1-bromopropane.

As found in dichloromethane, the first VAE (0.47 eV) of the geminal derivative bromochloromethane is significantly smaller than that of the longer-chain derivatives. The total anion current displays a maximum at ≤ 0.1 eV. At variance with the corresponding dichlorides, the DEA cross section of bromochloromethane is more than twice as large as that of 1-bromo-2-chloroethane, following the trend expected on the basis of the relative VAEs. However, it is to be pointed out that in the methane and ethane derivatives, the single maximum observed at ≤ 0.1 eV has a large contribution from the unresolved zero-energy signal, which can be severely affected by convolution with the electron beam resolution or the possible presence of traces of impurities with large cross sections at zero energy.

Mass analysis revealed that the observed total anion currents are essentially due to only the Br^- and Cl^- negative fragments. The ratios between the Br^- and Cl^- currents detected through a mass filter change significantly along the series. The signals were recorded at $m/e = 79$ and 35, but the ratios reported in the last column of Table 2 are already corrected for the various isotope abundances. In bromochloromethane, the Br^- current peaks at 0.08 eV, as calibrated against the SF_6^- signal at 0.00 eV, and is 30 times larger than the Cl^- current, which displays a rather broad (450 meV) signal peaking at 0.14 eV. In 1-bromo-2-chloroethane, the Br^-/Cl^- ratio drops to only 1.3, and both of the negative fragment currents are found to peak at 0.05 eV, with a weak shoulder at 0.3 and 0.4 eV for the Br^- and Cl^- anions, respectively. In 1-bromo-3-chloropropane and 1-bromo-4-chlorobutane, the measured Br^-/Cl^- ratios are 9 and 7.5, respectively. In the former, the $Br^-$and Cl^- currents were found to peak at about 0.3 and 0.8 eV, respectively, whereas in the latter, the Br^- current peaks at 0.3 eV and the Cl^- current at 0.5 eV. Several determinations of the Br^- and Cl^- peak energies

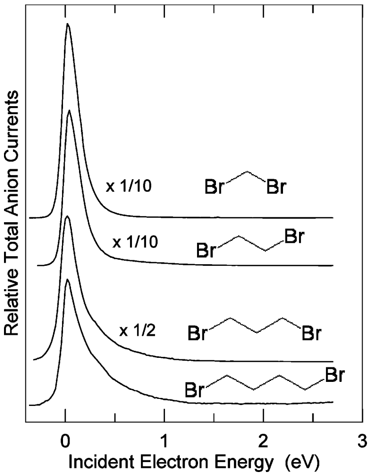

Figure 7. Total anion current as a function of incident electron energy in dibromomethane, 1,2-dibromoethane, 1,3-dibromopropane, and 1,4-dibromobutane.

in the DEA spectra of 1-bromo-3-chloropropane have recently been reported,[37−39] ranging from 0.3 to 0.47 eV for the former and from 0.4 to 0.75 eV for the latter.

An explanation of the relatively small Br^-/Cl^- ratio in 1-bromo-2-chloroethane is not obvious. The reason cannot be traced back to the calculated localization properties of the LUMOs. In addition to the MP2/6-31G(d) calculations, density functional theory B3LYP/6-31G(d) calculations have been carried out. Both theoretical methods predict the contribution from the σ^*_{C-Cl} MO to the LUMO to decrease with increasing length of the alkyl chain. Also, the calculated thermodynamic thresholds for C−Cl bond dissociation do not supply an explanation for the relatively high Cl^- current in the ethane derivative. According to both MP2 and B3LYP methods, the C−Cl bond dissociation energy in 1-bromo-2-chloroethane is slightly larger (0.12 and 0.03 eV, respectively) than that in bromochloromethane. However, the present finding is consistent with the nearly equal Br^- and Cl^- currents observed[38] in $CH_3CHBrCH_2Cl$ where the alkyl chain is longer, but the two halogen atoms are placed in vicinal positions as in 1-bromo-2-chloroethane. As a tentative explanation, the vertical anion state of 1-bromo-2-chloroethane could be formed in a vibrationally excited state, which strongly involves both C−Br and C−Cl stretching. B3LYP calculations predict the occurrence of such a normal mode with a wavenumber of 732 cm^{-1}, which is in agreement with the sharp feature displayed by the IR spectrum[39] of 1-bromo-2-chloroethane at this energy.

Figure 7 displays the total anion currents recorded in the series of the dibromoalkanes in the 0−3 eV energy range. In dibromomethane and 1,2-dibromoethane, a single peak is observed very close to zero energy. Calibration of the mass-selected Br^- current against SF_6^- located the maximum at 0.02 and 0.04 eV, respectively, in the two compounds. In agreement, the Br^- negative fragment was previously found[40] to peak at 0.1 eV. The evaluated absolute cross sections at these maxima (Table 2) are about (3.7 and 2.9) × 10^{-15} cm^2 in the methane and ethane derivatives, respectively, that is, about one order of magnitude larger than those measured in the corresponding bromochloro mixed derivatives. In 1,3-dibromopropane and 1,4-dibromobutane, the high-energy side of the zero-energy peak displays a distinct shoulder at about 0.4 eV. The absolute cross sections at 0.4 eV are evaluated to be about 10^{-16} cm^2, that is, 4 to 5 times larger than those of the corresponding bromochloro alkanes and about 30 times larger than those of linear monobromo alkanes.

In the dibromoalkanes, as found in the bromochloro counterparts and at variance with the dichloro counterparts, the DEA cross section of the methane derivative is slightly larger than that of the ethane derivative. However, an even larger difference would probably be expected on the basis of the sizeably smaller (about 1 eV) VAE of dibromomethane.

Conclusions

ETS and DEA spectroscopies have been used to measure, respectively, the energies of vertical electron attachment (VAEs) and the cross sections for total anion production as a function of the electron impact energy in geminal, vicinal, and distal dichloro, bromochloro, and dibromo alkanes. As expected on the basis of the ET spectra of monohalo alkanes, the bromo derivatives display better electron acceptor properties than their chlorine counterparts. All three series of dihalides show that the first anion state of the methane derivative, where the two halogen atoms occupy geminal positions, is sizeably more stable than that of the longer-chain derivatives. However, the magnitudes of the DEA cross sections of the dihaloethanes, despite the significantly lower stability of their first anion states, are comparable with those of the corresponding dihalomethane derivatives.

The energies supplied by HF/6-31G(d)//MP2/6-31G(d) calculations for the C−Cl and C−Br empty σ^* orbitals of the neutral molecules not only parallel the trends observed in the measured VAEs but also satisfactorily (and somewhat unexpectedly) reproduce the absolute values when scaled with a linear regression empirically calibrated only with the first VAE of a series of mono- and polychloroalkanes.

The first VAE remains nearly constant (1.1 to 1.2 eV) and only slightly smaller than that of the 1-bromoalkanes along the series 1-bromo-2-chloroethane, 1-bromo-3-chloropropane, and 1-bromo-4-chlorobutane; even replacement of the chlorine atom with a bromine atom to give the corresponding dibromides does not change the first VAE. In contrast, large variations of the DEA cross sections are observed both within each of the two series and upon going from the bromochloroalkanes to the corresponding dibromoalkanes.

The largest DEA cross sections are observed in the dibromoalkanes (about 3 × 10^{-15} cm^2 in the methane and ethane derivatives). The DEA cross sections of the bromochloroalkanes are found to be almost one order of magnitude smaller than those of the corresponding dibromides but about 20 times larger than those of the corresponding dichlorides and of the 1-bromoalkanes. Within each of the series of dihalides considered, the DEA cross sections of the methane and ethane derivatives are of the same order of magnitude and about one order of magnitude larger than those of the propane and butane derivatives.

All DEA spectra display a peak at zero energy and a maximum at higher energy, except for the bromochloro and dibromo derivatives of methane and ethane, where the two signals are not resolved.

Analysis of the $Br^-$and Cl^- currents in the bromochloroalkanes with a mass filter revealed that the Br^-/Cl^- ratio undergoes large variations along the series, with a maximum for the methane derivative and a minimum for the ethane derivative.

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