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Electron Attachment to Hydrogen Halide Clusters

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Negative ion production by endoergic charge transfer from fast alkali atoms to a crossed molecular beam of hydrogen halide clusters, \((HX)_n\), has been studied for HF, HCl, HBr, HI, and mixed HF, HBr clusters. Cluster ions corresponding to \(n\) up to 10 are readily detected, although the unit mass resolution required for full identification is only feasible for small clusters (masses \(\leq 100 \text{ amu}\)). Dissociative attachment to form the “solvated” halide or bilaehide anions, \([X(HX)]_{n-}\), is the predominant process. No evidence is found for any intact \((HX)_n^-\) ions.

Introduction

Often a single molecule cannot bind an excess electron, whereas a weakly bound cluster of the same molecules might be able to do so. Prototypical cases are the gas-phase water\(^1\) and carbon dioxide\(^2\) clusters, \((\text{H}_2\text{O})_n^-\) and \((\text{CO}_2)_n^-\). The hydrogen halides may also exemplify such systems. All attempts to attach electrons to HX monomers have resulted in dissociative attachment to form the halide ion, \(X^-\), with a cross section that decreases with increasing electronegativity of the halogen atom.\(^3\) Electronic structure calculations by Jordan and Wendoiloski indicate that \((\text{HF})_n^-\) is normally stable in some cases, but if so its autodetachment lifetime appears to be extremely short. Experimental evidence for relatively stable, negative dimer ions, \((HX)_2^-\), has been inferred from radiation chemistry. In discussing mechanisms for thermal electron capture by gaseous HCl + HBr, Armstrong and Nagra\(^4\) suggest that a previously proposed \((HX)_2^-\) intermediate\(^5,7\) is produced chiefly by electron attachment to \((HX)_2\) dimer molecules:

\[
e^- + (HX)_2 \rightarrow (HX)_2^- \quad (1,-1)
\]
\[
(HX)_2^- \rightarrow H + XHX^- \quad (2)
\]
\[
(HX)_2^- + M \rightarrow (HX)_3^- + M \quad (3)
\]

In this mechanism, reaction 2 is the major exit channel for HBr; but reactions -1 and 3 are dominant for HCl. The generation of negative dimer ions from the ambient neutral dimers and the subsequent collisional deactivation of these ions distinguish this mechanism from earlier proposals. Electronic structure calculations by Jordan and Wendoloski indicate that \((\text{HF})_n^-\) is stable.\(^6\) However, they caution that their calculations were restricted to linear configurations of both the neutral dimer (known experimentally to have a zig-zag geometry\(^10\)) and the dimer negative ion, and their method probably overestimated the electron affinity of \((\text{HF})_2^-\).

This tentative evidence is consistent with chemical intuition, which suggests that hydrogen halides involving the more electronegative halogens will be more likely to form stable negative dimer ions. It appears that both \((\text{HF})_2^-\) and \((\text{HCl})_2^-\) may be stable while \((\text{HBr})_2^-\) and presumably \((\text{HI})_2^-\) are not. In all cases, both dissociation of dimer ions and concurrent reaction processes are expected (when thermochemically allowed) to yield halide ions, \(X^-\) or \(X_2^-\), and especially the quite stable bilaehide ion (XHX\(^-\)) as observable products. “Solvated” halide ions, \(\text{Cl}^-\)(\(\text{HCl})_n\) with \(n = 1–4\), have been observed in the multiple collision environment of drift tubes.\(^1,12\) Yet results of swarm-beam experiments have been interpreted as excluding the possibility that XHX\(^-\) or \(X_2^-\) ions originate from \((\text{HX})_2\) species.\(^3\) This view contradicts the mechanism postulated for radiolysis experiments,\(^13\) in which \((\text{HCl})_2\) subsequently reacts to form the \(\text{Cl}^-\)(\(\text{HCl})_n\) species.\(^14\)

This paper reports attempts to observe intact negative cluster ions \((HX)_n^-\) with \(X = \text{F, Cl, Br, or I}\). Our method employs endoergic electron transfer from a fast alkali atom beam to a target beam of hydrogen halide clusters. The target beam contains a range of clusters, with \(n = 2–10\) or more. This is an advantage since dissociative attachment to the larger clusters offers another route to small \((HX)_n^-\) cluster ions \((m < n)\), whether or not direct formation of such ions occurs.

Experimental Procedure

The apparatus and techniques have been described in detail elsewhere.\(^15\) Fast rubidium atoms are generated by seeded supersonic expansion from a nozzle oven, using He or \(\text{H}_2\) as the diluent gas. The neutral molecular cluster beam is likewise produced by a supersonic expansion. Typical source conditions were as follows: stagnation pressure of hydrogen halide \(\sim 700\) torr, nozzle diameter \(\sim 0.008\) cm, nozzle-to-skimmer distance \(\sim 0.5\) cm. The various negative ions formed in single collisions at the intersection of the beams are detected and mass analyzed.

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by a quadrupole mass filter. Ion flight times are typically \( \sim 10^{-5} \) s. Signal pulses from the electron multiplier are capacitively coupled to pulse-counting electronics and signal averaging is employed as necessary. A reliable and accurate internal mass calibration is obtained from high-resolution mass spectra of \((SO_2)_n^-\) cluster ions in conjunction with a digital sweep generator. Unit mass resolution is essential because of the possibility of confusing the species \([XHX]^-\) and \((HX)_n^-\). In these experiments this was achieved for the HF and HCl systems although the largest cluster ion detectable with unit resolution depends on the available ion intensities and feasible averaging times (\( \sim 1 \) h). The only positive ion species observed with appreciable intensity was \( Rb^+ \), as in our previous work.\(^{16}\)

The relative translational energy in collisions between \( Rb \) and an \((HX)_n^-\) cluster is given to a good approximation by

\[
E_{rel}(n) \approx \frac{nE_B}{(m_A + n m_B)}
\]

Here \( m_A \) and \( m_B \) denote the masses of \( Rb \) and \( HX \), respectively. \( E_{lab} \) is the mean kinetic energy of the \( Rb \) atoms, which was scanned over a range of \( \sim 4-8 \) eV by adjusting the source temperature and diluent gas mole fraction. The energy resolution \( \Delta E_{rel}/E_{rel} \approx \Delta E_{lab}/E_{lab} \) is about 16% (fwhm). Threshold measurements for \((SO_2)_n^-\) clusters and several other systems\(^{15}\) indicate that this energy spread permits observation of a product anion at values of \( E_{lab} \) as much as 20% below the actual endoergic threshold.

### Negative Ions Observed

Table I gives estimates of the endoergic threshold energies \( E_{th} \) for production of \((HX)_n^-\), \((XHX)_n^-\), and \( X^- \) ions from \( Rb + (HX)_n^- \) collisions. These estimates are derived from thermochemical data and familiar formulas.\(^{15}\) Also listed are values of \( E_{rel} \) corresponding to the maximum available laboratory kinetic energy, taken as 9.6 eV (the nominal mean value increased by 20%). The light mass and high bond strength of HF are seen to impose rather stringent kinematic constraints: under our conditions, any ions formed from \( Rb + (HF)_n^- \) by single-collision processes must come from clusters larger than dimers. The requirement is

\[
n \geq \frac{(m_A - m_B)}{E_{th} / (E_{lab} - E_{th})}
\]

Thus, \((HF)_n^-\) can only come from clusters with \( n \geq 3, \)

<table>
<thead>
<tr>
<th>process</th>
<th>( Rb \rightarrow Rb^+ + e^- )</th>
<th>( HX \rightarrow H + X^- )</th>
<th>( X^- \rightarrow X + e^- )</th>
<th>( (XHX)^- \rightarrow (X^- + HX) )</th>
<th>( (HX)_2 \rightarrow 2HX )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Rb \rightarrow Rb^+ + e^- )</td>
<td>4.18</td>
<td>4.18</td>
<td>4.18</td>
<td>4.18</td>
<td>16</td>
</tr>
<tr>
<td>( HX \rightarrow H + X^- )</td>
<td>5.87</td>
<td>3.40</td>
<td>3.40</td>
<td>3.06</td>
<td>18</td>
</tr>
<tr>
<td>( X^- \rightarrow X + e^- )</td>
<td>3.40</td>
<td>3.61</td>
<td>3.36</td>
<td>3.06</td>
<td>18</td>
</tr>
<tr>
<td>( (XHX)^- \rightarrow (X^- + HX) )</td>
<td>1.31</td>
<td>1.03</td>
<td>0.78</td>
<td>0.5</td>
<td>19</td>
</tr>
<tr>
<td>( (HX)_2 \rightarrow 2HX )</td>
<td>0.26</td>
<td>0.10</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>20</td>
</tr>
</tbody>
</table>

Table I: Estimates of Threshold Energies (eV)


\(^{19}\) Yamdagni, R.; Kebarle, P. J. Am. Chem. Soc. 1971, 93, 7139.

chloride ion. This same pattern for the (HCl)$_2^-$ dimer ion would, of course, be shifted upward by one mass unit if it were present. It is difficult to ascertain whether (H$^{35}$Cl)$_2^-$ appears because of the artifacts on the low mass side of the peaks. The dimer species [(H$^{35}$Cl)(H$^{37}$Cl)]$^-$ and (H$^{27}$Cl)$_2^-$ are conspicuously absent, however. We estimate that any (HCl)$_2^-$ formed is well below 10% of the yield of (CIHCl)$_2^-$ observed.

The spectrum also shows the four-peak pattern corresponding to isotopic variants of Cl$^\cdot$(HCl)$_2$. Here the inadequate mass resolution would obscure any (HCl)$_2^-$; for the trimers we obtain only a crude limit, about 30% of the yield of Cl$^\cdot$(HCl)$_2$. Higher unresolved mass peaks were also observed, corresponding to cluster ions with $m$ up to 7.

**Hydrogen Bromide.** Resolved $^{79}$Br and $^{81}$Br peaks were clearly observed, but we were unable to achieve both unit resolution and a reasonable signal-to-noise ratio in the vicinity of (BrHBr)$^-$ or at higher masses. The 1:2:1 isotopic pattern characteristic of a two-bromine system gave an unresolved but symmetrical mass peak centered at mass 161. This undoubtedly corresponds to the (BrHBr)$^-$ ion. No (HBr)$_2^-$ was in evidence, since the high mass side of the peak did not show asymmetry. If there is any (HBr)$_2^-$, it must be 50% of the yield of (BrHBr)$^-$.

**Hydrogen Iodide.** Unresolved mass peaks corresponding to [I(HI)$_{m-1}$]$^-$ and/or (HI)$_m^-$ with $m = 1$ and 2 were observed, but estimates of the relative yields are not feasible.

**Mixed Halide Species.** During the runs with hydrogen bromide, cluster ions appeared that contained hydrogen fluoride which had been flushed from the gas line of the cluster beam source and evidently formed HF(HBr)$_n$ clusters in the supersonic expansion. Weak, unresolved signals were seen corresponding to [(HBr)$_{m-1}$]$^-$ and/or [HF(HBr)$_m$]$^-$ with $m = 3-12$. In studying electron capture reactions in HBr/HCl and HBr/H$_2$S mixtures, Armstrong$^2$ suggested that the principal negative ion products were (CIHBr)$^-$ and (BrH$_2$)$^-$, respectively.

**Rubidium Anions.** Particularly in the runs with hydrogen fluoride and hydrogen chloride, there appeared prominent “surface-born” negative ions at masses 85 and 87 with a 3:1 intensity ratio as seen in Figure 1. These peaks correspond to the isotopic components of the Rb$^-$ anion (stable by 0.49 eV with respect to electron detachment$^{22}$). The yield is markedly enhanced in the presence of the hydrogen halide cluster beam. Our observations are consistent with other experiments in this laboratory$^{23}$ which deliberately impinge halogen containing beams on alkali-coated surfaces and find remarkably efficient product formation of alkali anions and many other species.

**Discussion**

Our primary aim was to look for (HF)$_3^-$ and (HCl)$_3^-$ ions to test the recent proposals of their stability by Armstrong$^2$ and Jordan$^9$. We have found no evidence for the stability of these dimer ions or any other (HX)$_m^-$ cluster ions. Likewise we do not observe the X$^-_m$ ions seen in swarm-beam experiments.$^3$ At least for the single-collision charge transfer method we employed

$$\text{Rb} + (HX)_m^- \rightarrow \text{Rb}^+ + (HX)_m^- + \ldots$$

dissociative attachment to form the “solvated” halide or bihalide anions (with $m \leq n$) is clearly the dominant process. This conclusion of course is warranted only for the range of cluster sizes which we could examine with unit mass resolution. For the HBr case, our results agree with the Armstrong mechanism, and even for the HCl case do not contradict it. The mechanism postulates that the initially formed dimer ion, (HX)$_2^-$, is vibrationally excited but becomes stabilized by collisional deactivation. Since in our experiment the (HX)$_2^-$ ion, if formed, experiences no subsequent collisions, it might be expected to autoionize or dissociate long before it reaches the detector. Indeed, for (HCl)$_2^-$, the analysis given by Armstrong$^2$ implies an autoionization half-life of $\sim 10^{-12}$ s and a dissociation half-life of $\sim 3 \times 10^{-10}$ s, whereas the flight time from reaction zone to detector in our apparatus is $\sim 10^{-9}$ s.

Other features of the cluster ions as initially formed in our experiments are pertinent to assessing the stability of (HX)$_3^-$ dimer ions, however. (i) The electron transfer from alkali atom to target cluster can occur when the relative kinetic energy exceeds the difference between the alkali ionization potential and the cluster electron affinity. The excitation above the threshold for formation of dimer ions thus may be smaller than for dimer ions produced by the capture of thermal electrons in $\gamma$-ray irradiated vapors. (ii) The electron transfer that creates the cluster anion also produces an alkali cation, and its electric field induces vibrational relaxation of the anion.$^{24}$ The available evidence indicates that monomer and dimer anions are thereby fully relaxed to the ground vibrational state, corresponding to the adiabatic electron affinity, although this mechanism may become much less efficient for larger cluster anions.$^{15}$ (iii) Dissociative electron attachment to larger clusters would be expected to give some yield of intact dimer anions by (HX)$_2^-$ $\rightarrow$ (HX)$_2^- + \ldots$, if in fact bound dimer anions exist. The total yield of dimer anions would come from integrating over the distribution of larger clusters, which in our experiments had appreciable in-
tensity up to at least \( n \sim 10 \).

These three features invalidate the simplistic comparison of the (\( \text{HCl} \)) autoionization or dissociation half-life to flight time. In particular, the relaxation time for process (ii) is likely to be much shorter than those half-lives. For previously studied systems, the estimated relaxation time is of the order \( \sim 10^{-12} \) s, both from trajectory calculations\(^4\) and from observation of thresholds corresponding to the adiabatic rather than the vertical electron affinity.\(^5\) We conclude that our failure to detect (\( \text{HX}_2 \)) in these experiments at least casts doubt that such ions have appreciable stability.

**Acknowledgment.** We thank Doug Worsnop for lending us the digital sweep generator which he designed and built, and Professor David Armstrong for several helpful suggestions. We gratefully acknowledge support of this research by the National Science Foundations.

**Registry No.** HF, 7684-39-3; HCl, 7647-01-0; HBr, 10035-10-6; HI, 10034-56-2; Rb, 7440-17-7.

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**Molecular Beam Studies of \( \text{C}_6\text{F}_8 \), \( \text{C}_6\text{F}_3\text{H}_3 \), and \( \text{C}_6\text{H}_6 \) Complexes of HF. The Rotational Spectrum of \( \text{C}_6\text{H}_6\)-HF**

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An investigation of the complexes formed between HF and the aromatic species \( \text{C}_6\text{H}_6 \), \( \text{C}_6\text{F}_3\text{H}_3 \), and \( \text{C}_6\text{F}_6 \) has been carried out with the molecular beam electric resonance technique. Mass spectrometry indicates that HF forms a complex less easily as fluorine substitution increases on the aromatic ring. While insufficient HF complex was formed with the two fluorine-substituted benzenes to measure rotational spectra, spectroscopic constants have been obtained for \( \text{C}_6\text{H}_6\)-HF (\( B = 2048.540 (2) \) MHz, \( D_J = 3.1 (2) \) kHz, \( D_{JK} = 74 (1) \) kHz, \( \mu = 2.244 (4) \) D) and \( \text{C}_6\text{F}_3\text{H}_3\)-DF (\( B - D_{JK} = 2015.406 (6) \) MHz, \( D_J = 3.2 (4) \) kHz, \( eQ_{ID} = 280 (50) \) kHz, \( \mu = 2.282 (1) \) D). In the asymmetric average structure, the hydrogen end of HF points toward the benzene. The hydrogen atom is \( \sim 2.25 \) Å above the plane of the benzene molecule. The large amplitude motions present in this complex make it difficult to determine an equilibrium structure.

**Introduction**

The ability of molecules containing \( \pi \)-electrons to interact with Lewis acids has long been noted.\(^1\) Examples of molecular complexes formed as a result of this interaction range from weak "donor-acceptor" complexes observed in solution to more strongly bound organometallic compounds. Weakly bound species of this type are also believed to play a role in certain chemical reactions. The attack of a \( \pi \)-electron system by an electrophilic reagent is a familiar first step in many reaction mechanisms discussed in organic chemistry. In an attempt to better characterize the nature of this interaction, a systematic study of isolated molecular complexes formed between Lewis acids and unsaturated molecular systems has been started.

In particular, the Fourier transform microwave molecular beam technique has already been used to produce structures for the weak complexes ethylene-hydrogen fluoride and acetylene-hydrogen fluoride.\(^6\)\(^7\) The bonding arises from interaction of the acidic HF proton with the \( \pi \)-system of the hydrocarbon. The structure observed in each case is t-shaped, with the HF axis pointing toward the midpoint of the carbon-carbon bond. This structure is consistent with a HOMO-LUMO model of the interaction, in which the \( \pi \)-bonding molecular orbital of the hydrocarbon is the HOMO (highest occupied molecular orbital) and the \( \sigma^* \) antibonding molecular orbital of HF is the LUMO (lowest unoccupied molecular orbital).

In this paper, the results of a molecular beam study of the benzene-HF system is presented. The purpose of this study is to probe the interaction of a strong Lewis acid with an aromatic \( \pi \)-system from a structural viewpoint. The stereochemistry of this interaction has been of interest for some time, and, in particular, much experimental work has been done on complexes of benzene with the homonuclear diatomic halogen molecules. The results of these studies conflict, and there is some question as to whether the diatom lies along the \( \text{C}_6 \) symmetry axis of benzene, hence forming a symmetric molecule, or whether it interacts specifically with one of the carbon-carbon bonds, forming an asymmetric molecule. Structural studies on crystals\(^8\) of benzene-\( \text{Cl}_2 \) and benzene-\( \text{Br}_2 \) as well as infrared spectroscopy on benzene-\( \text{Br}_2 \) in the gas phase\(^9\) are indicative of a symmetric structure, while infrared spectroscopy of these species in low temperature matrices\(^10\) is consistent with the asymmetric structure.

Simple theoretical models for the interaction also provide conflicting structural predictions. A HOMO-LUMO model leads to the prediction of a nonsymmetric structure, since the symmetries of the benzene HOMO (an antisymmetric \( \pi \)-molecular orbital) and acid LUMO (a \( \sigma^* \) anti-