Electron Transfer to SF$_6$ and Oriented CH$_3$Br

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Received: June 15, 1999; In Final Form: July 26, 1999

Previous experiments have suggested that different negative ions are formed by electron transfer to different ends of a molecule. To investigate this possibility, a crossed molecular beam apparatus has been constructed to mass-analyze the ions produced in collisions between fast K atoms and oriented molecules. Initial studies are reported on ion formation in collisions of unoriented SF$_6$ and oriented CH$_3$Br. For lab energies $\approx 5-30$ eV, Br$^-$ is the only ion observed from CH$_3$Br, and its formation is favored by attack at the Br-end of CH$_3$Br. The Br and CH$_3$ ends have the same energetic threshold for forming Br$^-$. SF$_5^-$, SF$_6^-$, and F$^-$ ions are observed from SF$_6$ and O$_2^-$ from O$_2$. These ions are formed over a range of energies unlike those formed by electron attachment and suggest that the nascent negative ion can be stabilized by the accompanying positive K$^+$. 

I. Introduction

Steric considerations are an ingrained aspect of chemical thought and a number of experiments have recently directly probed the role of orientation in chemical reaction.$^{1-9}$ These effects seem to be especially significant in electron transfer between initially neutral species as shown by Xing et al.$^{10,11}$ In these experiments, positive ions were observed from collisions between neutral potassium atoms and CF$_3$Br molecules which had been oriented in space. Attack at the Br-end of the molecule produced more positive ions than at the CF$_3$-end. The energetic threshold for the Br-end was $\approx 0.7$ eV lower than for the CF$_3$-end, suggesting that attack at different ends of the molecule produced different negative ions.

These electron-transfer experiments exemplify the harpoon mechanism of Magee, et al.$^{12}$ in which an electron is transferred from an alkali metal atom to a halogen-containing molecule to form a transient ion-pair, which may then further interact to form neutral products. (Considerable evidence supports this mechanism, the most direct being the present observations that ions are formed if enough energy is available to separate the charges.$^{12-14}$) Transient negative ions are formed in many other chemical reactions, especially those in solution, the most obvious examples being those in electrochemical cells.

How is the electron transferred? Even since the days of J. J. Thompson,$^{15}$ the interaction of electrons with matter has been of enormous practical and theoretical interest.$^{16}$ Although both positive and negative ions can be formed by electron impact in the gas phase, attention has been mostly focused on positive ions since they are more robust and more convenient to handle. Any negative ions formed by electron attachment are inherently unstable because the total energy is above the dissociation limit to a free electron plus neutral atom or molecule. Even if a stable molecular ion exists, the Franck-Condon principle requires the nascent negative ion to be formed with the geometry of the neutral, which usually corresponds to the repulsive wall of the negative ion potential. Such a negative ion is thus most likely to autodetach (reform the electron and neutral) although molecular negative ions can dissipate energy by breaking chemical bonds to give radical negative ions.

In contrast to the gas phase, molecular negative ions are found in condensed phases because the solvent can deactivate the excited anion, and these anions play an important role in many chemical and biological electron-transfer processes. While it might thus seem that gas-phase (or molecular beam phase) experiments would be useless in addressing some issues in electron transfer, negative ions formed in atomic collision between neutrals are different from the negative ions formed by electron bombardment. Los and co-workers, for example, modeled ion formation in collision with alkali metal donors; they concluded that during the collision, “bond stretching” in the nascent molecular negative ion occurred due to the proximity of the positive alkali metal ion.$^{17}$ This stretching allowed the negative ion to more closely assume the geometry of the stable negative ion, and the electron affinity measured corresponded to the adiabatic (thermodynamic) electron affinity, being the difference in energy between the neutral in its ground-state geometry and the energy of the ion in its ground-state geometry. In contrast, electron attachment measures the vertical electron affinity, the energy difference between the neutral and negative ion with both in the geometry of the neutral. (This is likely to be negative; a vertical transition with the geometry of the neutral would usually lead to a repulsive portion of the anion potential.)

Formation of negative ions during collision, even during gas-phase collisions, is thus a potential tool for exploring molecular negative ions found in solution. To investigate the possibility of electron transfer being site specific, our oriented molecule apparatus has been modified to identify the ionic products in collisions between fast alkali metal atoms and oriented molecules. Methyl bromide is oriented, and SF$_6$ is used as a calibrant because it is spherically symmetric and has no mass combinations in common with CH$_3$Br. These collisions were expected...
end or CH₃ -end of CH₃ Br. The spectrum can be obtained for attack of the K atom at the Br- if no high voltage is applied, molecules pass through the hexapole without selection, and a weak, unselected, and random beam results. Likewise, no deflection or selection results for molecules without dipole moments, such as O₂ or SF₆, or for molecules without first-order Stark effects, such as CH₂CH₂. For these molecules a weak but random beam also results.

B. Fast Alkali Atoms. Alkali metal atoms are produced with energies in the 0–30 eV range by surface ionizing atoms on a hot W filament, accelerating the ions by a voltage on a grid, and then allowing the ions to resonantly charge-exchange with the alkali gas as they pass through the oven. Any residual ions in the beam are swept out by an external electric field, resulting in a beam containing only neutral species. The accelerating voltage is taken to be the nominal energy, and the well-known electron affinities for various SF₆ ions are used to calibrate the energy. Unfortunately, space charge effects greatly attenuate the beam at low energies, and very low count rates are observed near threshold.

C. Coincidence Time-of-Flight Mass Spectrometer. Ionizing collisions between the fast K atoms and the oriented molecules produce K⁺ ions and M⁻ ions which are detected in separate time-of-flight (TOF) mass spectrometers. The molecular beams are continuous so the time zero and transit time through the mass spectrometer is unknown. But the ions are created simultaneously and the (unknown) time zero is the same for both ions. If the mass of the positive ion (almost certainly K⁺) and the dimensions and voltages are known, then the time difference is a measure of the mass of the negative ion.

A schematic diagram of the mass spectrometer is shown in Figure 2. This design was inspired by those of Dunning and Meyer. The orientation of the symmetric-top molecule at the reaction center is determined by the direction of the local electric field which needs to be parallel or antiparallel to the relative velocity. Ions formed in the collision will be extracted along the electric field, so the mass spectrometer array is rotated 25° with respect to the K beam to provide a field roughly parallel (antiparallel) with respect to the relative velocity. To reverse the orientation of the molecules, the direction of the electric field must be reversed, requiring reversal of the polarity of all of the electrodes which in turn reverses the direction the ions travel. A given TOF detector will thus collect positive ions in one orientation and negative ions in the other. The two TOF detectors are thus made identical.

Ions formed in the electron-transfer collision are accelerated toward their respective detectors by the electric field between the two TOF detectors. The ions then enter a field-free drift tube, and are deflected upward by a 45° electrostatic mirror into a second field-free region. The 57 mm diameter electrodes are spaced 6 mm apart with a 25 mm diameter opening. Elements in the mirror section are 2 mm apart. The positive ion and negative ion TOF sections are separated by 14.5 mm and the overall “drift tube” distance (triangular region of Figure 2) is 128 mm. Grids are 95% transparent Ni mesh (Buckbee–Mears) and the ions are detected with Galileo microchannel plates with an active area 25 mm diameter. Typical operating voltages are ±1450, ±600, ±600, and 0 for D, A, M₁, and M₂, giving a field strength in the collision region of about 300 V/cm. Relatively high potentials were used to minimize the loss of ions with appreciable transverse velocity components.

To avoid charge-up problems associated with oil contamination, the entire mass spectrometer assembly is contained in a UHV chamber pumped by a Varian triode ion pump. The beams
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For a molecule such as SF$_6$, a variety of different negative ions could be produced, such as e$^-$, F$^-$, SF$_5$$^-$$^-$, and SF$_6$$^-$$^-$, and in some cases the lightest ion is the negative ion. The negative ion pulse was delayed with a Stanford Research Systems digital delay generator in order to accommodate these possibilities.

III. Results

Mass Spectra. Different detectors with different efficiencies must be used for different orientations of a molecule. To compare signals from the different detectors, a small amount of a nonorientable gas (SF$_6$) is added to the CH$_3$Br/He gas mixture in the nozzle beam reservoir; typically SF$_6$:CH$_3$Br:He was 3%:7%:90%. Reaction of SF$_6$ is independent of the electric-field arrangement, and can be used to account for the different detection efficiencies, as well as different beam intensities on different days. Figure 4 shows typical coincidence time-of-flight spectra taken on different days for such a mixture with a 15.5 eV (lab) K atom beam. At these energies considerable fragmentation occurs in SF$_6$ and the ions SF$_5$$^-$$^-$, F$^-$, and SF$_6$$^-$$^-$ are all observed. The only ion observed from CH$_3$Br is the Br$^-$ ion. An O$_2$ pair from a small leak was later sealed. A small number of electrons is observed from background collisions.

A difference in transit time is apparent for the two orientations, which can be understood from Figure 1. In the “straight-through” (ST) orientation, the K$^+$ ion is detected by TOF A, but in the “turn-around” (TA) orientation the positive ion is detected by TOF B. The initial velocity of the K atom is away from TOF B, and the K species must stop and turn around before heading to detector B. This makes the flight time for K$^+$ longer in the TA orientation, which can be seen in the arrival of the electron (which corresponds to a K$^+$, e$^-$ pair). The heavier negative ion is less affected by the choice of detector A or B, and its travel time is roughly constant in the TA and ST orientations. The time difference between the K$^+$ and the heavier negative ions in the TA orientation is then smaller than in the ST orientation, as shown in Figure 4.

If the energy of the fast atom is zero or if the fast-atom beam is blocked, there are no coincidences. If the atomic beam is energized but the molecular beam is blocked, there are small coincidence signals arising from collisions of fast atoms with...
background gases. These are discriminated against by taking data with the high-voltage hexapole field on and off, as illustrated in Figure 5. With the high voltage off, a weak unoriented beam of CH\textsubscript{3} Br and SF\textsubscript{6} results in the middle spectrum. When high voltage is applied, the SF\textsubscript{6} intensity is bigger and corresponds to attack at the Br-end of CH\textsubscript{3} Br.

Energy Dependence: SF\textsubscript{6}. The most abundant ion in the energy range covered in these experiments is the fragment ion, SF\textsubscript{5}\textsuperscript{−}, which is unambiguously identified because the mass is the same as that of I\textsuperscript{−} which we observe from CH\textsubscript{3}I. Smaller amounts of SF\textsubscript{4}\textsuperscript{−} and F\textsuperscript{−} are also observed. The experimental integrated intensity, \( I_{i}(E) \), of a negative ion (i) at energy E for a specific orientation (o = ST or TA) is given by

\[
S_{i}^{o}(E) = \sigma_{o}^{i}(E)I_{G}D^{o}
\]

where \( \sigma_{o}^{i}(E) \) is the cross section for formation of ion i at energy E from orientation o, \( I_{G} \) is the intensity of the gas beam, \( I_{K} \) is the intensity of the K beam (which varies as \( E^{3/2} \) because the source is space-charge limited\textsuperscript{11,27}), and \( D^{o} \) is a detector function which depends on orientation. The laboratory kinetic energy of the K atom is taken to be the accelerating voltage for the K\textsuperscript{+} ions inside the charge exchange oven. The CM energy is \( E_{CM} = \frac{1}{2}\mu(v_{e}^{2} + v_{g}^{2}) \) where \( \mu \) is the reduced mass, \( m_{G} + m_{o} \), \( v_{e} \) and \( m_{o} \) are speed and mass, respectively, and subscripts G and K denote gas or K.

Unfortunately, neither the absolute intensities nor the detector function are known, and they are likely to vary from run to run. But for a specific gas mixture, the intensities of all ions are measured under the same conditions of beam intensity and detector function. Since \( D^{o} \) is found to be roughly independent of energy, the unknown beam intensities and detector functions can be removed by defining the relative cross sections, \( \alpha_{o}^{i}(E) \), relative to SF\textsubscript{5}\textsuperscript{−} at 20 eV

\[
\alpha_{o}^{i}(E) = \frac{S_{i}^{o}(E)20^{3/2}}{S_{SF5}^{o}(20)E^{3/2}}
\]
Cross sections relative to SF$_5^-$ at 20 eV (lab) are shown in Figures 7–9 for SF$_5^-$, F$^-$, SF$_6^-$, and Br$^-$, respectively. For the SF$_6$ species, the relative cross sections are calculated using the sum of ion intensities (HV-on + HV-off) averaged over the TA and ST “orientations”.

**Orientation of CH$_3$Br.** The relative cross sections for Br$^-$ produced in the TA and ST orientations are shown in Figure 10, where the data have again been normalized to the SF$_5^-$ intensity at 20 eV in both the TA and ST configurations. For CH$_3$Br the relative cross sections shown in Figure 10 are the HV-on – HV-off difference illustrated in Figure 5.

The cross sections are clearly different, and depend on energy. To clearly emphasize the effect of orientation, we define the steric factor, $G$, as the cross section difference divided by the cross section sum,

$$G(E) = \frac{\sigma_{\text{TA Br}}(E) - \sigma_{\text{ST Br}}(E)}{\sigma_{\text{TA Br}}(E) + \sigma_{\text{ST Br}}(E)}$$

$G$ is zero if there is no orientation difference, and $G$ is one if only one end of the molecule is reactive. The steric factor for the formation of Br$^-$ is plotted in Figure 11 and shows that the orientation becomes more important at low energies, with the Br-end of CH$_3$Br being favored by a factor of $\approx 2$ at energies near 5 eV.

**IV. Discussion**

**Ion Formation in SF$_6$.** As anticipated, the dominant negative ion is SF$_5^-$, but SF$_6^-$ is formed in appreciable amounts at collision energies as high as 20 eV. This is in agreement with
are essentially collisions of "free" electrons. This is under collisions at 20 eV can easily transfer an electron to SF6, which simultaneously deactivate the excited negative ion. Thus, the collision. In contrast to the attachment of a free electron, a electron is not free, and the nucleus plays a profound role in represents the limiting behavior of low Rydberg atoms: the large values of principal quantum number, \( n \), electron behavior are observed at "intermediate" values of \( n \) electron is essentially a free-electron. But deviations from free classification suggests that stabilization of the negative ion is favored over autodetachment. The degree of stabilization will probably depend on both the donor and acceptor, since electron affinities measured with fast Rb atoms for CO2 clusters are believed not to be the adiabatic electron affinities suggesting incomplete relaxation of the cluster anions.

Energy Thresholds. The kinetic energy of the K atoms is assumed to be the accelerating potential for the K+ ions in the charge-exchange oven. In Xing’s earlier work the speed of the atoms was measured, and found to agree well with the nominal accelerating voltage. Unfortunately, subsequent modifications in the charge-exchange oven make this calibration suspect and the collision energy is calibrated using the thresholds for the various SF6 ions.

The apparent thresholds for formation of various ions, taken from Figures 7–10 are shown in Table 1. The energy scale is calibrated by linear interpolation of the SF6 ion thresholds, and the corrected Br− threshold after calibration of the beam energy is 4.05 eV, in good agreement with the theoretical threshold calculated from ionization potentials, electron affinities, and bond dissociation energies. (The leak causing the O2 impurity mentioned earlier was repaired before the lower energy scans were taken, and O2 was unavailable as a calibrant.)

Steric Effects in CH3Br. The only negative ion observed so far from CH3Br is Br−. This ion is found to be more likely formed in the turn-around orientation where the positive ion detector is TOF B in Figure 1. Since the hexapole field selects molecules in states in which the energy increases with field, the negative end of the molecule points toward negatively biased detector B. In this orientation the negative end of the molecule is attacked, and we assume the negative end is the Br-end of the molecule.

The Br-end of the molecule is the more reactive end at all energies, and the Br-end is roughly twice as reactive as the CH3-end at low energies. As shown in Figure 10, the Br-end and CH3-end cross sections have the same apparent threshold. This might seem in contradiction to the earlier data of Xing which reported somewhat larger reactivity ratios and which suggested that the Br-end and CH3-end might have different energetic thresholds.

But Xing detected only the positive ions formed in the collision. If a negative ion other than Br− is formed this would have been included in Xing’s experiments although it would not be included here. For example, if the parent negative molecular ion CH3Br− were formed, Xing might have measured its threshold in one orientation. (We have not observed CH3Br−, although we have independently observed the parent negative molecular ion CF3Br− and defer a detailed study to use a

**Table 1**

<table>
<thead>
<tr>
<th>ion</th>
<th>experimental threshold (eV)</th>
<th>theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF6−</td>
<td>4.63 ± 0.19</td>
<td>3.29a</td>
</tr>
<tr>
<td>SF5−</td>
<td>5.41 ± 0.10</td>
<td>4.49b</td>
</tr>
<tr>
<td>F−</td>
<td>6.26 ± 0.19</td>
<td>4.84a</td>
</tr>
<tr>
<td>Br− (CH3-end)</td>
<td>5.27 ± 0.03</td>
<td>4.05</td>
</tr>
<tr>
<td>Br− (Br-end)</td>
<td>5.29 ± 0.08</td>
<td>4.07</td>
</tr>
</tbody>
</table>

*These values used for energy calibration. a Data: IP(K) = 4.34+0.1 eV; EA(Br, F, SF6, SF5) = 3.36, 3.45, 3.05, 1.05, 4.2, 4.43 3.84+0.4 eV; BDE (F−SF6, CH3−Br) = 3.95, 3.08.

experiments is greatly stabilized, and may well be stable, but the lifetime has not yet been determined. Very few free electrons are seen, and these small signals seem to be from background processes, suggesting that stabilization of the negative ion is favored over autodetachment.

Extensive studies with Rydberg atoms have shown that for large values of principal quantum number, \( n \), Rydberg collisions are essentially collisions of “free” electrons, \( n \). Rydberg collisions and Rydberg electron collisions with a ground-state atom can produce a negative ion by electron attachment and the nearby nucleus can almost simultaneously deactivate the excited negative ion. Thus, collisions at 20 eV can easily transfer an electron to SF6, which can fragment to SF5− or be deactivated by interaction with the K+ core to form SF6−. (Similar considerations apply to O2; electron attachment to O2 yields O−, but as shown in Figure 4, we observe O2−, and not O−. The molecular negative ion is stable against autodetachment in only the first few vibrational levels,37 so the collision apparently produces an ion in a low-lying vibrational state.) Thus the SF6− observed in these

Figure 12. Schematic diagram of electron interactions with molecule AX. If AX− is bound, it is likely to have a weaker and longer bond. Attachment of a free electron to AX will occur in a vertical, Franck-Condon like process in which the nuclei do not move, and AX− will be formed in a state lying above the neutral molecule. This state is likely to rapidly autodetach the electron to reform the neutral plus electron, although it may also be stabilized by dissociation into fragments. The addition of a nearby positive ion core during electron attachment provides a “third body” which can stabilize the negative ion in a nonvertical process.
calibrant other than SF₆.) The present (K⁺, Br⁻) coincidence signals do not include any contribution from other ions and show that although the signal depends on orientation and energy, the threshold is determined only by the energy, as is to be expected from thermodynamics.

V. Summary

Collisions of fast potassium atoms with SF₆ and CH₃Br produce ions which have been identified. Ions from SF₆ are different from those expected from electron impact and suggest that the nascent K⁺ ion can play the role of a solvent and deactivate the nascent negative ion.

The CH₃Br molecule can be oriented prior to collision. More Br⁻ ions are formed when the Br-end of the molecule is attacked, but the energetic threshold is the same regardless of orientation.

Acknowledgment. We gratefully acknowledge financial support from the National Science Foundation and the Robert A. Welch Foundation. We have benefited from the previous experience in this lab gleaned by Howard Carman, Leon Phillips, Peter Harland, Guoqiang Xing, and Dock-Chil Che, and we thank them for their contributions. We thank Ken Smith and Mike Duncan for helpful discussions.

References and Notes

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