Steric Asymmetry in Electron Transfer from Potassium Atoms to Oriented Nitromethane (CH₃NO₂) Molecules

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Received: January 13, 2006

Electrons are transferred in collisions between potassium atoms and CH₃NO₂ molecules that have been oriented in space prior to collision. The electron transfer produces K⁺ ions, parent negative ions CH₃NO₂⁻, and the fragment ions e⁻, NO₂⁻, and O⁻ in amounts that depend on the energy. The positive and negative ions are detected in coincidence by separate time-of-flight mass spectrometers at various collision energies for both CH₃-end attack and NO₂-end attack. The steric asymmetry for electrons and CH₃NO₂⁻ is essentially zero, but the steric asymmetry for NO₂⁻ shows that NO₂⁻ is formed mainly in CH₃-end collisions. There is evidence that the electrons and NO₂⁻ have the same transient precursor, despite having different steric asymmetries. It appears likely that the precursor is formed by electron transfer mainly in collisions normal to the molecular axis leading to near zero steric asymmetry for the electron. This transient precursor can also eject an NO₂⁻ ion, which is more likely to be removed as KNO₂ salt when K⁺ ions are near the NO₂ end of the molecule, with the result that CH₃-end collisions seem to produce more NO₂⁻.

I. Introduction

Electron transfer plays a fundamental role in many chemical reactions.¹ In some instances, evidence of the transfer is obvious, such as in ion–molecule reactions;² but in many other cases, the electron transfer event is disguised by the Coulomb interaction. Electron transfer collisions can be directly studied by crossing beams of neutral reagents at speeds of about 10 times thermal speeds.³ At these speeds, enough energy is available to overcome the Coulomb attraction between ions formed in the electron transfer. Observation of the ions then provides direct evidence of the transfer.

Electron transfer to nitromethane produces several different negative ions⁴–⁸ (e⁻, O⁻, NO₂⁻, and CH₃NO₂⁻). We recently studied how the orientation of the molecule affected the production of the various ions by colliding fast Na atoms with CH₃NO₂ molecules that had been oriented by state selection in a hexapole electric field. The steric asymmetry for all of the ions was determined to be essentially zero, in contrast to other molecules previously studied. This was surprising because CH₃NO₂ has a high dipole moment (3.46 D)⁹ and displays evidence of forming a dipole-bound negative ion.⁷,¹⁰ The electron in the dipole-bound state (DBS) is loosely bound in an extended orbital at the CH₃ end of the molecule, and formation of the DBS is mostly likely by an electron from the sodium atom attacking at the CH₃ end of the molecule. This was not observed, leading us to conclude that there was no evidence of the dipole-bound state participating in the subsequent chemical reactions. The experimental observations were consistent with a collisionally induced distortion of the molecule into a bent geometry¹¹ similar to that of the anion. Calculations showed that in the bent geometry, the LUMO changed into a largely π*NO₂ orbital with concomitant occupation of this orbital via sideways collisions.⁴

II. Experimental Section

Supersonic beams of CH₃NO₂ are generated by mixing ~150 Torr helium with vapor from liquid CH₃NO₂ at 0 °C (~9 Torr). The beam passes through an inhomogeneous hexapole electric field containing no beam stops. When high voltage (HV) is applied to the rods, molecules in low-field seeking states are deflected toward the axis, and the beam intensity increases. A weak, uniform electric field is maintained on the molecules as they fly from the hexapole to the reaction center so that the initially inhomogeneous electric field is smoothly transformed into a uniform electric field. The molecules make adiabatic transitions from the inhomogeneous field to the uniform field where they are oriented with the negative end of the dipole (NO₂ in this case) pointing toward the negative field plate. Changing the polarity of the uniform field changes the laboratory direction of the molecule.¹⁶

The CH₃NO₂ beam intersects a beam of K atoms produced in a charge-exchange oven. Neutral atoms are surface ionized inside the oven, accelerated toward a slit, and drift field-free through the oven where they charge-exchange to produce a beam of fast atoms. Residual ions in the beam are removed by...
electrostatic deflection plates external to the oven. The beams cross inside a uhv chamber at an angle of 90° between identical time-of-flight (TOF) mass spectrometers lying in the plane of the two beams and arranged so that the field is roughly along the relative velocity of the collision. One TOF is biased to the two beams and arranged so that the field is roughly along time-of-flight (TOF) mass spectrometers lying in the plane of the orientation is random, and this enables us to normalize the detector efficiency for the two different TOF polarities.18

III. Results

To relate the present studies with solution-phase thermal energy electron transfer, the reaction was studied near the threshold for ion pair formation, from nominal lab energies of 6−20 eV, corresponding to CM energies in the 4−7 eV range. Potassium reacts with CH₃NO₂ to form K⁺ ions to start the TOF clock. Electrons, parent negative ions, CH₃NO₂⁻, and the fragment ions, NO₂⁻ and O⁻, stop the clock. Signals for all of these ions increase when the HV is turned on, showing that they (and the K⁺) arise from reaction with CH₃NO₂. Ions at mle = 32 are observed, but these are independent of the HV and are almost certainly due to O₂ from a leak. At substantially higher collision energy, O⁻ might result from CH₃NO₂, but this was not observed nor further investigated.

Energy Calibration. The nominal laboratory energy of the fast K atoms is the voltage applied to the surface ionization filament, but the voltage drop along the filament and various contact potentials inside the oven make it necessary to calibrate the energy. These experiments are not designed to determine thresholds: the intensity of the fast atom beam drops precipitously as the energy is decreased because the original ion beam in the K oven is space-charge limited. The reaction cross sections also decrease with energy, and taken together, these effects produce small signals that vanish near the respective thresholds.

Nominal CM threshold estimates for various ions are determined by a method previously discussed.4 We are able to fit signal, S, vs nominal CM energies, E, with a quadratic curve $S = a(E - Th)^n$ (E ≥ Th), where a accounts for different beam intensities, Th is the threshold energy, and n = 2. (Thresholds for the electron and the parent ion, CH₃NO₂⁻, required using n = 1.) The corrected CM energy is obtained by plotting the true thresholds vs the nominal CM energies as shown in Figure 1. The calibrated energy is similar to that determined for sodium, but the earlier suggestion that NO₂⁻ might display a threshold ~0.2 eV too high is not observed here, indicating that the uncertainty in the energy is ~0.2 eV.

Steric Asymmetry. The energy dependence of the signals can easily overwhelm the steric dependence, and to focus on the steric dependence of the signal, we define the steric asymmetry factor as

$$G(i) = \frac{\sigma_-(i) - \sigma_+(i)}{\sigma_-(i) + \sigma_+(i)}$$

where $\sigma_+(i)$ is the cross section for forming ions of mle = i. Thus $G = 1$ if the reaction occurs only on the negative end of the molecule, $G = -1$ if the reaction occurs only on the positive end, and $G = 0$ if there is no preference for positive/negative end. Absolute cross sections are not measured, but relative cross sections can be obtained from the difference in signal measured with high voltage on and off (ΔHV). Differences in detector efficiency and collection are accounted for by using the signals from randomly oriented molecules obtained when the HV is off.18

The steric asymmetry measured for parent negative ions, CH₃NO₂⁻, and the fragment ions, electrons, O⁻, and NO₂⁻, are shown in Figures 2−4. Electrons are shown in Figure 2, and the steric asymmetry is very small, apparently indicating that electron transfer occurs mainly in sideways collisions. The signals from O⁻ are too small and scattered to interpret.

The asymmetry for the parent negative ion, CH₃NO₂⁻, is shown in Figure 3. It is again small, essentially constant over the energy range studied, and reflects a preference for sideways attack.

The asymmetry for NO₂⁻ is shown in Figure 4 and is completely different from either that of the parent negative ion or that of the electron. The asymmetry is not small, and the production of NO₂⁻ is favored by attack at the positive, CH₃ end. As we shall discuss, we believe that NO₂⁻-end collisions are more likely to form salt molecules. These are not detected, but their formation would decrease the number of ions that are detected. Thus, salt formation in NO₂⁻-end collisions would
decrease the NO$_2^-$ ions that are ultimately detected in NO$_2^-$ collisions, making it appear that collisions at the CH$_3$ end are more likely to produce ions.

There is evidence for a diminution in NO$_2^-$ production at the NO$_2$ end of the molecule. We make separate measurements of the reactivity at the positive end and at the negative end of the molecule, and it is useful to examine these separate reactivities. The increase in signal when the hexapole is energized, $\psi$HV, is due to oriented molecules, and the signal with no voltage applied to the hexapole, $\psi$HV off, is due to randomly oriented molecules. Because the randomly oriented molecules cannot be oriented, this signal is independent of the TOF polarities. The ratio, $R(\psi)$HV)($\psi$HV off measures the reactivity of oriented molecules (in the positive or negative orientation) relative to the reactivity of (a different number of) randomly oriented molecules.$^{18}$ These separate measurements of $R^+$ and $R^-$ are shown in Figure 5, which shows that $R^+$ and $R^-$ for the sodium reactions and $R^+$ for potassium are all essentially the same, but $R^-$ for potassium is much smaller. Thus, about the same number of NO$_2^-$ ions are detected for CH$_3$-end attack with both sodium and potassium and for NO$_2$-end attack with sodium. But fewer NO$_2^-$ ions are detected for NO$_2$-end attack with potassium. This shows that NO$_2$-end attack with potassium is less effective (compared to sodium) in forming NO$_2^-$.

Electron transfer to the molecule produces a transient molecular negative ion that can be either bound or produce fragment ions. The fractions of the various ions that are produced are shown in Figure 6. The stable parent ion is the most intense ion near the threshold and monotonically decreases as the energy is increased. The fraction of electrons initially increases, maximizes near 0.6 eV, and thereafter decreases because the channel to form NO$_2^-$ has opened at 0.4 eV. The ion fractions for the analogous sodium reaction are very similar: the position of the maximum is within 0.2 eV of that in Figure 5 (reflecting our uncertainty in the energy scale) and is somewhat narrower. For the electron transfer from sodium, the NO$_2^-$ fraction is smaller and the electron fraction is concomitantly larger.

IV. Discussion

Electron transfer from a potassium atom to a nitromethane molecule produces parent negative ions, CH$_3$NO$_2^-$, and fragment ions, e$^-$, O$^-$, and NO$_2^-$, in proportions that mainly depend on the energy. In some respects, the results are similar to earlier results obtained with sodium atoms: the steric asymmetry for forming electrons and CH$_3$NO$_2^-$ is very small and slightly negative, suggesting that the electron is mainly transferred in collisions broadside to the dipole, with perhaps a slight bias for the CH$_3$ end of the molecule.

Leaving aside for the moment the glaring difference in the steric asymmetry between Na and K for forming NO$_2^-$, the similarities in steric asymmetries can be discussed in terms of...
the rough potential energy curves shown in Figure 7. This figure, adapted\textsuperscript{4} from a coherent discussion by Walker and Fluendy\textsuperscript{19} summarizing the optical spectra and electron energy loss data, helps interpret the asymmetry data.

Theory and experiment\textsuperscript{19} agree that the CH\textsubscript{3}NO\textsubscript{2} LUMO is $\pi^*\text{NO}$; the anion is bent, and thus, the geometry for the neutral curve is different from that of the $^2\text{B}_1$ state of the anion. At the lowest energies in our experiments, the electron must be transferred to this orbital to produce the parent negative ion, CH\textsubscript{3}NO\textsubscript{2}$. Increasing energy will produce vibrationally excited states of the B state, which lie in the continuum of the neutral molecule and free electron, and the molecular negative ion will autodetach an electron. Because the B state comprises the $\pi^*\text{NO}$ orbital, the electron will prefer sideways orientations, and the steric asymmetry for forming both the electron and the parent negative ion should be essentially zero, as observed. Cleavage of the C–N bond occurs, giving NaNO\textsubscript{2} in thermal experiments\textsuperscript{14,15} and NO\textsubscript{2}$^-$ at higher energies, such as those described here, by populating the $^2\text{A}_1$ state either by direct electron transfer or by internal conversion from the $^2\text{B}_1$ state.

At first glance, it appears that NO\textsubscript{2}$^-$ is formed differently from the two atomic donors, and that the longer-range electron transfer from K might well be into a dipole-bound state located on the CH\textsubscript{3} end of the molecule. However, we believe this is not the case for the following reasons: (1) for both Na and K, the electron fraction peaks near the opening of the channel to produce NO\textsubscript{2}$^-$ and it appears that there is a common precursor (probably the $^2\text{B}_1$ state) for the species that autodetaches and for the species that ultimately produces NO\textsubscript{2}$^-$; (2) if the precursor to NO\textsubscript{2}$^-$ were formed by an electron transfer to the CH\textsubscript{3} end of the molecule, the increase in reactivity due to oriented molecules relative to the random sample would be higher for potassium than for sodium for CH\textsubscript{3}-end attack. Figure 5 shows that the reactivity of K is the same as for Na for CH\textsubscript{3}-end attack. Moreover, Figure 5 shows that the reactivity at the NO\textsubscript{2} end of the molecule is lower, probably because NO\textsubscript{2}$^-$ ions are combining with K$^+$ ions nearby. The steric asymmetry compares the reactivity at the two ends, so the “preference for CH\textsubscript{3}-end attack” shown in Figure 4 is consistent with smaller NO\textsubscript{2}$^-$ signals from the NO\textsubscript{2} end shown in Figure 5.

We conclude that the precursor to autodetachment and to formation of NO\textsubscript{2}$^-$ is the same and that this precursor is formed by broadside collisions in which the electron is transferred into the $^2\text{B}_1 (\pi^*\text{NO})$ state. For NO\textsubscript{2}-end collisions with K, the NO\textsubscript{2}$^-\text{CH}_3$ bond stretching\textsuperscript{23}.

Figure 7. Highly schematic potential energy curves for neutral CHNO\textsubscript{2} and the two lowest-lying anion states, $^2\text{B}_1 (\pi^*)$, and $^2\text{A}_1 (\sigma^*)$. The reaction coordinate is the C–N distance at large energies but includes different anion geometries at small distances. Dashed portions of the anion curves indicate regions where the anion autodetaches, giving the neutral molecule plus an electron.

Figure 8. Adiabatic potential energy curves (schematic) for the interaction of Na with I, showing an avoided crossing near 7 Å where the diabatic curves cross. Neutral atoms could form ions by colliding along the path shown by arrowheads.

flux is reduced by ion recombination to make salt molecules, which are not detected. In potassium reactions to form NO\textsubscript{2}$^-$, the methyl end has not become more reactive, but rather the NO\textsubscript{2} end has become less reactive.

Why should potassium atoms be more likely than sodium atoms to form salt molecules? Consider electron transfer in an atomic system such as Na + I, shown in Figure 8. Neutral atoms would collide on a surface initially and clearly characterized as covalent, and the full arrowheads illustrate their motion. The diabatic “covalent” and “ionic” curves appear to cross at a distance $r_c$, where $e^2r_c=IP-\Delta A$, $IP$ is the ionization potential of the donor atom, and $\Delta A$ is the electron affinity of the acceptor. At the avoided crossing, the system is shown to stay on the blue adiabatic surface, but as the particles come closer together, they are better described as “ionic” and the arrowheads are changed to reflect this different character.\textsuperscript{20} A full collision requires that the particles recombine from one another, and they must traverse the same avoided crossing on the way out. If they make a diabatic transition on the outbound crossing, they will stay on the ionic curve (full red arrowheads) and separate as ions, provided they have enough energy. (Another path exploring the upper “covalent” surface would also produce ions if the first crossing were diabatic and the second adiabatic. Either way requires one adiabatic and one diabatic crossing.) The probability of the transition being diabatic is usually given by the Landau–Zener theory as\textsuperscript{21,22}

$$P_d = \exp \left( -\frac{4\pi H_{IC}^2}{\hbar v_j \frac{d}{dr}(H_{II} - H_{CC})} \right),$$

where $H_{IC}$ is the off-diagonal matrix element coupling the ionic and covalent curves ($H_{II}$ and $H_{CC}$), $v_j$ is the radial speed of the system through the crossing, and the other term in the denominator is the difference in slopes of the diabatic curves at the crossing.

This simple picture is qualitatively useful for discussing the much more complicated case of an atom and molecule colliding. For molecules, more than one dimension is required, because the potential energy depends on many more coordinates and we must consider intersecting surfaces. An important consequence of the increased dimensionality is that the outbound avoided crossing can be different from the inbound crossing because the molecule could start to fall apart in the time between the crossings. This effect is known as “bond stretching”. It is
Curves are drawn a distance $R$ from the centers of the C, N, or O atoms, where explains the difference between Na and K, and this is shown in Figure 9.

**Figure 9.** Schematic difference between electron transfer in Na-atom and K-atom collisions with CH$_3$NO$_2$. The inner red cloverleaf approximates the distance where M$^+$/CH$_3$NO$_2^-$ ion pair is formed; the green outer cloverleaf approximates the distance where MNO$_2$ is formed.

this difference between the inbound and outbound crossings that explains the difference between Na and K, and this is shown in Figure 9.

The (red) inner curves in Figure 9 are drawn a distance $R_{IN}$ from the centers of the C, N, or O atoms, where $R_{IN}$ is the M$^+$CH$_3$NO$_2$ ionic–covalent crossing distances (Na = 2.9 Å; K = 3.5 Å) for the initial reagents. Similarly, the outer (green) curves are drawn a distance $R_{OUT}$, but now from the centers of the N and the two O atoms, where $R_{OUT}$ is the M$^+$NO$_2$ ionic–covalent crossing distance for the products (5 and 7 Å, respectively). If electron transfer occurs from K in this model, the K atom will lie inside of the capture radius for KNO$_2$ (the red cloverleaf lies entirely within the green). This crude model thus suggests that there is a good chance of making the salt regardless of the location of the K atom. For sodium, on the other hand, there is a region near the CH$_3$ end where the Na$^+$CH$_3$NO$_2$ ion pair could be made (shaded in the figure), but which is outside the capture radius for the salt. Thus, some Na atoms near the methyl end cannot escape as salt because they are too far from the NO$_2$ moiety. This model is clearly highly oversimplified ($H_R$ is angle dependent and the methyl group is more than a small perturbation), but the general idea is clear that potassium is more likely to form salt, especially if the K$^+$ lies anywhere near the NO$_2^-$ end of the molecule.

**V. Summary**

Ionic products have been detected in coincidence for electron-transfer collisions with potassium and CH$_3$NO$_2$ molecules oriented before collision. The steric dependence for electrons and parent negative ions, CH$_3$NO$_2^-$, is similar to that previously found for sodium collisions. But the steric asymmetry for forming the K$^+$/NO$_2^-$ ion pair shows a strong preference for CH$_3$-end attack near the threshold. Separate measurements of the positive-end and negative-end reactivities show that fewer NO$_2^-$ ions are detected for potassium when it is incident on the NO$_2$ end because K has a greater tendency to form the KNO$_2$ salt for NO$_2$-end attack. A crude Landau–Zener model shows that K has a larger capture zone for formation of the salt than does Na, supporting the experimental observations. Again, there is no steric evidence for participation of the dipole-bound state.

**Acknowledgment.** We gratefully acknowledge support received for this work from the Robert A. Welch Foundation and the National Science Foundation. Acknowledgment is made to the Donors of the American Chemical Society Petroleum Research Fund for partial support of this research. C.R. thanks the Ford Foundation for a Predoctoral Fellowship.

**References and Notes**