J. Phys. Chem. A **2006,** *110,* 4697−4701

Steric Asymmetry in Electron Transfer from Potassium Atoms to Oriented Nitromethane (CH_3NO_2) Molecules

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Received: January 13, 2006

Electrons are transferred in collisions between potassium atoms and CH_3NO_2 molecules that have been oriented in space prior to collision. The electron transfer produces K^+ ions, parent negative ions $CH_3NO_2^-$, and the fragment ions e^-, NO_2^-, 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 CH_3-end attack and NO_2-end attack. The steric asymmetry for electrons and $CH_3NO_2^-$ is essentially zero, but the steric asymmetry for NO_2^- shows that NO_2^- is formed mainly in CH_3-end collisions. There is evidence that the electrons and NO_2^- 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 NO_2^- ion, which is more likely to be removed as KNO_2 salt when K^+ ions are near the NO_2 end of the molecule, with the result that CH_3-end collisions seem to produce more NO_2^-.

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 ions[4−8] (e^-, O^-, NO_2^-, and $CH_3NO_2^-$). We recently studied how the orientation of the molecule affected the production of the various ions by colliding fast Na atoms with CH_3NO_2 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 CH_3NO_2 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 CH_3 end of the molecule, and formation of the DBS is mostly likely by an electron from the sodium atom attacking at the CH_3 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 geometry[11] similar to that of the *anion.* Calculations showed that in the bent geometry, the LUMO changed into a largely π^*_{NO} orbital with concomitant occupation of this orbital via sideways collisions.[4]

To further probe the possible participation of the dipole-bound state in these reactions, we have extended the studies of orientation dependence to the reaction of potassium with CH_3NO_2. Potassium has a smaller ionization potential than sodium (4.34 vs 5.14 eV),[12] which increases the distance at which the electron is transferred and decreases the interaction between the nascent ions. Earlier experiments comparing these atoms in reaction with CF_3Br suggested that potassium interacted less strongly than sodium[13] with the nascent CF_3Br^-. However, in the present experiments, the two are remarkably similar, with the glaring exception that more NO_2^- results when the K is incident upon the CH_3 end of the molecule. We believe that this is a consequence of electron transfer favoring a sideways attack,[14,15] followed by the evolution of NO_2^- ions that are removed as the KNO_2 salt if the K^+ ion is in the vicinity of the NO_2 end. There is no steric evidence for participation of the dipole-bound state.

II. Experimental Section

Supersonic beams of CH_3NO_2 are generated by mixing ∼150 Torr helium with vapor from liquid CH_3NO_2 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 (NO_2 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 CH_3NO_2 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

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10.1021/jp060265l CCC: $33.50

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.[17] One TOF is biased to detect positive ions and the other to detect negative ions; the field between the two TOF units is about 300 V/cm and is reversed by swapping the polarity of the mass spectrometers. Ions are detected by microchannel plates and counted in coincidence because there is no time zero: pulses from positive ions start a clock, which is stopped by pulses from negative ions (delayed 4 μs to ensure that pulses from electrons formed in collision arrive after the start pulse.)[18]

The reactivity for positive-end attack and negative-end attack is determined by acquiring spectra at various laboratory energies with the hexapole focusing voltage on and off and with the two different TOF polarities. When the hexapole is not energized (HV off) the molecular beam is totally unaffected and 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 CH_3NO_2 to form K^+ ions to start the TOF clock. Electrons, parent negative ions, $CH_3NO_2^-$, and the fragment ions, NO_2^- 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 CH_3NO_2. Ions at $m/e = 32$ are observed, but these are independent of the HV and are almost certainly due to O_2 from a leak. At substantially higher collision energy, O_2^- might result from CH_3NO_2, 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 $S = a(E - Th)^n$ ($E \geq Th$), where a accounts for different beam intensities, Th is the threshold energy, and $n = 2$. (Thresholds for the electron and the parent ion, $CH_3NO_2^-$, 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,[4] but the earlier suggestion that NO_2^- 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

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

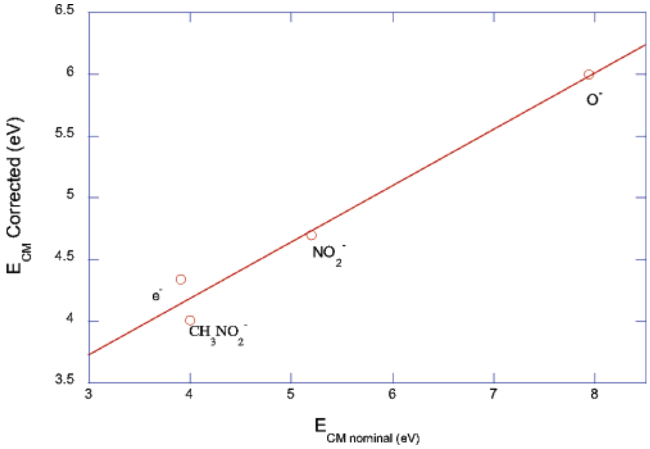


Figure 1. Energy calibration. Actual energy thresholds vs nominal experimental thresholds. Line is a least-squares fit.

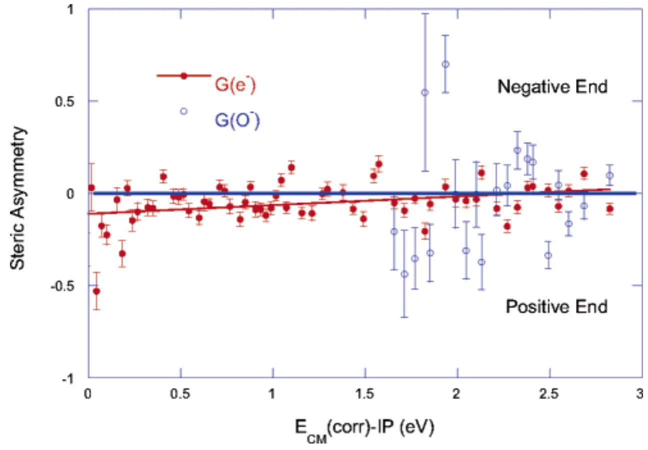


Figure 2. Steric asymmetry factors for electrons and O^- formed from nitromethane following electron transfer from K atoms. The line is a least-squares fit to the electron data.

where $\sigma_\pm(i)$ is the cross section for forming ions of $m/e = i$. 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, $CH_3NO_2^-$, and the fragment ions, electrons, O^-, and NO_2^-, 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, $CH_3NO_2^-$, 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 NO_2^- 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 NO_2^- is favored by attack at the *positive*, CH_3 end. As we shall discuss, we believe that NO_2-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 NO_2-end collisions would

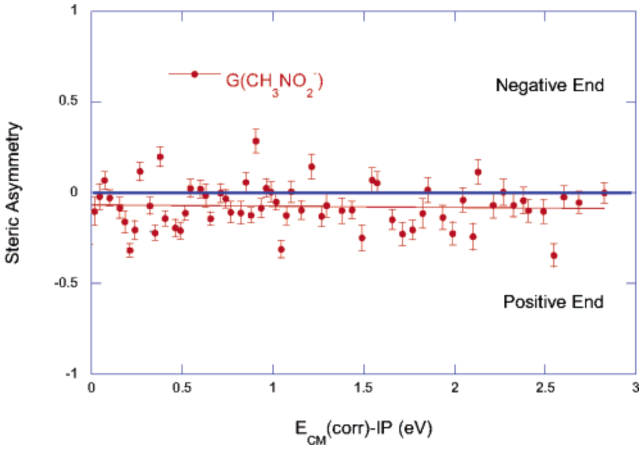


Figure 3. Steric asymmetry factor and linear least-squares fit for the parent negative ion, $CH_3NO_2^-$.

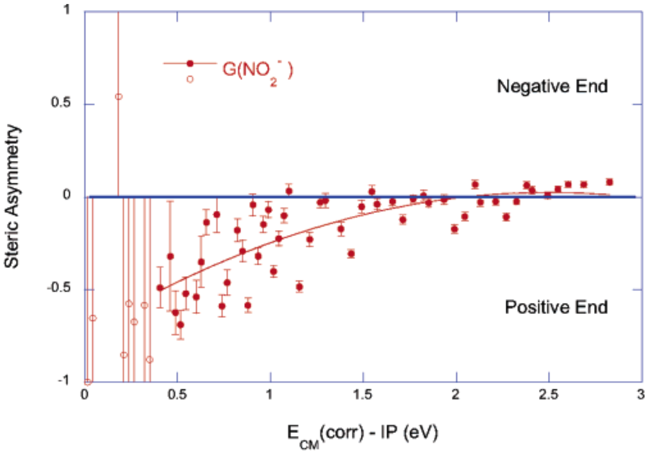


Figure 4. Steric asymmetry factor for formation of NO_2^-. Open symbols are data taken below the nominal threshold, and the line is a quadratic fit to the data above the threshold.

decrease the NO_2^- *ions* that are ultimately detected in NO_2-end 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, ΔHV, is due to *oriented* molecules, and the signal with no voltage applied to the hexapole, 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, $R_\pm = (\Delta HV)_\pm/HV_{off}$ measures the reactivity of *oriented* molecules (in the positive or negative orientation) relative to the reactivity of (a different number of) random 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^-.

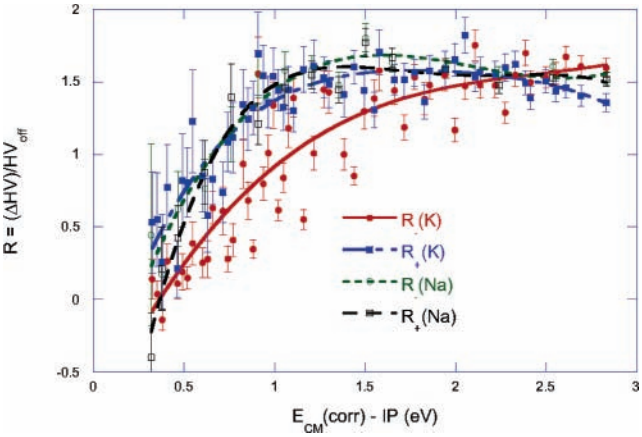


Figure 5. Increase in signal caused by focusing molecules in hexapole field relative to signal from **randomly** oriented molecules that pass through the field with HV = 0. Curves are 4th order polynomials, which smoothly represent the data. NO_2-end attack by potassium produces less NO_2^- than does CH_3-end attack and produces less NO_2^- than does sodium in either orientation.

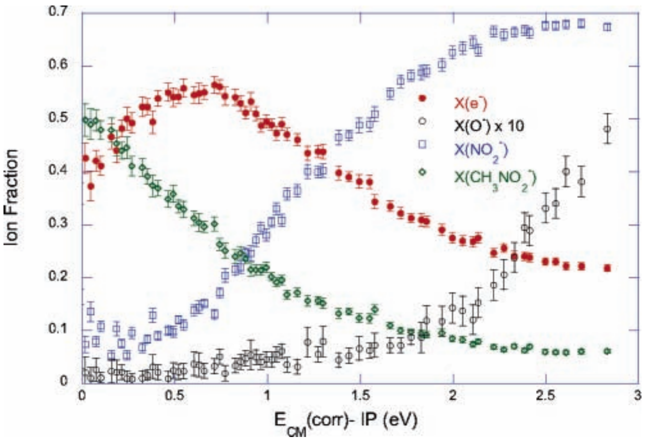


Figure 6. Average fractions of ions formed in positive and negative attack plotted vs collision energy. The formation of electrons is turned off by the opening of the channel to form NO_2^-.

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, $CH_3NO_2^-$, 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 $CH_3NO_2^-$ 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

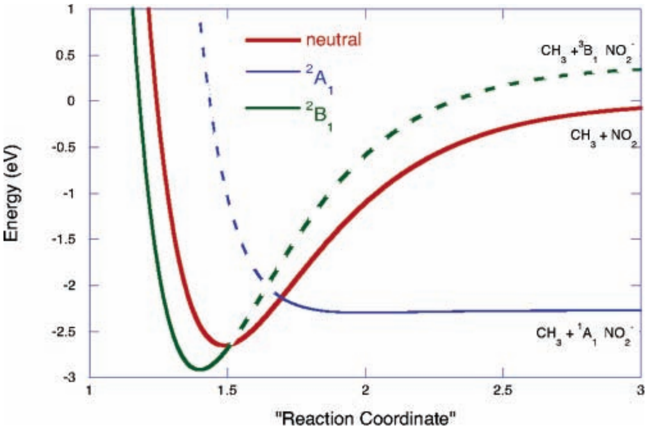


Figure 7. Highly schematic potential energy curves for neutral CH_3NO_2 and the two lowest-lying anion states, $^2B_1$ (π^*), and $^2A_1$(σ^*). The reaction coordinate is the C−N distance at large energies but includes different anion geometries at small distances. Dashed portions of the anion curves indicate regions where the anion autodetaches, giving the neutral molecule plus an electron.

the rough potential energy curves shown in Figure 7. This figure, adapted[4] from a coherent discussion by Walker and Fluendy[19] summarizing the optical spectra and electron energy loss data, helps interpret the asymmetry data.

Theory and experiment[19] agree that the CH_3NO_2 LUMO is π^*_{NO}; the anion is bent, and thus, the geometry for the neutral curve is different from that of the $^2B_1$ 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, $CH_3NO_2^-$. 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 π^*_{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 $NaNO_2$ in thermal experiments[14,15] and NO_2^- at higher energies, such as those described here, by populating the $^2A_1$ state either by direct electron transfer or by internal conversion from the $^2B_1$ state.

At first glance, it appears that NO_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_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_2^- and it appears that there is a common precursor (probably the $^2B_1$ state) for the species that autodetaches and for the species that ultimately produces NO_2^-; (2) if the precursor to NO_2^- were formed by an electron transfer to the CH_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_3-end attack. Figure 5 shows that the reactivity of K is *the same* as for Na for CH_3-end attack. Moreover, Figure 5 shows that the reactivity at the NO_2 end of the molecule is *lower,* probably because NO_2^- ions are combining with K^+ ions nearby. The steric asymmetry compares the reactivity at the two ends, so the "preference for CH_3-end attack" shown in Figure 4 is consistent with smaller NO_2^- signals from the NO_2 end shown in Figure 5.

We conclude that the precursor to autodetachment and to formation of NO_2^- is the same and that this precursor is formed by broadside collisions in which the electron is transferred into the $^2B_1$ (π^*_{NO}) state. For NO_2-end collisions with K, the NO_2^- flux is reduced by ion recombination to make salt molecules, which are not detected. In potassium reactions to form NO_2^-, the methyl end has not become more reactive, but rather the NO_2 end has become less reactive.

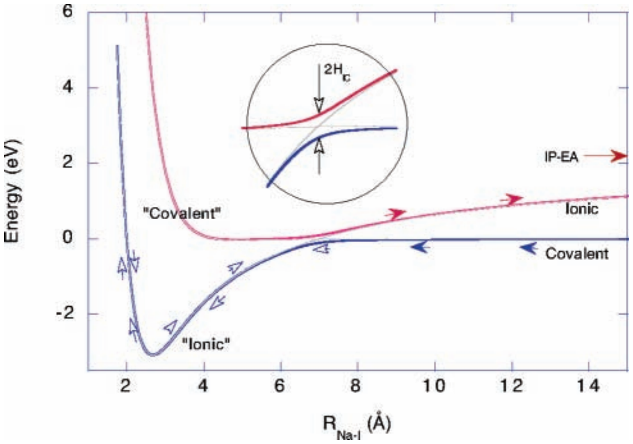


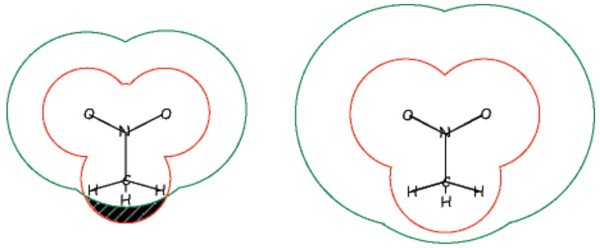
Figure 8. Adiabatic potential energy curves (schematic) for the interaction of Na with I, showing an avoided crossing near 7 Å where the diabatic curves cross. Neutral atoms could form ions by colliding along the path shown by arrowheads.

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 $e^2/r_c = IP - EA$, IP is the ionization potential of the donor atom, and EA 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.[20] A full collision requires that the particles recede 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[21,22]

$$P_d = \exp\left(\frac{-4\pi H_{IC}^{\ 2}}{h\upsilon_r\left|\frac{d}{dr}(H_{II} - H_{CC})\right|}\right)_{r_c}$$

where H_{IC} is the off-diagonal matrix element coupling the ionic and covalent curves (H_{II} and H_{CC}), υ_r 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[23]". It is



(Na) (K)

Figure 9. Schematic difference between electron transfer in Na-atom and K-atom collisions with CH_3NO_2. The inner red cloverleaf approximates the distance where the $M^+/CH_3NO_2^-$ 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 $M-CH_3NO_2$ 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 $Na-CH_3NO_2$ 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_{IC} 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_3NO_2 molecules oriented before collision. The steric dependence for electrons and parent negative ions, $CH_3NO_2^-$, 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.

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