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Steric Effects in Electron Transfer from Potassium to $\pi$-Bonded Oriented Molecules CH$_3$CN, CH$_3$NC, and CCl$_3$CN

Philip R. Brooks,* Peter W. Harland,† Sean A. Harris, Terry Kennair, Crystal Redden, and Jack F. Tate

Contribution from the Chemistry Department and Rice Quantum Institute, Rice University, Houston, Texas 77251

Received June 13, 2007; E-mail: brooks@python.rice.edu

Abstract: Electron transfer from K atoms to oriented CH$_3$CN, CH$_3$NC, and CCl$_3$CN is studied in crossed beams at energies near the threshold for forming an ion pair. For the methyl compounds, the dominant ions are K$^+$ and CN$^-$; the steric asymmetry is very small and energy-independent, characteristic of sideways attack with the electron apparently entering the $\pi^*$ orbital of the C=CCl bond. Migration of the electron to the $\sigma^*_{CC}$ orbital to break the C=CCl bond is greatly facilitated by interaction with the atomic donor. CH$_3$CN$^-$ is formed in collisions preferring CH$_3$-end attack, and the steric asymmetry becomes very large near threshold. CCl$_3$CN mostly forms Cl$^-$ in collisions slightly favoring the CCl$_3$ end with a small energy dependence with the electron apparently entering the $\alpha$ LUMO. CN$^-$ is formed in much smaller yield with a slight preference for the CN end. The parent negative ion CCl$_3$CN$^-$ is observed, and a lower limit for its electron affinity is estimated to be 0.3 eV. Fragment ions CCl$_2$CN$^-$ and CClCN$^-$ are also observed with upper limits for the quantity bond dissociation energy ($\text{BDE} - \text{EA}$) estimated to be 0.6 and 1.0 eV, respectively.

1. Introduction

Electrons bind nuclei together into molecules, and chemical reactions are a consequence of rearrangement of electrons around the nuclei involved. The transfer of electrons is thus fundamental to chemistry, but since few reactions produce charged particles under normal conditions, the participation of electrons is only rarely evident, such as in reactions in electric cells. But even though electron-transfer reactions are often disguised, they still play a central role in chemistry and biochemistry.1,2

The electron-transfer event is not the transfer of a free electron, but rather a curve-crossing between different diabatic electronic states3–5 approximately described by the Landau–Zener theory. For the case considered here, that theory considers the (avoided) crossing between a neutral diabatic potential energy curve and an ionic diabatic potential energy curve. The probability of an electron “jump” (actually an adiabatic transition from a neutral surface to an ionic surface) depends mainly on the species involved and their electronic potential surfaces. An electron may jump as the reagents approach or as the products recede. The overall probability can be very complex because the electron does not jump back.6 (This has been called “bond stretching” in simpler systems.) Without question, the electron-transfer process is a concerted event involving the properties of the donor and the acceptor.

Most chemical reactions lack the energy required to reach these curve crossings but occur in condensed phases because the solvent can act to activate the reagents and deactivate the product.8 This further complicates the overall process. To directly examine the electron-transfer event itself and avoid the obfuscation of the solvent, we study electron transfer from isolated atoms to simple isolated molecules in crossed molecular beams at collision energies high enough to separately detect the positive and negative ions formed by the electron transfer. This is still a concerted process, involving both the donor and the acceptor and their interaction but without the solvent. In contrast, free electrons can also interact with molecules in attachment processes that involve only the acceptor and are therefore not concerted reactions.9 Interactions with free electrons are of particular interest in studying the effects of radiation damage10–12 but are not directly related to the problem of electron transfer.

At energies close to the threshold for separating ions, the electron must be captured in the molecular LUMO, but the fate of the (probably unstable) transient negative ion depends on

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1 Present address: Chemistry Department, University of Canterbury, Christchurch, New Zealand.

Steric Effects in Electron Transfer to $\pi$-Bonded Molecules

2. Experimental Section

An atomic beam of hyperthermal potassium atoms intersects a beam of fast neutrals. Any residual ions are deflected out of the beam of fast neutrals. The time difference is read out by computer and the TDC is reset to await the next ion pair.

A computer acquires data and controls the experiment. For each energy of the atom chosen, coincidence TOF data are acquired for HV ~70 kV, molecules in some quantum states are attracted to the rods and defocused, whereas molecules in other states are deflected toward the axis and increase the intensity of the beam. These molecules are oriented in a (weak) electric field with $<\cos \theta > = \mathcal{M}/[\mathcal{J}(\mathcal{J}+1)]$, where $<\cos \theta >$ is the average of the cosine of the angle between the field and the top axis, and the quantum numbers $\mathcal{J}$, $\mathcal{K}$, and $\mathcal{M}$ correspond to the total angular momentum, its projection on the top axis, and its projection on the electric field, respectively. This deflection in the hexapole field selects molecules with $\mathcal{M} < 0$, corresponding to molecules in “high-energy” orientations where the positive end of the molecule points toward a positively charged plate. The molecules are oriented with respect to the local electric field, which gradually changes from that inside the hexapole to the uniform field between the two TOF mass spectrometers. The orientation of the molecule at the collision region can be changed by reversing the direction of the field, which is accomplished by interchanging the polarities of the TOF mass spectrometers.

The beams are continuous and the TOF voltages are DC so there is no time zero for the TOF. But an electron-transfer simultaneously produces a K$^+$ ion and a negative ion of unknown mass, and the difference in flight times is a signature of the mass of the negative ion. The ions in each mass spectrometer are detected with multichannel plate (MCP) detectors. The pulse from the positive ion MCP starts a time-to-digital converter (TDC), and the pulse from the negative ion MCP (after a 4 $\mu$s delay to ensure that the positive pulse always arrives first) stops the digitizer. The time difference is read out by computer and the TDC is reset to await the next ion pair.
on and HV off for positive-end approach and negative-end approach. The data acquired for HV off are from molecules that have not been state selected and are thus truly randomly oriented. These data are used to compare the sensitivities of the two MCP’s. The energies are randomly varied to avoid systematic drifts.

3. Results

3.1. Mass Spectra. Mass spectra of the negative ions for acetonitrile, CH$_3$CN, and methyl isocyanide, CH$_3$NC are very similar, but these differed enormously from that for trichloroacetonitrile, CCl$_3$CN, and are shown in Figure 1 for illustration. Although the count rate depends on the intensity of each beam, this was relatively constant for each molecule from run to run. Assuming beam intensity is proportional to the vapor pressure, cross sections relative to CN$^-$ from CH$_3$NC are evaluated from the average HV$_{ON}$ signal 3 eV above each ion’s threshold and plotted in Figure 1. Several points are apparent: whereas the cross section for forming CN$^-$ from CH$_3$NC is nearly the same for CH$_3$CN and CH$_3$NC, the cross section for forming CN$^-$ from CCl$_3$CN is some 2 orders of magnitude smaller. The cross section for forming Cl$^-$ from CCl$_3$CN is comparable to those for CN$^-$ from CH$_3$CN/CH$_3$NC, and the cross sections for forming CH$_3$CN$^-$ or CH$_3$NC$^-$ are about equal. Other ions are clearly produced in far smaller concentration. Electron signals for acetonitrile and methyl isocyanide apparently arise only from some background process, as previously reported.

3.2. Energy Calibration. To calibrate the collision energy, apparent laboratory thresholds were determined for each ion observed by plotting HV$_{ON}$ and HV$_{OFF}$ signals for positive end and negative end attack. The signal rates, $S$, for the various ions were fairly reproducible from day to day and these plots could be well-fit with a threshold and a quadratic for energies above threshold,

$$ S = a (E < E_{th}) $$

$$ S = a + b(E - E_{th}) + c(E - E_{th})^2 (E \geq E_{th}) $$

(1)

where $E$ is the accelerating voltage and $E_{th}$ is the apparent threshold. Thresholds are usually identical for positive end and negative end attack and representative thresholds are shown in Figure 2.

For any given ion pair, there is a minimum threshold energy, $E_{th}$, required to separate the ions so that they can be detected,

$$ E_{th} \geq IP + BDE - EA $$

(2)

where IP is the ionization energy of the alkali metal (K), EA the electron affinity of the species forming the negative ion, and BDE the bond dissociation energy of any bond that is broken. The inequality arises because one or more of the fragments could be excited. For various well-characterized ions (e$^-$, CN$^-$, CH$_3$CN$^-$, etc) thresholds could be calculated from values in the NIST webbook. Other salts such as Cl$^-$ from CCl$_3$CN relied upon bond dissociation energies estimated from related compounds. The center-of-mass thresholds from eq 2 were transformed to laboratory collision energies and plotted vs the experimental voltage thresholds as shown in Figure 3. Laboratory energies are used for this plot to display thresholds for CCl$_3$CN as well as those from CH$_3$CN and CH$_3$NC. Using the calibration from Figure 3, we evaluate the corrected lab energy for each accelerating voltage, and from the corrected lab energy, we calculate the CM energy. This energy will be used in subsequent plots.
Steric Effects in Electron Transfer to π-Bonded Molecules

ARTICLES

3.3. CH3CN and CH3NC. Electron transfer to acetonitrile (CH3CN) and methyl isocyanide (CH3NC) is remarkably similar. Both molecules yield mainly CN− with small amounts of CH3CN− and CH2NC− produced as the energy is increased. Very small signals corresponding to electrons and H− are observed, but the H− signal increases when the HV is applied whereas the electron signal does not. Since the HV focuses the symmetric top molecules, the beam intensity increases and the signals from reaction products involving the symmetric top molecule must also increase. The electrons observed are not from a molecule that focuses and are thus from some background process and not from CH3CN. A signal from O2− is also frequently observed (and is also independent of the HV), apparently from oxygen not removed by the freeze–thaw cycles. The O2− signals were helpful for mass and energy calibration, and no effort was made to eliminate them.

Signals from CN− require that the CH3−CN or CH3−NC bond be broken, and since these have different strengths, the CN− thresholds are considerably different, as shown in Figure 4. The energy has been calibrated using the data in Figure 2, and the thresholds shown, 4.03 and 5.56 eV, differ slightly from the results calculated using the literature, 4.84 and 5.73, reflecting an uncertainty of ~0.2 eV in our energy calibration.

The signals shown in Figure 4 suggest that production of CN− is favored for negative-end attack. Although this is true, the absolute signal (or difference here) also reflects swapping detectors to reverse the orienting electric field. We eliminate any detector bias by comparing signals obtained with the HV focusing field turned off: the molecules are truly randomly oriented when the HV is off and the signals are normalized to be identical.16

After normalizing the HV OFF signals we evaluate the experimental steric asymmetry factor, defined as

\[ G(E) = \frac{\sigma_-(E) - \sigma_+(E)}{\sigma_-(E) + \sigma_+(E)} \]

where \( \sigma_\pm (E) \) is the energy-dependent cross section for attack at the positive or negative end of the molecule. The steric asymmetry factor for CN− is shown in Figure 5 and that for CH3CN− is shown in Figure 6. For CN− from CH3CN the steric asymmetry is very small and slightly favors the CN end of the molecule. There is no dependence on energy, and the data for CH3CN are scattered about the line through the CH3CN data. (More data were taken with CH3CN because it was readily

Figure 4. HVON−HVOFF signal rates vs energy for CN− from CH3NC (round points) and CH3_CN (diamonds). Curves are least square quadratic fits with the thresholds indicated.

Figure 5. Steric asymmetry factor for producing CN− from CH3CN (red symbols) or from CH3NC (blue squares). Filled symbols refer to data taken using a tungsten wire in the charge exchange oven, open symbols taken using a rhenium wire. Thresholds for the molecules are denoted by arrows. The line is a linear least-square fit through the CH3CN data taken using a rhenium filament.

Figure 6. Steric asymmetry factor for producing CH3CN− from CH3CN (red circles) or CH3NC (blue squares). The thresholds are different and denoted by arrows. The curve is a smooth line drawn through the CH3CN data taken with a rhenium filament and is included only to show trend available.) The small value of G and its apparent energy independence strongly suggests that sideways attack is preferred for producing CN−.

The signals at mle = 40, corresponding to CH3CN− are much smaller than those at mle = 26 (CN−), and the steric asymmetry is a bit more scattered, but Figure 6 shows that attack at the positive (CH3) end of the molecule is clearly favored. The preference for CH3-end attack is strongest at energies near threshold and fades to zero as the energy is increased.

The signals at mle = 1 (H−) are very small but clearly depend on the hexapole voltage so they arise from CH3CN molecules. The steric asymmetry factor for H− is scattered, but as shown in Figure 7 the steric asymmetry for H− resembles that for forming CN− and is different from that for CH3CN−, the complementary ion formed if the C=H bond is broken.

Figure 8 shows the average ion fractions \( X = (X_+ + X_-)/2 \) as a function of energy, where \( X_\pm \) denotes the fraction in the positive or negative orientation. (The average is used because a steric effect for any one ion affects all the fractions and would be misleading.) The signal at mle = 1 (H−) is typically <1% of the signal, and we were not able to determine the threshold very well. The threshold for producing CH3CN− is about 7.5
eV and as that ion (and also apparently the H\(^-\)) is formed, the fraction of CN\(^-\) produced begins the fall off.

### 3.4. CCl\(_3\)CN. Ions Formed.

CCl\(_3\)CN is in many respects more interesting than CH\(_3\)CN/CH\(_3\)NC not only because the signal is higher at a given LAB energy, but also because more ionic species are formed. Negative ions were produced by CCl\(_3\) - CN collisions at nominal values of \(m/e\) 0, 26, 35, 73, 108, and 143, corresponding to the species e\(^-\), CN\(^-\), Cl\(^-\), ClCCN\(^-\), Cl\(_2\)CCN\(^-\), and Cl\(_3\)CCN\(^-\) (the parent ion). The chlorine isotopes caused broadening of the mass peaks for all the Cl-containing species.

The fraction of ions observed as a function of energy (analogous to Figure 8 for CH\(_3\)CN) is shown in Figure 9. The dominant ion is clearly Cl\(^-\) rather than CN\(^-\) which is not surprising since the C-Cl bond is \(\sim 2\) eV weaker than the C-CN bond. (The electron affinity of CN is only slightly greater than that of Cl.) CN\(^-\) increases exponentially from a threshold near 5.5 eV, and the parent negative ion decays exponentially with energy as expected. The free electron is always a very small signal and it should be noted that it does not increase at the expense of the parent negative ion, so the parent ion is chemically decomposing rather than auto-detaching an electron. Cl\(_2\)CCN\(^-\) is present in appreciable concentrations and the energy dependence is unusual.

Threshold energies were determined (after energy calibration) for the electron and the ions CN\(^-\), Cl\(^-\), CICC\(^-\), Cl\(_2\)CCN\(^-\), and Cl\(_3\)CCN\(^-\). The experimental and theoretical thresholds for the electron, CN\(^-\) and Cl\(^-\) agree reasonably well but they were used for calibration. Three of the ions, CICC\(^-\), Cl\(_2\)CCN\(^-\), and Cl\(_3\)CCN\(^-\), were not used in the calibration. In the case of the two fragment ions, the absence of reliable values for the BDEs precludes a realistic estimate of electron affinities but their thresholds may be used to deduce new information for the quantity (BDE - EA) and these are shown in Table 1. For the parent ion, where no molecular bond is broken, the threshold relation of eq 2 simplifies to

\[ E_{th} = g \times IP - EA \]

and EA is estimated to be \(\approx 0.3\) eV. The uncertainty in the values deduced from the thresholds could be as high as 0.2 eV as noted above.

### Steric Asymmetry.

The steric asymmetry factors for the various ions formed in the electron transfer from potassium to CCl\(_3\)CN are shown in Figures 10–14. In each case, the steric asymmetry factors are compared with those for the major ion, Cl\(^-\). Figure 10 clearly shows that the steric asymmetry for Cl\(^-\) and for CN\(^-\) is completely different: CN\(^-\) prefers negative-
end (CN-end) attack whereas Cl- slightly prefers positive-end (CCl3-end) attack. The steric asymmetry factor for CH3CN from Figure 5 is also plotted in Figure 10. Obviously the CN- steric asymmetry factors are significantly different for the two molecules. The steric asymmetry for Cl- is not only larger than that for CN- from acetonitrile but also shows a distinct energy dependence, and suggests that Cl- is likely to be formed by CCl3-end attack collisions.

Because of the smaller signals involved, less definitive conclusions can be reached with respect to the other ions formed. Figures 11 and 12 show that the free electron and the parent negative ion, CCl3CN- have very similar steric asymmetry factors possibly arising from a common precursor. Figures 13 and 14 show that CCl2CN- and CClCN- have different steric asymmetry factors from Cl- at higher energies, even though all of these ions involve rupture of the C-Cl bond.

4. Discussion

CH3CN/CH3NC. Acetonitrile and methylisocyanide behave similarly. Figures 5 and 6 show that while the molecular orientation has a large effect on the production of the cyanomethyl anion, CH2CN-, it has virtually no effect on the formation of the CN- anion, the major product following electron transfer. The steric asymmetry factor for CN-, G(CN-) = 0.05 and is independent of energy. It is not zero and reaction is only slightly favored by approaching the CN end of the molecule. In contrast, the steric asymmetry for CH2CN- depends on energy and favors approaching the CH3 end of the molecule. Hydride ions, H-, are formed, but in concentrations too low to evaluate the steric asymmetry. The parent negative ion, CH2CN-, is apparently not formed nor is the electron as we have observed in CH3NO2,29,30 t-butyl Br, 15,16 and CCl3CN.

In our preliminary report22 we concluded that CH2CN- was formed by attack at the CH3 end of the molecule but we were unable to rule out the importance of sideways attack in forming CN-. Whereas steric asymmetry factors for electron transfer into the ð* LUMO's found in saturated species such as CH3Br tend to be large and strongly energy dependent, the steric asymmetry factor for electron transfer into the ð* orbital of CH3NO2 was very small and essentially energy independent. Because of the very small, energy independent G(CN), we now believe that formation of CN- from CH3CN or CH3NC is favored by sideways attack, with the electron being transferred into the ð*CN LUMO. Similar behavior was observed in transfer to the ð*NO orbital in CH3NO2.29,30

A variety of experimental and theoretical evidence shows that the 3e ð*CN orbital is the LUMO in CH3CN.31 Photoelectron spectra characterize the occupied orbitals and different electron bombardment experiments interrogate the unoccupied orbitals. These experiments with free electrons include the following: (a) The overall transmission of a beam of energy selected

electrons reveals “resonances” in the cross section for transmission corresponding to transient states in the (electron + molecule) continuum. Measuring the energies of these resonances determines the vertical attachment energy of the transient negative ion, and the width of the resonance gives information about the lifetime of the transient negative ion via the uncertainty principle.\(^{(32)}\)\(^{(33)}\)\(^{(34)}\)\(^{(35)}\)\(^{(36)}\)\(^{(37)}\)\(^{(38)}\)\(^{(39)}\) (b) Transient negative ions are unstable and can decay by autodetaching an electron, with, perhaps, an energy different from the incident energy because the electrons have excited a vibration of the neutral molecule. Careful measurement of the energy loss of the electrons thus gives information about which vibrational modes have been excited.\(^{(35)}\) (c) The (energized) transient negative ion can decompose to give daughter ions, and identifying the ions and determining their energy dependence helps understand the fate of the excited transient negative ion.\(^{(19)}\)\(^{(20)}\)

For acetonitrile (and somewhat similarly for methyl isocyanide), electron transmission measurements show broad resonances near 2.9 and 6.7 eV.\(^{(33)}\)\(^{(34)}\)\(^{(36)}\)\(^{(37)}\) The resonance near 2.9 eV is similar to that in HCN and is attributed to capture into the doubly degenerate \(\pi^*_{CN}\) orbital. Electron energy loss spectroscopy at the 2.9 eV \(\pi^*\) resonance shows excitation of the \(v_2\) (\(C≡N\) stretch) and \(v_8\) (\(C–C≡N\) bend) vibrations, whereas at the 6.7 eV \(\sigma^*\) resonance the spectra are dominated by \(\text{CH}\) stretching modes, nicely corroborating molecular orbital predictions that the LUMO is 3e (\(\pi^*_{CN}\)) and the LUMO+1 is the 8a1 \(\sigma^*\) orbital.\(^{(34)}\)

Dissociative attachment of free electrons also supports resonances near 3 and 6 eV, producing at low energy (in order of abundance) \(\text{CH}_2\text{CN}^–\), \(\text{CHCN}^–\), and \(\text{CN}^–\). The \(\text{CN}^–\) signal is only about 1% of the \(\text{CH}_2\text{CN}^–\) signal at low energies\(^{(19)}\)\(^{(20)}\) in contrast to the present experiments where \(\text{CN}^–\) is about \(100\times\) the \(\text{CH}_2\text{CN}^–\) signal. MNDO calculations for the radical anions for various saturated nitriles show that the HOMO (for the anion) is the antibonding \(\pi^*_{CN}\) orbital with the excess charge centered on the CN. Formation of ground state \(\text{CN}^–\) requires that the \(\pi^*\) electron move to the \(\sigma^*_{CC}\) orbital which could occur via a predissociation where the \(\Pi\) and \(\Sigma\) curves cross as suggested in Figure 15.

From these theoretical and experimental observations we believe that the following picture emerges for low-energy electron transfer: Electrons are attached to \(\text{CH}_3\text{CN}\) by entering the \(\pi^*_{CN}\) orbital in the ground state geometry to give a transient negative ion of \(\Pi\) symmetry. This state lies in the electron−molecule continuum, being unstable with respect to autodetachment and having lifetime \(\approx\) femtoseconds. To form \(\text{CN}^–\), the \(\Pi\) state must live long enough to predissociate to the \(\Sigma\) state and the rapid autodetachment of the electron makes this unlikely. This accounts for the low yield of \(\text{CN}^–\) in the dissociative attachment experiments using free electrons. In the present experiments, however, the electron is not free, but is transferred from a potassium atom, and this significantly changes the simple picture painted above. Our previous experiments using different alkali metal atoms show that different donor atoms markedly affect not only the steric asymmetry but also the products formed.\(^{(18)}\) The potassium atom could induce a bending in the molecule as we have seen in the case of \(\text{CH}_3\text{NO}_2\)\(^{(29)}\) and affect the initial transfer or simply enhance the probability of the \(\Sigma–\Pi\) predissociation (Clark and Coulson proposed a similar mechanism for electron attachment in halobenzenes and noted that since a third body was involved a pressure dependence might be observed\(^{(38)}\)). The K atom could also be considered to quench the formation of \(\text{H}_2\text{CCCN}^–\) by opening the channel to the formation of \(\text{CN}^–\). Theoretical work\(^{(39)}\) also suggests that the K atom plays an important role in the process.

In summary, in the present electron-transfer experiments the steric asymmetry of the \(\text{CN}^–\) is nearly zero and is energy independent. This is not typical of alkyl halides, and \(\text{CN}^–\) is not simply a “super halogen.” The electron-transfer experiments produce \(\text{CN}^–\) in attack of the K atom “sideways” to the axis of the \(\text{CH}_3\text{CN}\) molecule. The electron is transferred to the \(\pi^*_{CN}\) orbital to produce a \(\Pi\) transient negative ion and interaction between the incipient \(\text{CH}_2\text{CN}^–\) and \(\text{K}^+\) enhances the curve crossing to the \(\Sigma\) state producing more \(\text{CN}^–\) than would be produced in the absence of the atomic interaction. (In the free electron experiments, the \(\Sigma–\Pi\) transition is not facilitated, and \(\text{CN}^–\) is far less likely to be formed.) The cyanomethyl anion, \(\text{CH}_2\text{CN}^–\) is preferentially produced in \(\text{CH}_3\)−end attack, with the electron being transferred into the \(\sigma^*\) LUMO+1. The large dipole moment for \(\text{CH}_3\text{CN}\) supports a dipole-bound state with a binding energy of \(\approx\) 12 meV,\(^{(40)}\) but the interaction between the nascent ions is apparently sufficiently large that we see no steric evidence for their participation.

**CCl\(_3\)CN.** The dominant signal from \(\text{CCl}_3\text{CN}\) is from \(\text{Cl}^–\) (even accounting for the fact that there are 3 C\(_\text{Cl}\)’s). Gaussian calculations showed that the LUMO for this molecule had changed to an orbital with \(\sigma^*\)\(_\text{CCl}\) character, and the steric asymmetry strongly resembles that from chloroform measured earlier.\(^{(17)}\)

The \(\text{CN}^–\) signal from \(\text{CCl}_3\text{CN}\) shows a much larger steric asymmetry than does \(\text{CN}^–\) from \(\text{CH}_3\text{CN}\), due partly to the better

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**Figure 15.** High-schematic potential curves for \(\text{CH}_3\text{CN}\), suggesting that vertical (Franck-Condon) attachment of an electron would produce a transient negative ion in a \(\Pi\) state evolving to excited \(\text{CN}^–\). A collision-enhanced predissociation from the \(\Pi\) state to the \(\Sigma\) state is necessary to give ground state \(\text{CN}^–\).
the rotationally averaged dipole moment and the extant are better oriented.

less prolate, higher values of \( K \) are populated and the molecules

\[
E_{\text{rot}} = Bh(J + 1) + (C - B)hK^2 \quad K = J, J - 1, \ldots, -J
\]

where the rotational constants are \( B = [h(8\pi^2 I_B)] \) and \( C = [h(8\pi^2 I_C)] \) and \( I_C, I_B \) are the moments of inertia about the unique \((C_i)\) axis of rotation and about an axis perpendicular to the \( C_i \) axis. High orientation thus requires rotational states with \( K \approx J \) which is favored by Boltzmann statistics if \( B > C \), \((I_C > I_B)\) [an oblate top] as exemplified by a bicycle wheel spinning about its axis. If \( C > B \), [a prolate top] as exemplified by a pencil spinning about its axis (or \( \text{CH}_3 \text{CN}\) ) high values of \( K \) are not favored by Boltzmann statistics. Thus it is much easier to spin \( \text{CCl}_3 \text{CN} \) about its axis than it is to spin \( \text{CH}_3 \text{CN} \) about its axis, favored by Boltzmann statistics. Thus it is much easier to spin \( \text{CCl}_3 \text{CN} \) about its axis than it is to spin \( \text{CH}_3 \text{CN} \) about its axis, and the distribution of orientations, \( P(\cos \theta) \), in our oriented beams is quite different between the two molecules. We have calculated \( P(\cos \theta) \) for the present molecules and for \( \text{CCl}_3 \text{H} \) for comparison using a procedure discussed elsewhere. This distribution can be characterized using a fourth-order Legendre polynomial fit

\[
P(\cos \theta) = \sum_{\ell=0}^{3} a_\ell P_\ell(\cos \theta)
\]

where \( P(\cos \theta) \) are the Legendre polynomials and \( a_0 = 0.5 \). The coefficients \( a_\ell \) are listed in Table 2 for the \( \text{HV}_{\text{ON}} - \text{HV}_{\text{OFF}} \) distribution together with \( <\cos \theta> \). As the molecules become less prolate, higher values of \( K \) are populated and the molecules are better oriented.

It is important to realize that the angle \( \theta \) is the angle between the rotationally averaged dipole moment and the extant electric field so the probability distribution \( P(\cos \theta) \) in the lab is the same for positive and negative attack orientations. The \( K \) atom explores the same distribution from different directions because the electric field is parallel to the \( K \) atom velocity in the negative-end attack orientation and antiparallel in the positive-end attack orientation.

We have used a simple cone-of-acceptance model to account for the different orientation distributions where the reaction probability is assumed to be one for attack angles less than some critical value, \( \chi_0 \), and zero otherwise. Integrating this model over the positive and negative attack orientations and comparing with the steric asymmetry factor gives \( \chi_0 \) for each energy. The values obtained are shown in Figures 17 and 18 for \( \text{CN}^- \) formation, respectively, together with sketches roughly indicating the different half angles. The allowed angles for \( \text{CH}_3 \text{CN} \) and \( \text{CH}_3 \text{NC} \) are about the same, \( \sim 155^\circ \), showing that any angle of attack is productive except for a \( 25^\circ \) half-angle cone at the \( \text{CH}_3 \) end. This cone apparently arises from some hard barrier since increasing the collision energy fails to overcome it. The cone of acceptance for producing \( \text{CN}^- \) from \( \text{CCl}_3 \text{CN} \) and \( \text{CCl}_3 \text{H} \) \( \chi_0 \) is measured from \( \text{Cl}_3 \) end, and lines are least-square fits.

| Table 2. \( \text{HV}_{\text{ON}} - \text{HV}_{\text{OFF}} \) Legendre Coefficients |
|-------------------------|---|---|---|---|
| \( a_0 \) | \( a_1 \) | \( a_2 \) | \( a_3 \) | \( R \) |
| \( \text{CH}_3 \text{CN} \) | -0.456 | -0.076 | -0.076 | 0.9986 | -0.304 |
| \( \text{CH}_3 \text{NC} \) | -0.469 | -0.067 | -0.071 | 0.9986 | -0.313 |
| \( \text{CCl}_3 \text{CN} \) | -0.723 | 0.111 | 0.027 | 0.99995 | -0.48 |
| \( \text{CCl}_3 \text{H} \) | -0.846 | 0.232 | 0.016 | 0.99996 | -0.56 |

\[ \text{Figure 16. Quantum probability distribution } P(\cos \theta) \text{ vs } \cos \theta \text{ calculated for } \text{HV}_{\text{ON}} - \text{HV}_{\text{OFF}} \text{ using apparatus geometry and molecular constants. Horizontal dash-dot line is for a random beam. The average } \cos \theta \text{ for } \text{CCl}_3 \text{CN} \text{ and } \text{CH}_3 \text{CN} \text{ are indicated by vertical bars with sketches of molecules with that orientation.} \]

\[ \text{Figure 17. Half angle of cone of acceptance for forming } \text{CN}^- \text{ from } \text{CH}_3 \text{CN}, \text{CH}_3 \text{NC}, \text{and } \text{CCl}_3 \text{CN}. \chi_0 \text{ is measured from } \text{Cl}_3 \text{ end, and lines are least-square fits.} \]

\[ \text{Figure 18. Half angle of cone of acceptance for forming } \text{Cl}^- \text{ from } \text{CCl}_3 \text{CN} \text{ and } \text{CCl}_3 \text{H}. \]
5. Summary

Electron transfer from potassium atoms to beams of oriented CH₃CN, CH₃NC and CCl₃CN gives K⁺ and various negative ions that are identified by coincidence time-of-flight mass spectrometry. The dominant ion from CCl₃CN is Cl⁻. All species produce CN⁻ (although its formation from CCl₃CN is severely depressed in favor of Cl⁻) CX₂CN⁻ (X = H or Cl) and small amounts of other ions. CCl₃CN produces a parent negative ion, CCl₃CN⁻ and ions corresponding to the removal of one or two chlorine atoms from the parent negative ion, CCl₂CN⁻ and CClCN⁻. The quantities (BDE - EA) for CCl₂CN⁻ and CClCN⁻ are estimated to be ≤0.6 and ≤1.0 eV, respectively, and the electron affinity of the molecular ion CCl₃CN⁻ is estimated to be ≥0.3 eV.

The steric asymmetry factors for CN⁻ from the methyl compounds are similar, energy independent and very close to zero, ever so slightly favoring the negative CN end of the molecule. This seems to be a signature of molecules that prefer sideways attack and we conclude that the electron is accepted into the πCN* LUMO. A cone-of-acceptance model suggests that all angles of attack are successful in initiating reaction except for a small cone-of-exclusion of half angle ~25° at the CH₃ end of the molecule. The steric asymmetry factor for CH₂CN⁻ strongly favors the positive CH₃ end and the absolute value becomes larger as the energy is decreased toward threshold, consistent with electron transfer into a σ* orbital at the CH₃ end of the molecule.

The steric asymmetry factor for CN⁻ from CCl₃CN is slightly larger (and noisier), favoring the negative end of the molecule. A cone of exclusion at the CCl₃ end appears to have a half angle ~55°. The dominant Cl⁻ ion is formed in attack of the σCC* LUMO at the positive end of the molecule, and these steric preferences confirm that the CN end of the molecule is still negative as would be predicted by dipole vector addition.

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