Effect of Isotopic Substitution upon the Gas Phase and Solution Electron Affinities of Nitrobenzene

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Abstract: Ion cyclotron resonance and electron spin resonance have been utilized to determine the equilibrium constant for the electron transfer from the nitrobenzene anion radical to 15N labeled nitrobenzene (Ph13NO2− + Ph15NO2 = Ph14NO2 + Ph15NO2−). It was found that the equilibrium constant is within experimental error of unity at 305 K. Molecular orbital calculations indicate that this might be accounted for by the shortening of the C=N bond and a counterbalancing lengthening of the N-O bonds upon electron attachment to nitrobenzene. An equilibrium constant that is much larger than unity can be observed in liquid ammonia at 208 K when K+ serves as the gegenion (K+ = 2.1). However, when Na+ serves as the gegenion, the solution electron affinity of Ph14NO2 is greater than that of Ph15NO2 (K+ = 0.4). These results are explained in terms of ion association. When the hydrogen atoms are replaced with deuterium, the gas phase electron affinity is decreased. A similar decrease is observed in liquid ammonia. In the gas phase this is attributed to the slight lengthening of all the C–H bonds upon electron attachment.

The equilibrium constant controlling the solution phase electron transfer between the naphthalene anion radical (NP−) and per-deuteriated naphthlene (NP-d6) has been shown to be significantly below unity (eq 1) and invariant with solvent choice. This

\[
\text{NP}^- + \text{M}^+ + \text{NP-d6} = \text{NP} + \text{NP-d6}^- + \text{M}^+ \tag{1}
\]

\[\Delta G^\circ = 410 \text{ cal/mol at } -120 \degree\text{C} \]

is due to the net reduction in molecular bond energy that is observed as NP is reduced to NP− coupled with the differences in the zero-point energies of NP and NP-d6.1,2 The facts that K+ is well below unity and the chemical reactivity of the anion radical is different than that of the neutral NP have allowed the use of reaction 1 for the enrichment of NP-d6 from a mixture of deuteriated and undeuteriated naphthalenes.1 Extrapolating from the above result, one might expect a similar displacement of the equilibrium involving the transfer of an electron from any anion radical to the corresponding neutral system where an atom residing at a position of high spin and charge density has been replaced with a heavier isotope of that atom. This idea could be nicely tested with the nitrobenzene (Ph3NO2−) system and its 15N analogue (Ph3NO2−). The nitrobenzene anion radical has a very large spin and charge density on the nitrogen atom.3 Further, the spin and charge densities on the nitrogen can be varied dramatically via changes in the solvent and/or counterion. The IR and Raman spectra for tetracyanoethylené (TCNE) that have been reported by Devlin and co-workers4,5 show that reduction of TCNE to the anion radical results in a lowering of the force constant for the C–C bond from 6.59 to 5.43 mdyn/Å. A similar decrease in the force constant for the C–N bond is observed. The reverse effect is seen for the C–C single bond; in this case the force constant increases upon reduction. Very similar results were obtained from the vibrational analysis of 7,7,8,8-tetracyanoquinodimethane (TCNO) and its 15N analogue (Ph3NO2−). The overall effect of the addition of an electron to conjugated molecules is best characterized as a strengthening of single bonds and a weakening of multiple bonds with a net reduction in bond order.7 Since the nitrogen atom in nitrobenzene is involved in both single and multiple bonding to the neighboring atoms, this simple generalization does not allow a prediction as to the direction in which the equilibrium for reaction 2 will lie. However, by changing

\[
\text{Ph3NO2}^- + \text{Ph3NO2} = \text{Ph3NO2} + \text{Ph3NO2}^- \tag{2}
\]

the spin density upon the NO2 group via changes in the solvent system, it should be possible to significantly alter the free energy of reaction 2. This prediction, if born out, would be in contrast to the results obtained for reaction 1, where the equilibrium constant is independent of the solvent used.1 Further, the intrinsic equilibrium constant for reaction 2 can be determined, as the nitrobenzene anion radical can be observed in the gas phase.8

Free energy changes of electron transfer, such as that from a radical anion to another π system, can be readily determined in the gas phase with ion cyclotron resonance spectroscopy9 and high-pressure pulsed mass spectrometry.10 An extensive scale of such free energy changes for electron-transfer reactions now exists, and it covers a range of 40 kcal/mol. In many cases these values have been equated with differences in the electron affinities (enthalpic quantities) by assuming that the entropy for electron transfer between aromatic π systems in the gas phase is zero.10a This assumption seems appropriate in the case of simple isotopic substitution, given the very small entropy changes observed for systems undergoing more dramatic geometry changes.

The AGo's measured in the gas phase should reflect predictions based on the zero-point energy arguments mentioned above.1,2 It should be pointed out that the zero-point energy data given in ref 2a and analyzed in ref 1 are erroneous and have been updated.25

Experimental Section

The gas-phase results were obtained with ion cyclotron resonance spectroscopy. The equipment and techniques for determining the gas-phase equilibria have been previously described,11 save for the following. The neutral pressure ratio for Ph3NO2/Ph3NO2-d6 was set by admitting a premixed (v/v) solution into the ICR spectrometer. The vapor pressure of the deutero compound should be ca. 3% greater than that of the protio form;12 this effect was corrected for in calculating the

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deuterium atoms. Indeed, we could not measure a statistically
overlap (hyperconjugation) with the C-H/C-D bonds. In the
aromatic results in a much smaller perturbation in the relative EA than
isotope effect is in line with other such values in the gas phase.
and magnitude (an average of 40 cal/mol per D) for the deuterium
deuterium isotope effect for the latter. The observed direction
proton-transfer equilibrium favors the light ion by 100 to 170
For deuterium substitution in CH,X-

\[ \text{PhNO}_2^+ + \text{H}_2 \rightarrow \text{PhNO}_2^+ + \text{H}_2 \]

A comparison of isotope effects on electron-transfer

\[ \Delta G^o = 0.19 \pm 0.05 \text{ kcal/mol at } 32 \degree C \]

and proton-transfer equilibria is valid because there is a secondary
deuterium isotope effect for the latter. The observed direction
and magnitude (an average of 40 cal/mol per D) for the deuterium
isotope effect is in line with other such values in the gas phase.
For deuterium substitution in CH,X- (X = O, NH2, S), the
proton-transfer equilibrium favors the light ion by 100 to 170
cal/mol per D.14 A larger effect is expected in these latter cases
than for the nitrobenzene, since the anionic orbitals have good
overlap (hyperconjugation) with the C-H/C-D bonds. In the
present work, only the relatively poor s-p overlap connects the
aromatic \( \pi \) system with the isotopically labeled atoms.

The replacement of the \( ^{14}\text{N} \) atom in this molecule with an
\( ^{15}\text{N} \) results in a much smaller perturbation in the relative EA
than does the replacement of each of the five hydrogen atoms with
deuterium atoms. Indeed, we could not measure a statistically
meaningful difference in the EAs of \( \text{PhNO}_2^+ \) and \( \text{PhN}^{14}\text{O}_2^+ \).

\[ \text{Table I. Equilibrium Constants and Free Energies of Electron Transfer} \]

\[ \begin{array}{cccc}
\text{from} & \text{to} & \Delta G^o & K_n \\
\text{PhNO}_2^+ & \text{PhNO}_2^+ & \text{PhNO}_2^+ & \text{PhNO}_2^+ \\
\text{PhNO}_2^+ & \text{PhNO}_2^+ & \text{PhNO}_2^+ & \text{PhNO}_2^+ \\
\text{PhH}_4\text{NO}_2^- & \text{PhH}_4\text{NO}_2^- & \text{PhH}_4\text{NO}_2^- & \text{PhH}_4\text{NO}_2^- \\
\end{array} \]

\[ \begin{array}{cccc}
\text{(NH}_3\text{H}, \text{K}^+) & \text{(NH}_3\text{H}, \text{K}^+) & \text{(NH}_3\text{H}, \text{K}^+) & \text{(NH}_3\text{H}, \text{K}^+) \\
\text{305} & \text{305} & \text{208} & \text{208} \\
\text{190} & \text{190} & \text{93} & \text{93} \\
\text{5} & \text{5} & \text{5} & \text{5} \\
\text{0.73} & \text{0.73} & \text{0.80} & \text{0.80} \\
\end{array} \]

five independent measurements the free energy change for reaction
2 in the gas phase was found to be \(-12 \pm 12 \text{ cal/mol} \) (Table I). In
the PhH\(_4\)NO\(_2^+\) system, the isotopically labeled atom has a p
orbital that is part of the \( \pi \) system, and the spin density of the
perturbation upon \( K_n \) is small.

In order to explore the reasons for the observed free energies of
electron transfer, we have performed semiempirical molecular
orbital calculations on nitrobenzene and its anion radical, using
MNDO and AM1 methods, contained in the AMPAC program.15
The nitro group is not handled especially well by the MNDO
method, with AM1 being somewhat improved. Nevertheless,
the general trends in these methods should be useful in rationalizing
the observed gas-phase data, especially since we are using iso-
desmic equilibria. The geometric and energetic parameters from
total geometry optimization are given in Table II. Both methods
give heats of formation for nitrobenzene that suggest too much
instability, although AM1 comes closer than MNDO to matching
the experimental value. The radical anions are too stable in both
cases, resulting in adiabatic electron affinities about twice that of
the experimental value.16 Both the neutral and the ionic forms
are planar. The geometry changes on electron attachment are
qualitatively similar in both methods: a shortening of the C-N
and a slight lengthening of all C-H bonds (0.0045,

\[ \text{Table II. Molecular Orbital Calculations: Bond Lengths (Å) and Energetics of Nitrobenzene and Nitrobenzene Anion Radical} \]

\[ \begin{array}{cccc}
\text{parameter} & \text{MNDO} & \text{AM1} \\
\text{PhNO}_2^+ & \text{PhNO}_2^+ & \text{PhNO}_2^+ & \text{PhNO}_2^+ \\
\text{N-O} & \text{1.210} & \text{1.207} & \text{1.207} & \text{1.207} \\
\text{C-N} & \text{1.4982} & \text{1.4962} & \text{1.4962} & \text{1.4962} \\
\text{C-C} & \text{1.4151} & \text{1.4406} & \text{1.4406} & \text{1.4406} \\
\text{C-N} & \text{1.4064} & \text{1.4004} & \text{1.4004} & \text{1.4004} \\
\text{C-C} & \text{1.4061} & \text{1.4192} & \text{1.4192} & \text{1.4192} \\
\text{C-H} & \text{1.0902} & \text{1.0912} & \text{1.0912} & \text{1.0912} \\
\text{C-H} & \text{1.0902} & \text{1.0984} & \text{1.0984} & \text{1.0984} \\
\text{HOMO (eV)} & \text{-10.313} & \text{-2.546} & \text{-2.546} & \text{-2.546} \\
\text{LUMO (eV)} & \text{-1.221} & \text{+4.834} & \text{+4.834} & \text{+4.834} \\
\Delta H^o (kcal/mol) & \text{37.5} & \text{-7.6} & \text{25.3} & \text{-14.8} \\
\text{E_A(\text{max}) (eV)} & \text{1.97} & \text{1.74} & \text{1.74} & \text{1.74} \\
\end{array} \]


(13) Bartmess, J. E.; Georgidas, R. M. Vacuum 1983, 33, 149.
Solution Electron Affinity of Nitrobenzene

The anion radical of PhNO₂-d₅ exhibits only three resolved ESR lines (Figure 1), and computer simulations of the spectra taken from mixtures of nitrobenzene and perdeuterated nitrobenzene clearly show that the solution electron affinity of the isotopically substituted material is less than that of nitrobenzene (Table I), reaction 5. This is in qualitative agreement with the gas-phase results.

\[
\text{PhNO}_2\cdot d_5^- + \text{PhNO}_2\cdot d_5^- = \text{PhNO}_2\cdot d_5^- + \text{PhNO}_2\cdot d_5^- + K^+
\]

(5)

Considering the above it would appear that ion association and solvation in liquid ammonia result in perturbations of the relative electron affinities and that ion association and ion solvation have the effect of decreasing the free energy change. However, a sample of Ph⁻¹¹NO₂⁻ + Ph⁻¹⁵NO₂⁻ that had been left in the a refrigerator for 1 week was fortuitously resubmitted to ESR analysis, and it was noted that the intensity of the Ph⁻¹⁵NO₂⁻ signal had decreased appreciably relative to that of the Ph⁻¹¹NO₂⁻. In fact the equilibrium constant for reaction 4 had fallen from 2.0 to 0.8. As the total anion concentration does not decrease and equilibrium involving electron exchange in solution is established in less than microseconds, the only viable explanation of this observation involves the slow addition of an agent to the anion radical solution from a reaction with the solvent or glass that perturbs the equilibrium constant.

In the previous experiment it was noted that the intensity of the Ph⁻¹⁵N0₂⁻ signal had decreased with a very deficient amount of potassium metal. The lower concentration of potassium metal in liquid ammonia results in perturbations of the bond energies (new ion-solvent and ion-gegenion interactions are formed) to yield a negative AG° (Table 1). Such a change might be expected, since solvation and ion association increase the spin and charge densities in the NO₂ group. Reaction 4 may not have a zero entropy change, since solvation in liquid ammonia result in perturbations of the relative intensities of the two simultaneously observed ESR lines (Figure 1),

A.°ν = 10.83 G, Aₜ(ortho) = 3.50 G, Aₜ(meta) = 0.90 G, Aₜ(ortho) = 4.00 G, all Aₜ = 1/6.52 of the respective Aₜ, and a ratio of PhNO₂-d₅⁻/PhNO₂-d₅⁻ = 4.0. An example of the ESR spectra and simulations for the Ph⁻¹⁴NO₂-Ph⁻¹⁵NO₂ system is given in ref 19.

in liquid ammonia with very deficient amounts of potassium metal, the relative intensities of the two simultaneously observed ESR spectra show that the equilibrium constant at -65 °C for reaction 4 when M⁺ is K⁺ is 2.1 ± 0.2 (ΔG° = -307 ± 10 cal/mol). It appears that the solvation and ion association with K⁺ results in sufficient perturbation of the bond energies (new ion-solvent and ion-gegenion interactions are formed) to yield a negative AG° (Table 1). Such a change might be expected, since solvation and ion association increase the spin and charge densities in the NO₂ group. Reaction 4 may not have a zero entropy change, since the ion association and solvent anion interactions are very dependent upon the temperature. However, it did not prove possible to explore the thermal dependence of K°, due to the fact that rapid electron transfer between the anion radicals and neutral molecules results too much line broadening at elevated temperatures to allow for the accurate determination of relative ESR intensities.

\[
\Delta G° = 93 ± 5 \text{ cal/mol at } -65 °\text{C}
\]

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