

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

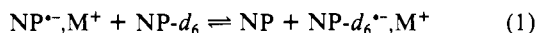
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Abstract: Ion cyclotron resonance and electron spin resonance have been utilized to determine the equilibrium constant for the electron transfer from the nitrobenzene anion radical to ¹⁵N labeled nitrobenzene ($\text{Ph}^{14}\text{NO}_2^{\cdot-} + \text{Ph}^{15}\text{NO}_2 \rightleftharpoons \text{Ph}^{14}\text{NO}_2 + \text{Ph}^{15}\text{NO}_2^{\cdot-}$). 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 ($K_{\text{eq}} = 2.1$). However, when Na^+ serves as the gegenion, the solution electron affinity of $\text{Ph}^{14}\text{NO}_2$ is greater than that of $\text{Ph}^{15}\text{NO}_2$ ($K_{\text{eq}} = 0.4$). These results are explained in terms of ion association. When the hydrogen atoms are replaced with deuteriums, 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.

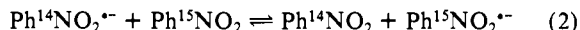
The equilibrium constant controlling the solution phase electron transfer between the naphthalene anion radical ($\text{NP}^{\cdot-}$) and perdeuteriated naphthalene ($\text{NP}-d_8$) has been shown to be significantly below unity (eq 1) and invariant with solvent choice. This



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

is due to the net reduction in molecular bond energy that is observed as NP is reduced to $\text{NP}^{\cdot-}$ coupled with the differences in the zero-point energies of NP and $\text{NP}-d_8$.^{1,2} The facts that K_{eq} 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 $\text{NP}-d_8$ 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 ($\text{Ph}^{14}\text{NO}_2$) system and its ¹⁵N analogue ($\text{Ph}^{15}\text{NO}_2$). 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 tetracyanoethylene (TCNE) that have been reported by Devlin and co-workers^{4,5} 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 4.54 mdyne/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 (TCNQ) and its anion radical.⁶ 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



the spin density upon the NO_2 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.¹⁰

The ΔG° 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.^{2b}

Experimental Section

The gas-phase results were obtained with ion cyclotron resonance mass spectrometry. The equipment and techniques for determining the gas-phase equilibria have been previously described,¹¹ save for the following changes. The neutral pressure ratios for $\text{PhNO}_2\text{-}h_5/\text{PhNO}_2\text{-}d_5$ were set by admitting a premixed (v/v) solution into the ICR spectrometer. The vapor pressure of the deuterio 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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Table I. Equilibrium Constants and Free Energies of Electron Transfer

electron transfer			<i>T</i> (K)	ΔG° (cal/mol)	K_{eq}
from	to	phase			
PhNO ₂ - <i>h</i> ₅ ^{•-}	PhNO ₂ - <i>d</i> ₅	gas	305	190 ± 50	0.73
PhNO ₂ - <i>h</i> ₅ ^{•-}	PhNO ₂ - <i>d</i> ₅	soln (NH ₃ , K ⁺)	208	93 ± 5	0.80
Ph ¹⁴ NO ₂ ^{•-}	Ph ¹⁵ NO ₂	gas	305	-12 ± 12	1.02 ^a
Ph ¹⁴ NO ₂ ^{•-}	Ph ¹⁵ NO ₂	soln (NH ₃ , K ⁺)	208	-307 ± 10	2.1
Ph ¹⁴ NO ₂ ^{•-}	Ph ¹⁵ NO ₂	soln (NH ₃ , Na ⁺)	208	378 ± 20	0.4

^a Repeated measurement of this equilibrium constant did not result in a statistically significant deviation from unity.

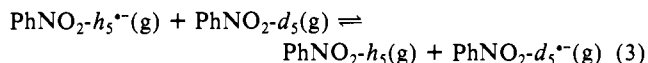
equilibrium constants. There was still appreciable liquid sample remaining in the foreline vessel during the experiment. This technique should result in a much more accurately known neutral pressure ratio than is commonly available.^{11,13} For the Ph¹⁵NO₂/Ph¹⁴NO₂ measurement, the usual ion gauge pressure measurement technique was used to set the two pressures separately, due to a lack of sample. The ion gauge sensitivity factors for the two isotopic forms are assumed to be the same.¹³ The equilibrium constants were measured at >20 collisions (5 to 7 × 10⁻⁶ Torr, ion gauge).

The solution-phase results were obtained with electron spin resonance spectroscopy. The equipment and techniques used for the reduction of nitrobenzene to its corresponding anion radical have already been described.^{3b} A total of 0.5 to 1.5 mmol of Ph¹⁴NO₂ mixed with Ph¹⁵NO₂ were reduced in about 25 mL of freshly distilled (from potassium metal) liquid ammonia with a very deficient amount (ca. 0.05 mmol) of potassium metal at -78 °C in an all-glass apparatus.^{3b} All of the reductions were carried out under high vacuum (ca. 10⁻³ Torr), and portions of the resulting anion radical solutions were then diluted with pure NH₃ to reduce the concentration of anion radical and neutral molecule sufficiently to allow well-resolved ESR spectra at -70 °C.

ESR spectra were recorded on a Bruker (IBM) ER-200 ESR equipped with a Varian temperature controller. Mole ratios of the anion radicals yielding a given ESR pattern were obtained via computer simulation of the simultaneously observed spectra. Accurate values for the ratios of anion radicals were obtained by expanding spectra and simulating expanded portions where minimal overlap of lines of the two species occurs, allowing for most precise matching of the relative intensities of the two spectra. The equilibrium constants were measured in this way from each of eight independently prepared samples, and the errors reported represent the standard deviations in these K_{eq} s.

Results and Discussion

Gas Phase. An equilibrium constant of 0.73 ± 0.06 was found for the electron transfer from PhNO₂-*h*₅^{•-} to PhNO₂-*d*₅ at 32 °C, reaction 3. A comparison of isotope effects on electron-transfer



$$\Delta G^\circ = 0.19 \pm 0.05 \text{ kcal/mol at } 32 \text{ }^\circ\text{C}$$

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 CH₃X⁻ (X = O, NH, 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 π system with the isotopically labeled atoms.

The replacement of the ¹⁴N atom in this molecule with an ¹⁵N 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 Ph¹⁵NO₂ and Ph¹⁴NO₂. From

Table II. Molecular Orbital Calculations: Bond Lengths (Å) and Energetics of Nitrobenzene and Nitrobenzene Anion Radical

parameter	MNDO		AM1	
	PhNO ₂	PhNO ₂ ^{•-}	PhNO ₂	PhNO ₂ ^{•-}
N-O	1.2120	1.2355	1.2021	1.2275
C-N	1.4982	1.4227	1.4862	1.4145
C _i -C _o	1.4151	1.4458	1.4046	1.4324
C _o -C _m	1.4064	1.4004	1.3932	1.3814
C _m -C _p	1.4061	1.4192	1.3953	1.4064
C _o -H	1.0913	1.0899	1.1034	1.0989
C _m -H	1.0902	1.0912	1.1008	1.0992
C _p -H	1.0902	1.0884	1.1011	1.0951
HOMO (eV)	-10.313	-2.546	-10.561	-2.365
LUMO (eV)	-1.221	+4.834	-1.069	+4.637
ΔH_f° (kcal/mol)	37.5	-7.6	25.3	-14.8
EA _{adiab} (eV)	1.97		1.74	

five independent measurements the free energy change for reaction 2 in the gas phase was found to be -12 ± 12 cal/mol (Table I). In the Ph¹⁵NO₂^{•-} system, the isotopically labeled atom has a p orbital that is part of the π system, and the spin density of the perturbation upon K_{eq} 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 isodesmic 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.¹⁰ 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 bond by 0.0717 Å and the C_{ortho}-C_{meta} bonds by 0.0277 Å, a lengthening of the N-O bonds by 0.025 Å and C_{ipso}-C_{ortho} by 0.0277 Å, and a slight lengthening of all C-H bonds (0.0045, 0.0016, and 0.0060 Å).

By the orbital electron analysis, in the anion, 0.39 of the added electron resides in the p orbitals of the nitro group and 0.03 in the σ framework of the -NO₂. The geometry changes parallel the observed isotope effects: isotopic substitution into a bond that lengthens on electron attachment results in favoring the light ion energetically, while substitution on a bond that shortens on electron attachment favors the heavier form. The lengthening of all of the C-H bonds upon electron attachment accounts for the positive free energy change of reaction 3, and the dramatic shortening of the C-N bond coupled with the lesser lengthening of the C-O bonds are in qualitative agreement with the small $|\Delta G^\circ|$ associated with the transfer of an electron from Ph¹⁴NO₂^{•-} to Ph¹⁵NO₂.

While the molecular orbital calculations seem to, at least qualitatively, account for the observed gas-phase relative EAs, a much more complicated situation exists for these same reactions in the solution phase. In solution ion association between the counterion and the electronegative NO₂ group in the anion radical may significantly alter the changes in bond lengths due to the fact that this ion association results in large perturbations in the spin and charge density on the NO₂ group.

Solution Phase. When mixtures of carefully measured quantities of Ph¹⁴NO₂ and Ph¹⁵NO₂ were reduced with potassium metal

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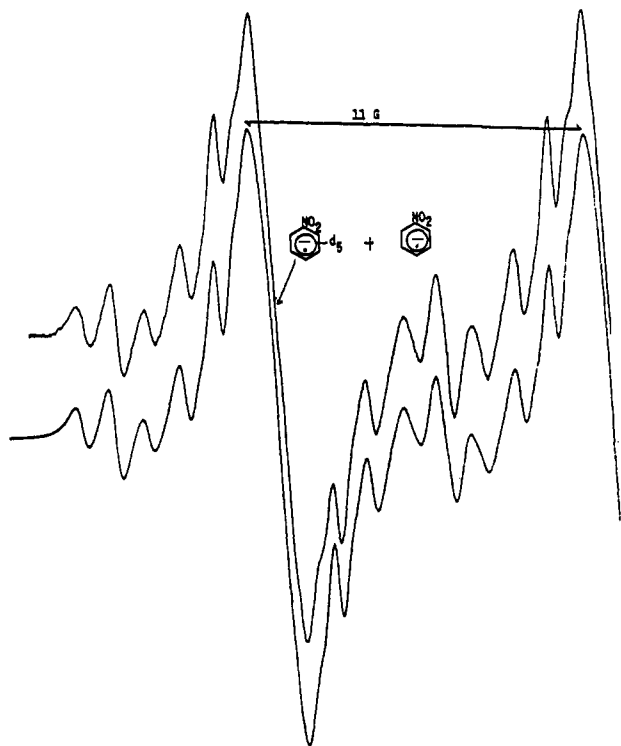


Figure 1. ESR spectrum (upper) recorded in liquid ammonia at $-65\text{ }^{\circ}\text{C}$ (only low field half shown) of a 3:1 mixture of $\text{PhNO}_2\text{-}h_5$ and $\text{PhNO}_2\text{-}d_5$ reduced with a very deficient amount of potassium metal. The lower spectrum is a computer simulation that was generated with use of the following parameters: $A^{14}\text{N} = 10.83\text{ G}$, $A_{\text{H}}(\text{ortho}) = 3.50\text{ G}$, $A_{\text{H}}(\text{meta}) = 0.90\text{ G}$, $A_{\text{H}}(\text{para}) = 4.00\text{ G}$, all $A_{\text{DS}} = 1/6.52$ of the respective A_{H} , and a ratio of $\text{PhNO}_2\text{-}d_5^{\cdot-}/\text{PhNO}_2\text{-}h_5^{\cdot-} = 4.0$. An example of the ESR spectra and simulations for the $\text{Ph}^{14}\text{NO}_2\text{-Ph}^{15}\text{NO}_2$ system is given in ref 19.

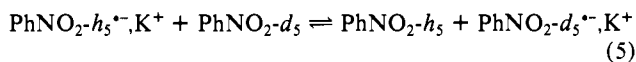
in liquid ammonia with very deficient amounts of potassium metal, the relative intensities of the two simultaneously observed ESR spectra show that the equilibrium constant at $-65\text{ }^{\circ}\text{C}$ for reaction 4 when M^+ is K^+ is 2.1 ± 0.2 ($\Delta G^{\circ} = -307 \pm 10\text{ cal/mol}$). It

$$\text{Ph}^{14}\text{NO}_2^{\cdot-}, \text{M}^+ + \text{Ph}^{15}\text{NO}_2 \rightleftharpoons \text{Ph}^{14}\text{NO}_2 + \text{Ph}^{15}\text{NO}_2^{\cdot-}, \text{M}^+ \quad (4)$$

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 ΔG° (Table I). Such a change might be expected, since solvation and ion association increase the spin and charge densities in the NO_2 group.³ 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_{eq} due to the fact that rapid electron transfer between the anion radicals and neutral molecules results in too much line broadening at elevated temperatures¹⁶ to allow for the accurate determination of relative ESR intensities.

The anion radical of $\text{PhNO}_2\text{-}d_5$ exhibits only three resolved ESR lines (Figure 1),¹⁹ 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.



$$\Delta G^{\circ} = 93 \pm 5\text{ cal/mol at } -65\text{ }^{\circ}\text{C}$$

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 $\text{Ph}^{14}\text{NO}_2^{\cdot-} + \text{Ph}^{15}\text{NO}_2^{\cdot-}$ that had been left in the refrigerator for 1 week was fortuitously resubmitted to ESR analysis, and it was noted that the intensity of the $\text{Ph}^{15}\text{NO}_2^{\cdot-}$ signal had decreased appreciably relative to that of the $\text{Ph}^{14}\text{NO}_2^{\cdot-}$. 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.

It has been previously observed that solvated electron solutions in liquid ammonia undergo cation exchange with the glass.¹⁷ That is, if a solution of $(\text{K}^+ + \text{e}^-)\text{NH}_3$ is generated via the dissolution of K metal in liquid ammonia in Pyrex glass, the species present after several hours is $(\text{Na}^+ + \text{e}^-)\text{NH}_3$. This is due to ion exchange of K^+ with the Na^+ in the glass. To provide evidence that a similar cation exchange was taking place in the nitrobenzene anion radical solutions, we reduced mixtures of $\text{Ph}^{14}\text{NO}_2$ and $\text{Ph}^{15}\text{NO}_2$ with sodium metal and submitted the resulting anion radical solutions to ESR analysis. The equilibrium constant for reaction 4 when Na^+ serves as the cation is 0.4 at $-65\text{ }^{\circ}\text{C}$. Thus, the free energy of reaction 4 in liquid ammonia is changed from a negative value to a positive value by simply changing M^+ from K^+ to Na^+ . Further, if the reduction is carried out with potassium metal and 0.2 M KI is added to the ammonia solution, then the equilibrium constant for reaction 4 is 2.1, and it does not vary with time. Under these conditions M^+ in reaction 4 remains K^+ due to its high concentration. Evidently, the electrostatic interactions between the NO_2 group and the cation result in sufficient perturbations in the C-N and N-O vibrational frequencies to drastically alter the equilibrium involving electron exchange between $\text{Ph}^{14}\text{NO}_2^{\cdot-}$ and $\text{Ph}^{15}\text{NO}_2$, reaction 4.

Finally it should be noted that the magnitude and range of isotope effects reported here for ^{14}N and ^{15}N are unprecedented and have obvious practical significance.¹⁸

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