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Isotopic Enrichments via Altered First and Second Solution Electron Affinities

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Abstract: Electron spin resonance experiments have been utilized to show that the solution electron affinity of benzene-$^{13}C_6$ is less than that of benzene by 0.24 kcal/mol and that the solution EA of benzene-d_6 is less than that of benzene by 0.44 kcal/mol. Perdeuteration of naphthalene, anthracene, or perylene results in a very similar lowering of the solution EA of the hydrocarbon as evidenced by the fact that the equilibrium constant for the electron transfer between the hydrocarbon anion radical, $X^{\bullet -}$, and the perdeuterated hydrocarbon, Xd ($X^{\bullet -} + Xd = Xd^{\bullet -} + X$), is less than unity. Likewise the second EAs of perdeuterated perylene and anthracene are lower than those of the unsubstituted hydrocarbons (K_{eq} for $X^{2-} + Xd^{\bullet -} = X^{\bullet -} + Xd^{2-}$ is less than unity). The free energy and enthalpy of electron transfer from the anthracene anion radical to perdeuterated anthracene is 0.41 kcal/mol and that from the anthracene dianion to the perdeuterated anion radical is 0.10 kcal/mol. The fact that these equilibrium constants are not equal to 1 enables one to use the difference in the chemical reactivity of the ions and neutral molecules to selectively isotopically enrich the hydrocarbons involved.

Both theory and ESR studies show that the symmetric (S) and antisymmetric (A) wave functions of benzene are degenerate.[1] However, an ESR study carried out in tetrahydrofuran (THF) and dimethoxyethane (DME) has shown that even the substitution of a deuterium on the benzene anion radical ($BZ^{\bullet -}$) removes the degeneracy of these two lowest antibonding MOs.[2] Alkyl groups produce a much larger splitting in the degeneracy of the S and A wave functions of $BZ^{\bullet -}$.[3-7] However, this effect is not purely an electronic one as was shown by the vibronic coupling calculations of Alper and Silbey.[8] Further, alkyl groups appear to destabilize both S and A wave functions, as evidenced by the fact that toluene has a smaller solution electron affinity than does benzene.[9] It must be kept in mind, however, that the relative electron affinities in solution are in part due to counterion and/or solvent interactions, as toluene has a larger EA than benzene in the gas phase.[10] We were motivated to see if deuteration analogously diminishes the solution electron affinity (forces K_{eq} for reaction 1 to less than unity) and if this decreased solution EA could be used for isotopic enrichment.

$$BZ^{\bullet -},K^+ + BZ\text{-}d_6 \rightleftharpoons BZ + BZ\text{-}d_6^{\bullet -},K^+ \qquad (1)$$

On the basis of Raman and IR studies carried out upon the neutral molecules and anion radicals of tetracyanoethylene (TCNE) and tetracyanoquinone (TCNQ), the effect of an added electron is best characterized as a strengthening of single bonds and a weakening of multiple bonds with a net reduction in molecular bond energies.[11] However, the situation is more complex for benzene when the static Jahn-Teller distortion, which must occur, is considered.[12] Since the ground state of the undistorted anion is degenerate, the Jahn-Teller distortion leads to a splitting of the e_{2g} and e_{1u} vibrational modes into an a_g and a b_{3g} vibration. Assignment of the observed Raman and IR spectra of the ion paired benzene anion radical assuming a C_{6v} structure shows that a a_g-b_{3g} doublet is found centered at 1540 cm^{-1} in $M^+BZ^{\bullet -}$, which is 55 cm^{-1} lower than the original 1595 e_2 vibration for benzene.[12]

Table I. Observed IR and Raman Frequencies in cm^{-1} for Benzene, Benzene-d_6, and Their Anion Radicals

assignment in benzene	C_6H_6	C_6D_6	$C_6H_6^{\bullet -}$	$C_6D_6^{\bullet -}$	contribution (cal/mol) to $\Delta G°$ for reaction 1
e_{2g} C-C stretch[a]	1595	1559	1540	1520	-91.5
e_{1u} C-C stretch[a]	1479	1333	1350	1235	-177
e_{2g} C-H in-plane bend[a]	1178	867	1185	860	+80.1
a_{1g} breathing	992	945	980	942	-25.7
b_{2u} C-C stretch	1309	1287	1260	1057	+518
e_{1u} C-H in-plane bend	1037	813	968	755	-31.5
total contribution to $\Delta G°$ = +272 cal/mol					

[a] These are degenerate modes of vibration.

On the other hand, the original 1178 cm^{-1} benzene C-H e_{2g} bending mode appears as a doublet centered at 1185 cm^{-1}.[12] These data suggest that the vibrations of $BZ^{\bullet -}$ resemble those of BZ except for the slightly altered stretching frequencies and split degeneracies. For the case of BZ-d_6, the original 1559 e_2 band drops only 39 cm^{-1} to 1520 cm^{-1} upon the addition of an electron. Thus, considering this degenerate e_2 vibration only, perdeuteration of the benzene ring system shoud result in a decrease in the free energy of reaction 1 of 2 × (55 - 39) cm^{-1} or some 91.5 cal/mol (Table I).

The 1178 degenerate C-H bending mode, discussed above, has a frequency of 867 cm^{-1} in BZ-d_6 and 860 cm^{-1} in BZ-$d_6^{\bullet -}$. Its influence is to raise the free energy of reaction 1 by 2 × [(1185 - 1178) - (860 - 867)] = +28 cm^{-1} or +80 kcal/mol. The Raman active b_{2u} C-C stretch at 1309 in benzene is found at 1260 cm^{-1} in the anion radical. The analogous band in the anion radical of perdeuteriobenzene is found at 1057 cm^{-1}. Miller[12b] has found that the 1309 cm^{-1} band in benzene is found at 1287 cm^{-1} in BZ-d_6. Thus, these stretching modes have the net effect of increasing the free energy of reaction 1 by +518 cal/mol.

Table I details the effect of all eight known IR and Raman active vibrations of BZ, BZ-d_6, $BZ^{\bullet -}$, and BZ-$d_6^{\bullet -}$ upon the free energy of reaction 1. On the basis of these eight bands only, the zero point energy effect would result in a free energy of reaction 1 of +272 kcal/mol. The remaining 22 of the 30 vibrational degrees of freedom have not been observed for all four species. However, based upon those that have been assigned for benzene[13]

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Figure 1. ESR spectra (upper) of a mixture of [benzene]/[benzene-d_6] = 0.36/1 reduced with a very deficient amount of potassium metal in THF and recorded at −100 °C. The computer simulation (lower) is based upon an anion radical ratio of [$BZ^{\bullet -}$]/[Bz-$d_6^{\bullet -}$] = 1.33/1.

and benzene-d_6 and those observed but unassigned for the anion radicals,[12a] most of them have a relatively small effect, and some are counteracting. Indeed it has been noted for other neutral molecule–anion radical comparisons that the frequencies below 700 cm^{-1} do not exhibit significant ionization shifts.[14] Further, it has been noted that the C–C stretching frequencies are the most influenced by the addition of the electron,[14] and we have accounted for all of these in Table I. Thus, the IR and Raman results reported in Table I predict that the solution electron affinity of BZ-d_6 is lower than that of BZ by about 300 cal/mol, and this should be reflected in the free energy and enthalpy of reaction 1.

Results and Discussion

When mixtures of carefully measured quantities of benzene (BZ) and perdeuterated benzene (BZ-d_6) were reduced with very deficient amounts of potassium metal in tetrahydrofuran (THF), the relative intensities of the two simultaneously observed ESR spectra (Figure 1) show that the equilibrium constant at −100 °C for reaction 1 is indeed well below unity as predicted earlier. The equilibrium constant was found to be 0.27 ± 0.02, and $\Delta G°$, which is identical with the enthalpy change,[9] is 440 ± 11 cal/mol. This value is in general agreement with that predicted based upon the zero point energy arguments.

The IR spectrum of the anion radical of benzene containing six ^{13}C atoms (BZ-$^{13}C_6$) is unknown. However, the C–C motions should be perturbed to a similar degree when neutrons are added to the C–H moieties whether they are added to the H or to the C atoms. The C–H motions would, of course, be affected to a much smaller extent when the neutrons are added to the C atoms. Thus the zero point energy argument would predict a free energy for reaction 2 that is somewhat smaller than 440 cal/mol. The ESR spectrum of BZ-$^{13}C_6$, readily generated in THF via K reduction, consists of two heptets, one due to six protons with a coupling constant of 3.75 and the other due to six ^{13}C's with a splitting of 2.70 G. This spectrum is, however, significantly contaminated with that for the anion radical of benzene. The BZ-$^{13}C_6$ was 98.2% ^{13}C (confirmed via mass spectral analysis), thus the source of the benzene contaminant must have been the solvent. A typical potassium reduction of a 4.5:1 [BZ-$^{13}C_6$]/[BZ] mixture yields ESR spectra consistent with a ratio of anion radicals [BZ-$^{13}C_6^{\bullet -}$]/[$BZ^{\bullet -}$] of 2/1 (accounting for the presence of $BZ^{\bullet -}$ as an impurity). Thus, the predicted situation was realized; see reaction 2 at −100 °C.

$$BZ^{\bullet -},K^+ + BZ\text{-}^{13}C^6 \rightleftharpoons BZ + BZ\text{-}^{13}C_6^{\bullet -},K^+ \qquad (2)$$

$$\Delta G° = 240 \pm 70 \text{ cal/mol};\ K_{eq} = 0.48 \pm 0.10$$

The measured equilibrium constant for reaction 2 is very dependent upon our ability to accurately account for the small

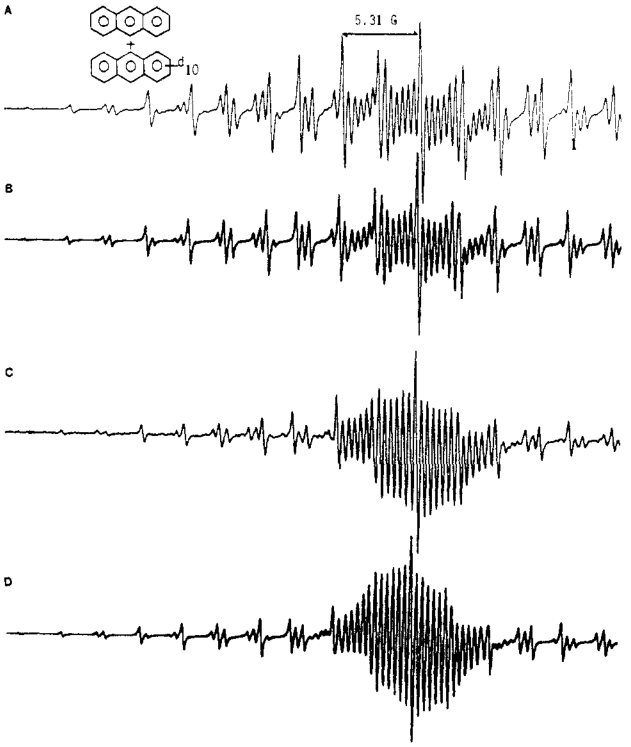

Figure 2. (A) The first 3/4 (low field portion) of the ESR spectrum generated from a reduction of a 0.21/1 mixture of [AN]/[AN-d_{10}] with a very deficient amount of potassium metal in THF. (B) A computer simulation of ESR spectrum A based upon a ratio of anion radicals of [$AN^{\bullet -}$]/[AN-$d_{10}^{\bullet -}$] = 0.65/1. (C) ESR spectrum of the same solution (as in A). However, the solution had been reexposed to the potassium metal and almost two moles of potassium per mole of hydrocarbon had been dissolved. (D) A computer simulation of spectrum C based upon a mole ratio of anion radicals of 0.15/1. All of the spectra were recorded at −100 °C.

amount of BZ in the solvent system. This is due to the fact that the $BZ^{\bullet -}$ ESR lines exactly superimpose upon the most intense lines for the BZ-$^{13}C_6^{\bullet -}$. For this reason the equilibrium constant for reaction 2 was verified by reducing mixtures of BZ-$^{13}C_6$ and BZ-d_6. The reduction of these mixtures has shown that the equilibrium constant for reaction 3 is 0.52 ± 0.05 at −100 °C.

$$BZ\text{-}^{13}C_6^{\bullet -},K^+ + BZ\text{-}d_6 \rightleftharpoons BZ\text{-}^{13}C_6 + BZ\text{-}d_6^{\bullet -},K^+ \qquad (3)$$

The division of K_{eq} for reaction 1 by that of reaction 3 yields 0.52, which is within experimental error of K_{eq} for reaction 2. This provides an independent confirmation for the free energy of reaction 2.

When a 5/1 ([AN-d_{10}]/[AN]) mixture of perdeuterated anthracene (AN-d_{10}) and anthracene is reduced with a very deficient amount of potassium metal in THF, the resulting ESR signal is consistant with a 1.5/1 mixture of the anion radicals ([AN-$d_{10}^{\bullet -}$]/[$AN^{\bullet -}$]). As the reduction is continued (more potassium is allowed to react with the mixture), the relative concentration of AN-$d_{10}^{\bullet -}$ to $AN^{\bullet -}$ increases (Figure 2). When very nearly two moles of K have been used for each mole of AN-d_{10} plus AN in the reaction vessel, the ratio of anion radicals is [AN-$d_{10}^{\bullet -}$]/[$AN^{\bullet -}$] = 6.7/1, and that of the dianions is 5/1. Any further addition of K metal results in the complete reduction of both materials to their respective dianions (AN-d_{10}^{2-} and AN^{2-}). From these data and a number of similar experiments the equilibrium constants for reactions 4 and 5 were found to be 0.30 ± 04 and 0.74 ± 0.02 at −100 °C, respectively.

$$AN^{\bullet -},K^+ + AN\text{-}d_{10} \rightleftharpoons AN\text{-}d_{10}^{\bullet -},K^+ + AN \qquad (4)$$

$$\Delta G° = 410 \pm 40 \text{ cal/mol}$$

$$AN^{2-},2K^+ + AN\text{-}d_{10}^{\bullet -},K^+ \rightleftharpoons AN^{\bullet -},K^+ + AN\text{-}d_{10}^{2-},K^+ \qquad (5)$$

$$\Delta G° = 100 \pm 9 \text{ cal/mol}$$

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Likewise, the potassium reduction of a 1:1 mixture of perylene (PY) and perdeuterated perylene (PY-d_{14}) yields an ESR signal that is predominantly due to the anion radical of perylene. However, as the reduction proceeds the relative concentration of PY-$d_{14}^{\bullet-}$ increases, and it is this species that is dominant after close to 2 mol of potassium per mol of hydrocarbon has been dissolved. Analysis of the spectra yields equilibrium constants of 0.40 ± 0.08 and 0.65 ± 0.02 for reactions 6 and 7, respectively, at −100 °C.

$$\mathrm{PY}^{\bullet-},\mathrm{K}^+ + \mathrm{PY}\text{-}d_{12} \rightleftharpoons \mathrm{PY} + \mathrm{PY}\text{-}d_{12}^{\bullet-},\mathrm{K}^+ \qquad (6)$$

$$\Delta G^\circ = 310 \pm 70\ \mathrm{cal/mol}$$

$$\mathrm{PY}^{2-},2\mathrm{K}^+ + \mathrm{PY}\text{-}d_{12}^{\bullet-},\mathrm{K}^+ \rightleftharpoons \mathrm{PY}^{\bullet-},\mathrm{K}^+ + \mathrm{PY}\text{-}d_{12}^{2-},2\mathrm{K}^+ \qquad (7)$$

$$\Delta G^\circ = 150 \pm 11\ \mathrm{cal/mol}$$

The reversal of the relative intensities of the ESR signals of the perdeuterated and undeuterated anion radicals in the PY and AN systems upon the addition of more metal clearly means that both the first and the second solution EAs of the perdeuterated systems are lower than those of the undeuterated hydrocarbons. The IR and Raman data for the anion radicals and dianions of PY-d_{12} and AN-d_{10} are unknown. However, Devlin and coworkers[15] have studied these spectra for AN, $\mathrm{K}^+\mathrm{AN}^{\bullet-}$, and $\mathrm{K}^+{}_2\mathrm{AN}^{2-}$ in the solid phase. It was noted that although certain bonds are weakened others are strengthened as a result of the one- and two-electron transfer to anthracene. Thus, although the transferred electron(s) has a net antibonding quality, an orderly decrease in the fundamental frequencies is not observed.[15] It is, however, this general bond alteration with the addition of electrons coupled with the increased mass due to the extra neutrons in the deuterated materials that renders both the first and second EAs of the perdeuterated anthracene and perylene lower than those of the undeuterated materials.

The equilibrium constant for the electron exchange between naphthalene (NP) and perdeuterated naphthalene (NP-d_8) in THF is 0.30 at 25 °C (reaction 8).[16] Water was added to a 1/1

$$\mathrm{NP}^{\bullet-},\mathrm{K}^+ + \mathrm{NP}\text{-}d_8 \rightleftharpoons \mathrm{NP} + \mathrm{NP}\text{-}d_8^{\bullet-},\mathrm{K}^+ \qquad (8)$$

NP/NP-d_8 mixture that had been reduced in THF with 0.5 mol of potassium per mol of hydrocarbon. The Birch reduction products (from reactions 9 and 10) were worked up and analyzed for the NP/NP-d_8 ratio. The products proved to contain a 0.65/1

$$2\mathrm{NP}^{\bullet-},\mathrm{K}^+ + 2\mathrm{H_2O} \rightarrow \mathrm{NP} + \mathrm{NPH_2} + 2\mathrm{KOH} \qquad (9)$$

$$2\mathrm{NP}\text{-}d_8^{\bullet-},\mathrm{K}^+ + 2\mathrm{H_2O} \rightarrow \mathrm{NP}\text{-}d_8 + \mathrm{NP}\text{-}d_8\text{-}\mathrm{H_2} + 2\mathrm{KOH} \qquad (10)$$

ratio of NP/NP-d_8. This enhanced mixture was then resubmitted to the same process. Analysis and workup of the second reaction mixture proved it to contain a 0.5/1 mol ratio of NP/NP-d_8. Thus, continually passing the isotope mixture through this process will continue to enrich the material in perdeuterated naphthalene. The procedure described above should be viable for the enrichment of a wide variety of isotopic materials.[17]

Experimental Section

The samples of perdeuterated benzene, anthracene, and naphthalene were purchased from Aldrich Chemical Co., checked for isotopic purity via mass spectral analysis, and used without further purification. The perdeuterated perylene was purchased from MSD Isotopes, Inc.

All anion radicals and dianions were generated under high vacuum in sealed glass containers via contact with a freshly distilled potassium metal mirror. The THF was distilled from a sodium potassium alloy directly into the evacuated apparatus, which was subsequently sealed from the vacuum system. Carefully weighed portions of the unsubstituted and isotopically substituted hydrocarbons were mixed and placed into breakseals, which were in turn placed into the apparatuses used for the reductions. Agitation of the evacuated apparatuses resulted in the breaking of the breakseals, consequent release of the substrates, and contact with the metal mirror.

A 230-mg sample consisting of 0.89 mmol of naphthalene and 0.85 mmol of deuterated naphthalene was prepared. The complete reduction of a 6-mg sample of this mixture with potassium metal in THF results in an anion radical solution that yields an ESR spectrum due to a 1/1 mixture of perdeuterated naphthalene anion radical/naphthalene anion radical. The remainder of this mixture was reduced with about 1.0 mmol of potassium metal (about 50% of the metal needed for a complete reduction to anion radical) in 20 mL of THF. After all of the potassium had dissolved, 800 mL of water was added to the solution, which contained both neutral molecule and anion radical in equal portions. The water mixture was extracted three times with ether, and the ether was evaporated. The remaining material was sublimed at room temperature. A 6-mg portion of this sublimed material was then completely reduced to anion radical with a large excess of potassium metal in THF. Analysis of the resulting ESR spectrum proved the mixture to consist of a 1.3/1 mixture of perdeuterated naphthalene/naphthalene. The remainder of this mixture was again reacted with sufficient potassium in THF under high vacuum to reduce half of it. This new anion radical–neutral molecule mixture was worked up in the same manner. After sublimation, complete reduction of a 6-mg sample of the mixture and ESR analysis showed it to consist of a 1.5/1 mixture of perdeuterated naphthalene/naphthalene.

ESR spectra were recorded on a Bruker (IBM) ER-200 ESR spectrometer 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 blowing up both the empirical spectra and the computer simulations, such that only the small portion (about 1/4) of the central region of each were recorded. The full spectra could then be simulated as shown in Figures 1 and 2.

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