Effect of Charge Distribution upon Condensed-Phase Electron Transfer between Isotopic Isomers

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EPR analysis of the anion radicals resulting from the partial potassium reduction of mixtures of perdeuteriated and perprotiated polyaromatics (*R and R, respectively) in tetrahydrofuran shows that the equilibrium constant for the reaction $R^{\bullet -},M^+ + {}^*R \rightleftharpoons R + {}^*R^{\bullet -},M^+$ is less than unity but that it is closer to unity for systems with large amounts of charge density on the ring juncture carbons. These EPR results predict that a separation of anion radical from neutral molecule would effect an isotopic separation. Removal of the THF leaves a solid mixture of neutral polyaromatic and the potassium anion-radical salt. Subsequent dissolution or sublimation of the neutral polyaromatics from the anion radical yields a mixture that is enriched in the heavy isotopic isomer, and reoxidation of the anion radical with iodine yields a mixture that is depleted in the heavy isotopic isomer. The room-temperature equilibrium constants obtained from these physical separations are not as large as those measured in solution due to lattice effects in the solid state.

The reports[1-6] of an equilibrium isotope effect involving the transfer of electrons from an organic anion-radical ion pair to its neutral isotopic isomer (reaction 1, where *R

$$R^{\bullet -},M^+ + {}^*R = R + {}^*R^{\bullet -},M^+ \qquad (1)$$

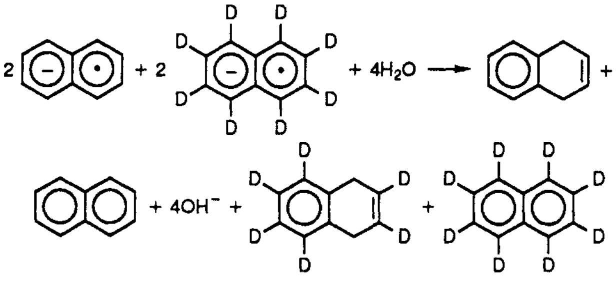
is the heavy isotopic isomer of R) have also led to some controversy, since the effect is believed by some to be larger than current theory can accommodate.[7] However, the H and D isotope effect that we initially observed via EPR measurements[1-4] has been confirmed with cyclic voltammetry data[8] and ion cyclotron resonance data.[9] Further, the effect in general has also led to actual isotope enrichments, which have been detected via mass spectral analysis,[2] scintillation counting,[10] EPR measurements,[1] and NMR measurements.[2] This work has been supported by observations made at Los Alamos National Laboratory.[8] There it was found that the reduction potential, measured versus a silver wire quasi-reference electrode and referenced to an internal potential standard [$(C_5H_5)_2Fe = (C_5H_5)_2Fe^+ + e^-$] of perdeuteriated naphthalene, is 13 ± 2 mV greater than that of naphthalene in THF with 0.1 M tetra-*n*-butylammonium tetrafluoroborate as the supporting electrolyte.[8] Their $\Delta E°$ corresponds to an equilibrium constant of 0.60 ± 0.05 at room temperature. Considering the experimental error and possible effects due to ion association, this is reasonably close to the room-temperature value extrapolated (assuming that $\Delta S° = 0$) from our EPR measurements (0.50 ± 0.03).[2] It is also possible that the entropy term is not exactly zero and $\Delta G° \neq \Delta H°$.

A positive free energy of electron transfer is also observed when mixtures of perdeuteriated naphthalene and naphthalene are partially reduced in THF. That is, the isotopically lighter isomer is preferentially reduced, and the equilibrium constant for reaction 2 is 0.26 at −120 °C.[1]

$$C_{10}H_8^{\bullet -},M^+ + C_{10}D_8 = C_{10}H_8 + C_{10}D_8^{\bullet -},M^+ \qquad (2)$$

$$\Delta G° = 466 \text{ cal/mol}$$

The fact that this equilibrium isotope effect can be taken advantage of to separate mixtures of $C_{10}H_8$ and $C_{10}D_8$ has been demonstrated by quenching the equilibrium mixture with water at room temperature, reaction 3. The proton-decoupled ^{13}C NMR analysis of the Birch reduction products clearly shows that the ratio of dihydronaphthalene to dihydrohexadeuterionaphthalene is greater for a partially reduced mixture of $C_{10}H_8$ and $C_{10}D_8$ than it is for a fully reduced mixture. Quantitative analysis of this NMR data in terms of the ratio of deuteriated to undeuteriated dihydronaphthalene (previously discussed in detail)[2] shows that the equilibrium constant is 0.41 ± 0.04 at 298 K.[2] If it is assumed that the entropy change for reaction 2 is close to zero, then K_{eq} from the EPR data at 298 K is $K_{eq} = e^{-466/298R} = 0.46 \pm 0.03$. Thus, the results from the physical separation followed by NMR analysis are in reasonable agreement with the EPR experiment.


(3)

The reduction of the solution electron affinity of the aromatics upon perdeuteriation appears to be general, since the free energy change for reaction 1 is well above zero when R represents benzene, naphthalene, or anthracene and *R represents their perdeuteriated analogues.[3] The preferential electron attachment to the light isotopic isomer can be qualitatively accounted for by the general weakening of the double bonds, which is much less than offset by the strengthening of the single bonds,[11-14] upon addition of an antibonding electron.[3] The resulting polyaromatic anion radicals in THF do exist as ion pairs,[15]

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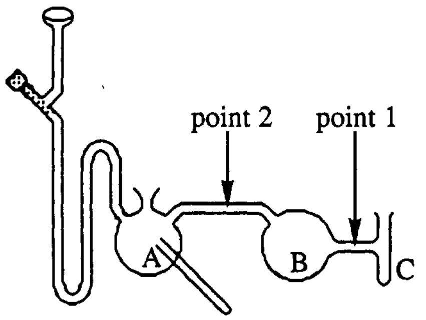

Figure 1. Apparatus used for the isotopic enrichment experiments by sublimation. See text for explanation.

and the electron transfer is accompanied by a transfer of the counterion as shown in reactions 1 and 2.

All of the aromatics, except benzene, have unsubstituted carbons, and it was expected that this would decrease the perdeuteriation effect upon the solution electron affinity. We were interested in gaining insight into how equilibrium constants for reaction 3 vary with the fraction of unprotiated carbons, as this information would allow insight into how the localization of charge and spin density on the anion radicals effects the electron transfer from the isotopically light to the isotopically heavy materials.

Experimental Section

Separations. Carefully weighed portions (0.2–2 mmol) of the polyaromatic and its perdeuteriated analogue were placed in bulb A of the apparatus shown in Figure 1. Tube C was then charged with approximately enough potassium metal to reduce half of the aromatics. Bulb A and tube C were sealed by glass-blowing techniques, and the apparatus was evacuated. A fresh potassium mirror was deposited in bulb B by distillation from tube C. Tube C was consequently sealed and cut from the apparatus, at point 1. Approximately 50 mL of dry THF was then distilled from NaK_2 into bulb A, the Teflon stopcock was shut, and the apparatus was removed from the vacuum line. Once the polyaromatic was completely dissolved in the THF, a small portion of this solution was poured into side arm E. This side arm was then removed from the apparatus and used as the control sample. The remainder of the THF solution was exposed to the potassium mirror until all of the metal had dissolved. The THF solution was then poured over into bulb A, with care, so as not to contaminate the U-tube with any of the solution. The THF was distilled back into bulb B to rinse any remaining THF solution; the rinse was then poured back into bulb A. The majority of the solvent was removed from the anion radical–neutral molecule mixture by cooling bulb B to −78 °C in a dry ice–acetone bath. Bulb B was then sealed from the apparatus at point 2. The apparatus was connected to the high-vacuum system (10^{-6} Torr) and left exposed for several hours to remove any remaining solvent. The U-tube was then cooled in a dry ice–acetone bath, while bulb A was placed in a heated (75–100 °C depending on the polyaromatic) oil bath. This resulted in sublimation of the unreduced polyaromatics, which were collected in the cooled U-tube. The polyarenes collected in the U-tube were submitted to mass spectral analysis along with the control sample.

In other experiments the anion radical–neutral molecule mixture was washed with hexane to selectively dissolve the neutral material from the salt. The hexane solution was separated from the insoluble anion-radical salt via filtration through a sintered glass frit. After several washings of the anion radical with hexane, this salt was reoxidized back to the neutral polyaromatic. An excess of I_2 dissolved in ether was added to the solid anion-radical salt remaining in bulb A. This addition liberated the polyaromatics $[2K^+R^{\bullet-} + I_2 = 2K^+I^- + 2R]$.[16] Once the reoxidized solution was removed from the apparatus, sodium thiosulfate was added to eliminate any excess I_2. After evaporation of the ether, the organic materials were sublimed.

Mass spectral data were collected on a Hewlett-Packard 5790/5970 GC–mass spectrometer system with a 30 m × 0.25 mm (i.d.) capillary column of methylphenyl silicone. Each sample was initially detected in the SCAN mode to check for any impurities. Detection methods were then set in the SIM (selected ion mode), focusing on the parent ions for calculation of isotopic ratios.

ESR Measurements. All anion radicals were generated under high-vacuum conditions in sealed glass containers via contact with a freshly distilled potassium metal mirror. Carefully weighed portions of the unsubstituted and isotopically substituted hydrocarbons were placed into the apparatus used for the reactions. THF was added, and the resulting solution was then recorded and simulated. The apparatus was then retrieved from the spectrometer, and the solution was reexposed to the metal mirror. This second exposure was continued until all of the neutral polyaromatic was reduced to the anion radical. At this time the ESR spectrum was again recorded and simulated. After this second recording, the apparatus was broken and water added to the THF solution. The resulting solution was then titrated with standard HCl to ensure that the solution did contain 1 mol of metal/mol of hydrocarbon at the time of the second ESR recording. *In all cases the ESR simulations for these fully reduced solutions yielded best agreement with the experimental spectra when* $[{}^*R^{\bullet-}]/[R^{\bullet-}]$ *was assumed identical with the ratio of heavy to light material added to the apparatus.* This agreement supports the fact that the ESR simulation technique yields accurate values for the ratios of isotopically heavy to light anion radicals. The partially reduced mixtures were best simulated with heavy to light anion-radical ratios that are much lower than the isotopic ratio of the materials used to prepare the reaction mixture.

ESR spectra were recorded on a Bruker (IBM) ER-200 ESR spectrometer equipped with a Bruker temperature controller. Mole ratios of the anion radical 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 a small portion (about one-fourth) of the central region was recorded. Most of the simulations were carried out under "blind" conditions. That is, the individual constructing the simulations did not know the [*R]/[R] ratio used in the sample preparation.

The computer program used to generate the spectral simulations is based upon the Bloch equations and rigorously accounts for line broadening caused by electron exchange between the radical and the nonparamagnetic species in solution. The computations are based on an expression for G (total transverse

$$G = \frac{iC}{(1/P_kA_k^{-1}) - (1/\tau)} \tag{4}$$

$$A_k = i(\omega_k - \omega) + T_2^{-1} + \tau^{-1} \tag{5}$$

magnetization) for exchange between multiple sites as generalized from Binsch's[17] two-site exchange model. The imaginary part of this equation corresponds to the relative absorption of electromagnetic radiation of a radical with N nuclear spin states as a function of ω (Larmor frequency), τ (lifetime), P_k (statistical population), ω_k (resonance frequency of the kth nuclear state), and T_2 (transverse relaxation time). C is an arbitrary scaling factor. Differentiating eq 4 and extracting the imaginary portion generates the observable ESR spectral simulation.

An empirical value for peak to peak intrinsic line width is used for the calculation of T_2, and τ is calculated as a function of hypothetical values for the rate constant for exchange (k_r) and the molar concentration of the nonparamagnetic species ([M]), eq 6.

$$\tau = (2k_r[\mathrm{M}])^{-1} \tag{6}$$

Initially, coupling constants are obtained from spectra of solutions of the isotopically pure radicals. Simulations generated

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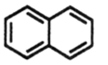
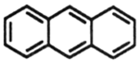
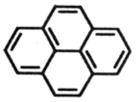
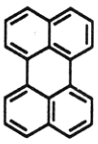
Table I. Equilibrium Constants for Reaction 1, Decrease in Solution Electron Affinity (ΔEA) (cal/mol) upon Perdeuteriation, Ratio of Protiated Carbons to Total Carbons, and Negative Charge Density on the Protiated Carbons Based upon the Hückel Molecular Approach

polyaromatic	K_{eq}(173 K), ΔEA = Δ$G°$	H/C	$\sum C_{i(H)}^2$	K_{eq}(298 K) (extrapolated)
	0.26 ● 0.04[a] 466 ± 53	1.0	1.0	0.46
	0.26 ● 0.05[b] 466 ± 67	0.80	1.0	0.46
	0.30 ± 0.04[b] 417 ● 46	0.71	0.97	0.50
	0.37 ± 0.06[c] 344 ● 65	0.63	0.89	0.56
	0.40 ± 0.6[c] 317 ± 69	0.60	0.82	0.59

[a] Data taken from ref 2. [b] Data taken in part from ref 2 and remeasured in this work. [c] Data taken from this work.

with these parameters are improved as necessary by trial variation of the exchange rate constant, with very careful attention to matching of observable line widths and shapes (by superimposition of simulated and real spectra on a light box). Then, the simulations of the two isotopic isomer anion radicals are computationally superimposed with concentration ratio as a new variable parameter.

Coupling constants and line widths of both species have to be meticulously adjusted in the simulations of mixtures, by reference to lines that are relatively free of overlap. The equilibrium constants produced by the concentration ratios used for the "best fits" are reproducible over several experiments with differing neutral molecule concentration ratios. "blind" simulations of fully reduced mixtures, used to test the accuracy of the fits, reproduce the concentration ratio of the prepared neutral mixtures. Further, the rate constants for electron exchange between neutral molecule and anion radical can be determined from these simulations, and they agree with the literature[15] values.

Results and Discussion

When carefully measured quantities of pyrene and perdeuteriated pyrene were reduced with very deficient amounts of potassium metal in THF, the two anion radicals were produced simultaneously and ESR analysis of the resulting solutions indicates that the equilibrium constant at −120 °C for reaction 3, where R = pyrene, is 0.37 ± 0.07. This corresponds to a standard free energy and enthalpy change of 344 cal/mol. The temperature dependence ESR studies that would be necessary to prove that $\Delta H° = \Delta G°$ are not feasible since the line broadening at elevated temperatures due to electron exchange is too great to allow the resolution needed for accurate K_{eq} measurements. It is clear from Figure 2 that large line widths would eliminate resolution of the hyperfine lines in the perdeuteriated anion-radical spectrum.

The results reported in Table I indicate that the equilibrium constant for reaction 1 deviates further from unity for those systems that can be deuteriated in positions of higher charge density. The deuterium substitution would have no effect if it took place on positions of zero spin density. The ring juncture carbons on naphthalene lie in a nodal plane in the LUMO, and no spin or charge density due to the added electron resides on these two carbons. In general, K_{eq} is further from unity for those systems where more of the excess charge density is located on the non ring juncture carbons.

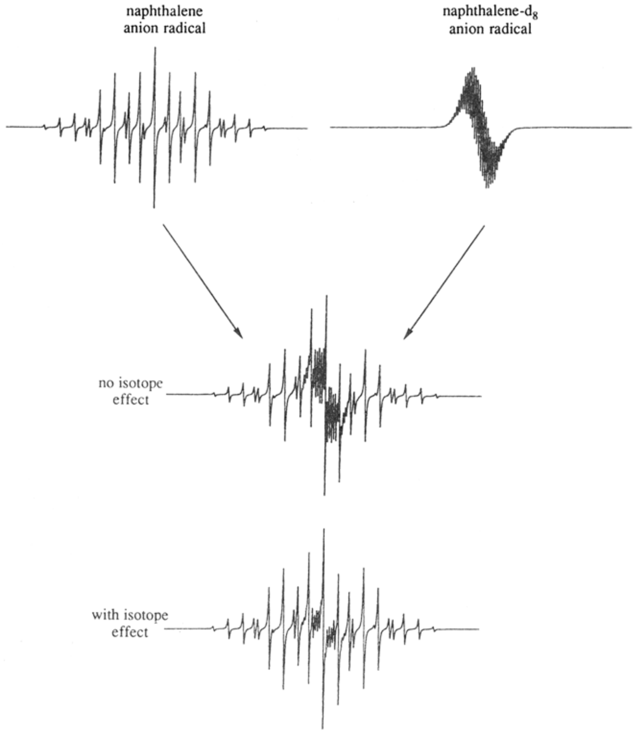


Figure 2. Example of how ESR is used as an analytical technique for the determination of the relative concentrations of anion radicals. These ESR results are used to predict the efficiency of the isotope separations. (Top left) Computer simulation of the ESR spectrum of the naphthalene anion radical. (Top right) Computer simulation of the spectrum of the perdeuteriated naphthalene anion radical. (Bottom) Two spectra combined in different ratios. The spectrum labeled "no isotope effect" was obtained by combining the spectra of $C_{10}H_8^{•-}$ and $C_{10}D_8^{•-}$ in a ratio of $[C_{10}H_8^{•-}]/[C_{10}D_8^{•-}] = 0.162$. The spectrum labeled "with isotope effect" is a computer simulation of the ESR spectrum based upon a ratio of anions of $[C_{10}H_8^{•-}]/[C_{10}D_8^{•-}] = 0.556$. When a mixture of naphthalene and naphthalene-d_8 ($[C_{10}H_8]/[C_{10}D_8] = 0.162$) is reduced with a very deficient amount of potassium metal in THF, the resulting solution yields an ESR spectrum (pictured in ref 3) that matches exactly that corresponding to a $[C_{10}H_8^{•-}]/[C_{10}D_8^{•-}]$ ratio of 0.556. These data indicate an equilibrium constant for reaction 2 of 0.162/0.556 = 0.29. The ratio of neutral species (0.162) is virtually unchanged from its original value, as only a small percentage is reduced. This is one example of many measurements. The average of all of the measurements is 0.26 ± 0.04.

After evaporation of the solvent, separation of the neutral molecule phase (phase 1) from the anion radical (phase 2) in a partially reduced mixture of hydrocarbon and perdeuteriated hydrocarbon should result in a partial separation of the isotopic materials, and the degree of separation should reflect the thermodynamic equilibrium constant. The neutral hydrocarbons in phase 2 can be recovered via the reoxidation with iodine. The solid-phase equilibrium constant is simply the mole ratio of the heavy to light isotopic isomers in phase 1 divided by that in phase 2:

$$K_{eq}(s) = \frac{([{*}R]/[R])_{phase1}}{([{*}R]/[R])_{phase2}} \qquad (7)$$

These room-temperature solid-phase equilibria can be compared to those observed in solution by simply extrapolating the equilibria data in Table I from 173 to 298 K [$K_{eq} = e^{-\Delta G°/298R}$] (Table II). It must be kept in mind that these are solution-phase equilibrium constants, and they do agree with the separations that have been carried

Table II. EPR-Measured Equilibrium Constants Extrapolated to 298 °C (K_{eq}(soln)) and Solid-Phase Equilibrium Constants (K_{eq}(s)) Obtained from the Separations of the Neutral Molecule from the Anion Radical at 298 K

polyaromatic	K_{eq}(soln)	K_{eq}(s)	ref
benzene	0.45	0.59 ± 0.04[a]	2
naphthalene	0.45	0.67 ± 0.05[b]	this work
anthracene	0.50	0.76 ± 0.05	this work
pyrene	0.56	0.75 ± 0.05	this work
perylene	0.59	0.74 ± 0.07	this work

[a] For the benzene separations, the K^+ in the solid anion-radical salt is encapsulated in 18-crown-6.[2] This may account for the better separation, and apparent smaller K_{eq}(s), in the benzene system compared to those of the naphthalene system. [b] If the separation of anion radical and neutral molecule for this system is carried out prior to the removal of the solvent by reaction of the anion radical with water, the equilibrium constant obtained from the separation (0.41 ± 0.04) is well within experimental error of K_{eq}(soln).[2]

out in solution;[2] however, the separations reported here take place in the solid phase after the removal of the solvent. The very small entropy change for reaction 1 allows meaningful extrapolations of the low-temperature data to room temperature.

Using the dissolution of pyrene in hexane to separate the neutral material from the anion-radical salt yields the room-temperature solid-phase equilibrium constant values shown in Table II. It might be argued that incomplete dissolution of the neutral material in the hexanes is an explanation for the difference in the solution K_{eq} and that measured in the solid phase (K_{eq}(s)) via physical separation. To see whether a different separation technique would bring the two into closer agreement, the experiments were repeated but, this time, the neutral molecule was sublimed from the anion-radical salt. This alteration of the method of anion radical–neutral molecule separation did not change the results. Thus, a chemical explanation is in order.

In solution, the rate of electron transfer between anion radical and neutral molecule is very fast. The second-order rate constants vary from 10^7 to 10^9 M^{-1} s^{-1}.[15] Consequently, there is no doubt that equilibrium (reaction 1) is established long before an analysis can be performed. Since the solid anion radical–neutral molecule mixture is generated by slowly evaporating the solvent (THF) from the solution, a state of thermodynamic equilibrium persists during solvent removal and possibly in the solid state. It was pointed out by a reviewer that the $M^+R^{\bullet-}(s)$ and R(s) may precipitate as microcrystals so that solid-state effects will not operate at the molecular level. It appears that the ΔG° values in the solid state (or supersaturated state) are not as large as they are in solution. Keep in mind that when the separations of anion radical and neutral molecule are carried out in the solution state via the reaction of the anion radical with water, the equilibrium constants measured via the EPR and separation techniques do agree.[2]

The solution electron affinities of the perdeuteriated polyarenes are smaller than those of the perprotiated materials due to the general decrease in bond order caused by addition of an electron to an antibonding molecular orbital. Raman and IR work carried out on perdeuteriated benzene, benzene, and their anion radicals show that the destabilization of the isotopically heavy material is greater upon electron attachment than is the destabilization of the isotopically light benzene.[11] Thus, the total effect comes from the fact that the extra destabilization for $^*R^{\bullet-}$, with respect to $^*R$, is due to the smaller decrease in zero point energy as compared to that of $R^{\bullet-}$ with respect to R; consequently, $K_{eq} < 1$. Thus, the anion-radical salt and unreduced neutral molecule that exist after a partial reduction of a mixture of the two isotopic isomers should be enriched in the isotopically light and isotopically heavy materials, respectively. This is in agreement with experiment.

The quantitative evaluation of the partition function ratio for the isotopic neutral molecules and anion radicals in the solid state would require a realistic model that relates to all of the vibrational degrees of freedom. In the solid phase the complicated lattice and perturbed molecular vibrations of the anion-radical salt are not amenable to calculation.

When supported by the EPR and separations work reported here, there can be no reasonable doubt that perdeuteriation decreases the condensed-phase electron affinity. These data further indicate that this decrease is greater in solution than in the solid phase. This is the same situation that was observed for the case of ^{13}C- and ^{14}C-substituted benzophenones. Physical separation of the ketyls from the neutral ketones showed an enrichment of the [^{14}C]benzophenone in the neutral material, but the separation, while in the right direction, was not as large as would be expected from the solution equilibrium measurements on the benzophenone/[^{13}C]benzophenone system.[5,10] The data objectively exists, and even if its interpretation in terms of established theory is awkward,[7,18,19] this does not invalidate it. Further, to maintain that our data are valid for H and D measurements only[7] implies the peculiarly illogical assumption that an error is being made that is dependent upon the materials under observation even though the experimental techniques are identical.

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