Table V. Single-Crystal X-ray Crystallographic Analysis

	compound 2c′	compound 4
A. Crystal Parameters		
formula	$C_{20}H_{23}N_3O_7S$ (449.5)	$C_{15}H_{13}N_3O_4S\cdot C_2H_7NO$ (392.4)
crystallization medium	dimethyl sulfoxide	acetonitrile
crystal size, mm	0.14 × 0.14 × 0.15	0.20 × 0.20 × 0.20
cell dimensions		
a =	10.018 (2) Å	12.823 (4) Å
b =	10.240 (3) Å	9.075 (4) Å
c =	11.351 (3) Å	9.954 (4) Å
α =	102.85 (2)°	123.01 (2)°
β =	110.71 (2)°	91.54 (3)°
γ =	93.16 (2)°	103.18 (3)°
V =	1050.4 (4) Å^3	929.5 (5) Å^3
space group	$P\bar{1}$	$P\bar{1}$
molecules/unit cell	2	2
density calcd, g/cm^3	1.42	1.40
linear absorptn factor, cm^{-1}	17.6	18.4
B. Refinement Parameters		
number of reflcns	2129	1921
nonzero reflcns ($I > 3.0\sigma$)	1359	1889
R index[a]	0.078	0.049
scale factor	1.694 (4)	0.750 (5)

[a] R index = $\sum ||F_o| - |F_c|| / \sum |F_o|$.

Crystal Structures. A representative crystal for each compound was surveyed, and a 1 A data set (maximum sin Θ/λ = 0.5) was collected on a Nicolet R3m/μ diffractometer for compound **2c′** and a Syntex P1 for compound **4**. Atomic scattering factors were taken from the International Tables for X-ray Crystallography.[18] All crystallographic calculations on **2c′** were facilitated by the SHELXTL[19] system, and those on **4** by the CRYM[20] system. All diffractometer data were collected at room temperature. Pertinent crystal, data collection, and refinement parameters are summarized in Table V.

In both cases, a trial structure was obtained by direct methods and refined routinely. Hydrogen positions were calculated wherever possible. The methyl hydrogens and hydrogen on oxygen were located by difference Fourier techniques. The hydrogen parameters were added to the structure factor calculations but were not refined. The shifts calculated in the final cycle of least-squares refinement were all less than 0.1 of their corresponding standard deviations. The final R index was 0.078 for compound **2c′** and 0.049 for compound **4**. The final difference Fouriers revealed no missing or misplaced electron density.

The refined structures were plotted (Figures 7 and 8) by using the SHELXTL plotting package. Coordinates, anisotropic temperature factors, distances, and angles are available as Supplementary Material (Tables S1-S10).

Acknowledgment. We gratefully acknowledge the substantial contributions of Andrew C. Braisted, who first isolated compound **2c′**, Diane Rescek, who conducted many of the NMR measurements, and Dr. B. W. Dominy, who performed the computations involved in Figure 7 and Table III.

Supplementary Material Available: Tables of atomic coordinates and isotropic thermal parameters (Table S1), bond lengths (Tables S2 and S7), bond angles (Tables S3 and S8), anisotropic thermal parameters (Table S4 and S9), H-atom coordinates and isotropic thermal parameters (Table S5), atomic coordinates (Table S6), and H-atom coordinates (Table S10) (10 pages). Ordering information is given on any current masthead page.

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Effect of Sequential Deuteriation upon the Solution Electron Affinity of Benzene

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Abstract: The sequential addition of deuteriums to the six possible sites in benzene results in a nonlinear decrease in the solution EA, and this decrease in the EA is independent of the relative positions of substitution and thus orbital splitting. A plot of the reciprocal of the number of deuteriums vs $1/(1 - K)$, where K represents the equilibrium constant for electron transfer from the anion radical of the protiated benzene to the deuterium-substituted benzene, is exactly represented by a parabolic curve. This relationship has been linearized.

There are only two stable annulene anion radicals that are capable of maintaining the shape of a regular polyhedron on the ESR time scale. In both of these systems the odd electron is equally distributed between the doubly degenerate orbitals, which are nonbonding in the case of [8]annulene and antibonding in the case of [6]annulene. The presence of an electron-releasing substituent on the anion radical of [8]annulene results in a splitting of the degeneracy of the singly occupied nonbonding molecular orbitals, with a consequent increase in the spin density in the Ψ_{n+} MO at the expense of that in the Ψ_{n-}.[1] The relative increase in the spin density in Ψ_{n+} is due to the fact that the energy of this MO increases upon substitution, while that for Ψ_{n-} remains unperturbed (Figure 1A). In contrast to this, a single electron-releasing substituent on the [6]annulene anion radical results in a relative decrease in the spin density in the symmetric wave function (Ψ_s), which is increased in energy.[2] The antisymmetric wave function (Ψ_a) is unperturbed by the presence of an electron-releasing substituent (Figure 1B).

In the simplest model, the odd electron in the [8]annulene moiety or [6]annulene moiety can be described as existing in linear

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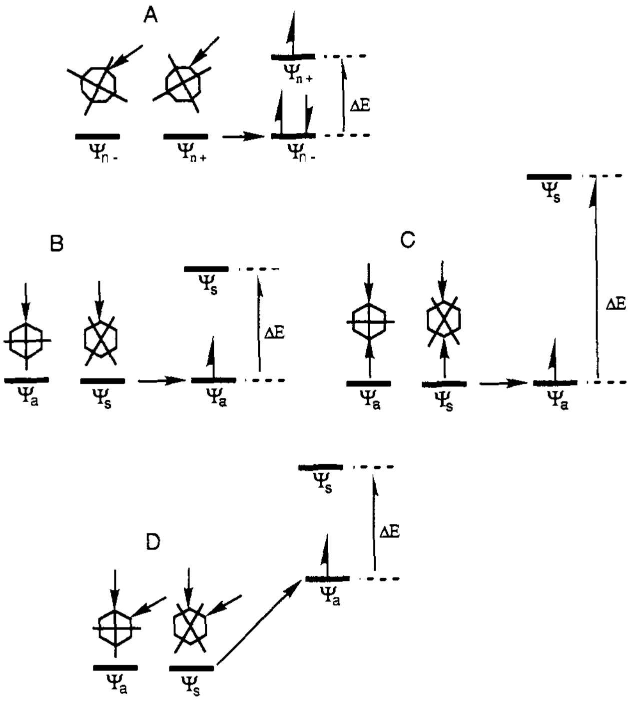


Figure 1. (A) Two nonbonding degenerate orbitals of planar [8]annulene (COT) split by an electron-releasing group. (B) Two antibonding degenerate orbitals of planar [6]annulene and their splitting due to the presence of an electron-donating group. (C and D) Splitting of the antibonding MO's in [6]annulene due to the presence of two electron-donating groups. The arrows point to the substituted positions on the ring.

combinations of the two formerly degenerate MO's, eq 1 and 2, respectively.[1,2] Both C_{n-} and C_s can be obtained from the ESR

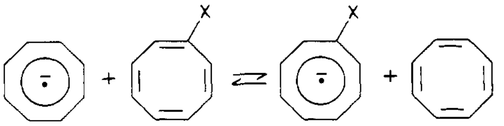
$$\Psi = C_{n-}\Psi_{n-} + C_{n+}\Psi_{n+} \tag{1}$$

$$\Psi = C_s\Psi_s + C_a\Psi_a \tag{2}$$

coupling constants. When π–π spin polarization is neglected, $C_{n-}^2 = A_{H(4)}/[A_{H(4)} + A_{H(3)}]$ and $C_s^2 = 3A_{H(para)}/[2A_{H(para)} + 4A_{H(meta)}]$. C_{n-} and C_s are related to the magnitude of the splitting of the degenerate MO's by the Boltzmann distribution, eq 3. An identical equation can be written for C_{n-} except that it would be in terms of ΔE for [8]annulene (COT).

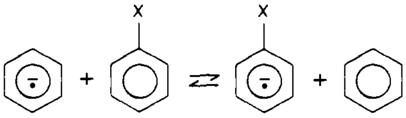
$$C_s^2 = 1/(e^{\Delta E/RT} + 1) \tag{3}$$

It has been shown that there is a rough correlation between ΔE, determined from ESR measurements as described above, and the enthalpy of electron transfer from the [8]annulene anion radical to monosubstituted [8]annulene in hexamethylphosphoramide (HMPA), reaction 4. When X = CH_3, ΔE = 450 cal/mol, and $\Delta H°$ for reaction 4 is 540 cal/mol.[3]



(4)

We might not expect a similar correlation between ΔE and the enthalpy for the electron transfer from [6]annulene anion radical to a monosubstituted [6]annulene, reaction 5, because the orbital



(5)

splitting leads to the prediction that each monosubstituted [6]annulene should have the same solution electron affinity as does [6]annulene. That is, the perturbing substituents cannot, to first order, change the energy of the highest filled MO of the benzene anion radical.[4] However, when X = $-CH_3$, the free energy and enthalpy change for reaction 5 is 506 cal/mol in a THF–DME mixture.[5]

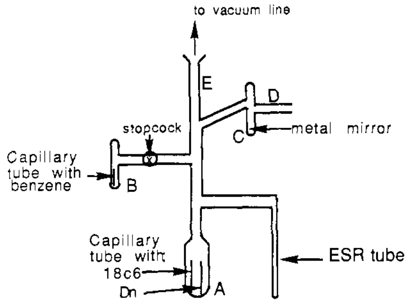
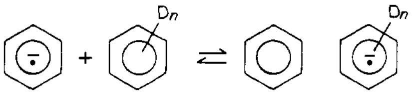


Figure 2. Apparatus used for the partial reduction of the mixtures of benzene and deuteriated benzenes.

Using the coupling constants $A_{H(para)}$ = 0.59 G and $A_{H(meta)}$ = 5.45 G reported for the toluene anion radical (X = $-CH_3$)[6] in reaction 5, $C_s^2 = 3(0.59)/[2(0.59) + 4(5.45)] = 0.077$ and ΔE = 859 cal/mol. This is a little larger (13%) than the 761 cal/mol calculated by Alper and Silbey,[7] but their calculation includes the effects of vibronic interactions. The sensitivity of the spin distribution to exceedingly small perturbations is greater for the [6]annulene systems than for the [8]annulene systems.[8c] This sensitivity is so great in the benzene system that a difference in the para proton (3.41 G) and the meta proton (3.92 G) splittings can be observed when one ring hydrogen is replaced by a single deuterium.[8a] The single deuterium splits the degeneracy of the two orbitals by about 50 cal/mol.[8a] This coupled with the fact that electron-releasing groups increase $\Delta G°$ of reaction 5 implies that the equilibrium constant for reaction 5 should be slightly less than unity when X = D. On the other hand, the ESR spectrum of the radical anion of monodeuteriated cyclooctatetraene exhibits no splitting of the degeneracy of the two nonbonding molecular orbitals.[8b–d]

We have recently developed an ESR technique for measurement of equilibrium constants for electron transfer between isotopic isomers.[9] When this technique was utilized, it was found that the free energy and enthalpy of electron transfer from benzene to perdeuteriated benzene is 440 ± 11 cal/mol.[9a] If it is naively assumed that each deuterium lowers the solution electron affinity by $^1/_6$ of this value, then a single deuterium should result in a free energy of reaction 5 (X = D) of about 70 cal/mol. This technique involves the partial reduction of a mixture of isotopic isomers followed by an ESR study of the resulting mixture of anion radicals. The relative concentrations of the two anion radicals can be measured via computer simulation of the ESR spectra. The technique has very recently been shown to be sensitive enough to allow the observation of isotopic perturbations in solution EA's that are as small as 50 cal/mol.[10] Thus, we were motivated to measure the free energy of reaction 6 where n varied from 0 to



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6 to gain insight into how sequential isotopic substitution affects solution electron affinity. It has already been demonstrated that

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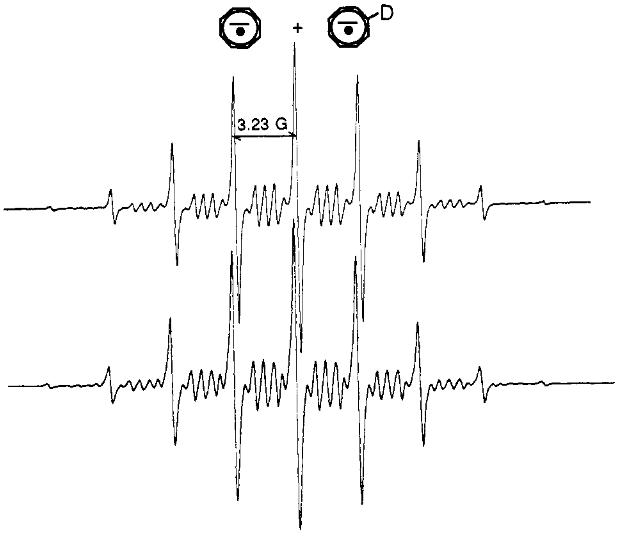

Figure 3. ESR spectrum (upper) and computer simulation (lower) resulting from the addition of 0.21 mmol of D_2O to about 10 mL of a hexamethylphosphoramide solution of 1.1 mmol of [8]annulene reduced by 1.7 mmol of potassium metal. The monodeuteriated [8]annulene anion radicals exhibits only one proton coupling constant for all seven protons, and thus there is no observed splitting of the degeneracy of the nonbonding MO's due to the presence of a deuterium. ΔE for the [8]-annulene system is 0 when the substituent is D.

nonunity equilibrium constants for electron-transfer reactions involving isotopic isomers (like reaction 6) can be used to physically separate the isotopic isomers involved.[11]

Experimental Section

Carefully weighed mixtures of benzene (D_0) and a specifically deuteriated benzene (D_n) were placed into separate capillary tubes, which were in turn sealed. The tube containing the benzene was placed into B of the apparatus shown in Figure 2. The capillary tube containing the D_n was placed into bulb A of the apparatus along with a very molar deficient quantity of 18-crown-6. After evacuation of the entire apparatus, a freshly distilled potassium mirror was deposited into bulb C from the side tube, which was subsequently sealed from the apparatus at point D. Dry THF was then distilled from a storage bulb containing NaK_2 directly into bulb A. The entire apparatus was then sealed from the vacuum system at point E. The apparatus was then shaken so as to break the tube containing the deuteriated benzene and expose the THF-deuteriated benzene–18C6 solution to the potassium mirror. The amount of anion radical formed was controlled by the amount of 18C6 (the limiting reagent) present in the solution. A sample of this resulting anion-radical solution was then poured into the EPR tube and subjected to EPR analysis. The apparatus was then removed from the spectrometer and shaken so as to rupture the capillary tube containing the benzene. This benzene was then allowed to fully mix with the already formed anion-radical solution, and a second EPR analysis was obtained. The second EPR spectrum always exhibited the presence of the anion radical of both D_n and D_0. The relative amounts of the two anion radicals in solution were accurately obtained from computer simulations of the EPR spectra as previously described.[9a]

When [8]annulene is reduced in hexamethylphosphoramide (HMPA) with potassium metal under high vacuum, the resulting solution exhibits the well-known 9-line pattern of the [8]annulene anion radical.[12] The addition of molar deficient (relative to the metal) amounts of D_2O to the anion-radical solution results in the simultaneous appearance of the monodeuteriated [8]annulene anion radical (Figure 3). This anion radical is characterized by seven protons with a coupling constant of 3.23 G and a single deuterium with a coupling constant of 0.54 G. In contrast to the monodeuteriated [6]annulene system the deuterium does not split the degeneracy of the MO's containing the odd electron within the resolution of the EPR experiment.

The deuteriated benzenes were purchased from MSD Isotopes Inc. (99+%) and used without further purification. The EPR spectra were recorded at −100 °C on an IBM (Bruker) ER-200D spectrometer equipped with an IBM variable-temperature unit.

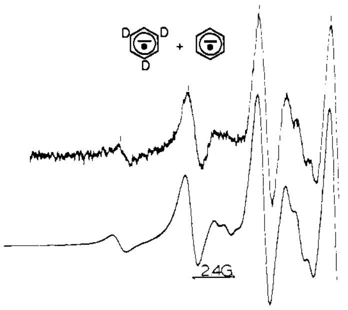

Figure 4. ESR spectrum recorded at −100 °C obtained from the partial reduction of a mixture of D_0 and 1,3,5-D_3 (upper) in THF with 18-crown-6. Below is the computer simulation of the spectrum assuming that K_{eq} for reaction 6 is 0.37. The small vertical arrows indicate the lines due to the anion radical of benzene.

Table I. K_{eq} and $\Delta G°$ for Reactions 6 at −100 °C

compd	K_{eq}	$\Delta G°$, cal/mol	$(1/n - {}^1/_6)^2$	$1/(1 - K_{eq})$
D_0	1.00	0.0	∞	∞
D_1	0.86 ± 0.01	50 ± 3	0.694	7.140
1,2-D_2	0.55 ± 0.02	207 ± 9	0.111	2.220
1,4-D_2	0.56 ± 0.02	202 ± 11	0.111	2.270
1,3,5,D_3	0.37 ± 0.04	344 ± 43	0.028	1.590
D_6	0.26 ± 0.02	475 ± 16	0.000	1.350

Results and Discussion

When a solution of 0.172 mmol of 1,3,5-trideuteriobenzene (1,3,5-D_3) in about 3 mL of tetrahydrofuran (THF) containing a very molar deficient amount of 18-crown-6 is exposed to a freshly distilled potassium metal mirror under high vacuum, a stable solution of the anion radical (1,3,5-$D_3^{\bullet-}$) is formed. The ESR spectrum of the anion radical is best simulated using coupling constants of 0.58 G for the three deuteriums and 3.82 G for the three hydrogens. A small amount of benzene anion radical was always present in these solutions as an impurity, and it is characterized by a 7-line pattern with a coupling constant of 3.82 G. The best computer simulation of this spectrum was obtained using an anion-radical mixture corresponding to $[1,3,5\text{-}D_3^{\bullet-}]/[D_0^{\bullet-}] = 5.42$. The addition of 0.018 mmol of benzene to this anion-radical solution via a break seal clearly results in a dramatic increase in the amplitude of the signal due to the benzene anion radical relative to that due to 1,3,5-$D_3^{\bullet-}$. This spectrum is best simulated using a ratio of $[1,3,5\text{-}D_3^{\bullet-}]/[D_0^{\bullet-}] = 1.70$ (Figure 4). If the solution electron affinities of 1,3,5-D_3 and D_0 had been identical ($K_{eq} = 1$), this anion-radical ratio would have been 4.86 instead of the 1.70 actually observed. Thus, the equilibrium constant for reaction 6, where $n = 3$, that best fits this experiment, and accounting for the benzene impurity (eq 7) in the original mixture,

$$K_{eq} = \{[1,3,5\text{-}D_3^{\bullet-}]/[D_0^{\bullet-}]\}\{([D_{0_i}] + [D_{0_a}])/[1,3,5\text{-}D_3]\} \quad (7)$$

is 0.37. The ratio $\{1,3,5\text{-}D_3^{\bullet-}]/[D_0^{\bullet-}\}$ is obtained via the ESR spectrum and the computer simulation. $[D_{0_i}]$ and $[D_{0_a}]$ represent the concentrations of the small benzene impurity ($[D_{0_i}] \ll [D_{0_a}]$) and the added benzene, respectively. The sum of these two concentrations represents the total benzene concentration. Carrying out this same procedure on three separate anion-radical solutions yields an average K_{eq} of 0.37 ± 0.04.

When monodeuteriobenzene (D_1) is reduced under the same conditions, the same splitting of the degeneracy of the antibonding molecular orbitals as previously reported[8a] was observed ($A_D = 0.57$ G, $A_{H(ortho)} = 3.93$ G, $A_{H(meta)} = 3.93$ G, $A_{H(para)} = 3.56$ G). The addition of benzene to the anion-radical solution resulted in a great enhancement of the signal for $D_0^{\bullet-}$ (present in the original solution only as a minor impurity), and computer simulations clearly show that $[D_1]/[D_0] > [D_1^{\bullet-}]/[D_0^{\bullet-}]$. The equilibrium constant for reaction 6 was found to be 0.86 ± 0.07 at −100 °C when $n = 1$.

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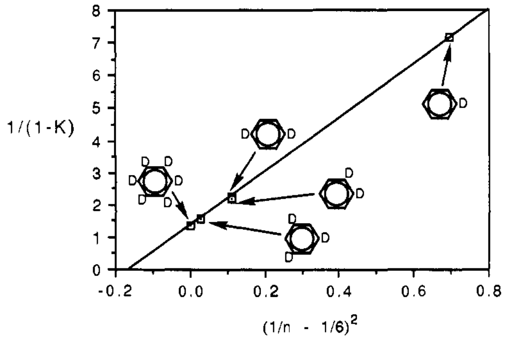

Figure 5. Plot of $1/(1 - K_{eq})$ for reaction 6 vs $(1/n - {}^1/_6)^2$.

Both the 1,2-dideuteriobenzene ($A_D = 0.53$ G, $A_H = 4.10$ G for 2 H's, and $A_H = 3.75$ G for 2 H's) and 1,4-dideuteriobenzene ($A_D = 0.52$ G and $A_H = 4.08$ G) anion-radical systems yield equilibrium constants for reaction 6 when $n = 2$ that are nearly identical with each other (0.55 and 0.56, respectively; Table I).

The data in Table I clearly show that it is impossible to generate a linear free energy relationship involving the equilibrium constant of reaction 6 with either the number of deuteriums or the splitting of the degeneracy of the antibonding MO's. This is in contrast to the fact that such a relationship has been constructed between the enthalpy of electron transfer from [8]annulene to monosubstituted [8]annulenes and the splitting of the degeneracy of the nonbonding MO's.[13]

Whenever an empirical parameter (in this case K_{eq} for reaction 6) has a limiting value in the absence of a perturbing component (in this case neutrons) and varies continuously with the amount of the perturbing component, the use of a weighted average equation is very helpful.[14-17] As most commonly used, the weighted average equation appears in the form introduced by Benesi and Hildebrand[17] and discussed in detail by Deranleau.[18] With the K_{eq} acting as the empirical parameter and the number of neutrons in the 6-membered ring system (n) acting as the peturbing component, the Benesi–Hildebrand equation as applied to this system appears as

$$1/(K_{eq}{}^0 - K_{eq}) = Z(1/n - {}^1\!/_6)^m/(K_{eq}{}^0 - K_{eq}') + 1(K_{eq}{}^0 - K_{eq}') \quad (8)$$

where Z is an unknown constant, $K_{eq}{}^0 = 1$ and represents the value of K_{eq} when $n = 0$, and K_{eq}' represents the hypothetical value of the equilibrium constant in the limit as n approaches infinity. The unknown parameters (K_{eq}' and Z) can be obtained from a plot of $1/(1 - K_{eq})$ vs $(1/n - {}^1/_6)^m$. When $m = 1$, such a plot is parabolic with a minimum near 0.0, implying that letting $m = 2$ would linearize the data. Indeed, plotting the data in Table I in the form represented by eq 8 when $m = 2$ yields a straight line with an x intercept of $-{}^1/_6$ and a slope of ${}^{50}/_6$ (Figure 5). The fact that the changes in K_{eq} resulting from the number of deuteriums going from 1 to 2 is much larger than that when the number of deuteriums goes from 3 to 6 is fortunate, since it obviates the experiments with the 4 and 5 deuterium systems. This keeps the cost of the project manageable.

It is clear from the data in Table I that relative positions of the deuteriums have no effect upon K_{eq} for reaction 6. This is evidenced by the following facts: (1) the 1,2-D_2 and 1,4-D_2 systems have nearly the same equilibrium constants; (2) the splitting of the orbital degeneracy is much larger for the 1,4-D_2 system than it is for the 1,2-D_2 system (Figure 1C,D); (3) the 1,3,5-D_3 system has no orbital splitting; (4) the 1,3,5-D_3 system yields a K_{eq} that is consistent with those systems for which there is a large orbital splitting. These facts eliminate any possibility of a relationship between ΔE and the electron-transfer equilibrium constant. It thus appears that the isotope effects observed here are due to zero-point vibrational changes and are not influenced by electronic effects. In a mathematical sense only, we can view the neutrons in these benzene systems as being spread out over all six possible positions in a way that is analogous to our view of the π electrons in the 6p orbitals.

Acknowledgment. We thank the National Science Foundation, donors of the Petroleum Research Fund, administered by the American Chemical Society, and Baxter Health Care for support of this work.

Appendix: A Rationalization of Equation 8

Consider a two-site model where site β represents a hypothetical benzene system with an infinite number of neutrons in the six hydrogen atoms. All spectroscopic, kinetic, and thermodynamic parameters of an isotopic isomer of benzene ($^*C_6H_6$) can be considered, in a mathematical sense, as weighted averages between those parameters for β and those for benzene. This is certainly true for the equilibrium constant controlling the electron transfer from benzene to $^*C_6H_6$, reaction 9.

$$C_6H_6{}^{\bullet -} + {}^*C_6H_6 \rightleftharpoons {}^*C_6H_6{}^{\bullet -} + C_6H_6 \quad (9)$$

If we treat this equilibrium constant as a weighted average of the equilibrium constant observed when $^*C_6H_6$ = benzene ($K^0 = 1$) and that when $^*C_6H_6 = \beta$, then K_{eq} is given by the product of K^0 and the mole fraction of C_6H_6 plus the product of K' and the mole fraction of β (eq 10). K' is the limiting equilibrium constant for reaction 9 as the number of neutrons in $^*C_6H_6$ approaches infinity (a black hole). The concentration of β is coupled to that of $^*C_6H_6$ by an imaginary reaction consisting of the ejection of m neutron clusters (η) from β, reaction 11. The equilibrium constant for "reaction" 11 is represented by Z and is given by eq 12.

$$K_{eq} = \{[C_6H_6]K^0 + [\beta]K'\}/\{[C_6H_6] + [\beta]\} \quad (10)$$

$$\beta = C_6H_6 + m\eta \quad (11)$$

$$Z = [C_6H_6][\eta]^m/[\beta] \quad (12)$$

Solving eq 10 for $[C_6H_6]$ and substituting this expression into eq 12 yields

$$Z = \{K_{eq} - K'\}[\eta]^m/\{K^0 - K_{eq}\} \quad (13)$$

Rearranging eq 13 leads to eq 14.

$$\{K^0 - K'\}/\{K^0 - K_{eq}\} = Z/[\eta]^m + 1 \quad (14)$$

Our final expression (eq 15) is obtained simply by dividing both sides of eq 14 by $(K^0 - K')$. A plot of $1/\{K^0 - K_{eq}\}$ vs $(1/[\eta])^m$ should yield a straight line with an intercept of $1/\{K^0 - K'\}$ and a slope of Z. In our case, with n deuteriums in $^*C_6H_6$, $(1/[\eta])^m$, which varies from 0 to infinity, must be replaced by a function of $(1/n)^m$ that also varies from 0 to infinity. Further, we must keep in mind that the number of possible substitution sites is limited to 6. The function $(1/n - {}^1/_6)^m$ satisfies these boundary conditions and leads directly to eq 8.

$$1/\{K^0 - K_{eq}\} = Z/[\eta]^m(K^0 - K') + 1/\{K^0 - K'\} \quad (15)$$

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