

Effect of ^{13}C Substitution on the Solution Electron Affinity of *p*-Benzoquinone

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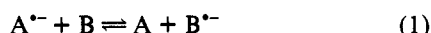
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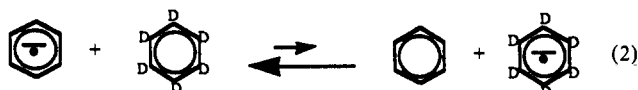
Abstract: An equilibrium isotope effect (confirmed via physical separation of the isotopic isomers involved) was observed via the EPR analysis of a mixture of benzoquinone and benzoquinone- $^{13}\text{C}_6$ competing for a deficient number of electrons in a tetrahydrofuran–liquid ammonia mixture. The K_{eq} for the reaction $\text{C}_6\text{H}_4\text{O}_2^- + ^{13}\text{C}_6\text{H}_4\text{O}_2 = \text{C}_6\text{H}_4\text{O}_2 + ^{13}\text{C}_6\text{H}_4\text{O}_2^-$ is 0.66 ± 0.04 at 200 K. An analogous competition for electrons between benzoquinone and perdeuterated benzoquinone shows no equilibrium isotope effect. The ^{13}C effect is attributed almost exclusively to the carbonyl carbons. The low spin density on the non-carbonyl positions renders the substitution of the protons with deuteriums and substitution of the non-carbonyl carbons with ^{13}C ineffective in altering the solution electron affinity.

Introduction

Over the years, EPR has proven to be an accurate analytical tool for the evaluation of relative concentrations of radicals,¹ and nearly 2 decades ago, free energy changes for electron transfer as small as 500 cal/mol were measured with a reported experimental error of only about 10 cal/mol.² These facts, along with the advances in EPR computer simulation efficiency and precision, make “the EPR technique”³ extremely useful for the study of electron-transfer reactions of the type shown in reaction 1.^{3,4}



More recently, we have made use of this EPR approach to investigate the free energy changes involved in reaction 1 when A and B are isotopic isomers.⁴ Specifically, when A represents benzene and B its perdeuterated analogue (reaction 2), K_{eq} was found to be 0.26 ± 0.01 at $-100\text{ }^\circ\text{C}$.^{1f} The non-unity value for



the equilibrium constant necessarily means that any separation of the neutral molecule from the anion radical will result in a partial separation of the isotopic isomers. In fact, separation of the neutral benzenes (labeled phase 1) from the benzene anion radicals, which were subsequently reoxidized back to benzenes via the addition of I_2 (labeled phase 2), did yield the expected partial separation. The C_6H_6 was enriched in phase 2, and the C_6D_6 was enriched in phase 1.⁴

Wolfsberg et al.⁵ have pointed out that the empirically derived magnitudes of reported carbon isotope effects (reaction 1) are at variance with conclusions based upon statistical mechanical calculations. Therefore, the suitability of the use of the EPR

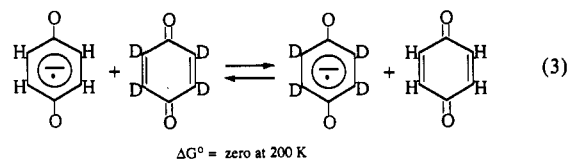
technique to obtain the equilibrium constants for reaction 1 when A and B represent isotopic isomers involving polarizable systems and isotopes heavier than H and D has been questioned.⁵ However, the long history of the technique for nonisotopic systems,³ the agreement between the EPR-measured K_{eq} values and the separation data,^{4,6} the manifestation of the effect in anion radical cleavage reactions,⁷ and the fact that the H and D cyclic voltammetry data⁸ are in good agreement with the EPR data leave no reasonable doubt that the technique yields valid and very useful results, at least for the H and D systems. It should be kept in mind, however, that the H and D effect was not directly questioned.⁵ The ^{13}C effect, on the other hand, was.⁵

We now wish to report the verification of the ^{13}C effect via physical separation of the neutral molecule and anion radical phases coupled with mass spectral analysis. We have carried out these experiments with systems in which the ^{13}C equilibrium isotope effect is enhanced via complete replacement of ^{12}C with ^{13}C .

Results and Discussion

Reaction 1 is very instructive in the case of benzoquinone ($\text{C}_6\text{H}_4\text{O}_2$) and isotopically substituted benzoquinone due to the symmetry of the system and the fact that many of the fundamental vibrational modes of the neutral $\text{C}_6\text{H}_4\text{O}_2$ and its anion radical have been observed empirically.⁹

When a THF–liquid ammonia solution at 200 K under high vacuum containing 0.0418 mmol of benzoquinone and 0.0411 mmol of perdeuterated benzoquinone is reduced with a very molar deficient quantity of freshly distilled sodium metal, both anion radicals are generated, and the relative concentrations of the two anion radicals are controlled by the rapid electron-transfer equilibrium, reaction 3. EPR analyses of such solutions show



that the $[\text{C}_6\text{D}_4\text{O}_2^-]/[\text{C}_6\text{H}_4\text{O}_2^-]$ ratio is within experimental error

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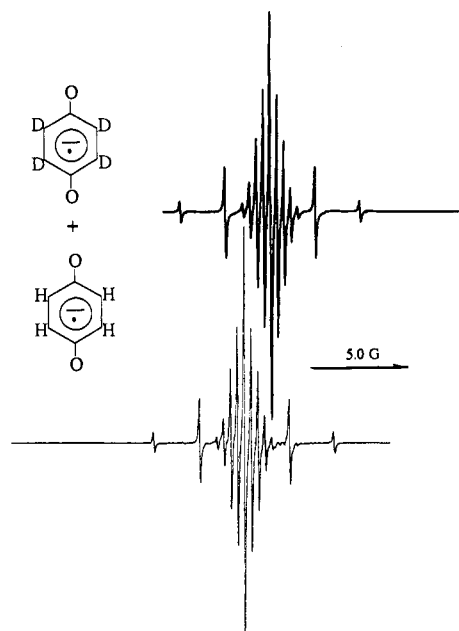
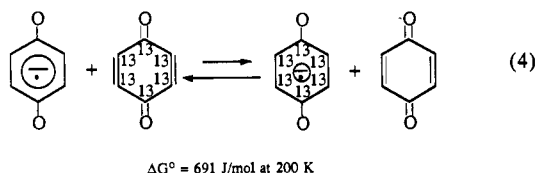


Figure 1. (Lower) EPR spectrum recorded at 200 K resulting from the partial sodium reduction of a mixture of perdeuterated benzoquinone and benzoquinone ($[\text{C}_6\text{H}_4\text{O}_2]/[\text{C}_6\text{D}_4\text{O}_2] = 1.02$) in a THF–liquid ammonia mixture. The simulation (upper) was generated using a ratio of anion radicals that is also 1.02. The coupling constants used in the simulation are $A_D = 0.367$ G and $A_H = 2.41$ G.

of the $[\text{C}_6\text{D}_4\text{O}_2]/[\text{C}_6\text{H}_4\text{O}_2]$ ratio, and thus $K_{\text{eq}} = 1.00 \pm 0.04$ at 200 K, Figure 1. However, when several identical experiments are carried out with mixtures of benzoquinone and benzoquinone- $^{13}\text{C}_6$ ($^{13}\text{C}_6\text{H}_4\text{O}_2$), the relative intensities of the simultaneously observed EPR spectra of $\text{C}_6\text{H}_4\text{O}_2^-$ and $^{13}\text{C}_6\text{H}_4\text{O}_2^-$ suggest that K_{eq} for reaction 4 is 0.66 ± 0.04 in a liquid ammonia–THF mixture at 200 K. This K_{eq} is an average of several measurements.



In one experiment performed at 220 K, 4.20 mg (0.037 mM) of $^{13}\text{C}_6\text{H}_4\text{O}_2$ and 4.22 mg (0.039 mM) of $\text{C}_6\text{H}_4\text{O}_2$ ($[\text{C}_6\text{H}_4\text{O}_2]/[^{13}\text{C}_6\text{H}_4\text{O}_2] = 1.05$) were dissolved in liquid ammonia–THF (15/1), and the mixture was reduced with a very deficient amount of sodium metal. The equilibrated anion radical solution yielded an EPR spectrum best simulated using a $[\text{C}_6\text{H}_4\text{O}_2^-]/[^{13}\text{C}_6\text{H}_4\text{O}_2^-]$ ratio of 0.63, Figure 2. Ion association is not a factor with this high NH_3 –THF ratio. This corresponds to an equilibrium constant for reaction 4 of 0.66 at 220 K. Assuming ΔS° to be insignificant, this converts to 0.63 at 200 K (a value included in the average reported above). Full reduction of the $^{13}\text{C}_6\text{H}_4\text{O}_2$ – $\text{C}_6\text{H}_4\text{O}_2$ mixtures (the addition of one mole of metal per mole of quinone) led to an EPR signal whose simulation yielded a $[\text{C}_6\text{H}_4\text{O}_2^-]/[\text{C}_6\text{H}_4\text{O}_2^-]$ ratio equal to the initial ratio of concentrations of neutral molecules. The concentration ratios for both the full and the partial reductions were also determined by means of computer simulations of expanded portions of the EPR spectra, see the Experimental Section and Figure 3. Further, these expanded areas allowed an accurate accounting of the line widths and line shapes. The line widths in the spectra of $^{13}\text{C}_6\text{H}_4\text{O}_2^-$ are, in part, controlled by g -tensor anisotropy. Note the broader lines in the low-field portion. This g -tensor anisotropy effect has been rigorously accounted for in the computer simulations, Figure 4.

It is predictable that the addition of an antibonding π -electron to these quinones would result in a general decrease in bond order,

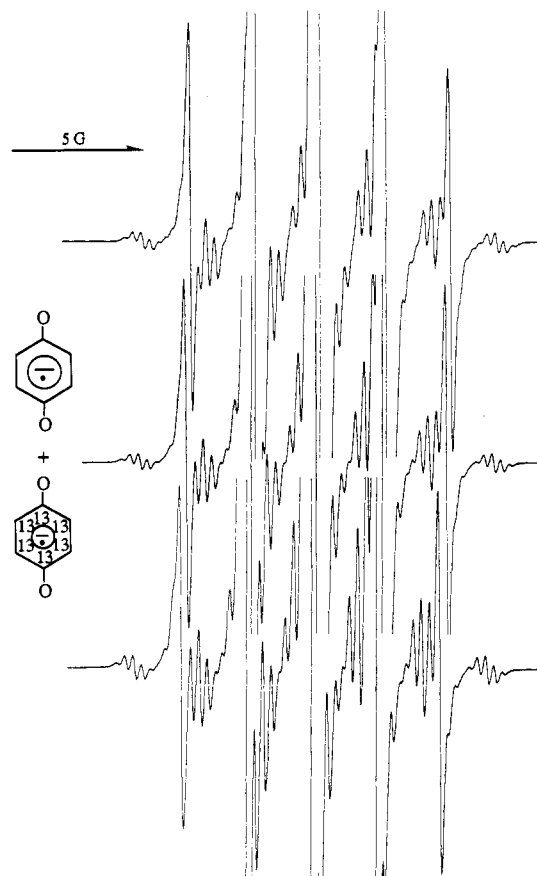


Figure 2. (Upper) EPR spectrum of a mixture of benzoquinone- $^{13}\text{C}_6$ and benzoquinone at 220 K generated from the partial sodium reduction of $^{13}\text{C}_6\text{H}_4\text{O}_2$ and $\text{C}_6\text{H}_4\text{O}_2$ in a $[\text{C}_6\text{H}_4\text{O}_2]/[^{13}\text{C}_6\text{H}_4\text{O}_2] = 1.05$ mole ratio in a THF–liquid ammonia solution. (Middle) A computer simulation, which *does include* the effects of g -tensor anisotropy. Note the line broadening of the low-field lines in both the real and the simulated spectra of the per- ^{13}C anion radical. The simulation was generated with coupling constants of $A_{^{13}\text{C}} = 1.750$ G (2 ^{13}C), $A_{^{13}\text{C}} = 0.30$ G (4 ^{13}C), and $A_H = 2.374$ G (4 H). The 1.750-G ^{13}C coupling was simulated utilizing couplings from two spin orientations with splittings of 2 and 1.5 G and a correlation time of 1.6×10^{-8} s. The orientation with the larger splitting was off-shifted by 0.151 G upfield from the other species. The ratio of anion radicals $[\text{C}_6\text{H}_4\text{O}_2^-]/[\text{C}_6\text{H}_4\text{O}_2^-]$ was 0.63. The ratio of neutral molecule to anion radical suggests an equilibrium constant (equilibrium isotope effect) for reaction 4 that is 0.66 at 220 K. (Lower) A computer simulation generated in exactly the same manner as described for the simulation above but with no equilibrium isotope effect ($[\text{C}_6\text{H}_4\text{O}_2^-]/[\text{C}_6\text{H}_4\text{O}_2^-] = 1/1.05$). Note that this simulation shows relatively more per- ^{13}C anion radical than does the empirical spectrum. The spectra and simulations are expanded by a factor of 10 in the vertical scale. Thus, the three center lines for $\text{C}_6\text{H}_4\text{O}_2^-$ extend off-scale.

with a consequent decrease in the C=O and C=C bond vibrational frequencies. Indeed, there is experimental indication that these bonds are weakened.^{9a,b} More recently, Chipman and Prebena^{9c} used ab initio calculations to predict and assign all of the 30 degrees of vibrational freedom in both the neutral $\text{C}_6\text{H}_4\text{O}_2$ and its anion radical. The agreement between the empirical studies carried out in solution and these ab initio calculations suggests that the attachment of an electron to $\text{C}_6\text{H}_4\text{O}_2$ either in solution or in the gas phase is best characterized in terms of a weakening of the C=O and C=C bonds and a strengthening of the C—C bonds.^{9c} The most significant decrease in vibrational frequency upon electron addition was observed in the C=O stretch. The a_g C=O stretch shifts 346 cm^{-1} , and the b_{1u} C=O stretch decreases by 521 cm^{-1} upon reduction, Table I. The increase in the C—C stretching frequency upon electron addition is, on the other hand, much smaller in magnitude and is offset by the decreases in the frequencies of the remaining vibrational degrees of freedom.

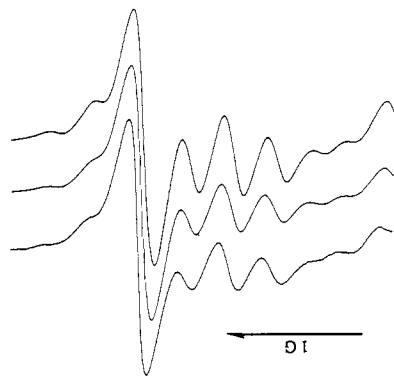


Figure 3. (Upper) Same EPR spectrum as that shown in Figure 2 but expanded in the horizontal direction. Only the high-field line of the benzoquinone spectrum and the local peaks from $^{13}\text{C}_6\text{H}_4\text{O}_2^-$ are shown. (Middle) Computer simulation expanded in the same way. The reorientation of the ^{13}C nucleus and the spin exchange, which yield the observed line widths, result in Lorentzian line shapes. The simulations include only the Lorentzian (no Gaussian) contribution. This is in agreement with theory for these homogeneously broadened spectra of solution-phase anion radicals. The line shapes fit the real spectrum perfectly as shown. (Lower) A computer simulation generated in exactly the same manner as described above but with no equilibrium isotope effect.

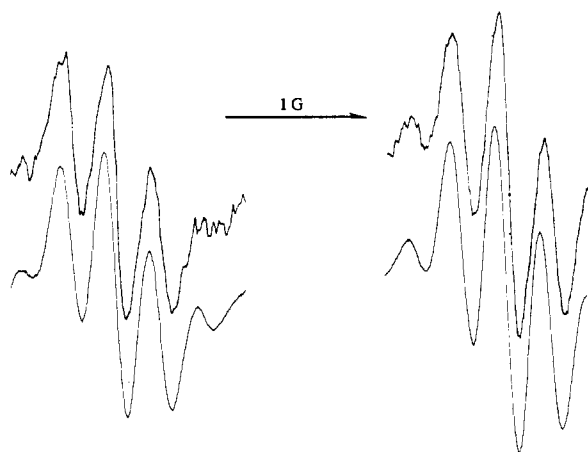


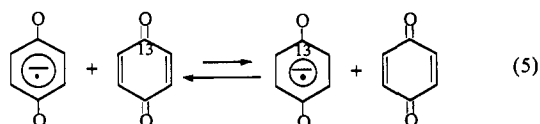
Figure 4. (Upper) Lowest and highest field portions of the EPR spectrum of benzoquinone- $^{13}\text{C}_6$. (Lower) Computer simulation generated as described in Figure 2. Note that the different line widths and line heights are accounted for in the simulation, which illustrates the effects of g -tensor anisotropy in the per- ^{13}C anion radical.

Table I. Calculated Fundamental C=O Stretch Vibrational Frequencies in *p*-Benzoquinone, *p*-Benzoquinone, and Carbonyl ^{13}C -Substituted *p*-Benzoquinone and *p*-Benzoquinone and $h\nu/2kT$ at 200 K

compd	$\omega(a_g)$, cm^{-1}	$\omega(b_{1u})$, cm^{-1}	$h\nu(a_g)c/$ $2kT$	$h\nu(b_{1u})c/$ $2kT$
$\text{C}_6\text{H}_4\text{O}_2$	1736	1716	6.242	6.171
$\text{C}_6\text{H}_4\text{O}_2^-$	1390	1195	4.999	4.297
$\text{C}_5\text{H}_4\text{O}^{13}\text{CO}$	1697 ^a	1678	6.103	6.034
$\text{C}_5\text{H}_4\text{O}^{13}\text{CO}^-$	1365	1169	4.909	4.204

^a $1736 \times \{[(12)(16)/(12+16)]/[(13)(16)/(13+16)]\}^{1/2} = 1697$.

The very large decrease in the a_g and b_{1u} frequencies would be expected to decrease the electron affinity of even a singly ^{13}C -substituted benzoquinone relative to that of its lighter isotopic isomer. The vast majority of any standard free energy difference for the electron transfer from *p*-benzoquinone to *p*-benzoquinone-*carbonyl*- ^{13}C ($\text{C}_5\text{H}_4\text{O}^{13}\text{CO}$, reaction 5) results from the



contribution of these two vibrational degrees of freedom, eq 6,

$$\Delta G^\circ = \Delta G^\circ(a_g) + \Delta G^\circ(b_{1u}) \quad (6)$$

where $\Delta G^\circ(a_g)$ can be calculated from the data in ref 9c, eq 7,

$$\Delta G^\circ(a_g) = -RT \left[\ln \frac{q_{\text{vib}}(\text{C}_6\text{H}_4\text{O}_2)q_{\text{vib}}(\text{C}_5\text{H}_4\text{O}^{13}\text{CO}^-)}{q_{\text{vib}}(\text{C}_6\text{H}_4\text{O}_2^-)q_{\text{vib}}(\text{C}_5\text{H}_4\text{O}^{13}\text{CO})} \right] \quad (7)$$

Each of the vibrational partition functions are given by $q_{\text{vib}} = e^{-h\nu/2kT}/(1 - e^{-h\nu/kT})$. At the temperatures (about 200 K) involved in these experiments, $1 \gg e^{-h\nu/kT}$, and therefore each $1 - e^{-h\nu/kT}$ term is equal to 1.00; the difference in the zero-point energies controls ΔG° , eq 8:

$$\begin{aligned} \Delta G^\circ(a_g) &= -RT[h\nu(a_g, \text{C}_6\text{H}_4\text{O}_2^-)/2kT - \\ &\quad h\nu(a_g, \text{C}_6\text{H}_4\text{O}_2)/2kT + h\nu(a_g, \text{C}_5\text{H}_4\text{O}^{13}\text{CO})/2kT - \\ &\quad h\nu(a_g, \text{C}_5\text{H}_4\text{O}^{13}\text{CO}^-)/2kT] \\ &= -RT[4.999 - 6.242 + 6.103 - 4.909] \\ &= +81.9 \text{ J/mol at 200 K} \end{aligned} \quad (8)$$

The free energy change due to the b_{1u} degree of vibrational freedom can be calculated in the same manner, and it amounts to

$$\begin{aligned} \Delta G^\circ(b_{1u}) &= -RT[4.297 - 6.171 + 6.034 - 4.204] \\ &= 73.6 \text{ J/mol} \end{aligned} \quad (9)$$

Based upon this argument, K_{eq} for the electron transfer from *p*-benzoquinone to *p*-benzoquinone-*carbonyl*- ^{13}C (reaction 5) is predicted to be about 0.91 at 200 K, which is larger than the empirical value (0.80),¹⁰ but only two of the 30 degrees of vibrational freedom have been taken into account.

If we keep in mind that there are two carbonyl- ^{13}C s in *p*-benzoquinone- $^{13}\text{C}_6$ and ignore the effect caused by ^{13}C substitution in the noncarbonyl carbons where the spin and charge densities are very low,¹¹ then an estimate of the value of K_{eq} for reaction 4, based upon the empirical results from reaction 5, is $(0.80)^2 = 0.64$ at 200 K. This is close to the average empirical values from the EPR work (0.66) described above.

The fact that this equilibrium constant deviates from unity necessarily means that any separation of the anion radical phase (phase 2) from the neutral molecule phase (phase 1) is, in net effect, a partial separation of the isotopic isomers involved. The equilibrium constant for the electron transfer (reaction 1) can be determined after the separation of the two phases and reoxidation of phase 2. It is simply the mole ratio of the heavy to light isotopic isomers in phase 2 divided by that in phase 1, eq 10, where [A] and [B] can be determined by mass spectral analysis.

$$K_{\text{eq}} = \frac{[\text{A}]/[\text{B}] \text{ (phase 2)}}{[\text{A}]/[\text{B}] \text{ (phase 1)}} \quad (10)$$

After evaporation of the solvent, the neutral phase was extracted from the anion radical phase via sublimation. The sublimations were carried out at ambient temperature, where it is well documented that these types of anion radical systems are thermodynamically and kinetically stable toward decomposition via electron transfer to the metal cation ($\text{C}_6\text{H}_4\text{O}_2^- \cdot \text{Na}^+(\text{solid}) \rightarrow \text{C}_6\text{H}_4\text{O}_2(\text{gas}) + \text{Na}(\text{solid})$).¹² The remaining solid anion radical was reoxidized with iodine and labeled phase 2. Mass spectral analysis of these two phases shows that K_{eq} obtained via eq 10 is 1.0 ± 0.05 for the $\text{C}_6\text{H}_4\text{O}_2$ - $\text{C}_6\text{D}_4\text{O}_2$ system and 0.75 ± 0.05 for the $\text{C}_6\text{H}_4\text{O}_2$ - $^{13}\text{C}_6\text{H}_4\text{O}_2$ system. Assuming that ΔS° is

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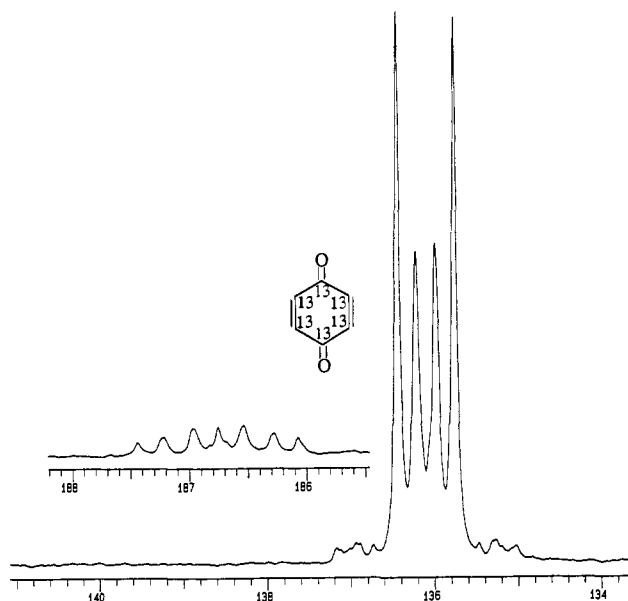


Figure 5. Proton-decoupled 75.5-MHz ^{13}C NMR spectrum of benzoquinone- $^{13}\text{C}_6$. Note the A_2B_2 pattern for the ring carbons at 136.10 ppm and both the long-range and the short-range ^{13}C - ^{13}C splitting in the carbonyl carbons at 187.78 ppm.

negligible for reaction 4, this corresponds to a K_{eq} of 0.65 ± 0.05 at 200 K. The equilibrium constants determined from the separations are in good agreement with the EPR results which, in turn, are qualitatively consistent with the statistical thermodynamic predictions. The statistical treatment does not account for solvation and ion association effects, and this is, in part, the justification for utilizing only a semiquantitative statistical treatment.

Experimental Section

Synthesis. The synthesis of benzoquinone- $^{13}\text{C}_6$ was carried out via the oxidation of phenol- $^{13}\text{C}_6$. A steel bomb was charged with 0.30 g (3.0×10^{-3} mol) of phenol- $^{13}\text{C}_6$, 0.50 g (7.8×10^{-3} mol) of Cu filings, 0.079 g (8.0×10^{-4} mol) of CuCl, 0.065 g (8.0×10^{-4} mol) of NaSCN, and approximately 10 mL of dimethylformamide. The bomb was sealed and pressurized to 30 atm with O_2 (deviation from this pressure greatly reduces the yield). The bomb was subsequently placed into a 70 °C oil bath and shaken vigorously for 3.5 h. The O_2 was released, the reaction mixture was filtered, and 10 mL of water was added. This mixture was then extracted with diethyl ether, and the ether layer was washed repeatedly with H_2O . The resultant yellowish organic layer was dried with Na_2SO_4 and subjected to a preparatory GC (Carbowax on Chromosorb column) purification. The synthesized $^{13}\text{C}_6\text{H}_4\text{O}_2$ (about 10 mg, 3% yield based upon the phenol put into the reaction mixture) yields the expected A_2B_2 ^{13}C NMR pattern for the chemically equivalent but magnetically nonequivalent non-carbonyl carbons (Figure 5). Most of the unconsumed phenol could be recovered from the GC separations. The initial phenol- $^{13}\text{C}_6$ (Cambridge Isotope Laboratories) was of 99% isotopic purity. The isotopic purity of the product (benzoquinone- $^{13}\text{C}_6$) is presumably the same. In any event, the presence of benzosemiquinone- $^{13}\text{C}_5$ could not be detected in the EPR spectra (Figure 2), and its presence was not accounted for.

Separations. An apparatus was constructed (glass blown) for the separations as follows. Two glass bulbs (A and B), each with Teflon (Du Pont) stopcocks and ball joints for connection to a vacuum line, were

connected to each other, with a stopcock between them. Bulb A also was connected to a test tube (C) and an EPR sample tube. Carefully weighed portions (0.5–1 mmol) of freshly sublimed benzoquinone and its isotopically heavy analogue were placed in bulb A of the apparatus. Tube C was then charged with approximately enough sodium metal to reduce half of the quinones. Tube C was sealed and the apparatus evacuated. A fresh sodium mirror was deposited in bulb A by distillation from tube C. Tube C was consequently sealed from the apparatus. Approximately 25 mL of dry THF and 5 mL of anhydrous liquid ammonia were then distilled from sodium metal into bulb A, the Teflon stopcock was shut, and the apparatus was removed from the vacuum line. The THF-liquid ammonia solution was exposed to the sodium mirror until all of the metal was dissolved. An EPR sample could be taken at this time. The THF-liquid ammonia mixture was then distilled into bulb B, and the neutral benzoquinones were simultaneously sublimed with the solvent. Bulbs A and B were then separated, and the anion radical phase (in bulb A) was reoxidized via the addition of a slight molar excess of I_2 in diethyl ether. The ether solution was filtered through sodium thiosulfate and norite, concentrated, and labeled phase 2. The neutral molecule phase in bulb B was also concentrated, and it was labeled phase 1. Both phases were submitted to GC mass spectral analysis, and K_{eq} was determined via eq 10.

Instrumental Measurements. 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. The equilibrium constant for electron transfer ($\text{C}_6\text{H}_4\text{O}_2^- + ^{13}\text{C}_6\text{H}_4\text{O}_2 = \text{C}_6\text{H}_4\text{O}_2 + ^{13}\text{C}_6\text{H}_4\text{O}_2^-$) was evaluated from

$$K_{\text{eq}} = \frac{[\text{abundance of } m/z = 114 \text{ (phase 2)}] / [\text{abundance of } m/z = 108 \text{ (phase 2)}]}{[\text{abundance of } m/z = 114 \text{ (phase 1)}] / [\text{abundance of } m/z = 108 \text{ (phase 1)}]}$$

EPR measurements⁶ and simulations¹³ were carried out as previously described on an IBM (Bruker) ER-200D spectrometer equipped with an IBM variable-temperature unit. It is important to note that K_{eq} values determined via the EPR measurements lie within the experimental error reported only if $<10\%$ of the quinones are reduced in the partial reductions, that is, when $[^{13}\text{C}_6\text{H}_4\text{O}_2^-]$ and $[\text{C}_6\text{H}_4\text{O}_2^-] \ll [^{13}\text{C}_6\text{H}_4\text{O}_2]_0$ and $[\text{C}_6\text{H}_4\text{O}_2]_0$, where $[^{13}\text{C}_6\text{H}_4\text{O}_2]_0$ and $[\text{C}_6\text{H}_4\text{O}_2]_0$ represent the total concentrations of quinones used in the reaction. The ratio $[^{13}\text{C}_6\text{H}_4\text{O}_2]_0 / [\text{C}_6\text{H}_4\text{O}_2]_0$ was obtained by careful weighing of the two materials. The thermodynamic value, $K_{\text{eq}} = [^{13}\text{C}_6\text{H}_4\text{O}_2^-][\text{C}_6\text{H}_4\text{O}_2] / [\text{C}_6\text{H}_4\text{O}_2][^{13}\text{C}_6\text{H}_4\text{O}_2^-] = [^{13}\text{C}_6\text{H}_4\text{O}_2^-]([\text{C}_6\text{H}_4\text{O}_2]_0 - [\text{C}_6\text{H}_4\text{O}_2^-]) / [\text{C}_6\text{H}_4\text{O}_2^-]([^{13}\text{C}_6\text{H}_4\text{O}_2]_0 - [^{13}\text{C}_6\text{H}_4\text{O}_2^-])$ and is less than 1.00. At low ($<10\%$) extent of reduction, this may be approximated as an apparent equilibrium constant, $K_{\text{app}} = [^{13}\text{C}_6\text{H}_4\text{O}_2^-][\text{C}_6\text{H}_4\text{O}_2]_0 / [\text{C}_6\text{H}_4\text{O}_2^-][^{13}\text{C}_6\text{H}_4\text{O}_2]_0$. However, as the extent of reduction becomes large, the ionic concentrations approach the corresponding initial neutral molecule concentrations, and K_{app} tends toward 1.00. To be sure that our reductions were carried out with appropriately deficient amounts of metal, we determined K_{app} as a function of contact time with the metal. At the lowest levels of reduction, K_{app} did not vary. However, as the level of reduction was increased, K_{app} approached 1.00 (where $[^{13}\text{C}_6\text{H}_4\text{O}_2^-]$ and $[\text{C}_6\text{H}_4\text{O}_2^-] = [^{13}\text{C}_6\text{H}_4\text{O}_2]_0$ and $[\text{C}_6\text{H}_4\text{O}_2]_0$, respectively). It should be noted that in liquid ammonia solution, these anion radicals are not involved in extensive ion association.

The NMR spectra were recorded on a Varian (Gemini) 300-MHz (^1H) NMR spectrometer.

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