# Free Energies of Electron Transfer from Ketyls to Isotopically Substituted Ketones

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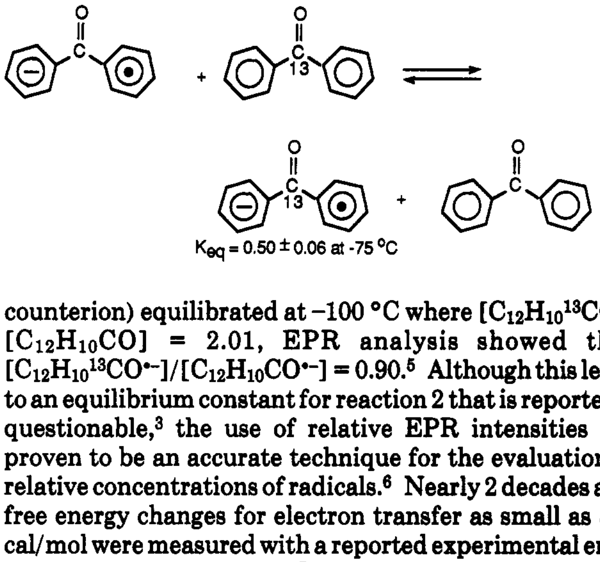
A series of electron transfer competition reactions between several isotopically different benzophenones was established in liquid ammonia. The resulting electron transfer ($A^{\bullet -} + B = A + B^{\bullet -}$) equilibrium constants were determined via EPR studies and via the physical separation of the anion radical phase from the neutral molecule phase. This anion radical–neutral molecule separation leads to a partial separation of the isotopic isomers involved due to the deviation of the equilibrium constants from unity. Mass spectral analysis of the two phases yields thermodynamic data for the electron transfer that is consistent with the EPR results: when A = benzophenone, $K_{eq}$ at −75 °C equals 0.52, 0.50, and 0.83 for equilibria involving B = perdeuteriated benzophenone, [*carbonyl*-$^{13}$*C*]benzophenone, and [*sym-dodeca*-$^{13}$C]benzophenone, respectively.

## Introduction

The theory of equilibrium isotope effects has been well understood and has been successfully applied to both verification and prediction of experimental results.[1] Even with the Born–Oppenheimer approximation and the assumption of the harmonic oscillator–rigid rotor approximation the theory is semiquantitative.[2] Theory and experiment show that, in a dynamic oxidation reduction equilibrium, the isotopically heavy materials will tend to concentrate in the species having larger force constants at the site(s) of isotopic substitution.[3] Thus, it was not a surprise (in a qualitative sense) that the equilibrium constants for electron transfer from the anion radicals of polyaromatic hydrocarbons ($A^{\bullet -}$) to their deuteriated isotopic analogues (B) (reaction 1) were found to be less

$$A^{\bullet -} + B \rightleftharpoons A + B^{\bullet -} \qquad (1)$$

than unity.[4] It has been stipulated that the D/H effects reported[4] do not exceed easily set theoretical upper limits.[3] On the other hand, theoretical analysis has suggested that the $^{13}C/^{12}C$ equilibrium isotope effect reported for the benzophenone ($C_{12}H_{10}CO$) system (reaction 2)[5] is problematic.[3]



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The equilibrium constant for reaction 2 was measured by monitoring the relative intensities of the EPR signals of $C_{12}H_{10}CO^{\bullet -}$ and $C_{12}H_{10}{}^{13}CO^{\bullet -}$ in a solution containing known quantities of $C_{12}H_{10}CO$ and $C_{12}H_{10}{}^{13}CO$.[5] In a particular experiment in a liquid ammonia solution ($Na^+$, counterion) equilibrated at −100 °C where $[C_{12}H_{10}{}^{13}CO]/[C_{12}H_{10}CO] = 2.01$, EPR analysis showed that $[C_{12}H_{10}{}^{13}CO^{\bullet -}]/[C_{12}H_{10}CO^{\bullet -}] = 0.90$.[5] Although this leads to an equilibrium constant for reaction 2 that is reportedly questionable,[3] the use of relative EPR intensities has proven to be an accurate technique for the evaluation of relative concentrations of radicals.[6] 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.[7] These facts along with the advances in EPR computer simulation processes (faster computers allowing practical use of rigorous line width algorithms, leading to more precise high resolution simulations) make "the EPR technique"[8] extremely viable for the study of electron transfer reactions of the type shown in reaction 1.[9]

This same EPR approach was used to investigate the free energy changes involved in reaction 3, the results of which have remained unchallanged in the literature. These results have been utilized by other workers as a tool for the investigation of reaction mechanisms[10] and to ratio-

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[†] This author previously published under the name Gerald R. Stevenson.

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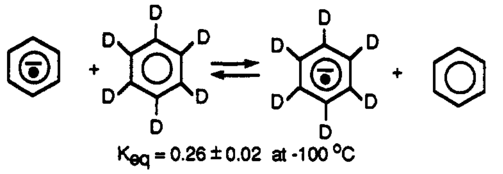


(3)

nalize their own results concerning other chemical problems.[11,12] It is readily conceivable that the relative solution electron affinities of the $^{13}C/^{12}C$ systems can be similarly utilized. Thus, it is important that the $^{13}C$ effect be established (or discounted) to the same degree of certainty as is the $^{2}H$ effect, which has been confirmed via electrochemical techniques.[4c,d]

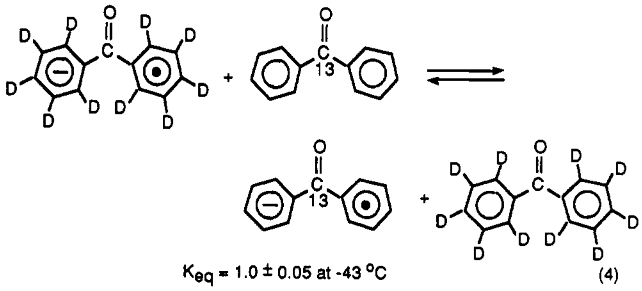
The nonunity value for the equilibrium constant (e.g. reaction 3) necessarily means that any separation of the neutral molecule from equilibrated anion radical will result in a partial separation of the isotopic isomers. In fact, separation of the neutral benzenes (labeled phase I) from the benzene anion radicals, which were subsequently oxidized back to benzenes via the addition of $I_2$ (labeled phase II), did yield the expected partial separation according to mass spectral and NMR analyses of the two phases.[9] The $C_6H_6$ was enriched in phase II and the $C_6D_6$ was enriched in phase I.[9] Thus, we do not have to rely solely upon the EPR technique for determination of the equilibrium constants for reactions 1–3.

Due to the fact that $C_{12}H_{10}CO$ and $C_{12}H_{10}{}^{13}CO$ differ by only one mass unit, it is very difficult to determine the relevant equilibrium constant via the separation of anionic (later reoxidized) and neutral phases followed by mass spectral analysis. The P + 1 peak of the light and P − 1 peak of the heavy species interfere with the parent peaks of the heavy and light isotopic isomers, respectively. To circumvent this difficulty we have studied the equilibria involving the perdeuteriated benzophenone ($C_{12}D_{10}CO$) and [*sym-dodeca*-$^{13}$C]benzophenone ($^{13}C_{12}H_{10}CO$) systems. Here the large mass differences obviate the mass spectral analytical difficulties in the analysis of the two phases.

## Results and Discussion

**EPR Measurements.** The reduction of a 25-mL liquid ammonia solution of a mixture of $C_{12}D_{10}CO$ (1.53 mmol) and $C_{12}H_{10}{}^{13}CO$ (0.0153 mmol) with a very molar-deficient amount of potassium metal results in a deep blue paramagnetic solution. After further dilution with liquid ammonia the EPR spectrum, recorded at 230 K, shows the presence of both $C_{12}D_{10}CO^{\bullet-}$ and $C_{12}H_{10}{}^{13}CO^{\bullet-}$ (Figure 1). The EPR spectrum is best simulated when it is assumed that the ratio of anion radicals ($[C_{12}D_{10}CO^{\bullet-}]/[C_{12}H_{10}{}^{13}CO^{\bullet-}]$) is 100/1. Since the ratio of anion radical isotopic isomers is the same as the ratio of neutral isotopic isomers, the solution electron affinity of $C_{12}D_{10}CO$ and $C_{12}H_{10}{}^{13}CO$ must be about the same. Several such experiments do indeed yield an average value of $K_{eq}$ for reaction 4 that is unity (1.00 ± 0.05).

An analogous EPR experiment at 230 K (Figure 2) was carried out with a partial reduction of a 15.05/1 mixture of $[C_{12}D_{10}CO]/[C_{12}H_{10}CO]$. The resulting blue solution yielded an EPR spectrum whose simulation shows that the ratio of anion radicals is $[C_{12}D_{10}CO^{\bullet-}]/[C_{12}H_{10}CO^{\bullet-}] = 8.5/1$. This particular experiment suggests an equilibrium constant for reaction 5 of 0.56 at −43 °C. Several such experiments give an average value, which when adjusted to −75 °C (assuming $\Delta S° = 0$), of 0.52 ± 0.04.



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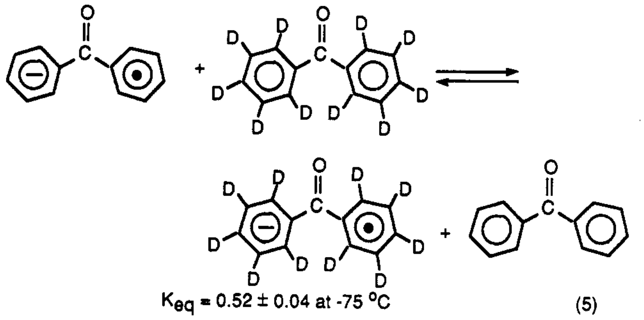

(5)

Reactions 4 and 5 can now be used in a thermochemical cycle (Scheme I) to authenticate the previously published value for reaction 2. The resulting free energy for reaction 2 ($\Delta G°_2$) corresponds to an equilibrium constant of 0.52 at −75 °C, which is in excellent agreement with that reported in ref 5. Interestingly, the effect of a single $^{13}C$ substitution in the carbonyl position, the position of highest spin and charge density, is about the same as that from the ten deuterium substitutions on the ring carbons.

While the "EPR technique" leads to self-consistent solution electron affinity results (Scheme I vs ref 5b), we need not rely totally upon this approach. The mass difference between $C_{12}H_{10}{}^{13}CO$ and $C_{12}D_{10}CO$ is 9 atomic mass units, and that between $C_{12}H_{10}CO$ and $C_{12}D_{10}CO$ is 10 atomic mass units. This precludes the analytical problems (discussed in the introduction) involved in the use of the physical separation technique for mixtures of $C_{12}H_{10}{}^{13}CO$ and $C_{12}H_{10}CO$. Indeed, $\Delta G°_2$ can be obtained from the thermochemical cycle shown in Scheme I via physical separation and mass spectral analysis of $C_{12}H_{10}{}^{13}CO/C_{12}D_{10}CO$ and $C_{12}H_{10}CO/C_{12}D_{10}CO$ mixtures. This is the topic of the next section.

**Separations.** A mixture of 0.582 mmol of $C_{12}H_{10}CO$ and 0.884 mmol of $C_{12}D_{10}CO$ was reduced with about 0.7 mmol of K metal, and the solvent (liquid $NH_3$) was removed under reduced pressure. The solid ketones (phase I) were removed from the ketyls (phase II) via extraction with hexane, and phase II was reoxidized with iodine (e.g. reaction 6). Mass spectral analysis (Figure 3) of the two

$$1/2I_2 + K^+C_{12}D_{10}CO^{\bullet-}{}_{(solid)} \rightarrow K^+I^-{}_{(solid)} + C_{12}D_{10}CO \quad (6)$$

phases then showed that phase II was enriched and phase I accordingly depleted in the isotopically light material. Thus, $\alpha = K_{eq} = 0.57 = \{[C_{12}D_{10}CO]/[C_{12}H_{10}CO]_{(phase\ II)}\}/\{[C_{12}D_{10}CO]/[C_{12}H_{10}CO]_{(phase\ I)}\}$ for this particular experiment. Measurements from several reactions yielded $\alpha$ =

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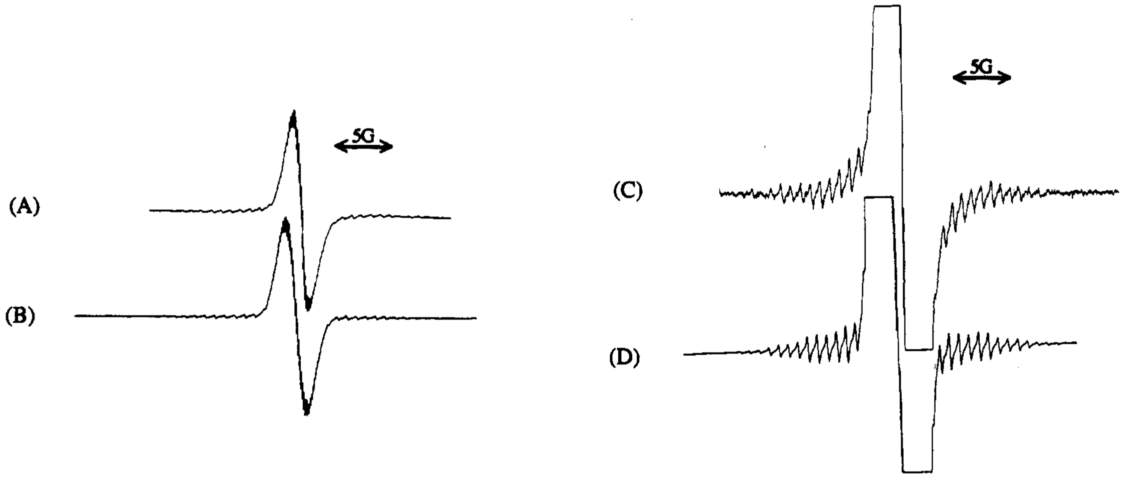


**Figure 1.** (A) An EPR spectrum recorded at 230 K of a mixture of $C_{12}D_{10}CO$ and $C_{12}H_{10}{}^{13}CO$ in a ratio of 100/1 and reduced with a very molar-deficient amount of potassium metal in liquid ammonia. This rather large ratio favoring the perdeuteriated material insures a relatively unperturbed EPR signal from the $C_{12}D_{10}CO^{\bullet-}$ while the unoverlapped peaks of the $C_{12}H_{10}{}^{13}CO^{\bullet-}$ can still be observed in the low- and high-field portions of the spectrum. A more detailed view of the peaks from $C_{12}H_{10}{}^{13}CO^{\bullet-}$ can be obtained by simply expanding the spectrum in the *y* direction. (B) A computer simulation of spectrum A generated using a ratio of 100/1 for the two anion radicals and the coupling constants: $a_H = 3.44$ (2 H's), 2.61 (4 H's), 0.864 (4 H's), and $a_{^{13}C} = 9.20$ G; $a_D = 0.520$ (2 D's), 0.400 (4 D's), 0.134 (4 D's). (C) The same spectrum shown above but with the gain increased by a factor of 10. (D) The computer simulation with the gain augmented by a factor of 10.

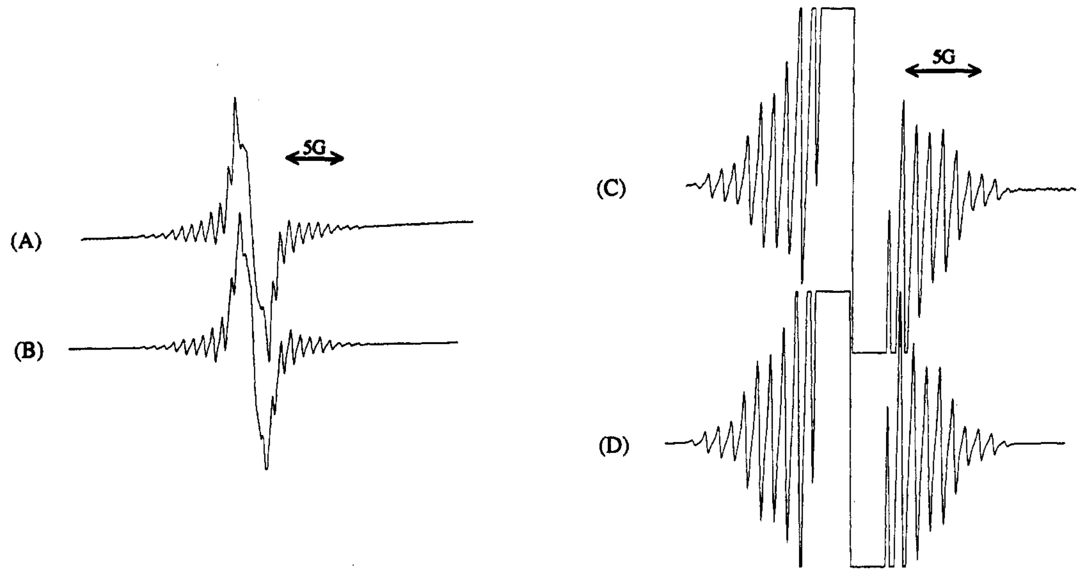


**Figure 2.** (A) An EPR spectrum recorded at 230 K of a mixture of $C_{12}D_{10}CO$ and $C_{12}H_{10}CO$ in a ratio of 15.05/1 and reduced with a very molar-deficient amount of potassium metal in liquid ammonia. (B) A computer simulation of spectrum A generated using a ratio of 8.5/1 for the two anion radicals and the coupling constants: $a_H = 3.44$ (2 H's), 2.61 (4 H's), 0.864 (4 H's). (C) The same spectrum shown above but with the gain increased by a factor of 10. (D) The same computer simulation but with the gain increased by a factor of 10.

**Scheme I** [a]

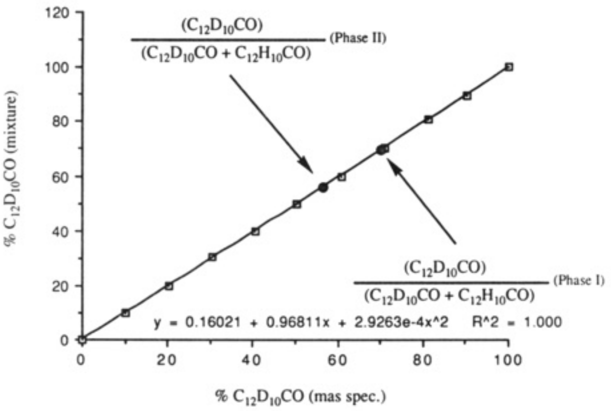
$$\begin{array}{ll}
C_{12}D_{10}CO^{\bullet-} + C_{12}H_{10}{}^{13}CO = C_{12}H_{10}{}^{13}CO^{\bullet-} + C_{12}D_{10}CO & \Delta G°_4 = 0 \\
C_{12}D_{10}CO^{\bullet-} + C_{12}D_{10}CO = C_{12}H_{10}CO + C_{12}D_{10}CO^{\bullet-} & \Delta G°_5 = 1076 \\
\hline
C_{12}H_{10}CO^{\bullet-} + C_{12}H_{10}{}^{13}CO = C_{12}H_{10}CO + C_{12}H_{10}{}^{13}CO^{\bullet-} & \Delta G°_2 = 1076
\end{array}$$

[a] ΔG° at −75 °C in J/mol.

$K_{eq} = 0.57 \pm 0.04$ at 298 K, reaction 5. Assuming a negligible $\Delta S°$, this is equivalent to $K_{eq} = 0.43 \pm 0.04$ at −75 °C, which is reasonably close to the value obtained from the EPR data (reaction 5).

Similar mixtures of $C_{12}H_{10}{}^{13}CO$ and $C_{12}D_{10}CO$ were reduced and treated in the same manner. However, both phases exhibited the same mass spectral ratios, indicating that no separation of the two isotopic isomers took place upon the separation of the anionic and neutral materials. Thus, the physical separation technique in conjunction with Scheme I indicates a slightly larger isotope effect than suggested by the previously reported[5] value of ΔG° for reaction 2.

On the basis of the previous observation that deuterium substitution in positions of high charge and spin density leads to larger attenuations of the solution electron affinity than does substitution at positions of low charge and spin density,[4e] it was anticipated that an analogous situation would exist in the case of $^{13}C$ substitution. Nearly half of the charge and spin density resides on the carbonyl carbon of $C_{12}H_{10}CO^{\bullet-}$;[13] consequently $^{13}C$ substitution at this position is expected to result in the largest $^{13}C$ attenuation of the solution EA of $C_{12}H_{10}CO$.



$$K_{eq} = \frac{\dfrac{(C_{12}D_{10}CO)}{(C_{12}D_{10}CO + C_{12}H_{10}CO)}\ \text{(Phase II)}}{\dfrac{(C_{12}D_{10}CO)}{(C_{12}D_{10}CO + C_{12}H_{10}CO)}\ \text{(Phase I)}} = 0.57$$

**Figure 3.** A plot of the percentage of $C_{12}D_{10}CO$ in mixtures containing $C_{12}D_{10}CO$ and $C_{12}H_{10}CO$ vs that calculated based upon the relative intensities of parent peaks (192 and 182) from the mass spectrometer. The exact equation for the resulting curve and the correlation constant are shown. The mass spectral-based percentages determined for the anionic and neutral phases of a partially reduced mixture of $C_{12}D_{10}CO$ and $C_{12}H_{10}CO$ are indicated by the circles on the plot. Note that the percentage of $C_{12}D_{10}CO$ is higher in the neutral phase (phase I) than in the anionic phase (phase II).

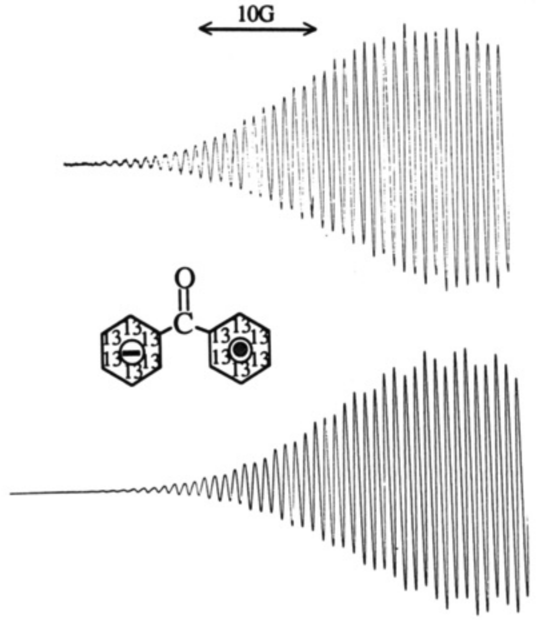


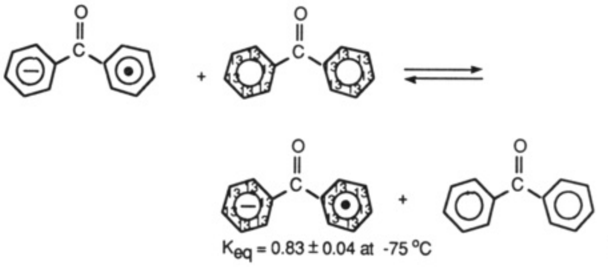
**Figure 4.** Low-field portion of the EPR spectrum of $^{13}C_{12}H_{10}CO^{\bullet-}$ recorded at 230 K in liquid ammonia. Potassium serves as the counterion, and the computer simulation shown directly below was generated with the following coupling constants: $a_{^{13}C}$ = 6.86 (2 C's), 3.56 (2 C's), 6.14 (4 C's), and 2.67 (4 C's).

The anion radical of the [*sym-dodeca*-$^{13}$C]benzophenone ($^{13}C_{12}H_{10}CO^{\bullet-}$) yields an EPR spectrum that is interesting and qualitatively interpretable, Figure 4. However, mixtures of this anion radical with that of $C_{12}H_{10}CO$ yield an EPR pattern that is too complex to permit the quantitative determination of relative anion radical concentrations. The separation technique discussed above circumvents this problem and allows the determination of the equilibrium constant for reaction 7.

**Table I. Equilibrium Constants for Electron Transfer from the Ketyls Shown in the First Column to the Neutral Benzophenones Shown in the Top Horizontal Row at −75 °C**

| | $C_{12}H_{10}CO$ | $C_{12}D_{10}CO$ | $C_{12}H_{10}{}^{13}CO$ | $^{13}C_{12}H_{10}CO$ |
|---|---|---|---|---|
| $C_{12}H_{10}CO^{\bullet-}$ | 1.0 | 0.52[a] | 0.50[a] | 0.83[b] |
| $C_{12}D_{10}CO^{\bullet-}$ | 1.92 | 1.0 | 1.0[a] | 0.63[c] |
| $C_{12}H_{10}{}^{13}CO^{\bullet-}$ | 2.0 | 1.0 | 1.0 | 0.60[c] |
| $^{13}C_{12}H_{10}CO^{\bullet-}$ | 1.20 | 1.59 | 1.67 | 1.0 |

[a] Equilibrium constant taken from EPR data. [b] Equilibrium constant taken from separation data. [c] Equilibrium data taken from thermochemical cycle.



(7)

The two experimental techniques for evaluating $K_{eq}$ for electron transfer were coupled with thermochemical cycles analogous to that shown in Scheme I. This allowed determination of electron transfer equilibrium constants for the reactions involving all pairs of species, Table I.

## Conclusions

The EPR evidence that the solution electron affinity of benzophenone is measurably reduced upon replacement of the carbonyl carbon with $^{13}$C,[5] which has been contested,[3] has been quantitatively substantiated indirectly via a series of measurements of relative solution electron affinities related by a thermochemical cycle. This $^{13}$C effect has been verified via both EPR data and the fact that the physical separation of the anionic and neutral materials involved in the electron competition equilibria (reaction 1) results in a partial separation of the isotopic isomers involved.

The attenuation of the electron affinity via the substitution of the carbonyl carbon with $^{13}$C is greater than that caused by substitution of all of the ring carbons combined. This is attributed to the fact that the carbonyl moiety has the highest charge and spin density in the benzophenone anion radical.

## Experimental Section

**Materials.** The synthesis of [*sym-dodeca*-$^{13}$C]benzophenone was carried out via the Friedel–Crafts phenylation of carbon tetrachloride and subsequent dehalogenation of the product as described by Marvel and Sperry.[14] [*per*-$^{13}$C]Benzene was used in place of benzene. The $C_{12}D_{10}CO$ and $C_{12}H_{10}{}^{13}CO$ were purchased from Cambridge Isotope Laboratories and MSD Isotopes, respectively, and used without further purification.

**Separations.** Carefully weighed portions (typically 0.01–1 mmol) of the benzophenone and its isotopically heavy analogue were placed in bulb A of the apparatus shown in Figure 5. In a specific experiment, 0.0364 mmol of [*dodeca*-$^{13}$C]benzophenone and 0.619 mmol of benzophenone were loaded into bulb A. Tube

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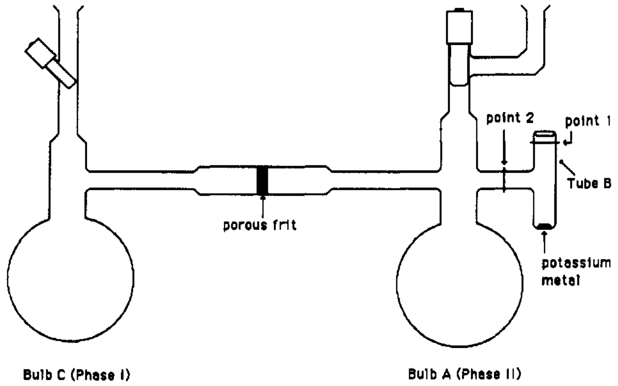

**Figure 5.** Apparatus used for the separation of the benzophenone ketyls from the ketones.

B was then charged with approximately enough potassium metal to reduce half of the ketones. Tube B was sealed at point 1 and the apparatus evacuated. A fresh potassium mirror was deposited in bulb A by distillation from tube B. Tube B was consequently sealed from the apparatus at point 2. Approximately 30 mL of liquid ammonia were then distilled from potassium metal into bulb A, the Teflon stopcock was shut, and the apparatus was removed from the vacuum line. The liquid ammonia solution was exposed to the potassium mirror at −78 °C until all of the metal had dissolved. The liquid ammonia was then removed under reduced pressure, and the remaining neutral ketones were dissolved in freshly distilled hexane at room temperature. The solution of ketones was then passed through the glass frit into bulb C. This last process was repeated to ensure complete separation of the neutral and anionic phases. Bulbs A and C were then separated, and an excess of $I_2$ in diethyl ether was added to the anion radical phase (in bulb A). The ether solution was filtered through sodium thiosulfate and activated charcoal, concentrated, and labeled as phase II. The neutral molecule phase in bulb C was also concentrated and labeled as phase I. Both phases were submitted to GC-mass spectral analysis. The ratios of the heavy to light isotopic isomers were found to be 0.0972 in phase II and 0.111 in phase I $[^{13}C_{12}H_{10}CO]/[C_{12}H_{10}CO]_{(\text{phase II})}/[^{13}C_{12}H_{10}C)]/[C_{12}H_{10}CO]_{(\text{phase I})} = 0.0972/0.111 = 0.88$). An average value for $K_{eq}$ at 25 °C from several such experiments is 0.88 ± 0.04. This corresponds to a $K_{eq}$ for reaction 7 of 0.83 ± 0.04 at −75 °C. This general process was utilized for all of the mixtures featured in the results and discussion section.

**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. The SIM (selected ion mode) was used, focusing on the parent ions for calculation of isotopic ratios. In the case of the perdeuteriated benzophenone–[*carbonyl*-$^{13}$C]benzophenone system for example, the mass spectrometer was calibrated by injecting diethyl ether solutions of weighed portions of $C_{12}D_{10}CO$ and $C_{12}H_{10}{}^{13}CO$. The spectral results were then plotted as shown in Figure 3. The ether solutions of the phase I and phase II mixtures were then injected in an identical manner. The equilibrium constant for electron transfer (reaction 4) was evaluated from eq 8, Figure 3.

$$K_{eq} = \frac{[\% m/z = 192]/[\% m/z = 183]_{(\text{phase II})}}{[\% m/z = 192]/[\% m/z = 183]_{(\text{phase I})}} \tag{8}$$

EPR measurements were carried out as previously described on an IBM (Bruker) ER-200D spectrometer equipped with an IBM variable temperature unit.[5] It is important to note that the $K_{eq}$'s determined via the EPR measurements lie within the experimental error reported only if less than 10% of the ketones are reduced in the partial reductions. To accurately determine line widths for use in simulations of the EPR spectra of the mixtures, we initially recorded the low-field 5-G portion of the spectra. These expanded partial spectra were best simulated using the same line width for both spectral components when the low-field portions were used.

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