Altered Condensed-Phase Electron Affinities of Carbonyl-¹³C-, -¹⁴C-, and -¹⁷O-**Substituted Ketones**

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Electron spin resonance experiments have shown that the solution electron affinities of both benzoquinone (BQ) and benzophenone (BZO) in liquid ammonia are diminished when a ¹³C replaces the ¹²C in the carbonyl position. For the reaction $*\hat{R} + R^{-1}$ \Rightarrow *R** + R, where *R represents the ¹³C-substituted material (either BZO-13C or BQ-13C), the equilibrium constants (K_{eq}) are 0.80 and 0.50 at -75 °C for the BQ and BZO systems, respectively. The reduction of radioactive samples of benzophenone (mixtures of BZO and BZO-14C, ¹⁴C substitution at the carbonyl carbon) with deficient amounts of sodium metal in liquid ammonia followed by removal of the ammonia leaves a solid mixture of benzophenone and benzophenone ketyl. Sublimation of the neutral benzophenone from the anion radical salt produces benzophenone that is enhanced in radioactivity relative to the starting BZO/BZO-14C mixture. This enhancement in radioactivity is consistent with the equilibrium constant again being less than unity when *R represents the ¹⁴C-substituted benzophenone. In contrast to these results, substitution of the oxygen atom with ¹⁷O results in an increase in the relative solution electron affinity. This is explained in terms of the increase in "bonding" involving the oxygen upon reduction, due to ion association.

A simple electron-transfer reaction from an anion radical (R⁻⁻) to a neutral molecule where one of the atoms has been substituted with another isotope of the same element (*R) results in the formation of the anion radical of the isotopic isomer (*R*-) and R, reaction 1. The equilibrium constants for several reactions

$$\mathbf{R}^{\bullet-} + \mathbf{R} \rightleftharpoons \mathbf{R}^{\bullet-} + \mathbf{R} \tag{1}$$

of this type have been observed to deviate considerably from unity,^{1,2} which suggests a means of enrichment of the isotopic isomer.^{3,4} For a gas-phase reaction the equilibrium constant K_{eq} is given in terms of the molecular partition functions (Q)

$$K_{eq} = [Q(*R^{\bullet-}) Q(R) / Q(R^{\bullet-}) Q(*R)] \exp(-\Delta E_0 / RT)$$
(2)

where ΔE_0 represents the potential energy difference, and the entropy change for the reaction is given by the natural logarithm of the preexponential term multiplied by the gas constant. According to the Born-Oppenheimer approximation,⁵ the potential energy (ΔE) does not change for the vast majority of reactions upon isotopic substitution.⁶ However, for reaction 1 ΔE_0 becomes the difference in the gas-phase electron affinities of *R and R, and this difference is not always negligible.⁷ The equilibrium isotope effect (EIE) is defined as the equilibrium constant for the reaction without the presence of isotopic isomers (for reaction 1 this value is unity) divided by K_{eq} .⁶ Gas-phase studies of reaction 1 were carried out where R represented nitrobenzene (PhNO₂) and *R represented pentadeuterionitrobenzene.7a The ion cyclotron resonance results showed the EIE to be significantly greater than unity $(K_{eq} = 0.73 \pm 0.06)$.^{7a} Based upon MNDO calculations of bond length changes upon electron attachment, the EIE was attributed to the ΔE_0 term in eq 2. For large organic anion radicals in the solvated state it is very difficult to obtain the partition functions necessary for the meaningful application of eq 2. The difficulty of obtaining partition functions for solvated multiatomic anion radicals is enhanced due to ion association. An effect of ion association is evidenced by the observation that the presence of either sodium or potassium cations seems to have an effect upon the equilibrium constant for reaction 1 when R and *R are PhNO₂ and Ph¹⁵NO₂, respectively.^{3,7a} However, eq 2 has been applied to isotope-exchange reactions involving solvated atomic ions with impressive success.7b

The competition for electrons described in reaction 1 can be utilized for the physical enrichment of isotopic material, and it is this aspect of reaction 1 that renders it of practical value.⁴ For the cases where the EIE deviates from unity, the isotopic enrichment can be accomplished as easily as the anion radicals can be separated from the neutral molecules.

Isotopic enrichment is often expressed in terms of the deviation of the isotopic ratio in the enriched material from that of natural abundance in parts per thousand, eq 3.8

$$\delta = \{[*R] / [R](sample) - [*R] / [R](standard)\} / \{[*R] / [R](standard)\} / ([*R] / [R](standard)] (3)$$

Since there are ordinarily only small differences in the properties of the isotopic species, the separation factors are close to unity, and to obtain significant enrichments a large number of separation stages must be employed.8

There are at least two obvious simple schemes for anion-neutral-molecule separation. One involves the addition of a substance to the solution that will selectively react with the anion (i.e., water) followed by the separation of the reaction products from the unreacted substrates. The other scheme involves physical separation of the neutral and anionic material via their very different vapor pressures. This latter scheme involves the solid state. We have found that isotopic enrichment can be effected with either technique.

Results and Discussion

The reduction of p-benzoquinone (BQ) in liquid ammonia with a very deficient amount of potassium metal results in a solution of the anion radical in the presence of a large excess of neutral molecule (ca. 0.01 M). The EPR spectrum of this mixture exhibits broadened hyperfine lines due to Heisenberg exchange. Diluting a portion of this solution with pure ammonia and recording the spectrum at -75 °C yields a sufficiently well-resolved spectrum $(A_{\rm H} = 2.40 \text{ G} \text{ and peak to peak line width} = 0.10 \text{ G})$ to allow observation of the ¹³C satellites due to the natural abundance of ¹³C in the carbonyl positions ($A_{13C} = 1.65$ G). The ¹³C splitting from the methylene carbons is much too small for observation and

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Figure 1. EPR spectra (recorded at -75 °C) of the benzoquinone anion radical in liquid ammonia. The reduction was carried out with a very deficient amount of potassium metal. Only the high-field side of the center line of the 1:4:6:4:1 pentet from the carbonyl-¹²C system is shown (A). The ¹³C satellites are observed on each side of the center line and are separated by 1.65 G. The high-field ¹³C satellite is shown after a 10-fold magnification (B). Below this is a computer simulation (C) of a mixture of BQ⁻⁻ and BQ-13C⁻⁻. This best fit is obtained when the [BQ^{•-}]/[BQ-13C^{•-}] ratio is 65:1. This simulation (C) exactly matches the experimental spectrum in both the central (A) region (either on scale or with 10-fold magnification) and the ¹³C satellite region. A second simulation (D) was generated using a 44:1 [BQ*-]/[BQ-13*-] ratio, which corresponds to the natural abundance of carbonyl-¹³C in BQ^{•-} (2.22%). Simulation D also matches the experimental spectrum in the central region exactly. However, the ¹³C satellite in this simulation is too large to fit the experimental ¹³C satellite (B). The simulations were generated with peak to peak line widths of 0.122 G. When the reduction is carried out with a stoichiometric amount of potassium metal, the resulting spectrum is best simulated with a 44:1 anion radical ratio.

is buried under the huge signal from the all ¹²C anion radical.

From natural abundance, 2.2% of the anion radicals in the solution should contain a ¹³C carbonyl atom. However, computer simulations of the EPR spectra clearly show that there is considerably less than 2.2% ¹³C represented, Figure 1. That is, the ¹³C satellites of each of the five lines for BQ^{•-} have an intensity that is less than 1.1% of the peak due to BO^{•-}. On the other hand, when the solution is reduced by one mole of potassium metal for each mole of BQ, as opposed to a very deficient amount of potassium metal, the computer simulations best fit the experimental spectra when the anion radical is considered to contain 2.2% ¹³C in the carbonyl position. Five independent measurements of the equilibrium constant for reaction 1, where *R represents benzoquinone-carbonyl-¹³C (BQ-13C), clearly show that K_{eq} is less than unity, reaction 4.





The reduction of carefully weighed mixtures of benzophenone (BZO) and benzophenone-carbonyl- ^{13}C (BZO-13C) with very deficient amounts of sodium metal in liquid ammonia results in the simultaneous observation of the ESR spectra of BZO⁻⁻ and

TABLE I: Millimoles of Anion Radical and Neutral Molecule Present after the Reductions of an Original "Hot" Mixture of BZO and BZO-14C Along with the Radioactivity of the Original BZO:BZO-14C Mixture (dpm[S]) and of the Mixtures Recovered from the Partial Reduction (dpm[R]) and the ¹⁴C Enrichment

mmol of R*-	mmol of R	dpm[S] ^a × 10 ⁻⁵	$\frac{dpm[\mathbf{R}]^b \times}{10^{-5}}$	enrichment (δ) , parts/thousand
0.31	0.39	2.68 ± 0.03	2.90 ± 0.04	82
0.66	0.77	2.68 ± 0.03	2.97 ± 0.04	109
0.89	1.29	2.68 ± 0.03	2.98 ± 0.04	113
0.76	0.42	2.68 ± 0.03	2.96 ± 0.04	107

^a This represents the decompositions per minute/millimole of the original mixture. It did not vary from day to day. b This represents the decompositions per minute/millimole of the material sublimed from a partially reduced sample of the original mixture.

BZO-13C⁻⁻. Computer simulations of the spectra from a number of different solutions show that the equilibrium constant for reaction 1 where R = BZO-13C is well below unity, reaction 5.

$$BZO^{-}$$
, $Na^+ + BZO-13C \Rightarrow BZO + BZO-13C^{-}$, Na^+ (5)

$$K_{eq} = 0.50 \pm 0.06$$
 in NH₃ at -75 °C

Both reactions 4 and 5 suggest that the separation of the anionic material from the neutral material would effect a partial separation of the two isotopes. Indeed, the addition of water to the ammonia solution containing BZO- and BZO-13C - and subsequent workup and purification (sublimation) of the remaining BZO showed it to be significantly enriched in ¹³C at the carbonyl position ($\delta =$ +78).

Since ¹⁴C is of considerable importance in anthropological dating, we were motivated to utilize reaction 1, where *R represents BZO-carbonyl- ${}^{14}C$ to see if we could effect an enhancement in the radioactivity of samples consisting of a mixture of hot (BZO-14C) and cold (BZO-12C) benzophenones.

When 0.6-5.0 mmol samples of a radioactive $(0.02-0.16 \ \mu \text{Ci})^9$ mixture of BZO-14C and BZO-12C are reduced with deficient amounts of sodium metal in 20-40 mL of liquid ammonia at -78 °C, the concentrations of the hot and cold anion radicals and neutral molecules are controlled via reaction 6. Unfortunately

$$BZO^{\bullet-}.Na^+ + BZO-14C \Longrightarrow BZO + BZO-14C^{\bullet-}.Na^+$$
 (6)

there is no way of directly measuring the equilibrium constant for reaction 6, since ¹⁴C does not have a nuclear spin, and the β radiation emanating from it comes from the solution as a whole. Thus, in order to see if an EIE other than unity can be obtained by applying reaction 1 to this carbon-14-substituted system, an actual separation must be effected. Since both the Birch reduction products and unreacted BZO's would be radioactive it is more appropriate to attempt the enrichment via sublimation of the unreduced BZO's from the anion radical after solvent removal.

The deep blue ammonia solutions were exposed to high vacuum at -78 °C until all of the ammonia was evaporated, leaving a solid organometallic salt together with the unreacted BZO's. The anion radical salt that remains after the removal of the NH₃ has been previously characterized as Na⁺(NH₃)BZO^{-.10} The unreacted BZO's could be easily sublimed from this salt by warming the mixture to 160 °C under high (10⁻⁶ Torr) vacuum.¹¹ Alternatively, dry ether could be added to the solid ketyl-ketone mixture. As only the neutral ketone is soluble in the ether, this effects a separation of the ketyl and ketone.

Comparison of the radioactivity of the recovered samples to that of the original unreacted mixture showed the benzophenones recovered from the anion radical mixture to be enhanced in radioactivity, Table I. Further enhancement of the radioactivity can be achieved by simply partially reducing the recovered ma-

⁽⁹⁾ Pure BZO-14C yields 0.0624 Ci/mmol.

^{(10) (}a) The composition of the solid salt left after the evaporation of the (10) (a) The composition of the solid san tert after the evaporation of the ammonia was determined as described in ref 10b. (b) Stevenson, G. R.;
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^{5366.}



Figure 2. (Upper, A) Part (starting 10.0 G from the low-field end) of the ESR spectrum of a sample that was produced via the partial reduction of a 1.0 to 10.5 mixture of $C_{12}H_{10}C^{17}O$ and $C_{12}H_{10}C^{16}O$. The vertical arrow indicates the first line of the spectrum of $C_{12}H_{10}C^{16}O^{-\tau}$. Keep in mind that this line also has a contribution from the ¹⁷O species. (B) The computer simulation of the upper spectrum computed by using a ratio of heavy anion radical to light anion radical of 0.36. This corresponds to an equilibrium constant of $[C_{12}H_{10}C^{17}O^{-\tau}][C_{12}H_{10}C^{16}O]/[C_{12}H_{10}C^{16}O^{-\tau}] = 0.36 \times 10.5 = 3.8$. (C) The spectrum of the same solution after the addition of 0.10 M NaI. Note the reduction in the relative intensity of the spectrum due to $C_{12}H_{10}C^{17}O^{-\tau}$.

terials with sodium in liquid ammonia and working up this reaction mixture in the same manner. Table I shows that significant enrichment of the 14 C material can be obtained by this technique and that the electron attachment favors the cold BZO over the hot (heavy) BZO.

Due to the fact that the spin and charge densities are high in both the carbonyl carbon and oxygen atoms, it is expected that the condensed-phase electron affinity of BZO containing an isotopically altered oxygen atom should also be different from that of the unsubstituted BZO. Benzophenone enriched in ¹⁷O was prepared by warming benzophenone in a mixture of ¹⁷O-enriched water, dioxane, and a trace of HCl to 100 °C for 48 h as previously described.¹² When a sample of this ¹⁷O-enriched benzophenone (BZO-17O) was reduced in liquid ammonia with one mole of sodium for each mole of total benzophenone, the resulting blue solution yielded an ESR spectrum that was best simulated by using a combination of the spectra of BZO*- and BZO-17O*- in the ratio $[BZO^{-}]/[BZO-17O^{-}] = 0.095$. On the other hand, when the reduction of this enriched benzophenone isotopic mixture was carried out with very deficient amounts of sodium metal in liquid ammonia, the ESR spectrum of the resulting solution clearly exhibited a higher ratio of [BZO-170^{•-}]/[BZO^{•-}] than that for the complete reduction of this mixture. Computer simulations yield a best fit of the spectrum (Figure 2) when an equilibrium constant of 3.8 ± 0.31 at -75 °C is used for the reaction

$$BZO^{\bullet-} + BZO-17O \rightleftharpoons BZO + BZO-17O^{\bullet-}$$
(7)



Figure 3. (Center) The first portion (starting just downfield of the first line due to BZO*-) of the ESR spectrum recorded at -75 °C from a sample containing a [BZO]/[BZO-13C] ratio of 0.497 reduced with a very small amount of sodium metal in liquid ammonia. The first four lines from BZO⁻⁻ are marked with the vertical arrows and represent the first four lines of the 1:4:6:4:1 pentet due to the four meta protons. (Upper) This is the best fit computer simulation and was obtained by using a ratio of $[BZO-13C^{\bullet-}]/[BZO^{\bullet-}] = 0.90$, which corresponds to an equilibrium constant of 0.45 for reaction 4. The coupling constants used in the simulation are 3.65 G (2 H), 2.65 G (4 H), and 0.86 (4 H). A 9.66 G splitting for the ¹³C was added to produce the simulation for BZO-13C⁻⁻. The peak to peak line width is 0.190 G and is broadened, for the most part, due to electron exchange. (Lower) This simulation was generated exactly as described for the upper simulation except that the ratio [BZO-13C^{•-}]/[BZO^{•-}] was considered to be 1/0.497, which would correspond to an equilibrium constant for reaction 4 of 1.0 (no thermodynamic isotope effect). Note the much better agreement of the simulation that includes the isotope effect (upper) than that without the isotope effect (lower). There is no conceivable set of parameters (line widths, coupling constants, and anion radical ratios) other than those used to generate the upper simulation that will generate a simulation similar to the real spectrum. Several real experiments and their simulations yield an average value for K_{eq} for reaction 5 of 0.50 \pm 0.06.

Since the added electron lies predominantly in the carbonyl moiety in an antibonding molecular orbital, the bond loosening caused by the addition of this electron should render the gas-phase electron affinities of the heavy isotopic isomers, with either the presence of 13 C, 14 C, or 17 O smaller than those of the light (normal) isotopic materials. This expected order of electron affinities is observed in solution, also, for the case of BZO and BZO-13C. However, when the oxygen atom as opposed to the carbon atom is isotopically substituted, the heavy isotopic isomer has the larger solution electron affinity. This is explained by the fact that in liquid ammonia the anion radicals exist in the form of ion pairs¹³ as shown in the structure

The strong interaction between the negatively charged oxygen atom and the gegenion is essentially an ionic bond. This Coulombic attraction is present only after the addition of the extra electron. Thus, this "bond" is not just strengthened but is, rather, created upon addition of the extra electron, and bond formation increases the relative electron affinity of the isotopically heavy

⁽¹³⁾ Smith, W. H.; Bard, A. J. Am. Chem. Soc. 1975, 97, 5203.

species relative to that of the light. The ion association does not directly involve the carbon atom, which is why the isotopically light material has the greater solution electron affinity when isotopic substitution takes place on the carbon atom.

If this explanation is correct, then the addition of extra sodium ions to the solution would result in association between the ion pair and the added Na⁺ at a site other than the already associated oxygen atom (ion aggregation). This would result in a weakening of the original ion pair, and we should observe a decrease in the concentration of $C_{12}H_{10}C^{17}O^{\bullet-}$ relative to that of $C_{12}H_{10}C^{16}O^{\bullet-}$. The addition of sodium iodide to a solution of these two anion radicals in the presence of the two neutral molecules did indeed result in a significant decrease in the relative concentration of the isotopically heavy anion radical, Figure 2.

Experimental Section

Samples of either BZO or BQ ranging in size from 0.03 to 1.3 mmol were reduced in 25-35 mL of liquid NH₃ at -78 °C on a freshly distilled alkali metal mirror. Samples of these solutions could be prepared for ESR analysis by simply pouring a very small portion of the solution into the bottom of a ESR tube and then filling the remainder of the tube by distilling ammonia into the tube from the original anion radical solution. The solutions were diluted sufficiently to allow the observation of well-resolved spectra at -75 °C. The ESR spectra were recorded with a Brucker (IBM) ER-200 ESR spectrometer equipped with a IBM ER 4111 variable-temperature controller.

Mole ratios of the anion radicals yielding the given ESR pattern were obtained via computer simulation of the simultaneously observed spectra. Accurate values for the ratios of the two isotopically different anion radicals were obtained by expanding the spectra and simulating expanded portions where minimal overlap of lines of the two species occurs, allowing for more precise matching of the relative intensities of the two spectra. For spectra obtained from the complete reduction (one mole of metal added for each mole of substrate) the best fit was always obtained from a simulation that consisted of a ratio of anion radicals that was the same as in the original mixture. For example, the complete reduction of benzoquinone yields an ESR pattern that is best simulated with a mixture of BQ and BQ-13C that is 2.2% of the paramagnetic material in the form of BQ-13C⁻⁻. However, when only a partial reduction was carried out, the best fit was always obtained with the use of much lower ratios of heavy anion radical to light anion radical than the ratios of heavy to light materials used in the reaction.

The computer program used to generate the spectral simulations are based upon the Bloch equations and rigorously account for line broadening caused by electron exchange between radical and nonparamagnetic species in solution. The computations are based on an expression for G (total tranverse magnetization) for exchange between multiple sites as generalized from Binsch's¹⁴ two site exchange model. The imaginary portion of this equation

$$G = \frac{iC}{1/\sum (P_{k}A_{k}^{-1}) - 1/\tau}$$
(8)

$$A_{k} = i(w_{k} - w) + T_{2}^{-1} + \tau^{-1}$$
(8a)

corresponds to the relative absorption of electromagnetic radiation of a radical with N nuclear spin states as a function of w (Larmor frequency), τ (lifetime), p_k (statistical population), w_k (resonance frequency of the kth nuclear state), and T_2 (transverse relaxation time). C is an arbitrary scaling factor. Differentiating eq 8 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 9.

$$\tau = (2k_{\rm r}[{\rm M}])^{-1} \tag{9}$$

(14) Binsch, G. Top. Stereochem. 1968, 3, 104.

Initially, coupling constants are obtained from spectra of solutions of the isotopically pure radicals. Simulations generated using 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 and possible g shift (shift in spectral centers) as new variable parameters.

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 literature¹⁵ values.

Simulation of a 50:50 mixture of BQ and BQ-13C produces five lines, each with pairs of satellites whose intensities equal in sum those of the main lines. A portion of a real spectrum and its simulation used to obtain an empirical value for the equilibrium constant for reaction 4 is shown in Figure 1.

BZO-14C/BZO Measurements. A mixture of hot (purchased from Pathfinder Laboratories Inc.) and cold benzophenones was made up such that the ¹⁴C concentration was high enough for convenient counting and small enough for relatively safe handling. This original mixture was used as the radioactivity standard, and it yielded $(2.676 \pm 0.002) \times 10^5$ decompositions/minute/millimole (dpm[S]), Table I. Samples of this mixture (0.6–5.0 mmol) were dissolved in 20-40 mL of very dry liquid ammonia (the ammonia was distilled onto the BZO from potassium metal under high vacuum). The exposure of these solutions to freshly distilled sodium resulted in the formation of the deep blue solutions of the benzophenone ketyl. After complete dissolution of the molar deficient sodium, the ammonia was distilled from the apparatus under high vacuum at -78 °C. After complete removal of the ammonia, the solid mixture was exposed to high vacuum for about an hour at room temperature. Some of the solid neutral molecule could than be sublimed from this mixture into a U-tube that was kept at -78 °C and placed between the apparatus containing the mixture and the high vacuum system, by warming the solid mixture to 160 °C. The amount of anion radical generated during the reduction is necessarily the same as the amount of metal that dissolved in the ammonia solution containing the excess BZO, and it was determined by titration as previously described.¹⁶

The benzophenone recovered from the U-tube was recrystallized from methanol-water and dried under high vacuum. Accurately weighed samples (about 12 mg) of the mixture of hot and cold benzophenones recovered in this manner were dissolved in toluene containing Omnifluor as the scintillation solvent. The radioactivity associated with each sample was determined by using a Packard Tri-carb 460C-460D liquid scintillation system. Isotopic enrichments (δ values) were determined by comparison of the radioactivity of the recovered mixture in decompositions/minute/millimole (dpm[R]) with that of the original mixture (dpm-[S]).

BZO-13C/BZO Measurements. After the partial reduction of the benzophenone in liquid ammonia was complete, about 10 mL of water was distilled onto the ammonia solution and allowed to react with the anion radical. The ammonia was then allowed to evaporate and the remaining solid was dissolved in 50 mL of ether. The ether solution was washed several times with water. The ether solution was then dried with sodium sulfate and the

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Ed.; Wiley: New York, 1974; Vol. 2, pp 59-69.
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^{(17) (}a) Khatkale, M. S.; Devlin, J. P. J. Phys. Chem. 1979, 83, 1636. (b) Khatkale, M. S.; Devlin, J. P. J. Chem. Phys. 1979, 60, 1851.

ether removed under reduced pressure. The dry product was then recrystallized from methanol-water, dried, and sublimed. This benzophenone was then mixed with an equal number of moles of 3-pentanone and dissolved in 10 mL of CDCl₃. A similar mixture was made with the original (unreacted) benzophenone. $^{13}\mbox{C}$ NMR spectra in the carbonyl region were recorded for both solutions. Enrichments or depletions of the ¹³C isotope in the BZO via the reduction were determined by comparing the ratio of the heights of the pentanone and BZO ¹³C NMR lines (recorded on a FX-90-Q Jeol NMR spectrometer) in the original and reacted mixtures. The benzophenone recovered from the reaction mixture yielded no smaller signal (within experimental error) for the carbonyl carbon relative to that of the pentanone than did the same amount of unreacted material with the same amount of pentanone. Care was taken to assure that the pulse delay, number of pulses, pulse width, and other spectral parameters were kept the same when accumulating the data for the standards and recovered materials. However, the NMR experiments described above can be used to investigate larger changes in the ¹³C concentration at specific positions. Mass spectral analysis, on the other hand, can only point out changes in the bulk ¹³C content.

BZO-170/BZO Measurements. The benzophenone (BZO) was enriched with ¹⁷O by heating sealed tubes containing 1.0 g of BZO dissolved in 10 mL of dioxane with 1.0 mL of $H_2^{17}O$ (65%) containing a trace amount of HCl as previously described.¹² The dioxane was then evaporated, and the remaining mixture was extracted with ether. The ether solutions were dried with magnesium sulfate, and the ether was removed under reduced pressure. The enriched benzophenone was recrystallized from methanolwater, dried under vacuum, and sublimed. The chemical reductions, the recording of the ESR spectra, and the spectral analysis were carried out as described for the BZO/BZO-13C systems.

Conclusions

The solutions electron affinities (EA's) in liquid ammonia of

benzoquinone and benzophenone are significantly reduced by the presence of a seventh or eighth (in the case of benzophenone) neutron on the carbonyl carbon(s), and this fact can be utilized to enrich mixtures of the isotopic materials. One way to effect the enrichment is to quench the reaction in liquid ammonia with water and separate the hydrogenated and unreacted materials. Another way to separate the anionic material from the neutral material is to remove the solvent and sublime the neutral molecule from the ketyl salt.

On the basis of the Raman and IR studies carried out upon the neutral molecules and anion radicals of tetracyanoethylene and tetracyanoquinone, the net effect of an added electron is to lower the bond energies.¹⁵ It is in part this zero point energy effect that lowers the solution electron affinity of BZO where one or more extra neutrons is placed on the carbonyl carbon. However, this intrinsic property is combined with environmental interactions that are present in the condensed phases to yield very different relative solution and solid-state electron affinities. Indeed, the formation of the Coulombic interaction between the oxygen atom in the benzophenone anion radical and the sodium cation in the ketyl-Na⁺ ion pair renders the partition function of the BZO-170^{•-},Na⁺ ion pair larger than that of the BZO^{•-},Na⁺ ion pair resulting in the larger solution electron affinity of the heavy isotopic isomer.

The zero point energy argument can be used to predict the thermal dependence of K_{eq} . Unfortunately, we have not had success in the interpretation of the EPR spectra recorded at elevated temperatures due to the rapid (line broadening) electron exchange between anion radical and neutral molecule.

Acknowledgment. We thank NSF (Grant CHE-841127) for support of this work.

Registry No. BQ, 106-51-4; BZO, 119-61-9; BQ*-, 3225-29-4; BZO*-, 16592-08-8; ¹⁴C, 14762-75-5.

COMMENTS

Torsional Frequency of the Biphenyl Molecule

Sir: This article comments upon recent work of Akiyama et al.¹ on the problem of internal rotation in biphenyl. The problem of the potential function for internal rotation and the associated torsional frequency is a controversial one in spite of considerable efforts.1-6 One of the basic obstacles in the more complete understanding of the nature of internal rotation in biphenyl is the fact that the molecule changes geometry substantially from the gas phase to the solid or liquid. The equilibrium dihedral angle between the planes of the phenyl rings is $45 \pm 10^{\circ}$ in the gas phase,⁷ 22° in the melt,⁸ and 0° in the crystal at room temperature.⁹⁻¹¹ The fundamental problem in the spectroscopic investigations, for more than two decades, was the assignment of

the torsional mode in different phases. A number of authors concluded that in the crystal the frequency of the torsional mode is around $60-70 \text{ cm}^{-1.12-14}$ Such a conclusion was recently supported by a number of model calculations.¹⁵⁻¹⁷ In their work Akiyama et al.¹ compared a calculated frequency of the torsion from the geometry of the free molecule ($\theta = 37^{\circ}$) with the early observed neutron scattering data for the polycrystalline sample, i.e., the data obtained from a sample with a molecular geometry $\theta = 0^{\circ.18}$ For biphenyl one should make clear distinction between the torsional frequency of the free molecule and the molecule in the crystal lattice, because of the substantial change in molecular geometry between these two phases. The energy levels for torsional motion of the phenyl ring for the free molecule are calculated by solving the Schrödinger equation for periodic internal potential, and for the gas phase of biphenyl it was done by Carreira et al.² The usual assumption is that the potential for internal rotation of one molecular group can be expressed as a Fourier series. In

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