and the thermal internal energy tend to offset each other: coincidentally the predicted long-time appearance energy for this dissociation (1.2 eV) is seen to be equal to E_0 at 375 K.

Conclusion

The dissociation kinetics of TTBB ion are well described by RRKM modeling, which gives strong support to the validity of the QET picture of the dissociation. It is noteworthy that the dissociation was found to be *slower* than predicted from the loose transition state analogous to the transition state for TBB ion dissociation. If localized bond breaking were to take place prior to complete equilibration of the internal energy the dissociation would be expected to be faster than the RRKM prediction.

The 0 K conventional kinetic shift is large, as expected, shifting the 0 K threshold upward from 1.2 to 2.4 eV (giving approximately a doubling of the threshold). The intrinsic kinetic shift is less (0.7)

eV), but still a large fraction of E_0 . In terms of attempting to establish the dissociation thermochemistry by daughter ion appearance measurements, the present results reinforce a point which is clear in recent work: For larger ions, the effects of kinetic shifts and thermal energy content on the observed threshold are so large that the appearance energy of daughters has essentially no relation to the true dissociation thermochemistry. Only by measuring the dissociation rate as a function of energy, deconvoluting the contribution of thermal internal energy, and extrapolating to E_0 can the true dissociation activation energy be determined from measurements of daughter ion intensities.

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Strong Environmental Effects upon ΔG° of Electron Transfer between an Anion Radical and Its Perdeuteriated Analogue

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The free energy change for electron transfer from the anion radical of nitrobenzene to perdeuteriated nitrobenzene (PhNO2-+ PhNO₂- d_5 = PhNO₂ + PhNO₂- d_5) has been determined via solution-phase EPR measurements and physical separation of the neutral nitrobenzenes from the solid anion-radical salts. This free energy is largest in hexamethyl-phosphoramide $(\Delta G^{\circ} = 1400 \text{ J/mol})$ where the anion radical exists free of ion association and hydrogen bonding. In liquid ammonia, where the anion radicals are strongly hydrogen bonded through the NO_2 group, this free energy is only 389 J/mol. The addition of extra sodium cations to the ammonia solution results in a further decrease in ΔG° to 243 J/mol where it is of the same magnitude as in the solid-state anion radical where the interaction between the cation and anion radical is very strong. Ion association and hydrogen bonding pull spin and charge density into the NO₂ group and away from the phenyl ring where isotopic substitution takes place, resulting in a smaller equilibrium isotope effect. In HMPA the isotope effect is even larger than in the gas phase due to stronger solvation of the phenyl moiety than of the NO_2 group in this solvent.

Introduction

Gas-phase isotope effects can, in principle, be explained and predicted with statistical mechanical models to a degree that may even exceed the accuracy obtained from the direct measurements of these effects. The cases of the disproportionations of oxygen-16,18 $(2^{16}O^{18}O = {}^{16}O^{16}O + {}^{18}O^{18}O)^{1}$ and HD (2HD = HH)+ DD)² are well-studied examples where the improvement of the instrumentation seems to result in experimental equilibrium constants that approach the predicted values. Excellent agreement between statistical mechanical calculations and solution equilibrium isotope effects have been observed.³ However, since the solvation of ions involves a variety of solvent-ion and cation-anion vibrational interactions that are difficult to account for in detail, these statistical mechanical agreements are best when charged species are not involved. Solvation, of course, often has profound effects upon the thermodynamics controlling the formation of charged species. Note the 1970 discovery that the gas-phase electron affinity (EA) of the *tert*-butoxy radical is greater than that of the methoxy radical, while in solution quite the reverse is observed.⁴ These two solution- or gas-phase electron affinities control the electron transfer between methoxide and the tertbutoxy radical $(CH_3O^- + (CH_3)_3CO^- = CH_3O^- + (CH_3)_3CO^-)$.

Theoreticians did not predict (in print) this gas-phase observation, nor, to our knowledge, is there a good statistical model describing the relative solution electron affinities of the alkoxy and hydroxy radicals. Despite this, Wolfsberg and co-workers⁵ used statistical mechanical arguments to question the empirically derived relative solution electron affinities for a series of isotopic isomers. A later report by some of the same authors further points out how important statistical mechanical models are in testing the experimental validity of solution-phase isotope effects.³ It must be kept in mind that the construction of a theoretical model for the difference in the EA's of alkoxy radicals is very different than the construction of such a model for the maximum isotope effects. The point remains, however, that the inclusion of solvent effects may not be straightforward.

In 1986 EPR experiments on electron-transfer reactions (reaction 1) yielded evidence indicating that the solution electron affinities of both perdeuteriated benzene and (13C)₆benzene are considerably less than that of normal benzene, reactions 1 and 2.6 Given the magnitude of ΔG° in reaction 2 (186 J/mol/¹³C),

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we were motivated to look for an analogous ¹³C equilibrium isotope effect in a system where the isotopically heavy material is enriched at only a single position. It was reasoned that the larger spin and charge densities on the carbonyl carbon of a ketyl relative to those on a carbon atom in the benzene anion radical should augment the effect in this former system. Indeed, (carbonyl-¹³C)benzophenone was found to have a significantly lower solution EA than does normal benzophenone, reaction 3.7 It was this and similar



 $\Delta G^{\circ} = 1280 \text{ J/mol}$ (3)

reports of heavy-atom equilibrium isotope effects⁷ that were the target of Wolfberg's⁵ criticism, which stated that no reasonable statistical mechanical model can support the reported ΔG° 's. The H/D effects were not specifically criticized,⁵ but the critique could suggest doubt as to the viability of the EPR technique. The general technique, however, is well established.

Over the years EPR has proven to be an accurate analytical tool for evaluation of relative concentrations of radicals,⁸ and nearly two 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.⁹ These facts along with the advances in EPR computer simulation processes make "the EPR technique"10 extremely viable for the study of electron-transfer reactions of the type shown in reaction 4.10

$$A^{*-} + B = A + B^{*-}$$
 (4)

The H and D isotope effect that we initially observed via EPR measurements,^{4,5} has been confirmed with cyclic voltammetry data¹¹ and ion cyclotron resonance data.¹² Further, the effect

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in general has also led to actual isotope separations, which have been detected via mass spectral analysis,13 scintillation counting,14 EPR measurements,⁶ and NMR measurements.¹⁵ While no laboratory is immune to error concerning a particular measurement, there can be no reasonable doubt as to the viability of the EPR technique for determining the free energy changes of electron transfer, and the evidence obtained by other techniques and from other laboratories constitutes overwhelming validation of our measurements of ΔG° of electron transfer for systems involving isotopic isomers. This indicates the probability of error in either the applicability of the types of calculations used in Wolfsberg's critique or the use of unsuitable assumptions.

In view of the recent successes of quantum mechanics (no exceptions reported to date) especially in relationship to Bell's inequality,¹⁶ there seems almost no doubt that quantum-mechanics-based statistical mechanical models represent models for the macroscopic thermodynamic world that are fundamentally correct. However, the statistical mechanical method for extrapolating from the quantum-mechanical world to the macroscopic scale is dependent upon detailed knowledge of all of the quantum-mechanical phenomena in which each part of the system under study is involved. For solvated ionic systems this is not always available. Here we wish to report empirical gas-phase, solution-phase, and solid-phase equilibrium isotope effects where media considerations have altered the intrinsic equilibrium constants to a degree that would render a statistical mechanical treatment in conjunction with the common assumptions erroneous.

Results and Discussion

Solutions of nitrobenzene or perdeuteriated nitrobenzene in liquid ammonia will dissolve small amounts of sodium metal to form the respective anion radicals, which yield strong well-resolved EPR spectra that are characterized by a nitrogen splitting of 10.2 G and ortho, meta, and para proton splittings of 3.50 (0.54), 0.90 (0.13), and 4.00 (0.61) G, respectively. The reduction of a 1:1 mixture of $PhNO_2 + PhNO_2 - d_5$ with 1 mol of sodium per mole of total nitrobenzene produces a solution yielding an EPR spectrum that is best simulated by assuming a 1:1 mixture of $PhNO_2^{-}$ + $PhNO_2 - d_5^{\bullet-}$. However, when the sodium metal is present in a molar deficiency, the resulting EPR spectrum clearly exhibits a greater relative concentration of the isotopically light anion radical. Simulation of a number of such spectra resulting from various mixtures of these two materials shows that the equilibrium constant for reaction 5 is 0.80 ± 0.03 at -63 °C.

In liquid ammonia, there is considerable hydrogen bonding between the nitro group and the solvent protons,¹⁷ which pulls



charge and spin density into the NO2 group and results in the large $A_{\rm N}$ relative to that in non-hydrogen-bonding solvents such as hexamethylphosphoramide (HMPA), where A_N is only 8.48 G.¹⁸ Further, the strong hydrogen bonding in ammonia inhibits ion association with the gegon ion.¹⁹ The addition of extra Na⁺ (i.e.,

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NaI) shifts reaction 6, which is fast on the EPR time scale, to

the right resulting in an increase in the observed $A_{\rm N}$.¹⁹ It was expected that this shift of charge and spin density from the ring system, where isotopic substitution takes place, to the NO₂ group would diminish the equilibrium isotope effect (shifting the value of K_{eq} closer to unity). Indeed, when the same experiments described above were carried out in liquid ammonia after adding 0.3 M NaI, A_N increased from 10.2 to 11.5 G, and K_{eq} for reaction 7 increased to 0.87 ± 0.04 at -63 °C.

In the solid state the interaction between the anion radical and cation is also intimate, as it accounts for the lattice energy of the salt. To study the electron transfer in the solid state the anion radicals of PhNO₂-d₅ and PhNO₂ were generated in tetrahydrofuran (THF) via the reduction of a mixture of $PhNO_2-d_5$ and PhNO₂ with a molar deficiency of sodium metal in THF. After the formation of the anion radicals, the solvent was removed under reduced pressure. Once all of the THF was evaporated, the solid anion-radical salt and neutral nitrobenzenes were present in the apparatus.²⁰ The separation of the neutral nitrobenzenes phase (phase 1), via dissolution in hexane, from the anion radical (phase 2) results in a partial separation of the isotopic materials, and the degree of separation should reflect the thermodynamic equilibrium constant for the electron transfer from the solid anion radical to the nitrobenzene. The neutral hydrocarbons were recovered from phase 2 via their reoxidation with iodine (Na⁺- $PhNO_2^{\bullet-} + \frac{1}{2}I_2 \rightarrow NaI + PhNO_2$). The equilibrium constant for the electron transfer involving the solid anion-radical salt is simply the mole ratio of the heavy to light isotopic isomers in phase 1 divided by that in phase 2, eq 8. The ratios of [PhNO₂-

$$K_{eq(s)} = \frac{\left([PhNO_2 \cdot d_5]/[PhNO_2]\right)_{phase 1}}{\left([PhNO_2 \cdot d_5]/[PhNO_2]\right)_{phase 2}}$$
(8)

 d_{5} /[PhNO₂] in the two phases were determined by mass spectral analysis and yield a value for $K_{eq(s)}$ of 0.90 ± 0.02 at +25 °C, reaction 9.

$$Na^{+} \bigodot_{(s)}^{NO_{2}} + D_{0}^{NO_{2}} + D_{0}^{NO_{2}} + D_{0}^{NO_{2}} + O_{(s)}^{NO_{2}} + O_{(s)}^{N$$

From Table I, it appears that the intimate interaction between the anion radical and sodium cation does result in a general lowering of the observed free energy change for the electrontransfer reaction. The ΔG° for the electron transfer involving the ion pair (reaction 7) and that involving the solid anion-radical salt (reaction 9) are both significantly smaller than that involving the unassociated hydrogen-bonded anion radical (reaction 5). The electron transfer involving the ion pairs in liquid ammonia is shifted to the right to about the same degree as that in the solid phase possibly due to the synergistic effects of hydrogen bonding and ion association in the former case. After simple extrapolation of these solid-phase room-temperature equilibria data from 298 to 173 K $[K_{eq} = e^{-\Delta G^{e}/173R}]$ they can be compared to the low-tem-



Figure 1. (Upper) EPR spectrum of a partially reduced mixture of nitrobenzene and nitrobenzene-ds in HMPA at 25 °C. (Lower) Computer simulation of this spectrum using a ratio of $[PhNO_2-d_5]/$ $[PhNO_2^{*-}] = 5.5$. Since the ratio of $[PhNO_2 - d_5]/[PhNO_2] = 10$, the implied equilibrium constant for reaction 10 is 0.55. The average equilibrium constant from several such measurements is 0.57 ± 0.02 . This corresponds to a free energy change of 1.4 kJ/mol and extrapolates to $K_{eq} = 0.38$ at 173 K.

perature data taken in solution, Table I. The very small entropy changes for reactions 5 and 9 allow meaningful extrapolations of the room-temperature data to low temperature.

In solution, the rate of electron transfer between anion radical and neutral molecule is very fast. The second-order rate constants vary from 10⁷ to 10⁹ M⁻¹ s⁻¹.^{10c} Consequently, there is no doubt that equilibria (reactions 5, and 7) are established long before an analysis can be performed. Since the solid anion-radicalneutral-molecule mixture is generated by slowly evaporating the solvent (THF) from the solution, a state of thermodynamic equilibrium persists during the solvent removal and in the solid state.

Since the nitrobenzene anion radical can be generated free of ion association and free of hydrogen-bonding interactions in HMPA, it was expected that the free energy of electron transfer from $PhNO_2^{-}$ to $PhNO_2 d_5$ in this solvent would be larger than that obtained in liquid ammonia. Simulations of the EPR data obtained from solutions containing partially reduced mixtures of PhNO₂ and PhNO₂- d_5 show that K_{eq} for reaction 10 in HMPA

is 0.57 at 25 °C, Figure 1. This free energy change is even larger than that measured in the gas phase by ion cyclotron resonance $(\Delta G^{\circ} = 790 \pm 200 \text{ J/mol})$,¹² suggesting that the HMPA solvates the ring portion of the anion radical to a greater extent than it does the nitro group, producing a reverse solvent effect.

Experimental Section

HMPA Studies. The sodium reduction of nitrobenzene in HMPA results in the formation of both the ion pair and free solvated ions, which appear simultaneously upon EPR observation.¹⁸ To avoid this problem, we reduced the carefully weighed mixtures of the nitrobenzenes ($PhNO_2 + PhNO_2 - d_5$) in THF with a very deficient amount of sodium metal under high vacuum. The

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TABLE I: Equilibrium Constant and Free Energy Change for the Electron Transfer PhNO2⁺⁺ + PhNO2⁺ = PhNO2 + PhNO2⁺ d⁺

medium	ΔG° , J/mol	K _{eq} (173 K)	method	ref	no. of expts	
gas phase	790 ± 190	0.58	ICR	12		
$NH_1 + K^+$	389 ± 21	0.76	EPR	this work	4	
solid salt	261 ± 29	0.83	phys sepn	this work	4	
$NH_{3} + K^{+} + Na^{+}$. I ⁻	243 ± 42	0.84	EPR	this work	5	
$HMPA + Na^+$	1400 ± 30	0.38	EPR	this work	3	



Figure 2. Apparatus used for the reduction of the $PhNO_2 \cdot d_3 + PhNO_2$ mixtures in liquid NH₃. The nitrobenzenes are sealed in capillary tubes, which are in turn placed into the tubes marked E, and the NaI is sealed into capillary tubes, which are placed into the tubes marked D.

THF was then removed under reduced pressure, and HMPA was distilled from potassium metal directly into the apparatus containing the solid anion-radical salts. This afforded nitrobenzene anion-radical solutions, which exhibited only the free solvated ion $(A_N = 8.48 \text{ G})^{18}$ upon EPR analysis. Computer simulations of these spectra yielded the ratio of anion radicals ([PhNO₂-d₅-]/[PhNO₂-d₅-]) that was used to obtain K_{eq} for reaction 10 (Figure 1).

Liquid NH₁ Studies. Carefully weighed portions of PhNO₂ and PhNO₂-d₅ were sealed into glass capillary tubes and placed into tubes D of the apparatus shown in Figure 2. Similar capillary tubes charged with weighed portions of sodium iodide were sealed under argon and placed into tubes E of the apparatus. Tubes D and E were subsequently sealed. With the entire apparatus evacuated, potassium metal was distilled from tube A to form a mirror in tube B. Tube A was then sealed from the apparatus (arrow). With bulb C in a dry ice/acetone bath, ammonia was then distilled from potassium metal through the vacuum line into the apparatus. The apparatus was removed from the vacuum system after closing of the stopcock, and a small portion of the ammonia was allowed brief contact with the potassium mirror. The resulting solvated electron solutions were then poured into the EPR sample tubes, which were subsequently sealed from the apparatus at the point indicated by the arrow.

Agitation of the EPR sample tubes ruptured the capillary tubes containing the nitrobenzenes resulting in the formation of the anion radicals. After thorough mixing, the EPR spectra were recorded. The tubes were then agitated in a direction perpendicular to that used to break the nitrobenzene-containing tubes so as to break the tubes containing the NaI. After dissolution of the NaI, the EPR spectra were again recorded. In this way the EPR spectra of the same anion-radical solutions, with and without added Na⁺, could be directly compared to each other.

Physical Separations. The separations of the isotopic materials were carried out in a manner that is analogous to that described

for the isotopic isomers of benzene.¹⁵ Mixtures of PhNO₂ and PhNO₂- d_5 were reduced with about a 50% deficiency of sodium metal in THF under high vacuum. The THF was then removed under reduced pressure, and hexane was distilled through the vacuum system onto the remaining anion-radical salt and neutral nitrobenzenes. The resulting hexane/nitrobenzene solution was passed through a sintered glass frit to separate it from the insoluble anion-radical salts. The neutral nitrobenzenes were recovered from the hexanes, distilled, and labeled phase I.

After several washings of the anion-radical salts with hexane to ensure complete removal of the neutral nitrobenzenes, the anion radicals were reoxidized with I_2 in ether. The reoxidized material in ether was washed with a sodium thiosulfate solution and water. The ether solution was then dried over magnesium sulfate. After evaporation of the ether, the nitrobenzenes were vacuum distilled and labeled phase II. The relative amounts of PhNO₂ and PhNO₂-d₅ in phase I and phase II were determined via gas chromatography/mass spectral analysis.

Instrumentation and Materials. The phase I and phase II nitrobenzene samples were subjected to analysis on a Hewlett Packard 5790/5970 gas chromatograph/mass spectrometer system with a 30-m, 0.25-mm-i.d. capillary column of methyl silicone. Measurements were made in the scan mode. The samples were checked against standard mixtures of PhNO₂ and PhNO₂- d_5 .

EPR spectra were recorded on a Bruker ER-200 EPR spectrometer equipped with a Bruker ER-4111 variable temperature controller. The computer simulations were carried out as previously described.⁷

The nitrobenzene- d_5 in 99% isotopic purity was purchased from Cambridge Isotope Laboratories.

Conclusions

The free energy change controlling electron transfer from the anion radical of nitrobenzene to perdeuteriated nitrobenzene is strongly dependent upon charge and spin density around the ring system where isotopic substitution takes place, which is, in turn, dependent upon the medium. In the gas-phase, this free energy is about twice as large as it is in liquid ammonia solution, where the anion radical acts as a hydrogen-bonding proton acceptor with the ammonia (PhNO₂ ·····H₃N). This free energy (ΔG°) in liquid ammonia is further decreased by the presence of ion association with the sodium cation (PhNO₂^{•-}, Na⁺). In HMPA, where PhNO₂⁻⁻ is not involved in either hydrogen bonding or ion association, ΔG° is even larger than in the gas phase. This is probably best explained by the stronger solvation of the ring system than of the nitro group in this solvent. The observed equilibrium isotope effect is strongly dependent upon the charge and spin density in the area of isotopic substitution, which is, in turn, dependent upon the specific anion-radical-counterion and anion-radical-solvent interactions. Statistical mechanical predictions of these condensed-phase equilibrium constants would necessarily be erroneous if they did not take both of these interdependent effects (solvation and charge density shifts) into account. Since solvation effects are still not well understood on a quantum-mechanical level, meaningful calculations could prove formidable.

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Registry No. PhNO₂, 98-95-3; PhNO₂- d_5 , 4165-60-0; Na, 7440-23-5; PhNO₂⁻⁺, 12169-65-2; PhNO₂- d_5^{+-} , 65119-76-8; NaI, 7681-82-5; PhNO₂- d_5^{+-} Na⁺, 135189-85-4; D₂, 7782-39-0.