The results are given in Figure 10. When compared with the experimental results in Figure 9, it gives a rough idea of the reliability of the mechanism of conversion from one type of molecular motion to another.

Conclusion

The thermodynamic properties of the liquid phase of toluene have given us access to two sets of information. The first follows from the examination of the expansivity coefficient. Its behavior as a function of pressure conforms to the general rule, but its behavior as a function temperature classifies toluene in the "complex" liquid category. The nature of this "complexity" may be examined through the behavior of the heat capacity C_v as a function of volume, giving us the second set of information. A discussion on the qualitative aspects of the phenomenon leads us to conclude that there is a measurable conversion from one type of molecular motion to another taking place at low temperature in the high-density region.

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Appendix

I. The Compressibility $\Delta \kappa(T,p)$. Following step S2, the integral of eq 9 is determined where $\alpha(T,p)$ is given by eq 17a-17c. Putting down

$$w = a_1/a_2$$
 and $\Omega = \frac{\alpha_0(1-w)}{a_2}$

we operate the change of variable $X^2 = (m_0 - w)/(w - m_\lambda)$; the result is

$$\Delta \kappa(T,p) = \frac{\Omega(m_0 - w)}{p_c(m - w)^2} \Biggl\{ \frac{(m_0 - m)^2}{(m - m_\lambda)^{1/2}(m_0 - w)} + \frac{(m_0 - w)(m - m_\lambda)^{1/2}}{2(w - m_\lambda)} + (4m - 3m_0 - w) \varsigma \Biggr\}_{T_t}^T (A1)$$

where the function ζ takes one of the following two forms depending on the value of m:

case 1:
$$m > w$$

ζ=

$$\frac{1}{2(m-w)^{1/2}} \ln \left[\frac{(m_0-w)^{1/2}}{(m-w)^{1/2}} \frac{(m-w)^{1/2} + (m-m_\lambda)^{1/2}}{(w-m_\lambda)^{1/2}} \right]$$
(A2)

case 2: m < w

$$\zeta = \frac{1}{2(w-m)^{1/2}} \arcsin\left[\frac{(w-m)}{(w-m_{\lambda})}\right]^{1/2}$$
(A3)

II. The Reference Isotherm for the Compressibility $\kappa(T_r,p)$ ($T_r = 178.2 \text{ K}$).

$$\kappa(T_{r},p) = \frac{A_{1}}{(p+A_{2})^{2}}$$
(A4)

III. The Molar Volume V(T,p). Following step S6 and with the same change of variable as in (I), we find

$$\ln \frac{V(T,p)}{V(T_{r},p)} = \frac{2\Omega(m_{0} - w)}{m - w} \left\{ \frac{(m_{0} - w)(m - m_{\lambda})^{1/2}}{2(w - m_{\lambda})} - \frac{(m - w)(m - m_{\lambda})^{1/2}}{m_{0} - w} + (4m - 3w - m_{0})\zeta \right\}_{T_{r}}^{T} (A5)$$

where ζ is given by eq A2 or A3 according to the sign of (m - w).

IV. The Reference Isotherm for the Volume $V(T_r,p)$.

$$\ln \frac{V(T_{r,p})}{V(T_{r,p}=0)} = \left[\frac{A_1}{p+A_2}\right]_{p=0}^p$$
(A6)

 $V(T_r,p=0) = 95.73 \text{ cm}^3 \text{ mol}^{-1} \text{ at } T_r = 178.2 \text{ K}.$ Registry No. Toluene, 108-88-3.

Equilibrium Studies by Electron Spin Resonance. 17. The Effect of a Methyl Group on the Solution Electron Affinity of Nitrobenzene

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Electron spin resonance studies have shown that the free energy of electron transfer from the ion-associated anion radical of nitrobenzene to p-methylnitrobenzene ($PhNO_2^{\leftarrow}, Na^+ + CH_3 - PhNO_2 = PhNO_2 + CH_3 - PhNO_2^{\leftarrow}, Na^+$) in liquid ammonia is 1.52 kcal/mol. The free energies of ion association for both anion radicals were measured, and these values were used in a thermochemical cycle to obtain the free energy of electron transfer involving the unassociated ions. This free energy of electron transfer is 1.4 kcal/mol, which is identical with the difference in the electron affinities of $PhNO_2$ and CH_3 - $PhNO_2$ in the gas phase. It was found that the ion association constant increased from 320 to 381 for $PhNO_2^{\leftarrow}$ and from 380 to 450 for CH_3 - $PhNO_2^{\leftarrow}$ when the solvent is changed from ammonia to methylamine. The increase in the ion association constant caused by placing it on the nitrobenzene anion radical.

Introduction

In a mixture of dimethoxyethane (DME) and tetrahydrofuran (THF), where anion radicals exist exclusively as ion pairs, it has been shown that the relative solution electron affinity of toluene

is smaller than that of benzene by 0.51 kcal/mol, reaction $1.^1$ In contrast to this the electron affinity (EA) of toluene is greater

⁽¹⁾ Lawler, R. G.; Tabit, C. T. J. Am. Chem. Soc. 1969, 91, 5671.

than that of benzene in the gas phase, reaction $2.^2$ This would



 $\Delta G_1^\circ = \Delta H_1^\circ = +0.51 \text{ kcal/mol}$

$$(\mathbf{g}) + (\mathbf{g}) \neq (\mathbf{g}) \neq (\mathbf{g}) + (\mathbf{g}) \neq (\mathbf{g}) = (\mathbf{g}) + (\mathbf{g}) = (\mathbf{g})$$

 $\Delta G_2^\circ = \Delta H_2^\circ = -0.92$ kcal/mol

indicate that the decreased affinity for an electron exerted by the methyl group in solution is not due to an intrinsic electron releasing character of the methyl group but is due to its ability to inhibit the stabilizing interaction between the anion and the solvent and/or the counterion. This steric inhibition of solvation and possibly ion association is evidently important enough to reverse the relative electron affinities of benzene and toluene.

It has not been possible to determine the role of ion association in this reversal. This is due to the fact that these two anion radicals exist only as ion-associated species in the ethereal solvent systems. Further, in solvents where these ions may exist in the free solvated state, such as HMPA and liquid NH₃, these two anion radicals are unstable toward the neutral hydrocarbon and the solvated electron. However, it has recently been reported that the nitrobenzene anion radical can be observed either as the ion-associated species (PhNO₂^{•-},Na⁺) or as the unassociated solvated ion (PhNO₂^{•-}) in liquid ammonia, reaction 3, where X = H.³ This,

 $X-PhNO_2^{\bullet-}(soln) + Na^+(soln) \rightleftharpoons X-PhNO_2^{\bullet-}, Na^+(soln) \quad (3)$

$$\Delta G_3^\circ = -2.3 \text{ kcal/mol at } -75 \circ \text{C in NH}_3 \text{ when X} = \text{H}$$

 $PhNO_{2}^{\bullet-}(g) + CH_{3} - PhNO_{2}(g) \Longrightarrow$ $PhNO_{2}(g) + CH_{3} - PhNO_{2}^{\bullet-}(g) (4)$

$$\Delta G_4^\circ = \Delta H_4^\circ = \pm 1.4 \text{ kcal/mol}$$

coupled with the recent report of the relative gas-phase electron affinities (reaction 4) of both PhNO₂ and *p*-methylnitrobenzene (CH₃-PhNO₂),⁴ makes it possible to determine the relative solution EA's of these two ions in the presence of ion pairing and in its absence. When this information is coupled with the relative gas-phase EA data, a complete thermodynamic picture of the role of the methyl group upon relative solvation energies and ion association energies and their effect upon EA changes due to solvation and ion association can be obtained.

Results and Discussion

As with the case of nitrobenzene,³ the reduction of CH_3 -PhNO₂ in liquid ammonia leads to a light orange solution that yields a well-resolved ESR spectrum for the CH_3 -PhNO₂ anion radical, Figure 1. Both the nitrogen hyperfine coupling constant (A_N) and the g value are sensitive functions of the concentration of Na⁺ in the solution due to the formation of the ion pair as shown in reaction 3 where X = CH₃. The same situation was realized when methylamine served as the solvent.

The obvious line-width alternation observed in the ESR spectra (Figure 1) and the gradual increase in A_N accompanied with increases in the Na⁺ concentration show that reaction 3 is fast on the ESR time scale. As the concentration of Na⁺ is increased via the addition of sodium iodide to the anion radical solution, the line-width alternation effect first increases then decreases, Figure 1. At the higher concentrations of Na⁺, no line-width

TABLE I: Ion Association Constants (K_{eq} for Reaction 3) and ESR Parameters (in gauss) for Anion Radicals in Ammonia and Methylamine

anion radical	solvent	K _A	$A_{\rm N}^{0}$	<i>A</i> _N ′
PhNO ₂ •-	NH ₃	320 ± 30	10.2	11.5
PhNO ₂ •-	CH_3NH_2	381 ± 21	10.1	11.5
CH ₃ -PhNO ₂	NH ₃	380 ± 10	10.47	11.83
CH ₃ -PhNO ₂	CH_3NH_2	450 ± 40	10.3	11.8

alternation is evident, and there are no further increases in A_N with the additional augmentations of $[Na^+]$ via the addition of NaI to the solution. This indicates that reaction 3 is shifted far to the right under these conditions, and that the observed value for A_N is that for the ion-associated species (A_N') . As the concentration of the anion radical solutions is decreased, the ESR pattern approaches that of the unassociated anion radical. However, for the cases of PhNO₂^{•-} and CH₃-PhNO₂^{•-} in methylamine and for CH₃-PhNO₂^{•-} in ammonia, continuous dilution of the solutions led to the ESR signals growing too weak to allow observation before the anion radical solutions were sufficiently dilute to allow the measurement of the coupling constants for the solvated free ions (A_N^0) .

Equation 5 is commonly applied to ion association equilibria, when the two-site model applies as it does in reaction $3^{.3,5}$ To

$$K_{\rm A} = (A_{\rm N} - A_{\rm N}^{0}) / \{ [{\rm Na}^+] (A_{\rm N}' - A_{\rm N}) \}$$
(5)

utilize eq 5 it is necessary to be able to measure both A_N' and A_N^0 independently as in the case of nitrobenzene in liquid NH₃.³ Equation 5 must be rearranged to accommodate the situations where only one of the limiting values of A_N can be observed.⁶ In the cases described above, where only A_N' can be independently measured, eq 5 takes the form described in eq 6, which predicts that a plot of $1/(A_N' - A_N)$ vs the concentration of Na⁺ is linear⁷ and has a slope of $K_A/(A_N' - A_N^0)$ and an intercept of $1/(A_N' - A_N^0)$.⁷

$$1/(A_{N}' - A_{N}) = K_{A}[Na^{+}]/(A_{N}' - A_{N}^{0}) + 1/(A_{N}' - A_{N}^{0})$$
(6)

Such plots are indeed linear, Figure 2, and yield values for K_A of 381 ± 21 , 450 ± 40 , and 380 ± 10 for PhNO₂⁻⁻ in methylamine and CH₃-PhNO₂⁻⁻ in methylamine and NH₃, respectively, Table I. The larger values of K_A for CH₃-PhNO₂ anion radical in both solvents is due to the apparent electron releasing character of the methyl group in solution, which increases the spin and charge densities on the NO₂ group. This is supported by the fact that both A_N' and A_N^0 are larger for CH₃-PhNO₂⁻⁻ than for PhNO₂⁻⁻ in both solvents, Table I. It proved to be impossible to obtain the thermal dependence of K_A over a sufficient temperature range to obtain enthalpy and entropy changes for reaction 3 due to line broadening from electron exchange in these low-viscosity solvents.

From Table I it is clear that the degree of ion association is greater in methylamine than it is in ammonia. This is best explained in terms of the facts that there is one less proton available to hydrogen bond with the anion radical in methylamine and methylamine has a lower dielectric constant (17.9 as opposed to 24.8 for NH₃ at -75 °C).⁸ The quantitative effect of the methyl group upon K_A appears to be the same whether the methyl group is placed in the para position of the nitrobenzene or on the solvent, Table I.

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Figure 1. ESR spectra of CH_3 -PhNO₂⁻⁻ in methylamine at -75 °C. The upper and lower spectra were recorded from the same anion radical solution. However, the Na⁺ concentration is 0.0019 M in the solution yielding the upper spectrum, while it is 0.031 M in the solution yielding the lower spectrum. Note the obvious line-width alternation in the upper spectrum due to the rapid formation and dissociation of ion pairs. This is absent in the lower spectrum due to the fact that only the ion-associated anion radical is present.

When mixtures of equal molar amounts of CH_3 -PhNO₂ and PhNO₂ are reduced by very deficient amounts of sodium metal in either NH₃ or CH₃-NH₂, the resulting ESR spectra show the presence of the nitrobenzene anion radical only. However, when a 20:1 molar ratio of CH₃-PhNO₂ to PhNO₂ is reduced in either NH₃ or methylamine in the presence of 0.10 M NaI, the ESR spectra for the two ion pairs (PhNO₂^{•-},Na⁺ and CH₃-PhNO₂^{•-},Na⁺) can be observed simultaneously (Figure 3). Computer simulations of the ESR spectra generated from the reduction of mixtures with concentration ratios varying from 18:1 to 22:1 show that the equilibrium constant for reaction 7 is 0.032 \pm 0.001 in liquid ammonia.

$$\frac{PhNO_{2}^{\bullet-}, Na^{+}(soln) + CH_{3} - PhNO_{2}(soln) \Rightarrow}{PhNO_{2}(soln) + CH_{3} - PhNO_{2}^{\bullet-}, Na^{+}(soln) (7)}$$

The free energy of reaction 7 can be used as shown in Scheme I to obtain the free energy of electron transfer from the free solvated nitrobenzene anion radical to p-methylnitrobenzene to yield the free solvated anion radical of CH₃-PhNO₂ and PhNO₂, reaction 8. From Table II it is clear that the free energies of

$$PhNO_{2}^{\bullet\bullet}(soln) + CH_{3} - PhNO_{2}(soln) \rightleftharpoons PhNO_{2}(soln) + CH_{3} - PhNO_{2}^{\bullet\bullet}(soln) (8)$$

electron transfer for the free ions (reaction 8) are slightly more positive than those for the ion pairs (reaction 7). This is the case

in both of the solvent systems. This is, of course, due to the more excenergetic association of the CH_3 -PhNO₂^{•-} with the cation. SCHEME I

PhNO₂^{•-},Na⁺ + CH₃-PhNO₂ →
PhNO₂ + CH₃-PhNO₂^{•-},Na⁺
$$\Delta G_7^\circ$$

PhNO₂^{•-} + Na⁺ → PhNO₂^{•-},Na⁺ ΔG_3°
CH₃-PhNO₂^{•-},Na⁺ → CH₃-PhNO₂^{•-} + Na⁺ ΔG_4°
PhNO₂^{•-} + CH₃-PhNO₂ → PhNO₂ + CH₃-PhNO₂^{•-}
 $\Delta G^\circ = \Delta G_7^\circ + \Delta G_3^\circ + \Delta G_4^\circ$

The free energies of electron transfer in the gas phase (reaction 4) were obtained by monitoring the relative concentrations of the two anion radicals trapped for several seconds in an ion cyclotron resonance cell.⁴ The standard deviation in the free energy change was not reported, but we can assume that it is about 0.1 kcal/mol from the fact that two significant figures are reported (ΔG° in the gas phase is 1.4 kcal/mol at 380 K). The value for K_{trans} in the gas phase at -75 °C is 0.029 based upon this free energy. After five independent measurements of the equilibrium constant for reaction 8 (K_{trans}), we find that our value of 0.0271 ± 0.0035 at -75 °C is well within experimental error of the value reported for the electron transfer in the gas phase (reaction 4), Table II. The large difference in the free energy of electron transfer from the benzene anion radical to methylbenzene that one observes upon

TABLE II: Thermodynamic Parameters for Electron Transfer from the Nitrobenzene Anion Radical to p-Methylnitrobenzene at -75 °C

solvent	state	reaction	K _{trans}	ΔG° , kcal/mol	ref	
gas phase	free ions	4	0.029	$+1.40 \pm 0.10^{a}$	4	
ammonia	free ions	8	0.0271 ± 0.0035	$+1.42 \pm 0.05$	this work	
ammonia	ion pairs	7	0.0322 ± 0.0010	$+1.35 \pm 0.02$	this work	
CH ₃ NH ₂	free ions	8	0.035 ± 0.016^{b}	$+1.32 \pm 0.20$	this work	
CH ₃ NH ₂	ion pairs	7	0.041 ± 0.014	$+1.26 \pm 0.13$	this work	

^a The experimental error taken from ref 4 is estimated from the significant figures reported in the measurement of ΔG° . ^b The experimental error (standard deviation) in the equilibrium constants and consequently the free energy changes are much larger for the systems in methylamine. This is due to the fact that the ESR line widths are 4-5 times larger in this solvent than in ammonia.



Figure 2. Plot of $1/(A_N' - A_N)$ in G^{-1} vs the molar concentration of Na⁺ for the anion radical of nitrobenzene in liquid methylamine at -75 °C. The intercept and slope of this line yields the ion association constant. The dotted line results from plotting the activities as opposed to the concentrations on the x axis. Activities should not be used in these plots.

going from the gas phase to a solution media, reactions 2 and 1 respectively, is not observed for the case of the electron transfer from the nitrobenzene anion radical to methylnitrobenzene, reactions 4 and 8, respectively. This may be due to the fact that, in the case of the toluene anion radical, the methyl group is only one carbon removed from the positions of high charge density (the ortho carbons) in the anion radical. This allows the methyl group to sterically hinder the approach of solvent to the anion. This steric inhibition of solvation is not observed in the *p*-methylnitrobenzene anion radical, since the majority of the charge density is located out on the nitro group, which is located far enough from the methyl group to be solvated without hindrance.

The presence of the methyl group on the nitrobenzene anion radical decreases the free energy of ion association, which has the effect of decreasing the free energy of electron transfer from the unsubstituted anion radical to the methyl-substituted system. This same ion association effect must be present in the toluene-benzene system. Yet, the steric inhibition of solvation caused by the methyl group on the anion radical of toluene is enough to obviate the relatively small effects of ion association.

Experimental Section

The reductions of PhNO₂ and CH₃-PhNO₂ in liquid ammonia and in liquid methylamine were carried out on a freshly distilled metal mirror in an all-glass apparatus at -80 °C under high vacuum as previously described.³ Bone dry methylamine and ammonia were distilled from potassium metal directly into the apparatus through the vacuum line.

The ESR spectra were recorded on a Bruker (IBM) ER 200 ESR spectrometer equipped with a Varian temperature controller.

Even though there are techniques for estimating some activity coefficients for solvent-separated ion pairs,⁹ there is no reliable basis for estimating them under the conditions of these experiments. Thus, activity coefficients have been omitted. A number of similar studies were carried out in a variety of solvents including dimethoxyethane,^{10a} dimethyl sulfoxide,^{10b} hexamethyl-





Figure 3. ESR spectrum (recorded at -75 °C) of a 20.1:1 mole ratio mixture of *p*-methylnitrobenzene to nitrobenze in liquid ammonia containing 0.10 M NaI to ensure that both anion radicals are ion associated. The reduction was carried out with a very deficient amount of sodium metal. The first three lines (marked with arrows) represent the first 1:2:1 triplet from the meta protons on CH₃-PhNO₂⁻⁻,Na⁺. The distance between the two lines marked with the horizontal arrow represents the nitrogen coupling constant for the nitrobenzene anion radical ion pair. The lower spectrum is a computer simulation generated by assuming a mole ratio of anion radicals ([PhNO₂⁻⁻,Na⁺]/[CH₃-PhNO₂⁻⁻,Na⁺]) of 1.55. The spectral centers are marked with arrows, and only the low-field portions of the spectra are shown.

phosphoramide,^{10c} and tetrahydrofuran,^{10d} and in liquid ammonia itself.^{10e} In these cases and all others (to our knowledge) concentrations, not activities, have been used to obtain the thermodynamic parameters for ion association.

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Registry No. PhNO₂, 98-95-3; PhNO₂⁻⁻, 12169-65-2; PhNO₂⁻⁻, Na⁺, 34480-34-7; *p*-MePhNO₂, 99-99-0; CH₃-PhNO₂⁻⁻, 34509-96-1; CH₃-PhNO₂⁻⁻, Na⁺, 103346-56-1.

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