Solvation Enthalpies of Organic Anion Radicals

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Received April 2, 1979

Abstract: An experimental technique is described for the calorimetric determination of anion radical solvation enthalpies. The method involves the calorimetric measurement of the heat of reaction of an anion radical solvated in tetrahydrofuran (THF) or hexamethylphosphoramide (HMPA) with deoxygenated water. This measured enthalpy can then be used in a thermochemical cycle to obtain the solvation enthalpy of the gas-phase anion and sodium cation. Surprisingly, the enthalpies of solvation in THF (ΔH° for $\pi^-\cdot_g + Na^+_g \rightarrow \pi^-\cdot,Na^+_{THF}$) are very close to -180 kcal/mol for a variety of hydrocarbon anion radicals ($\pi^-\cdot$) including those where π = naphthalene, anthracene, tetracene, phenanthrene, pyrene, and perylene. This is explained in terms of the fact that the anion radicals are always ion associated with the sodium cation in THF. However, in HMPA there is no ion pairing. Thus, in this solvent the single ion heat of solvation of the anthracene anion radical could be obtained (ΔH° for $\pi^-\cdot_g \rightarrow \pi^-\cdot_{HMPA}$). This enthalpy turns out to be -72 kcal/mol. This is much more exothermic than was expected and represents about 86% of that for the single ion heat of solvation of Na^+ in HMPA.

Introduction

The capture of a free gas-phase electron by a gaseous acceptor (A) to yield the solvated anion radical ($A^-\cdot$) is much more exothermic than the same reaction to form the gas-phase anion radical, the difference being the enthalpy of solvation (ΔH°_{solv}) of the anion radical. The commanding role of anion solvation in controlling the thermodynamic stabilities of organic anions was demonstrated by the classic observations of Brauman and Blair.[1] Despite the obvious importance of solvation enthalpies in controlling the stabilities and chemistry of organic anion radicals, no experimental solvation enthalpies for these species have been reported except for a single attempt to correlate the threshold of photorejection of an electron from a rhodium electrode into hydrocarbon acceptors with their solvation energies.[2] However, Hush and Blackledge[3] carried out a series of MO calculations which were used in conjunction with Born-type interaction terms to estimate the solvation heats for several anion radicals in tetrahydrofuran (THF). Their prediction for the solvation energy of the anthracene anion radical in THF is -18 kcal/mol. Here, we wish to report an experimental determination of the solvation enthalpies of a series of polyacene anion radicals in THF and in hexamethylphosphoramide (HMPA). Further, we will show that the estimations of Hush and Blackledge are very high.

No estimations for the solvation enthalpies of anion radicals in HMPA have been made. However, HMPA is known to be an excellent solvent for anion radical formation with alkali metals owing to its strong ability to solvate cations.[4] On the other hand, HMPA is thought to be a particularly poor solvent for anions, since the anion is sterically prohibited from close approach to the electropositive phosphorus owing to the methyl groups.[5] This, it has been said, leaves the anion practically unsolvated in HMPA.[5] From this, it is expected that the single ion heat of solvation of anion radicals in HMPA would be close to zero. To test these predictions, we have measured the experimental heat of solvation of the anthracene anion radical in HMPA.

Experimental Section

A small quantity of sodium or potassium metal was placed into bulb C of the apparatus shown in Figure 1. After the bulb was sealed at point E, bulb B was charged with an excess of the aromatic hydrocarbon. The entire system was then evacuated and the alkali metal distilled to form a mirror in bulb A. After bulb C was sealed off at point F, the solvent (THF or HMPA) was distilled into B through stopcock 1. The hydrocarbon solution was then allowed to react with the alkali metal mirror until complete dissolution of the alkali metal. The anion radical solution was finally passed through the glass frit into bulb D, which was subsequently sealed from the apparatus. The thin-walled glass bulbs were placed into a modified cell of a Parr solution calorimeter as described previously.[6] The entire cell plus bulb was immersed in 100 mL of deoxygenated water in the calorimeter. After thermal stabilization, the bulb was broken, allowing its contents to react with the water. The change in the temperature (ΔT) in the calorimeter due to the reaction of the salt with water and the heat of solution of the solvent in water were measured.

After the reaction, the contents of the calorimeter was titrated with standardized HCl to obtain the amount of anion radical salt in the bulb. The broken glass was then collected and weighed, and the amount of solvent in the bulb was taken as the difference in the weight of the intact bulb plus its contents and the sum of the weights of the salt, neutral hydrocarbon, and glass.

The anion radical solutions were fired immediately after their preparation. NMR analysis of the calorimeter contents showed only the dihydro compounds and the unchanged hydrocarbons after the firings. Although the products and the mechanisms of reaction for the water protonation of the anion radicals studied here have been the subject of many reports, the enthalpy of hydrogenation of perylene (PE) and the structure of the dihydroperylene produced via the reaction of the PE anion radical with water are still unknown.

It should be noted that both THF and HMPA are completely miscible with water, but neither the dihydropolyacenes nor the polyacenes are soluble in the water-THF or water-HMPA mixtures left in the calorimeter after the reaction takes place.

The hydrocarbons were purchased from Aldrich Chemical Co. and sublimed before use except for tetracene, which was used without further purification. All of the anion radical solutions did exhibit ESR signals consistent with the particular polyacene anion radical under study.

The THF was distilled from the benzophenone ketyl and stored under vacuum over NaK_2. It was then distilled directly into the apparatus shown in Figure 1. The HMPA was distilled from calcium hydride and stored over molecular sieves 4A. It was then distilled from potassium metal directly into the evacuated apparatus for anion radical preparation.

Results and Discussion

Since the heat evolved in the calorimeter is not only due to the reaction of the anion radical with water but also due to the aquation of the solvent, it is necessary to first determine the amount of heat evolved from this latter process. Thus, samples of pure THF and HMPA were placed into the evacuated glass bulbs, which were crushed under 100 mL of deoxygenated water in the calorimeter. Plots of the amount of solvent in the glass bulbs vs. the temperature change in the calorimeter were found to be linear, Figure 2.

From Figure 2 the temperature change in the calorimeter due to the aquation of the solvent for any anion radical solution can be determined. Subtracting this from the total observed temperature change in the calorimeter yields that due to the reaction of the anion radical with the water. The reactions of

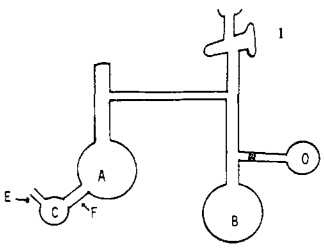

Figure 1. Apparatus used for the formation of the anion radical solutions. The solution is transferred into bulb D, which is then sealed from the apparatus and placed into the calorimeter cell.

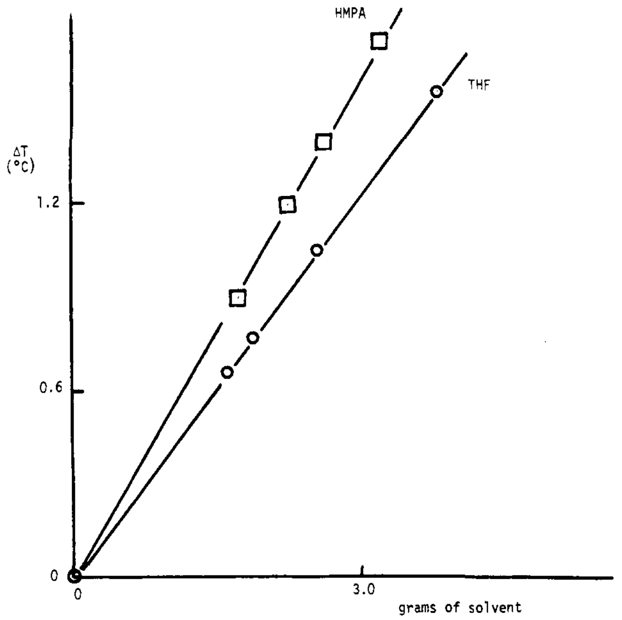

Figure 2. Plots of the change in temperature of the calorimeter vs. the grams of HMPA (□) or THF (○). The slopes of the lines are 0.528 and 0.407 deg/g for HMPA and THF, respectively.

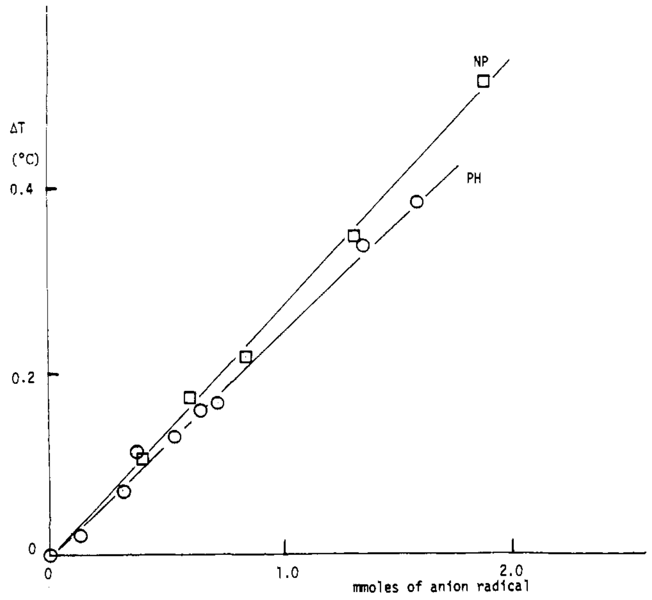

Figure 3. Plots of the change in temperature of the calorimeter vs. the millimoles of anion radical sealed into the evacuated glass bulbs. The upper line contains the data points for the naphthalene anion radical (□), and the lower line contains those for the phenanthrene anion radical (○). The anion radical solvent is THF.

Table I. Enthalpies of Reaction of THF Solvated Anion Radicals with Water

reaction (eq)	anion radical	$\Delta H°$, kcal/mol	amount of anion radical sealed into the glass bulbs, mmol
(1)	$TE^{-}\cdot,NA^{+}$	−17.6 ± 0.8[a]	0.1-0.5
(2)	$AN^{-}\cdot,Na^{+}$	−28.9 ± 1.4	0.1-0.8
(3)	$NP^{-}\cdot,Na^{+}$	−31.4 ± 0.9	0.2-1.8
(4)	$PH^{-}\cdot,Na^{+}$	−28.9 ± 0.8	0.1-1.6
(5)	$PY^{-}\cdot,Na^{+}$	−16.2 ± 0.4	0.2-0.8
(6)	$PE^{-}\cdot,Na^{+}$	−22.7 ± 2.0	0.1-1.2

[a] The errors are standard deviations, which were determined by propagating the standard deviation in the lines.

the THF solvated anion radicals of anthracene (AN),[8] naphthalene (NP),[9] tetracene (TE),[10] pyrene (PY),[11] perylene (PE),[12] and phenanthrene (PH)[13] with water take place with well-established stoichiometries that are depicted in eq 1-6. It must be remembered that the anion radicals are ion paired with the sodium cation in THF.[14]

Plots of the change in the temperature of the calorimeter, minus that due to the solvent (ΔT due to the anion radical), vs. the millimoles of anion radical in the glass bulbs are linear, i.e., Figure 3. The slopes of the lines are proportional to the enthalpies of the reactions shown in eq 1-6, Table I.

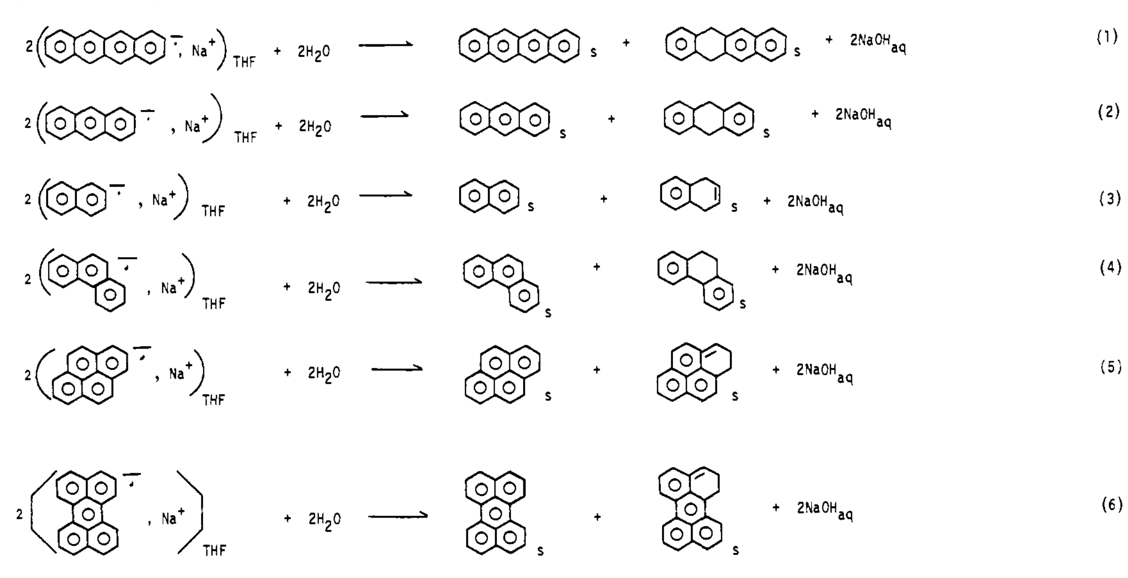

Table II. Enthalpies of Reaction

reaction		$\Delta H°$, kcal/mol, for π =						
		NP	AN	TE	PH	PY	PE	ref
$\pi H_{2_s} + \pi_s +$ $2NaOH_{aq}$	$\rightarrow 2(\pi^{-}\cdot,Na^{+}) +$ $2H_2O_{liq}$	62.8	57.8	35.2	57.8	32.4	45.4	
$2Na^0{}_s + 2H_2O_{liq}$	$\rightarrow 2NaOH_{aq} + H_{2_g}$	−88.2	−88.2	−88.2	−88.2	−88.2	−88.2	15
$2Na^0{}_g$	$\rightarrow 2Na^0{}_s$	−51.8	−51.8	−51.8	−51.8	−51.8	−51.8	16
$2Na^+{}_g + 2e^-{}_g$	$\rightarrow 2Na^0{}_g$	−236.8	−236.8	−236.8	−236.8	−236.8	−236.8	17
$\pi_s + H_{2_g}$	$\rightarrow \pi H_{2_s}$	−3.2	−17	−12.5	−7.7	−2.7	−15[a]	18[c]
$2\pi_g$	$\rightarrow 2\pi_s$	−34.8	−46.8	−59.6	−43.4	−45.0	−60.0	19
$2\pi^-\cdot_g$	$\rightarrow 2\pi_g + 2e^-{}_g$	7.0	25.5	52.9	14.2	26.6	48.8	20
$\pi^-\cdot_g + Na^+{}_g$	$\rightarrow (\pi^-\cdot,Na^+)$	−172.5[b]	−178.7	−180.4	−178.0	−182.8	−178.8	

[a] The enthalpy of hydrogenation of PE has not been reported. This number is just an estimation based upon the other hydrocarbons. [b] By propagating the errors in the various measurements, the final error is estimated to be ±4 kcal/mol. The hydrogenation reactions yielding these heats of hydrogenation give the same dihydropolyacene as do the anion radical-water reactions.

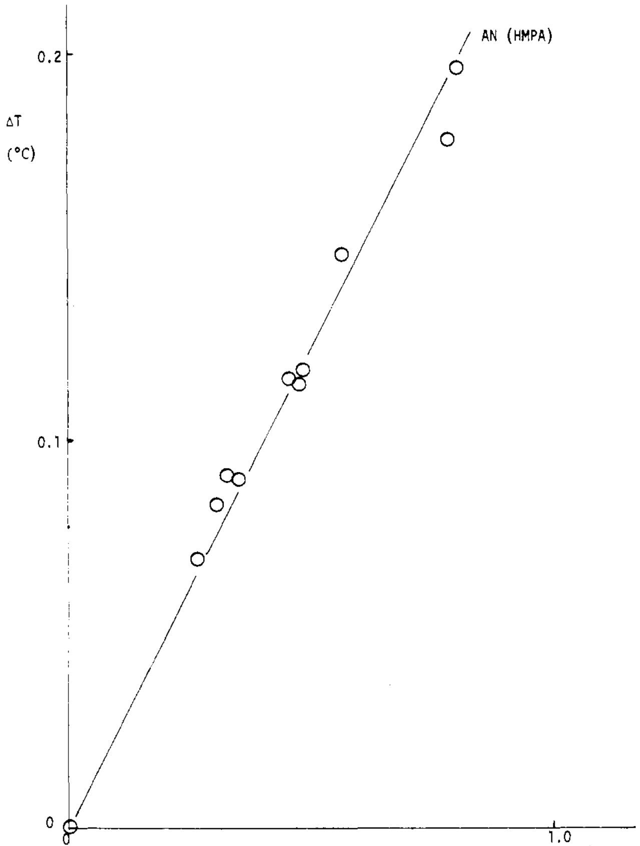

Figure 4. Plot of the change in temperature of the calorimeter vs. the millimoles of anthracene anion radical sealed into the evacuated glass bulbs. The anion radical solvent is HMPA.

Many effects must be considered in the interpretation of these enthalpies, but they do show the expected trend in the linear series (NP, AN, Te) of being more exothermic for the smaller anions. It is also interesting to note that the enthalpy of reaction of these anion radicals with water varies from about 40 to 90% of the enthalpy for the reaction of sodium metal with water. Thus, these solvated anion radicals react very exothermically with water.

Of much more significance are the solvation enthalpies of the anion radical systems, which are given by the enthalpy of the reaction shown in eq 7, where π represents the π-conjugated polyacene.

$$\pi^-\cdot_g + Na^+{}_g \rightleftarrows (\pi^-\cdot,Na^+)_{THF} \qquad (7)$$

The enthalpies of solvation can be calculated via a thermochemical cycle as shown in Table II.

The most striking feature of the data given in Table II is the fact that the enthalpies of solvation of the separated gas-phase ions to form the solvated ion pairs are within experimental error for all of the anion radicals studied. It was expected that the smaller systems would yield more exothermic enthalpies, as they should interact more strongly with the solvent. The data, however, can be explained in terms of the ion association. The smaller anion radicals form tighter ion pairs with the sodium cation owing to their more localized charge densities. These tighter ion pairs interact more weakly with the solvent owing to the smaller effective charge creating the ion-induced THF dipoles. The stronger solvent-ion interactions formed in the larger anion radical systems counterbalance their more endothermic ion association enthalpies.

Solutions of the anthracene anion radical in HMPA were also fired in the calorimeter using the same procedure. Again, the only hydrocarbons in the calorimeter after the reaction were anthracene and 9,10-dihydroanthracene. It must be remembered that in HMPA the anthracene anion radical is free from ion association from the sodium cation,[4,21] and the reaction is given by[22]

$$2AN^-\cdot + 2Na^+ + 2H_2O \rightarrow AN + ANH_2 + 2NaOH_{aq} \qquad (8)$$

A plot of the change in the temperature of the calorimeter due to the anion radical vs. the millimoles of anion radical in the evacuated glass bulbs is linear, Figure 4. The enthalpy taken from the slope of the line is −27.8 ± 0.5 kcal/mol.

If this enthalpy is combined with the heat of reaction of sodium with water, the heat of vaporization of sodium metal, the ionization potential of sodium, the heat of hydrogenation of anthracene, and the electron affinity of anthracene in a thermochemical cycle, the enthalpy for the reaction shown in eq 9 is found to be −179.8 ± 3 kcal/mol.

$$AN^-\cdot_g + Na^+{}_g \rightarrow AN^-\cdot_{HMPA} + Na^+{}_{HMPA} \qquad (9)$$

Since the ions are free from association with each other in HMPA and the single ion heat of solvation of the sodium cation has been measured in this solvent, the single ion heat of solvation of the anthracene anion radical can be obtained. Subtracting −108 kcal/mol (the single ion enthalpy of solvation of the sodium cation in HMPA)[23] from the enthalpy of the reaction depicted in eq 9 yields a value of −72 kcal/mol for the solvation enthalpy of $AN^-\cdot$ in HMPA:

$$AN^-\cdot_g \rightarrow AN^-\cdot_{HMPA} \quad \Delta H° = -72 \pm 6 \text{ kcal/mol} \qquad (10)$$

The single ion heat of solvation for the sodium cation used in this calculation is not absolutely valid, since it is ultimately based upon the extra thermodynamic assumption called the

Table III. Single Ion Heats of Solvation in HMPA and Heats of Solvation of Separated Ions in THF to Form Solvated Ions

substance	solvent	heat of solvation, kcal/mol	ref
Li^+	HMPA	−141	23
Na^+	HMPA	−108	23
K^+	HMPA	−93	23, 24
AN^-	HMPA	−72	this work
$Na^+ + AN^-$	THF	−186[a]	this work

[a] This is the heat of solvation of the gas-phase ion assuming that the heat of ion-pair dissociation in THF is about −7 kcal/mol.

TATB assumption.[24] With this assumption it is assumed that the enthalpy of solvation of Ph_4As^+ is the same as that of Ph_4B^-. Even though the validity of this assumption has been questioned, it is probably of use here where the effects are large.

In view of the fact that anion radicals are thought to remain practically unsolvated in HMPA,[4,5,23] this enthalpy is much more exothermic than was expected. The steric hindrance around the electropositive phosphorus center in HMPA does not prevent strong anion solvation. In fact, the heat of solvation of the anthracene anion radical in HMPA is about 86% of that for the sodium cation, Table III.

From this study, single ion heats of solvation of the cation and anthracene anion radical in THF are not possible to determine. This is the case, since $AN^-\cdot$ and the alkali metal cation are always associated (tightly ion paired) with each other in THF.[25] However, from the work of Hirota[25] and others it is clear that the ion association enthalpy for the Na^+ cation with $AN^-\cdot$ is no larger than 10 kcal/mol and is probably close to 7 kcal/mol. From this we conclude that the sum of the solvation enthalpies of Na^+ and $AN^-\cdot$ together must be about $-179 - 7 = -186$ kcal/mol. Thus the solvation enthalpies estimated via the calculations of Hush and Blackledge[3] are not nearly exothermic enough.

Other than our preliminary communication, this represents the first report of anion radical solvation enthalpies.[26]

Acknowledgment. We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

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Graph-Theoretical Formulation of London Diamagnetism

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Abstract: A graph-theoretical method is presented for estimating the London diamagnetism, i.e., the diamagnetic susceptibility arising from a cyclic conjugated system of an organic compound. This method is based on the generalized version of Sachs' graph-theoretical theorem, and enables one to save much labor which would otherwise be needed. Moreover, the present approach enables one to analyze London diamagnetism to extract information about the susceptibility contributions of individual π rings in a polycyclic conjugated compound. An illustrative application to biphenylene is described in conjunction with its aromaticity.

Introduction

The diamagnetic anisotropy of a cyclic conjugated compound arises primarily from ring currents induced in its π-electron system. This picture, first proposed by Pauling,[1] was formulated in quantum-mechanical terms by London in 1937.[2] Diamagnetism due to ring currents is then termed London diamagnetism. His molecular orbital (MO) method for conjugated hydrocarbons placed in a uniform magnetic field was an extension of the simple Hückel MO model.[3] The diamagnetic susceptibility due to ring currents is hereafter called the diamagnetic susceptibility of a conjugated system. It is an important quantity because of its close correlation with aromaticity.[4,5]

0002-7863/79/1501-5913$01.00/0