Calorimetric Disproportionation Enthalpies

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Abstract: An experimental technique is described for the calorimetric determination of enthalpies of disproportionation of anion radicals. The technique involves the calorimetric determination of the heats of reaction of the anion radical and dianion with water in a solution calorimeter. Thus, the thermodynamic stabilities of the anion and dianion are also obtained. The enthalpies of disproportionation of the anthracene and tetracene anion radicals were found to be +7.1 and +27.7 kcal/mol, respectively. The more endothermic disproportionation of the tetracene anion is explained in terms of its greater thermodynamic stability than the anthracene anion radical and the fact that the anthracene dianion forms tighter ion pairs with the sodium cation than does the tetracene dianion. This ion association effect results in the two dianions having the same thermodynamic stability relative to their respective neutral molecules

Introduction

Hydrocarbon dianions are unknown in the gas phase, and only one uncontested report of an organic dianion has appeared.[1] However, in ethereal solvents dianion solvation and ion association effects allow anion radicals ($\pi^{-}\cdot$) to disproportionate:

$$2\pi^{-}\cdot,\ M^{+} \rightleftarrows M^{+},\ \pi^{2-},\ M^{+} + \pi \qquad (1)$$

Thus, much insight into the solvation and ion association of anion radicals and dianions can be gained through accurate knowledge of the thermodynamic parameters controlling disproportionation.[2]

Several experimental techniques have been developed for the determination of the enthalpies of anion radical disproportionation.[3,4] Even the best and most recent of these techniques[5] involves the use of $\ln K_{eq}$ vs. $1/T$ plots. In all of these cases either the assumption that $\Delta H°$ is not a function of temperature ($\Delta C_p = 0$) is made, or actual curvature of the van't Hoff plots is observed.[5] Thus, these techniques may have an inherent error, as wide temperature ranges are needed to obtain meaningful data. Here, we would like to report a simple calorimetric technique, requiring only a solution calorimeter, for the determination of disproportionation enthalpies along with a comparison of the enthalpy of disproportionation for the tetracene anion radical measured calorimetrically with that determined using the most recently reported method.

Results and Discussion

Tetrahydrofuran (THF) solutions of the anthracene and tetracene anion radicals were placed into thin-walled glass bulbs. These bulbs were broken under 100 mL of deoxygenated water in a Parr solution calorimeter, and the change in the temperature of the calorimeter due to the heat of reaction of the anion radical with the water and the heat of solution of the THF in water was recorded. The heat of aquation of the THF can be subtracted out after carrying out the measurement with pure THF in the glass bulbs. After subtraction of the heat due to the THF–water interaction, the remaining heat is due to the reaction depicted in eq 2, where the sole contents of the calorimeter are anthracene (π = A) and 9,10-dihydroanthracene ($\pi H_2 = AH_2$) or tetracene (π = T) and dihydrotetracene ($\pi H_2 = TH_2$).

$$2\pi^{-}\cdot,\ Na^{+} + 2H_2O \rightleftarrows \pi + \pi H_2 + 2NaOH_{aq} \qquad (2)$$

A simple plot of the change in temperature of the calorimeter, minus that due to the THF, vs. the millimoles of anion radical in the glass bulbs was found to be linear, and the slopes of the lines are proportional to the enthalpy of the reaction shown in eq 2 (Figure 1). Similar plots for the reactions of the dianions with water are also linear, and the slopes of these lines are proportional to the enthalpies of the reactions depicted in the equation

$$\pi^{2-},\ 2Na^{+} + 2H_2O \rightleftarrows \pi H_2 + 2NaOH_{aq} \qquad (3)$$

The dianion solutions were prepared via exhaustive reduction of the neutral molecule with excess sodium metal, and the only organic product found in the calorimeter was the dihydro compound.

The enthalpies of reaction of the dianions and anion radicals with water are listed in Table I along with our measurement of the enthalpy of reaction of lithium metal with water. The value we obtained using this simple technique for the reaction of Li^0 with water is in excellent agreement with the literature value.[6]

By simply subtracting the enthalpies of reaction with water for the dianion and anion radical, the enthalpy of disproportionation ($\Delta H°_{dis}$) can be obtained (Table II). The enthalpies of reaction with water for A^{2-}, $2Na^{+}$ and T^{2-}, $2Na^{+}$ are within experimental error, and only one line is drawn for the dianions in Figure 1.

The enthalpy of disproportionation of the anthracene anion radical has never been determined by any other experimental technique. However, that for the tetracene anion radical in THF has recently been reported by Szwarc and co-workers[7] where their new potentiometric technique was utilized.[3] Their enthalpy of 27 kcal/mol is in excellent agreement with our calorimetric results.

From Table II the enthalpy of disproportionation of $T^{-}\cdot$ is more than three times as endothermic as that of $A^{-}\cdot$. Considering electron–electron repulsion energies only, this is a very surprising result. However, Szwarc and co-workers[8] have shown that the tighter ion association between the dianion and the two cations for the smaller dianion systems more than overcomes the increased electron–electron repulsion as evidenced by the decrease in the free energy of disproportionation with the decreasing size of the hydrocarbon dianion. This effect has been explained in terms of the fact that the coulombic energy between the anions and cations in π^{2-}, $2M^{+}$ can be larger than twice that in two $\pi^{-}\cdot$, M^{+} ion pairs.[8]

From the above arguments it may seem surprising that, relative to the neutral molecules, the thermodynamic stability of the two dianions is about the same (Table I, Figure 1). It is the relative stability of the anion radicals that results in the more endothermic disproportionation of the tetracene anion radical ($T^{-}\cdot$). The two tetracene anion radicals are more stable than the two anthracene anion radicals by about 22 kcal/mol (Table I).[9] This more than overcomes the 20.6 kcal/mol difference in the enthalpies of disproportionation. Thus, the increased coulombic interaction in the smaller dianion (A^{2-}) is

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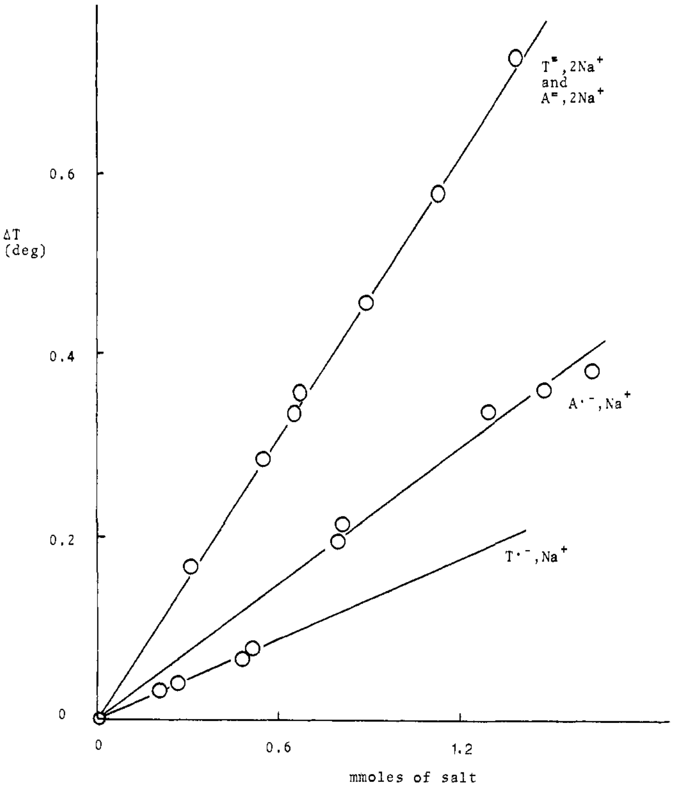

Figure 1. Plots of the change in the temperature of the calorimeter vs. the millimoles of salt sealed in the glass bulbs. The upper line contains the data points for both the tetracene (O) and anthracene (O) dianions, as both of these solvated dianions yield the same heat of reaction with water. The lower lines represent the reaction of the anion radicals with water. The millimoles of salt in the sealed glass bulbs was obtained after the heat measurement by titrating the calorimeter contents with HCl.

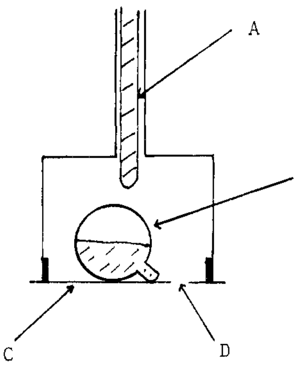

Figure 2. Calorimetric cell used for the determination of the heats of reaction of the dianion and anion radical salts with water. (A) represents the push rod which is used to break the glass bulb. It extends outside of the calorimeter. (B) represents the glass bulb containing the anion radical or dianion solution. (C) represents the Teflon bottom of the cell, which separates from the cell when struck by the push rod. (D) represents a small hole in the bottom of the cell to allow water to enter the cell before the reaction is initiated.

Table I. Measured Enthalpies of Reaction with Water for the Following Substances

substance	$\Delta H°$, kcal/mol
Li^0	-53.5 ± 0.5[a]
$(A^{-}\cdot, Na^{+})_{THF}$	-28.9 ± 1.3[b]
$(A^{2-}, 2Na^{+})_{THF}$	-64.9 ± 1.3
$(T^{-}\cdot, Na^{+})_{THF}$	-17.6 ± 0.7
$(T^{2-}, 2Na^{+})_{THF}$	-62.9 ± 1.4

[a] The literature value for this enthalpy is −53.1 kcal/mol.[6] [b] The errors are obtained from a propagation of the standard deviations of the slopes.

Table II. Enthalpies of Reaction

reaction	$\Delta H°$, kcal/mol, for π = T	$\Delta H°$, kcal/mol, for π = A
$2(\pi^{-}\cdot, Na^{+})_{THF} + 2H_2O \rightarrow \pi + \pi H_2 + 2NaOH_{aq}$	-35.2	-57.8
$\pi H_2 + 2NaOH_{aq} \rightarrow (\pi^{2-}, 2Na^{+})_{THF} + 2H_2O$	$+62.9$	$+64.9$
$2(\pi^{-}\cdot, Na^{+})_{THF} \rightarrow (\pi^{2-}, 2Na^{+})_{THF} + \pi$	$+27.7$	$+7.1$

enough to just maintain its thermodynamic stability equal to that of T^{2-} and overcome the increased electron–electron repulsion energy. It is the greater thermodynamic stability of the tetracene anion radical added to the coulombic effect in the dianions that results in $T^{-}\cdot$ having the more endothermic disproportionation.

The experimental technique described here not only allows a calorimetric determination of disproportionation enthalpies but can also be utilized to investigate the individual thermodynamic stabilities of the ions involved. The present work does not indicate that there are large errors in the van't Hoff plots previously used to obtain enthalpies of disproportionation; in fact, the results obtained here for the tetracene anion radical are well within experimental error with those reported by Szwarc and co-workers.[7]

Experimental Section

The dianion salts were prepared by exhaustive reduction on a freshly distilled sodium metal mirror in THF, and the anion radical solutions were prepared via reduction with a deficient amount of sodium metal. The solutions were then passed through a glass frit and sealed into thin glass bulbs. The glass bulbs were placed into a modified cell of a Parr solution calorimeter as shown in Figure 2. The entire cell plus bulb was immersed in 100 mL of deoxygenated water in the calorimeter. After thermal stabilization, the push rod was struck, breaking the bulb and releasing the Teflon bottom of the cell. The change in temperature (ΔT) in the calorimeter due to the reaction of the salt with water and the heat of solution of the THF in water were measured. No other processes need to be considered, such as the precipitation of the hydrocarbons from solution. This is the case since the enthalpies measured and reported in Table I are for the reactions depicted in eq 2 and 3 where πH_2 and π represent the solid hydrocarbons.

After the reaction, the contents of the calorimeter were titrated with standardized HCl to obtain the amount of salt in the bulb. The broken glass was then collected and weighed, and the amount of THF 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 and glass.

The anion radical and dianion solutions were fired immediately after their preparation. NMR analysis of the calorimeter contents showed only the dihydro compounds for the dianion firings and a mixture of the dihydro compounds and the unchanged hydrocarbons for the anion radical firings. A sample of the anthracene dianion was fired in D_2O, and the NMR analysis showed that 9,10-dideuterioanthracene is the only organic product. The NMR integrations are only accurate to about 3%; thus some of the dianion may be protonated by the solvent prior to the calorimetric analysis. This possible error must, however, be smaller than the experimental error reported in Table I.[10]

The anthracene was recrystallized from methanol to a constant melting point, and the tetracene (Aldrich Chemical Co.) was used without further purification. Later experiments with unpurified anthracene gave identical results. The THF was distilled from sodium benzophenone ketyl and stored over NaK_2 under vacuum. It was then distilled directly into the reaction vessel.

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(9) The thermodynamic stabilities mentioned in the text are relative to the respective neutral dihydromolecules. The enthalpies of hydrogenation are about the same for anthracene and tetracene; therefore $T^{-}\cdot$, Na^{+} is 28.9–17.6 kcal/mol more stable relative to T than $A^{-}\cdot$, Na^{+} is relative to A (Table I).
(10) Even AH^{-} must yield some heat upon reaction with water. Thus, the error caused by any protonation of A^{2-} with THF must be much smaller than 3%.

Carbonium Ions in Solution. 9. The Relationship between Carbocations in Superacid and Solvolysis Transition States

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Abstract: The heats of ionization, ΔH_i, of various alkyl chlorides to stable carbocations in SbF_5–solvent mixtures correlate remarkably well with the free energies of activation of limiting solvolysis of the same chlorides in ethanol. The slope of the correlation line, 0.89, suggests that "carbocation character" is very largely developed in solvolysis transition states. Simple secondary chlorides, i.e., 2-propyl, cyclopentyl, and 2-butyl, subject to nucleophilic solvent assistance, do not exhibit limiting ("pure" S_N1) behavior on ethanolysis. Uncorrected solvolysis data for these substrates do not correlate with ΔH_i (SbF_5–SO_2ClF), but the same data, corrected for the amount of nucleophilic solvent assistance, correlate well. In contrast, ΔH_i values for these same substrates in the SbF_5–CH_2Cl_2 mixture correlate better with uncorrected, rather than with corrected, solvolysis free energies, indicating that the less stable carbocations are subject to specific solvation effects. All these results confirm the long-held presumption that limiting solvolysis rates are reliable measures of carbocation stabilities. Exceptions are noted. For example, stereoisomeric 2-*exo*- and 2-*endo*-norbornyl substrates (secondary as well as tertiary) both give the same carbocation on ionization but their solvolysis rates differ by 10^2–10^3. Only the exo solvolytic data correlate with ΔH_i, showing that the exo but not the endo transition states are related closely to the resulting carbocations. ΔH_i for 2-*exo*-norbornyl chloride among all the compounds reported here displays a unique sensitivity to solvent variation relative to the other cations. Although this differential solvation effect may doubtless be interpreted in various ways, we note that it conforms with theoretical prediction that σ bridged ions should show different responses to solvation than their classical counterparts. By means of our correlations of ΔH_i vs. limiting solvolysis rates and a previous correlation with gas-phase heats of ionization estimates are made of the contribution of covalent bonding from more nucleophilic solvents (ethanol, acetic acid, and even trifluoroacetic acid) in the solvolysis transition states of methyl and ethyl tosylates. In methyl tosylate ethanolysis nucleophilic assistance by solvent reduces the free energy of activation from an estimated 58 kcal/mol for the hypothetical limiting process to the observed value of 24.5 kcal/mol.

Introduction

For over half a century organic chemists have gained powerful insight into the mechanisms of polar reactions in solution through the concept of carbonium-ion-like intermediates. The daring suggestions of Meerwein and Whitmore, especially as developed by the Ingold–Hughes school, Bartlett, and Winstein, provided a rationale both for interpreting and predicting the response of an enormous range of reactions to change in structure and conditions.[2] Solvolysis reactions, in which an amphiprotic solvent serves also as the attacking nucleophile, have been the proving ground for developing the carbonium ion theory of substitution displacement reactions, primarily through structure–rate studies. A major intellectual tool for inferring the relative stabilities of unstable carbonium ions, or ion pairs, has been the postulate[3–5] that their structures and energies are well modeled by solvolysis transition states. Thus, it has often been an article of faith that S_N1 solvolysis rates for a series of similar compounds under similar conditions generally reflect directly the stabilities of their carbocationoid intermediates. However, we know now that the reactivity–selectivity principle is not universally applicable to organic reaction rates; the reasons for failure are not clearly understood.[6] Thus, it is not a foregone conclusion that there should be a close relationship between a solvolysis transition state and a carbocation intermediate. This article deals directly with this problem.

Recently one of us with his associates[7] succeeded in demonstrating that solvolysis data involving an enormous range of substrates and solvents could be correlated in terms of a single mechanistic continuum. In this view the principal difference between S_N1 and S_N2 solvolysis is the degree of nucleophilic assistance from the solvent.[8] A treatment was proposed for correcting the rates of nucleophilically assisted solvolysis to reveal the free energies of activation which would be expected for limiting S_N1 behavior.

Concurrently, two of us developed rigorously authenticated methods for measuring the heats of ionization of many typical aliphatic and alicyclic halides to stable carbocations in superacidic media at low temperatures under conditions developed by Olah.[9] The method has been described[10a] as have the effects of solvent and ionic structure[10b] on thermodynamic stability. We now compare the relationship between the energies of forming carbocations as measured calorimetrically under stable ion conditions with those inferred from solvolysis

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