insufficient for distinguishing between these and other alternatives for the mechanism of electron transfer.

Entrapping PtO_2 in the interior of DHP vesicles of system I resulted in the prompt reoxidation of $MV^{+}\cdot$ (Figure 7). The rate constant for this process at ca. 10^{-6} M PtO_2 concentration, $k_7 = 7.7 \times 10^5$ s^{-1}, is an order of magnitude greater than that reported previously for using 1.25×10^{-3} M poly(vinyl alcohol) stabilized colloidal platinum in aqueous solutions.[35] Apparently, very small amounts of PtO_2, localized in the inner pools of DHP vesicles, provide superior catalytic powers and obviate the need for polymer stabilization[35] in order to observe the dynamics of platinum mediated catalysis. Dispersed PtO_2 have large catalytic surfaces and act as microelectrodes.[53-55] Photolysis of PtO_2 carrying DHP vesicles of system I leads to the net consumption of only EDTA. Figure 9 shows the schematics of the hydrogen generating system.

An important feature of the present system is the extremely low concentration of sensitizer ($Ru(bpy)_3^{2+}$), acceptor (MV^{2+}), and catalysts (PtO_2) used. Comparable aqueous systems utilized several orders of magnitude higher concentrations of these components with much less efficiency.[30,33,46,56-60] Currently we are determining hydrogen and deuterium yields quantitatively under various experimental conditions and continue to exploit surfactant vesicles to mimic photosynthesis.

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Solid State Disproportionation Enthalpies

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Abstract: Using calorimetric techniques, we have measured the heats of reaction of several solid anion radical and dianion salts with water. These heats of reaction have been coupled in a thermochemical cycle to yield the first enthalpies of disproportionation for anion radicals in the solid phase. The enthalpies of disproportionation ($\Delta H°$ for $2Na^{+}A^{-}\cdot(s) \rightleftarrows Na^{+}_2A^{2-}(s) + A(s)$) range from −13.6 when A is pyrene to +8.8 kcal/mol when A represents tetracene. The enthalpy of disproportionation for the pyrene salt is the most exothermic anion radical disproportionation yet reported and is largely controlled by the crystal lattice energies of the dianion and anion radical salts.

The equilibria of radical anion disproportionation in solution have been extensively studied,[1-8] and mostly through the efforts of Szwarc and co-workers[1-6] a rather complete picture has been developed explaining anion radical disproportionation in molecular terms. The effects of solvation and ion association fit consistently into this picture.

Despite the extensive work on disproportionation in solution, not a single report has appeared concerning anion radical disproportionation in the solid state. Solid state anion radical disproportionation cannot be studied via equilibria measurements due to the very long reaction times that are necessary to reach an equilibrium state. These very long reaction times are due to the very slow migration of electrons and counterions between crystals of anion radical ($M^{+}A^{-}\cdot$), dianion ($M^{+}_2A^{2-}$), and neutral species (A). The kinetic problems can be circumvented by the use of calorimetric methods. Here we wish to report the first enthalpies of anion radical disproportionation in the solid state, eq 1.

$$2M^{+}A^{-}\cdot(s) \rightarrow A(s) + M^{+}_2A^{2-}(s) \qquad (1)$$

Experimental Section

Tetrahydrofuran (THF) solutions of the anion radical or dianion of polyacene hydrocarbons were generated via the reduction of the polyacene with an equal molar or a large excess of sodium metal, respectively.[9,10] After complete formation of the anion radical or dianion salts

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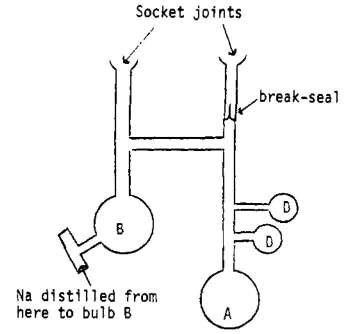

Figure 1. Apparatus used for the dianion and anion radical generation.

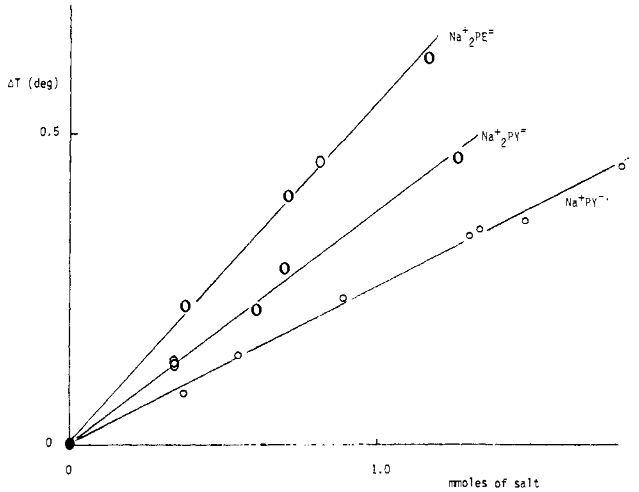

Figure 2. Plots of the change in the temperature of the calorimeter vs. the millimoles of anion radical or dianion salt in the evaculated glass bulbs. The enthalpy of reaction of the salt with water is obtained by multiplying the slope of the line by −119.3 cal/deg.

Table I. Enthalpies of Reaction (kcal/mol)

polyacene	$\Delta H^\circ_{\text{anion}}$	$\Delta H^\circ_{\text{dianion}}$	$\Delta H^\circ_{\text{d,solid}}$	$\Delta H^\circ_{\text{d,THF}}$
tetracene	−33.4 ± 0.6	−75.6 ± 1.8	+8.8 ± 2.1	+27[a]
perylene	−32.0 ± 1.0	−66.8 ± 1.3	+2.8 ± 1.9	+27[b]
anthracene	−41.1 ± 0.3	−79.1 ± 0.9	−3.1 ± 1.0	+7[a]
pyrene	−29.4 ± 0.7	−43.2 ± 1.3	−13.6 ± 1.9	

[a] These data were taken from ref 6. [b] These data were taken from ref 8.

Table II. Crystal Lattice Energies and Electron Affinities (kcal/mol)

polyacene	EA_1	U_1	$EA_1 + 2U_1$	$EA_2 + U_2$	$\Delta H^\circ_{\text{vapor}}$[12]
tetracene	26.5	164.6	355.7	380.2	−29.8
perylene	24.4	169.5	363.4	390.6	−30.0
anthracene	12.7	166.6	345.9	372.5	−23.5
pyrene	13.3	170.6	354.5	390.6	−22.5

Scheme I

$$\begin{array}{ll}
A(g) \rightarrow A(s) & -\Delta H^\circ_{\text{vapor}} \\
A^{-}\cdot(g) \rightarrow A(g) + e^{-}(g) & EA_1 \\
A^{-}\cdot(g) + e^{-}(g) \rightarrow A^{2-}(g) & -EA_2 \\
2Na^{+}A^{-}\cdot(s) \rightarrow 2A^{-}\cdot(g) + 2Na^{+}(g) & 2U_1 \\
A^{2-}(g) + 2Na^{+}(g) \rightarrow Na^{+}{}_2A^{2-}(s) & -U_2 \\
\hline
2Na^{+}A^{-}\cdot(s) \rightarrow A(s) + Na^{+}{}_2A^{2-}(s) & \Delta H^\circ_{\text{d,solid}} = (EA_1 + 2U_1) - (EA_2 + U_2) - \Delta H^\circ_{\text{vapor}}
\end{array}$$

in bulb B of the apparatus shown in Figure 1, the solution was poured over into bulb A. Most of the THF was removed from the salt by placing bulb B in liquid nitrogen. After several hours, bulb B was sealed off from the apparatus. The remainder of the apparatus containing the salt was then placed on a high vacuum line, with a liquid nitrogen trap between the apparatus and the manifold, and the break-seal broken. After 48 h the apparatus was sealed off from the high vacuum (10^{-6} mm of Hg) line just below the break-seal. The solid salt was then poured into the thin-walled glass bulbs (D), which were sealed off from the apparatus. The glass bulbs (D) were crushed under 100 mL of deoxygenated water in a modified Parr solution calorimeter as previously described.[8] A simple titration of the calorimeter contents with a standardized HCl solution yielded the quantity of salt that was in a given glass bulb.

The formation of the dianion and anion radical salts was monitored via ESR. During the course of the formation of a dianion salt the ESR spectral intensity would increase then decrease. The signal would finally disappear after complete formation of the dianion.

To ensure that no THF was left incorporated into the crystal lattice of the dry salts, D_2O was added to the salts and the solution submitted to NMR analysis. No THF signal was observed in the D_2O. In these experiments, D_2O was added to the samples in a vacuum system fitted with a gas buret and a Toepler pump so that any liberated deuterium gas could be measured. No noncondensable gases were liberated from the reactions of the solid salts with D_2O.

In separate experiments the anion radical of anthracene was generated in the manner described above. However, in these experiments several ESR tubes were connected to bulb A of the apparatus in place of the thin-walled bulbs. In this way the intensity of the ESR spectra of the anion radical solution could be monitored as the THF was quantitatively distilled from the anion radical solution. The ESR experiments were carried out on a Varian E-4 ESR spectrometer that is interfaced with a MINC II PDP/11 computer system. The ESR signal from the anthracene anion radical (exhibiting a single fast exchange line) was fed directly into the computer for double integration. All of the ESR samples were run consecutively while maintaining all of the settings on the ESR constant. Thus, the values for the double integrals are proportionate to the anion radical concentration.

NMR spectra were run on a Perkin-Elmer R-32 90-MHz NMR spectrometer.

The hydrocarbons were sublimed before use, and the THF was distilled from the benzophenone ketyl and stored over NaK_2 under vacuum. The errors reported in the enthalpies measured in the calorimeter were propagated from the standard deviations in the slopes of the lines shown in Figure 2.

Results and Discussion

The change in the temperature of the calorimeter is due strictly to the reaction of the salt with water to produce the dihydro polyacene and sodium hydroxide.

$$Na^{+}A^{-}\cdot(s) + H_2O(l) \rightarrow NaOH(aq) + {}^{1}/{}_{2}A(s) + {}^{1}/{}_{2}AH_2(s) \quad (2)$$

$$Na_2{}^{+}A^{2-}(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + AH_2(s) \quad (3)$$

After completion of the reaction, the solid dihydro hydrocarbon or the dihydro hydrocarbon with the polyacene can be seen floating in the water.

Plots of the millimoles of salt in the bulbs vs. the change in the temperature of the calorimeter are linear (Figures 2 and 3), and the slopes of the lines are proportional to the enthalpies of the reactions depicted in eq 2 and 3. The heat capacity of the calorimeter is 119.3 ± 0.8 cal/deg as previously reported.[9]

By simply subtracting the enthalpy of the reaction depicted in eq 3 ($\Delta H^\circ_{\text{dianion}}$) from twice that depicted in eq 2 ($\Delta H^\circ_{\text{anion}}$) the enthalpy of disproportionation ($\Delta H^\circ_{\text{d,solid}}$) in the solid state can be obtained, Table I. The anthracene, tetracene, and perylene systems were chosen for this study since they are the only ones for which solution enthalpies of disproportionation are known.

The dianions and anion radicals exist either as tight or loose ion pairs in THF and the disproportionation must be written in terms of the ion-associated species, eq 4. From Table I, there

$$2Na^{+},A^{-}\cdot(THF) \rightarrow A(THF) + Na^{+},A^{2-},Na^{+}(THF) \quad (4)$$

is no obvious correlation between the enthalpies of disproportionation in THF and those for the solid-state disproportionation, eq 5.

$$2Na^{+}A^{-}\cdot(s) \rightarrow A(s) + Na^{+}{}_2A^{2-}(s) \quad (5)$$

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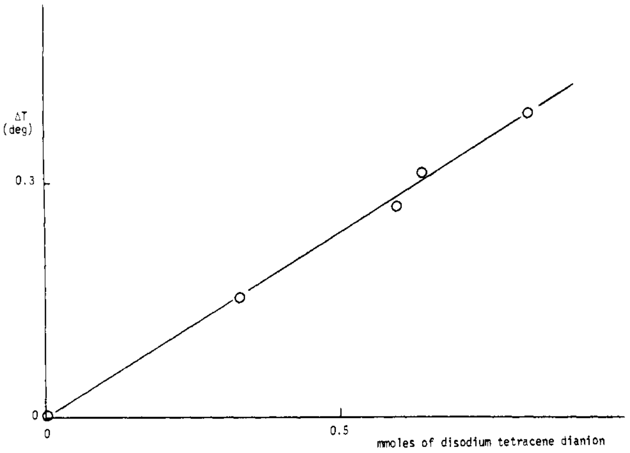

Figure 3. Plot of the change in the temperature of the calorimeter vs. the millimoles of solid tetracene dianion salt in the evacuated glass bulbs.

In THF both the dianions and anion radicals are ion associated with the sodium cation.[1] However, in the solid state the questions of crystal lattice energies replace those of ion association and ion solvation. Very little is known about dianion crystal lattice energies, but it appears that the crystal lattice energies of anion radicals do not vary much from one polyacene anion to another.[9] The solid-state disproportionation enthalpy is a sensitive function of crystal lattice energies (U) and electron affinities (EA) as shown in Scheme I.

The values for EA_1 are well known,[11] and those for U_1 can be calculated from the enthalpies of reaction of the anion radical salts with water as previously described,[9] Table II. Neither the second electron affinities nor the dianion crystal lattice energies are known, but from Table II it appears that even the relatively small differences in the crystal lattice energies and in the electron affinities combine to generate large differences in the disproportionation enthalpies for the solid polyacene anion radicals. A combination of crystal lattice energies and electron affinities results in the most exothermic disproportionation enthalpy yet observed (−13.6 kcal/mol for the solid pyrene anion radical). For all of the anions studied in both phases, the enthalpy of disproportionation in the solid state is between 24 and 10 kcal/mol more exothermic than in solution.

Table III. Volume of THF in the Initial Sample Divided by the Volume Remaining after Evaporation (A) and the Ratios of the Double Integrals of the ESR Spectra of the Anthracene Anion Radical in Solution (B)

A	B	A	B
1.00	1.00	1.53	1.68
1.19	1.49	2.79	2.62
1.47	1.47		

Two impurities that may have existed in the solid dianion solutions are neutral sodium metal caused by electron transfer back to the metal from the dianion and anion radical together with the neutral hydrocarbon. The first possibility has been eliminated, since the addition of water to the solid salts does not yield any hydrogen gas. The possibility that the anion radicals could change to neutral molecule and dianion as the THF was being evaporated also had to be eliminated. From Table III it is clear that the relative intensity of the ESR signal after THF evaporation does not decrease relative to the ratio of the initial THF volume to the final THF volume. In fact, the data would indicate that the anion radical concentration was increasing even faster than can be accounted for by concentration effects. However, the double integration method does incorporate relatively large errors. In the last sample, when more than 60% of the THF had been evaporated, some precipitation of the solid anion radical could be observed.

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Study of the Photolysis of Dimethyl-*s*-tetrazine Using a Holographic Technique

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Abstract: A holographic technique is used to investigate the photochemical action spectrum of the second step in the two-photon photodissociation of dimethyl-*s*-tetrazine (DMST) in poly(vinylcarbazole) (PVK). We are able to show from these measurements that the previously observed transient absorption in the 600–700-nm spectral region is not directly involved in the second step absorption that leads to photodissociation. Furthermore, from the very fact that holograms can be produced with modest laser powers in this system, we are able to conclude that the intermediate in the second step cannot have a lifetime on the nanosecond or shorter time scale.

The photodissociation of tetrazine and its substituted derivatives has been the subject of many recent investigations.[2-8] This interest has been stimulated by the suggestion that the photodissociation might be useful as a means of isotope separation.[3b] It has also

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