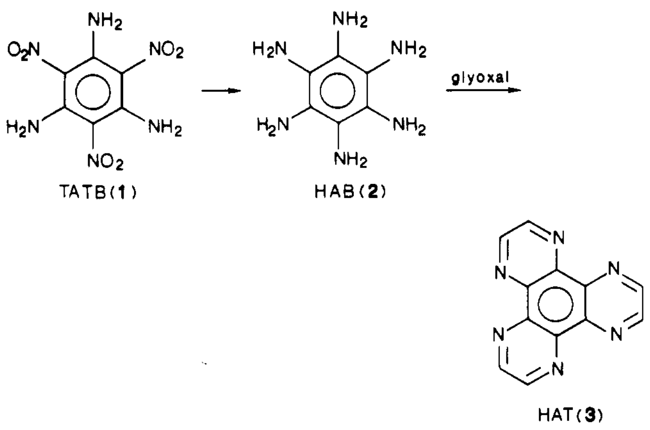
Scheme I



better than 75% yield based on TATB.

Although the modified reduction procedure reported here has not been tested on other polynitroarenes, we believe that it would be generally useful method for the synthesis of polyaminoarenes from the corresponding polynitroarenes. It would also be of interest to examine the reduction of other types of substrates with sodium in liquid ammonia in the presence of very high hydrogen donor concentrations.

Experimental Section

Infrared spectra were taken on a Nicolet 5DXE FT-IR instrument. Microanalyses were performed by Galbraith Laboratories. TATB was purchased from Chemtronics, Inc. and used as received. All other reagents were used as received. *Caution! TATB is a military explosive. Although relatively insensitive to accidental detonation, it should be used only in small quantities with appropriate safety precautions.*

Preparation of HAB (2). A 1-L 3-neck flask equipped with mechanical stirrer, gas inlet, and gas condenser was charged with TATB (1; 7.1 g, 27.5 mmol) and methanol (137 mL, 3.39 M). Approximately 400 mL of ammonia was then condensed into the flask. Stirring was started and sodium (16 g, 696 mmol) added in small pieces at a rate sufficient to cause gentle reflux of the ammonia. After the sodium addition was complete and the blue color discharged, the gas condenser was removed and the ammonia allowed to evaporate. When the mixture reached room temperature, the solids were collected by vacuum filtration and washed with ethanol and finally diethyl ether to give 2 (4.39 g, 26.1 mmol) as a cream-colored solid in 95% yield. This material was of sufficient quality to use without purification but decomposed significantly on standing in air for 24 h. Aqueous solutions of 2 decomposed completely in 24 h. On heating in air 2 darkened at 150 °C and decomposed at 240–255 °C (lit.[3] decomposition point (in H_2) 247–248 °C). IR (KBr, cm^{-1}): 3353, 3269, 1644, 1490.

Preparation of HAT (3). Technical grade 40% aqueous glyoxal (approximately 50 mL) was cooled in an ice bath and freshly prepared HAB (4.39 g, 26.1 mmol) added in portions to the stirred solution. After the addition was complete, the solution was allowed to warm to room temperature. A copious precipitate appeared within 1 h. After stirring for 18 h, the mixture was poured into 300 mL of water, and the solids were collected by vacuum filtration. The solids were washed well with water, ethanol, and diethyl ether and then dried to give HAT (5.05 g, 21.7 mmol) in 83% yield as a tan solid. Of this 2.38 g was continuously extracted for 48 h with 500 mL of chloroform. Decolorizing carbon (0.15 g) was added to the chloroform solution, and the solution was gently boiled for 15 min. The solution was cooled to room temperature and poured onto a column of 500 g of dry alumina. A yellow band eluted in the middle of the HAT elution. Two fractions were collected. Evaporation of eluent before the yellow band gave 0.40 g of HAT as a white solid. Anal. Calcd for $C_{12}H_6N_6$: C, 61.54; H, 2.56; N, 35.90. Found: C, 61.57; H, 2.64; N, 35.56. The IR spectrum was identical with that of material prepared by previously reported methods. IR (KBr, cm^{-1}): 1968, 1469, 1377, 1328, 1223, 1096, 871.

Evaporation of the remaining eluent gave 1.95 g of HAT as a white solid, with an IR spectrum identical with that of the preceding fraction. Anal. Found: C, 61.25; H, 2.66; N, 36.00.

Registry No. 1, 3058-38-6; 2, 4444-26-2; 3, 79790-37-7; glyoxal, 107-22-2.

Voltammetry in (Toluene)$_3$-Tetrabutylammonium Tetrafluoroborate, a Novel Liquid "Hydrocarbon Electrolyte"

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The electrochemical voltammetric behavior of organic substances, involving as it generally does the generation of charged intermediates, is very sensitive to the nature of the medium in which the experiments are conducted.[1-5] A variety of homogeneous and heterogeneous processes can be affected by changes in the solvent and/or supporting electrolyte. For example, many studies have shown that the electrochemical reduction of aromatic hydrocarbons is highly sensitive to the presence of proton donors in the medium.[1-3] Furthermore, since ion-pairing effects can be important in such studies, the polarity of the solvent can have a major effect upon the electrochemical behavior of substances dissolved in it. For this reason, our attention was recently attracted by the report of a novel liquid "hydrocarbon electrolyte" solvent system composed of tetrabutylammonium tetrafluoroborate and toluene in 1:3 molar ratio.[6] We were interested in the potential utility of this solvent (which we refer to herein as T3–TBATFB) for studies on the voltammetric behavior of aromatic hydrocarbons as well as intrigued by the possibility that this solvent might present a "hydrocarbon-like" microenvironment in which to carry out electrochemical experimentation. Little information was provided concerning such matters in the original publication, which was devoted to the voltammetry of an iron–sulfur cluster. We have examined the voltammetry of several aromatic substrates in this novel solvent system. Our results indicate that such voltammetry, with a few exceptions, resembles to a surprising degree that of the same substances in a typical dipolar aprotic solvent, dimethylformamide (DMF).

Cyclic voltammetry was carried out at a mercury-coated platinum electrode[7] at a scan rate of 500 mV s^{-1} and DC polarography was carried out at a conventional dropping mercury electrode. The cyclic voltammogram of perylene in T3–TBATFB, scanned from −1.20 to −2.75 V (vs. Ag/0.1 M $AgNO_3$ in acetonitrile) and back is shown in Figure 1. The most characteristic features of this voltammogram are the presence of a reversible couple at −2.00 V, an irreversible reduction peak at −2.58 V, and an oxidation peak at −1.46 V, which is not present if the initial potential scan

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Table I. Voltammetry of Aromatic Compounds

compound	solvent	method[a]	$-E_1$, V[b]	$-E_2$, V[b]	$E_1 - E_2$, V	$E_{pa} - E_{pc}$, mV
pyrene	T3–TBATFB	CV	2.46	3.06	0.60	73
perylene	T3–TBATFB	CV	2.04	2.58	0.54	67
9,10-DPA	T3–TBATFB	CV	2.25	2.69	0.44	100
anthraquinone	T3–TBATFB	Py	1.27	1.75	0.48	57[c]
pyrene	DMF	CV	2.49	3.09	0.60	57
perylene	DMF	CV	2.12	2.68	0.56	56
9,10-DPA	DMF	CV[d]	2.25	2.87	0.62	60
tetracene	DMF	CV	2.01	2.61	0.60	55
tetracene	DMF	CV[e]	2.03	2.63	0.60	66
pyrene	THF	CV	2.48	3.01	0.53	78
pyrene	THF	Py	2.44	2.96	0.52	
perylene	THF	CV[e]	2.00	2.47	0.47	340
tetracene	THF	CV[e]	2.07	2.58	0.51	323

[a] CV = cyclic voltammetry (at a mercury-coated platinum electrode, except where noted); Py = DC polarography. [b] Potentials measured relative to Ag/0.1 M $AgNO_3$. [c] $E_{1/4} - E_{3/4}$; see ref 3, p 38. [d] Hanging mercury drop electrode; data from ref 12. [e] Carbon electrode.

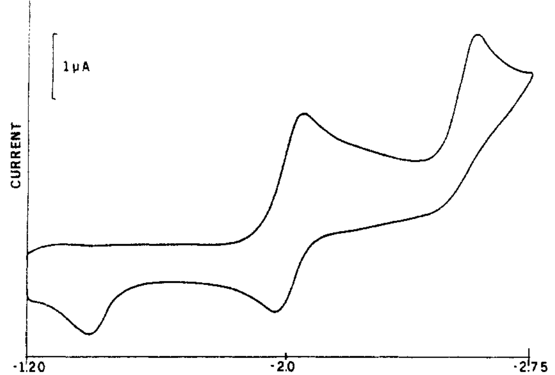

Figure 1. Cyclic voltammogram of perylene in (toluene)$_3$–tetrabutylammonium tetrafluoroborate, scanned from −1.20 V to −2.75 V (vs. Ag/0.1 M $AgNO_3$) and back, at a mercury-coated platinum electrode.

Scheme I

$$\underset{1}{\mathrm{ArH}} + e^- \rightarrow \underset{2}{\mathrm{ArH}^{\bullet}} \qquad E_1 \tag{1}$$

$$2 + e^- \rightarrow \underset{3}{\mathrm{ArH}^{2-}} \qquad E_2 \tag{2}$$

$$3 + H^+ \rightarrow \underset{4}{\mathrm{ArH}_2^-} \tag{3}$$

$$3 + H^+ \rightarrow \underset{5}{\mathrm{ArH}_2\bullet} \tag{4}$$

is reversed at −2.2 V. Essentially identical behavior is exhibited by perylene and 9,10-diphenylanthracene.

This behavior is remarkably similar to that exhibited by these, and many other, PAH's in dipolar aprotic solvents such as DMF, acetonitrile, and dimethyl sulfoxide.[1–4] In such solvents, and evidently also in T3–TBATFB, the electrochemical reduction of such substances follows the sequence outlined in Scheme I. The substrate (**1**) is reduced to the corresponding radical anion (**2**) at potential E_1 (eq 1), and **2** is generally long-lived under such conditions, hence the reversible nature of the couple at E_1. Radical anion **2** is reduced to a dianion (**3**) at a more negative potential E_2 (eq 2), accounting for the second reduction step. However, **3** is usually much more highly basic than **2** and rapidly abstracts a proton from the medium to produce a monoanion (**4**) (eq 3).[8] This accounts for the irreversible nature of the second step and also for the (irreversible) oxidation step at −1.46 V, which is due to oxidation of **4** to a short-lived neutral radical. The similarity of the voltammograms of PAH's in T3–TBATFB and solvents such as DMF goes beyond a general resemblance. Reduction potentials measured in the two types of medium are almost identical, indicating that the liquid–liquid junction potentials between acetonitrile (the solvent for the reference electrode) and T3–TBATFB and typical dipolar aprotic solvents are very similar. More surprisingly, $E_1 - E_2$, the spacing in volts between the first and second reduction potentials, and $E_{pa} - E_{pc}$, the difference in volts between the anodic and cathodic peak potentials at E_1, are also very similar (Table I). These parameters measure two different, though related, properties of the solvent system. $E_{pa} - E_{pc}$ is generally larger than the theoretical value of 56 mV in solvents of high electrical resistance, because of incomplete compensation of the *iR* drop between the reference and working electrodes.[9] It appears from the data in Table I that the electrical resistance of T3–TBATFB is slightly higher than that of DMF, but much more like DMF than THF, which is known to have high electrical resistance.[10] As has been noted previously,[4,11] the value of $E_1 - E_2$ is related to differential ion-pairing phenomena.

This may be seen by subtraction of eq 2 from eq 1 to give eq 5, from which it may be seen that $E_1 - E_2$ is a

$$1 + 3 \rightleftarrows 2\ 2 \qquad E_1 - E_2 = -\Delta G/nF \tag{5}$$

measure of the tendency of the radical anion **2** to disproportionate into starting material and dianion. Dianions generally have a considerably higher tendency toward ion-pairing to the cation of the supporting electrolyte than do radical anions; therefore conditions conducive to ion-pairing (small cations, low dielectric solvents) stabilize the left side of eq 3 more than the right, causing $E_1 - E_2$ to decrease.[4,11] The values of $E_1 - E_2$ in T3–TBATFB and DMF are larger than the corresponding values in tetrahydrofuran, a much less polar and less electrically conductive solvent,[10] indicating that hydrocarbons dissolved in T3–TBATFB do not find themselves in a "hydrocarbon-like" microenvironment. This solvent appears just like a typical dipolar aprotic solvent to substrates dissolved in it. This is at least partly understandable in terms of the high salt content of the medium (the mole fraction of tetrabutylammonium tetrafluoroborate in T3–TBATFB is 0.54; T3–TBATFB is 1.62 M in TBATFB), but one might then have expected this to increase the degree of

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(8) (a) The second reduction step in such solvents is reversible when they are subjected to rigorous purification.[8b] (b) Jensen, B. S.; Parker, V. D. *J. Am. Chem. Soc.* **1975**, *97*, 5211.

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ion-pairing by a mass-action effect and thus also to decrease $E_1 - E_2$. We explored this point further by measuring the DC polarogram of anthraquinone in T3–TBATFB. This substrate is more sensitive to ion-pairing effects than are hydrocarbons, because of the higher electronegativity of oxygen over carbon and the consequent higher charge carried by the two oxygen atoms in the dianion.[1] The spacing between the first and second polarographic waves was found to be 0.48 V, which may be compared with a spacing of 0.65 V for anthraquinone in DMF containing 0.1 M tetrabutylammonium iodide (TBAI).[1] The difference between the two solvents, while real, is relatively small.

The only point at which ordinary electrochemical experimentation in T3–TBATFB was found to produce results significantly different from those in DMF was in the effects of added proton donors upon the voltammetry of PAH's in the respective solvents. Addition of increasing amounts of proton donors to such solutions is known to produce a gradual increase in the height of the first wave, with corresponding decrease in the height of the second wave, until at high proton donor concentration the first wave has doubled in height and the second has disappeared.[1-3] This behavior is caused by protonation of the radical anion **2** to afford neutral radical **4**, whose reduction potential is well negative of E_1, so that **4** is reduced as soon as it is formed. In the case of 9,10-diphenylanthracene in DMF with phenol as proton donor, a phenol:hydrocarbon ratio of ca. 20:1 is required (for 1 mM hydrocarbon) to effect a 50% increase in the height of the first wave and a ratio of between 50 and 200:1 to double the height of this wave.[12] In T3–TBATFB, however, 1:1 and 10:1 phenol:hydrocarbon ratios, respectively, sufficed to create the same effects upon wave height. Thus phenol appears to be a noticeably better proton donor in T3–TBATFB than it is in DMF. We presume that this is because DMF is the better hydrogen-bond acceptor and that therefore phenol, being hydrogen-bonded to DMF, is not as good a proton donor in this solvent. It is already well-known that water is a very poor proton donor in DMF and Me_2SO, to which it is very tightly hydrogen-bonded, and that it is a much better proton donor in acetonitrile, a poorer hydrogen-bond acceptor.[13]

Finally, we note that the reduction potentials of unsaturated hydrocarbons are very similar in DMF and THF,[14] in contrast to reported[15] results for alkyl halides, sulfonates, and unsaturated carbonyl compounds.

Experimental Section

Toluene was distilled from sodium immediately before use. Tetrabutylammonium tetrafluoroborate was prepared by the metathetic reaction between tetrabutylammonium iodide and tetrafluoroboric acid.[16] (Toluene)$_3$–tetrabutylammonium tetrafluoroborate was prepared by stirring the salt with an excess of toluene.[6] It was found necessary to keep solutions of the "hydrocarbon electrolyte" covered with a thin layer of toluene during voltammetry in order to prevent slow evaporation of solvent and consequent precipitation of the toluene-free salt. Cyclic voltammetry and polarography were carried out in a Brinkmann cell, Model EA874/875-20. The reference electrode consisted of a silver wire immersed in a 0.1 M solution of silver nitrate in acetonitrile, contained in a length of heavy-walled Teflon-brand tubing sealed at one end with a short length in porous Vycor. The potential of this electrode is +0.35 V vs. SCE.

Acknowledgment. Financial support was provided by the National Science Foundation (CHE-8502078).

Registry No. T3, 429-42-5; TBATFB, 108-88-3; pyrene, 129-00-0; perylene, 198-55-0; 9,10-diphenylanthracene, 1499-10-1; anthraquinone, 84-65-1; phenol, 108-95-2.

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Communications

On the Driving Force for the Symmetric Structure of Benzene and the Allyl Radical: σ or π?[1]

Summary: The conclusion of Hiberty and co-workers that the symmetric structures of benzene and the allyl radical are preferred to those with alternating bonds because of the σ bond energy is shown to be critically dependent upon the choice of the C=C length in the alternating structure. Use of a more appropriate value reverses their controversial conclusions.

Sir: Recently Hiberty and co-workers have argued that the symmetric structures of benzene and the allyl radical are superior to those with alternating bonds because of the energetic preferences of the σ bonds and that in fact the π system itself prefers an asymmetric structure.[2,3] In this paper I show that their arguments rest critically on a questionable assumption concerning the bond distances for the alternating structure and that if more appropriate values are used, their conclusions are reversed and the traditional view—that the symmetrical structure is due to π electrons—is recovered.

Hiberty and co-workers compare the σ and π energies of benzene with all bond lengths chosen as 1.400 Å to a structure with bonds of alternating lengths of 1.34 and 1.4627 Å. They find that the σ energy is better in the symmetrical structure by about 17 kcal mol^{-1}, that the π energy is worse by about 11 kcal mol^{-1}, and that overall the symmetric is preferred by about 6 kcal mol^{-1}. They do not discuss the choice of bond distances assumed for their structures, but clearly that for the symmetrical

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