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The Electrochemical Reduction of 9,10-Diphenylanthracene

K. S. V. Santhanam and Allen J. Bard¹

Contribution from the Department of Chemistry, The University of Texas, Austin, Texas 78712. Received January 22, 1966

Abstract: The electroreduction of 9,10-diphenylanthracene (DPA) in dimethylformamide solutions was studied by polarography, cyclic voltammetry, chronopotentiometry, and coulometry. The results generally confirmed the mechanism proposed for the reduction of aromatic hydrocarbons based on polarographic experiments. Coulometric experiments demonstrated that with sufficient care in solution preparation 1 Faraday per mole of DPA was consumed and fairly stable solutions of DPA^- could be obtained. The protonation of DPA^- by hydroquinone was also studied. The half-wave potential for the reduction of DPA to DPA^- was shown to be equal to that calculated by molecular orbital theory, using an angle between the 9- and 10-phenyl groups and the anthracene nucleus based on electron spin resonance measurements. An explanation of the pronounced streaming which occurs at mercury electrodes during oxidation of DPA^- is given.

The electrochemistry of aromatic hydrocarbons in aprotic solvents has been the subject of a number of studies.² These investigations are of interest because the radical ions which are formed at the electrode may undergo further chemical or electrode reactions. Further interest lies in the correlation between the polarographic half-wave potentials for the reduction of the hydrocarbon (R) to its radical anion ($\text{R}^{\cdot-}$) with electron affinities, ultraviolet absorption frequencies, or parameters calculated by molecular orbital (MO) theory.^{2,3} Although the results of dc and ac polarography fit very well with assumed mechanisms and the known chemistry of aromatic hydrocarbons (e.g., reduction with alkali metals), very few studies have been made using some of the more recent electrochemical techniques such as cyclic voltammetry and chronopotentiometry. Neither have electrochemical studies been made of the radical anions themselves. Furthermore, the coulometric reduction of these compounds at the first reduction plateau gave evidence of a two-electron reduction,⁴ which was ascribed to the reaction of $\text{R}^{\cdot-}$ with the solvent (dimethylformamide) producing RH^{\cdot} , which was reduced in a second one-electron step at these potentials. This finding seemed at variance with the known stability of $\text{R}^{\cdot-}$, as observed through optical and electron spin resonance (esr) studies. Finally, although theoretical considerations lead to the predication that the protonated radical (RH^{\cdot}) should reduce at less cathodic potentials than R, no direct attempts have been made to obtain RH^{\cdot} and study its electrochemistry.

The aim of this investigation was to study the electrochemical reduction of an aromatic hydrocarbon by a variety of electrochemical techniques, in order to confirm and extend the previously described mechanisms. The choice of 9,10-diphenylanthracene (DPA) was based on interest in this substance in chemiluminescence experiments.⁵ Furthermore, a comparison of elec-

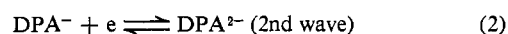
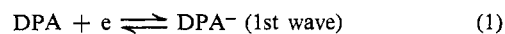
trochemical and esr parameters with those calculated by MO theory can provide information about the extent of nonplanarity of DPA.

The electrochemical reduction of DPA and oxidation of DPA^- in the absence of proton donors will be described first. Then the effect of proton donors will be discussed. Finally a correlation of the observed half-wave potentials and those predicted by MO theory will be given and an explanation of the stirring effect which occurs during the electrooxidation of anion radicals will be presented.

Results

Voltammetric Methods. The polarographic reduction of DPA in a *N,N*-dimethylformamide (DMF) solution containing 0.1 *M* tetra-*n*-butylammonium iodide (TBAI) showed two well-defined waves (Figure 1) with half-wave potentials ($E_{1/2}$) of -1.84 and -2.46 v vs. an aqueous saturated calomel electrode (sce). The values of $E_{3/4} - E_{1/4}$ for the two waves (Tómes criterion of reversibility⁶), 0.06 and 0.08 v, respectively, suggested that the first wave involved a reversible one-electron reduction and the second an irreversible one-electron reduction. The diffusion currents of both waves varied as the square root of the head of the dropping mercury electrode (dme). The diffusion current constants for the first and second waves were 5.35 and 9.95, respectively.

These results are consistent with the mechanisms proposed previously for the reduction of aromatic hydrocarbons² and can be represented as



where HS represents the solvent. Further justification for this mechanism is given below.

A cyclic voltammogram of DPA in DMF containing 0.1 *M* TBAI at a hanging mercury drop electrode (hmde) is shown in Figure 2, curve 1. A clear anodic peak on the reverse scan is shown for the oxidation of DPA^- , but, at slow scan rates, no reversal peak is observed for the second wave. At higher (greater than

(1) To whom correspondence and request for reprints should be directed.

(2) This work has been reviewed in (a) G. J. Hoijtink, *Ric. Sci., Suppl.*, **30**, 217 (1960); (b) G. J. Hoijtink, *Rec. Trav. Chim.*, **76**, 885 (1957); (c) M. E. Peover in "Electroanalytical Chemistry. A Series of Monographs on Recent Advances," Vol. II, A. J. Bard, Ed., Marcel Dekker, Inc., New York, N. Y., in preparation.

(3) (a) A. Maccol, *Nature*, **163**, 178 (1949); (b) F. A. Matsen, *J. Chem. Phys.*, **24**, 602 (1956); (c) G. J. Hoijtink, *Rec. Trav. Chim.*, **74**, 1525 (1955).

(4) D. E. G. Austen, P. H. Given, D. J. E. Ingram, and M. E. Peover, *Nature*, **182**, 1784 (1958).

(5) (a) E. A. Chandross and F. I. Sontag, *J. Am. Chem. Soc.*, **86**, 3179 (1964); (b) R. Visco and E. A. Chandross, *ibid.*, **86**, 5350 (1964); (c) K. S. V. Santhanam and A. J. Bard, *ibid.*, **87**, 139 (1965).

(6) J. Tómes, *Collection Czech. Chem. Commun.*, **9**, 12 (1937).

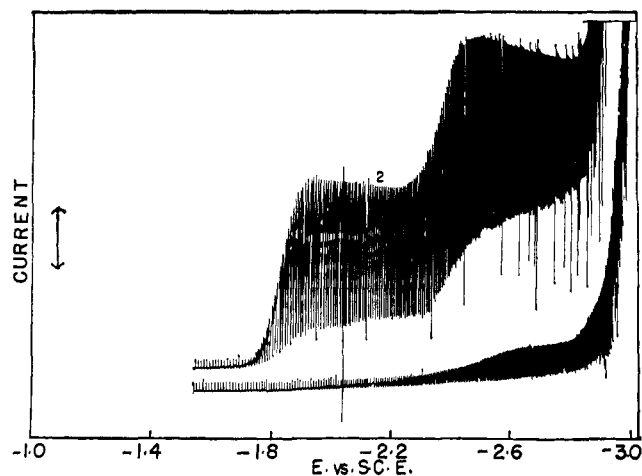


Figure 1. Polarogram for reduction of 9,10-diphenylanthracene. The solution was (lower curve) supporting electrolyte (0.1 M TBAI) in DMF (upper curve) with 3 mM DPA. Current arrow represents 1.9 μ A.

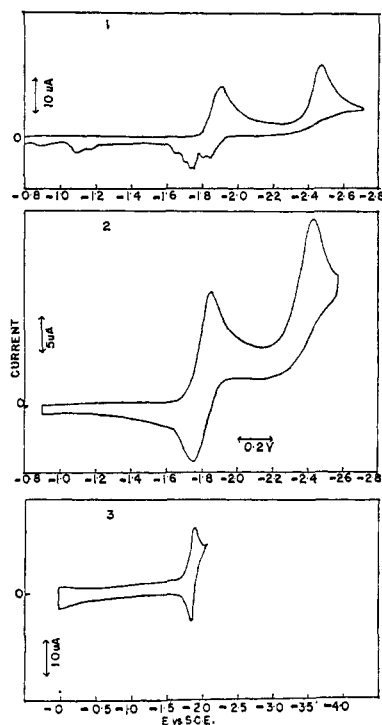


Figure 2. Cyclic voltammetry of 9,10-diphenylanthracene. The solution contained 0.1 M TBAI in DMF and (1) 3 mM DPA at hmde; (2) 1.5 mM DPA at HMDE; (3,) 3 mM DPA at platinum disk electrode.

3 mM) concentrations of DPA, the anodic peak shows multiple peaks, and often the appearance of many other peaks as the scan is continued to more anodic potentials. Observation of the hmde during this peak shows vigorous streaming of the blue radical, DPA^- , around the electrode. Similar behavior has been observed in other systems.⁷ As the concentration of DPA is decreased, the current density involved in the electrode process decreases, and the peaks become smoother. At a concentration of 1.5 mM DPA a smooth peak is obtained (Figure 2, curve 2). This

(7) See, for example, Figure 3 in R. H. Philp, Jr., T. Layloff, and R. N. Adams, *J. Electrochem. Soc.*, **111**, 1189 (1964).

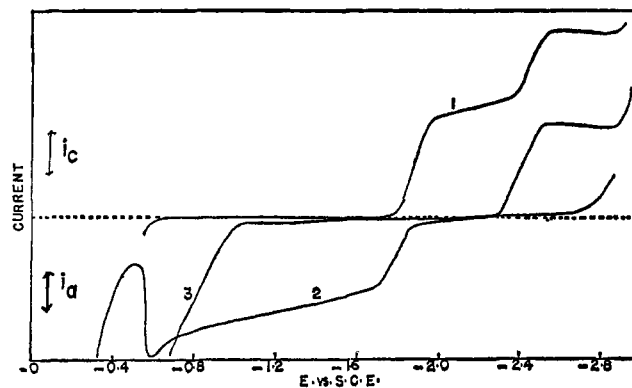


Figure 3. Polarograms during various stages of reduction of 4.2 mM 9,10-diphenylanthracene in 0.1 M TBAI in DMF at mercury pool electrode: (1) before reduction; (2) after reduction at -2.0 V vs. s.c.e (current arrow, $i_c = 4 \mu\text{A}$, $i_a = 16 \mu\text{A}$).

streaming also gives rise to pronounced maxima in the polarographic oxidation of DPA^- (see below) and is discussed later. At a plain platinum electrode, cyclic voltammograms do not show this streaming behavior, even at higher concentrations of DPA (Figure 3, curve 3). Typical results of cyclic voltammetric (linear potential sweep chronoamperometry with reversal) experiments at a hmde and platinum disk electrode are shown in Table I. At a platinum electrode, the ratio of the peak current of the first cathodic wave to that of the reverse anodic wave, i_{pc}/i_{pa} , was about 1, as expected for the formation of a radical species which is stable during the time of the measurement. Similar results are obtained with the hmde at 1.56 mM DPA, although i_{pc}/i_{pa} is somewhat larger. With higher DPA concentrations, stirring at the electrode surface

Table I. Cyclic Voltammetric Data for First Waves in the Reduction of 9,10-Diphenylanthracene^a

Sweep rate, mv/sec	i_{pc} , μA	i_{pa} , μA	i_{pc}/i_{pa}	E , vs. s.c.e.		
				E_{pc}	E_{pa}	$E_{pc} - E_{pa}$
Hanging Mercury Drop Electrode ^b						
Concn = 1.56 mM						
67.1	10.3	8.1	1.27	-1.88	1.82	-0.06
153	15.0	11.8	1.27	-1.88	-1.82	-0.06
222	18.1	15.0	1.16	-1.89	-1.82	-0.06
312	21.8	18.1	1.21	-1.89	-1.83	-0.06
476	26.8	23.1	1.16	-1.89	-1.83	-0.06
714	31.8	26.2	1.21	-1.91	-1.81	-0.10
Concn = 2.58 mM ^c						
67.1	21.2	12.4	1.71	-1.93	-1.87	-0.06
153	31.2	18.8	1.66	-1.95	-1.85	0.10
222	36.2	23.6	1.53	-1.95	-1.85	-0.10
312	42.4	28.8	1.47	-1.96	-1.85	-0.11
476	50.6	33.8	1.49	-1.97	-1.85	-0.12
714	58.8	42.4	1.38	-1.97	-1.85	-0.12
Platinum Disk Electrode ^d						
Concn = 1.56 mM						
152	12.8	11.8	1.08	-1.90	-1.85	-0.05
222	15.9	14.4	1.10	-1.90	-1.85	-0.05
312	18.8	17.5	1.03	-1.90	1.85	-0.05
476	23.1	21.2	1.09	-1.90	-1.85	-0.05
714	30.6	27.5	1.11	-1.95	-1.85	-0.10

^a The solution was 0.1 M TBAI in DMF. Scan reversed at a potential 40 mv more negative than E_p . ^b Area = 0.083 cm². ^c Stirring in this solution makes the location of E_{pa} difficult. Potentials in this solution may also include some uncompensated iR drop. ^d Area = 0.031 cm².

becomes significant and values of i_{pc}/i_{pa} appreciably greater than 1 are obtained. The value of $E_{pc} - E_{pa}$ is close to the value for a reversible one-electron reaction, 0.057 v, and E_{pc} is essentially independent of scan rate.⁸ These results are in agreement with reaction I proposed for the reduction.

The second reduction wave in cyclic voltammetric experiments shows, at a scan rate of 67 mv/sec, a peak at -2.50 v *vs.* sce, which shifts toward more negative potentials with increasing scan rate. This observation and the fact that at high values of scan rate (20 v/sec) the suggestion of a reversal peak for the second wave becomes apparent are indicative of a reversible electrode reaction followed by an irreversible chemical reaction (case VI in the work of Nicholson and Shain⁸). Ac polarography also gives evidence of a small peak at the potential of the second peak.⁹

Typical results obtained by chronopotentiometry are shown in Table II. In general the reversal transition times (τ_b) at a hmde are much shorter than the expected one-third of the forward transition times (τ_f), even at rather short transition times, probably because of the stirring effect. At platinum τ_b values are less than one-third of τ_f at longer transition times but become equal to $1/3 \tau_f$ at short τ values. Since the radical is known to be stable over the time of the measurement and stirring does not occur at platinum (as shown by equality of i_{pc} and i_{pa} in cyclic voltammetry in similar time intervals), the short τ_b values in chronopotentiometry must be ascribed to other causes. One cause is the residual current at the potentials of reduction of DPA, due to electrolysis of the supporting electrolyte and residual impurities in the DMF. At long transition times (small currents) this can amount to an appreciable fraction of the applied current density, increasing τ_f and decreasing τ_b . At short transition times (large currents), this contribution is small and the results fit closely to expected diffusion-controlled behavior for reversal and cyclic chronopotentiometry.¹⁰ Typical values for relative transition times at a current of 52.8 μ a are 1.0, 0.29, 0.60, and 0.33 for the first through fourth transitions, compared to the theoretical values of 1.0, 0.33, 0.59, and 0.36 for a diffusion-controlled reaction.

Controlled Potential Coulometry. Coulometric experiments at a mercury pool electrode controlled at a potential on the diffusion plateau of the first wave (-2.00 v *vs.* sce) were undertaken to study the stability of DPA^- and also to prepare solutions of DPA^- which could be subjected to further electrochemical studies. The results for the coulometric reduction of DPA and anthracene were found to be very dependent upon the conditions under which the electrolysis was carried out (Table III). When the electrolysis was performed in purified DMF with pure nitrogen (high-purity nitrogen passed over hot copper and presaturated with DMF) bubbling through the solution, a steady-state current appreciably higher than the background current (e.g., 1.38 ma *vs.* 600 μ a) was attained, so that an apparent number of electrons per molecule, n_{app} , much larger than 2 would be calculated.

(8) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).

(9) M. E. Peover also has found an ac polarographic peak at the potential of the second reduction wave for DPA (private communication).

(10) H. B. Herman and A. J. Bard, *Anal. Chem.*, **35**, 1121 (1963).

Table II. Chronopotentiometric Data for Reduction of DPA^-

Concn (C), mM	Current density (i_0), ma/cm ²	Transition times, sec		$i_0 \tau_f^{1/2} / C$ (ma sec ^{1/2} /cm ² mM)
		Forward τ_f	Reverse τ_b	
Hanging Mercury Drop Electrode				
1.56	0.130	1.85	0.30	0.11
	0.110	2.65	0.60	0.11
1.90	1.976	0.0256	0.0048	0.16
	1.409	0.0620	0.0106	0.18
	0.909	0.135	0.030	0.18
	0.621	0.325	0.070	0.18
2.59	0.290	0.60	...	0.08
	0.130	5.0	1.25	0.11
	0.10	8.2	2.2	0.11
Platinum Disk Electrode				
1.56	0.280	3.2	0.37	0.32
	0.180	9.4	0.90	0.35
1.90	3.740	0.0144	0.0048	0.27
	2.620	0.0320	0.0104	0.25
	1.726	0.0800	0.026	0.26
	1.190	0.180	0.060	0.26
2.59	0.350	5.45	0.52	0.31
	0.270	7.60	0.90	0.29
	0.180	9.4	1.25	0.21

^a Solution was 0.1 M TBAI in DMF.

Table III. Controlled Potential Coulometric Results^a

Compound	Conditions	Concn, mM	n_{app}
A. Effect of Solution Conditions on n_{app} for Reduction of DPA and A ^b at -2.0 v <i>vs.</i> sce			
A and DPA	N ₂ bubbling, 25°	0.60-1.92	Steady state reached
DPA	N ₂ over surface, 25°	0.57	1.31
DPA	Vacuum line, 25°	1.19	1.15
A	Vacuum line, 25°	2.83	1.24
DPA	N ₂ bubbling, 3°	0.93	1.11
DPA	N ₂ over surface, 3°	0.62-0.93	1.06
A	N ₂ over surface, 3°	0.77	1.08
DPA	Vacuum line, 3°	1.19	0.95
B. Other Effects and Reversal Coulometry ^c			
A	-2.0 v, 7.5 mM phenol added	0.55	1.98
DPA	-2.6 v (reduction at second wave)	8.49	2.06
DPA ⁻	-1.4 v, reversal coulometry (oxidation)	1.99	0.91
DPA ⁻	-1.4 v, reversal coulometry vacuum line, 3°	1.99	0.88
DPA ⁻	-1.4 reversal coulometry N ₂ over surface, 25°	1.16	0.69

^a The solution was 30-50 ml of DMF containing 0.1 M TBAI; the cathode was a mercury pool with a projected area of about 10 cm² and the anode was a silver wire isolated by a sintered-glass disk and an agar plug. Electrolysis times were 30-40 min. ^b DPA = 9,10-diphenylanthracene, A = anthracene. ^c Conditions: vacuum line at 25°, unless noted otherwise.

This behavior is usually characteristic of a catalytic process in which the product of the electrode reaction undergoes a chemical reaction leading to regeneration of the original species. When the nitrogen gas was only passed over the surface of the solution during the electrolysis (after preliminary deaeration), a lower steady-state current was attained, although the n_{app} value was still considerably larger than 1. When the coulometric experiments were carried out at low tem-

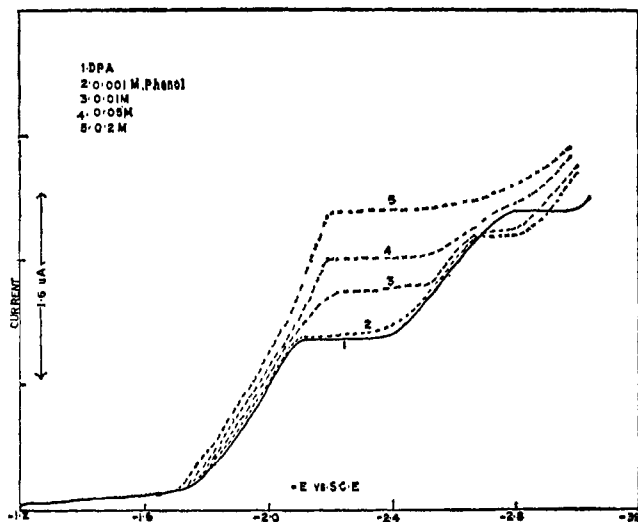


Figure 4. Polarograms for reduction of 1.0 mM 9,10-diphenylanthracene in 0.1 M TBAI in DMF with the addition of various amounts of phenol.

perature or on the vacuum line (see Experimental Section), n_{app} values close to the expected value of 1.0 were obtained. The nature of the secondary process is not known, although it probably involves a trace component in the gas stream. Small amounts of oxygen might be involved by the following process



followed by reaction of O_2^- with the solvent. The potential for the reduction of O_2 to O_2^- is about -0.8 v *vs.* sce,¹¹ so that DPA^- is a sufficiently strong reductant for reaction 4. On a vacuum line, after the DPA^- had been produced, passage of purified helium (passed through anhydrous magnesium perchlorate, hot copper turnings, and activated carbon at liquid nitrogen temperatures) over the surface of the solution produced little or no decomposition of the radical. The radical produced on the vacuum line or at low temperatures was quite stable and could be transferred to an esr sample cell and observed with little change in concentration over several hours. Further evidence for the stability of DPA^- was obtained by reversal coulometry experiments,¹² where the radical was produced and then oxidized at a controlled potential of -1.40 v *vs.* sce (Table III). Values of n_{app} near 1 were obtained for the oxidation for a total time of the reduction and oxidation of 60 to 80 min.

These results differ from those obtained by Pointeau, Favade, and Delhaes,¹³ who electrogenerated anthracene radical anion in a microcell contained inside an esr cavity, and observed the decay of the radical anion. These authors found a second-order decay of anthracene radical anion with a half-life, at concentrations similar to those in this study, of 10 to 15 min. Radicals produced and introduced into the esr cavity by the technique described above were much more stable than this. In experiments in which a small amount of air was introduced in filling the esr sample cell, the radical showed appreciably faster decay. For example,

(11) D. L. Maricle and W. G. Hodgson, *Anal. Chem.*, **37**, 1562 (1965).

(12) A. J. Bard and S. V. Tatwawadi, *J. Phys. Chem.*, **68**, 2676 (1964).

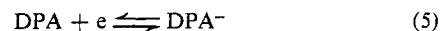
(13) R. Pointeau, J. Favade, and P. Delhaes, *J. Chim. Phys.*, **1129** (1964).

in one experiment, after an "induction period" of about 30 min, the radical decayed by a first-order reaction with a half-life of about 45 min.

These results also differ from previous coulometric results⁴ which yielded an n_{app} value near 2. However, small amounts of proton donors, probably including water, lead to protonation of the radical, followed by a one-electron reaction, leading to an over-all two-electron reaction (see entry in Table III). Coulometric reduction at potentials on the second plateau of the polarographic wave (-2.60 v *vs.* sce) yields an n_{app} value near 2, as expected.

Voltammetry of DPA^- . Polarograms for a DPA^- solution in various stages of reduction are shown in Figure 3. The polarogram for the solution containing DPA^- (curve 2, Figure 3) shows an anodic wave with a large maximum which abruptly drops to near the expected diffusion value near the potential of the electrocapillary maximum (ecm) in this medium, -0.70 v *vs.* sce. The shape of the anodic wave is very similar to that found by Okinaka, Kolthoff, and Murayama¹⁴ for the anodic oxidation of zinc amalgam and probably can be explained by a similar mechanism (see Discussion). The reduction wave for DPA^- to DPA^{2-} occurs at the same potentials as the second polarographic wave in the reduction of DPA . Further reduction at a potential of -2.60 v *vs.* sce results in the disappearance of all waves (curve 3) because of the rapid protonation of DPA . Cyclic voltammetry of a DPA^- solution is shown in Figure 5 (curve 2). The very large anodic current for the oxidation is due to the same stirring effect as has been previously described.

Effect of Proton Donors. The polarographic behavior of DPA in the presence of a proton donor, such as phenol, is essentially as previously described for other aromatic hydrocarbons by Hoijtink and co-workers^{15a} and Given and Peover.^{15b} Typical results are shown in Figure 4. With addition of a proton donor, HX, the reaction at the first plateau becomes an ece-type reaction



probably followed by protonation of DPAH^- . Since DPAH is even easier to reduce than DPA , this leads to an increase in the height of the first wave, until, at high enough concentrations of HX, only a single two-electron wave is obtained. Coulometric reduction in the presence of phenol at a potential of -2.0 v *vs.* sce yields an n_{app} of 2 (Table III).

To investigate further the effect of proton donors and to test if any of the protonated species could be observed electrochemically, the effect of addition of hydroquinone to a solution of DPA^- was examined.¹⁶

(14) Y. Okinaka, I. M. Kolthoff, and T. Murayama, *J. Am. Chem. Soc.*, **87**, 423 (1965).

(15) (a) G. J. Hoijtink, J. Van Schooten, E. DeBoer, and W. I. Aalbersberg, *Rec. Trav. Chim.*, **73**, 355 (1954); (b) P. H. Given and M. E. Peover, *J. Chem. Soc.*, 385 (1960); *Collection Czech. Chem. Commun.*, **25**, 3195 (1960).

(16) Although phenol has been shown to be a good protonating agent and has been used successfully in these kind of measurements,^{15b} we found it difficult to remove the last traces of water, oxygen, or other impurities which tended to destroy the radical. Hydroquinone apparently works as well; it shows no reduction or oxidation waves in the region of interest.

The results are shown in Figure 5. An explanation of the curves follows. Curve 1 is the usual cyclic voltammogram for DPA; i_{pc} was $21.8 \mu\text{a}$. Curve 2 is the oxidation peak for DPA^- after a controlled potential coulometric reduction. Upon addition of hydroquinone, protonation of DPA^- , reaction 6, occurs. However since the E° of the DPAH^- - DPAH^- couple is more positive than that of the DPA - DPA^- couple, DPA^- is a strong enough reductant to reduce DPAH , and the protonation is immediately followed by



so that the over-all effect of adding HX can be considered to be



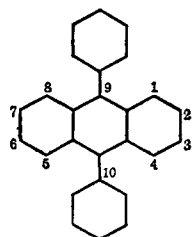
Curve 3 shows the effect of addition of an amount of hydroquinone insufficient to consume all of the radical. The new oxidation wave which appears at -0.69 v *vs.* sce may be the oxidation of DPAH^- to DPAH . The expected E° for the DPAH - DPAH^- couple on the basis of MO calculations is -0.85 v *vs.* sce (see Discussion). When 10.36 mmoles of hydroquinone per liter has been added, the blue color of the radical DPA^- has completely disappeared; see curve 4, showing only a reduction wave of DPA to DPA^- ($i_{pc} = 8.8 \mu\text{a}$) and oxidation waves (on reversal) of DPA^- and DPAH^- ($7.5 \mu\text{a}$). According to the proposed mechanism, the concentration of DPA at this stage should be half of the original amount, so that i_{pc} should be about $10.9 \mu\text{a}$. The lower value actually obtained may be due to some continued protonation of DPAH^- to DPAH_2 either by a slow continuous reaction or in the presence of a local excess of hydroquinone during its addition to the solution. Curve 5 shows the result of the addition of a large excess of hydroquinone, 0.47 M . All DPAH^- is now protonated, and the wave due to the reduction of DPA ($i_{pc} = 16.2 \mu\text{a}$) is twice as high as in curve 4, since the reduction is proceeding *via* a two-electron process (reactions 5, 6, and 7). The reverse wave at these potentials has disappeared.

Discussion

MO Correlations. It has been shown⁸ that the polarographic $E_{1/2}$ can be correlated to the energy of the lowest available orbital, by equations of the form

$$E_{1/2} = m_{m+1}\beta + c \quad (10)$$

where m_{m+1} is the root of the MO secular equation corresponding to the lowest nonoccupied π orbital, β is the effective resonance integral for the series of compounds, and c is taken as a constant for a series of hydrocarbons. The correlation for DPA is interesting since the phenyl groups in the 9- and 10-positions do not lie in the plane of the anthracene ring because of



steric repulsion between the *ortho* hydrogens on the phenyls and the hydrogens on the anthracene nucleus

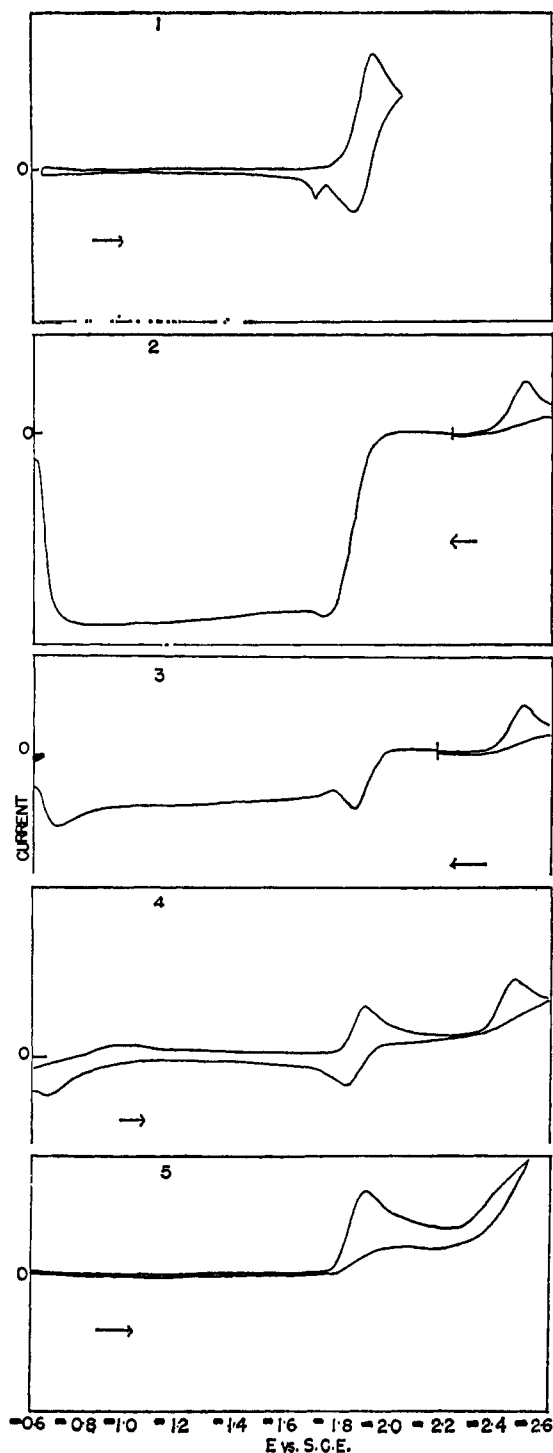


Figure 5. Cyclic voltammetry of 2.6 mM 9,10-diphenylanthracene and its radical anion in 0.1 M TBAI in DMF with the addition of varying amounts of hydroquinone: (1) DPA , before reduction; (2) DPA^- ; (3) $\text{DPA}^- + 4 \text{ mmoles}$ of hydroquinone/l.; (4) $\text{DPA}^- + 10.4 \text{ mmoles}$ of hydroquinone/l.; (5) $\text{DPA} + 0.47 \text{ M}$ hydroquinone. The current sensitivity in curve 2 is twice that in curves 1, 3, 4, and 5. Arrow indicates direction of initial scan.

at positions 1, 4, 5, and 8. The effect of this non-planarity is to lower the β value between the phenyl rings and the anthracene nucleus. On the basis of an optimal assignment of relative electron densities calculated by Hückel MO theory to the esr spectrum of DPA^- , a β value of 0.37 was found.¹⁷ This value

(17) L. O. Wheeler, K. S. V. Santhanam, and A. J. Bard, *J. Phys. Chem.*, **70**, 404 (1966).

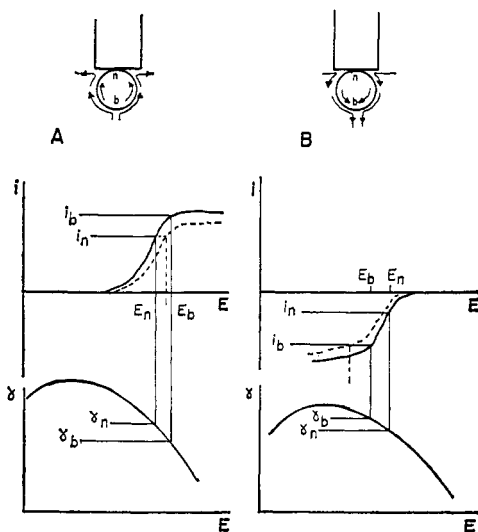


Figure 6. Representation of streaming occurring at mercury drop electrode during (A) reduction and (B) oxidation at potentials more negative than the ecm. E_n , i_n , and γ_n are the potential, current density, and surface tension at the neck of the drop, respectively; E_b , i_b , and γ_b refer to the bottom of the drop. Dashed curves indicate effect of concentration depletion on E .

corresponds to an angle between the phenyl ring and the anthracene nucleus, θ , of about 68° (assuming β varies as the cosine of θ ¹⁸), and a value of m_{m+1} of -0.396 . Using Hoijtink's correlation values of $c = -0.85$ and $\beta = 2.54 \pm 0.090$ ^{3c} in (10) leads to a predicted value of $E_{1/2}$ of -1.855 ± 0.036 , in excellent agreement with the measured value of -1.84 .

The value for the $E_{1/2}$ for DPAH can be calculated assuming that protonation of DPA^- occurs in the 9- or 10-position (the position of highest electron density).³ If protonation occurs at the 9-position, conjugation with the phenyl ring in this position no longer occurs and the resulting DPAH effectively has the same energy levels as triphenylmethyl. Since for this molecule $m_{m+1} = 0$, one predicts an $E_{1/2}$ of -0.85 v vs. sce for DPAH.

Anodic Streaming. The streaming phenomenon which occurs during oxidation of DPA^- in cyclic voltammetric experiments, and which is especially pronounced in polarography and cyclic voltammetry in DPA^- solutions, can be explained by the theory presented for polarographic maxima of the first kind.^{14,19} A schematic representation of the situation leading to streaming phenomena is shown in Figure 6 and is described below. Because of shielding of a portion of the drop by the base of the capillary, the current density differs at different locations around the drop and is lower at the neck or point of attachment of the drop than at the base.²⁰ This uneven current density distribution will cause an uneven potential distribution over the solution side of the electrode-solution interface. For an oxidation, the potential at the bottom

of the drop, E_b , will always be more positive than the potential at the neck of the drop, E_n . For a reduction, E_b is more negative than E_n . Since the surface tension of the mercury-solution interface, γ , is a function of potential, it will differ at the base and the neck. For reductions at potentials negative to the ecm (e.g., aromatic hydrocarbons), the surface tension at the neck, γ_n , will be larger than the surface tension at the base, γ_b . For oxidations in this potential region, $\gamma_b > \gamma_n$. Tangential stirring occurs in the direction from lower to higher γ ,²¹ so that for a reduction in this region, stirring will be in an upward direction from bottom to neck; for an oxidation stirring will be downward from neck to bottom. Therefore stirring occurs during both the reduction and oxidation reactions at the mercury drop. Abrupt maxima and more vigorous stirring are observed during anodic reactions rather than during cathodic ones because of concentration changes occurring as the solution passes over the electrode surface, as was pointed out by Levich.^{19a} In the case of reductions (upward streaming), the solution passes from the bottom toward the neck, so that the concentration at the neck of the electrode is somewhat smaller than that in the bulk. This tends to make the potential at the neck more negative, the difference in potential between bottom and neck, $\Delta\psi$, smaller, so that the degree of stirring is reduced. On the other hand, for oxidations (downward stirring) the concentration is depleted at the bottom, and the potential at the bottom tends to be more positive, increasing $\Delta\psi$ and the extent of stirring. The effects on the positive side of the ecm are the reverse of those just described; cathodic stirring will be more pronounced than anodic stirring in this potential region. These stirring effects are readily observable during voltammetry of DPA, since the radical DPA^- is colored a deep blue. During reduction at a hmde, a steady streaming of DPA^- outwards from the top of the capillary is observed, as would be the case for an upwards streaming of the solution. During oxidation of DPA^- a violent downward and outward streaming of the solution is observed. One would predict from the explanation given that polarographic oxidations of hydrocarbon and other radicals occurring at potentials negative to the ecm will frequently show maxima and stirring behavior. Indeed Maricle and Hodgson recently found this to be true for the oxidation of O_2^- (and other radical anions).¹¹ These effects should be especially pronounced in nonaqueous solutions of rather high resistance, R , since¹⁴

$$\Delta\psi = R\Delta i \quad (11)$$

so that large potential differences will arise even for small differences in current densities at different regions of the drop, Δi .

The ramifications of this stirring in electrochemical studies at mercury electrodes in nonaqueous solutions are clear. Diffusion coefficients, D , determined by electrochemical studies at mercury electrodes based on calculations assuming only mass transfer by diffusion may be significantly in error. Recently a comparison of D values determined by electrochemical and tracer methods was made,²² where it was observed that

(21) Reference 19a, p 380.

(22) T. A. Miller, B. Prater, J. K. Lee, and R. N. Adams, *J. Am. Chem. Soc.*, **87**, 121 (1965).

(18) M. J. S. Dewar, *J. Am. Chem. Soc.*, **74**, 3345 (1952).

(19) (a) V. G. Levich, "Physicochemical Hydrodynamics," Prentice-Hall, Englewood Cliffs, N. J., 1962, pp 561-590; (b) M. von Stackelberg and R. Doppelfeld, *Advan. Polarog. Proc. Intern. Congr.*, 2nd Cambridge, Engl., 1959, **1**, 68 (1960).

(20) R. De Levie (*J. Electroanal. Chem.*, **9**, 331 (1965)) has recently pointed out that in a dme uneven current distribution may also arise because of eccentric growth of the mercury drop. At a hmde, however, nonuniformity in the current distribution must arise from other sources, such as shielding.

electrochemically determined diffusion coefficients were almost always much larger than those determined by tracer techniques and seemed to be less probable values. The explanation advanced for these differences²² was based on the occurrence of rapid following reactions (e.g., protonation) leading to an erroneous assignment to the effective number of electrons involved in the electrode reaction. An alternate explanation based on the occurrence of stirring during the reactions can also be presented, since in many cases the extent of following reactions during the time of the electrochemical measurement (3–5 sec) is known to be small. The stirring may also lead to misinterpretation of mechanisms of reactions based on cyclic voltammetric or chronopotentiometric data assuming diffusion control. For example, even at times as short as 25 msec reversal waves were less than the expected one-third for chronopotentiometric reduction of DPA at a hmde, even though the conditions were such that the DPA⁻ was clearly stable as determined by voltammetry at platinum electrodes and coulometry.

Experimental Section

The final purification of the solvent and the filling of the electrochemical cell were performed on a vacuum line; the cell and a schematic diagram of the vacuum line are shown in Figure 7. The vacuum line was conventional and was evacuated to about 10^{-5} mm. The cell was connected to the line by means of an O-ring ball joint, and had provision for introduction of a dme, hmde, or platinum electrode through a standard taper ground joint on the top of the cell (not shown) and for a reference electrode and auxiliary electrode chamber, also through ground joints. A mercury pool at the bottom of the cell was used in coulometry. The DMF was stored overnight over anhydrous copper sulfate and distilled under vacuum into an intermediate storage flask, in which it was stored over molecular sieve until use. The mercury and supporting electrolyte with or without DPA was introduced into the cell which was cooled with liquid nitrogen and evacuated several times to remove traces of air and water. The cell was then cooled with liquid nitrogen and DMF was distilled into it from the storage flask. This was thawed and refrozen at least once. Some experiments were with the cell under vacuum, *i.e.*, at the vapor pressure of solution. In most experiments the cell was brought to atmospheric pressure by introducing helium through the vacuum line. The helium (99.995% pure) was passed successively through anhydrous magnesium perchlorate, copper turnings (heated to 350°), and activated charcoal at liquid nitrogen temperature and finally to the

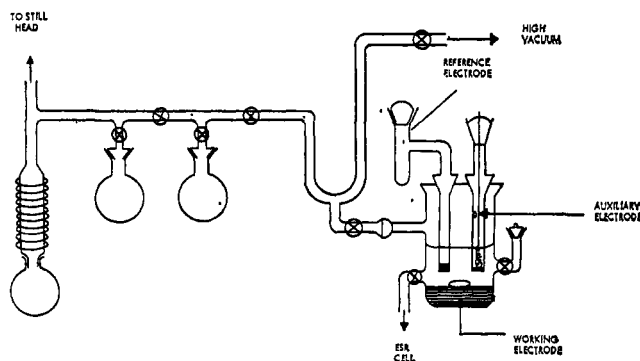


Figure 7. Schematic diagram of vacuum line and electrolysis cell.

vacuum line. Connection to the tank valve was made with copper tubing, which was connected to the glass tubing by a Kovar-glass seal. The use of rubber or Tygon tubing in this line introduced impurities. The auxiliary electrode was a silver wire. The reference electrode was an aqueous sce connected *via* an agar plug and sintered glass disk to a salt bridge containing the test solution and closed at the end by a fine porosity sintered glass disk. The failure to use an intermediate salt bridge would sometimes lead to the introduction of potassium ion and water into the cell, although an aqueous sce containing a fresh agar-KNO₃ plug could sometimes be used without deleterious effects. Stirring was by means of a magnetic stirrer.

The voltammetric experiments were carried out using a multi-purpose instrument employing operational amplifier circuitry with a three-electrode configuration, similar to those discussed in the literature.²³ Controlled potential coulometry was carried out using a previously described apparatus.²⁴

DPA was obtained from Aldrich Chemical Co. and was used without further purification; the melting point of this material was within 1° of the literature value. TBAI was obtained from Southwestern Analytical Chemicals (Austin, Texas).

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(24) A. J. Bard, *Anal. Chem.*, **35**, 1121 (1963).