

Electrochemistry in Media of Intermediate Acidity. VII.¹ Redox Equilibria of Anthracene Cation Radicals, Dications, and Cationic Addition Products

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Abstract: The redox behavior of anthracene, 9-phenylanthracene, and several 9,10-disubstituted anthracenes was examined in both acidic and aprotic media. Reversible or quasireversible cation radical-dication redox couples were observed for the 9,10-diarylanthracenes. In the presence of trifluoroacetic acid the dications of 9,10-disubstituted anthracenes react to give 9-trifluoroacetoxy substituted cations. Similar cations substituted at the 9 position with hydroxy and methoxy were observed and their spectral data recorded. Arenium ions (protonated anthracenes) were found to undergo anodic oxidation about 1.5 V more anodic than the parent bases.

The anodic oxidation of anthracenes has been studied extensively and they have been used as model compounds in order to establish the reaction pathways of anodically generated intermediates. Thus, the first indication of the mechanism of anodic substitution emerged from Lund's study of the anodic pyridination of anthracene² in which he observed that the two-electron oxidation of anthracene in the presence of pyridine was accompanied by the formation of a 9,10-dipyridinium salt. Later, the oxidation of anthracene to bianthrone was observed in acetonitrile³ and a mechanism was postulated involving the electrochemical formation of 9-anthrone followed by air oxidation.⁴ Coulometric and product studies⁵ later showed that bianthrone is the electrochemical product and detailed studies were made of several anodic reactions of anthracenes including hydroxylation,⁶ acetoxylation,⁷ and methoxylation.⁸

The anthracenes, particularly 9,10-diphenylanthracene (DPA), were instrumental in establishing the one-electron oxidation pathway of aromatic hydrocarbons in aprotic media. The latter was firmly established by three groups working independently in different solvents, acetonitrile,⁹ dichloromethane,¹⁰ and nitrobenzene.¹¹ DPA was also used as a model substrate to provide convincing evidence for the ECE mechanism for anodic substitution reactions.¹² A second irreversible oxidation of DPA was observed in the voltammetric studies⁹⁻¹¹ which was attributed to the oxidation of the initially formed cation radical to a reactive dication. Sioda¹³ found that oxidation of DPA in acetonitrile at

the potential of the second oxidation stage resulted in the formation of 9,10-diphenyl-9,10-dihydroxy-9,10-dihydroanthracene which he proposed formed by reaction of the dication with water. The reaction of the DPA dication with an unspecified nucleophile to give a short-lived cationic addition product was proposed on the basis of the observation of a voltammetric peak during cyclic voltammetry of DPA in several solvent-electrolyte systems¹⁴ which was cited in support of the ECE mechanism. An alternative mechanism for anodic pyridination of DPA has been proposed, involving disproportionation of the anodically generated cation radical to a dication which reacts with the nucleophile¹⁵ in analogy to the mechanism proposed for the hydroxylation of the thianthrene cation radical.¹⁶ The disproportionation mechanism has been questioned in both the latter cases.^{17,18}

All previous voltammetric studies have concluded that aromatic dications are extremely reactive species and reversible cation radical-dication redox behavior has therefore only been observed in very few cases.^{19,20} This, as well as the absence of convincing evidence for the existence of the cationic ECE product of anodic substitution, leaves an uncertainty in the mechanism of cation radical reactions. Without more clearly defined voltammetric data, equilibrium constants for disproportionation cannot be determined and, thus, this mechanism remains a possibility. Here we report reversible oxidation of anthracene cation radicals to dications and present definitive spectral evidence for the nature of the ECE product of several anthracenes.

Experimental Section

Apparatus. Voltammetry was carried out with a three-electrode multi-purpose voltammetry unit constructed by Mr. S. Laursen after a design of Dr. W. White, University of Kansas. Voltammograms were recorded on Watanabe x-y recorders, Model WX 431.

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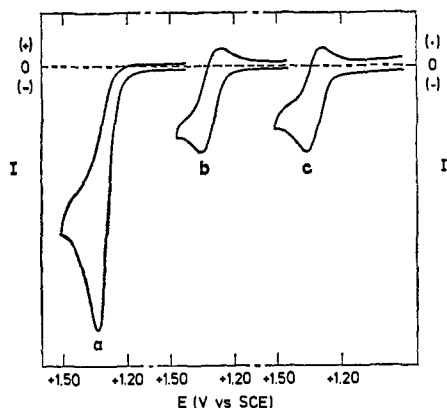


Figure 1. Cyclic voltammograms of anthracene (1.0 mM) in (a) dichloromethane, (b) dichloromethane over neutral alumina, and (c) dichloromethane-TFA-TFAn (18:1:1). Supporting electrolyte was *n*-Bu₄NBF₄ (0.2 M); voltage sweep rate, 86 mV/sec.

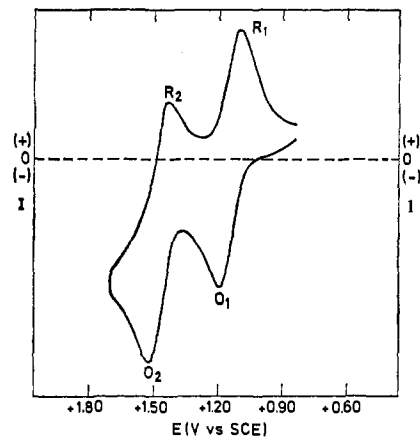


Figure 2. Cyclic voltammogram of DAA (0.5 mM) in CH₂Cl₂-TFAn-TFA (45:5:1) containing *n*-Bu₄NBF₄ (0.2 M); voltage sweep rate, 86 mV/sec.

Constant-current electrolyses were conducted with Juul Electronic power supplies, Model B 41. The cell used for voltammetry and coulometry was a two compartment enclosed vessel with anode and cathode chambers separated by sintered glass (G-4). The temperature was controlled from -80 to +40° with a Ultra Kryostat, UK 80 DW.

Platinum gauze electrodes were used for coulometry and Beckman platinum buttons (No. 39273) were used as working electrodes for voltammetry.

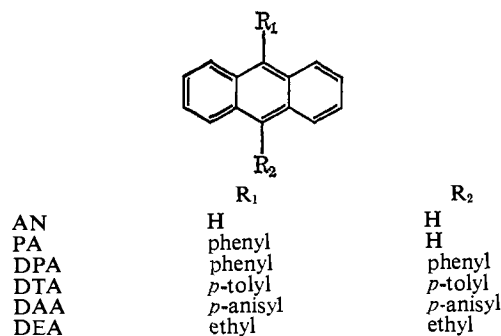
Uv and visible spectra were recorded on a Unicam SP 1800 ultraviolet spectrophotometer.

Reagents. Acetonitrile was purified by the method described by Moe.²¹ Trifluoroacetic acid (TFA) was Schuchardt, Munich, containing less than 0.5% water and was used without further purification. Trifluoroacetic anhydride (TFAn) was Fluka (purum) and was used without further purification. All other solvents were reagent grade and purified by passing through a column of neutral alumina (Woelm, W200). The supporting electrolyte was tetra-*n*-butylammonium fluoroborate.

9,10-Disubstituted anthracenes were prepared by reaction of the appropriate Grignard reagent with anthraquinone and reduction of the resulting 9,10-diol with phenylhydrazine in acetic acid²² (the structures were confirmed by mass spectrometry). 9,10-Diphenyl-9,10-dimethoxy-9,10-dihydroanthracene was prepared by treatment of the diol with dilute methanolic sulfuric acid.²³

Results

The anthracenes studied are



Reversible Voltammetry of Anthracene and 9-Phenylanthracene. The voltammogram of AN in dichloromethane containing *n*-Bu₄NBF₄ (0.2 M) recorded at a voltage sweep rate of 86 mV/sec is shown in Figure 1a. Figure 1b is the voltammogram of a portion of the same solution in which neutral alumina was suspended before

recording the voltammogram. Figure 1c is the voltammogram of another portion of the solution to which TFA (5%) and TFAn (5%) were added. The irreversible oxidation peak (Figure 1a) corresponds to a cascade of electron transfers coupled with chemical reactions producing a complex product mixture of the kind formed when the reaction is conducted in wet acetonitrile.⁵ On the other hand, the voltammograms recorded in the presence of the very effective nucleophile scavengers, alumina (Figure 1b) and TFAn (Figure 1c), indicate reversible one-electron transfers giving the anthracene cation radical, which is stable under the conditions of slow sweep cyclic voltammetry. Completely reversible voltammograms were observed for PA in either acetonitrile or dichloromethane containing the nucleophile scavengers.

Dications by Two Consecutive One-Electron Oxidations of 9,10-Diarylanthracenes. The voltammetric behavior of DAA in CH₂Cl₂-TFAn-TFA (45:5:1) is illustrated in Figure 2. On the anodic sweep, two oxidation peaks were observed (O₁ and O₂) and their reduction counterparts (R₁ and R₂) were seen on the cathodic segment of the cycle. The peak separations for both couples were about 70 mV and the current functions,²⁴ $i_p/v^{1/2}C$, were constant for both oxidation steps indicating that both of the couples are reversible one-electron transfers. Potential and current function data are summarized in Table I.

The one-electron charge transfers are further illustrated by the constant-current coulometry⁵ of DAA in the same solvent (Figure 3). The concentrations of substrate, cation radical, and dication were monitored by the limiting currents for the various species at a solid micro electrode in stirred solution. Before oxidation DAA showed the voltammogram in Figure 3a. After 1.0 min at 25 mA, the limiting currents for both DAA and DAA^{•+} were measured (Figure 3b). This procedure was repeated again after 2.0 and 3.0 min and a plot of i_L for either DAA or DAA^{•+} vs. time showed that the reaction was complete after the passage of 1 faraday/mol (3.22 min required at 25 mA to oxidize 0.05 mmol). Figures 3d-g illustrate the procedure for the oxidation of DAA^{•+} to DAA²⁺. Once again 1.0 faraday/mol was consumed.

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Table I. Voltammetric Data for the Oxidation of DAA in CH₂Cl₂-TFAn-TFA (45:5:1)

Sweep Rate (mV/sec)	E_{1a}^a	E_{1c}^a	i_{1a}^b	$i_{1a}/v^{1/2}C$	E_{2a}^a	E_{2c}^a	i_{2a}^b	$i_{2a}/v^{1/2}C$
43	1.19	1.12	19	5.6	1.51	1.45	16	4.8
86	1.19	1.12	26	5.6	1.52	1.45	24	5.2
105	1.19	1.12	28	5.4	1.52	1.45	27	5.4
161	1.20	1.12	35	5.4	1.52	1.45	34	5.4
210	1.20	1.11	39	5.4	1.53	1.44	38	5.2

^a Measured vs. Ag|Ag⁺ (0.1 M), expressed vs. the saturated aqueous calomel electrode (sce). ^b Current in μ A for a substrate concentration of 0.5 mM.

Table II. Oxidation of Diarylanthracenes to Cation Radicals and Dications^a

Solvent	DAA				DTA				DPA			
	E_{1a}	E_{1c}	E_{2a}	E_{2c}	E_{1a}	E_{1c}	E_{2a}	E_{2c}	E_{1a}	E_{1c}	E_{2a}	E_{2c}
Acetonitrile	1.15	1.09	1.37	1.30	1.19	1.13	1.63 ^b		1.23	1.17	1.69 ^b	
Nitrobenzene	1.16	1.10	1.42	1.35	1.22	1.15	1.72 ^b		1.27	1.21	1.78 ^b	
Dichloromethane	1.18	1.12	1.48	1.41	1.23	1.16	1.75 ^b				<i>b</i>	
CH ₂ Cl ₂ -TFAn-TFA ^c	1.19	1.12	1.52	1.45	1.23	1.16	1.79 ^d		1.28	1.21	1.90 ^d	
CH ₂ Cl ₂ -FSO ₃ H ^e	<i>f</i>				1.22	1.15	1.77	1.69	1.27	1.20	1.90	1.82

^a Supporting electrolyte was *n*-Bu₄NBF₄ (0.2 M). Potentials are vs. sce at 86 mV/sec. ^b Quasireversible peak. ^c 45:5:1. ^d The dication reacts with trifluoroacetate ion. See the following section. ^e 100:1, *t* = -34°. ^f DAA is sulfonated by FSO₃H.

The visible spectrum of DAA²⁺ prepared in the above manner showed an absorption maximum at 520 nm (ϵ 40,600). The spectrum of DAA²⁺ generated independently by dissolution of 9,10-di-*p*-anisyl-9,10-dihydroxy-9,10-dihydroanthracene in methanesulfonic acid was identical with the anodically generated species.

The dications of DPA and DTA are so reactive, that it was not possible to obtain two reversible couples for these compounds in CH₂Cl₂-TFAn-TFA (45:5:1). Reversible cation radical-dication redox behavior was observed in CH₂Cl₂-FSO₃H (100:1)²⁵ at -34°.

In acetonitrile, nitrobenzene, and dichloromethane at room temperature, reversible (DAA) or quasireversible (DPA and DTA) oxidation of the cation radicals to the corresponding dications was observed.²⁶ The data are summarized in Table II.

Reaction of Anthracene Dications with Nucleophiles. The cation radicals of DPA, DTA, and DEA are all oxidized irreversibly in TFA or CH₂Cl₂-TFAn-TFA (45:5:1). The reaction of DPA²⁺ with TFA is illustrated by the voltammograms of Figure 4. The cyclic voltammogram of DPA in the above solvent shows a reversible one-electron peak at +1.28 V (O₁)²⁷ and a second irreversible peak (O₂) at +1.90 V. On the cathodic going sweep, the cation radical reduction peak R₁ appeared at +1.21 V and a new peak (R_C)²⁸ was observed at +0.80 V. Constant-current electrolysis (25.0 mA) was carried out until 1.0 faraday/mol had been consumed leaving a solution of DPA^{·+}, as was shown

(25) The effect of FSO₃H is probably due to protonation of nucleophilic impurities in the solvent; protonation of the substrates requires approximately 7% FSO₃H. See also the last section.

(26) In order to observe reversible behavior in these solvents, it was necessary to make the voltammetric measurements with solutions in contact with a drying agent, neutral alumina, in the manner recently described.²⁰

(27) The potentials given in *J. Electroanal. Chem.*, **38**, App. 9 (1972) are all 0.40 V too low due to an error in the potential of the reference electrode.

(28) The nature of the reduction peak, R_C, is dependent upon the nucleophiles in solution and is due to the reduction of cations of structure 5. From here on this reduction peak will be identified according to the nature of R (structure 5) assuming that R is derived from the best nucleophile in solution. Thus, when TFA is the only nucleophile present we label the reduction peak R_C^{TFA} or when the solution contains water R_C^H or methanol R_C^{Me}.

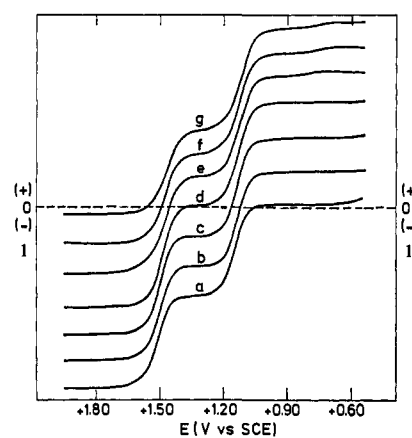


Figure 3. Stirred solution voltammograms of DAA during constant-current coulometry in CH₂Cl₂-TFAn-TFA (45:5:1). Time of oxidation at 25.0 mA (in min): (a) 0, (b) 1.0, (c) 2.0, (d) 3.22, (e) 4.22, (f) 5.22, (g) 6.22.

by the fact that R₁ (Figure 4b) was the same height as O₁ (Figure 4a) before oxidation. The fact that R_C^{TFA} of this solution was still small indicates the species giving rise to this reduction is not formed from the cation radical. Electrolysis for an additional 1.0 faraday/mol resulted in almost complete consumption of the cation radical as shown by the height of O₂ and R₁, for oxidation and reduction, respectively, of the cation radical being very small. What is remarkable is that R_C^{TFA} grew to almost double the original height of O₁ showing that it is due to a product stable in the medium and corresponds to a two-electron reduction. Constant-current coulometric reduction of the latter solution resulted in the consumption of 2.0 faradays/mol and the quantitative regeneration of DPA as shown by the magnitude of the voltammetric peak current (O₁) as compared to the original solution of DPA.

The potential of R_C^{TFA} is +0.80 V. When a solution identical with that used in Figure 4a was treated incrementally with water, the reduction peak at +0.80 V first began to broaden and then a new peak (R_C^H) began to appear at +0.65 V. When the water concentration

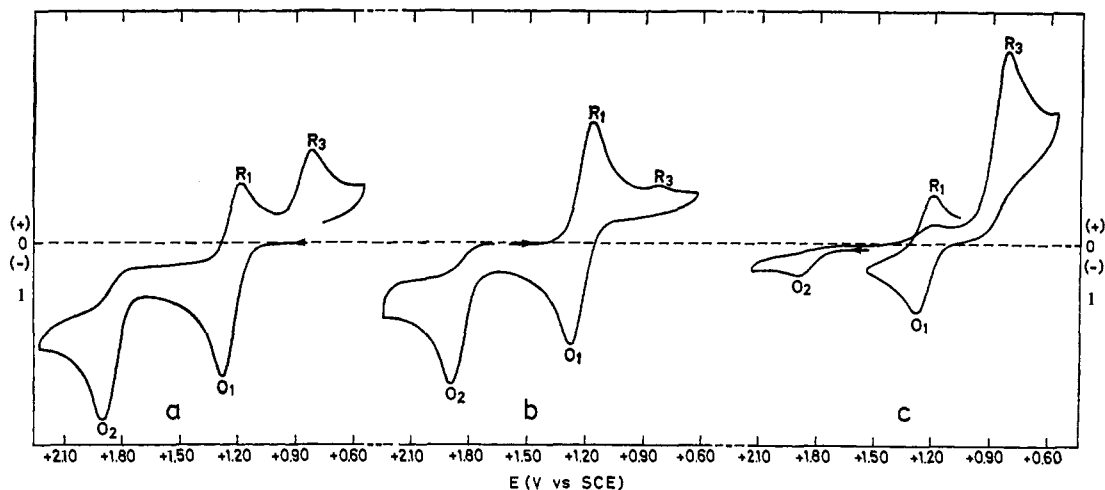


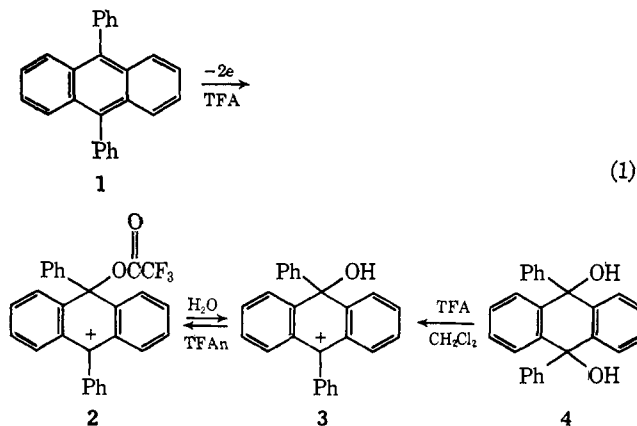
Figure 4. Cyclic voltammograms of (a) DPA (1.0 mM), (b) DPA \cdot^+ (1.0 mM), (c) (DPA-OCCF $_3$) $^+$ (1.0 mM) in CH $_2$ Cl $_2$ -TFAn-TFA (45:5:1) containing *n*-Bu $_4$ NBF $_4$ (0.2 M); voltage sweep rate, 86 mV/sec.

Table III. Monocations Formed by Reaction of Anthracene Dications with TFA or H $_2$ O a

Substrate	Peak potentials							
	TFA b				H $_2$ O c			
	O $_1$	R $_1$	O $_2$	R $_C^{TFA}$	O $_1$	R $_1$	O $_2$	R $_C^H$
DAA	1.18 d	1.10 d	1.44 d	0.57 d	1.17	1.10	1.47	0.54
DTA	1.23	1.16	1.79	0.76	1.21	1.15	1.73	0.60
DPA	1.28	1.21	1.90	0.80	1.25	1.19	1.84	0.65
DEA	1.13 e	1.06 e	1.88 e	0.68 e				

a Supporting electrolyte was *n*-Bu $_4$ NBF $_4$ (0.2 M). Potentials are vs. sce at 86 mV/sec. b Solvent system: CH $_2$ Cl $_2$ -TFAn-TFA (45:5:1). c Solvent system: CH $_2$ Cl $_2$ -TFA (5:1) containing 1% water. d Solution containing potassium trifluoroacetate (saturated). e Solvent system: CH $_2$ Cl $_2$ -TFA (2:1).

was 0.6 M, R $_C^{TFA}$ was completely gone leaving only R $_C^H$. Thus the species undergoing reduction is different in the presence of water; however, R $_C^{TFA}$ could be completely restored by the addition of TFAn which consumed the water. The species giving rise to R $_C^H$ was also formed on dissolution of 9,10-dihydroxy-9,10-diphenyl-9,10-dihydroanthracene in CH $_2$ Cl $_2$ -TFA (5:1) as shown both by comparison of the visible spectra (λ_{max} 452 nm (ϵ 23,400)) and the cyclic voltammograms. Treatment of the latter solution with TFAn resulted in the disappearance of R $_C^H$ in the voltammogram accompanied by the appearance of R $_C^{TFA}$. Thus, the species giving rise to R $_C^{TFA}$ and R $_C^H$ are **2** and **3** (eq 1).



The behavior of DTA parallels that of DPA while DEA forms a cation analogous to **2** of limited stability. Under the conditions where the other compounds give

monocations such as **2**, DAA gives a dication (previous sections) and R $_C^{TFA}$ cannot be detected in the cyclic voltammogram. However, if trifluoroacetate ion is added to the solution, R $_C^{TFA}$ is observed with DAA. Voltammetric data under conditions where monocations analogous to **2** are formed are summarized in Table III.

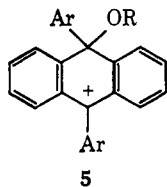
The potential of R $_C^{TFA}$ was found to be strongly dependent on the acidity of the solvent system, and therefore the values were very difficult to reproduce. In Table IV are summarized the potentials of R $_C^{TFA}$ rela-

Table IV

Solvent system	R $_1$ - R $_C^{TFA}$, V
TFA-TFAn (1:1)	0.275
TFA	0.320
CH $_2$ Cl $_2$ -TFA (5:1)	0.390
CH $_2$ Cl $_2$ -TFAn-TFA (45:5:1)	0.410
TFA-H $_2$ O (9:1)	0.410

tive to R $_1$ for DPA in five different solvent systems, where the cation formed was derived from TFA.

Formation of Substituted Anthracene Monocations in Acidic Media. 9,10-Diaryl-9,10-dihydroxy-9,10-dihydroanthracenes undergo an ionization reaction upon dissolving in TFA or dichloromethane-TFA to give the monocations, **5** (R = H), which revert to the corresponding cation radical on standing. The lifetime of these cations can be increased to almost stability by adding approximately 1% water to the solvent system. With DAA **5** is in all cases very unstable, the first



species detected being DAA^{2+} in a water-free system. Spectral data of the monocations are given in Table V.

Table V. Spectral Data for Anthracene Monocations^a

Structure of 5		λ_{max} , nm	ϵ^b
Ar	R		
Ph	H	452	23,400
Ph	COCF_3	429	26,400
<i>p</i> -Tol	H	442, 501	24,200, 14,300
<i>p</i> -Tol	COCF_3	430, 521	28,400, 17,200
<i>p</i> -An	CH_3^c	440, 577	16,800, 11,800
<i>p</i> -An	COCF_3	439, 590	17,000, 13,200

^a Solution of the corresponding 9,10-diol in dichloromethane-TFA (5:1) containing 1% water, TFA, or methanol. ^b Calculated by extrapolation to the time for mixing; temperature, 25°. ^c The H compound is so reactive, that it is impossible to get a reliable ϵ value. The λ values are the same for the two ions.

Anodic Oxidation of Protonated Anthracenes (Arenium Ions). In strongly acidic media, the anthracenes are monoprotonated.²⁹ The 9,10-diarylanthracenes are protonated in dichloromethane containing fluorosulfonic acid. Voltammetric and spectral data for the proton adducts of DPA, DTA, and DEA are summarized in Table VI. The voltammetry of the arenium

Table VI. Voltammetric and Spectral Properties of Anthracene Proton Adducts

Substrate	E_{ArH^+} ^a	$E_{\text{Ar}\cdot^+}$ ^a	$E_{\text{Ar}\cdot^+}$ ^{a,b}	λ_{max} , nm	ϵ
DPA	2.73	1.95	1.20	415	42,600 ^c
DTA	2.51	1.85	1.16	417, 492	42,400, 19,900 ^c
DEA	3.00			415	46,200

^a Solvent: Dichloromethane containing fluorosulfonic acid (7%) and tetrabutylammonium fluoroborate (0.2 M). Peak potentials are expressed in V vs. sce and measured at the sweep rate 86 mV/sec; temperature, -34°. ^b Reduction peak of $\text{Ar}\cdot^+$. ^c Calculated by extrapolation to the time for mixing; temperature, 25°.

ions is exemplified by the cyclic voltammograms for DPA (Figure 5) in dichloromethane containing fluorosulfonic acid (7%). On the first anodic sweep, the only peak observed was that for the proton adduct (O_3) and on the cathodic going sweep reduction peaks, R_2 due to DPA^{2+} and R_1 due to $\text{DPA}\cdot^+$, were observed.

Discussion

The effect of reducing the nucleophilicity of a solvent system upon the lifetime of reactive aromatic cations is dramatically illustrated by the voltammograms for the oxidation of anthracene in dichloromethane (Figure 1a) and in dichloromethane containing either neutral alumina (Figure 1b) or small amounts of TFA and TFA_n (Figure 1c). Thus, for the first time complete

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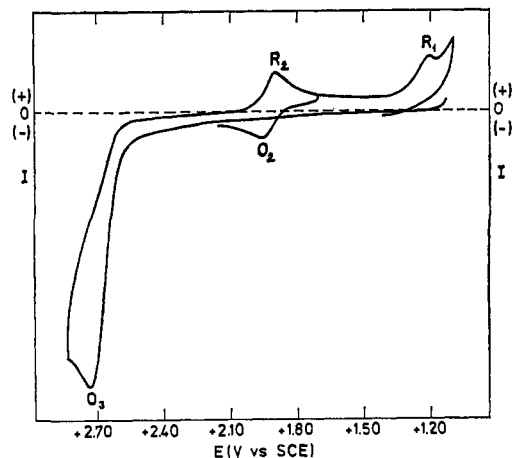
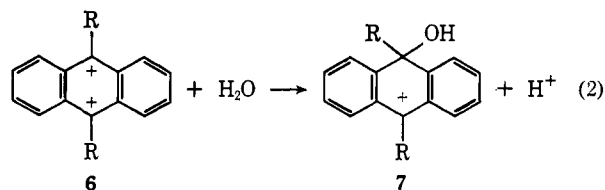


Figure 5. Cyclic voltammogram of the DPA proton adduct in dichloromethane containing FSO_3H (7%) and $n\text{-Bu}_4\text{NBF}_4$ (0.2 M); voltage sweep rate, 86 mV/sec; temperature, -34°.

reversibility was observed for the 1e oxidation of anthracene to the anthracene cation radical.

Previous work^{9-11,13,30} has shown that in general, 9,10-disubstituted anthracenes give relatively stable cation radicals but in no case has the reversible oxidation of cation radicals to dication been reported. The voltammetry of DAA in acetonitrile has recently been characterized as consisting of a quasireversible one-electron transfer producing the cation radical and a second totally irreversible charge transfer taking place about 165 mV more anodic than the first.³⁰ In the mixed solvent system, $\text{CH}_2\text{Cl}_2\text{-TFA}_n\text{-TFA}$ (45:5:1), voltammetric results clearly indicate that the two consecutive one-electron transfers for oxidation of DAA approach reversibility (Table I and Figure 2). Obviously, the reversibility of the second charge transfer is a consequence of the stability of the dication in the solvent system used. This is further demonstrated by the fact that the dication could be prepared coulometrically (Figure 3) and characterized by comparison of the electronic absorption spectrum of the anodically generated species with that of the dication prepared by dissolving the corresponding diol in methanesulfonic acid.

What is in even stronger contrast to previous work is that the reversible oxidation of $\text{DAA}\cdot^+$ to DAA^{2+} could be observed in the three common aprotic solvents: acetonitrile, nitrobenzene, and dichloromethane (Table II). The latter observations were made possible by the "super" drying action of suspended alumina in the voltammetric solutions.²⁰ The observation of reversible redox behavior in the latter media is very important in that the instability of anthracene dications can now definitely be assigned to the rapid reaction with water (eq 2) present in trace amounts in the carefully

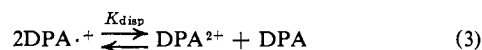


dried solvents as has previously been proposed for the reaction of DPA^{2+} in acetonitrile.¹³ Thus, reactions of

(30) V. D. Parker, *Chem. Commun.*, 848 (1969).

the dications with the solvents do not appear to be important, at least not on the voltammetric time scale.

The high degree of stability of DAA²⁺ is in part due to the presence of the methoxy groups. In acetonitrile and nitrobenzene only small reduction currents for the dications of DPA and DTA could be observed during cyclic voltammetry at 86 mV/sec while reversible voltammetry was observed in dichloromethane containing trace amounts of FSO₃H (Table II). The latter measurements were made at low temperature (−34°), a technique which has recently been shown to be of great value in extending the lifetimes of electrode-generated intermediates.^{19,31,32} Although complete reversibility was not observed for the formation of DPA²⁺ and DTA²⁺, the observation of partial reversibility indicates that the potentials measured under these conditions are not greatly affected by post electron transfer kinetic processes and thus the difference, $E_{2a} - E_{1a}$, can be used as a close approximation for the difference in standard electrode potentials, $E_2^0 - E_1^0$. The equilibrium constant for the disproportionation of DPA^{·+} (eq 3) in



acetonitrile has been estimated to be equal to 4×10^{-6} based on a value of 320 mV measured for $E_{2a} - E_{1a}$.¹⁵ The latter points out the fact that caution must be taken in using relative electrode potentials as an estimate of relative E^0 's, especially if both electrode processes do not fulfill the criteria of reversibility since large errors may be encountered due to electrode potential shifts due to rapid follow-up reactions. Under the conditions of near reversibility, we find that $E_{2a} - E_{1a}$ for DPA in acetonitrile is equal to 460 mV which gives an estimate of $K_{\text{disp}} = 10^{-8}$. A factor of greater than 100 between the irreversible¹⁵ and our near reversible measurement is very critical in assessing the validity of mechanisms proposed for the reactions of DPA^{·+}. A disproportionation mechanism has been proposed for the pyridination of DPA^{·+}.¹⁵ However, a recent kinetic investigation has verified that the reaction is first order in both DPA^{·+} and pyridine which rules out the disproportionation.³³

In the preliminary communication²⁷ of this work, we pointed out that the failure of previous attempts to observe **10** (Nu = pyr⁺) during the anodic pyridination of 9,10-diphenylanthracene posed a serious difficulty to the unequivocal assignment of that mechanism.¹² In previous work it was necessary to assume that oxidation of the radical (9) occurred sufficiently cathodic of E_1 that oxidation occurred very rapidly after the formation of 9. However, this assumption could not be verified experimentally. Support of the assignment of the EC_NE mechanism was later given by the observation of a voltammetric peak during rapid sweep cyclic voltammetry which was assigned to the reduction of a cation such as **10**.¹⁴ However, the observation of a voltammetric peak of unknown origin must be considered as weak evidence when it cannot be matched with that of the known species or supported by other data.

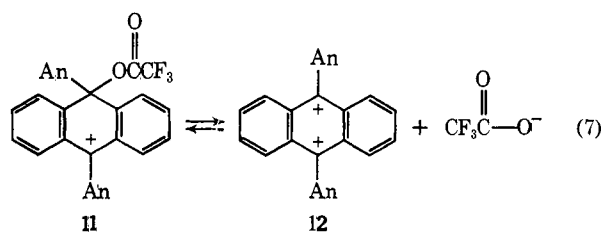
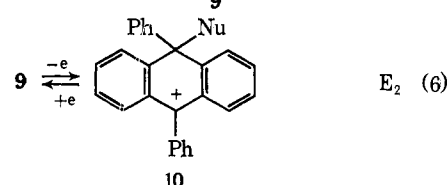
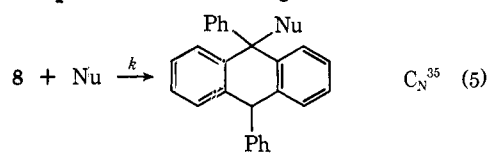
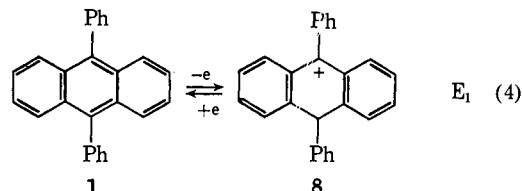
Monocations of general structure **5** were observed for

(31) R. P. Van Duyne and C. N. Reilly, *Anal. Chem.*, **44**, 142, 153, 158 (1972).

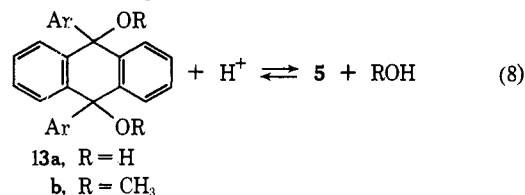
(32) K. Bechgaard and V. D. Parker, *J. Amer. Chem. Soc.*, **94**, 4749 (1972).

(33) U. Svanholm and V. D. Parker, *Acta Chem. Scand.*, **27**, 1454 (1973).

all the 9,10-disubstituted anthracenes during oxidation in dichloromethane containing TFA (Table III).³⁴ In the case of DAA the monocation could only be observed in the presence of trifluoroacetate ion since in its absence the equilibrium between the monocation **11** and the dication **12** greatly favors the dication. Solutions



of monocations (**5**) are readily prepared by dissolving either the diols (**13a**) or the dimethoxy compounds (**13b**) in TFA. Reduction potentials R_C^H for **5** (R = H) in

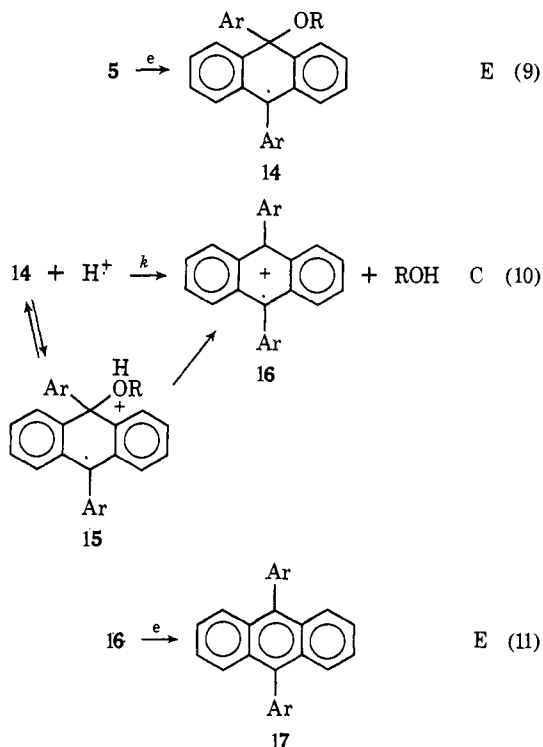


CH₂Cl₂-TFA (4:1) from DPA, DTA, and DAA are recorded in Table III. In this case all three cations are reduced from 450 to 600 mV more cathodic than the corresponding cation radical. The potential of R_C is affected both by the nature of the OR group and by the nature of the medium. The effect of the OR group is that expected from the electron-donating or -withdrawing tendencies of the group with electron-withdrawing OC(O)CF₃ lowering the reduction potential of **5** relative to that when OR is electron-donating OH or OCH₃. The reduction of **5** produces the anthracene **17** in an ECE reaction (eq 9–11). The rate of the homogeneous step (eq 10) depends on the ability of RO[−] to act as a leaving group and in general the best leaving groups

(34) The most characteristic spectral feature of **5** is the strong ($\epsilon = 2 \times 10^4$) band at about 440 nm (Table V), which is comparable to the corresponding band for the triphenylmethyl cation (441 nm, $\epsilon = 3.78 \times 10^4$): S. F. Mason, *Quart. Rev.*, *Chem. Soc.*, **15**, 335 (1961).

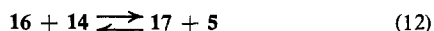
(35) Here we use the subscript N to specify the nature of the chemical step of the ECE mechanism as a reaction of the electro-generated species with a nucleophile as proposed earlier.³⁶

(36) V. D. Parker and Lennart Ebersson, *Tetrahedron Lett.*, 2843 (1969).



are the weakest bases.³⁷ Thus, CF_3CO_2^- is a better leaving group than HO^- or CH_3O^- and the protonated forms (15) are all much better leaving groups than the parent bases. The effect of acidity is to increase the rate of reaction 10 and this kinetic step can have a profound effect on the potential of R_c as expected for an ECE reaction.³⁸ The most interesting feature of the reduction of 5 (eq 9–11) is that this reaction sequence is the exact reverse of the ECE mechanism proposed for the anodic pyridination of DPA.¹²

In discussing ECE mechanisms it is implied that the second electron transfer, for example, eq 11, need not occur at the electrode but also takes place in solution as shown in eq 12. This "nuance" to the ECE mech-



anism has been pointed out and demonstrated by Feldberg and coworkers.^{39–41} Marcoux⁴² has recently implied that this refinement has been ignored by workers studying anodic substitution reactions. However, it should be pointed out that in assigning the ECE mechanism to the pyridination of DPA¹² as well as other related reactions, the occurrence of homogeneous electron-transfer reactions was assumed but the viewpoint and notation of Adams were followed.⁴³

(37) For a discussion, see J. March, "Advanced Organic Chemistry: Reactions, Mechanism and Structure," McGraw-Hill, New York, N. Y., 1968, pp 290–293.

(38) R. S. Nicholson and I. Shain, *Anal. Chem.*, **37**, 178 (1965).

(39) M. D. Hawley and S. W. Feldberg, *J. Phys. Chem.*, **70**, 3459 (1966).

(40) R. N. Adams, M. D. Hawley, and S. W. Feldberg, *J. Phys. Chem.*, **71**, 851 (1967).

(41) S. W. Feldberg, *J. Phys. Chem.*, **75**, 2377 (1971).

(42) L. S. Marcoux, *J. Phys. Chem.*, **76**, 3254 (1972).

(43) Adams makes the following statements regarding ECE reactions.⁴⁴ "In spite of the reality and calculational importance of the 'second' chemical step, it seems preferable to retain the shorthand ECE for all electrochemical reactions with a chemical step interposed between two charge transfers. The ECE designation seems preferable since it indicates that additional electrons are observed as current flow experimentally, regardless of whether the detailed reaction is ECE or ECC."

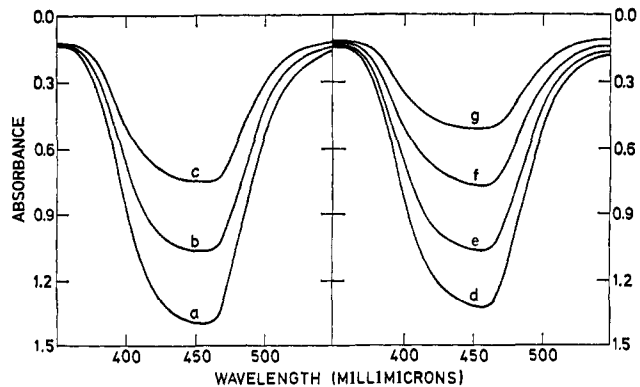
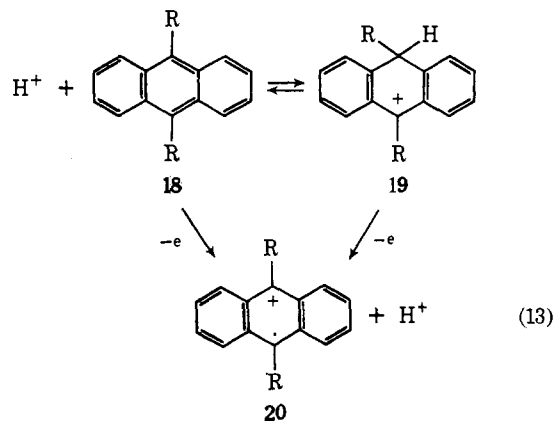


Figure 6. Visible absorption spectra of 5 (Ar = Ph and R = H) in dichloromethane containing TFA, H_2O , CF_3COO^- , and 13a (Ar = Ph). $[\text{5}] + [\text{13a}] = 1.0 \times 10^{-2} \text{ M}$. The concentrations of TFA, H_2O , and CF_3COO^- respectively are: (a) 0.80, 0.42, and 0.015; (b) 0.80, 0.51, and 0.015; (c) 0.80, 0.60, and 0.015; (d) 0.98, 0.60, and 0.015; (e) 0.98, 0.67, and 0.015; (f) 0.98, 0.75, and 0.015; (g) 0.98, 0.83, and 0.015.

The cations, 5 (R = H or Me), are more stable in TFA when water or methanol is present. This suggests that the rapid conversion of 5 to the corresponding cation radicals in pure TFA involves equilibria between 5 and the dications. The latter equilibria may be suppressed by the presence of water, methanol, or $\text{CF}_3\text{C(O)ONa}$ as demonstrated in Figure 6. We suspect that the failure to find a suitable equilibrium expression is due to changes in the dissociation equilibrium of TFA in the presence of H_2O and CH_3OH . There are inconsistencies in the literature regarding the acidity of neat TFA. Older indicator work⁴⁵ suggests that neat TFA is indeed a strong acid while newer⁴⁶ conductivity studies suggest that it is weak acid.

The protonation of anthracenes (18) in acidic media to form adducts of structure 19 has been recognized for some time.⁴⁷ The spontaneous oxidation of aromatic hydrocarbons to the corresponding cation radicals on dissolving in strong acids such as concentrated sulfuric acid has been attributed to protonation followed by oxidation of the corresponding proton adduct 19 producing the cation radical 20.²⁹ The latter postulate



implies that the adducts (19) are sufficiently easily oxidized that relatively weak oxidants such as oxygen or

(44) R. N. Adams, "Electrochemistry at Solid Electrodes," Marcel Dekker, New York, N. Y., 1969, p 252.

(45) H. H. Hyman and R. A. Garber, *J. Amer. Chem. Soc.*, **81**, 1847 (1959).

(46) M. G. Harriss and J. B. Milne, *Can. J. Chem.*, **49**, 1888 (1971).

(47) V. Gold and F. L. Tye, *J. Chem. Soc.*, 2172, 2181, 2184 (1952).

sulfur trioxide can bring about the conversion of **19** to **20**. Voltammetric measurements (Table VI and Figure 5) virtually rule out such oxidation mechanisms. For example, the proton adduct of DPA is oxidized at a platinum electrode with a peak potential of +2.73 V *vs.* the sce in dichloromethane containing FSO₃H (7%) while DPA^{•+} is reduced irreversibly at +1.20 V to produce DPA which is immediately protonated. This would imply that the oxidation of unprotonated DPA should occur with a peak potential of about +1.26 V in the latter medium which compares favorably to the observed values of +1.23, +1.27, and +1.27 in neutral acetonitrile, nitrobenzene, and dichloromethane, respectively (Table II). Thus, the proton adduct is oxidized about 1.5 V more anodic than is DPA. Protonated forms of DTA and DEA are likewise much more difficultly oxidized than the corresponding substrates. These results suggest that oxidation of protonated aromatic compounds is a very unfavorable process and that oxidation of aromatic hydrocarbons on dissolving in strong acid proceeds by reaction of the unprotonated form (**18**) which exists in equilibrium with the proton adduct (**19**).

In dichloromethane containing FSO₃H (7%), the

proton adduct of DEA is stable at room temperature while the corresponding adducts of DPA and DTA are short lived, having half-lives of the order of 5 min. In the latter two cases, it was necessary to extrapolate to the time of mixing in order to obtain extinction coefficients. The instability appears to be connected with the aromatic groups substituted at the 9 and 10 positions and suggests sulfonation⁴⁸ as the substrate consuming reaction since FSO₃H has recently been shown to be a potent sulfonation agent.⁴⁹

In conclusion, it should be pointed out that the observation of oxidation of proton adducts, reversible cation radical-dication redox equilibria, the "elusive" monocations derived from ECE reactions, and the cathodic ECE reaction of the monocations which is the reverse of the ECE mechanism of anodic substitution has only been described for the "model" system, 9,10-disubstituted anthracenes. However, we feel that these "model" systems can be referred to with confidence in interpreting results of other anodic electrode processes.

(48) It is of interest to note that DPAH⁺ disappears according to a second-order rate law while the consumption of DTAH⁺ is cleanly first order. These reactions are being investigated.

(49) U. Svanholm and V. D. Parker, *J. Chem. Soc., Perkin Trans. 2*, 962 (1972).

Electrochemical Oxidation of the Enolate of Dibenzoylmethane

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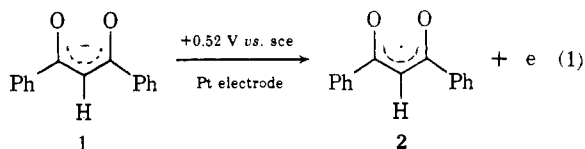
Abstract: The anodic oxidation of the enolate of dibenzoylmethane, **1**, at platinum anodes in dimethyl sulfoxide as solvent has been studied by cyclic voltammetry, controlled potential coulometry, and analysis of electrolytic products. The oxidation proceeds in an initial one-electron step forming the dibenzoylmethyl radical, **2**. Radical **2** is short-lived, reacting by dimerization to 1,1,2,2-tetrabenzoylthane (**4**) and by hydrogen atom abstraction forming dibenzoylmethane **3**. As expected, the fraction of **2** reacting by dimerization increases as the concentration of **1** is increased. Though **3** and **4** are the products formed at short times, complete electrolysis of the solution produces tetrabenzoylethylene (**7**) and additional **3**. **7** is formed from **4** by proton transfer from **4** to unreacted **1** followed by anodic oxidation of the resulting anion to **7**. The hydrogen abstraction reaction of **2** was suppressed when benzonitrile was used as solvent. The cathodic reduction of 2-bromo-1,3-diphenyl-1,3-propanedione was also studied. Both the two-electron product, **1**, and the 1,3-diketone, **3**, were formed. Radical **2** is probably an intermediate in this reduction.

The electrochemical oxidation of the anions of esters, 1,3-diketones, and nitroalkanes has been investigated by numerous workers.¹ Dimeric products are often formed in good yield but other products are also found.²⁻⁶ The relevant experimental conditions governing the type and distribution of products have not been established and very little information is available concerning the individual steps in the reaction sequence. In this paper we report a voltammetric

study of the anodic oxidation of the enolate of dibenzoylmethane, **1**, at platinum electrodes in dimethyl sulfoxide (DMSO) as solvent.

Results and Discussion

Cyclic Voltammetry. The electrochemical oxidation of **1** was studied using its tetra-*n*-butylammonium salt. The observed oxidation is consistent with a one-electron oxidation to the neutral radical, **2**, which reacts



very rapidly *via* two competing chemical reactions. One of these is hydrogen abstraction by the radical to

(1) (a) N. L. Weinberg and H. R. Weinberg, *Chem. Rev.*, **68**, 449 (1968); (b) K. Nyberg in "Organic Electrochemistry," M. M. Baizer, Ed., Marcel Dekker, New York, N. Y., 1973, pp 718-724.

(2) S. P. Mulliken, *Amer. Chem. J.*, **15**, 523 (1893).

(3) T. D. Binns and R. Brettle, *J. Chem. Soc. C*, 336 (1966).

(4) R. G. Cooks, D. H. Williams, K. M. Johnston, and J. D. Stride, *J. Chem. Soc. C*, 2199 (1968).

(5) R. Brettle and D. Seddon, *J. Chem. Soc. C*, 2175 (1970).

(6) T. E. Neal, Ph.D. Thesis, University of North Carolina, Chapel Hill, 1970.