the benzenesulfonyl derivative. The DMN derivative displays an M^+ that is the base peak, while the M^+ is 29% of the base peak for the DMB derivative. All of the aromatic Schiff bases examined thus far display a prominent ion corresponding to a cleavage of the N^α–C^α bond of the second amino acid residue from the N-terminus (Table I, column d). There is no apparent relationship between the electron-withdrawing properties of the aromatic moiety and the relative intensity of the "d" cleavage. The spectra of the *p*-diethyl- and *p*-dimethylaminocinnamylidene ester derivatives of **1** (Table I) were found to be comparable in their ease of interpretation although differences in the distributions of ion intensities were noted. This suggests that dimethylamino and diethylamino substituents should have about the same effect.

Many of the peptide mass spectra discussed above exhibit two properties which are pertinent to the problem of peptide sequencing by EI mass spectrometry. These features are (1) relatively intense molecular and high *m/e* sequence ions, and (2) suppression or elimination of McLafferty fragmentations and other side-chain cleavages in certain derivatives. It has been well documented that substituent groups within a molecule can have a decided effect on the EI mass spectrum of the molecule.[10,11] Numerous studies have shown that the ionization potential (IP) of a molecule with an aryl amino or dimethyl amino group is significantly lower than that of the unsubstituted molecule or one with another substituent.[12,13] It has been suggested that the fragmentation observed is a function of the difference between the IP of the molecule and the appearance potential (AP) of the fragment(s), *i.e.*, the greater the Δ(AP − IP), the less likely the fragmentation will be observed.[14,15] The Schiff base ester derivatives of **1** (Table I) examined in this study appear to bear out this contention if the IP's of model compounds are taken as estimates of the IP's of the peptide derivatives.[16] Wachs and McLafferty[17] have shown that an aryl substituent greatly affects the relative amount of McLafferty fragmentation through intervening σ bonds and that an aryl amino group almost completely suppresses the fragmentation in the model compound studied.

Audier[18] has demonstrated the generalization that when a fragmentation takes place in EI mass spectroscopy the positive charge remains on the fragment with the lowest IP. Bursey and McLafferty[19] recorded similar observations for a series of para-substituted aceto- and benzophenones. The EI mass spectra reported here of peptide derivatives containing an aryl dimethyl amino group are in contrast with previously reported chemical ionization mass spectra of peptide derivatives which contain both the C- and N-terminal sequence identifying ions.[20]

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An Electrochemical and Spectrophotometric Study of Fluorene and the Fluorene Carbanion in Dimethylformamide, Dimethyl Sulfoxide, and Acetonitrile[1]

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The reduction behavior of the nonalternant aromatic hydrocarbon fluorene is investigated in DMF, DMSO, and acetonitrile, and compared and contrasted to that of alternant hydrocarbons. It is concluded that the normal electrochemical sequence does not occur on formation of the fluorene anion radical at the electrode in protic media, or when self-protonation occurs in aprotic media. Polarographic and coulometric data indicate that, rather than the usual reduction of a double bond, with a two-electron change, three electrons per molecule of fluorene are transferred under protic conditions, and reactive intermediates are formed which yield colored products on addition of oxygen. These products are unstable and decay rapidly to fluorenone under uv light. Spectrophotometric data of the colored intermediates are given, along with that of the fluorene anion radical.

It has been known for several years that chemical and electrochemical reduction of alternant aromatic hydrocarbons in aprotic solvents yields relatively stable anion radicals, which degrade by reaction with solvent and/or impurities. In the presence of electroinert proton donors such as phenol and resorcinol the anion radical abstracts a proton from the donor, and the resultant neutral radical is further reduced and protonated.[3] This sequence is the so-called electrochemical–chemical–

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electrochemical (ECE) mechanism. It is of considerable interest to determine whether nonalternant benzenoid hydrocarbons act in a similar manner. Certain nonalternant aromatic compounds which have undergone substantial study in this regard are those in which a methylene group acts as a bridge between two parts of a benzenoid system. As the bridge methylene contributes to the aromaticity of the molecule through hyperconjugative effects, these compounds can be considered nonalternant. The methylene hydrogens of such systems are somewhat acidic ($pK_a = 20–25$),[4-6] and it has been shown in an electrochemical study of a molecule of this type, 4,5-methylenephenanthrene, that even in aprotic media the usual ECE process takes place, to a small degree, *via* self-protonation, yielding the carbanion in addition to the unstable neutral radical.[6] It was demonstrated that 9,10-dihydro-4,5-methylenephenanthrene was a final reduction product in both protic (this is the exclusive product in protic solution) and aprotic media; *i.e.*, the most reactive double bond is reduced, in the manner of alternant hydrocarbons.[6] However, the reduction mechanism for the similar nonalternant hydrocarbon fluorene has not been clarified despite considerable study. It has previously been suggested that its reduction with alkali metal yields the carbanion, not *via* the ECE sequence, but by a loss of a hydrogen atom from the anion radical.[7] Janzen and Gerlock[8a] and Casson and Tabner[8b] also appear to favor this decomposition route of the initially formed anion radical (to the carbanion) rather than the ECE sequence, while Eisch and Kaska do propose an ECE mechanism involving the parent, RH_2, acting as a proton donor.[9]

In order to add to the understanding of the electrochemistry of nonalternant hydrocarbons and to attempt a resolution of the above differences it was decided to study the reduction of fluorene in several aprotic solvents, dimethylformamide (DMF), acetonitrile (MeCN), and dimethyl sulfoxide (DMSO), under both aprotic and protic conditions. It was also desired to determine whether dihydrofluorene is a final product of reduction, both in aprotic and protic media, as would be expected if the usual ECE sequence is followed in the case of fluorene.

All of the reduction reactions were carried out electrochemically, as changes in reactant and product concentration could be easily followed polarographically and spectrophotometrically, and reaction conditions could be controlled more exactly than with an active metal reductant.

Experimental Section

Instrumental.—Polarographic and constant-potential coulometric electrolyses were carried out using a three-electrode system, the details of which have been reported elsewhere.[6,10] The constant potential coulometry experiments were carried out in a flow cell which allowed the macroscopic electrolysis at a mercury pool to continue while the instantaneous polarographic diffusion current was measured at a dropping-mercury electrode. This cell system has been described previously.[11] The reference electrode in all cases was an anodized silver wire immersed in a 0.01 *M* $AgClO_4$–0.1 *M* *tert*-butylammonium perchlorate (TBAP) solution of the particular solvent being studied. Details of the construction of the reference and salt-bridge compartments are found elsewhere.[10]

Solutions were deoxygenated by bubbling with nitrogen which had been passed through a gas train consisting of a tube of hot copper wool to remove traces of oxygen, a magnesium perchlorate tube to remove water, and a presaturator containing the solvent system under study. Solutions to be electrolyzed in the flow cell were deaerated for at least 1 hr.

Simultaneous electrochemical–spectrophotometric experiments were performed utilizing the above-mentioned flow cell in the Cary 14 recording spectrophotometer. Polarographic determination of *n* (apparent) values was carried out at 25.0 ± 0.1°. Certain experiments carried out to produce the fluorene anion radical in high concentration were effected at a mercury pool in both DMF and MeCN at reduced temperatures in a 1-cm quartz spectrophotometer cell. The mercury electrode was frozen with liquid nitrogen while the electrolysis was proceeding. Electrolyses performed at these lower temperatures in the sample compartment of the Cary 14 spectrophotometer enabled the visible spectrum of the anion radical to be obtained.

Fluorenone concentrations, as massive electrolysis products, were determined, in aprotic media, *via* the limiting current of the two one-electron reduction waves, −1.71 and −2.45 V in DMF, −1.53 and −2.64 V in DMSO, and −1.63 and −2.16 V in MeCN. In protic media the fluorenone was separated from other products and reactants by passing the electrolyzed solution through a column of neutral alumina. The resulting yellow product was still heavily contaminated with TBAP, which was then removed by adding toluene to the mixture. Several treatments precipitated virtually all of the TBAP.

Infrared analyses of electrolysis products were performed with the Perkin-Elmer 337 spectrophotometer using the usual KBr pellet technique.

Chemicals and Solutions.—All solvents used were Matheson Coleman and Bell Spectroquality grade. The DMF was purified according to the method of Moe.[12] It was found that fresh solvent had to be prepared weekly, as some deterioration occurred. DMSO and MeCN were used as received, but all three solvents were stored over Linde Type 4A Molecular Sieves, and as used, had very small (<0.2 μA) polarographic background currents prior to breakdown. The fluorene (Baker photosensitizer grade) was used as received. The resorcinol (Matheson Coleman and Bell) was recrystallized several times from ethanol, the final product being large, colorless crystals. The TBAP (Southwestern Analytical Chemicals, Inc., Austin, Texas) was dried *in vacuo* at 60° for several hours, or over silica gel for over 1 week. All chemicals were stored over silica gel prior to use.

Fluorene electrolysis solutions were generally 1.00 m*M* except for the massive protic electrolysis experiments, which utilized 0.05 *M* solutions of both fluorene and resorcinol.

Results and Discussion

Aprotic Conditions.—Under certain conditions, using DMF which was rigorously dried and deoxygenated, the blue-green anion radical of fluorene could be seen at room temperature on the surface of the mercury pool electrode during exhaustive electrolysis. This was somewhat unexpected, even though Van Duyne and Reilley indicate that DMF is an excellent solvent for the study of radical anions.[13a] Normally, however, no color was seen, nor was this color ever seen at room temperature in MeCN or DMSO regardless of experimental conditions. At temperatures reduced to the

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[7] G. W. H. Scherf and R. K. Brown, *Can. J. Chem.*, **38**, 2450 (1960).

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[12] N. S. Moe, *Acta Chem. Scand.*, **21**, 1389 (1967).

[13] (a) R. P. VanDuyne and C. N. Reilley, *Anal. Chem.*, **44**, 142 (1972). (b) Because of the severe reaction conditions employed, the spectra actually obtained were quite noisy, and a smoothed, average curve is shown. The position of λ_{max} is probably ±5 nm.

TABLE I

POLAROGRAPHIC AND SPECTRAL DATA FOR FLUORENE, FLUORENE ANION RADICAL, FLUORENE CARBANION, AND FLUORENONE ANION RADICAL IN MeCN, DMF, AND DMSO

Solvent	$E_{1/2}$ of RH$_2$ redn,[a] V	λ of RH$^-$,[b] nm	RH$^-$ oxidation wave max	$t_{1/2}$ of RH$^-$, min	λ of RH$^-$ + O$_2$ reaction,[c] nm	λ of protic electrolyzed intermediate,[d] nm	λ of RH$_2\cdot^-$, nm	λ of R=O$\cdot^-$,[e] nm
MeCN	-3.0_3	368	−1.13	13	422	448	693 ± 5	545
		425 (sh)			533			
		453			642			
		481						
		514						
DMF	−3.130	371	−1.17	30	557	510	708 ± 5	553
		425 (sh)			648			
		456						
		485						
		520						
DMSO	−2.910	362, 371	−1.00	100		507		
		430 (sh)						
		~455						
		482						
		~515						

[a] Vs. Ag/AgClO$_4$ (0.01 M); RH$_2$ = fluorene. [b] The short-wavelength band is about ten times as intense as the quartet. [c] Products of oxygen addition to electrolyzed fluorene in aprotic media; each band is a different species. [d] Products of oxygen addition to electrolyzed fluorene in protic media. [e] R=O$\cdot^-$ = fluorenone anion radical.

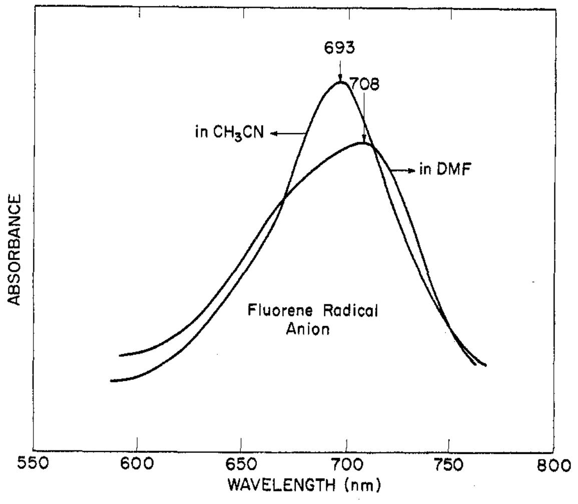


Figure 1.—Visible spectrum of the fluorene anion radical in DMF and MeCN. The actual spectra were much noisier than shown.[13] $T = <-20°$.

point that the mercury pool electrode was frozen, the radical anion was sufficiently stable and formed in high enough concentration so that a spectrum (Figure 1)[13b] could be obtained. Our spectral results in DMF and MeCN are in good agreement with those of Casson and Tabner in ethereal solvents.[5b]

Polarographically, fluorene exhibited essentially reversible one-electron reduction waves in both aprotic DMF and DMSO. Plots of $E_{1/2}$ vs. log $i/i_d - i$ (where i_d = the diffusion limited current) yielded slopes of 58–61 mV/decade, in good agreement with the theoretical Nernstian behavior. In aprotic MeCN, however, the polarographic limiting current is much larger than expected for a one-electron change, and constant-potential electrolysis yielded an n value around 2.0. The background breakdown of the MeCN–0.1 M TBAP solvent system begins around −3.10 V, which is near the fluorene half-wave potential. It appears that electron transfer, near the electrode, from fluorene to solvent and/or direct solvent system reduction is occurring. Either of these processes would account for the high n values.

Coulometric reduction at a Hg pool yielded an electron change value, n, only slightly greater than 1.0 over the first 20–30% of the electrolysis in DMF and DMSO. In MeCN, the proximity of background breakdown caused n to be erratic and much higher than 1.0.

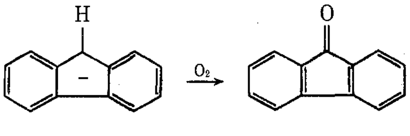
In all three aprotic solvents, electrolysis at or near the current limiting plateau potentials (−3.20 to −3.35 V in DMF, −3.05 V in DMSO, and −3.05 V in MeCN under aprotic conditions) of the fluorene reduction wave yields as one product the fluorene carbanion, as evidenced by a change of the solution from colorless to yellow-orange. This species has a very sharp and intense band around 370 nm, and a quartet of less intense bands farther out in the visible region (Table I) in all three solvents.[14,15] The build-up of this product could

(14) (a) A. Streitwieser, Jr., and J. I. Brauman, *J. Amer. Chem. Soc.*, **85**, 2633 (1963). (b) G. Häfelinger and A. Streitwieser, Jr., *Chem. Ber.*, **101**, 657 (1968). (c) Qualitatively, the stability of the carbanion (in the absence of air) varies considerably in the three solvents, as shown in Table I. The order of the anion stability, DMSO > DMF > MeCN, is explainable in terms of the solvating ability of the three solvents. MeCN solvates anions very weakly, DMSO very strongly, while DMF is intermediate in strength. Degradation of the anion in these experiments probably occurs by reaction with traces of oxygen and/or carbon dioxide, or with water or other impurities. In basic solvents carbanion stability is greatly enhanced.[14a] Indeed, if the anion is formed with potassium *tert*-butoxide in DMF, so that an excess of base is present, the half-life is over 6 hr.

(15) Hogen-Esch and Smid [T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, **88**, 307 (1966)] have postulated the existence of both contact and solvent-separated ion pairs of the fluorene anion in several solvents. Where solvent separation occurs, for strongly solvating conditions, the position of the short-wavelength band is said to be fixed at 373 nm, while contact ion pairing shifts the band anywhere from 368 to 346 nm. In both MeCN (λ_{max} 368 nm) and DMF (λ_{max} 371 nm) only one band was observed in the present study. It is likely that this indicates rather poor solvation of the anion by MeCN, yielding only the "free" ion. This is reasonable, as MeCN does not solvate anions particularly strongly. For DMF, however, strong solvation of the anion is indicated. In DMSO two short-wavelength bands are observed. At low carbanion concentrations λ_{max} is 362 nm, while at higher concentrations a band at 372 nm becomes predominant. Hogen-Esch and Smid also report these two peaks in DMSO, and attribute the shorter wavelength band to the free ion. However, this explanation does not seem reasonable; first, dilution would be expected to cause even more extensive solvation; and, second, no free ion would be expected in the extremely strongly solvating DMSO medium. Anion–anion interaction at higher concentrations may be responsible for the shift in wavelength.

be followed spectrophotometrically during the course of the electrolysis. Streitwieser has discussed this spectrum in some detail.[14a,b] Anion build-up can also be followed polarographically, as the carbanion possesses a characteristic oxidation wave with a very distinctive maximum (Table I) in all three solvents. It is of interest to note that no other product was detected in measurable quantities by either of these methods.[14c]

If air is admitted to an aprotic DMF, DMSO, or MeCN solution containing the fluorene carbanion, immediate decay of the carbanion is observed, as evidenced by the simultaneous disappearance of both the fluorene carbanion polarographic oxidative wave and its visible absorption spectrum. Russell and coworkers[16] have shown that oxygen reacts rapidly with the fluorene anion; so this result was not unexpected. However, a result that was unexpected is that when air was admitted to the electrolyzed DMF or DMSO solution containing the carbanion the fluorene remaining unelectrolyzed was considerably reduced in concentration. In fact, if the electrolysis was carried out to about 40 or 50% (*i.e.*, judging from the size of the fluorene polarographic wave, 40 or 50% of the original RH_2 had been reduced), and then terminated, and oxygen admitted to this solution of RH_2 and RH^-, the RH_2 remaining unelectrolyzed *completely* disappeared. In addition, the amount of fluorenone which resulted was much larger than expected, appearing in approximately equimolar amounts to the *original* RH_2 concentration. Dehl and Fraenkel also observed the formation of a yellow species, presumably the anion of fluorene, during electrolysis in DMF, but, because of molecular oxygen impurity, obtained the ketone directly during the course of the electrolysis.[17] In MeCN at least three intermediates are observed on addition of air to the carbanion solution,[18] but the degradation (uv light) product of all three is also the ketone. No other major product was found in any of the three solvents. Therefore, it would appear that, while self-protonation does indeed occur to some extent for aprotic reduction of fluorene, yielding the carbanion, RH^-, and neutral protonated radical, $RH_3\cdot$ (these are the electrochemical and chemical steps of the ECE sequence), this sequence is not stoichiometric and does not go to completion in the usual manner. We suggest a possible, nonspecific reaction pathway below, based on approximately 50% electrolysis of the RH_2, which is consistent with the above observations.



(electrochemical) $RH_2 + e^- \rightleftarrows RH_2\cdot^-$ (1)

(chemical) $RH_2\cdot^- + RH_2 \longrightarrow RH^- + RH_3\cdot$ (self-protonation) (2a)

or $RH_2\cdot^- + SH \longrightarrow S^- + RH_3\cdot$ (SH = solvent and/or impurities) (2b)

(electrochemical) $RH_3\cdot + e^- \not\longrightarrow RH_3^- \xrightarrow{H^+} RH_4$ (final steps of usual ECE sequence) (3)

$$RH_3\cdot \xrightarrow{\text{solvent}} Q^* \quad (4)$$

$$Q^* + RH_3 + O_2 \longrightarrow 2R{=}O + 2H\cdot \text{ or } 2H^+ \quad (5)$$

$$RH^- + O_2 \longrightarrow R{=}O + OH^- \quad (6)$$

The ratio of fluorenone produced to RH_2 originally present should have a maximum value of about 0.5 if all $RH_2\cdot^-$ species react with neutral RH_2 (an unlikely occurrence) and the usual ECE pathway occurs, and 1.0 for the alternate route indicated above. Experimentally a ratio near 1.0 was obtained, indicating that nearly all of the RH_2 originally present was converted to the ketone although only one-half of it was reduced at the electrode. The above very generalized sequence of reactions is consistent with this fact, as well as with an n value of 1.0. The experimental evidence also indicates that the second electrochemical step, which normally leads to the second protonation and the RH_4 species, does not occur. Rather, it appears as if the $RH_3\cdot$ somehow reacts with solvent or impurities to form an anaerobically stable species, Q*, which, in the presence of unreacted RH_2 and O_2, yields the ketone. This conclusion is strongly indicated by the fact that the 50% RH_2 unelectrolyzed also yields fluorenone. Of course, that RH^- formed *via* the self-protonation (2a) also forms the ketone.

Protic Conditions in DMF and DMSO.—From the reaction pathway shown above it is seen that the species RH_3^-, if formed under protic conditions, ought to favor the usual ECE mechanism; in fact reduction in the presence of a large excess of proton donor should yield no carbanion, as self-protonation should be swamped out, and, therefore, no fluorenone if the usual ECE sequence is followed. Carrying out the reduction under protic conditions was expected to answer the

[16] (a) G. A. Russell, A. J. Bemis, E. J. Geels, E. G. Janzen, and A. J. Moye in "Oxidation of Organic Compounds," Vol. I, Advances in Chemistry Series, No. 75, American Chemical Society, Washington, D. C., 1968, pp 174–202. (b) G. A. Russell in "Free Radicals in Solution," IUPAC, Division of Organic Chemistry, International Symposium, Ann Arbor, Mich., 1966, Butterworths, London, 1967, pp 185–206.

[17] R. Dehl and G. R. Fraenkel, *J. Chem. Phys.*, **39**, 1793 (1963).

[18] In most cases exhaustive electrolysis of fluorene in MeCN produced (besides the fluorene anion) a pink species as reduction progressed. When air was admitted *slowly* to a solution of fluorene anion in MeCN the same pink species was obtained. This is not the fluorenone ketyl radical, as λ_{max} for the ketyl does not quite match that for the pink species (Table I). A short while after the pink species begins to form, a very large band appears at 422 nm. A band with the same characteristics is observed when fluorenone itself is electrolyzed at a mercury pool. This yellow species may be the fluorene pinacol discussed by Korsun and Nekrasov [A. D. Korsun and L. N. Nekrasov, *Elektrokhimiya*, **4**, 1501 (1968)] which forms during the electrolysis of fluorenone.

If air is admitted *rapidly* to a solution of the fluorene anion in MeCN, a blue species, λ_{max} 642 nm, forms immediately, to the exclusion of the pink species. Under these conditions the band at 422 nm does not form.

When air is admitted at intermediate rates, both the blue and the pink species are observed, as is the yellow (422 nm). In most cases fluorenone is not formed concurrently with these species. That the formation of these "intermediates" results from reaction of oxygen with the carbanion is indicated by the fact that the anion formed by the reaction of potassium *tert*-butoxide with fluorene yields the same species with oxygen.

Sunlight degrades the pink species to fluorenone in under 1 min, while the blue takes several minutes to degrade to the same product. In the dark the blue lasts for days, while the pink decomposes in several hours. All efforts to isolate and characterize these products (pink, blue) failed as rapid degradation to the ketone resulted.

In DMF both slow and rapid admission of air to an anion solution resulted in immediate formation of fluorenone in nearly all cases. Occasionally, however, the intermediate red and blue species were obtained (Table I). In DMSO, no product other than fluorenone was ever obtained.

As the blue product formed in excess oxygen, some form of peroxy structure is likely, although Sprinzak [Y. Sprinzak, *J. Amer. Chem. Soc.*, **80**, 5449 (1958)] claims that no peroxide intermediate forms in the oxidation of fluorene anion to ketone in pyridine. In addition Hock, *et al.* [H. Hock, S. Lang, and G. Knauel, *Chem. Ber.*, **83**, 227 (1950)], claim that the fluorene hydroperoxide is colorless.

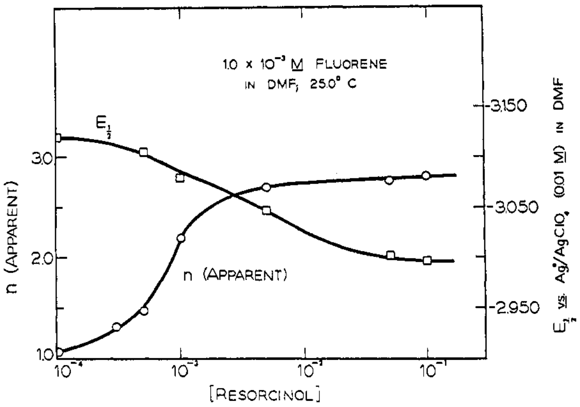


Figure 2.—Plots of n(apparent), the ratio of the polarographic limiting current of the fluorene reduction wave in resorcinol media to that in aprotic solvent, and the polarographic reduction half-wave potential of fluorene *vs.* resorcinol concentration in the DMF–resorcinol–TBAP solvent system.

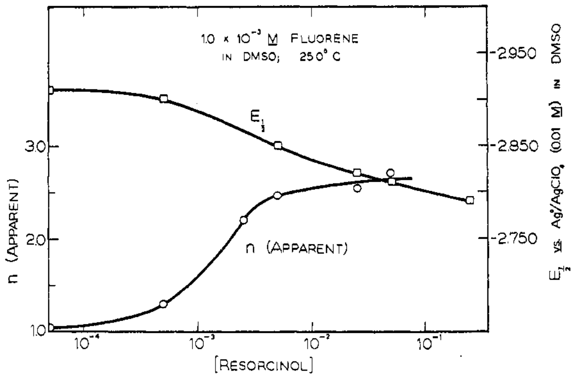


Figure 3.—Plots of n(apparent), the ratio of the polarographic limiting current of the fluorene reduction wave in resorcinol media to that in aprotic solvent, and the polarographic reduction half-wave potential of fluorene *vs.* resorcinol concentration in the DMSO–resorcinol–TBAP solvent system.

questions of whether RH_3^- formed at all in protic media, whether a pathway to fluorenone exists other than *via* the carbanion, RH^-, as does appear to be the case under aprotic conditions, and whether the twice-protonated species RH_4, dihydrofluorene, is the major product. (This is the usual ECE product and is the situation found for 4,5-methylenephenanthrene.) To test this hypothesis and to see if fluorene deviates from the usual sequence in protic, as in aprotic conditions, the reduction of fluorene was carried out in the presence of a large excess of resorcinol as an electroinert proton donor in all three solvents.

In Figures 2 and 3 there are plotted the n(apparent) values [n(apparent) $= i/i_d$, where i is the polarographic limiting current in the various protic media, and i_d is the diffusion limited current, in aprotic conditions, obtained in DMF and DMSO] *vs.* resorcinol concentration. The polarographic half wave potential is also shown as a function of resorcinol concentration. It can be seen that n(apparent) reaches a maximum value of about 2.8 in DMF and 2.7 in DMSO, indicating an electron change in protic media approaching a value of 3.0. In order to confirm this result, exhaustive electrolyses (at -3.10 V in DMF, and at -2.9 to -3.0 V in DMSO) of 1 mM fluorene solutions were carried out at a mercury pool in 0.01 M resorcinol medium. According to the modified Faraday expression the polarographic

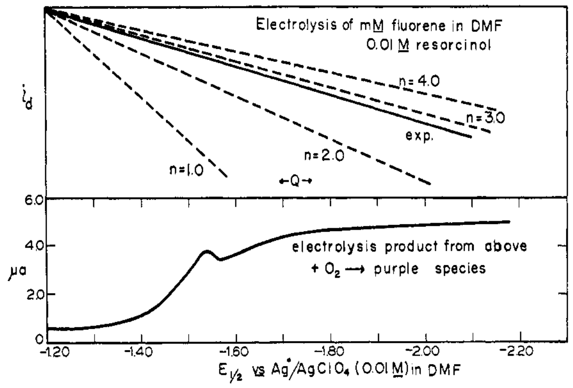


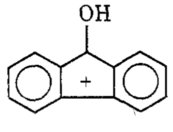
Figure 4.—The fluorene polarographic diffusion current, i_d, as a function of Q, the total amount of charge passed in the electrolysis of 1.0 mM fluorene in 0.01 M resorcinol–0.1 M TBAP–DMF. Shown below is the polarographic reduction wave of the purple solution resulting from addition of oxygen to the above electrolyzed solution.

diffusion current, i_d, is expected to yield a straight line when plotted *vs.* Q, the total charge passed in the electrolysis.[6] That is,

$$i_d = i_{d_0}\left(1 - \frac{Q}{nFVC_0}\right) \tag{7}$$

where Q = total charge passed in the electrolysis, recorded *vs.* i_d, the polargraphic diffusion current at time $= t$; i_{d_0} = polarographic diffusion limited current at $t = 0$; V = volume of solution; C_0 = original concentration of fluorene in molarity; n and F have their usual meaning.

Figure 4 shows the observed results as well as the theoretical results to be expected for n values from 1 to 4. Experimentally, an n value of just under 3.0 was observed over the entire span of the exhaustive electrolysis. As expected, no indication of any measurable fluorene carbanion concentration was found spectrophotometrically, nor was any observed polarographically. The electron change of 3.0 indicates that a reactive species is formed, as reduction of a double bond in the usual ECE sense requires but two electrons and yields a stable dihydro product. Addition of air to the system after electrolysis in protic DMF and DMSO results in the gradual formation of a purple species, likewise indicating that a reactive intermediate is present. However, as the electrolyzed solution is colorless before admission of air, the reactive species is most likely not a radical or radical ion. Formation of the purple species takes several hours to complete, also indicating that the electrolysis product is not a radical. In order to confirm this, the esr spectra of both the colorless electrolysis solution and the purple solution resulting on admission of air were examined. In neither case was any evidence for a radical species obtained. The polarographic wave associated with the purple species (in protic media) is shown in Figure 4. The relatively low cathodic reduction potential suggests that some type of oxygenated species (which is easily reduced) has been formed. The purple solution, formed in both DMF and DMSO, exhibited an unusually broad visible spectrum, extending from 450 nm to 650 nm (Figure 5). Extensive attempts to isolate this species met with failure, as decoloration occurred for all separation methods tried. It was observed that in sunlight this purple solution was converted to a bright yellow after a few hours. In order to obtain sufficient material for investigation, exhaustive electrolyses were carried out, in DMF, on more concentrated solutions (0.05 *M* fluorene, 0.05 *M* resorcinol). Again no anion is formed during electrolysis and, again, the dark brown-purple solution formed with admission of air. This solution, which exhibited an absorbance peak with similar maximum and shape to the purple compound formed under more dilute conditions, was warmed slightly, and was converted completely to the purple. When exposed to uv light it also turned yellow, yielding *fluorenone* as the major product. This purple species can be identified as being the cation



of the ketone. The spectrum is virtually identical with that normally obtained when fluorenone is dissolved in concentrated sulfuric acid.[19] It is interesting to note that this protonated species cannot be formed by approaching from the opposite direction (addition of fluorenone to a nonaqueous solution containing excess proton donor). It is not stable and can only be obtained during the decay of the colorless electrolysis product, or under the forcing conditions of very high proton activity. In addition, several other products were observed, as minor constituents, during separation; none of these could be isolated and identified. It should be mentioned, however, that *none of these minor products resembled* (even remotely) *a dihydro* or higher reduced form of fluorene, which would result from the usual ECE process.

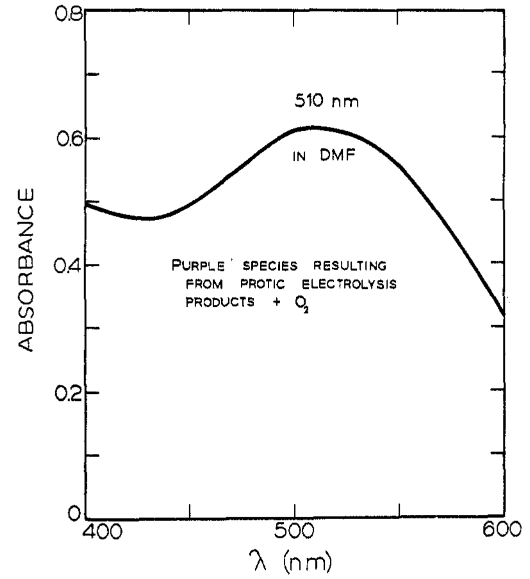
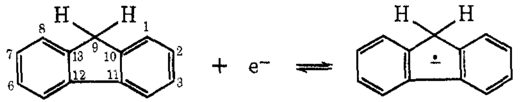


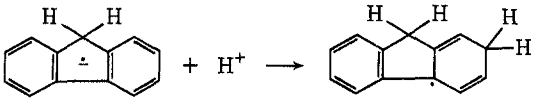
Figure 5.—Visible adsorption spectrum of the purple solution resulting from addition of O_2 to electrolyzed 1.0 m*M* fluorene–0.01 *M* resorcinol–0.1 *M* TBAP–DMF.

Therefore, under protic, just as under aprotic conditions, it appears as if the normal ECE sequence is not followed. Instead of a dihydrofluorene, the product, after oxidation with air, is a protonated form of fluorenone (perhaps ion pair stabilized) which is degraded to fluorenone on uv light treatment. The intermediate species formed on electrolysis in protic media appears to be more stable than those formed under aprotic conditions, as the purple product (protic conditions) takes several hours to form completely after oxygen is admitted, while the red and blue intermediate species in MeCN,[18] and fluorenone itself in DMF and DMSO (aprotic conditions), form immediately in the presence of air. One might conclude that under protic conditions, in view of the three-electron change, a dimeric species is formed, accounting for the fact that the colorless species is not a radical. These dimers might then react with oxygen and be further degradable to fluorenone under uv light. The spectral changes of both 9,9′-bifluorene and bifluoronylidene with excess proton donor present were studied as these compounds were exposed to uv light in the presence of oxygen. Although the bifluoronylidene did convert to fluorenone, there was no spectral evidence of the purple intermediate or any of the intermediates described above. Likewise, none of the spectral data obtained on the electrolysis solutions gave any evidence of bifluoronylidene or any oxygenated intermediate of it. Also, because of the dilute nature of the electrolysis solutions, it is unlikely that reactive radical intermediates would form the coupled dimer in quantitative yield; one would expect numerous decay paths for a radical of fluorene, especially in view of the excess proton donor. Consistent with the experimental observation that the intermediate product reacts with oxygen to form a protonated fluorenone cation species and this oxidized intermediate can be degraded (with uv light) to fluorenone is the proposition that the point of attack in the oxidation of the colorless reduction product is at the 9 (bridging) position. Also, the fact that an apparent *n* value of 3 is observed with no evidence of dimerization or higher order polymerization on reduction permits one to speculate on a possible mechanism for the electroreduction of fluorene in protic media (which can be either a large excess of the parent hydrocarbon or an added acidic organic species). As Casson and Tabner[8b] have determined the spin density of the fluorene radical anion (I) to be greatest at the 2 position, and, as the proton donor obviously causes a follow-up chemical reaction, the first two steps in the reaction are probably[9] eq 8 and



(8)

I



(9)

II

9, which are the same as the first two steps in a typical aromatic hydrocarbon reduction in the presence of a proton donor. Fessenden and Schuler have determined the spin density of the cyclohexadienyl radical

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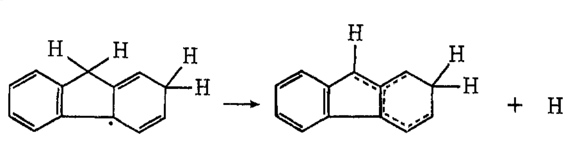
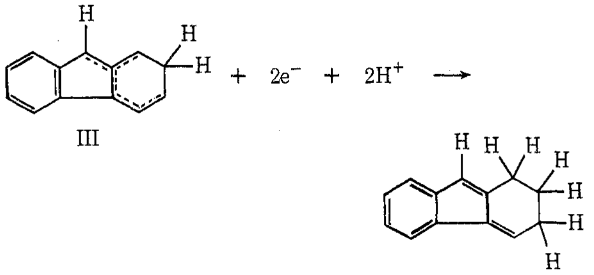
(19) (a) J. Michl, R. Zahranik, and P. Hochman, *J. Phys. Chem.*, **70**, 1732 (1966). (b) The structural characteristics of the spectrum of the purple species are identical with those of fluorenone in concentrated H_2SO_4. There is a slight difference in the peak maximum; 510 nm in DMF and 540 nm in concentrated H_2SO_4. However, this is not surprising for such different solvent systems. It is assumed that the species formed in concentrated H_2SO_4 is the simple protonated form of fluorenone, as dilution of the acid with H_2O results in complete recovery of the fluorenone. It is interesting that this protonated species is formed in the protic nonaqueous media under these conditions as the effective acid strength of these nonaqueous solution is certainly much less than that of concentrated H_2SO_4.

system to be greatest at the para position, *i.e.*, at the sp^2-hybridized carbon opposite the sp^3 carbon atom.[20] By analogy, then, we speculate that the electron in the fluorene radical is localized in the π orbital on the number 11 carbon as indicated by structure II in reaction 9, and we argue *post facto* that the normal ECE second electron transfer is either kinetically or thermodynamically unfavorable. We simply do not find any evidence of tetrahydrofluorene, the product expected if a second electron transfer occurs. Apparently, the electrode potentials applied are not large enough to force a second electron into species II, although the more negative potentials of lithium metal reduction will accomplish this.[9] As we have identified hydrogen gas being evolved on electrochemical reduction under these conditions and other investigators[8,21] have suggested that hydrogen is a product of the metal mirror reduction of fluorene, we suggest that species II then undergoes an elimination of H· to form III.



II III (10)

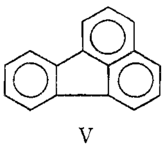
Species III would be expected to be easily reduced at the potentials employed in the electrolysis to form IV.



III IV (11)

This mechanism accounts for the $n_{app} = 3$ and a product which does not exhibit an esr spectrum. We suggest that species IV is the colorless electrolysis product that we obtain under protic conditions. As partially reduced fluorene compounds such as the tetrahydro and hexahydro species are known to oxidize under relatively mild conditions,[22] it is certainly possible that species IV would oxidize in the presence of O_2 to form the cation I and eventually yield fluorenone.

Although we have no direct evidence for the proposed intermediates and product, II, III, and IV, respectively, an indirect test of this sequence is possible. This mechanism predicts that, if the loss of H· from the 9 carbon is prevented or not possible (reaction 10), the subsequent further reduction of a double bond to give an $n_{app} = 3$ cannot occur. We have, therefore, examined the reduction of fluoranthene (V) (which has no proton at the analogous 9 position of fluorene) under identical conditions of solvent and proton donor concentration. We find that the limiting current of the first one-electron wave for fluoranthene does *not* increase with increasing concentration of proton donor. However, the value of the $E_{1/2}$ does shift positive as a function of added proton donor, indicating that the proton donor does bring on a follow-up chemical reaction of some kind. This is exactly as would be expected if the loss of a 9-position hydrogen was a determining step in the mechanism of the three-electron ECE mechanism for fluorene.



V

Protic Conditions in MeCN.—Because of the proximity of the fluorene reduction wave to background breakdown in MeCN, definitive protic electrolysis data was more difficult to obtain than in DMF or DMSO. Nevertheless, exhaustive electrolysis (at −3.05 V) of fluorene in resorcinol medium was performed in MeCN. No evidence of fluorene carbanion was found, similar to the situation in DMF and DMSO. An i_d *vs.* Q slope equivalent to an n value of about 2.5 was obtained. It seems, therefore, as if a three-electron transfer path may also occur in MeCN.

When air is admitted to the electrolyzed fluorene solution in MeCN (0.01 M in resorcinol) a yellowish coloration gradually appears, which becomes somewhat brownish on standing. The visible spectrum exhibits one broad band, similar to that observed for the purple solution in DMF and DMSO, but λ_{max} is 448 nm rather than about 500 nm. Ultraviolet light causes this "intermediate" to break down into several components, one of which appears to be fluorenone. Therefore, a reactive intermediate also seems to form in the protic electrolysis of fluorene in MeCN, as in DMF and DMSO. While this oxygenated intermediate has a different color than formed in DMF and DMSO (yellow *vs.* purple), it is possible that it is the same or a closely similar species, and merely shifted toward shorter wavelengths. Admittedly, though, this shift is larger than one would expect merely from solvent effects.

Conclusions

Several statements can be made, in conclusion, about the fluorene system. First, it appears as if the anion radical, $RH_2\cdot^-$, is somewhat more stable in dipolar, aprotic solvents than had been thought previously,[8a] as it could rather easily be seen at lowered temperatures in DMF and MeCN, and in carefully prepared DMF at room temperature. Presumably, if extensive care (such as drybox conditions) were taken to remove oxygen and impurities, the anion radical produced in dilute fluorene solutions should be even more stable in these solvents.

Secondly, of the three solvents studied, the one most suited for the study of the fluorene anion appears to be DMSO. This is no doubt related to its strong solvating tendency. The relatively acidic acyl proton of the DMF molecule probably results in lowered carbanion stability in that solvent,[23] while MeCN is just not a good solvating agent toward anions.

Finally, it appears that the fluorene anion radical does not degrade *via* the usual ECE reaction sequence of alternant hydrocarbons, but, rather than the second

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[20] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **38**, 773 (1963).

[21] B. J. Bitman and I. Skorokhodov, *Teor. Eksp. Khim.*, **6**, 418 (1970); N. L. Bauld and J. H. Zoller, *Tetrahedron Lett.*, **No. 10**, 885 (1967).

[22] W. Treibs and E. Heyner, *Chem. Ber.*, **90**, 2285 (1957).

[23] M. D. Malbin and H. B. Mark, Jr., *J. Phys. Chem.*, **75**, 2992 (1969).

electrochemical step, forms anaerobically stable reaction intermediates under both protic and aprotic reduction conditions. Whereas normally under protic conditions a two-electron change and addition of two protons to a double bond to form a dihydro product is found for alternant hydrocarbons, fluorene reduction under the same conditions does not lead to a dihydro or any other stable reduction product.

As was pointed out earlier, fluorenone is also formed as a major product of the electrochemical reduction of fluorene under aprotic conditions, as expected, but in greater amounts than the ECE mechanism would allow; unexpectedly, no dihydrofluorene is found here either. It appears as if one of the reaction intermediates, possibly the product of $RH_3\cdot$ reaction with solvent, in the presence of oxygen, reacts very readily with unelectrolyzed fluorene, in a second pathway to the ketone besides that through the carbanion. A significant solvent effect is observed in that addition of oxygen to the electrolyzed aprotic fluorene solution leads to different colored intermediates in MeCN than in DMF and DMSO. The major and final product in all three solvents is, however, fluorenone.

As different intermediates are observed depending on whether protic or aprotic conditions obtain, it is clear that different pathways to the ketone exist. One fact seems consistent, however, that the second electrochemical step ($RH_3\cdot + e^- \rightarrow RH_3^-$) does not occur in either case, and up to reaction 10 the sequences are probably the same.

Further study is necessary to establish the nature of the differencs in the reaction pathways and intermediate stabilities (the inability to isolate the purple cation species is puzzling, and further investigation is in progress) and to define the nature of the reaction products formed in both protic and aprotic conditions. Nevertheless, it seems clear from this work that fluorene does not follow the normal ECE sequence. It would be of interest to study other nonalternant hydrocarbons to determine if the above behavior is common with nonalternant species or peculiar to the fluorene-type structure.[24]

Registry No.—Fluorene, 86-73-7; dimethylformamide, 68-12-2; dimethyl sulfoxide, 67-68-5; acetonitrile 75-05-8; fluorene anion radical, 34484-03-2; fluorene carbanion, 35782-20-8; fluorenone anion radical, 37439-74-0.

Acknowledgment.—The authors wish to express their thanks to David B. Knight and Philip J. Hamrick, Jr., for helpful discussions concerning this investigation. Professor Hamrick was also kind enough to provide us with some 9-substituted fluorene compounds used in this study.

[24] We have some evidence that 9,10-dihydrophenanthrene also exhibits an *n* value of about 3.0 under protic conditions in DMF, but further study of this system is necessary. It should be noted that this species is also a cross-conjugated, biphenyl-related compound.

Reduction with Trichlorosilane. II.
Mechanistic Study of Reduction of Methyl Acetate to Ethyl Methyl Ether

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The kinetics of the previously reported reduction of alkyl aliphatic carboxylates with trichlorosilane under γ and photoirradiations was studied by using methyl acetate as a starting material. Initially the stoichiometry corresponded to $CH_3COOCH_3 + 3Cl_3SiH \rightarrow C_2H_5OCH_3 + SiCl_4 + HSiCl_2OSiCl_3$. However, since trichlorosiloxydichlorosilane behaved similarly to trichlorosilane, the amount of trichlorosilane consumed at the later stage of the reaction was smaller than 3 mol and the amount of trichlorosiloxydichlorosilane produced was less than 1 mol. Acetaldehyde was detected together with ethyl methyl ether by glpc analysis. The formations of intermediates, acetal type and α-chloroethyl methyl ether, were supported by several results. These intermediates gave acetaldehyde during glpc analysis, and were converted to ethyl methyl ether under irradiations with trichlorosilane. A free-radical chain mechanism *via* these intermediates was proposed. The rate of methyl acetate consumption is derived as $-\mathrm{d}[\text{methyl acetate}]/\mathrm{d}t = k(\text{dose rate})^{1/2} \times [\text{trichlorosilane}]$ by assuming that recombination of $CH_3\dot{C}(OSiCl_3)OCH_3$ radicals predominates over other termination steps. This rate equation is consistent with the results obtained by kinetic determinations. A small amount of benzene added to the reaction system was found to strongly retard the reaction, suggesting that benzene acts as a scavenger of trichlorosilyl radical.

In paper I of this series,[1] we reported that trichlorosilane can reduce alkyl aliphatic carboxylates, in some cases quantitatively, to dialkyl ethers under γ irradiation, and proposed that the reaction may proceed by a free-radical chain mechanism. However, the detailed mechanism has remained unsettled.

$$\mathrm{RCOOR'} \xrightarrow[\mathrm{Cl_3SiH}]{\gamma\ \mathrm{ray}} \mathrm{RCH_2OR'}$$

Also, one could not explain why carboxylic esters containing an aryl group in either R or R′ of RCOOR′ could not be reduced by this reaction. In the present paper we have established the reaction mechanism of methyl acetate with trichlorosilane under γ and photoirradiations. In addition, we found that addition of a catalytic amount of benzene to the reaction system greatly retarded the reaction. This retarding effect is interpreted by assuming that benzene acts as a scavenger of trichlorosilyl radical. This effect explains why carboxylic esters containing an aryl group cannot be reduced.

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(1) J. Tsurugi, R. Nakao, and T. Fukumoto, *J. Amer. Chem. Soc.*, **91**, 4587 (1969).