

CHAIN REACTIONS IN SEVERAL 9-SUBSTITUTED FLUORENES AND
BIFLUORENYLS INDUCED BY ELECTROGENERATED BASES

by

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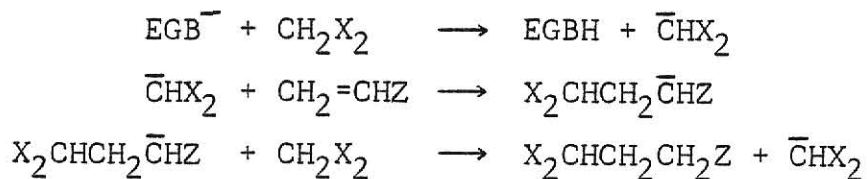
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INTRODUCTION

Chain reactions which are induced by the initial electrochemical generation of the chain-carrying species have been reported for several reaction types, including certain aromatic nucleophilic substitutions,¹ cis-trans isomerization of olefinic compounds,² ligand exchange³ and isomerization⁴ of organic complexes, and the formation of olefins and azines upon the oxidation⁵ and reduction⁶ of certain diazoalkanes, respectively.

Electrogenerated bases have also been reported to induce chain reactions. The reaction of oxygen with electrogenerated fluorenyl anion to form fluorenone⁷ is one such example. Baizer et al.⁸ have reported the use of electrogenerated bases produced from the reducible activated olefins or azobenzene in a base catalyzed reaction. In that reaction, only 1-10% of the olefins need to be reduced in order to initiate the catalytic reaction. The electrogenerated base may be an initially formed radical anion or the product of subsequent reactions of that species. The mechanism involves the abstraction of a proton from the donor compound by an electrogenerated base (EGB⁻) producing the carbanion of that compound which then reacts with the olefin to give the product.



In this thesis, three additional chain reactions which are induced in several 9-substituted fluorenes and bifluorenyls by electrogenerated bases have been studied. Although either a

fluorene (FlH_2) or a bifluorenyl ($(\text{FlH})_2$) that is substituted in the C_9 position is involved in all processes, the three types of



chain reactions differ significantly: electrochemically induced elimination of methanol occurs from 9-methoxybifluorenyl (FlHF1OCH_3); carbon-carbon bond cleavage occurs in the indirectly electrogenerated conjugate bases of 9-hydroxybifluorenyl (FlHF1OH) and 9,9'-dihydroxybifluorenyl ($(\text{FlOH})_2$); and an electrocatalyzed homogeneous redox reaction ensues between azobenzene (PhN=NPh) and either 9-fluorenol (FlHOH) or 9-fluorenylamine (FlHNH_2).

EXPERIMENTAL

Instrumentation

Cyclic voltammetric and chronoamperometric experiments were performed with three-electrode potentiostats which incorporated circuits for electronic correction of ohmic loss between the reference and the working electrodes.⁹ Control of the potentiostat and the acquisition and processing of the chronoamperometric data were performed with a laboratory digital computer (PDP 11/34, Digital Equipment Corp.). Readout for cyclic voltammetric studies with a scan rate of 0.5 V/s or less was to a Moseley 7035B x-y recorder; the readout for more rapid scan rates (0.66 to 100 V/s) was to a Tektronix Model 564 oscilloscope which was equipped with Type 2A63 and 2B67 plug-ins and a Model C-12 Polaroid camera. The three-electrode potentiostat which was used for the exhaustive, controlled-potential electrolyses has also been described.¹⁰

Cells, electrodes and electrolysis procedures

All electrochemical experiments were performed on an all-glass vacuum line. The solvent, dimethylformamide, was transferred into the cell on a vacuum line by trap-to-trap distillation. Traces of oxygen, if present, were removed by several freeze-pump-thaw cycles. The surface of all working electrodes was platinum. All potentials listed are with respect to a cadmium amalgam which is in contact with dimethylformamide that is saturated with both sodium chloride and cadmium chloride (Type A-III);¹¹ this electrode is reported to have a potential of -0.75 V vs. SCE .¹² Dual reference electrodes were used in the rapid-scan cyclic voltammetric experiments which were performed at -22°C and -51°C .¹³ The second reference electrode, which was a platinum wire in series with a $0.1\text{ }\mu\text{f}$ capacitor, was placed in parallel with the cadmium amalgam electrode.

The extent of large-scale electrolyses was monitored periodically by cyclic voltammetry. At the conclusion of the experiment, the electrolysis mixture was protonated in a dry helium atmosphere with an appropriate proton donor (e.g., diethyl malonate (DEM)). The mixtures were then analyzed directly by high performance liquid chromatography (HPLC).

Chromatography

The products of the electrolyzed solutions were separated by HPLC using a 6.35-mm diameter, 25-cm length stainless steel column packed with LiChrosorb RP8, 10- μm particle size. The eluting solvent was a mixture of methanol and water; the ratio of the mixture was dependent upon the nature of the products being analyzed.

The flow rate of the eluting solvent was 1 ml/min. The detector and the solvent pump were Altex Scientific Inc., Model 153 analytical UV detector and Model 110A solvent metering pump, respectively. The wavelength used in these analyses was 254 nm. Calibration curves for standards of all products were constructed daily.

Chemicals

Dimethylformamide (Burdick and Jackson) was purified by passage through a column of alumina (80-200 mesh, Brockman activity 1, activated at 600°C overnight) and was collected over a mixture of activated Davison 4A molecular sieves and alumina. This procedure was carried out in a dry, nitrogen-filled glovebag.

9-Fluoreno1,¹⁴ 9-hydroxy-9,9'-bifluorenyl,¹⁵ 9,9'-dihydroxy-bifluorenyl,¹⁶ 9-methoxy-9,9'-bifluorenyl,¹⁷ and 9,9'-bifluorenylidene¹⁸ were synthesized according to literature procedures; all other compounds were commercially available. Purities of all compounds were verified by melting point determination and by HPLC.

RESULTS AND DISCUSSION

I. 9-Methoxy-9,9'-bifluorenyl (FlHF1OCH₃)

The electrocatalyzed elimination of methanol from FlHF1OCH₃.

The cyclic voltammetric behavior of FlHF1OCH₃ in DMF-0.1 F (n-Bu)₄NClO₄ (Figure 1a) consists of three irreversible cathodic processes on the first negative-going sweep, three anodic waves due to intermediates and the reduced forms of products on the reverse, positive-going sweep, and five cathodic waves on the second negative-going sweep. The reduction process at -1.56 V

- Figure 1 (a) Cyclic voltammogram for the reduction of a 2.81 mM solution of FlHF10CH_3 in DMF - 0.1 $\text{F}(\text{n-Bu})_4\text{NClO}_4$ at 23°C. The scan rate at a spherical platinum working electrode is 0.2 V/s.
- (b) Same as (a) except that 2.61 mM PhN=NPh is now present. The numbers 1 and 2 represent the first and second cycles, respectively.

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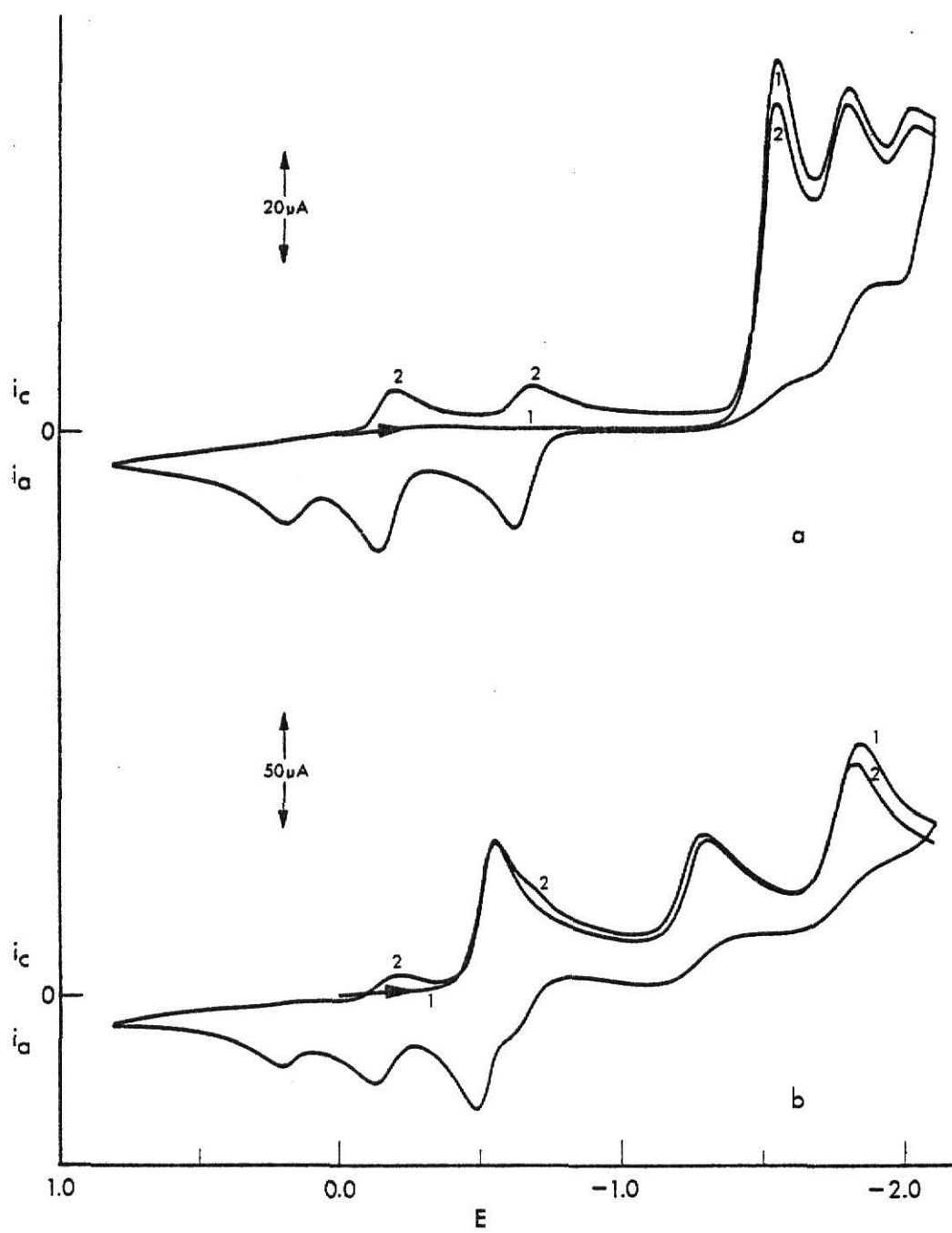
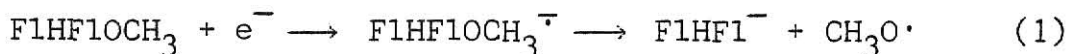


Figure 1

is due to FlHF1OCH_3 and is irreversible at all scan rates up to 100 V/s. The cathodic peaks at -1.82 and -2.07 V are attributed to the reduction of the conjugate bases of FlHF1OCH_3 and $(\text{FlH})_2$, respectively. Assignment of the $\text{Fl}(\text{OCH}_3)\text{Fl}^-$ process is based upon the behavior of FlHF1OCH_3 in the presence of the electro-generated base, PhN=NPh^{2-} (Figure 1b). The stepwise reduction of PhN=NPh occurs more readily than that of FlHF1OCH_3 ($E_{p,c} = -1.56$ V) and affords first the stable anion radical, $\text{PhN=NPh}^{\cdot-}$, at -0.58 V and then the unstable dianion, PhN=NPh^{2-} , at -1.30 V. The latter species rapidly abstracts the C_9 proton from FlHF1OCH_3 , resulting in the loss of cathodic peaks due to FlHF1OCH_3 and FlHF1^- at -1.56 and -2.07 V, respectively, and the appearance of peaks assigned to the reduction and oxidation of $\text{Fl}(\text{OCH}_3)\text{Fl}^-$ at -1.82 and 0.18 V, respectively (compare Figures 1a and 1b). The reversible couples near -0.20 and -0.68 V in Figures 1a and 1b are due to the stepwise reduction of bifluorenylidene (Fl=Fl) to its stable dianion and were identified by comparison to an authentic sample. The formation of Fl=Fl is kinetically controlled and occurs when methoxide ion is slowly eliminated from $\text{Fl}(\text{OCH}_3)\text{Fl}^-$. The identification of FlHF1^- as the species giving rise to the cathodic peak at -2.07 V in Figure 1a was made in a manner analogous to that for $\text{Fl}(\text{OCH}_3)\text{Fl}^-$. The electrogeneration of PhN=NPh^{2-} in the presence of $(\text{FlH})_2$ results in the loss of the cathodic peak for the irreversible reduction of $(\text{FlH})_2$ near -1.68 V and the appearance of a cathodic peak for the one-electron reduction of FlHF1^- to its relatively stable dianion radical, $\text{FlHF1}^{2\cdot-}$, at more negative potential ($E_{p,c} = -2.07$ V).¹⁹

The $\text{Fl}(\text{OCH}_3)\text{Fl}^-$ and FlHFFl^- reduction processes are also kinetically controlled. At -51°C and a scan rate of 10 V/s, no wave for the reduction of $\text{Fl}(\text{OCH}_3)\text{Fl}^-$ is evident. However, as the scan rate is slowly decreased, the wave due to $\text{Fl}(\text{OCH}_3)\text{Fl}^-$ emerges while the relative magnitude of the FlHFFl^- cathodic peak decreases. This behavior excludes heterolytic cleavage of the carbon-oxygen bond and the formation of $\text{FlHF}\text{Fl}\cdot$ and CH_3O^- as a mode of $\text{FlHF}\text{FlOCH}_3^-$ decomposition. If methoxide were formed, it should rapidly abstract a proton from unreacted starting material, thereby causing the immediate appearance of the cathodic wave for the reduction of $\text{Fl}(\text{OCH}_3)\text{Fl}^-$ at -1.82 V. However, kinetic behavior can be expected if $\text{FlHF}\text{FlOCH}_3^-$ decomposes by radical β carbon-oxygen bond scission, affording FlHFFl^- and $\text{CH}_3\text{O}\cdot$ as fragments (eq. 1). Kinetic control of the $\text{Fl}(\text{OCH}_3)\text{Fl}^-$ and FlHFFl^- processes should result when FlHFFl^- slowly abstracts the C_9 proton from unreacted starting material (eq. 2). The methoxy radical presumably abstracts a hydrogen atom from a component of the solvent-electrolyte system, although no attempt was made to ascertain the source of hydrogen in the product.



The coulometric reduction of $\text{FlHF}\text{FlOCH}_3$ in the absence of an added proton donor must involve a chain reaction, as evidenced by the fact that the passage of only 0.1 electron per molecule of $\text{FlHF}\text{FlOCH}_3$ consumes about 80% of the starting material (entry 1, Table). The principal product of this reaction is $\text{Fl}=\text{Fl}$. In the presence of diethyl malonate, $\text{Fl}=\text{Fl}$ and two of its stepwise

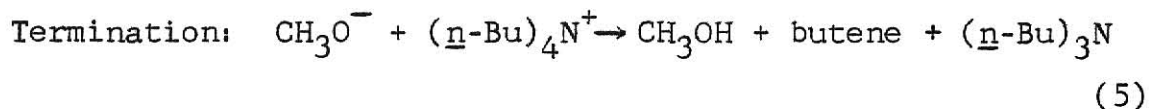
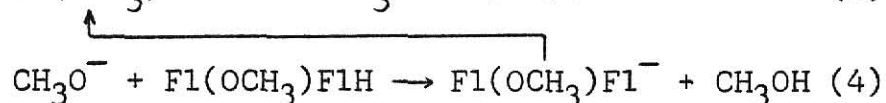
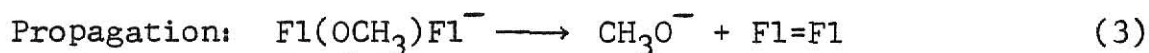
Table. Coulometric Data and Product Studies for the Controlled Potential Electrolytic Reductions
of Several 9-Hydroxy and 9-Methoxy Derivatives of R1fluorenyl

Entry No.	Compound	Conc., mM	E _{applied} , V	n	Proton Donor; Conc., mM	Products, % yield						
						FlHOR	FlH ₂	Fl=O	FlHF1OR	(Fl(OH)) ₂	(FlH) ₂	Fl=Fl
1	FlHF1OCH ₃	2.97	-1.55	0.10			0.5	0.6	21			76
2	FlHF1OCH ₃	2.97	-1.50	1.0	DEM; 36		8	0.9	68		16	7
3	FlHF1OH	3.35	-1.20	0.05			4.9	50				
4	FlHF1OH	2.99	-1.60	1.0	DEM; 36	3	25	11	52		10	2
5	(FlOH) ₂	3.70	-1.20	0.20		49	1.0	4.7				

reduction products, $(\text{FlH})_2$ and FlH_2 , are formed in large yield (entry 2, Table). Significantly, no FlHOCH_3 is formed in this reaction. This is additional evidence that FlHFloCH_3^- decomposes by scission of the carbon-oxygen bond and not by carbon-carbon bond cleavage as does $(\text{FlH})_2^-$.⁷

The proposed scheme for the electroreduction of FlHFloCH_3 .

The proposed scheme for the electrocatalyzed elimination of methanol from FlHFloCH_3 in the absence of added proton donors is described by eqs. 1 and 2 above and eqs. 3-5 below. After



homolytic cleavage of the carbon-oxygen bond in FlHFloCH_3^- , FlHF1^- abstracts a proton from unreacted starting material to give $(\text{FlH})_2$ and $\text{Fl}(\text{OCH}_3)\text{Fl}^-$. As evidenced by the effect which electrogenerated PhN=NPh^{2-} has upon the redox behavior of FlHFloCH_3 , $\text{Fl}(\text{OCH}_3)\text{Fl}^-$ then eliminates CH_3O^- , the chain-carrying species, to give $\text{Fl}=\text{Fl}$, the principal product (eqs. 3 and 4). In the presence of DEM, the relative amount of abstraction of the C_9 proton from FlHFloCH_3 by CH_3O^- and FlHF1^- is decreased, as demonstrated by the reduced yield of $\text{Fl}=\text{Fl}$ under these conditions (entry 2, Table). The formation of FlH_2 in the presence of DEM occurs when FlHF1^- is trapped by the proton donor; subsequent reduction of $(\text{FlH})_2$ at the applied potential then affords FlH_2 .⁷

The formation of $\text{Fl}=\text{Fl}$ when the electroreduction of FlHFloCH_3

is effected in the presence of DEM is not indicative of an alternate product-forming channel for this species. The failure to capture electrogenerated bases completely upon the addition of DEM as a proton donor is observed frequently when large delocalized anions such as FlHF1^- , FlH^- , Fl^-NNH , FlOH^- , and FlNH_2^- are involved.¹⁹ Similarly, slow proton transfer between carbon acids and large delocalized anions is often observed in the gas phase, including reactions such as these that are thermodynamically favorable.²⁰

II. 9-Hydroxy-9,9'-bifluorenyl (FlHF1OH) and 9,9'-dihydroxybifluorenyl ((FlOH)₂)

The reduction of FlHF1OH.

The cyclic voltammetric behavior of FlHF1OH at a platinum cathode in DMF-0.1 M $(\text{n-Bu})_4\text{NClO}_4$ is illustrated in Figure 2. Although the reduction of FlHF1OH ($E_{p,c} = -1.42$ V when $\nu = 0.2$ V/s and $T = 23^\circ\text{C}$) is irreversible at all scan rates up to 100 V/s in the temperature range $-51^\circ\text{C} \leq T \leq 23^\circ\text{C}$, several electroactive products arise from the decomposition of FlHF1OH^- on the reverse, positive-going sweep. By comparison to authentic samples, the anodic wave at -0.46 V arises from the concomitant oxidation of fluorenone anion radical (Fl=O^\cdot) and the conjugate base of fluorenone (FlOH^-), while the anodic wave near 0.16 V arises principally from the oxidation of 9-fluorenyl anion (FlH^-). The product of the anodic process at -0.46 V is Fl=O , which is reduced stepwise to its dianion on the second, negative-going sweep at -0.52 and -1.32 V. Subsequent reaction of Fl=O^{2-} with unreacted FlHF1OH causes the reduction of Fl=O^\cdot to Fl=O^{2-} to occur irreversibly

Figure 2 Cyclic voltammogram for the reduction of a 3.35 mM solution of FlHF10H in DMF - 0.1 M (n-Bu)₄NClO₄ at a spherical platinum electrode. The scan rate is 0.2 V/s; the temperature is 23°C. The scan is initiated in the negative-going direction at 0.0 V. The numbers 1 and 2 represent the first and second cycles, respectively.

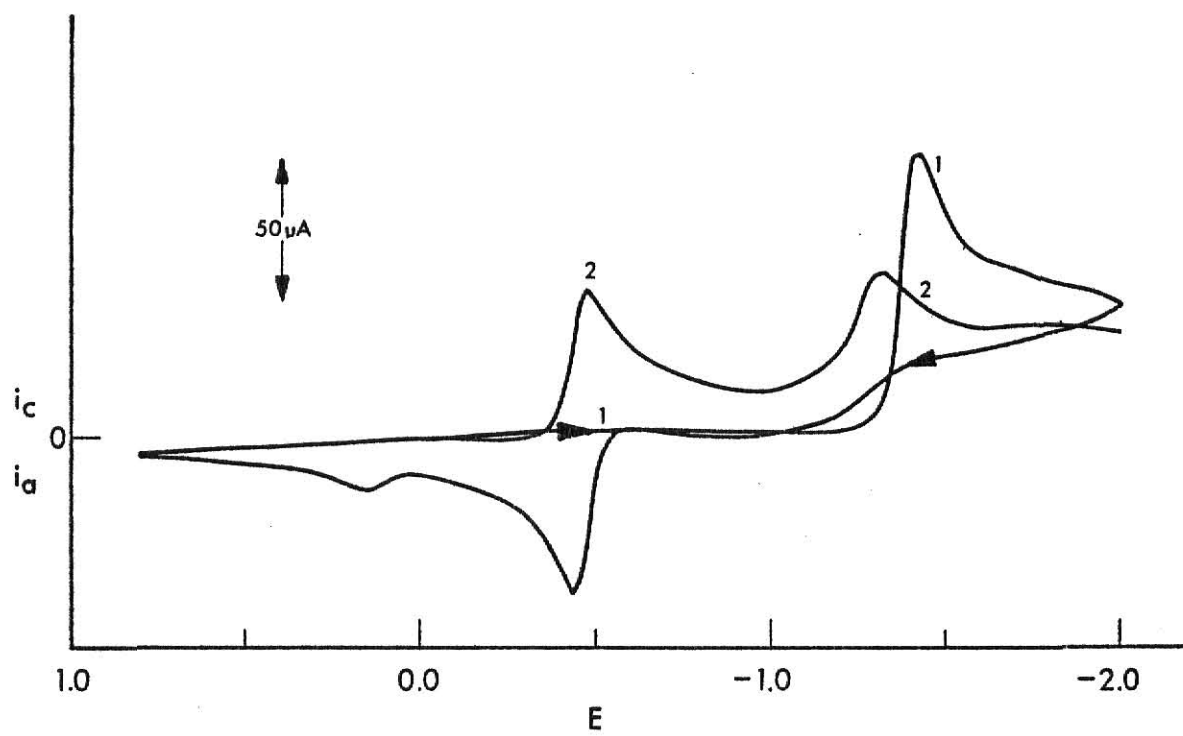


Figure 2

and to shift the cathodic peak for this process positively approximately 0.2 V from its normal, reversible potential. The oxidation of the other principal intermediate, FlH^- , affords both bifluorenyl ($(\text{FlH})_2$) and fluorene (FlH_2).⁷ The small, cathodic waves which are just evident on the negative-going sweep near -1.68 and -1.90 V are due in part to these species.

The occurrence of rapid, follow-up chemical reactions which afford a more readily reduced product is evidenced by the crossing of the current-potential curve near -1.34 V on the first cycle.²¹ This phenomenon is indicative of a chain process, an interpretation which is substantiated by the coulometry results. When electrolysis was halted arbitrarily at $n = 0.05$ electrons per molecule of FlHF1OH , no evidence of any unreacted FlHF1OH was found by cyclic voltammetry. Analysis of the products by HPLC showed that Fl=O and FlH_2 were formed in equimolar amounts and that together they accounted for all starting material (entry 3, Table).

The effect of DEM on the reduction of FlHF1OH .

The effect of DEM on the cyclic voltammetric behavior of FlHF1OH is illustrated in Figure 3: the cathodic wave for the irreversible reduction of FlHF1OH is shifted negatively to -1.70 V, a prominent couple appears at -1.90 V for the reduction of FlH_2 to its anion radical, a barely discernible wave arises near -2.07 V for the reduction of FlHF1^- , and the anodic waves due to FlOH^- and FlH^- in Figure 2 disappear. An HPLC analysis of a partially electrolyzed solution showed that, in addition to unreacted starting material, five products were formed: $(\text{FlH})_2$, 10%; FlH_2 , 25%; Fl=O , 11%; FlHOH , 3%; Fl=Fl , 2%; and FlHF1OH , 52% (entry 2,

Figure 3 Cyclic voltammogram for the reduction of a 3.23 mM solution of F1HF1OH in the presence of 6.46 mM DEM in DMF - 0.1 M (n-Bu)₄NClO₄. The scan is initiated in the negative-going direction at 0.0 V and at a rate of 0.2 V/s. The working electrode is spherical platinum; the temperature is 23°C.

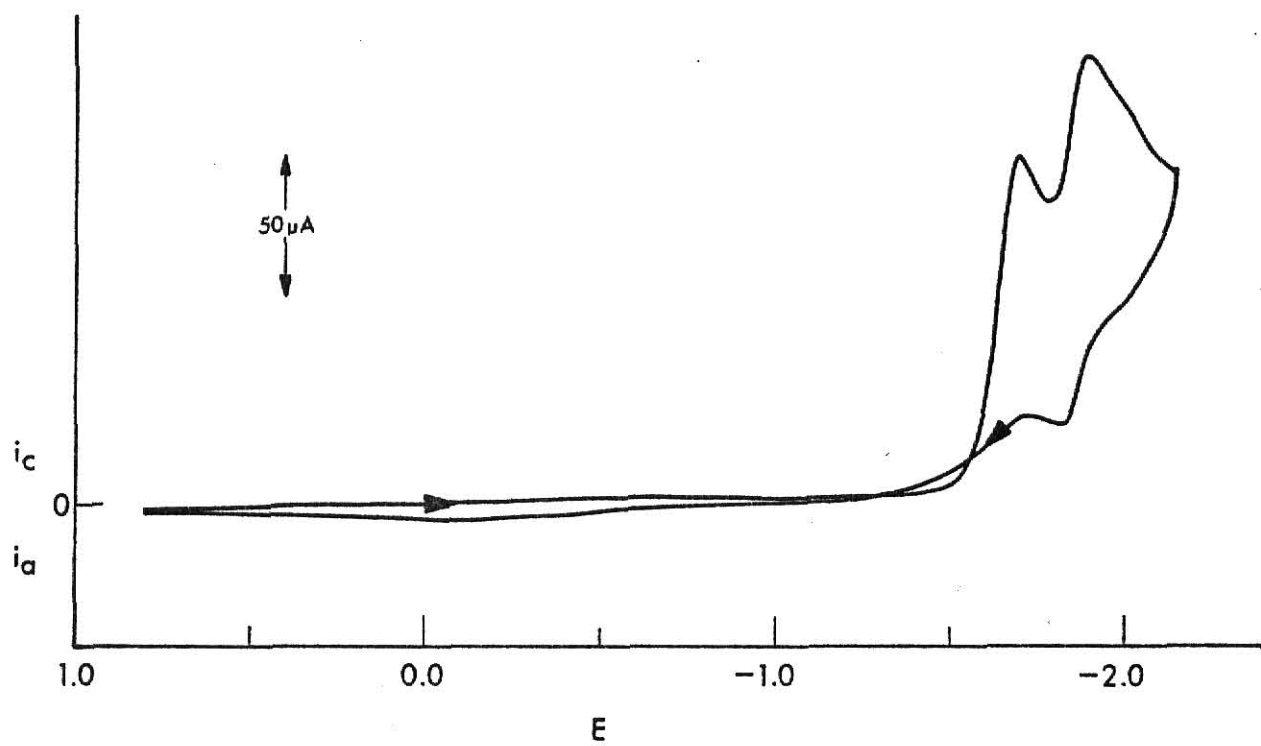


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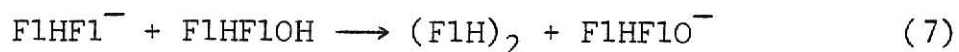
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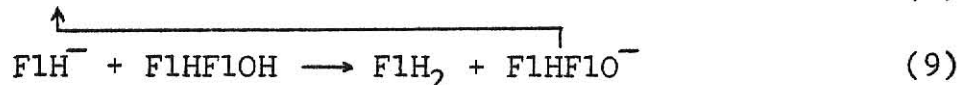
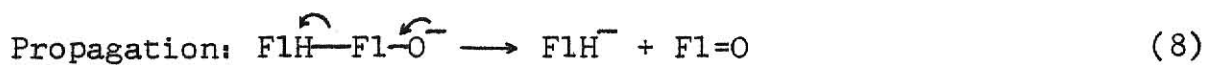
The effect of FlH^- and OH^- in the redox behavior of FlHF1OH .

The addition of FlHF1OH to a solution of either electro-generated FlH^- or $(\text{CH}_3)_4\text{NOH}$ results in the immediate disappearance of the cathodic wave for FlHF1OH and the appearances at more positive potentials of cathodic peaks for the stepwise reduction of Fl=O to its dianion. The reduction of Fl=O^\cdot to Fl=O^{2-} is irreversible, presumably because of the protonation of Fl=O^{2-} by the FlH_2 that is produced by the electrocatalyzed decomposition of FlHF1OH . HPLC analysis of the products formed by the reaction of FlHF1OH with OH^- showed that Fl=O and FlH_2 were formed in a 1:1 ratio. No other products were detected.

Decomposition pathway for FlHF1OH .

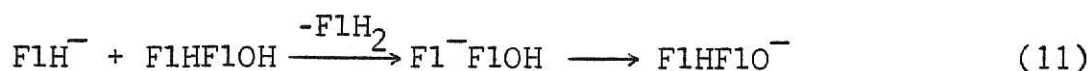
The absence of an anodic wave for reoxidation of FlHF1OH^\cdot at a scan rate of 100 V/s limits the lifetime of this anion radical to a maximum of 10^{-3} s. Since $(\text{FlH})_2$ formation is significant when reduction of FlHF1OH is effected in the presence of DEM, decomposition of FlHF1OH^\cdot by radical β carbon-oxygen bond scission to give FlHF1^- and OH^\cdot is suggested (eq. 6). FlHF1^- is then proposed in the absence of an added proton donor to abstract the hydroxylic proton from unreacted starting material (eq. 7) while the hydroxyl radical either abstracts a hydrogen atom from a component of the solvent-electrolyte system or is reduced.



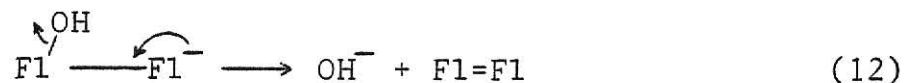


Propagation of the chain reaction involves heterolytic cleavage of the carbon-carbon bond in $\text{FlHF1O}^{\cdot-}$ to give $\text{Fl}=\text{O}$ and $\text{FlH}^{\cdot-}$, followed by the abstraction of a proton from FlHF1OH by $\text{FlH}^{\cdot-}$, the chain-carrying species. Termination of the chain occurs when $\text{FlH}^{\cdot-}$ abstracts a proton from $(\underline{n}\text{-Bu})_4\text{N}^+$, the cation of the supporting electrolyte. This scheme predicts that $\text{Fl}=\text{O}$ and FlH_2 should be formed in equimolar amounts, a prediction which is in excellent agreement with the experimental results (entry 3, Table).

The abstraction of the hydroxylic proton from FlHF1OH by $\text{FlH}^{\cdot-}$ has been written here (eq. 9). However, this pathway cannot be distinguished on the basis of our experiments from an alternative two-step process which involves, first, the abstraction of the C₉ proton from FlHF1OH by $\text{FlH}^{\cdot-}$ to give $\text{Fl}^{\cdot-}\text{F1OH}$, followed by an intramolecular 1,3-proton shift in this species to afford $\text{FlHF1O}^{\cdot-}$ (eq. 11).



Cleavage of the carbon-oxygen bond in $\text{Fl}^{\cdot-}\text{F1OH}$ in a manner analogous to $\text{Fl}(\text{OCH}_3)\text{Fl}^{\cdot-}$ is also plausible and might explain the small amount of $\text{Fl}=\text{Fl}$ that is formed in this reduction (eq. 12).



The formation of $\text{Fl}=\text{O}$ and FlHOH when electroreduction of FlHF1OH is effected in the presence of DEM requires comment.

Although this result might suggest that radical β carbon-carbon bond scission is a competing mode of FlHF1OH^- decomposition (eq. 13), we believe that the formation of Fl=O and FlHOH is

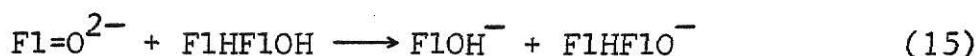
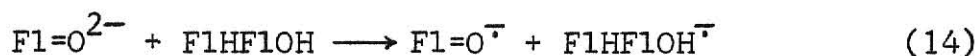


another artifact of slow proton transfer from DEM to FlHF1^- and FlH^- . In order to shut down the reactions which give rise to Fl=O and its reduction product, FlHOH (eqs. 7 and 9), the presence of relatively strong oxygen or nitrogen acids during the electroreduction of FlHF1OH would be required in order to capture all FlHF1^- and FlH^- afforded by reactions 6 and 8. Unfortunately, the acids which can effect protonation rapidly are also electroactive on platinum at the potentials that are required to reduce FlHF1OH . Although we did not attempt these electrocatalyzed reactions on other electrode surfaces, the electroreduction of FlHF1OCH_3 was shown above not to afford carbon-carbon bond cleavage products in either the presence or absence of DEM. Thus, since FlHF1OCH_3^- undergoes only radical β carbon-oxygen bond scission (eq. 1), it is reasonable to expect that FlHF1OH^- will behave similarly.

The effect of the electrocatalytic action of fluorenone on the cathodic peak potential of FlHF1OH .

It was noted above that the addition of DEM causes the cathodic peak for FlHF1OH to shift negatively approximately 0.3 V at room temperature. In addition, both scan rate and temperature affect the location of the cathodic peak potential. All effects, however, are manifestations of the electrocatalytic action of Fl=O on FlHF1OH . In the absence of DEM, Fl=O , which is afforded as a

product of the catalytic FlHF1OH decomposition reaction, is reduced stepwise and reversibly to its dianion. Either irreversible electron transfer from $\text{Fl}=\text{O}^{2-}$ to FlHF1OH (eq. 14) or the abstraction of a proton from FlHF1OH by $\text{Fl}=\text{O}^{2-}$ (eq. 15) could initiate the chain reaction for the decomposition of FlHF1OH (eqs. 6-10).



Since the crossing of the current-potential curve (Figure 2) requires these reactions to be rapid at 23°C, the reduction of FlHF1OH appears at the same potential as that for the reduction of $\text{Fl}=\text{O}^{\cdot-}$ to $\text{Fl}=\text{O}^{2-}$. In the presence of DEM, the electrocatalyzed reaction of FlHF1OH with $\text{Fl}=\text{O}^{2-}$ is interdicted because of protonation of $\text{Fl}=\text{O}^{2-}$; the reduction of FlHF1OH then occurs by heterogeneous electron transfer near -1.68 V. The absence of appreciable electrocatalyzed reaction of FlHF1OH with $\text{Fl}=\text{O}^{2-}$ at -51°C and/or rapid scan rate presumably is the result of the decreased relative rate at which $\text{Fl}=\text{O}$ is produced by reactions 7-9.

The electrocatalyzed cleavage of the carbon-carbon bond in $(\text{FlOH})_2$.

The cyclic voltammetric reduction of $(\text{FlOH})_2$ at a platinum cathode in DMF-0.1 F $(n\text{-Bu})_4\text{NClO}_4$ is illustrated in Figure 4a. Although $(\text{FlOH})_2^{\cdot-}$ is too unstable to give a corresponding anodic wave on the reverse, positive-going sweep, several other cathodic and anodic processes arise from its decomposition. The large anodic wave at -0.46 V is due to the concomitant oxidation of $\text{Fl}=\text{O}^{\cdot-}$ and FlOH^- .¹⁹ The product of both oxidations, $\text{Fl}=\text{O}$, is then reduced stepwise to its anion radical and dianion at -0.52

- Figure 4 (a) Cyclic voltammogram of a 3.38 mM solution of $(\text{FlOH})_2$ in DMF - 0.1 M $(\text{n-Bu})_4\text{NPF}_6$ at 23°C. The scan rate at the 0.25 cm² planar platinum working electrode is 0.2 V/s.
- (b) Cyclic voltammogram of an electrolyzed solution of 2.33 mM $(\text{FlOH})_2$ in DMF - 0.1 M $(\text{n-Bu})_4\text{NClO}_4$ at 23°C. The electrolysis was effected at a potential of -1.20 V and was terminated after the passage of 0.2 electrons per molecule of $(\text{FlOH})_2$. The working electrode for the cyclic voltammetric experiment was spherical platinum; the scan rate was 0.2 V/s.

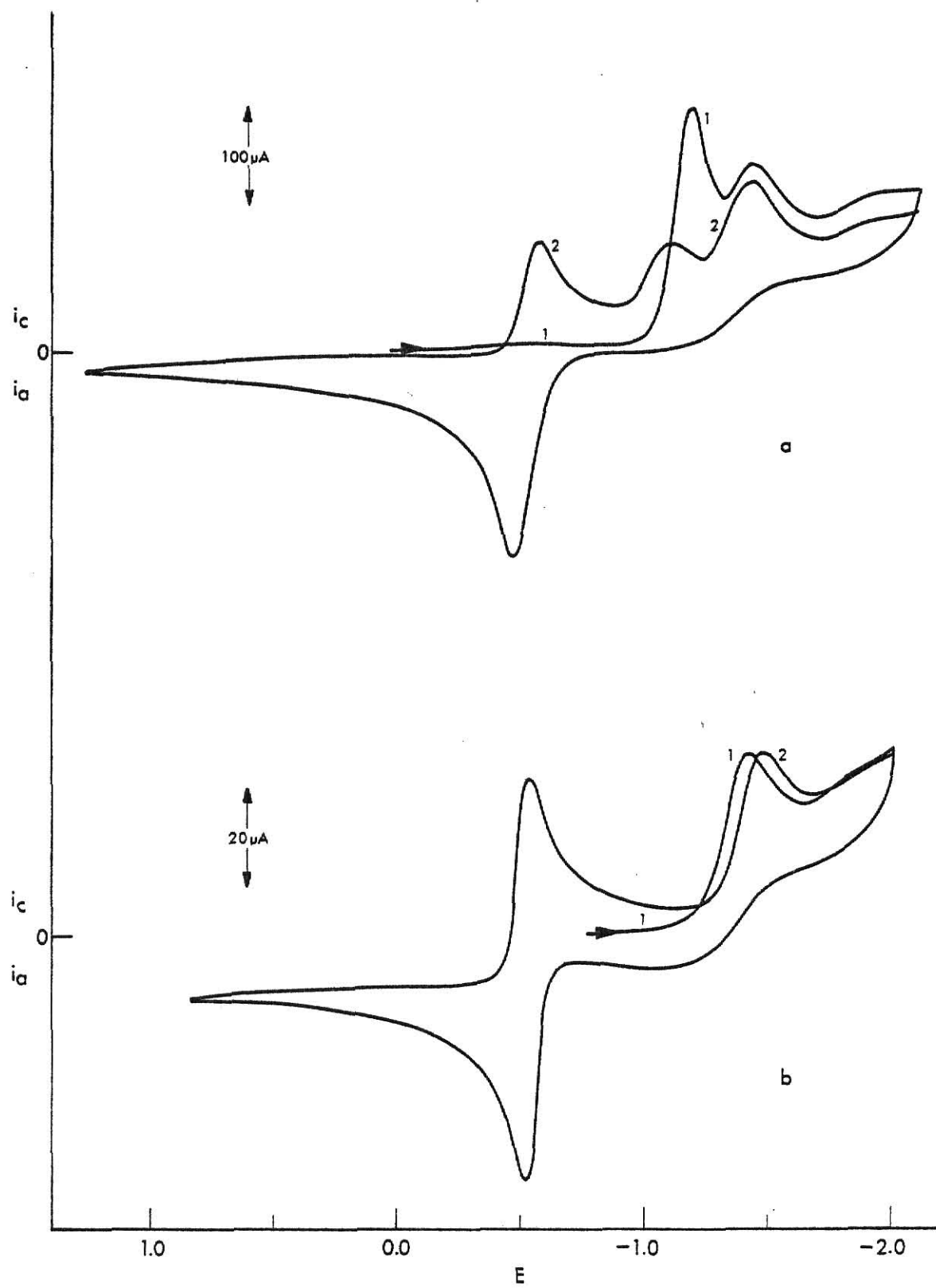


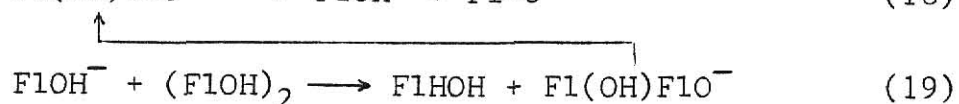
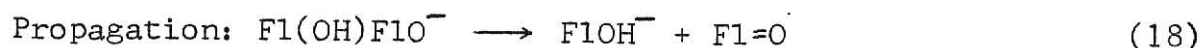
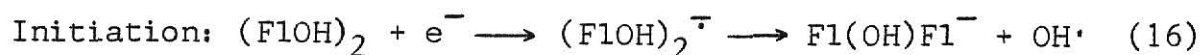
Figure 4

and -1.48 V, respectively. The latter reduction is irreversible, most probably as a result of protonation of $\text{Fl}=\text{O}^{2-}$ by unreacted $(\text{FlOH})_2$. The small cathodic wave near -1.85 V is due principally to FlHOH and its reduction products.¹⁹

Electrolysis of $(\text{FlOH})_2$ was generally complete after the passage of only 0.2 electrons per molecule (entry 5, Table). Analysis of the electrolyzed solution by HPLC showed that $\text{Fl}=\text{O}$ and FlHOH were formed in approximately equimolar amounts; the combined yields of these species accounted for nearly all starting material. Cyclic voltammetric examination of the electrolyzed solution showed a reversible couple due to $\text{Fl}=\text{O}/\text{Fl}=\text{O}^{\cdot-}$ near -0.52 V and an irreversible cathodic peak due to $\text{Fl}=\text{O}^{\cdot-}/\text{Fl}=\text{O}^{2-}$ near -1.36 V (Figure 4b). Loss of chemical reversibility for the latter reduction results from the protonation of $\text{Fl}=\text{O}^{2-}$ by FlHOH . Since $\text{Fl}=\text{O}$ and FlHOH are formed in equal molar amounts by the electrocatalyzed decomposition of $(\text{FlOH})_2$, the effect of the proton transfer reaction is to eliminate the cathodic wave for FlHOH that normally occurs near -1.85 V.

The proposed scheme for the electroreduction of $(\text{FlOH})_2$.

The proposed pathway for the electrocatalyzed transformation of $(\text{FlOH})_2$ into $\text{Fl}=\text{O}$ and FlHOH is analogous to that for FlHF1OH above. Radical β carbon-oxygen bond scission in $(\text{FlOH})_2^{\cdot-}$ (eq. 16),



Termination: $\text{FlOH}^- + (\underline{n}\text{-Bu})_4\text{N}^+ \rightarrow \text{FlHOH} + (\underline{n}\text{-Bu})_3\text{N} + \text{butene}$ (20)

followed by the abstraction of a proton from unreacted $(\text{FlOH})_2$ by $\text{Fl}(\text{OH})\text{Fl}^-$ (eq. 17), gives $\text{Fl}(\text{OH})\text{FlO}^-$. Propagation of the chain reaction involves carbon-carbon bond cleavage in $\text{Fl}(\text{OH})\text{FlO}^-$ (eq. 18), followed by the abstraction of a proton from $(\text{FlOH})_2$ by FlOH^- (eq. 19).

The feasibility of reactions 16-19 is demonstrated by the effect of added $(\text{CH}_3)_4\text{NOH}$ on the cyclic voltammetric behavior of $(\text{FlOH})_2$: the addition of this base causes the immediate disappearance of the cathodic wave attributed to $(\text{FlOH})_2$ and the appearance of two reversible couples assigned to the stepwise reduction of Fl=O to its dianion. No cathodic wave is observed for the reduction of FlHOH at its normal potential ($E_{p,c} = -1.85 \text{ V}$), however, since this species is deprotonated under these conditions to give FlOH^- which is subsequently oxidized at the same potential as Fl=O^- .¹⁹

Carbon-carbon and carbon-oxygen bond cleavage in the electroreduction of $(\text{FlOH})_2$ have been previously reported by Michel *et al.*²² However, these earlier workers neither identified the intermediates that gave rise to these modes of bond cleavage nor determined that the transformation of $(\text{FlOH})_2$ into Fl=O and FlHOH was a chain process induced by the electrogenerated base, $\text{Fl}(\text{OH})\text{Fl}^-$.

III. 9-Fluorenol (FlHOH) and 9-fluorenylamine (FlHNNH_2)

The electrocatalyzed oxidations of FlHOH and FlHNNH_2 with azobenzene (PhN=NPh).

The third type of chain process was observed when an attempt was made to prepare the conjugate bases of FlHOH and FlHNNH_2 using

$\text{PhN=NPh}^{\cdot-}$ and PhN=NPh^{2-} as the electrogenerated bases. The goal of this work was to prepare the more stable isomers of the conjugate bases of FlHOH and FlHNH_2 and to compare their electrochemical and chemical properties to those of electrogenerated FlOCH_3^- and $\text{FlN(CH}_3)_2^-$, respectively.

The effect which electrogenerated $\text{PhN=NPh}^{\cdot-}$ has upon FlHNH_2 and FlHOH is more apparent by cyclic voltammetry for FlHNH_2 . In the absence of azobenzene, a single cathodic peak is observed on the first negative-going sweep for the reduction of FlHNH_2 near -1.87 V (Figure 5a). Although this process is irreversible at this scan rate and temperature, an anodic peak, which is assigned to the irreversible oxidation of FlNH_2^- , is seen at -0.48 V on the reverse sweep. The product of FlNH_2^- oxidation, Fl=NH , is then reduced at -0.90 V on the second negative-going sweep. Although the reduction of Fl=NH to its anion radical is reversible in the absence of proton donors, the process is rendered irreversible here because of proton transfer to $\text{Fl=NH}^{\cdot-}$ from unreacted FlHNH_2 .

The addition of azobenzene ($[\text{FlHNH}_2]/[\text{PhN=NPh}] = 2.0$) results in the disappearance of the FlHNH_2 cathodic wave at -1.87 V (Figure 5b). The three new cathodic waves which appear on the first negative-going sweep are attributed to the reduction of PhN=NPh to its anion radical at -0.58 V, the reduction of Fl=NH to its anion radical at -0.90 V, and the irreversible reduction of the small amount of remaining $\text{PhN=NPh}^{\cdot-}$ to its dianion at -1.40 V. The relatively large anodic peak which is seen on the reverse sweep near -0.50 V is due to the concomitant oxidation of FlNH_2^- and unreacted $\text{PhN=NPh}^{\cdot-}$.

- Figure 5 (a) Cyclic voltammogram for the reduction of a 1.43 mM solution of FlHNH_2 in DMF - 0.1 $\text{F}(\text{n-Bu})_4\text{NClO}_4$ at 23°C . The scan rate at a spherical platinum working electrode is 0.2 V/s.
- (b) Same as (a) except that 0.71 mM PhN=NPh has now been added.
- (c) Cyclic voltammogram of the solution in (b) after electrolysis at an applied potential of -0.65 V and the passage of 0.3 electrons per molecule of PhN=NPh .

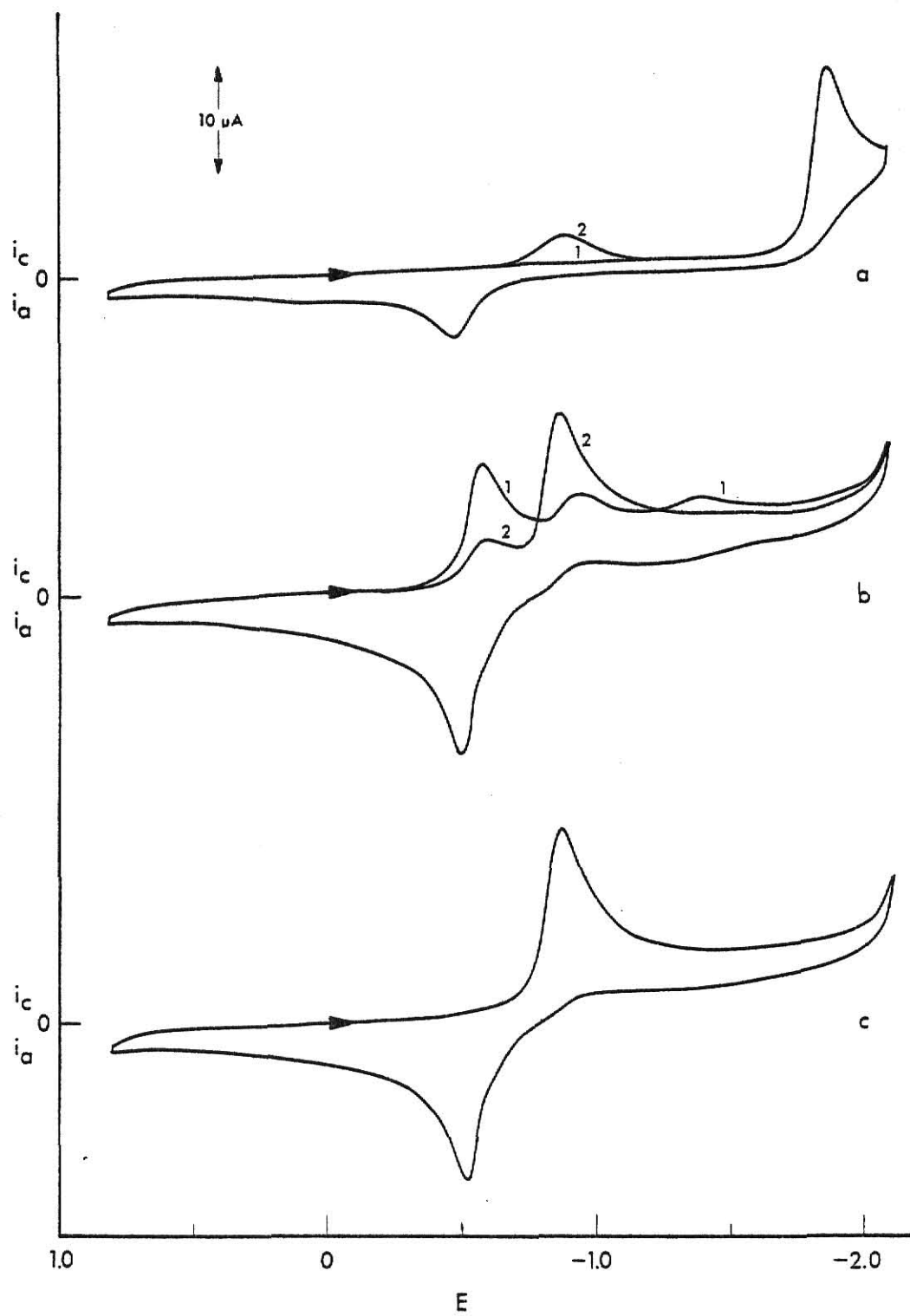


Figure 5

It is important to note that this cyclic voltammetric behavior cannot be the result of FlHNH_2 functioning simply as a proton donor for PhN=NPh^+ . If this were the case, an appreciable cathodic wave would not be expected for the reduction of Fl=NH on the first cathodic scan. In addition, when a constant potential electrolysis was effected at an applied potential of -0.65 V, approximately 80% of the FlHNH_2 and nearly all of the PhN=NPh was consumed after the passage of only 0.3 electrons per molecule of PhN=NPh . Cyclic voltammetric analysis of the electrolyzed solution showed only a single, irreversible peak due to the reduction of Fl=NH at -0.90 V and a corresponding anodic peak for the oxidation of FlNH_2^- at -0.48 V on the reverse sweep (Figure 5c). HPLC analysis gave the following product distribution: Fl=NH , 81%; FlHNH_2 , 17%; Fl=O , 1%; PhNHNHPh , 88%; and PhN=NPh , 12%. The observance of PhN=NPh among the final products is believed to result from the ready air oxidation of PhNHNHPh which occurs prior to and during the HPLC analysis of the electrolyzed solution.

Additional evidence for an electrochemically induced chain reaction is found in the chronoamperometric results. When the electrode potential is stepped from 0.0 V, where both PhN=NPh and an excess amount of FlHNH_2 are electroinactive, to -0.70 V, which is sufficiently negative to reduce only PhN=NPh to PhN=NPh^+ , slowly decreasing values of $it^{1/2}$ are observed for the first one second (Figure 6). The current then decreases abruptly to zero by four seconds, and remains near that value for the remainder of the experiment. This behavior is reminiscent of the $\vec{E}C\vec{E}$ chain process described by Feldberg³ and results when the initial electrode

Figure 6 Chronoamperometric data for the reduction of 1.70 mM PhN=NPh and 5.23 mM FlHNH₂ in DMF - 0.1 F (n-Bu)₄NClO₄ at a 0.25 cm² planar platinum electrode. The applied potential of -0.70 V is sufficiently negative to reduce PhN=NPh to its anion radical and sufficiently positive to oxidize Fl=NH⁻ to Fl=NH.

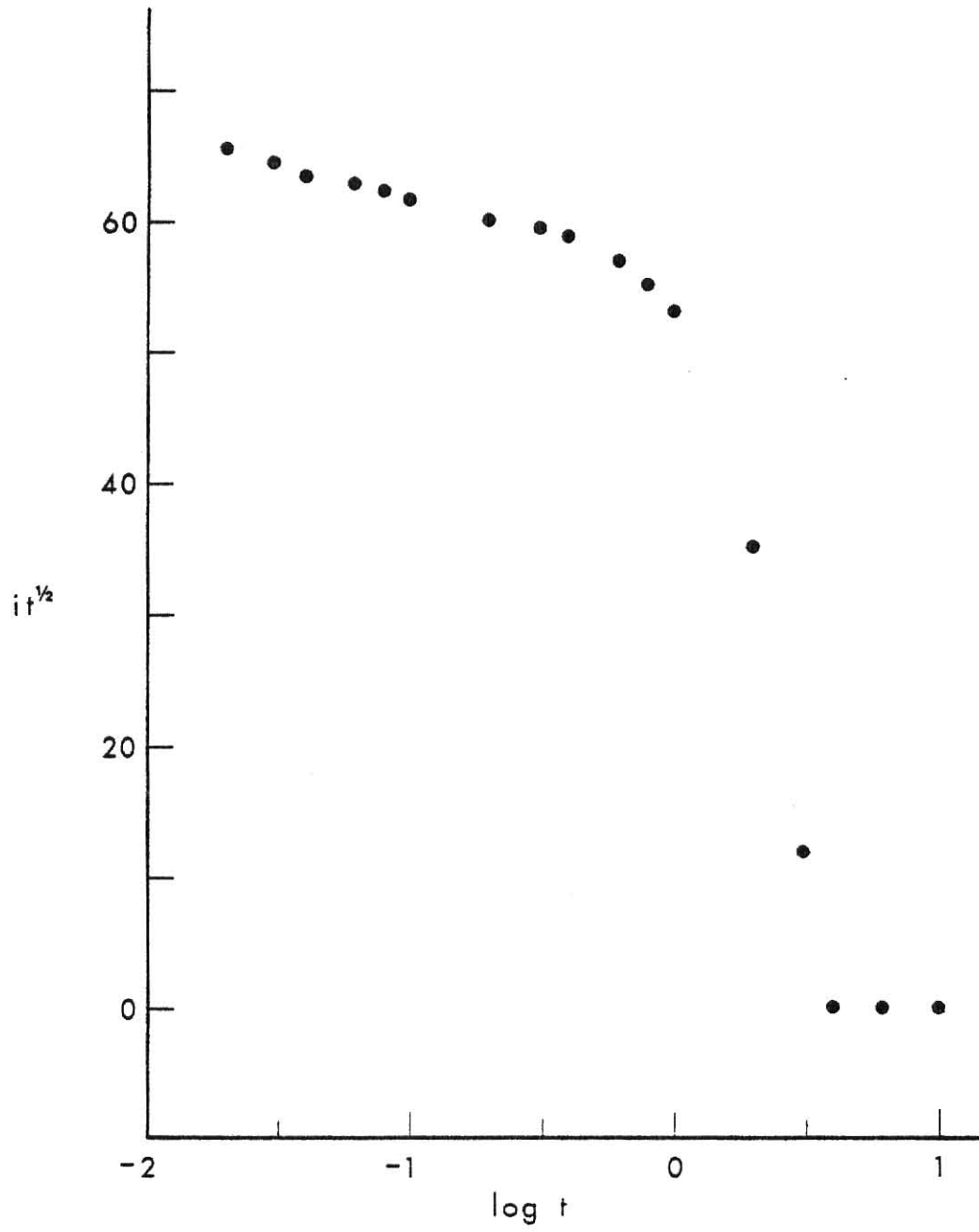
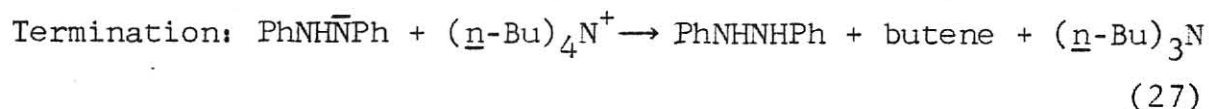
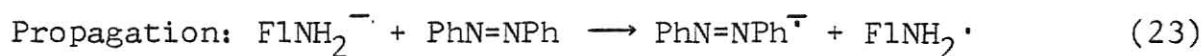


Figure 6

reduction product undergoes a homogeneous chemical reaction to afford a product which is oxidized at the applied potential. Although the actual shape of the $i t^{1/2}/C$ vs. $\log k t$ curve is also a function of the standard reduction potentials of the starting material and the product of the chemical reaction, a current which decays approximately exponentially is predicted.³

Similar cyclic voltammetric and coulometric results were obtained for the electrocatalyzed reaction of PhN=NPh with FlHOH . Product studies conducted after the arbitrary termination of a controlled potential electrolysis at the point $n = 0.1$ electron per molecule of FlHOH showed that 90 μmoles of the 114 μmoles of FlHOH which were originally present had been oxidized to Fl=O while 82.5 μmoles of PhN=NPh had been reduced to PhNHNHPh . Since the cathode potential of -0.8 V was insufficiently positive to oxidize FlOH^- ($E_{p,a} = -0.46$ V) to Fl=O , a reasonable explanation for these and the related results with FlHNH_2 is an electrochemically induced chain reaction. The pathway is illustrated for FlHNH_2 (eqs. 21-27).



The homogeneous chemical reactions consist of slow proton transfer from FlHNH_2 to electrogenerated $\text{PhN=NPh}^{\cdot-}$ (eq.22), the reduction of PhN=NPh by $\text{FlNH}_2^{\cdot-}$ (eq. 23) and proton transfers from FlNH_2^{\cdot} and FlHNH_2 to $\text{PhNHNPh}^{\cdot-}$ (eqs. 24 and 26, respectively). The final product of these solution reactions in the Feldberg³ formulation is $\text{Fl=NH}^{\cdot-}$, which is either oxidized electrochemically at the applied potential or reduces PhNHNPh in bulk solution (eq. 25). Since equimolar amounts of PhN=NPh and FlHNH_2 are consumed, and since the oxidation of FlHNH_2 to Fl=NH and the reduction of PhN=NPh to PhNHNPh each involves a two electron, two proton process, zero current results at this applied potential when all intervening chemical reactions are rapid.

CONCLUSIONS

The electrochemical reductions of several 9-substituted fluorenes and bifluorenyls have shown how the electrogenerated bases can be produced to catalyze chemical reactions. In the first series, $\text{FlHF1}^{\cdot-}$ generated from the carbon-oxygen bond cleavage of the electrogenerated anion radical of FlHF1OCH_3 abstracts the C_9 proton from unreacted starting material producing the corresponding conjugate base, $\text{Fl(OCH}_3\text{)Fl}^{\cdot-}$, which then eliminates the methoxide ion to give Fl=Fl . In the second series, the electrogenerated anion radicals of FlHF1OH and $(\text{FlOH})_2$ undergo the carbon-oxygen bond cleavage to give their corresponding electrogenerated bases, $\text{FlHF1}^{\cdot-}$ and $\text{Fl(OH)Fl}^{\cdot-}$, respectively. These species then abstract the hydroxylic proton from their unreacted starting materials causing the carbon-carbon bond cleavage of those starting compounds. In the third series, PhN=NPh has been

used as a base precursor in the reactions with FlHOH and FlHNH_2 . The electrogenerated azobenzene anion radical abstracts a proton from either FlHOH or FlHNH_2 to give the conjugate bases of those compounds. FlOH^- and FlNH_2^- then undergo a series of proton and electron transfer reactions to unreduced PhN=NPh to give hydrazobenzene (PhNHNHPh) and Fl=O and Fl=NH , respectively.

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CHAIN REACTIONS IN SEVERAL 9-SUBSTITUTED FLUORENES AND
BIFLUORENYLS INDUCED BY ELECTROGENERATED BASES

by

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ABSTRACT

Three types of chain reactions that are induced by electro-generated bases were studied. In the first series radical β carbon-oxygen bond scission in the electrogenerated anion radical of 9-methoxybifluorenyl (FlHF1OCH_3) affords OCH_3^\cdot and FlHF1^- . The latter species then abstracts the C_9 proton from unreacted FlHF1OCH_3 to give bifluorenyl ($(\text{FlH})_2$) and the corresponding conjugate base, $\text{Fl}(\text{OCH}_3)\text{Fl}^-$. The propagation cycle involves the slow loss of OCH_3^- from $\text{Fl}(\text{OCH}_3)\text{Fl}^-$, followed by the rapid abstraction of a proton from FlHF1OCH_3 by OCH_3^- to regenerate $\text{Fl}(\text{OCH}_3)\text{Fl}^-$. The final products of the base-induced transformation are bifluorenylidene ($\text{Fl}=\text{Fl}$) and CH_3OH . In the second series radical β carbon-oxygen bond scission in the electrogenerated anion radicals of 9-hydroxybifluorenyl (FlHF1OH) and 9,9'-dihydroxybifluorenyl ($(\text{FlOH})_2$) gives OH^\cdot and FlHF1^- and $\text{Fl}(\text{OH})\text{Fl}^-$, respectively. Subsequent steps include the abstraction of a hydroxylic proton from unreacted starting material by the electrogenerated base, followed by the heterolytic cleavage of the carbon-carbon bond in the resulting anions, FlHF1O^- and $\text{Fl}(\text{OH})\text{FlO}^-$. Fluorenone ($\text{Fl}=\text{O}$) and fluorene (FlH_2) are formed in equimolar quantities as the final products from FlHF1OH while $(\text{FlOH})_2$ affords $\text{Fl}=\text{O}$ and fluorenol (FlHOH). The third type of chain process is initiated when electrogenerated azobenzene anion radical (PhN=NPh^\cdot) abstracts a proton from either FlHOH or 9-fluorenylamine (FlHNNH_2). Electron transfer from the conjugate bases, FlOH^- and FlNH_2^- , to unreduced azobenzene then causes a series of proton and electron transfer reactions to ensue which results in the reduction of PhN=NPh to hydrazobenzene (PhNHNHPh) and the oxidation of FlHOH and FlHNNH_2 to $\text{Fl}=\text{O}$ and $\text{Fl}=\text{NH}$, respectively.