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Electrochemical Studies of 3,4-Dimethoxypropenyl
Benzene, Voltammetry and Controlled Potential
Oxidation at a Rotating Platinum Electrode
in Acetonitrile

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ELECTROCHEMICAL STUDIES OF 3,4-DIMETHOXYPROPENYL BENZENE
VOLTAMMETRY AND CONTROLLED POTENTIAL OXIDATION AT A
ROTATING PLATINUM ELECTRODE IN ACETONITRILE

A thesis submitted by

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SUMMARY

Although a wide variety of both chemical and biochemical oxidants have been utilized in the study of lignin and the so-called lignin model compounds, comparatively little attention has been paid to the electrochemical method of oxidation. The present investigation is the first application of the techniques of voltammetry and controlled potential electrolytic oxidation to the study of compounds containing the C_6-C_3 nucleus.

It has been shown that 3,4-dimethoxypropenylbenzene can be oxidized by a two-electron, irreversible process at a rotating platinum electrode in 0.5M sodium perchlorate-acetonitrile solution containing pyridine. The course of the reaction has been established by means of voltammetric and coulometric studies as well as by the isolation and identification of a dipyridiniumdiperchlorate of 3,4-dimethoxypropenylbenzene. The utility of the electrochemical method of oxidation is illustrated by the almost quantitative yield of the latter compound obtained in a preparative scale oxidation. Previous attempts to obtain addition products of the propenylphenol ethers have either produced the desired product in comparatively low yield or in some cases not at all. In most chemical oxidations of these compounds a variety of oxidation products is obtained.

The results suggest that by suitable modification of the supporting electrolyte-solvent system, similar additions of other nucleophilic groups such as the acetate or hydroxyl ions might be obtained without the formation of a variety of undesirable side-products.

In unbuffered acetonitrile, 3,4-dimethoxypropenylbenzene gives three waves corresponding to one-electron oxidation steps. Wave I was investigated in most

detail since a one-electron removal has been suggested as the initiating reaction in the polymerization of lignin precursors.

Wave I has been shown to correspond to a diffusion-controlled, one-electron oxidation which fulfills substantially the various criteria for voltammetric reversibility. Controlled potential electrolysis of 3,4-dimethoxypropenylbenzene in unbuffered acetonitrile is characterized by a rapid decrease in current accompanied by the liberation of from 0.5 to 1.0 hydrogen ions per electron transferred. The rapid decrease in current has been attributed to the combined effects of oxidation and acid-catalyzed dimerization of 3,4-dimethoxypropenylbenzene under the influence of the liberated hydrogen ion. This has been shown by the isolation of dimethyldiisoeugenol as the major product of the electrolysis as well as by separate kinetic studies of the effect of perchloric acid on the diffusion current constant in the absence of electrolytic oxidation.

The primary oxidation product obtained was a purple-colored material which appeared to be a dimeric perchlorate of 3,4-dimethoxypropenylbenzene. Treatment of the material with sodium hydroxide yielded a product whose infrared spectrum was characteristic of a substituted tetralin. A tentative mechanism has been proposed to account for the formation of this material as well as the liberation of hydrogen ion which involves free radical dimerization at the beta carbons of the side chains followed by ring closure. The absence of significant quantities of other oxidation products as shown by chromatographic investigation suggests that the intermediate carbonium ion radical is stabilized in some manner at the electrode surface permitting the dimerization of the intermediate in a preferred orientation. This behavior is suggestive of the directing influence characteristic of many enzymatic oxidation reactions.

The results obtained in this study indicate that the electrochemical method may provide the basis for a study of the conditions necessary for and the reactions leading to the formation of lignans. The first requirement as shown by the present studies is a means for the removal of hydrogen ion liberated in the reaction. If this requirement is met it is expected that high yields of these dimers could be obtained. Extensions of these studies to include compounds more closely related to coniferyl alcohol would be of interest in connection with the previous studies of the enzymatic oxidation of these compounds.

Although no detailed studies of the electrode reactions corresponding to Waves II and III were carried out, it has been shown that four electron oxidations of 3,4-dimethoxypropenylbenzene may be obtained by the addition of suitable reagents to the acetonitrile solution. This is a sufficiently drastic oxidation to effect cleavage of the side chain; however, further studies will be required to determine whether or not selective oxidation of the side chain may actually be obtained.

INTRODUCTION

"Oxidation is one of the most important of the reactions used for the degradation of an organic compound in order that its structure may be studied. Such a method, however, is useful only when it gives oxidation products which still have some of the basic structure of the molecule or one of its building stones. Unfortunately, protolignin and isolated lignins are very susceptible to oxidation and are extensively destroyed, even with relatively mild oxidizing agents." (1)

This situation described by Brauns has prompted the investigation of a wide variety of chemical oxidizing agents and their application to both the oxidative degradation of lignin and the so-called lignin model compounds. Our interest in the method of electrochemical oxidation may be summarized by the following questions. Can this technique be used to provide milder and more selective oxidation of lignin for structural studies than is obtained by the usual chemical oxidants? Is there sufficient similarity between enzymatic and electrochemical oxidation of lignin model compounds to permit the use of the latter technique in the study of the reactions responsible for the formation of lignin?

A partial answer to the first question has been given by the results obtained by Bailey and Brooks (2) in the electrolytic oxidation of several types of lignin in 1% aqueous sodium hydroxide solution at a lead anode. Butanol lignin yielded 81.6% of identified products with an increase in oxygen content of only 5% indicating, according to Brauns (3), a very mild oxidation. The oxidation products, however, were relatively low molecular weight materials indicating rather extreme degradation of the starting lignin. In spite of Brauns' observation (4) that the results are of far-reaching importance in determining the structure of lignin, no further studies of the electrolytic oxidation of lignin appear to have been undertaken.

Prior to the study of Bailey and Brooks, the only other reference to the electrolytic oxidation of a lignin material was made by König (5), who reported the oxidation of a barium lignosulfonate at a platinum anode in a solution of dilute sulfuric acid. From the anolyte, which had a pronounced odor of vanillin, König isolated a compound which appeared to be succinic acid.

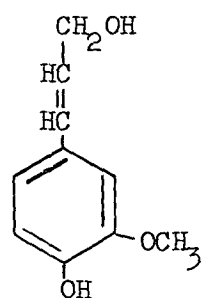
Since lignin is presumably formed by a process of oxidative dehydrogenation of so-called lignin "building stones," the electrochemical behavior of these compounds is also of interest. Electrochemical oxidations often lead to the formation of dimers or other oligomeric products. Hence, a study of the electrochemical behavior of lignin building stones and related compounds may provide information concerning the formation of lignin as well as its degradation.

Although the exact nature of the building stones is not known, Brauns (6) has described them as methoxylated p-hydroxyphenylpropane compounds with varying degrees of oxidation of their side chains. Coniferyl alcohol (I) which is usually taken as the primary representative of this class of compounds polymerizes to ligninlike materials. In addition, a series of dimers, trimers, and other oligomers are obtained. The linkages occurring in the latter compounds are believed by some investigators to be characteristic of those occurring in lignin (7).

Although no studies have been made of the electrochemical oxidation of coniferyl alcohol itself, oxidations of several closely related materials have been reported. In 1897 a patent was issued to von Heyden (8) for the electrolytic oxidation of isoeugenol (II) to vanillin (III). Lowry and Moore (9), however, were unable to repeat the work and obtained only a dark-colored material which was insoluble in ether and water.

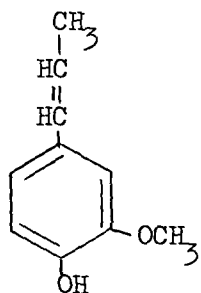
Fichter and Christen (10) studied the same oxidation and succeeded in obtaining vanillin by decreasing the temperature to 12°C. (compared to 60°C. specified in the patent). The yield was only 14%, however, and the greater portion of the isoeugenol was converted to an intractable material or mixture of materials.

In an attempt to determine the reason for the formation of "resins," Eichter and Christen studied the oxidation of propylguaiacol (IV). Except for the formation of small amounts of dipropylguaiacol the results obtained were essentially the same. This indicated that the unsaturation of the side chain was not responsible for the tarring reactions.



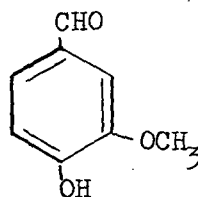
(I)

Coniferyl
Alcohol



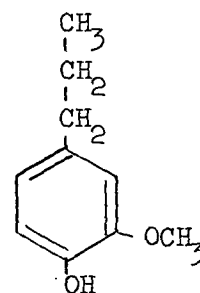
(II)

Isoeugenol



(III)

Vanillin



(IV)

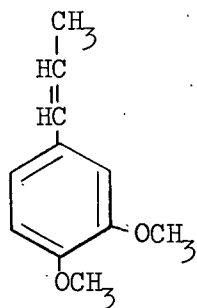
Propylguaiacol

Since the formation of tars is typical of both the chemical and electrolytic oxidation of many phenolic compounds, the phenolic group was blocked by methylation to give 3,4-dimethoxypropenylbenzene (V)¹. Oxidation of the latter compound under the same conditions used previously yielded 77.8% veratraldehyde (VI) and 12.7% veratric acid (VII). A similar oxidation of 4-methoxypropenylbenzene (VIII)²

¹ In subsequent discussions the abbreviation 3,4-DMPB will be used to represent 3,4-dimethoxypropenylbenzene.

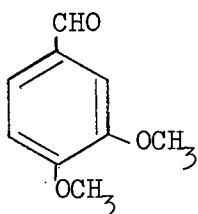
² In subsequent discussions the abbreviation 4-MPB will be used to represent 4-methoxypropenylbenzene.

produced 52% anisaldehyde (IX) and 25.4% anisic acid (X). A smooth cleavage of the side chain was also effected by conversion of the phenolic group of isoeugenol to the sulfuric acid ester. In this case 53.4% vanillin and 25.7% vanillic acid (XI) were obtained after electrolytic oxidation and removal of the sulfuric acid ester group by treatment with caustic.



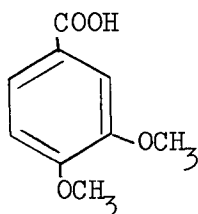
(V)

3,4-Dimethoxypropenylbenzene



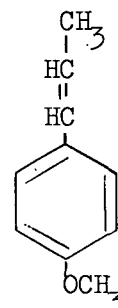
(VI)

Veratraldehyde



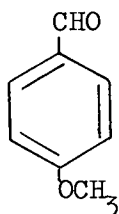
(VII)

Veratric Acid



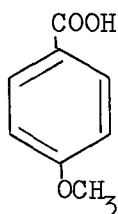
(VIII)

4-Methoxypropenylbenzene



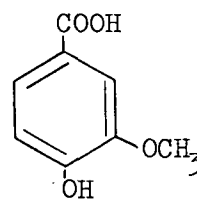
(IX)

Anisaldehyde



(X)

Anisic Acid



(XI)

Vanillic Acid

Although many other electrolytic studies of organic compounds might be mentioned, the results obtained in most cases are of questionable value because of inadequate descriptions of experimental conditions. In addition, little or no attention has been paid to the potential at the working electrode. The latter comment applies to all of the oxidations described above of both lignin and simple phenylpropane compounds.

The importance of the electrode potential which has long been recognized by some experimenters (11-14) was dramatically illustrated by Lingane, et al. (15) in 1943. At the same time Lingane showed that the polarographic, or more generally, voltammetric technique could be used as a "convenient technique to establish the optimum conditions for electrochemical oxidation or reduction reactions" (15).

The general applicability of Lingane's method has now been demonstrated in a wide variety of studies. However, comparatively few of these have dealt with electrochemical oxidation reactions. No previous controlled potential oxidations have been reported of compounds containing the phenylpropane nucleus.

STATEMENT OF THE PROBLEM

In view of the fact that no systematic electrochemical studies have as yet been made of even relatively simple compounds of the phenylpropane type it was decided that the initial studies could be most profitably directed toward this end. The premises upon which this decision was based were that studies of the simpler lignin model compounds would suggest the most promising directions for future studies of more complex compounds as well as aid in the interpretation of the electrochemical behavior of the more complex materials.

Coniferyl alcohol (I), for example, contains three readily oxidizable groups, the phenolic hydroxyl, the carbon-carbon double bond, and the primary alcohol group. Preliminary examinations of related materials containing each of these groups by itself would provide information concerning the relative stability of the various groups toward oxidation as well as the type of reactions to be expected from each of the functional groups under a given set of experimental conditions. To be sure, the presence of more than one of the functional groups on the same compound may lead to new and more complicated reactions so that more than simple interpolation from the data already accumulated may be necessary. This, however, merely serves to emphasize the importance of beginning the studies with relatively simple compounds.

The material chosen for the present investigation was 3,4-dimethoxypropenylbenzene (V). This compound retains the basic structure of coniferyl alcohol. The primary hydroxyl group is absent, however, and the phenolic group has been blocked by methylation. With respect to the latter alteration, the compound is more characteristic of the C_6-C_3 units after incorporation into the lignin molecule.

The goals of the present investigation may be summarized as follows:

- (1) to apply the techniques of voltammetry and controlled potential electrolytic oxidation to the study of some propenylphenol ethers, particularly 3,4-dimethoxypropenylbenzene, and
- (2) to supplement the electrochemical studies with the isolation and identification of the reaction products.

It is hoped that the information gained will suggest further studies in line with the ideas discussed earlier as well as increase our understanding of the nature of electrochemical oxidation reactions in general.

In accord with Elving's observation, "The electron is one of the most versatile of reagents, and its addition or removal from an organic compound via an electrode should be more extensively investigated by the organic chemist" (16).

BACKGROUND OF THE PROBLEM

THE CHEMICAL OXIDATION OF PROPENYLPHENOL ETHERS

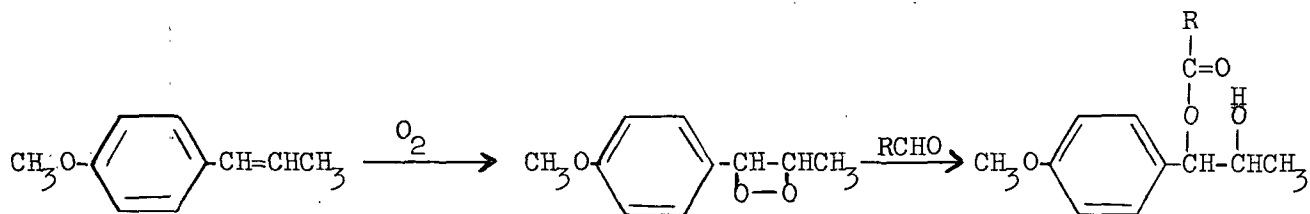
Since the electrolytic oxidation of a compound often parallels the course of a specific chemical oxidation, previous studies of the chemical oxidation of representative propenylphenol ethers will be reviewed briefly.

Oxidations of 4-MPB have been carried out employing air and sunlight (17-19); nitric acid in the presence of mercuric nitrate and lead nitrate as catalysts (20); potassium dichromate (21); hydrogen peroxide in the presence of osmium tetroxide (22); hydrogen peroxide in the presence of vanadium pentoxide and chromium trioxide (23); and chromic acid (24). The primary point of attack in all cases was the carbon-carbon double bond with the formation of one or more of the products, anisaldehyde (IX), anisic acid (X), acetaldehyde, and acetic acid.

Ozone, as expected, also attacks the double bond (25-27). The ozonides of 4-MPB and 3,4-DMPB are unstable and decompose spontaneously. The aldehydes formed are converted by further ozonization to acids and per-acids when all of the original propenylphenol ether has been consumed (28). In the presence of water, anisic acid and anisaldehyde are the major products from the ozonization of anethole (29).

Although most of the chemical oxidations reported lead to side chain cleavages with the formation of acids and aldehydes, this reaction is always accompanied by competing side reactions and further oxidations of the primary oxidation products. In some cases, the major products are something other than the simple acids and aldehydes.

Air and sunlight, for example, cause not only the simple cleavage of the 4-MPB side-chain, but also lead to the formation of other "deep-seated oxidations" (17). This is illustrated by the detailed study of Schulz (19), who obtained good yields of esters, both anisates and acetates, in addition to anisaldehyde and anisic acid. The esters are formed according to Schulz by the following reactions:



Other reactions which were observed include the demethylation of 4-MPB, nuclear oxidation to phenols, and nuclear degradations. The formation of dimers, trimers, and other higher oligomeric compounds of undetermined composition was also reported.

Schulz concluded from a study of a number of similar compounds that the relative oxidation velocities depended primarily on the degree of polarization of the double bond. The autooxidation of 4-MPB was apparently not affected by an increase in the oxygen overpressure up to 20 atmospheres nor by illumination.

Oxidation of 4-MPB by peracetic acid yields an acetate and anethole oxide (30-31). Lead tetraacetate oxidation of 4-MPB yields glycols, monoacetates, diacetates, and a number of other more complex products (32). Perbenzoic acid oxidation of propenylbenzenes usually leads to the formation of the corresponding substituted ethylene oxides (30).

3,4-Dimethoxypropenylbenzene is oxidized by alkyl nitrites in the presence of hydrochloric acid to give veratraldehyde as the primary oxidation product (33).

In at least one case the primary point of attack was the methyl group rather than the unsaturated carbon-carbon linkage. Monti (34), in an attempt to oxidize propenyl derivatives to give disubstituted products without cleavage of the double bond, used selenium dioxide as the oxidizing agent. 4-MPB yielded p-methoxy-cinnamaldehyde, while 3,4-DMPB was not attacked at all.

The propenylphenol ethers, although readily oxidized by many chemical oxidants, are more stable to oxidation than the corresponding phenols. Wacek and Kratzl (35) were unable to oxidize propenylbenzene or its methoxy-substituted derivatives. Isoeugenol, on the other hand, yielded almost quantitative amounts of vanillin. Similar compounds with oxygen in the side chain cinnamaldehyde (PhCH-CHCHO) and benzalacetone (PhCH-CHCOMe) were easily oxidized to benzaldehyde with only traces of benzoic acid.

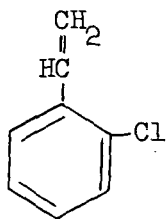
POLYMERIZATION OF PROPENYLPHENOL ETHERS

In almost all of the chemical oxidations of propenylphenol ethers, varying quantities of tars, resins, and other polymeric materials are formed. These polymers may arise as a result of ionic or free radical polymerizations or as a result of condensations of oxidation products of the reactions. Since electrolytic oxidations lead to the formation of free radicals or carbonium ions in the primary electrode reactions, a consideration of these mechanisms is pertinent to the present investigation.

On the basis of a very limited amount of information, it seems doubtful that free radical polymerizations of the propenylphenol ethers occurs to any appreciable extent. Royals (36) notes that "the simple aliphatic alkenes such as ethylene or isobutylene undergo free radical polymerization with considerable difficulty and are best polymerized under the influence of strong acid catalysts." Although

alkenes carrying negative substituents undergo vinyl polymerization much more readily under the influence of free radical reagents, "the unit of structure =CH_2 is apparently necessary to vinyl polymerization reactivity; thus, symmetrically disubstituted, trisubstituted and tetrasubstituted alkenes fail to undergo free radical polymerizations" (36).

Turner (37), in a study of the copolymerization of 4-MPB with o-chlorostyrene (XII), observed that "1,2-disubstituted ethylenes exhibit a specific reluctance to add to themselves in free radical copolymerization reactions." Although this has usually been attributed to steric effects, sterically hindered compounds which do not polymerize by a free radical mechanism can undergo ionic polymerizations with no apparent difficulty.



(XII)

o-Chlorostyrene

The acid-catalyzed copolymerization of o-chlorostyrene with 4-MPB yielded a copolymer much richer in 4-MPB than the corresponding monomer mixture in all concentrations. Peroxide-catalyzed reactions, on the other hand, gave polymers much poorer in 4-MPB. Thus, the more highly substituted 4-MPB monomer adds more easily to either 4-MPB or o-chlorostyrene carbonium ions than does o-chlorostyrene monomer. In radical polymerization, 4-MPB monomer is much less reactive with the o-chlorostyrene radical and is very unreactive with the 4-MPB radical.

Turner concluded from his studies that 1,2-disubstitution on the ethylenic double bond does not play as pronounced a steric role in ionic polymerizations as in the radical type (37).

In accord with Turner's observations, few cases of the free radical polymerization of the propenylphenol ethers have been reported in the literature. References to the ionic polymerizations of these compounds, on the other hand, are abundant.

The catalyst-solvent systems which have been applied to the study of the ionic polymerizations of the propenylphenol ethers include: iodine in toluene (38-41); stannic chloride in benzene (42-44); boron fluoride in dioxane, methyl alcohol, benzene, and petroleum ether (45); hydrochloric acid in methyl alcohol (46-48); zinc chloride in concentrated hydrochloric acid (49-50); aluminum chloride in ethylene oxide (51); ferric chloride in ethylene oxide (52-55); trichloroacetic acid (56); and formic acid (57-58).

In general, the course of the reaction depends on the concentration and strength of the electrophilic catalyst, the dielectric constant of the solvent, the temperature and the length of time the reaction is allowed to proceed. Of equal importance is the polarization and polarizability of the double bond of the monomer and the stability of the monomeric, dimeric, etc., carbonium ions formed. In the case of aryl-substituted alkenes, the polarizability of the aromatic nucleus also plays a role in determining the course of the reaction.

In a comprehensive study of dimeric propenylphenol ethers published in a series of some twenty-odd papers, Müller takes up the acid and iodine-catalyzed polymerization of some propenylphenol ethers including 4-MPB and 3,4-DMPB. The

reader is referred to two of the papers (41, 59) for an excellent discussion of this subject. The studies of Müller will be referred to in more detail in a later section of the present report.

VOLTAMMETRY AND CONTROLLED POTENTIAL ELECTROLYSIS

Principles and Terminology

The principles of voltammetry and controlled potential oxidation have been described in detail elsewhere and only the salient features will be reviewed here. Voltammetry, in brief, is the study of the current-potential relationships obtained during the electrolysis of a solution between a microelectrode and some standard reference electrode. The plot of current (i) versus potential (E) is referred to as a voltammogram. In the special case where the microelectrode is a dropping mercury electrode, the study is referred to as polarography and the current-potential plot as a polarogram.

For any specified set of conditions (e.g., solvent, pH, temperature, etc.), there is a certain potential required for the reduction or oxidation of the compound under study. Assuming that this potential is below the decomposition potential of the supporting electrolyte-solvent system, a sigmoid shaped curve will be obtained which is called a voltammetric wave. If the compound is oxidized or reduced in more than one step at potentials differing by approximately 0.15 volts or more or if more than one electroactive species is present a series of two or more sigmoid shaped curves are obtained as shown in Fig. 1.

As the applied voltage is increased, the concentration of the electroactive species at the electrode surface decreases until it becomes nearly zero. Further increases in potential will thus result in no increase in current. The current

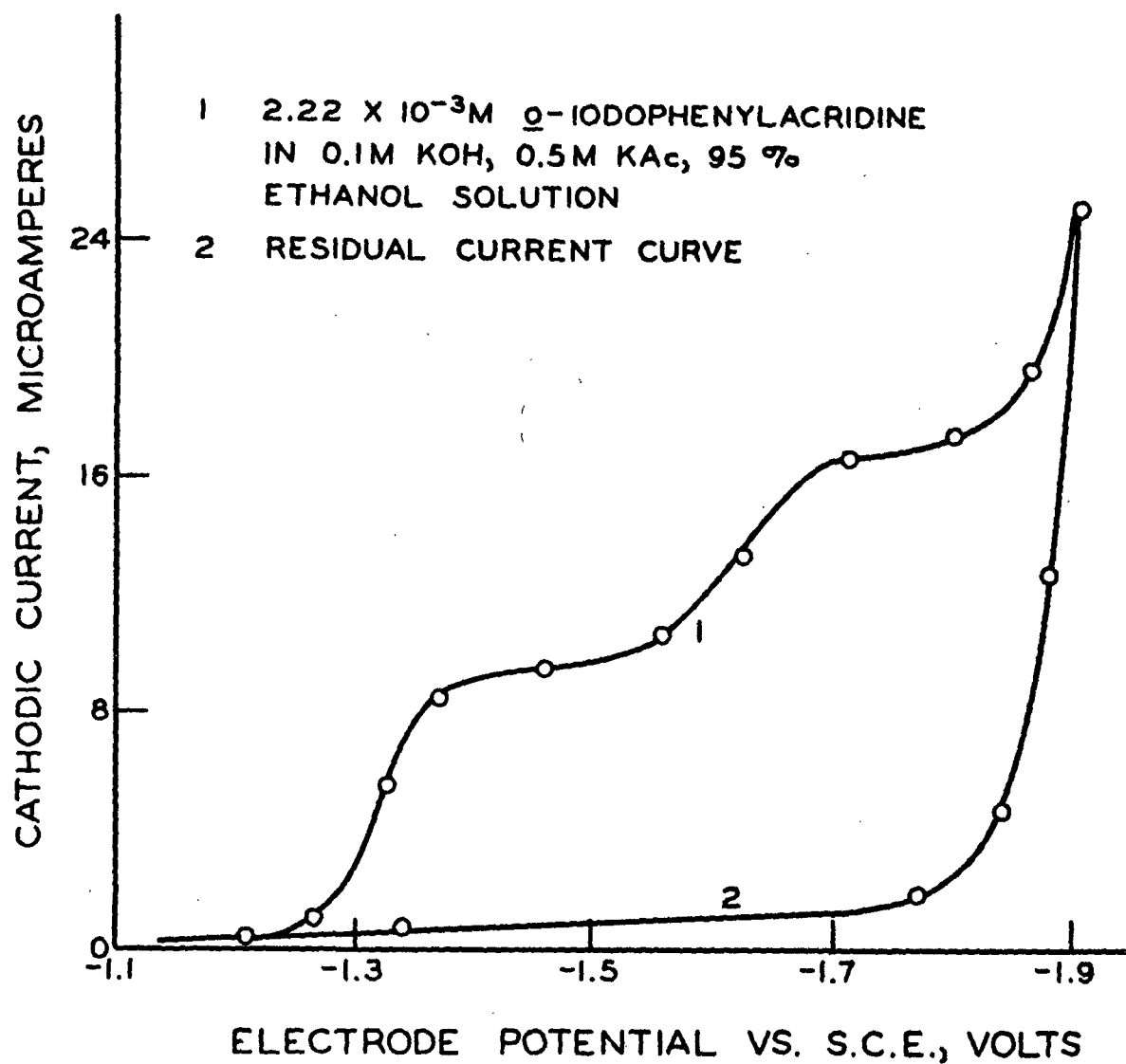


Figure 1. Polarogram of *o*-Iodophenylacridine
According to Lingane (15)

level at this point is referred to as the diffusion current (i_d) and is proportional to the size of the electrode, the concentration gradient existing between the surface of the electrode and the bulk of the solution, the diffusivity of the molecule, (D), and the number of electrons (n) involved in the electrode reaction, as well as a number of other factors. The diffusion current (i_d) divided by the concentration of the electroactive species is the diffusion current constant (I_d).

The potential corresponding to the current level midway between the diffusion current height and the residual current is called the half-wave potential ($E_{1/2}$). The residual current is the current obtained for the solvent-electrolyte system in the absence of the electroactive species under study.

Elving (60) has summarized the quantities available from polarographic measurements as follows:

- (a) half-wave potential as a measure of the ease of electron transfer for a particular environment;
- (b) current flow as a measure of the concentration of the electroactive species;
- (c) slope of the polarographic wave as an index to the number of electrons involved in the potential-determining step of a reversible electrode reaction (its significance for irreversible reactions is not yet clear); and
- (d) number of electrons involved in the current-producing process (calculated from the Ilkovic equation) as an indication of the nature of the over-all electrode reaction.

Other information less directly obtained from the polarograms has been summarized as follows:

- (e) variation of $E_{1/2}$ with pH as an indication of the role of hydrogen ions in the potential-determining process of the electrode reaction; and
- (f) variations of the current with drop-time (effective head of mercury), temperature, and concentration of active species from which the nature of the current-controlling process (diffusion, kinetic, or adsorption) can be evaluated.

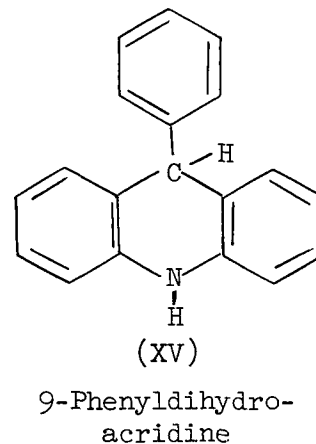
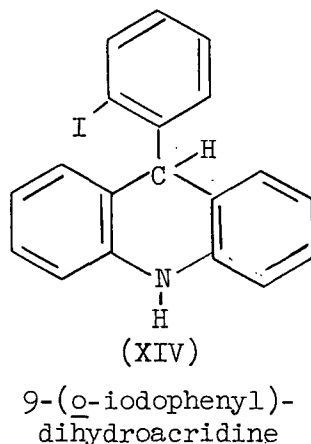
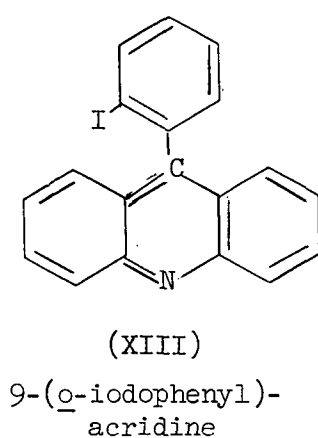
With certain minor modifications, the statements of Elving are equally applicable to the case of voltammetric studies carried out at a solid electrode.

The use of the voltammetric or polarographic technique as a pilot method to determine the optimum conditions for controlled potential electrolysis is best illustrated by reference to Lingane's now classical study of the reduction of 9-(o-iodophenyl)-acridine (XIII) (15). The reduction of this compound occurs in two steps and, hence, two polarographic waves will be obtained if the energy requirements for the two steps differ by a sufficient amount.

After making a number of preliminary polarographic runs at various pH's, and using different solvent, buffers, etc., Lingane was able to find a set of conditions which yielded the expected double wave as shown in Fig. 1.

By controlling the potential at the anode in a large-scale electrolysis at a value corresponding to the beginning of the first plateau, Lingane was able to obtain 9-(o-iodophenyl)-dihydroacridine (XIV) with a 100% current yield and a 90% material yield.

A similar oxidation at a potential corresponding to the beginning of the second plateau yielded phenyldihydroacridine (XV) in 95% yield and the current consumption was within 5% of the theoretical.



These experiments serve to emphasize not only the importance of the electrode potential but also the utility of the electrochemical method of electrolysis. Before the polarographic studies were made all attempts to prepare the intermediate reduction product using chemical reducing agents either resulted in no reduction at all or complete reduction to the phenyldihydroacridine.

Perhaps the most important advantage of this technique is the simplicity with which a wide variety of conditions of pH, solution composition, temperature, buffer systems, electrolytes, etc., can be examined in order to determine the optimum conditions for large-scale electrolyses, or if the reaction in question will even occur. In the traditional approach, electrolyses would have been carried out at each of a number of arbitrarily chosen conditions, the products isolated, identified and total yields determined before any judgement could be made of the relative merits of any given set of conditions.

Although this technique obviously offers a much more rational approach to the problems of electrochemical oxidation and reduction reactions and greatly reduces the labor involved in the study of any particular compound, it does not solve all of the problems which might be encountered. The voltammograms are representative of the primary electrode reactions and do not in general provide information concerning the course of secondary reactions such as rearrangements, of the primary oxidation products, reactions with the solvent or other solution species, condensations, etc. Thus, the final proof of any proposed electrochemical reaction mechanism ultimately rests with the isolation and identification of the reaction products.

Another serious limitation to this technique is the fact that it is applicable only at potentials below the decomposition point of the solvent-electrolyte

system. At higher potentials, the reaction of interest will be overshadowed by the large current arising from the decomposition of the solvent-electrolyte system. Thus, the maximum potential for oxidations in aqueous media is about 1.0 volts versus the saturated calomel electrode at low pH and only about 0.8 volts at high pH.

ELECTROCHEMICAL STUDIES IN ACETONITRILE

It is possible to extend this range considerably by carrying out the voltammetric studies in a nonaqueous solvent. Perhaps the most commonly employed of these and the one chosen for the present study is acetonitrile. This solvent with sodium perchlorate as the supporting electrolyte has a useful potential range of approximately -1.5 to +1.8 volts versus the saturated calomel electrode. In addition, it has good solvent properties for many organic molecules including the propenylphenol ethers. The most serious disadvantage connected with working in such a system is the difficulty involved in buffering the system.

A review of the voltammetric studies which have been carried out in acetonitrile up to 1957 has been given by Geske (61). Investigations since that time which are pertinent to the present study are discussed elsewhere in this report. For further details concerning the use of acetonitrile as a solvent for electrochemical studies the reader is referred to a recent paper by Billon (62) and several earlier publications by Kolthoff, et al. (63-64).

VOLTAMMETRIC STUDIES AT A PLATINUM ELECTRODE

Although the dropping mercury electrode is commonly employed for use in studies of reduction reactions, it is generally of limited value for oxidation studies because of its low oxidation potential. Hence, a solid electrode such as

gold, graphite, or more frequently, platinum is normally used. Unfortunately, the solid electrodes possess some particularly undesirable features.

The most serious disadvantage is that the voltammetric behavior of a particular compound is often dependent to a considerable degree on the past history of the electrode. A platinum electrode, for example, may give completely different results depending upon whether the surface has been oxidized or reduced before running the voltammogram. Similar differences may be observed between "shiny" and platinized platinum surfaces. Finally, the formation of an insoluble film on the electrode surface may cause a significant reduction in the height of the voltammetric waves or give rise to "peak" voltammograms. In the extreme case, attempts to retrace the voltammogram without cleaning the electrode surface may result in a trace of the residual current curve.

A dropping mercury electrode, on the other hand, continuously presents a clean, reproducible surface during the course of successive voltammograms. It seems reasonable to assume that this is the primary reason why the great majority of electrochemists have become so preoccupied with the study of reduction reactions.

A review of the use of both stationary and solid microelectrodes has been given by Geske (61) which need not be repeated here. The reader is also referred to the papers by Anson (65-66) concerning the effect of surface oxidation on the behavior of platinum electrodes and to the papers of Kolthoff, et al. (67) and Iaitinen, et al. (68) on the electrolytic formation and dissolution of oxide films on platinum electrodes.

EXPERIMENTAL

CHEMICALS

Four-liter batches of practical-grade acetonitrile (Matheson, Coleman, and Bell) were shaken briefly with 100-ml. portions of saturated potassium hydroxide, dried over anhydrous sodium carbonate and distilled two to three times from phosphorus pentoxide (93). All distillations were made through a five-foot column packed with glass helices. The column was provided with external heating units for temperature control and a tilting funnel-timer device for automatic control of the reflux ratio. Several hundred milliliters of acetonitrile were discarded at the beginning and end of each distillation. The middle cut from the final distillation was collected and stored in an all-glass, covered container equipped with a glass siphon tube and stopcock for subsequent delivery of the acetonitrile. The final distillation was carried out under nitrogen and the nitrogen atmosphere was maintained over the stored acetonitrile by means of a nitrogen-filled balloon.

Water content of the purified acetonitrile was one to two millimolar as measured by the Karl-Fischer titration. The ultraviolet spectra showed less absorption than commercially available spectral-grade acetonitrile.

Reagent-grade, anhydrous sodium perchlorate (G. F. Smith) was found to contain appreciable quantities of water and fine particles of black, water-insoluble material. The sodium perchlorate was dissolved in water, filtered, recrystallized and dried in a vacuum oven at 140°C. for 24 hours before use. No water could be detected in one-gram samples of the freshly dried sodium perchlorate. The dried material was stored in a desiccator in a covered, dark bottle over phosphorus pentoxide.

Tetraethylammonium perchlorate was prepared from sodium perchlorate (G. F. Smith) and tetraethylammonium bromide (Eastman) according to the procedure of Kolthoff and Coetzee (94). The sodium perchlorate solution, however, was made ten molar rather than one-tenth molar as directed in the reference.

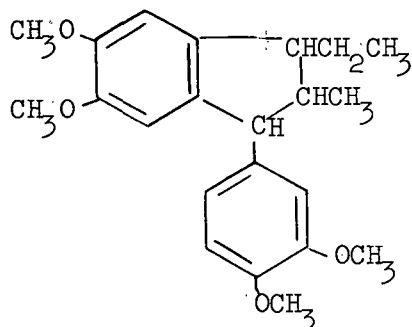
Tetraethylammonium hydroxide (Eastman) was obtained and used in the form of a 10% aqueous solution. A 0.5M stock solution of perchloric acid in glacial acetic acid was prepared by adding sufficient acetic anhydride to a 70% solution of double-distilled lead-free perchloric acid (G. F. Smith) to consume the water and diluting to the required volume with glacial acetic acid.

Reagent-grade pyridine (Mallinckrodt, Baker) and spectral-grade pyridine (Matheson, Coleman, and Bell) gave a deformed voltammetric wave in 0.5M sodium perchlorate-acetonitrile solution at approximately 1.5 volts vs. S.C.E. The several grades of pyridine were combined and distilled under nitrogen through the five-foot, packed column previously described. The distilled pyridine was stored in a dark, all-glass container equipped with a siphon tube. Voltammograms of the distilled pyridine showed no waves.

Prepurified nitrogen (Matheson, Coleman, and Bell) passed through separate tubes of magnesium perchlorate and phosphorus pentoxide was used in all distillations and for deaerations of the voltammetric test solutions. In the latter case the nitrogen was also passed through a series of bubbling tubes containing acetonitrile which were immersed in the constant temperature bath.

3,4-DMPB (Brothers Chem. Co.) was vacuum distilled under nitrogen to a constant refractive index and stored in dark, covered bottles. The compound was redistilled after several months. No apparent differences were observed in the voltammetric behavior of freshly distilled and aged 3,4-DMPB.

1-Veratryl-2-methyl-3-ethyl-5,6-dimethoxy indan (dimethyldiisoeugenol XVI) was prepared from 3,4-DMPB by treatment of the latter with zinc chloride and hydrochloric acid (95). This procedure yielded wartlike clumps of very tiny needles which melted at 93-95°C. after three recrystallizations from methanol. This compound is presumably a dimorphic form of the alpha-racemate of the indan (96).



(XVI)(XVIa)(XVIb)

Dimethyldiisoeugenol

An attempt to prepare the 106° m.p. alpha-racemate of the indan by refluxing 3,4-dimethoxypropenylbenzene with sulfuric acid (97) yielded fine, white needles (XVIa) which melted at 88°C. Three recrystallizations from methanol failed to increase the melting point. Although 88°C. is the reported melting point for the crude product from this preparation, the 106° isomer is normally obtained by repeated recrystallizations from alcohol. Since the two materials have different infrared spectra in the crystalline form and identical spectra in solution it seems probable that the two materials are dimorphic forms of the same stereoisomer. Repeated recrystallization from methanol results in the conversion of the less stable 88° m.p. dimorph to the more stable form melting at 105°C. (XVIb).

APPARATUS

The voltammetric cell used in the present study was patterned after a general description given by Kolthoff and Coetzee (94). The cell shown in Fig. 2 consists of an anode compartment of 40 ml. capacity (A) and a saturated calomel reference electrode (B). Both compartments of the cell are water-jacketed and maintained at $25.0 \pm 0.05^\circ\text{C}$. with water from a constant temperature bath.

A glass receptacle provided with a fine-grade frit (G) and filled with a portion of the test solution is used to separate the anode compartment from the agar bridge (I). Since the solution in the glass receptacle is contaminated by water and potassium chloride from the agar side-arm, the liquid level in the receptacle is maintained below that in the anode compartment to prevent bulk flow of the contaminated solution into the anolyte.

As observed previously by Kolthoff (94), a solid plug formed in the end of the agar bridge after prolonged immersion in the acetonitrile solution. This could be minimized by keeping the agar-bridge immersed in a solution of saturated (aqueous) potassium chloride between runs. The presence of the plug, however, seemed to have little effect on the measured cell resistance contrary to Kolthoff's findings.

The cell is provided with the usual bubbling tube (F) for deaeration of the test solution with nitrogen. A second inlet tube is used to direct the nitrogen over the surface of the solution while recording the voltammograms.

Anodes were constructed from short lengths of platinum wire sealed into the tips of soft-glass tubes (D). The platinum wire was heated in an oxygen flame to provide a rounded tip and a smooth, shiny surface before sealing into the glass

- A ANODE COMPARTMENT - WATER JACKETED,
40-ML. CAPACITY
- B CALOMEL REFERENCE ELECTRODE -
WATER JACKETED
- C SARGENT 600 R.P.M. SYNCHRONOUS MOTOR
- D PLATINUM WIRE ANODE
- E MERCURY-FILLED, GLASS TUBE
- F NITROGEN INLETS
- G FRITTED RECEPTACLE FOR AGAR BRIDGE
- H MULTIPLE CAPILLARY BUBBLING TUBE
- I AGAR BRIDGE
- J DRAIN TUBE
- K TEFLON COVER

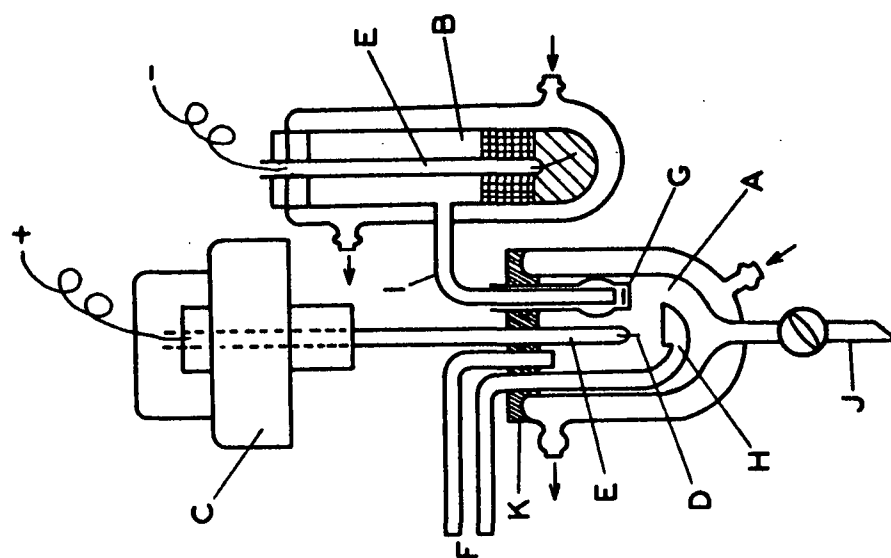


Figure 2. Voltammetric Cell (Scale = 1 in./cm.)

tube. Three different anodes were used during the course of the present study as follows: No. 1, 18-gage platinum wire, 0.303 sq. cm. exposed surface; No. 2, 22-gage platinum wire, 0.062 sq. cm. exposed surface; No. 3, 24-gage platinum wire, 0.0075 sq. cm. exposed surface.

Electrode No. 1 was used in most of the preliminary studies but was abandoned at the suggestion of Geske (86) in favor of the electrodes with much smaller surface area. The smaller electrodes proved to have a number of advantages and were used for the majority of voltammetric studies. Use of the smaller electrodes permitted the running of a series of voltammograms in the same solution without significantly altering the concentration of the electroactive species. In addition, the smaller electrodes were not subject to gross alterations in the stirring conditions at the electrode surface which had been obtained with the large electrode by accidental bending of the platinum wire.

The anode was rotated by means of a 600-r.p.m. Sargent synchronous motor in all voltammetric studies. Stroboscopic measurement gave a value of 618 r.p.m. for the actual rate of rotation.

The cell used for preparative-scale controlled potential oxidations is shown in Fig. 3. In principle, the cell is identical to the polarographic cell described above except that an auxiliary mercury pool cathode (F) is provided to carry the much larger electrolysis currents. The anode (E) used in the electrolysis cell was a commercially made 10 sq. cm. platinum gauze electrode. As in the case of the voltammetric cell, the anode potential is measured with respect to the saturated calomel electrode (C). Other features of the cell are detailed in Fig. 3.

Potential-current curves were obtained with a Sargent-Heyrovsky polarograph, Model XII used in conjunction with a Sargent Chart Recorder with a 1 second full-

- 600-ML. CAPACITY
- A ANODE COMPARTMENT-WATER JACKETED
 B CATHODE COMPARTMENT-400-ML. CAPACITY
 C CALOMEL (SAT.) HALF CELL-WATER JACKETED
 D MOTOR
 E PLATINUM MESH ANODE
 F MERCURY POOL CATHODE
 G TEFLON JACKET
 H TEFLON RECEPTACLE FOR MERCURY
 I NITROGEN INLET TUBES
 J FRITTED RECEPTACLE FOR AGAR BRIDGE
 K 50/30 B AND S JOINT
 L MERCURY CONTACT
 M BRASS SHAFT
 N CONTACT WIRE
 O FINE FRIT

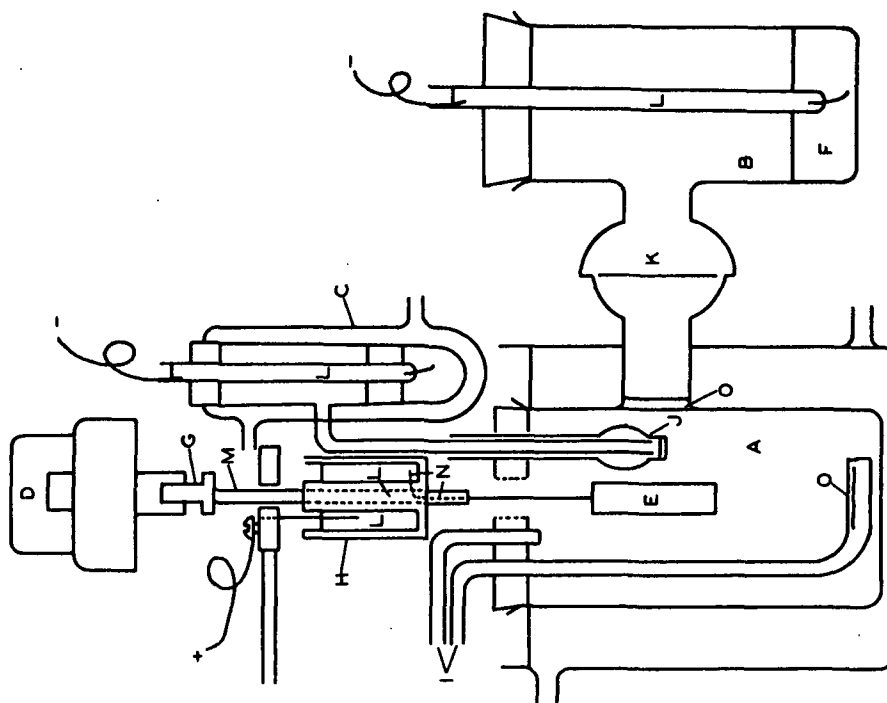


Figure 3. Cell for Controlled Potential Electrolyses (Scale = 1 in./cm.)

scale response. Controlled potential electrolyses were carried out using an Analytical Instruments Inc. Potentiostat. Potentials were checked before running the voltammograms and periodically during the course of controlled potential electrolyses by means of a Leeds and Northrup Student Potentiometer.

Resistance measurements were made initially with a Leeds and Northrup Conductivity Bridge; however, resistances were found to vary significantly with the voltage applied across the cell. Satisfactory results were obtained when the instrument was replaced with a General Radio Z-Y bridge, Type 1603-A. A Hewlett-Packard Audio-oscillator Model 200B provided a 3700 cycle/second A.C. current source and a Type 502 Tektronix, Inc. oscilloscope served as a null detector. Resistance measurements were made with an applied voltage of less than 0.05 volts. The resistance of the voltammetric cell varied between 1700 and 2000 ohms.

Infrared curves were run on a Perkin-Elmer Model 21 spectrophotometer. Ultraviolet curves were obtained with a Beckman Model DK2 spectrophotometer. Refractive indices were measured with a Bausch and Lomb Abbé refractometer.

All weighings were made on an analytical balance enclosed in a dry-box. Relative humidity within the dry-box was usually maintained between 5-10% by means of a silica gel column and blower together with trays of phosphorus pentoxide. In the humid summer months the relative humidity sometimes rose to 20% within the dry-box.

VOLTAMMETRIC PROCEDURE

Stock solutions of 0.5M sodium perchlorate in acetonitrile were prepared fresh each morning and used for the day's voltammetric runs. Ten milliliter stock solutions, usually 0.25M in the compound under investigation and 0.5M in sodium

perchlorate were similarly prepared each day even though stock solutions several weeks old showed no significant changes in voltammetric behavior.

Twenty-five milliliters of the supporting electrolyte-solvent stock solutions were pipetted into the cell and deaerated by passing dried nitrogen through the solution for approximately 10 minutes. The cleaned electrode was introduced into the cell and a residual current curve recorded. The desired quantity of the electroactive species was introduced into the cell by means of a micropipet and after thorough mixing of the solution with a stream of nitrogen the cleaned electrode was inserted and the voltammogram recorded. In most cases the addition of compound caused negligible changes to the total volume of solution (e.g., 0.04% to 0.2%) and no corrections were made to the concentrations. Where larger quantities of electroactive material or added compounds such as acid or base were required the appropriate corrections were made or the solutions were prepared individually in volumetric flasks.

The cell was thermostatted at $25.0 \pm 0.2^{\circ}\text{C}$. for all voltammetric runs. It was found that a significant reduction in cell resistance could be obtained by force-filling the frit from above (88). The effectiveness of the frit in preventing contamination from the agar bridge is shown by the absence of a chloride wave in a solution which had been in the cell for more than 10 hours.

All voltammograms were recorded at a polarization rate of 2.95 millivolts per second unless otherwise specified. Curves were corrected for residual currents and iR drop through the cell in all cases. A level diffusion plateau was not obtained even after correction for residual current. Hence, the diffusion currents were estimated by fitting a french curve closely to the upper portion of the wave and drawing in the level portion.

During the course of the present study all of the more commonly employed methods for cleaning the electrode surface were investigated with varying degrees of success. All voltammograms included in the present report were obtained on an electrode which had been cleaned by one of the following three methods. The particular cleaning method is specified for all voltammograms.

1. The electrode was soaked in concentrated nitric acid or dichromate cleaning solution for several minutes, rinsed with distilled water and reduced in a solution of ferrous ammonium sulfate acidified with concentrated sulfuric acid. The electrode was then thoroughly rinsed with distilled water followed by acetonitrile and transferred to the cell where it was allowed to equilibrate for several minutes before running the voltammogram.
2. The electrode was cleaned in hot dichromate cleaning solution for 3 minutes, rinsed with distilled water and acetonitrile and equilibrated in the test solution as above.
3. The electrode was shorted to the calomel electrode between runs until the current decreased to zero.

EXPERIMENTAL RESULTS AND DISCUSSION

VOLTAMMETRY OF 3,4-DIMETHOXYPROPENYL BENZENE

3,4-Dimethoxypropenylbenzene (3,4-DMPB) gives a series of voltammetric waves at a platinum electrode in 0.5M sodium perchlorate-acetonitrile solution. The number, positions, and heights of the waves are dependent upon the concentration of 3,4-DMPB, the condition of the electrode surface (e.g., oxidized vs. reduced), and the presence of acid, base, or water in the solution. Because of the complexity of the electrochemical behavior of 3,4-DMPB, the primary emphasis in the present study has been placed on the elucidation of the electrode reactions causing the first wave.

VOLTAMMETRIC BEHAVIOR IN UNBUFFERED ACETONITRILE

In unbuffered, 0.5M sodium perchlorate-acetonitrile solution, 3,4-DMPB gives three voltammetric waves at a rotating platinum electrode. A typical curve is shown in Fig. 4.

The waves have poorly defined diffusion plateaus and for this reason it is not possible to obtain accurate estimates of the diffusion current constants ($\underline{I_d}$). Thus, reproducibility of the $\underline{I_d}$ values was poor, particularly in the case of Waves II and III. Since the half-wave potentials ($\underline{E_{1/2}}$) were selected as the potentials corresponding to one-half of the diffusion current the reproducibility of these values suffered in a similar manner.

The $\underline{E_{1/2}}$ for Wave I is 0.98 ± 0.03 volts vs. the saturated calomel electrode* (S.C.E.). The $\underline{E_{1/2}}$'s for Waves II and III are approximately 1.2 and 1.4 volts vs.

* The abbreviation S.C.E. is used throughout the discussion to refer to the saturated calomel reference electrode.

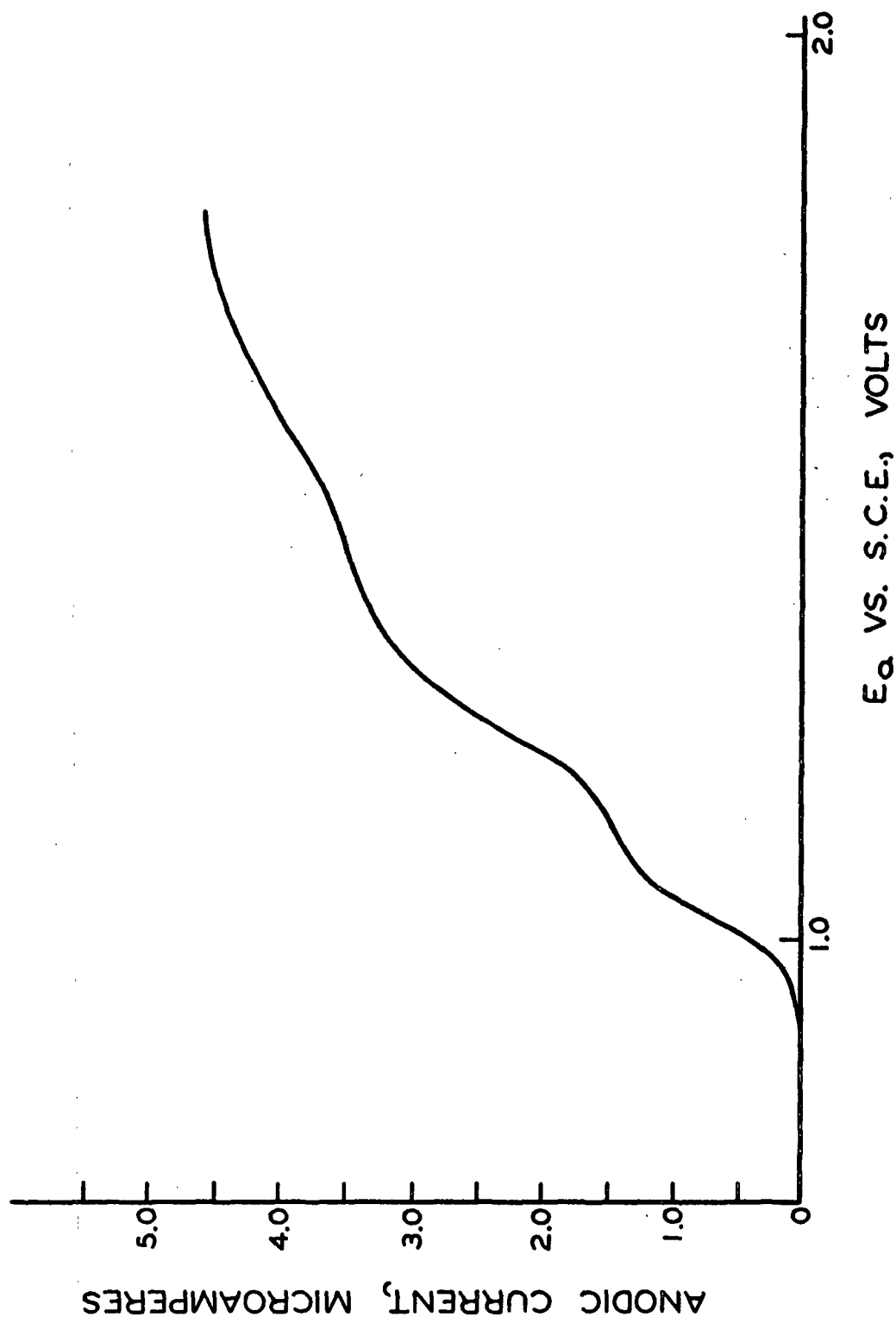


Figure 4. Voltammogram of 0.3068M 3,4-DMPB in 0.5M Sodium Perchlorate-Acetonitrile Solution.
Electrode No. 3, Cleaning Procedure No. 1.

S.C.E. at low concentrations of 3,4-DMPB and increase with increasing concentration of the compound. Waves II and III are poorly defined and in some cases appear as a single drawn-out wave. The $\underline{I_d}$'s of Waves II and III proved to be extremely erratic, but were usually between one and two times the height of Wave I.

Current Controlling Process

In Table I are given the $\underline{I_d}$'s for Waves I and II measured at temperatures of 25.7, 31.0, and 37.1°C. These values have been used to calculate the temperature coefficients of the diffusion current constants according to the following equation (69):

$$\underline{x} = (\underline{I_d}^{-2}/\underline{I_d}^{-1})^{1/\underline{n}} - 1$$

$\underline{I_d}^{-1}$ and $\underline{I_d}^{-2}$ are the diffusion current constants measured at temperatures $\underline{T_1}$ and $\underline{T_2}$, respectively, and \underline{n} is equal to $\underline{T_2} - \underline{T_1}$. The average value for the temperature coefficients over the intervals 25.7-31.0°C. and 31.0-37.1°C. was found to be 0.03 for both waves.

TABLE I

TEMPERATURE DEPENDENCE OF $\underline{I_d}$ AND $\underline{E_{1/2}}$ FOR WAVES I AND II OF
3,4-DMPB IN 0.5M SODIUM PERCHLORATE-ACETONITRILE SOLUTION
ELECTRODE NO. 2, CLEANING PROC. NO. 1

Concn. of 3,4-DMPB, M/l.	Temp., °C.	$\underline{E_{1/2}}$ vs. S.C.E., volts		$\underline{I_d}$, μ amp.-l./mmol.	
		I	II	I	II
0.467×10^{-4}	25.7	1.029	1.237	14.2	15.0
0.934×10^{-4}	31.0	1.016	1.220	17.1	17.7
0.934×10^{-4}	37.1	1.003	1.229	19.8	20.9
Temp. Range, °C.		Temp. Coeff. of $\underline{I_d}$			
		Wave I	Wave II		
25.7-31.0		0.035	0.032		
31.0-37.1		<u>0.025</u>	<u>0.028</u>		
		0.030	0.030		

In normal polarography at a dropping mercury electrode the temperature dependence of the diffusion current of an electroactive species is predicted by means of the Ilkovic equation (70).

$$i_d = knD^{1/2} C_m^{2/3} t^{1/6}$$

where i_d is the diffusion current, n is the number of electrons transferred per molecule of electroactive species, D is the diffusion coefficient of the electroactive species, C is its concentration, m is the rate of flow of mercury, and t is the drop time. In the present discussion, the only variable of interest is the diffusion coefficient (D) which has been shown to be the primary factor determining the temperature dependence of the diffusion current. All other quantities in the above equation have comparatively small temperature coefficients. Differentiation of the equation with respect to temperature shows that the temperature coefficient of the diffusion current is approximately equal to one-half of the temperature coefficient of the diffusion coefficient. For most organic molecules the temperature coefficients of the diffusion currents are of the order of 1-2% per degree (71).

In the case of a rotating solid electrode it has been shown (72) that at a constant angular velocity the diffusion current is given by the following expression:

$$i_d = knCD^a$$

where n is the number of electrons involved in the electrode reaction, C is the concentration of electroactive species, D is the diffusion coefficient, and $\log k$ is a constant proportional to the electrode area. The constant a has the value 0.66 according to Nightingale (72) and others.

Assuming that in this case also the temperature dependence of the diffusion coefficient is the primary factor governing the temperature dependence of the

diffusion current, it follows that the latter is approximately equal to two-thirds of the temperature coefficient of \underline{D} . This is approximately 1.33 times that observed in normal polarograms. Hence, the expected temperature coefficients of the diffusion currents of organic molecules are 1.3 to 2.7% per degree.

The value of 3% per degree obtained in the present study compares favorably with the values predicted for a diffusion-controlled process. It should be noted, however, that the above comparison cannot be taken as conclusive proof that diffusion is the rate-controlling step. The low value obtained does appear to eliminate chemical reaction occurring in the diffusion layer as the rate-controlling step (73).

As a further indication that the reaction is diffusion controlled it might be noted that the current height is dependent upon the rate of rotation of the electrode. For a diffusion-controlled process the current is proportional to the seventh power of the peripheral velocity of the rotating electrode (74).

Because of the irreproducibility of the third wave no measurements were made of the temperature dependence of the diffusion current.

Estimation of the Electrode n-Values

The expression previously given for the diffusion current at a rotating electrode may be written in terms of the diffusion current constant ($\underline{I_d}$) as follows:

$$\underline{I_d} = \underline{i_d}/\underline{C} = \underline{knD^a}$$

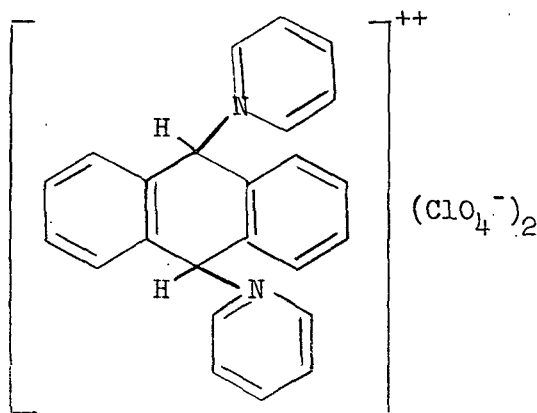
Thus, if successive voltammograms are run on two different electroactive materials which have approximately the same diffusivity, the ratio of $\underline{I_d}$'s will be given by:

$$\underline{I_d}^{-1}/\underline{I_d}^{-2} = \underline{n_1}/\underline{n_2}$$

provided the same cell and electrode is used and the rate of rotation of the electrode is maintained constant.

This relationship permits an estimate to be made of the \underline{n} -value of an unknown electrode reaction by comparison of the diffusion current constant with that obtained for a material of similar diffusivity whose electrode reaction is known.

Lund (75) has shown that anthracene undergoes a two-electron oxidation at a rotating platinum electrode in 0.5M sodium perchlorate-acetonitrile solution in the presence of pyridine. This has been confirmed by both coulometry and isolation and identification of 9,10-dihydroanthranyldipyridinium diperchlorate (XVII).



(XVII)

9,10-Dihydroanthranyldipyridinium
diperchlorate

3,4-DMPB also forms a dipyridinium diperchlorate in the presence of pyridine as will be shown later. In addition, the molecular weights of anthracene and 3,4-DMPB are identical. Thus, anthracene appears to be an ideal reference compound for use in estimating the \underline{n} -values of 3,4-DMPB. Comparative voltammetric data for anthracene and 3,4-DMPB are given in Table II.

TABLE II

VOLTAMMETRIC DATA FOR ANTHRACENE AND 3,4-DMPB IN UNBUFFERED
0.5M SODIUM PERCHLORATE ACETONITRILE SOLUTION AND
FOR ANTHRACENE IN THE PRESENCE OF PYRIDINE.
ELECTRODE NO. 3, CLEANING PROC. NO. 1

Compound	Concn. of Compound, $\underline{M} \times 10^3$	Concn. of Pyridine, $\underline{M} \times 10^3$	$\underline{E}_1/2$ vs. S.C.E., volts	\underline{I}_d , $\mu\text{amp.} - \underline{E}_1/2 / \text{mmol.}$
Anthracene	0.243	0.0	1.158	21.0
Anthracene	0.446	0.0	1.153	20.6
Anthracene	0.446	0.0	1.130	18.8
Anthracene	0.243	12.5	1.041	13.8
Anthracene	0.446	12.5	1.031	13.0
3,4-DMPB	0.141	0.0	0.991	6.4
3,4-DMPB	0.109	0.0	1.005	6.3
3,4-DMPB	0.205	0.0	0.989	6.4
3,4-DMPB	0.461	0.0	0.989	6.3

The average value for the \underline{I}_d of anthracene in the presence of pyridine was found to be 13.0. The corresponding value for Wave I of 3,4-DMPB in unbuffered solution is 6.34, approximately one-half of the anthracene value. Wave I thus corresponds to a one-electron oxidation reaction. As will be shown later, the height of Wave I doubles in the presence of pyridine indicating a two-electron reaction. Coulometry and isolation of a dipyridinium diperchlorate conclusively establishes the correctness of this estimate.

Hydroquinone, which is frequently used as a reference compound in voltammetric studies in acetonitrile (76-78) had an \underline{I}_d of 11.5 in unbuffered solution. The normally assumed two-electron oxidation of hydroquinone in acetonitrile is in accord with the comparisons of \underline{I}_d 's given here.

Lund (75) has suggested that anthracene as well as a number of other aromatic compounds are oxidized in a two-electron step in acetonitrile to yield divalent carbonium ions. The isolation of a dipyridinium perchlorate of anthracene from the oxidation of anthracene in the presence of pyridine is offered as proof of this mechanism. In the present study, an $\underline{I_d}$ of 19.25 was obtained for anthracene in unbuffered acetonitrile solution. This value corresponds closely to a three-electron oxidation step.

Thus, the conclusion arrived at by Lund appears to be valid only when pyridine is present in the solution. In unbuffered solution the electrode reaction may be quite different. The three electron oxidation step might be explained, for example, by a one-electron oxidation of anthracene followed by dimerization and a four-electron oxidation of the dimer.

Reversibility of the Electrode Process

Voltammetric electrode reactions are often classified as either reversible or irreversible processes. It should be noted that the electrode reactions in voltammetric studies occur at finite rates and, hence, cannot be considered strictly as thermodynamically reversible reactions. As Lingane has observed, however, "there are many cases where the potential of a working electrode is so slightly greater than the reversible potential computed from the concentration at the electrode surface that the difference between the two approaches experimental error" (79). When this is found to hold for a particular voltammetric process it is convenient to refer to the process as reversible. In the following discussions the term reversible is used in this restricted sense.

For a reversible anode reaction of the type



the current-potential relationship is described by the following equations (80):

$$E_a = E_{1/2} + (0.0591/n) \log [i/(i_d - i)] \quad (2)$$

$$E_{1/2} = E^{\circ} + (0.0591/n) \log (f_o k_R)/(f_R k_o) \quad (3)$$

where E_a , E° , and $E_{1/2}$ are the anode potential, the standard potential of the half-reaction occurring at the electrode, and the anode potential corresponding to a current of $i_d/2$, respectively. The symbols f_o and f_R refer to the activity coefficients of the oxidized and reduced species, and k_o and k_R are constants related to the diffusion coefficients of the oxidized and reduced species by the following equation:

$$(k_o/k_R) = (D_o/D_R)^{2/3} \quad (4)$$

The primary criterion of reversibility of an electrode reaction is that a plot of $\log [i/(i_d - i)]$ versus E_a give a straight line with slope equal to $0.0591/n$. Any deviation of the slope greater than 3-5 millivolts is, according to Meites, "fairly conclusive proof of some degree of irreversibility" (81). A further requirement for voltammetric reversibility is that the half-wave potential be constant and independent of the concentration of the electroactive species.

In order to apply these tests for reversibility it is necessary to have an independent estimate of the n -value of the electrode reaction. That is, Equation (2) cannot be used both as a test of reversibility and to estimate the n -value (82). The reason for this is evident from the corresponding current-voltage relationship shown by many irreversible reactions (83):

$$E_a = E_{1/2} + (0.0591/\alpha n) \log [i/(i_d - i)].$$

As in the case of a reversible reaction the half-wave potential is constant and independent of the concentration of the active species. In addition, a straight-line logarithmic plot is obtained. However, the slope in this case is given by $0.0591/\alpha n$ where α often has a value less than one. Thus, for a two-electron, irreversible reaction with α equal to 0.5, the logarithmic plot will be identical to that obtained for a one-electron reversible reaction.

Figure 5 illustrates the typical logarithmic plots obtained for Wave I of 3,4-DMPB in unbuffered 0.5M sodium perchlorate-acetonitrile solution over a ten-fold concentration range. The $E_{1/2}$'s are constant within experimental error and independent of concentration. The n -value calculated from the slopes of the log plots is in agreement with that predicted on the basis of diffusion current constants as discussed in the preceding section.

Wave I thus appears to behave as a reversible electrode reaction. At the lowest concentration of 3,4-DMPB, however, the deviation of the slope is somewhat greater than the 3-5 millivolts limit suggested by Meites, indicating possibly some degree of irreversibility.

With regard to the question of reversibility, one additional comment might be made concerning the variation of $E_{1/2}$ with temperature. Meites (84) has observed that for "homogeneous," reversible reactions the quantity $dE_{1/2}/dT$ may be either positive or negative, but it is rarely greater than about 1 mv./degree. An irreversible reaction has a temperature coefficient of the order of several millivolts per degree. A temperature coefficient of this magnitude is, according to Meites, "fair evidence for the irreversibility of a reaction" (84).

In the present experiments, the $E_{1/2}$ of Wave I decreases by 2.5 mv./degree over the temperature range 25.7-31.0°C. and by 2.1 mv./degree over the range

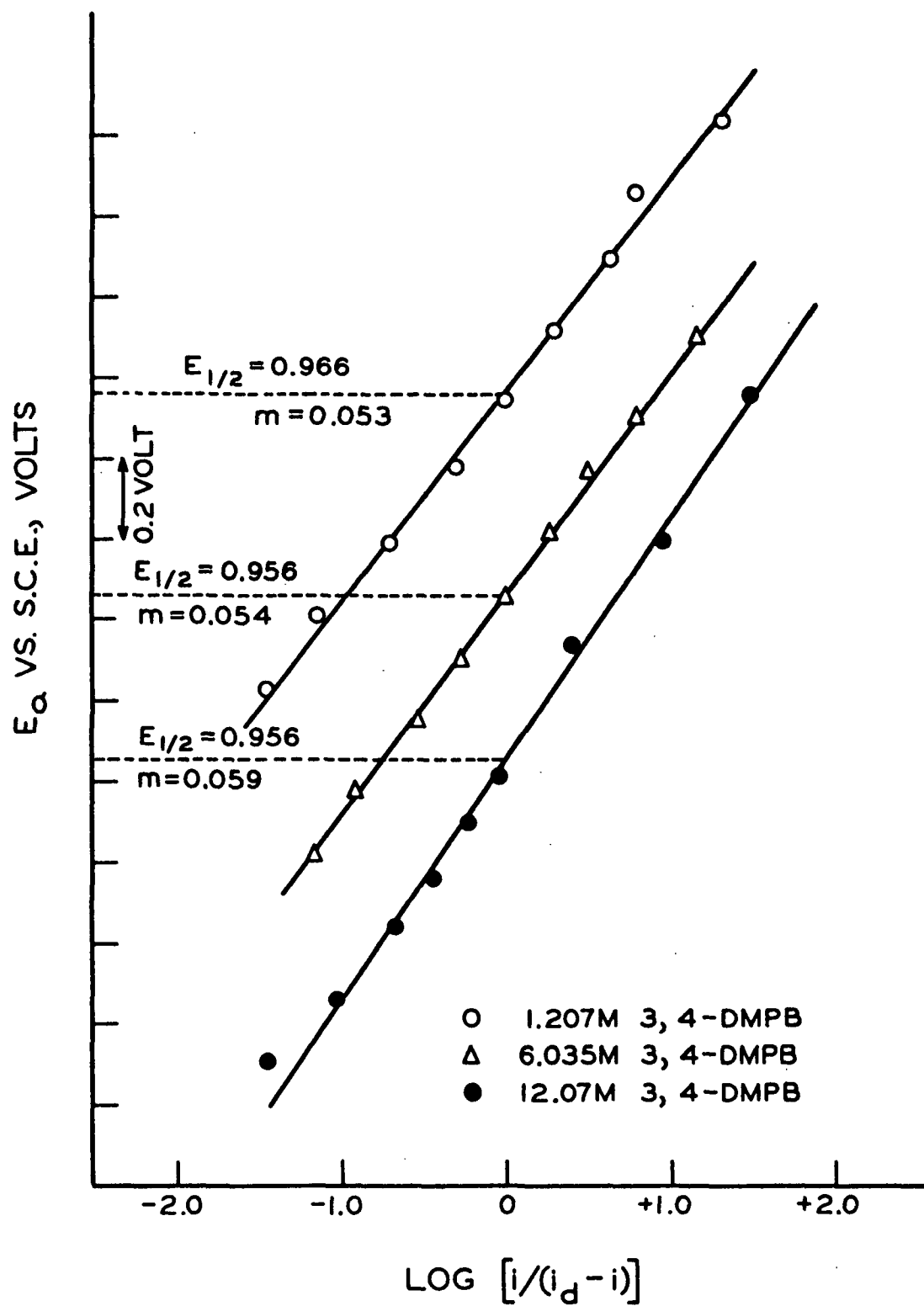


Figure 5. Anode Potential vs. $\text{Log } [i/(i_d - i)]$ 3,4-DMPB in 0.5M Sodium Perchlorate-Acetonitrile Solution. Electrode No. 2, Cleaning Proc. No. 3. Wave I.

31.0-37.1°C. These values are sufficiently high to indicate again some degree of irreversibility for the electrode reaction.

For purposes of comparison, logarithmic plots of $\underline{E_a}$ vs. $\log[i/(i_d - i)]$ for Wave II are given in Fig. 6. Although the half-wave potentials are reasonably constant the slope of the log plot is significantly greater than $0.0591/\underline{n}$ even for an assumed \underline{n} -value of one. At negative values of the log term the data points show a systematic deviation from the straight-line plot. This behavior is characteristic of an irreversible electrode reaction.

Influence of the Oxidation State of the Electrode Surface

During the course of the present study, a variety of electrode cleaning procedures were tried in an attempt to improve the reproducibility of the voltammetric data. It was found that the type of cleaning procedure employed had a pronounced effect on the voltammetric behavior of 3,4-DMPB in unbuffered acetonitrile solution. Ultimately, it was shown that the differences observed depended primarily upon whether the electrode surface was left in an oxidized or reduced condition by the pretreatment method. This same effect has been observed by a number of other investigators as indicated earlier.

Table III summarizes the results of a series of voltammograms run on 3,4-DMPB in unbuffered, 0.5M sodium perchlorate-acetonitrile solution using an electrode which had been preoxidized by treatment with dichromate cleaning solution. Similar data is presented in Table IV for a cathodically reduced electrode. In order to show more clearly the differences obtained between the two pretreatment procedures the data of both tables is given in graphical form in Fig. 7.

On a reduced electrode surface the $\underline{E}_{1/2}$ of Wave I is constant and independent of the concentration of 3,4-DMPB over a 60-fold concentration range. A slight trend

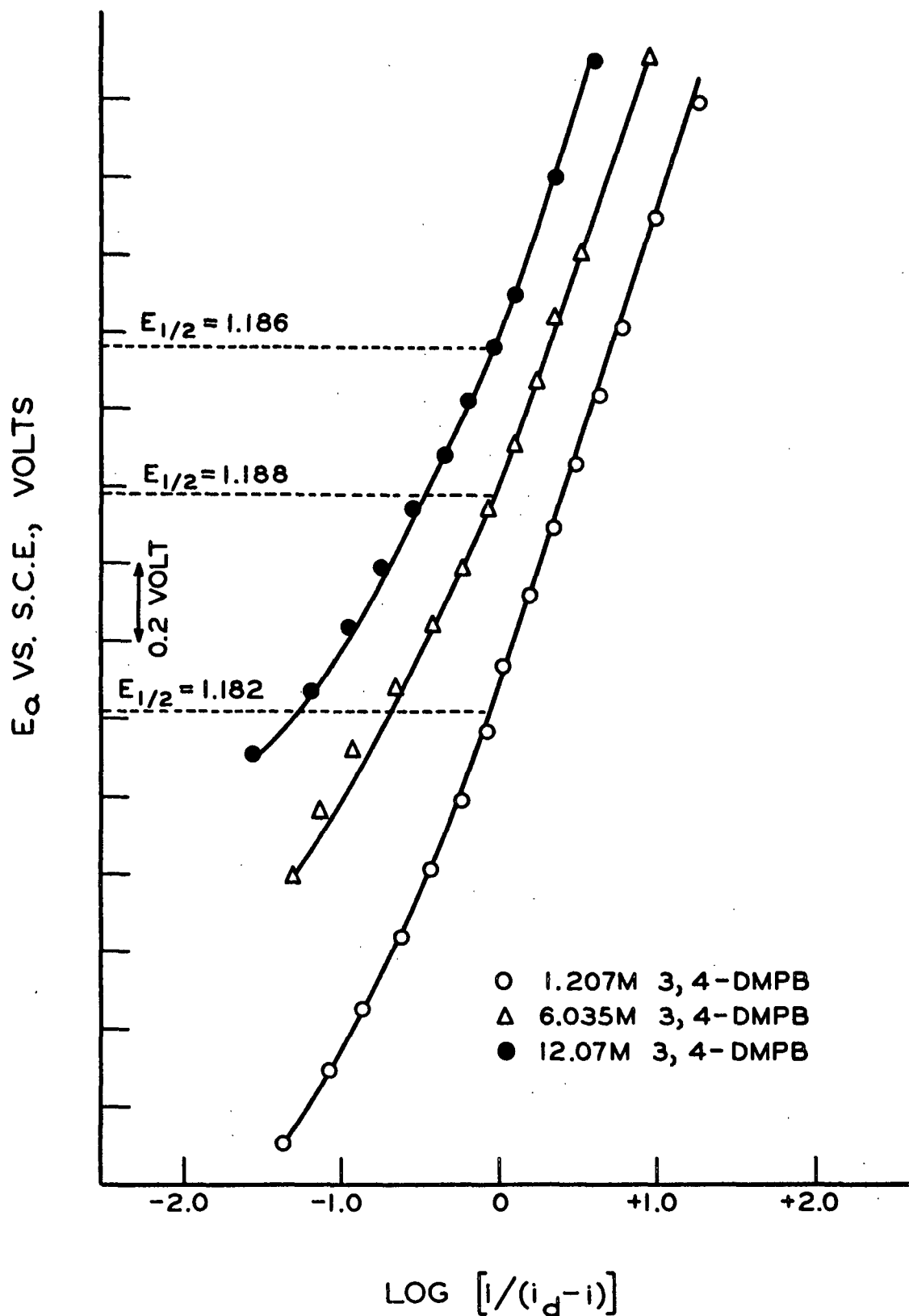


Figure 6. Anode Potential vs. $\text{Log} [i/(i_d - i)]$ 3,4-DMPB
in 0.5M Sodium Perchlorate-Acetonitrile Solution.
Electrode No. 2, Cleaning Proc. No. 3. Wave II.

TABLE III

VOLTAMMETRIC DATA FOR 3,4-DMPB IN UNBUFFERED 0.5M SODIUM
 PERCHLORATE-ACETONITRILE SOLUTION.
 ELECTRODE NO. 2, CLEANING PROC. NO. 2-OXIDIZED ELECTRODE

Concn. of 3,4-DMPB, <u>M</u>	<u>E</u> _{1/2} vs. S.C.E., volts		<u>I</u> _d , μ amp.-l./mmole	
	I	II	I	II
0.507 x 10 ⁻⁴	1.027	1.236	--	--
0.507 x 10 ⁻⁴	1.029	1.239	--	--
0.507 x 10 ⁻⁴	1.009	1.216	12.81	14.78
0.507 x 10 ⁻⁴	1.012	1.236	12.81	14.78
1.02 x 10 ⁻⁴	1.017	1.235	--	--
1.02 x 10 ⁻⁴	1.022	1.230	12.81	15.77
1.02 x 10 ⁻⁴	1.031	1.238	12.82	15.77
6.09 x 10 ⁻⁴	1.010	1.224	11.49	15.76
6.09 x 10 ⁻⁴	0.992	1.189	11.09	15.19
11.16 x 10 ⁻⁴	--	1.196	10.75	14.19
16.24 x 10 ⁻⁴	0.981	1.193	11.40	16.32
36.53 x 10 ⁻⁴	0.972	1.163	11.50	14.33
61.9 x 10 ⁻⁴	0.984	1.204	11.95	16.46

TABLE IV

VOLTAMMETRIC DATA FOR 3,4-DMPB IN UNBUFFERED 0.5M SODIUM
PERCHLORATE-ACETONITRILE SOLUTION.
ELECTRODE NO. 2, CLEANING PROC. NO. 3-REDUCED ELECTRODE

Concn. of 3,4-DMPB, <u>M</u>	<u>E</u> _{1/2} vs. S.C.E., volts		<u>I</u> _d , μ amp.- <u>l.</u> /mmole	
	I	II	I	II
1.21 x 10 ⁻⁴	0.977	1.205	11.6	19.1
2.41 x 10 ⁻⁴	0.976	1.202	10.8	18.9
6.04 x 10 ⁻⁴	0.970	1.190	11.6	19.9
12.07 x 10 ⁻⁴	0.977	1.222	11.6	19.9
24.14 x 10 ⁻⁴	0.971	1.273	11.6	18.8
60.35 x 10 ⁻⁴	1.012	1.303	12.4	18.2

toward decreasing $\underline{E}_{1/2}$ with increasing concentration of 3,4-DMPB is observed when a preoxidized electrode is used. The magnitude of the decrease is only 0.04-0.05 volts over a 120-fold concentration range and may be attributable to some other factor.

Similarly, no trend is observed in the values of the diffusion current constant over the entire concentration range for either the reduced or the oxidized electrode. The behavior of Wave I is in accord with the observations made earlier concerning the reversibility of the potential-determining electrode reaction.

The $\underline{E}_{1/2}$ for Wave II shows the same trend toward decreasing values with increasing concentration of 3,4-DMPB as was indicated for Wave I on an oxidized electrode. Furthermore, the ratios of $\underline{E}_{1/2}$ -II/ $\underline{E}_{1/2}$ -I appear to be constant and independent of the concentration of 3,4-DMPB. This strongly suggests that the decrease in $\underline{E}_{1/2}$ with increasing concentration of 3,4-DMPB for both waves is not indicative of a concentration dependence of $\underline{E}_{1/2}$ for either wave.

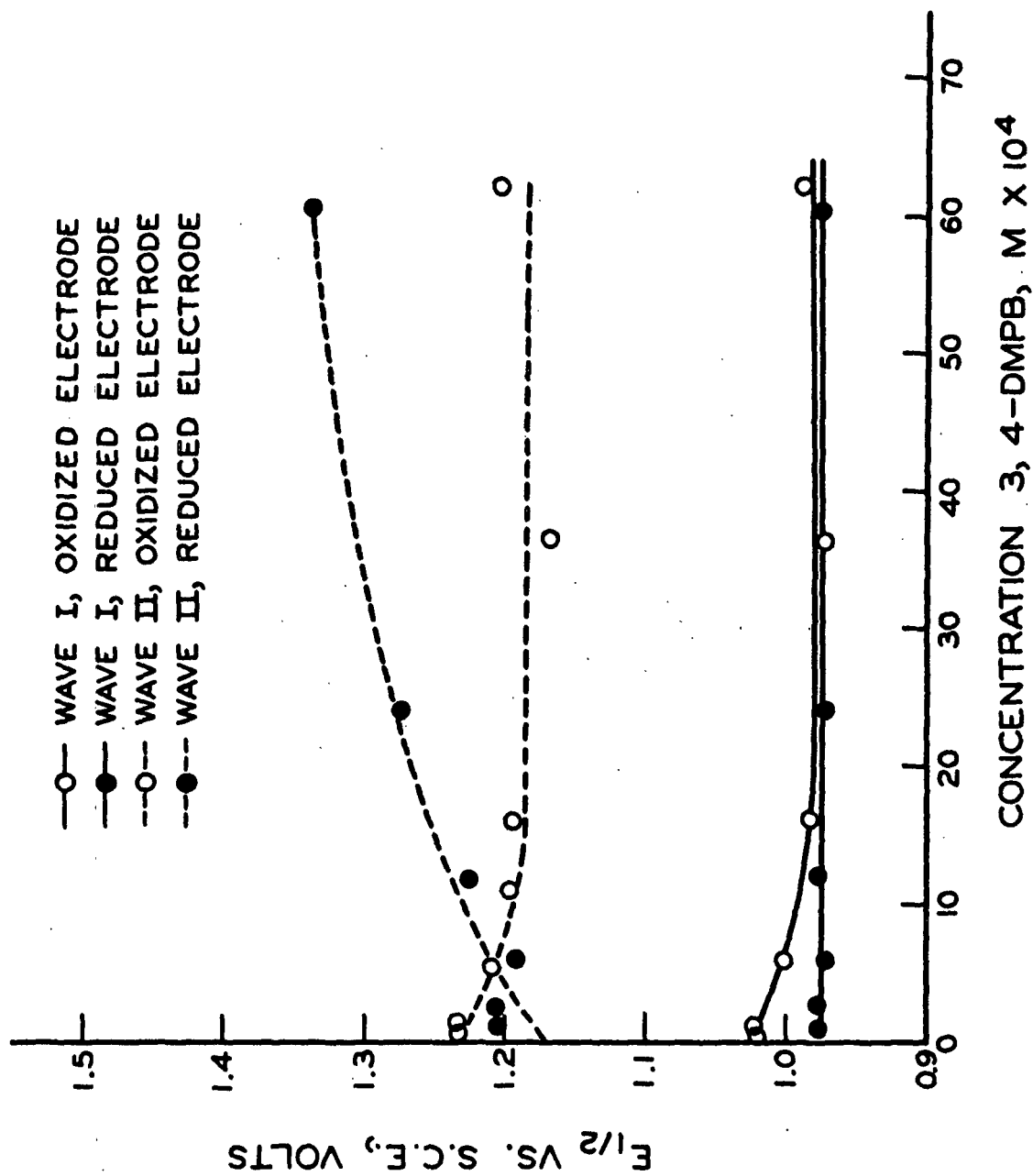


Figure 7. $E_{1/2}$ vs. Concentration of 3,4-DMPB.

Plots of Data: Tables III and IV

Considerably different behavior is exhibited by Wave II on a reduced electrode surface. In this case an increase in half-wave potential of approximately 0.1 volt is observed for a 50-fold increase in concentration of 3,4-DMPB. At the same time, however, the diffusion current constant for Wave II on a reduced electrode is 25% greater than that obtained on an oxidized electrode. Furthermore, there is no indication of a third wave in the voltammograms obtained on a reduced electrode. A third wave is present, however, in the voltammograms obtained on the oxidized electrode although the wave is very poorly defined.

Thus, it appears likely that the concentration dependence observed for Wave II on a reduced electrode may have arisen as a result of a merging of Waves II and III. It is not possible to decide conclusively from the data whether the concentration dependence is in fact exhibited by Wave II or III.

The results obtained serve to emphasize the importance of selecting the electrode pretreatment procedure with caution. Except for a few earlier studies which are included in the present report, the data obtained is referred to a reduced electrode surface. In all cases the type of electrode pretreatment is given together with the voltammetric data.

VOLTAMMETRIC BEHAVIOR IN THE PRESENCE OF BASE

Although the concentration independence of the half-wave potential of Wave I in unbuffered acetonitrile suggested a pH independent process it was desirable to establish this fact conclusively. For this reason, an investigation of the effect of acid and base on the voltammetric behavior of 3,4-DMPB was undertaken.

In order to be of any practical value in voltammetric studies, the acid or base chosen must be sufficiently soluble in acetonitrile to permit the addition of

a large excess with respect to the electroactive species. In addition, the acid or base must be stable to oxidation over the potential range in which the voltammetric waves of the compound under investigation occur. In the present section the suitability of various bases is considered.

Inorganic bases such as sodium and potassium hydroxide are virtually insoluble in acetonitrile (85) and tetraethylammonium hydroxide is soluble only to about 1-2 mM. For this reason, previous electrochemical studies carried out in acetonitrile have employed primarily organic bases such as pyridine (61, 75, 78), 1,3-dimethylurea (86), and diphenylguanidine (62, 76).

In the present study the effect of dimethylurea, pyridine, and tetraethylammonium hydroxide was investigated. Tetraethylammonium hydroxide, in addition to having a low solubility was found to give a wave at approximately 0.98 volts vs. S.C.E. Since this is the potential at which the first wave of 3,4-DMPB occurs, tetraethylammonium hydroxide was not suitable for use in the present investigation.

Pyridine

Reagent-grade pyridine from a number of suppliers as well as spectral-grade pyridine was found to give a peak wave in the residual current curve. The peak wave was removed by distilling the pyridine through a five-foot, packed column in a nitrogen atmosphere. After distillation a residual current curve was obtained for a 0.5M sodium perchlorate-acetonitrile solution made one molar in pyridine which was only slightly higher than that obtained in the absence of pyridine.

The voltammetric data for 3,4-DMPB obtained in the presence of pyridine is summarized in Table V. A typical voltammogram is shown in Fig. 8. Comparison

TABLE V

VOLTAMMETRIC DATA FOR 3,4-DMPB IN 0.5M SODIUM PERCHLORATE-
ACETONITRILE SOLUTION 1.0M IN PYRIDINE
ELECTRODE NO. 2, CLEANING PROC. NO. 2

Concn. of 3,4-DMPB, $\underline{M} \times 10^3$	$\underline{E}_{1/2}$ vs. S.C.E., volts	\underline{I}_d , $\mu\text{amp.} \cdot \underline{L} / \text{mmole}$
0.052	1.070	19.3
0.104	1.060	18.3
0.208	1.045	15.1
0.417	1.064	17.8
1.46	1.094	11.0
3.54	1.086	13.6

of the data with that obtained for 3,4-DMPB in unbuffered acetonitrile (Table III) shows that a marked increase in \underline{I}_d was obtained for Wave I. The increase approached a twofold increase at low concentrations of 3,4-DMPB suggesting a change in the electrode process from a one to a two-electron oxidation. Concurrently with the increase in \underline{I}_d both Wave II and Wave III were eliminated.

With increasing anodic potential the current was observed to decrease to low values as shown in Fig. 8. This effect is usually taken to indicate the formation of an insoluble film or tar on the electrode surface which acts as an effective barrier to the transfer of electrons. Similar film formation on a platinum electrode in the presence of pyridine was observed by Geske in a study of the oxidation of iodide ion (61), Rogers and Lord in the oxidation of phenylenediamines (87), and Vermillion in the oxidation of hindered phenols (88).

That the surface of the electrode was in some way altered was confirmed by attempts to retrace the voltammograms without cleaning the electrode between runs.

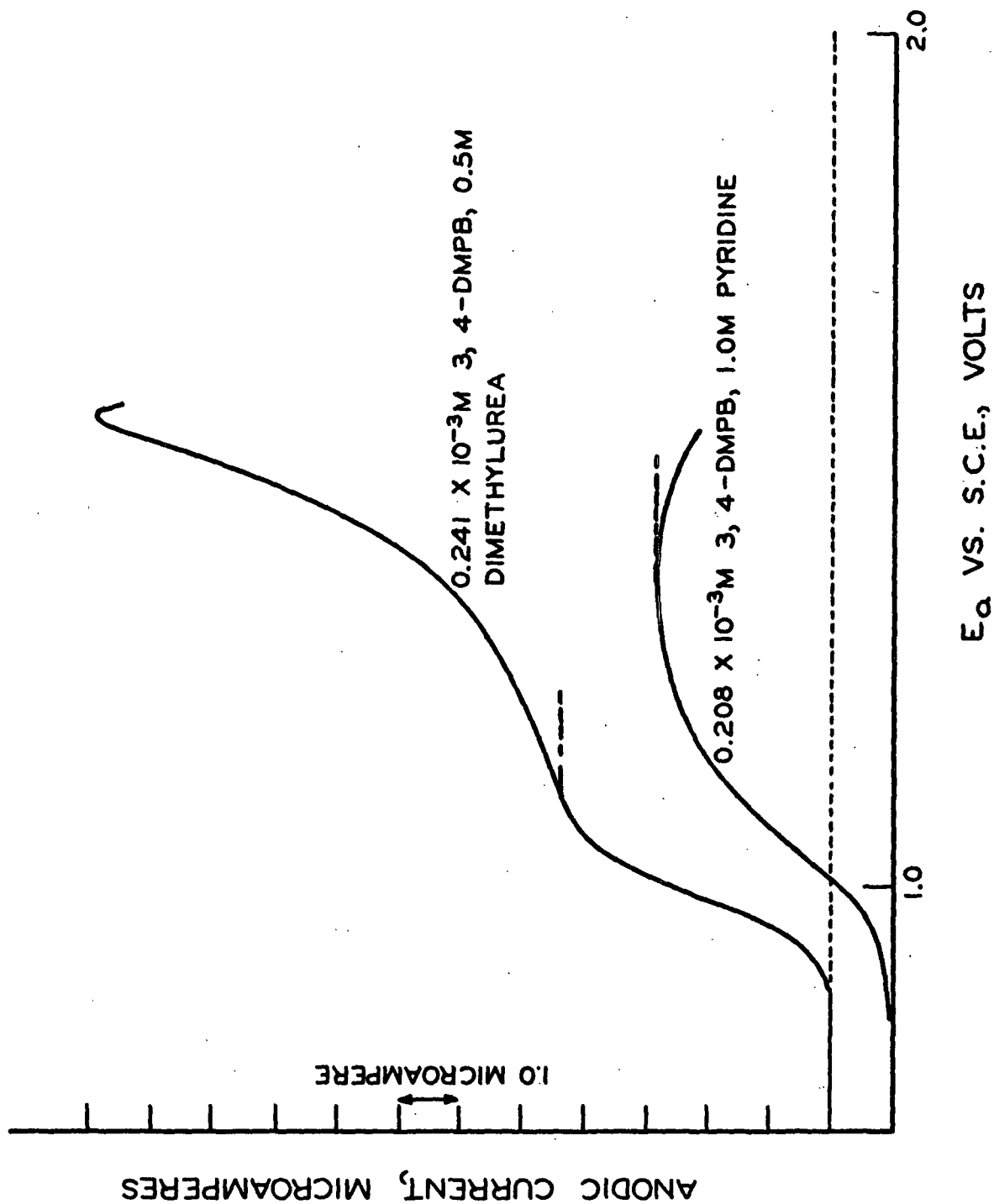


Figure 8. Voltammograms of 3,4-DMPB in 0.5M Sodium Perchlorate-Acetonitrile in the Presence of Pyridine (Curve 1) and Dimethylurea (Curve 2)

In every case a significant reduction was obtained in the height of the voltammetric wave. Attempts to remove the "film" by cathodic reduction were only partially successful. Voltammograms comparable to those obtained initially were obtained only after cleaning the electrode surface with nitric acid or dichromate cleaning solution.

At high concentrations of 3,4-DMPB a reduction in the $\underline{I_d}$ is observed. It is believed that this decrease is not attributable to a change in the nature of the electrode reaction of 3,4-DMPB, but rather is a reflection of the more rapid formation of the film on the electrode. This conclusion is substantiated by the almost quantitative recovery of 3,4-DMPB-dipyridinium diperchlorate (XVIII) from the oxidation of a solution initially containing high concentrations of both 3,4-DMPB and pyridine (see p. 63).

The $\underline{E}_{1/2}$ of the wave obtained in the presence of pyridine is somewhat higher than that obtained in unbuffered solution. When similar voltammograms were run on a reduced electrode, the half-wave potential averaged 0.962 volts which agrees with the results obtained in unbuffered acetonitrile within experimental error.

As in the case of experiments run in unbuffered acetonitrile, the half-wave potential was constant and independent of concentration. Plots of $\log [i/(\underline{i_d} - i)]$, however, gave a slope greater than 0.0591. In some cases the log plots deviated significantly from a straight-line plot. Both the slope and the shape of the log plot are typical of an irreversible reaction.

Dimethylurea

Reagent-grade symmetrical dimethylurea was found to give a peak in the residual current curve at approximately 1.44 volts vs. S.C.E. The peak was not removed

by a single recrystallization of the compound. Although the peak occurred at a sufficiently high potential to allow examination of the effect of dimethylurea on the first wave of 3,4-DMPB, the high residual current and the variability in peak potential left much to be desired.

The results of the voltammetric studies carried out in 0.5M dimethylurea at a reduced electrode are given in Table VI, and a typical voltammetric curve is shown in Fig. 8.

TABLE VI

VOLTAMMETRIC DATA FOR 3,4-DMPB IN 0.5M SODIUM PERCHLORATE-
ACETONITRILE SOLUTION 0.5M IN 1,3-DIMETHYLUREA.
ELECTRODE NO. 2, CLEANING PROC. NO. 3

Concn. of 3,4-DMPB, $\underline{M} \times 10^3$	$\underline{E}_{1/2}$ vs. S.C.E., volts		\underline{I}_d , $\mu\text{amp.} \cdot \underline{l.}/\text{mmole}$	
	I	II	I	II
0.121	0.985	1.497	19.9	27.3
0.241	0.994	1.509	18.2	22.4
0.604	0.985	1.499	18.2	15.7
1.21	0.999	1.499	16.6	12.4
2.41	0.987	1.520	16.6	14.1
6.04	1.009	1.534	14.1	13.8

The addition of dimethylurea had essentially the same effect as the addition of pyridine. That is, Wave I was significantly increased in height while the half-wave potential remained unaffected. Incidentally, the studies of dimethylurea were carried out at a reduced electrode and the half-wave potential obtained was comparable to that obtained on a reduced electrode in both unbuffered acetonitrile and in the presence of pyridine.

One major difference observed between the effect of pyridine and that of dimethylurea was that in the latter case a second wave was observed. Pyridine, it will be recalled, eliminated both the second and third waves.

The second wave, or more accurately, peak wave obtained in the presence of dimethylurea occurred at approximately the same potential as that given by dimethylurea itself. The magnitude of the wave, however, is considerably greater than that obtained for dimethylurea in the corresponding residual current curve. The only explanation which can be offered for these observations at the present time is that the "film" forming reaction leading to the peak curve for dimethylurea occurs at a slower rate when 3,4-DMPB is present in the solution and undergoing simultaneous oxidation at the electrode. This, however, appears to be at variance with the decrease in $\underline{I_d}$ of Wave I with increasing concentration of 3,4-DMPB.

Plots of $\log [i/(\underline{i_d} - i)]$ vs. $\underline{E_a}$ also gave a slope greater than 0.059 indicating clearly the irreversibility of the electrode reaction. This effect is similar to that obtained by the addition of pyridine.

VOLTAMMETRIC BEHAVIOR IN THE PRESENCE OF WATER AND ACETIC ANHYDRIDE

The most probable impurities which acetonitrile might contain are water and the various hydrolysis products of acetonitrile such as acetamide, ammonium acetate, ammonia, and acetic acid (89). Of these, water and acetic acid are probably the most important both from the standpoint of quantity and also with regard to probable influence on the voltammetric behavior of 3,4-DMPB. Thus, it was of interest to investigate the effect of both compounds on the electrochemical behavior of 3,4-DMPB.

Water content of the freshly distilled acetonitrile was monitored by means of the Karl-Fischer titration and the quantity found was always in the range of $1-2 \times 10^{-3} \text{M}$. Significant variations from this level in the final voltammetric solutions, however, might be caused by introduction of water during the necessary weighing, mixing, and transferring of the solutions to the cell, by contamination from the agar bridge, or by the addition of the supporting electrolyte containing small amounts of water.

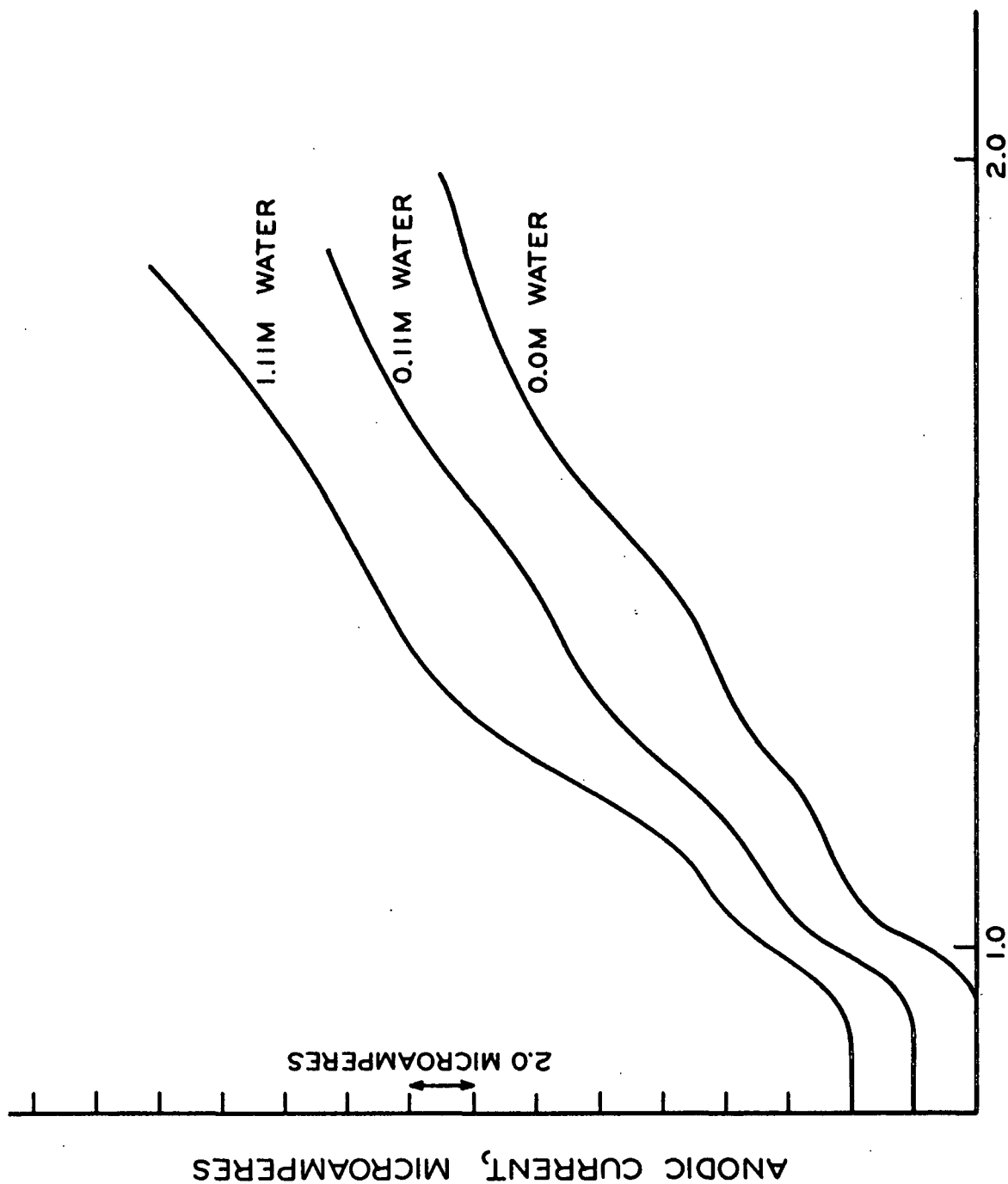
Table VII shows the effect of varying quantities of water on the voltammetric behavior of 3,4-DMPB. Representative voltammograms are shown in Fig. 9. As anticipated from the behavior of 3,4-DMPB in unbuffered solution, water had no effect on either the half-wave potential or the diffusion current constant of Wave I.

TABLE VII

VOLTAMMETRIC DATA FOR 3,4-DMPB IN 0.5M SODIUM PERCHLORATE-ACETONITRILE SOLUTION CONTAINING VARYING QUANTITIES OF ADDED WATER.
ELECTRODE NO. 2, CLEANING PROC. NO. 1

Concn. of 3,4-DMPB, $\text{M} \times 10^3$	Concn. of H_2O , M	$E_{1/2}$ vs. S.C.E., volts		I_d , $\mu\text{amp.} \cdot \text{cm}^2/\text{mmole}$	
		I	II	I	II
0.266	0.0	1.019	1.242	13.24	9.8
0.266	0.011	0.989	1.230	13.24	10.8
0.266	0.111	0.982	1.197	13.24	18.2
0.266	1.11	0.986	1.202	13.24	24.9

The diffusion current constant for Wave II on the other hand shows a steady increase with increasing concentration of water. At a water concentration of 1.11M the I_d of Wave II is approximately double that of Wave II in the absence of



E_a VS. S.C.E., VOLTS

Figure 9. Voltammograms of 3,4-DMPB in 0.5M Sodium Perchlorate-Acetonitrile Solution. Electrode No. 2, Cleaning Procedure No. 1.

water and approximately double that of Wave I. Further increases in water concentration up to 11.1M had no significant effect on the $\underline{I_d}$ of Wave II. The $\underline{E_{1/2}}$ of Wave II also shows a downward trend with increasing water content.

The results of these experiments show that variations in the water content of the "dry" acetonitrile would have no effect on the voltammetric behavior of Wave I. In the case of Wave II it was shown that water does have a significant effect on its voltammetric behavior. However, in view of the relatively large amounts of water required to produce significant changes in the latter, it does not appear that variations in water content alone could account for the variability observed in unbuffered acetonitrile.

In order to examine the behavior of 3,4-DMPB in solutions containing less than the usual 1-2 mmol. water content, a series of voltammograms was run in acetonitrile solutions made 0.2M in acetic anhydride. The experimental results are summarized in Table VIII. Comparison of the data with that given in Table VII shows the rather surprising result that the effect of 0.2M acetic anhydride is identical within experimental error with that of 1.11M water.

TABLE VIII

VOLTAMMETRIC DATA FOR 3,4-DMPB IN 0.5M SODIUM PERCHLORATE-
ACETONITRILE SOLUTION CONTAINING 0.2M ACETIC ANHYDRIDE.
ELECTRODE NO. 2, CLEANING PROC. NO. 3

Concn. of 3,4-DMPB, $\underline{M} \times 10^3$	Concn. of Acetic Anhydride, \underline{M}	$\underline{E_{1/2}}$ vs. S.C.E., volts		$\underline{I_d}$, $\mu\text{amp.} - \underline{I_d}/\text{mmole}$	
		I	II	I	II
0.098	0.2	0.995	1.208	13.3	22.4
0.196	0.2	1.012	1.229	12.2	20.4
0.490	0.2	0.994	1.207	13.3	21.4
0.980	0.2	0.985	1.207	11.2	18.0
1.96	0.2	0.995	1.214	11.2	20.4

It should be noted that the acetonitrile solutions contain a minimum of 1-2 millimolar water and the addition of acetic anhydride will result in the formation of a similar quantity of acetic acid. Thus, the observed change in the $E_{1/2}$ and I_d of Wave II may be due to the acetic acid formed rather than the acetic anhydride itself.

In the presence of either acetic anhydride or water, 3,4-DMPB also gives a very ill-defined third wave which is approximately equal in height to Wave I. Thus, the ratio of I_d -I: I_d -II: I_d -III is about 1:2:1 as compared to 1:1:1 or 1:2:0 obtained in unbuffered acetonitrile.

VOLTAMMETRIC BEHAVIOR IN THE PRESENCE OF ACID

Acetic Acid

As indicated in the previous section, the effect of acetic acid on the voltammetric behavior of 3,4-DMPB is of interest to the present study since this acid represents one of the more probable impurities which might be present in the acetonitrile. Its effect is also of interest in connection with the results obtained for acetic anhydride discussed in the previous section.

As shown in Table IX, acetic acid had no effect on Wave I. Waves II and III, on the other hand, appeared to merge giving a single, drawn-out wave. The I_d of the latter was comparable to the combined I_d 's of Waves II and III obtained in the presence of either acetic anhydride or water. The $E_{1/2}$ of the wave fell between the values obtained for Waves II and III in unbuffered solution.

Perchloric Acid

The independence of $E_{1/2}$ and I_d of Wave I of the concentration of 3,4-DMPB or the presence of water indicates that the potential-determining electrode reaction

TABLE IX

VOLTAMMETRIC DATA FOR 3,4-DMPB IN 0.5M SODIUM PERCHLORATE-
ACETONITRILE SOLUTION CONTAINING 1.0M ACETIC ACID.
ELECTRODE NO. 2, CLEANING PROC. NO. 3

Concn. of 3,4-DMPB, $\underline{M} \times 10^3$	$\underline{E}_{1/2}$ vs. S.C.E., volts		\underline{I}_d , $\mu\text{amp.-l./mmole}$	
	I	II	I	II
0.121	1.007	1.337	12.1	31.9
0.241	1.007	1.340	11.6	33.1
0.604	1.010	1.325	10.8	33.1
1.21	0.995	1.320	10.8	30.7
2.41	1.012	1.328	9.9	29.8
6.04	1.003	--	0.99	--

does not involve the participation of hydrogen ion. Controlled potential electrolysis of 3,4-DMPB at a potential corresponding to $\underline{E}_{1/2}$ of Wave I, however, results in the liberation of hydrogen ion (vide infra). Thus, it was of interest to investigate the effect of hydrogen ion on the voltammetric behavior of 3,4-DMPB.

It has already been shown that acetic acid has no effect on either the half-wave potential or the diffusion current constant of Wave I. Acetic acid, however, is virtually undissociated in acetonitrile and, hence, an extremely weak acid (90). A better choice for the study of hydrogen ion effect is perchloric acid. This acid according to Kolthoff (90) is the only one of the common strong acids which is also a strong acid in acetonitrile.

Table X shows the results of a series of voltammograms of 3,4-DMPB run in 0.5M sodium perchlorate-acetonitrile solution with increasing concentrations of perchloric acid. The absence of hydrogen ion participation in the potential-determining electrode reaction corresponding to Wave I is shown by the constancy of the

$E_{1/2}$. A similar independence of $\frac{I_d}{d}$ for Wave I was observed for acid concentrations up to 1.32 millimolar.

TABLE X

VOLTAMMETRIC DATA FOR 3,4-DMPB IN 0.5M SODIUM PERCHLORATE-ACETONITRILE
SOLUTION CONTAINING VARYING QUANTITIES OF ADDED PERCHLORIC ACID.
ELECTRODE NO. 3, CLEANING PROC. NO. 3

Concn. of 3,4-DMPB, $M \times 10^3$	Concn. of Perchloric Acid, $M \times 10^3$	$E_{1/2}$ vs. S.C.E., volts		$\frac{I_d}{d}$, $\mu\text{amp.-l.}/\text{mmol.}$	
		I	II	I	II
0.111	0.0	1.005	1.234	6.3	10.8
0.111	0.02	1.004	1.230	6.3	10.8
0.111	0.12	1.007	1.234	6.8	10.8
0.111	0.22	1.013	1.241	6.8	10.8
0.111	1.32	1.006	1.253	6.8	10.8

Wave II shows a very slight trend toward increasing $E_{1/2}$ with increasing concentration of perchloric acid. The relative change in $E_{1/2}$ for a 60-fold increase is less than 0.02 volts which is within experimental error. Since Wave II corresponds to an irreversible process no conclusions may be drawn concerning the possible participation of hydrogen in the electrode reaction.

A third wave was also obtained in the present experiments. As in preceding experiments, the wave was poorly defined. The $\frac{I_d}{d}$ of this wave appeared to be somewhat lower than Wave I.

CONTROLLED POTENTIAL ELECTROLYSIS

Isolation and identification of the final products of an electrochemical process by itself will seldom establish conclusively the nature of the potential-determining electrode process. It is equally true, however, that voltammetric

studies unsupported by a demonstration of the nature of the oxidation or reduction products can seldom serve as any more than a basis for speculation concerning the course of an electrochemical reaction. The latter statement is particularly true in the case of organic compounds which exhibit complex voltammetric behavior. Thus, electrochemical studies and isolation and identification of the final products are both of primary importance in the study of organic electrode processes.

As indicated earlier, the present investigation is directed primarily toward the elucidation of the electrochemical reactions corresponding to Wave I. This wave corresponds to a one-electron oxidation in unbuffered acetonitrile or in the presence of acid or water and a two-electron oxidation in the presence of base. Controlled potential electrolyses were thus carried out in both unbuffered acetonitrile and in acetonitrile containing added pyridine. The latter reaction is considerably less complicated and will be taken up first.

CONTROLLED POTENTIAL ELECTROLYSIS IN THE PRESENCE OF PYRIDINE

Six-hundred milliliters of acetonitrile, 0.5M in sodium perchlorate and 1.0M in pyridine were added to the anode compartment of the electrolysis cell and 400 ml. of 0.5M sodium perchlorate in acetonitrile to the cathode compartment. The solution was pre-electrolyzed at 1.2 volts vs. S.C.E. for one hour during which time the anolyte developed a pale yellow color and the current decreased to a low value. After the addition of 4.99 g. (0.028 moles) of 3,4-DMPB to the anode compartment, the electrolysis was continued for eight hours at 1.2 volts vs. S.C.E. The pale yellow color of the anolyte intensified only slightly during the electrolysis.

During the oxidation, 4.1 g. (0.023 moles) of 3,4-DMPB were consumed as estimated from the heights of the initial and final currents. The theoretical

current consumption for a two-electron oxidation is 4440 coulombs. Actual current consumption was determined as 4285 coulombs by integration of the current-time curve. The calculated n -value is thus 1.93 electrons per molecule in agreement with the voltammetric data.

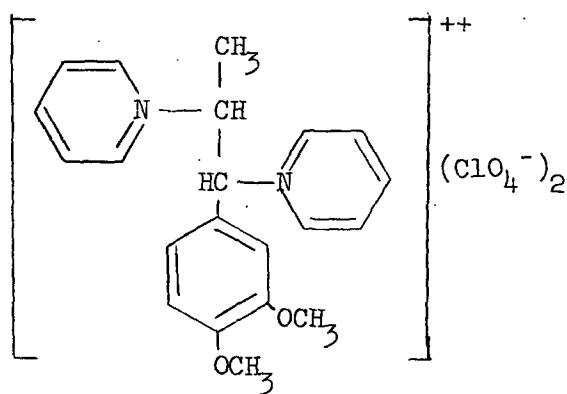
At the completion of the electrolysis the anolyte was transferred to a rotating evaporator where it was concentrated to a small volume under vacuum at temperatures below 40°C. The anolyte was then poured into 200 ml. of ice-water causing the precipitation of a white, crystalline material. Concentration of the aqueous phase and standing in the refrigerator for several days yielded a further quantity of the same material. The total air-dried yield was 12.5 g. Two recrystallizations from 90% ethanol-water gave fine, white crystals which melted at 110°C. (uncorr.).

The compound was found to be soluble in mixed alcohol-water and less soluble in either water or alcohol alone. The compound was soluble in acetone, chloroform, and acetonitrile and insoluble in benzene and ether. Addition of 5% nitron* in 10% (aqueous) acetic acid to an aqueous solution of the compound gave a heavy precipitate of nitron perchlorate. Heating on a platinum foil caused the compound to explode. When the material was heated with a little sodium hydroxide solution it gave off the unmistakable odor of pyridine. These tests, together with the coulometric data, suggests that the compound is a dipyridinium diperchlorate of 3,4-DMPB (XVIII). The theoretical yield for a dipyridinium diperchlorate (based on the consumed 3,4-DMPB) is 12.3 grams. Since most of the unreacted 3,4-DMPB might be expected to precipitate together with the diperchlorate upon addition of water, a crude yield of 13.2 g. would be expected. The crude yield of the dipyridinium

* 4,5-Dihydro-1,4-diphenyl-3,5-phenylimino-1,2,4-triazole.

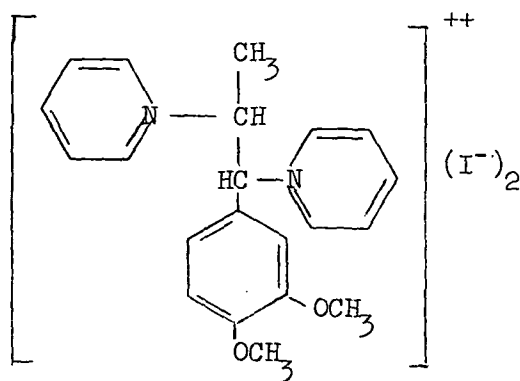
diperchlorate is thus approximately 95% of theoretical. Elemental analysis gave the following results. (Found: C, 47.93, 47.96; H, 4.70, 4.61; N, 5.15; Cl, 12.94; O (by difference), 29.31. Calcd. for $C_{21}H_{24}N_2O_{10}Cl_2$: C. 47.11; H 4.52; N 5.23; Cl 13.24; O 29.89) The infrared spectrum of the compound is shown in Fig. 10.

Addition of an excess of sodium iodide to a solution of the diperchlorate in 90% ethanol-water caused the solution to turn a bright yellow color. After several days standing in the refrigerator a quantity of bright yellow needles was obtained which melted at $174^\circ C$. (decomp.). Iodide analysis indicates the compound to be a dipyridinium diiodide of 3,4-DMPB (XIX). (Found: I, 38.9%, 38.9%; Calcd. for $C_{21}H_{24}N_2O_2I_2$: I 42.8%).



(XVIII)

3,4-DMPB-dipyridinium
diperchlorate



(XIX)

3,4-DMPB-dipyridinium
diiodide

The somewhat low values for iodide are probably due to the presence of small amounts of unchanged diperchlorate which was extremely difficult to remove from the diiodide. After three recrystallizations, the infrared spectrum of the diiodide still showed a small absorption band at 9 microns typical of the perchlorate

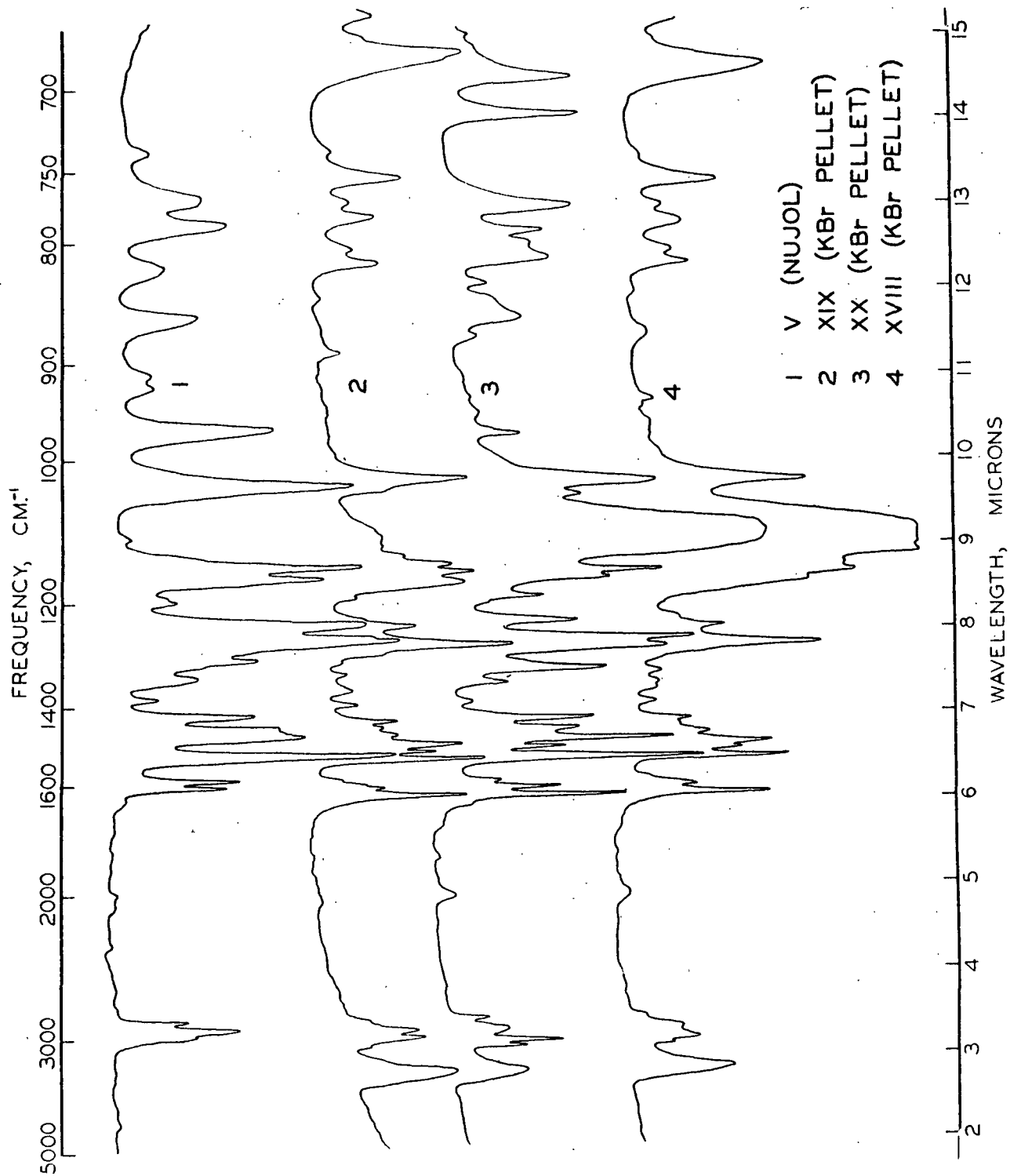


Figure 10. Infrared Spectra of 3,4-DMPB and Certain Derivatives

group (Fig. 8). The contamination by perchlorate may also be responsible for the decomposition on melting.

Treatment of the diperchlorate with two equivalents of sodium hydroxide in aqueous solution yielded pale yellow needles (XX) melting at 235°C. after two recrystallizations from water. A strong odor of pyridine was noted upon addition of the sodium hydroxide. The compound gives a precipitate with nitron acetate, explodes upon heating on a platinum foil and shows the typical perchlorate absorption band at 9 microns. No further work was done on the characterization of this material.

CONTROLLED POTENTIAL ELECTROLYSIS IN UNBUFFERED SOLUTION--WAVE I

Six hundred milliliters of 0.5M sodium perchlorate in acetonitrile were added to the anode compartment of the electrolysis cell and 400 ml. of the same solution to the cathode compartment. After pre-electrolysis for 30 minutes at 1.5 volts vs. S.C.E. (no color development) 10.075 g. (0.0565 moles) of 3,4-DMPB were added to the anode compartment. The control potential was reset to 0.95 volt vs. S.C.E. before starting the electrolysis.

Almost immediately upon application of the potential, an intense cherry-red color developed in the vicinity of the anode which rapidly spread throughout the anolyte. At the same time an extremely rapid decrease in current was observed. At the end of one-half hour of electrolysis the current had decreased to less than 25% of the initial current. After the initial drop-off, the current leveled off and remained essentially constant for the next eight hours of electrolysis. During this time the color of the solution changed from a cherry red to an intense purple.

At the end of eight hours the potential was decreased to 0.0 volt vs. S.C.E. for several minutes and then returned to the 0.95-volt setting. This caused a

current increase to approximately 30% of the initial level. The electrolysis was continued for eight more hours during which time the current decreased to 5% of the initial level. At the end of 17 hours of electrolysis the potential was again decreased to 0.0 volts for several minutes as before. Reapplication of the control potential returned the current to 25% of the original level. At this point the electrolysis was terminated. Integration of the current-time curve indicated that approximately 58% of the 3,4-DMPB was oxidized assuming a one-electron oxidation mechanism.

During the electrolysis, 2-3 ml. samples of the anolyte were removed at various reaction times. One milliliter aliquots of the samples were diluted to 50 ml. with 50% acetonitrile-water solution and titrated potentiometrically with 0.01M sodium hydroxide. The titration procedure was checked by titrating known amounts of perchloric acid in 50% acetonitrile-water solutions. Agreement between the known hydrogen ion concentrations and the analytical values was within 1%. The titration curves are given in Fig. 11 for both the anolyte samples and the known perchloric acid solutions.

During the early stages of electrolysis, approximately one hydrogen ion was liberated per molecule of 3,4-DMPB assuming a one-electron oxidation mechanism. This value gradually decreased to approximately 0.5 hydrogen ions per molecule as the electrolysis continued. The experimental results are shown graphically in Fig. 12.

The anolyte from the oxidation was placed in the refrigerator and allowed to stand overnight. No precipitate formed* and the solution was concentrated under

* In several preliminary oxidations carried out under identical conditions except that the concentration of 3,4-DMPB was 50% or less of that in the present oxidation, 5-10 mg. of yellow needles were obtained in every case by allowing the solution to stand overnight. The material sublimed at 335°C. and its I.R. spectrum was identical in every respect with that of 2,3,6,7-tetramethoxyanthraquinone (XXI).

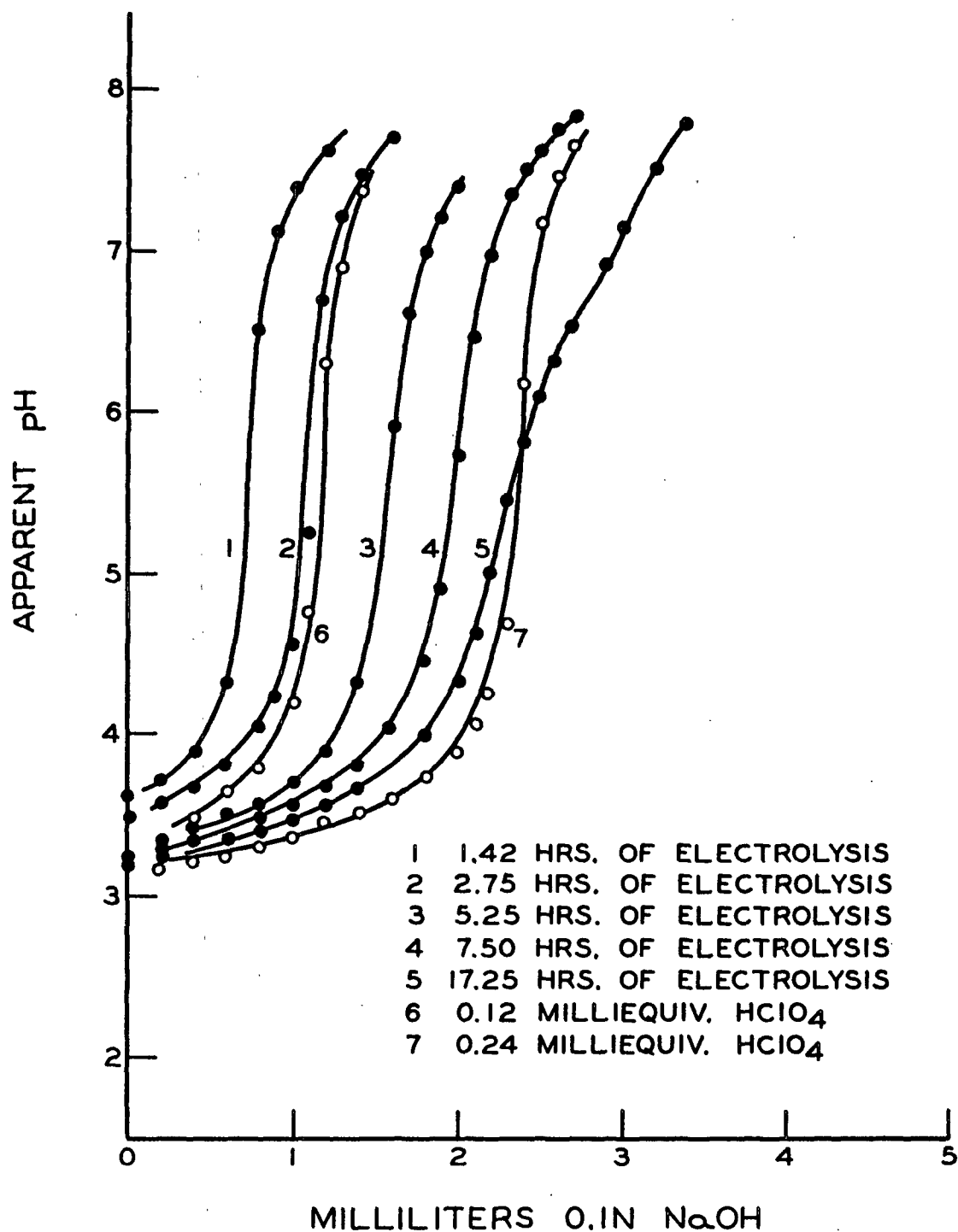


Figure 11. Potentiometric Titration Curves in
 50% Acetonitrile-Water Solution
 (Curves 1-5: 1 ml. Samples of Anolyte;
 Curves 6-7: Known Concentrations of Perchloric Acid)

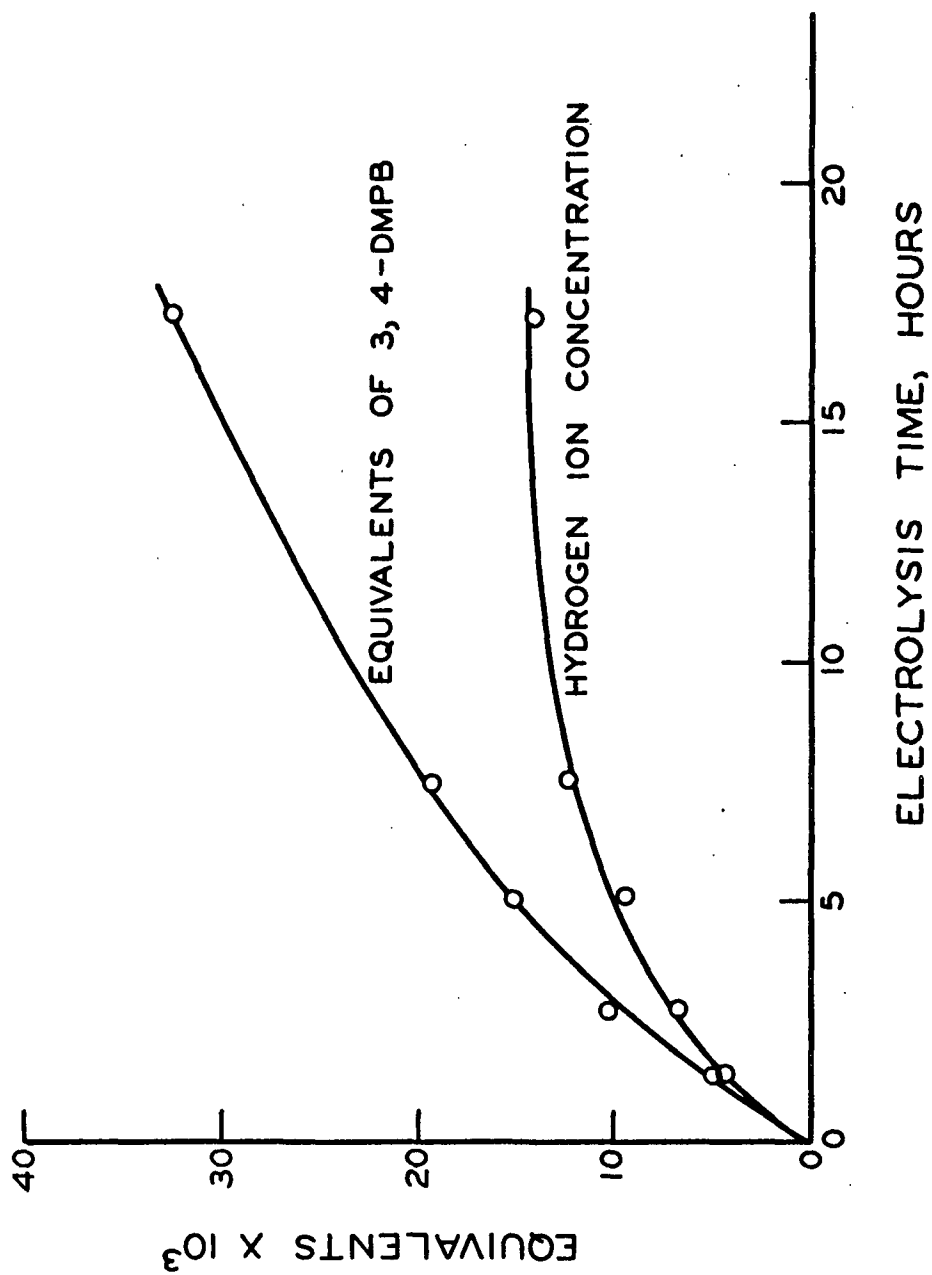


Figure 12. Equivalents of 3,4-DMPB Consumed and Equivalents of Hydrogen Ion Liberated as a Function of Electrolysis Time

vacuum in a rotating evaporator to near dryness. The concentrated anolyte was added to 1000 ml. of ether causing the precipitation of the sodium perchlorate and a dark, purple-colored material. The latter was removed by extraction with chloroform. Solids contents of the ether and chloroform solutions determined on small aliquots were 8.73 g. and 2.91 g., respectively.

Concentrating the two solutions under vacuum and storing overnight in the refrigerator led to the formation of a small quantity of white platelets in both solutions. These were removed by suction filtration, washed with a little methanol, and dried over phosphorus pentoxide. The compound gave a heavy precipitate with nitron in aqueous acetic acid and liberated ammonia when heated with a little aqueous sodium hydroxide solution. The material was found to be extremely water soluble and melted above 360°C . Its infrared spectrum matched that of ammonium perchlorate.

This material is undoubtedly formed by the hydrolysis of acetonitrile in the presence of perchloric acid and small quantities of water. The simultaneously formed acetic acid was observed in the anolyte from an earlier oxidation by means of gas chromatography. The chloroform and ether solutions were extracted with water in a separatory funnel and all fractions reserved for chromatographic investigation as described below.

The following fractions were spotted on Whatman No. 1 filter paper and developed by means of descending chromatography using methanol as the developer:

- a. chloroform fraction
- b. ether fraction
- c. residual solid in methanol
- d. chloroform fraction after water extraction
- e. ether fraction after water extraction
- f. aqueous extract of the chloroform fraction
- g. aqueous extract of the ether fraction
- h. untreated anolyte

The developed chromatograms were examined under an ultraviolet light for fluorescent materials and sprayed with 10% concentrated nitric acid in concentrated sulfuric acid. The results are summarized in Table XI.

TABLE XI

PAPER CHROMATOGRAMS OF PRODUCTS OBTAINED IN THE ELECTROLYTIC
OXIDATION OF 3,4-DMPB IN UNBUFFERED 0.5M SODIUM
PERCHLORATE-ACETONITRILE SOLUTION

Fraction	Treatment	0.0	R _f Values and Color		0.92-0.95
			0.8-0.82		
a	(a)	pink	<u>blue</u>		red-or.
	(b)	-	-		<u>purple</u>
b	(a)	pink	<u>blue</u>		red-or.
	(b)	-	-		<u>rose</u>
c	(a)	-	-		-
	(b)	-	-		-
d	(a)	-	-		pink
	(b)	-	-		<u>purple</u>
e	(a)	-	-		white
	(b)	-	-		<u>rose</u>
f	(a)	white	<u>blue</u>		pink
	(b)	-	-		-
g	(a)	white	<u>blue</u>		white
	(b)	-	-		-
h	(a)	-	<u>blue</u>		pink
	(b)	-	-		<u>violet</u>

Note: Descending chromatography, methanol developer, Whatman No. 1 filter paper. Heaviest spots are underlined. (a) ultraviolet light; (b) concentrated HNO₃-concentrated H₂SO₄.

The same solutions were also spotted on silica gel thin-layer chromatograms. These were prepared by spreading a thin layer of a slurry of 10 g. of silica gel*

* Silica gel for thin layer chromatography according to Stahl, E. Merck, A-G., Darmstadt, Germany.

and 18 ml. of water on 8 by 11 inch glass plates. The plates were dried in an oven at 110°C. for several hours before use. A variety of developing agents were tried including methanol, ethanol, propanol, acetonitrile, chloroform, tetrahydrofuran, glacial acetic acid, and a number of mixtures of these solvents. Methanol was found to give the most satisfactory development and only the results obtained with this solvent are included here.

The chromatograms were examined for fluorescent materials under ultraviolet light and sprayed with 10% concentrated nitric acid-concentrated sulfuric acid as before. The results are summarized in Table XII.

TABLE XII

THIN LAYER CHROMATOGRAMS OF PRODUCTS OBTAINED IN THE
ELECTROLYTIC OXIDATION OF 3,4-DMPB IN UNBUFFERED
0.5M SODIUM PERCHLORATE-ACETONITRILE SOLUTION

Fraction	Treatment	R_f Values and Colors				
		0.0	0.3-0.33	0.5	0.7-0.73	0.8-0.83
a	(a)	blue	blue	-	<u>blue</u>	-
	(b)	-	-	-	-	<u>purple</u>
b	(a)	blue	blue	-	<u>blue</u>	-
	(b)	-	-	-	-	<u>rose</u>
c	(a)	-	-	-	-	-
	(b)	-	-	-	-	-
d	(a)	-	-	-	-	-
	(b)	-	-	-	-	<u>purple</u>
e	(a)	-	-	-	-	-
	(b)	-	-	-	-	<u>rose</u>
f	(a)	blue	blue	blue	<u>blue</u>	-
	(b)	-	-	-	-	-
g	(a)	blue	blue	blue	<u>blue</u>	-
	(b)	-	-	-	-	-
h	(a)	blue	-	-	<u>blue</u>	-
	(b)	-	-	-	-	<u>violet</u>

Note: Ascending chromatography, methanol developer, silica gel layer. Heaviest spots are underlined. (a) ultraviolet light; (b) concentrated HNO₃-concentrated H₂SO₄.

Aqueous Phases

The blue fluorescent materials observed on the chromatograms were separated from the ether and chloroform solutions by extraction with water. Concentration of the aqueous phases in a rotating evaporator yielded several hundred milligrams of white crystals (XXII) which melted partially at 174°C. and completely at 194°C. After one recrystallization from methanol the melting point was 184-194°C.

Although the silica gel chromatograms indicated the presence of at least four different fluorescent materials, the size of the spots indicated that only one compound (XXII) (R_f 0.70 on silica gel; R_f 0.80 on paper) was present in significant quantity. The other three compounds were present in concentrations too low to show up at all on the paper chromatograms.

The fluorescent material melting at 184-194°C. gave a precipitate with nitron acetate and its infrared spectrum (Fig. 13) shows the perchlorate absorption band as well as a carbonyl absorption band. The absence of ester and carboxyl groups was shown by the ferric hydroxamate test and litmus tests for hydrogen ion, respectively.

It was shown that addition of an aqueous solution of perchloric acid to 3,4-DMPB resulted in the rapid formation of a material which imparted a strong blue fluorescence to the solution. The chromatographic behavior of this material was similar to that of the fluorescent compound described above. Thus, the fluorescent compound obtained in the electrolytic oxidation of 3,4-DMPB appears to be a secondary product formed by the action of perchloric acid formed during the oxidation on unreacted 3,4-DMPB. For this reason and because of the small quantity of compound obtained no further work was done on the characterization of the material.

It might be noted, however, that the properties of the compound are very similar to those of 2,3,6,7-tetramethoxy-9-ethylanthrone (XXIII) and its carbonium salts (91).

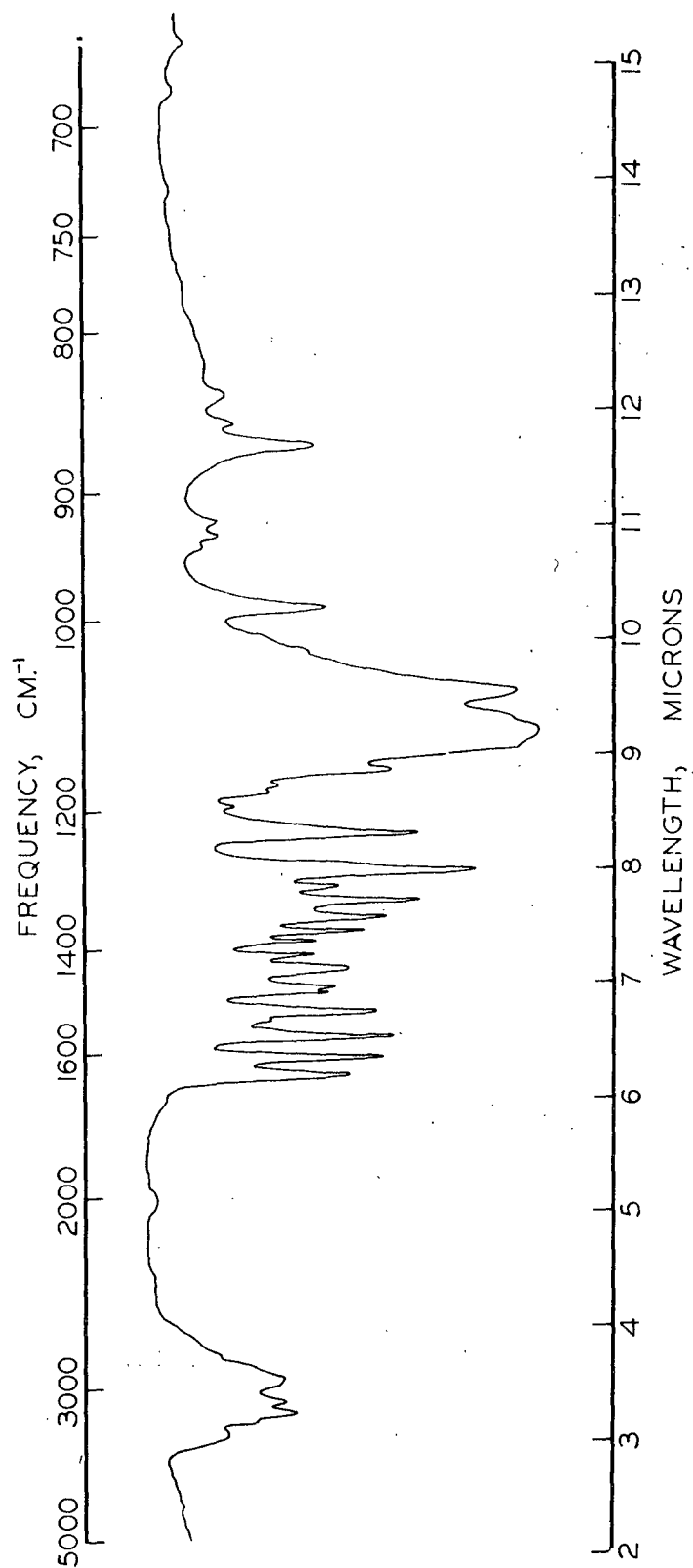
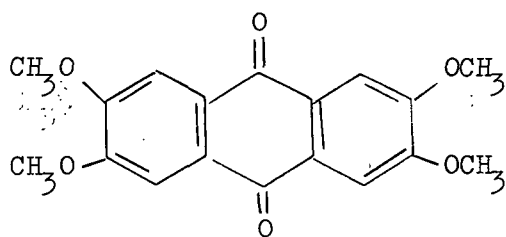
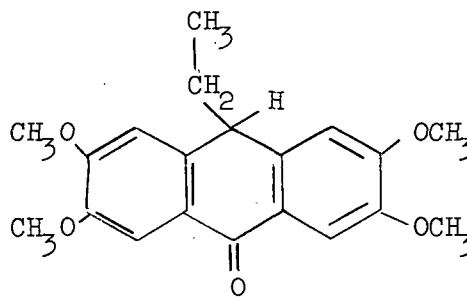


Figure 13. Infrared Spectrum of Compound XXII (KBr Pellet)



(XXI)

2,3,6,7-Tetramethoxy-
anthraquinone



(XXIII)

2,3,6,7-Tetramethoxy-9-
ethylanthrone

Ether Phase

The ether solution after extraction with water was concentrated in a rotary evaporator under vacuum to give a dark-colored oil. Addition of methanol to the oil and several days standing in the refrigerator produced small wartlike clusters of tiny needles. The crude material weighed 3 g. and melted at 95°C. No attempt was made to recover the remainder of the product in the ether solution since the chromatographic data indicated the presence of only a single material.

When the crude product was recrystallized from methanol, small clusters of needles formed first followed by a small quantity of long, slender needles. The two materials melted at 105 and 88°C., respectively, after mechanical separation and drying over phosphorus pentoxide. The infrared spectra (KBr pellets) of the 88°C. m.p. material was identical with the 88°C. m.p. isomer (XVIa) of dimethyldiisoeugenol obtained by the action of sulfuric acid on 3,4-DMPB.

The infrared spectra (KBr pellets) of the solid 88°C. m.p., 105°C. m.p., and also the 95°C. m.p. (XVI) isomer of dimethyldiisoeugenol obtained by the action of zinc chloride and hydrochloric acid on 3,4-DMPB were found to be very similar but not identical. The compounds appear to be dimorphic forms of a single stereoisomer of dimethyldiisoeugenol since the infrared spectra of all three compounds

run in carbon tetrachloride solution are identical in every respect. The infrared spectra are shown in Fig. 14. Ultraviolet spectra of the three materials in ethanol were also identical.

Chromatograms of dimethyldiisoeugenol showed spots with R_f 0.80-0.82 (silica gel) and 0.92-0.94 (paper). The spots were an intense rose color after spraying with concentrated nitric acid-concentrated sulfuric acid, but showed no fluorescence under ultraviolet light. This behavior is identical with that observed for the material in the ether phase of the anolyte. Dimethyldiisoeugenol, although obtained in comparatively large quantity from the anolyte is not an oxidation product of 3,4-DMPB.

Chloroform Phase

The only other product which appeared to be present in significant amounts was the purple-colored material (XXIV) present predominantly in the chloroform extract. The R_f values of this compound on both silica gel and paper were essentially the same as the R_f values for dimethyldiisoeugenol suggesting that this compound may also be a dimer of 3,4-DMPB.

The chloroform solution after extraction with water was concentrated to a small volume and stored in the refrigerator. Prolonged standing yielded no crystalline material. A purple-colored solid was obtained by precipitation with carbon tetrachloride from the chloroform solution. All attempts to recrystallize the material were unsuccessful. Treatment of (XXIV) with sodium hydroxide yielded a pale-yellow solid (XXV) in small quantity.

The infrared spectra of (XXIV) and (XXV) are given in Fig. 15. The spectrum of (XXIV) is characteristic of an organic perchlorate. The spectrum of (XXV) shows

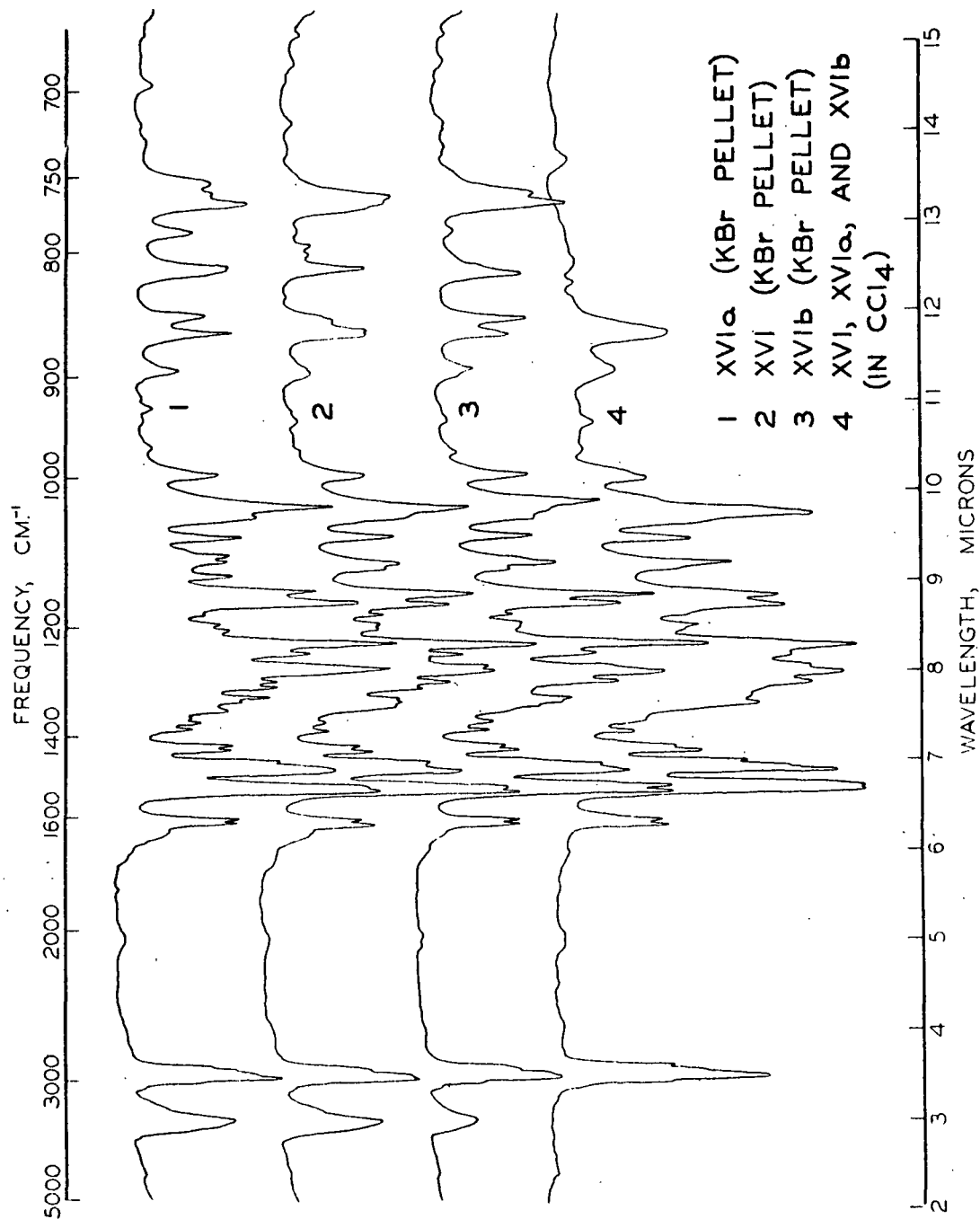


Figure 14. Infrared Spectra of Dimethyldiisoeugenol

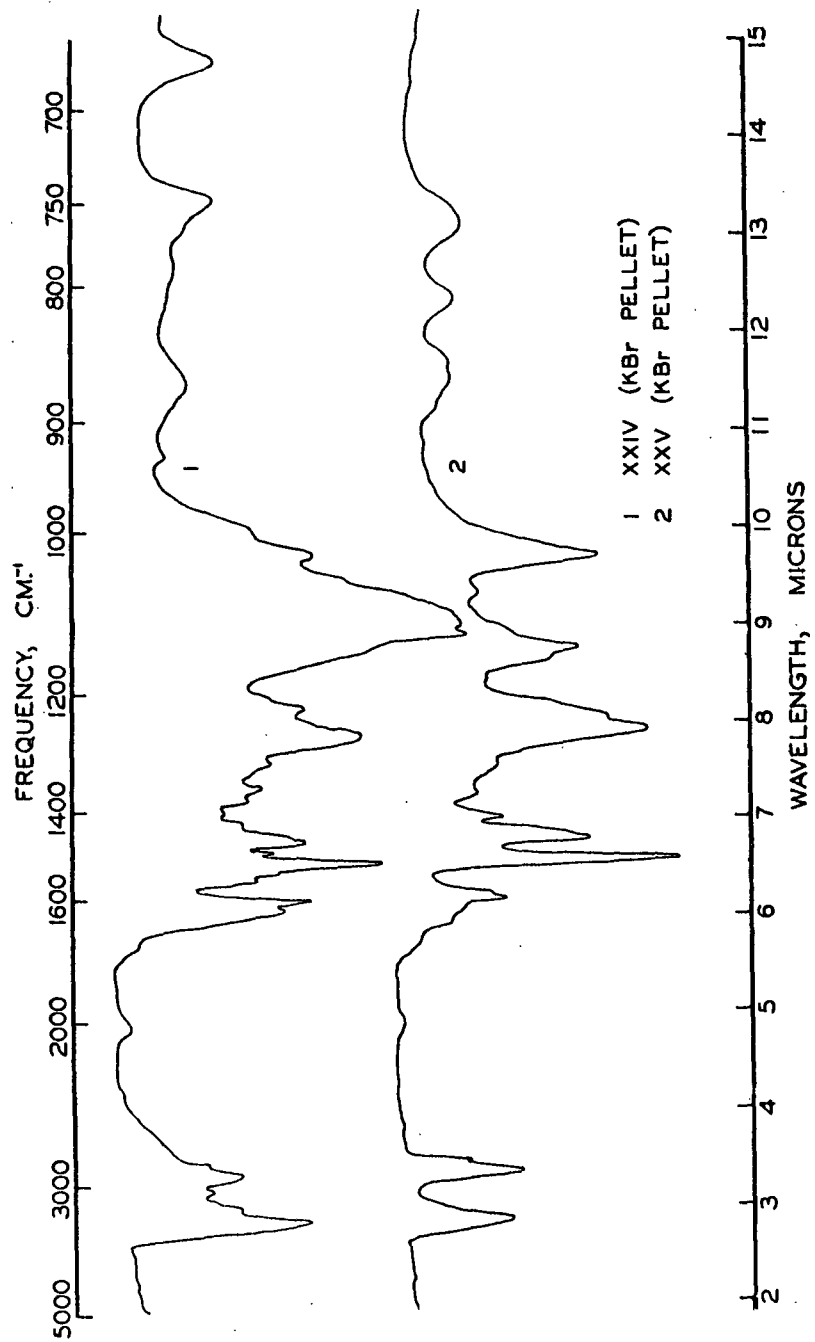
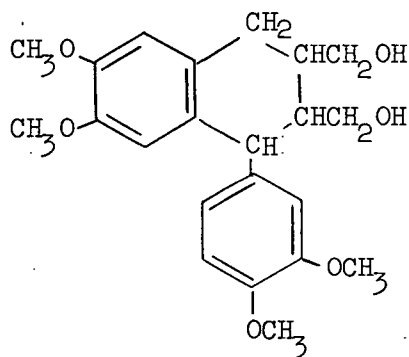


Figure 15. Infrared Spectra of Compounds XXIV and XXV

no perchlorate absorption bands and it bears a striking resemblance to that of 1,2-trans-2,3-cis-1-(3,4-dimethoxyphenyl)-1,2,3,4-tetrahydro-6,7-dimethoxy-2,3-naphthalenedimethanol (XXVI) (92). The infrared spectrum of Compound XXV, however, shows no hydroxyl absorption bands.



(XXVI)

1-(3,4-Dimethoxyphenyl)-1,2,3,4-tetrahydro-6,7-dimethoxy-2,3-naphthalenedimethanol

The details of the isolation procedures are summarized in Fig. 16.

THE ACID-CATALYZED DIMERIZATION OF 3,4-DMPB

It will be recalled that in the controlled potential oxidation of 3,4-DMPB in unbuffered acetonitrile an abnormally rapid decrease was obtained in the current level. A possible reason for this is suggested by the presence of hydrogen ion and dimethyldiisoeugenol in the anolyte from the oxidation. That is, the hydrogen ion generated in the primary electrode process or more likely in a subsequent secondary reaction, catalyzes the dimerization of unoxidized 3,4-DMPB to yield dimethyldiisoeugenol. Thus, a more rapid current decrease would be expected since the 3,4-DMPB is being removed both by electrolytic oxidation and by acid-catalyzed dimerization. These conclusions are valid, however, only if the dimethyldiisoeugenol is oxidized at a higher potential than the 3,4-DMPB or has a lower $\underline{I_d}$ at the same potential.

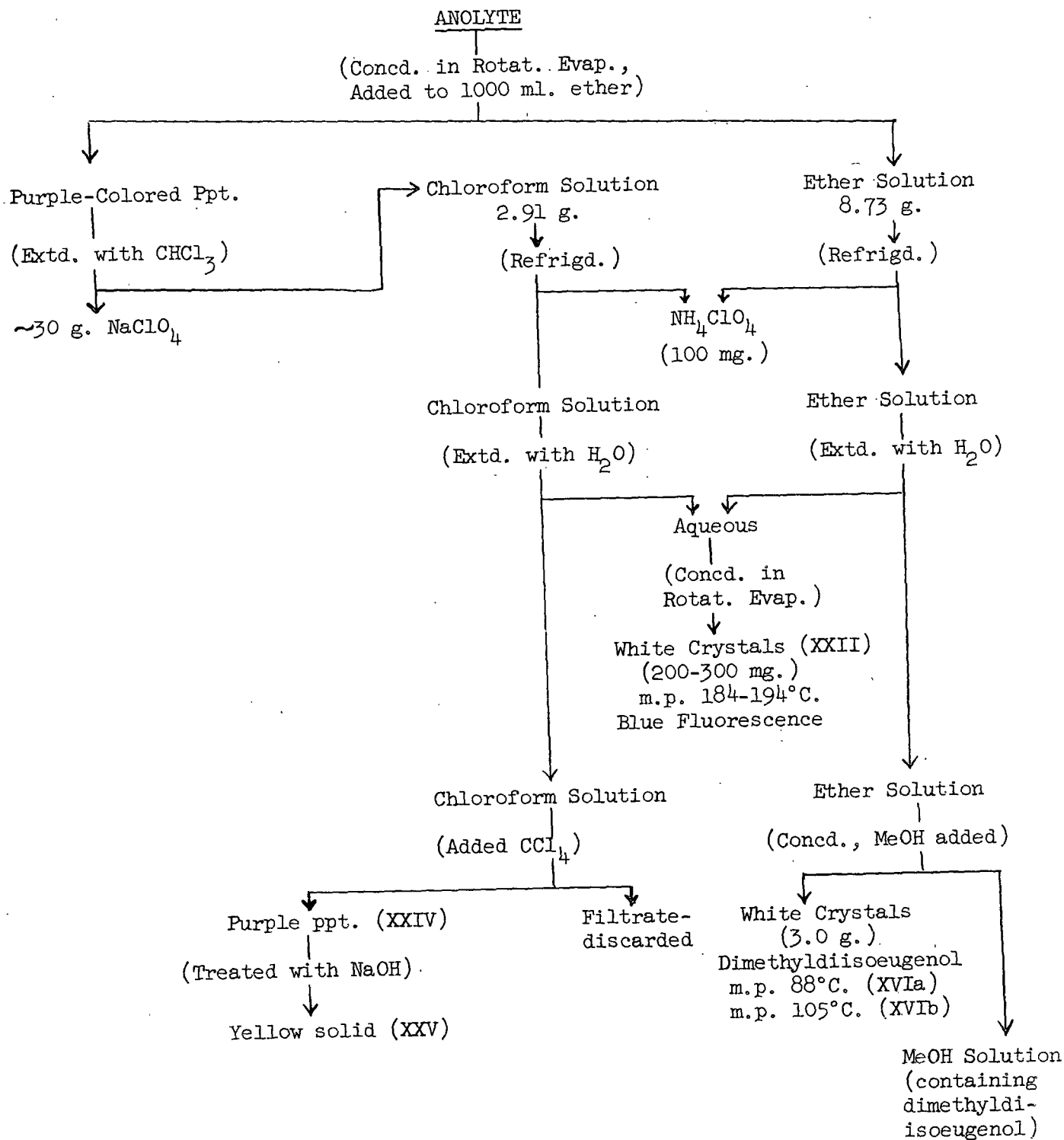


Figure 16. Isolation of Products from the Electrolytic Oxidation of 3,4-DMPB in Unbuffered 0.5M Sodium Perchlorate-Acetonitrile Solution

In order to test this hypothesis, 25 ml. of a $1.0\text{M} \times 10^{-3}\text{M}$ solution of 3,4-DMPB in 0.5M sodium perchlorate-acetonitrile were added to the voltammetric cell and a voltammogram recorded. The electrode was removed, cleaned (Proc. No. 1), and replaced in the cell. One-hundred microliters of 0.5M perchloric acid in glacial acetic acid were then added to the cell, the solution mixed with a vigorous stream of nitrogen and a current reading made at an anode potential of 1.05 volts vs. S.C.E. Similar current readings were taken at approximately 5 minute intervals during the early stages of the reaction and approximately once every half-hour after the initial sharp drop-off in current had taken place. Between measurements the E.M.F. switch was turned off. At the end of the run the electrode was again cleaned and a voltammogram recorded.

Similar experiments were carried out with 250, 500, and 5000 microliters of 0.5M perchloric acid added to the solution of 3,4-DMPB in acetonitrile. Since the E.M.F. was applied across the cell only long enough to make a current reading, less than 0.5% of the observed current drop could be attributed to electrolysis of the 3,4-DMPB.

The experimental results given in Fig. 17 show the rapid decrease in current attributable to the presence of hydrogen ion. Based on the data obtained, a hydrogen ion concentration of approximately 0.1M would cause by itself a decrease in current to 25% of the original value even in the absence of electrolytic oxidation. Thus, the rapid decrease in current observed in the electrolysis may be accounted for completely by the combined effect of oxidation and acid-catalyzed dimerization.

Typical voltammograms run before treatment with perchloric acid and after prolonged contact with acid are shown in Fig. 18. The voltammograms obtained after acid treatment are very well defined although the heights of the waves are less

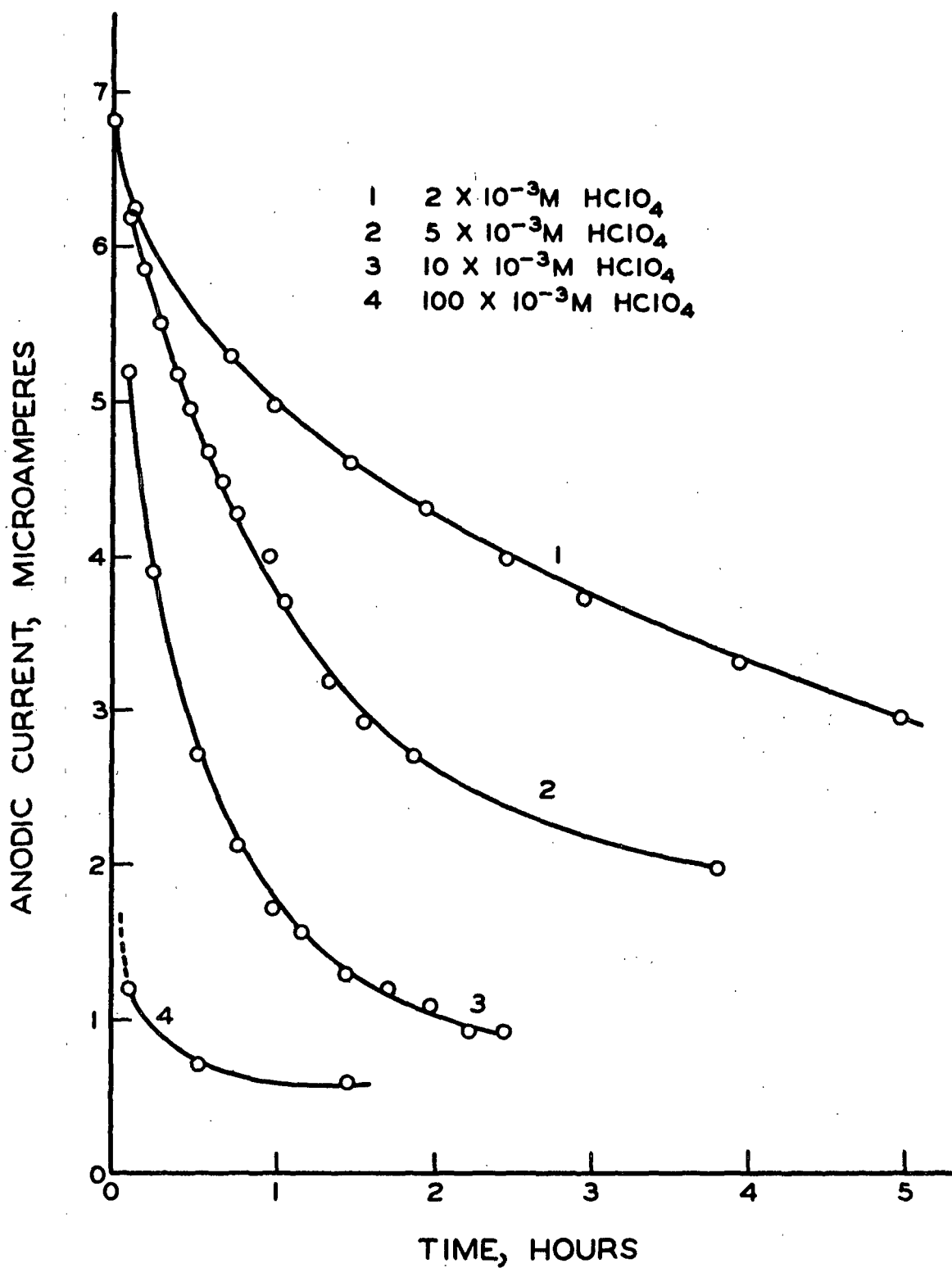


Figure 17. Decrease in Current Due to the Acid-Catalyzed Dimerization of 1.092 Millimolar 3,4-DMPB in 0.5M Sodium Perchlorate-Acetonitrile

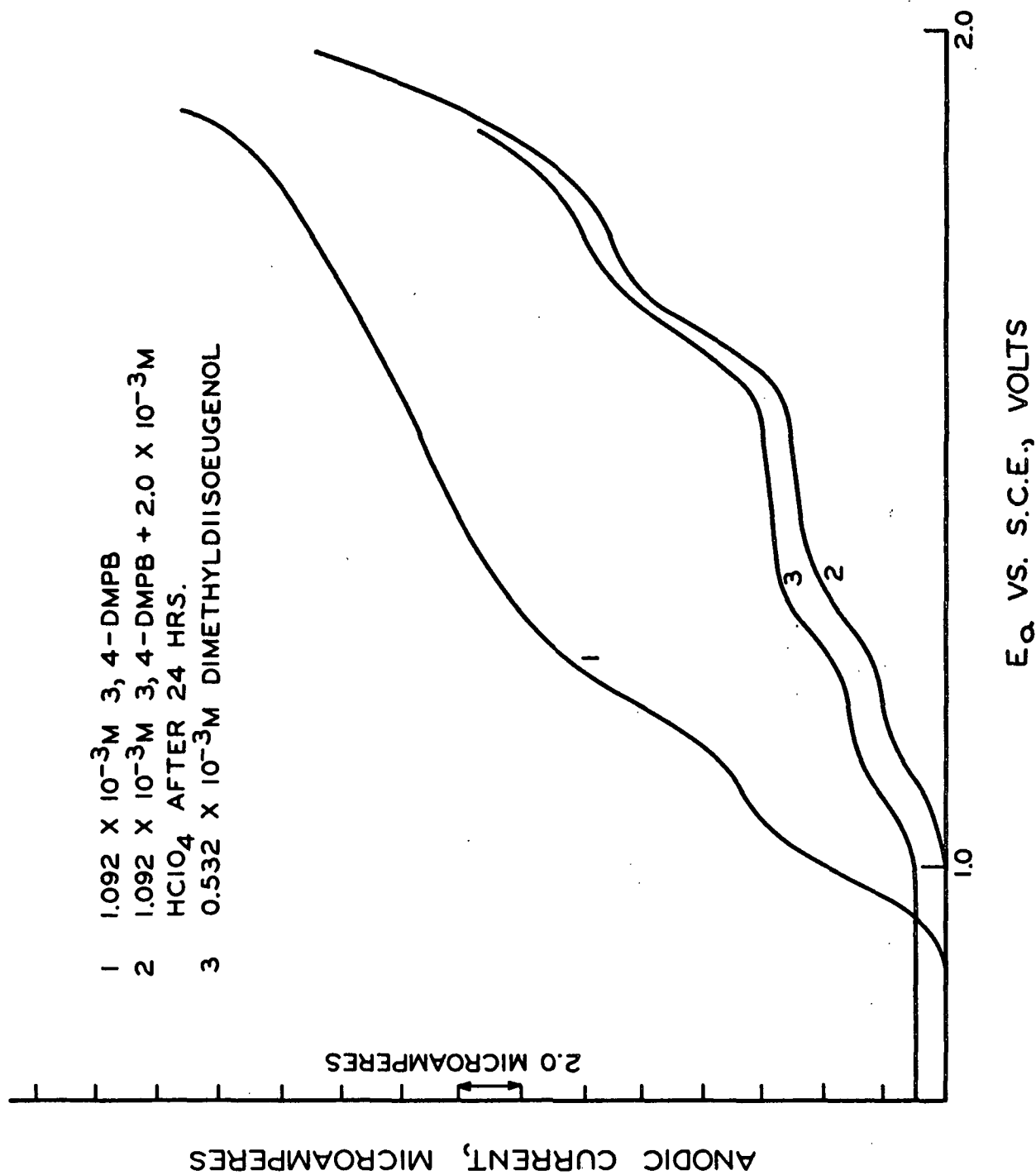


Figure 18. Voltammograms in 0.5M Sodium Perchlorate-Acetonitrile Solution

than 50% of the original heights. These results are in accord with the expected behavior for dimerization. That is, complete dimerization would effectively reduce the concentration of electroactive species by 50% and since the molecule formed is twice the size of the original monomer a further reduction in $\frac{I_d}{d}$ would be expected due to the decreased diffusivity of the larger molecule.

For comparison purposes a voltammogram of the 95°C. m.p. isomer of dimethyldiisoeugenol is also included in Fig. 18. The concentration of the dimethyldiisoeugenol is approximately that of the dimer formed by the action of perchloric acid. As shown, the two curves are very nearly identical with respect to the number of waves, the half-wave potentials of the waves, and the diffusion current constants. This evidence, together with the actual isolation of dimethyldiisoeugenol as one of the products from the electrolytic oxidation of 3,4-DMPB, clearly establishes the reason for the rapid decrease in current observed in the oxidation.

With the nature of the product thus established it seemed worthwhile to attempt a somewhat more detailed description of the process. It has been shown that if styrene or 4-MPB is dimerized by the action of deuterated hydrochloric acid both the dimer and the unreacted monomer will contain deuterium (98). Furthermore, the rate of dimerization is strongly dependent upon the acid concentration. This suggests a reaction mechanism of the following type (98)



in which the second step is a slow, irreversible process. Thus, the rate of consumption of A will be given by:

$$-\frac{dA}{dt} = k(AH^+)(A) = kK_{eq}(A)^2(H^+) \quad (3)$$

where:

$$K_{eq} = \frac{(AH^+)}{(A)(H^+)} \quad (4)$$

and therefore will be first order with respect to hydrogen ion and second order with respect to A. If the hydrogen ion is present in sufficiently large quantity to be treated as a constant or if the concentration of AH^+ is negligibly small with respect to the hydrogen ion concentration, Equation (3) may be integrated to give the familiar second-order rate equation:

$$1/A_2 - 1/A_1 = kK_{eq}(H^+)(t_2 - t_1) \quad (5)$$

Assuming that the equilibrium position of Reaction (1) is far to the left and that the only significant contribution to the current is given by 3,4-DMPB monomer and dimethyldiisoeugenol, the following expressions may be written:

Letting a = concentration of 3,4-DMPB at $t = 0$
 and $(a-x)$ = concentration of 3,4-DMPB at $t = t$
 $x/2$ = concentration of dimethyldiisoeugenol

Then

$$i = k(a-x) + (0.1)(x/2) \quad (6)$$

where i is taken as a positive quantity for purposes of convenience. The factor 0.1 is included in the second term since the current height for dimethyldiisoeugenol is 0.1 times that of an equal concentration of 3,4-DMPB at the potential used for the experiments.

Solving for $(a-x)$ in terms of a and i in Equation (6) gives:

$$(a-x) = [i - 0.05ka]/0.95k \quad (7)$$

Using Equation (5) with $A = (a-x)$ and the data of Fig. 17 the plots shown in Fig. 19 were obtained. Although some deviation from a straight-line plot is obtained

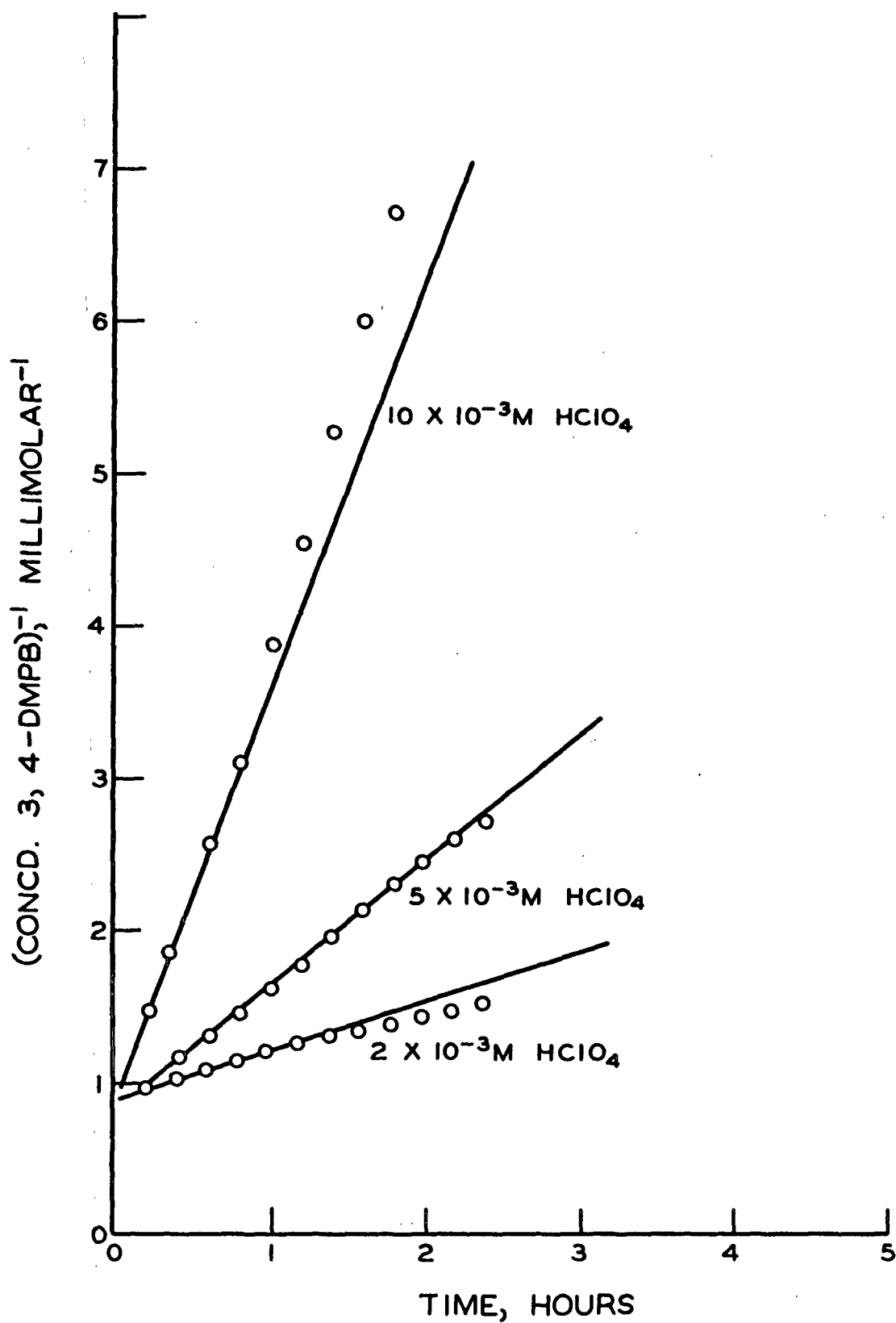


Figure 19. Second Order Plot for the Acid Catalyzed Dimerization of $1.092 \times 10^{-3} \text{ M}$ 3,4-DMPB in 0.5 M Sodium Perchlorate Acetonitrile

at longer times the data is in surprisingly good agreement with Equation (5) in view of the assumptions made in the derivation.

Since the slope is equal to $\frac{kK_{eq}}{[H^+]}$ where the only variable is (H^+) the predicted values for hydrogen ion concentrations of 2.0×10^{-3} , 5.0×10^{-3} , and $1.0 \times 10^{-2} M$ should have the ratio 1:2.5:5.0. The actual ratio obtained using the initial portion of the plots was 1:2.5:7.9.

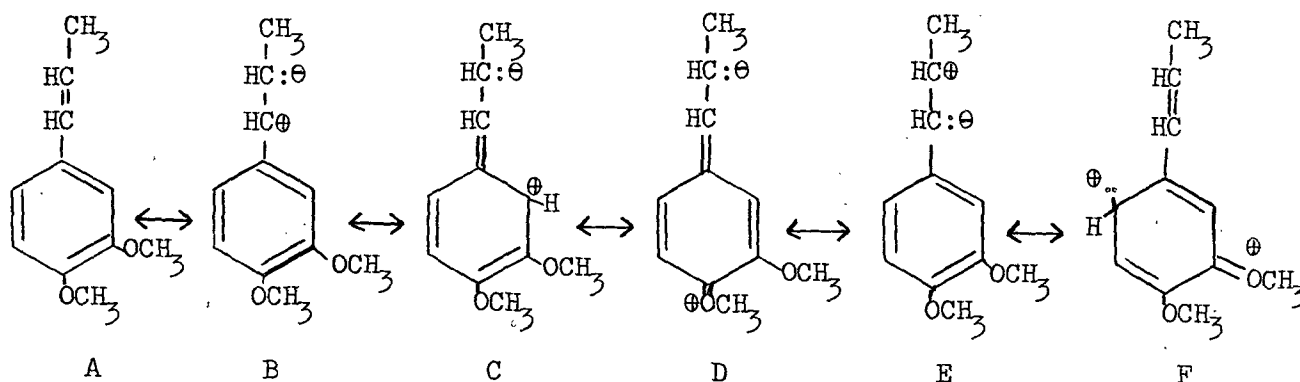
It would be of interest to extend these studies. However, the present investigation is not concerned primarily with the acid-catalyzed dimerization of 3,4-DMPB and no further work was done in this area.

One further observation made in the investigation of the acid-catalyzed dimerization of 3,4-DMPB appears pertinent to the present study. That is, an immediate formation of a cherry-red color was observed upon adding perchloric acid to a solution of 3,4-DMPB in acetonitrile. Thus, the red color observed in the electrolysis of 3,4-DMPB is probably a result of the liberation of perchloric acid at the anode and the formation of a halochromic salt with the unoxidized 3,4-DMPB. The more intensely colored, purple material appears to accumulate only slowly during the electrolysis.

SUMMARY AND INTERPRETATION OF EXPERIMENTAL RESULTS

It has been shown that 3,4-DMPB gives three voltammetric waves at a rotating platinum electrode in unbuffered acetonitrile. The first wave corresponds to a diffusion-controlled, one-electron electrode reaction which substantially fulfills the various criteria for voltammetric reversibility. Although hydrogen ion is not involved in the potential-determining electrode reaction this species is liberated in a secondary reaction to the extent of approximately one to two hydrogen ions per two electrons transferred.

In the 3,4-DMPB molecule the strong donor tendency of the p-methoxylated phenyl nucleus effects an electron shift in the direction of the beta carbon atom. Thus, of the representative contributing structures to the resonance hybrid shown below, B, C, and D are most important in describing the hybrid. Structures such as E, and F contribute little to the description of the molecule.

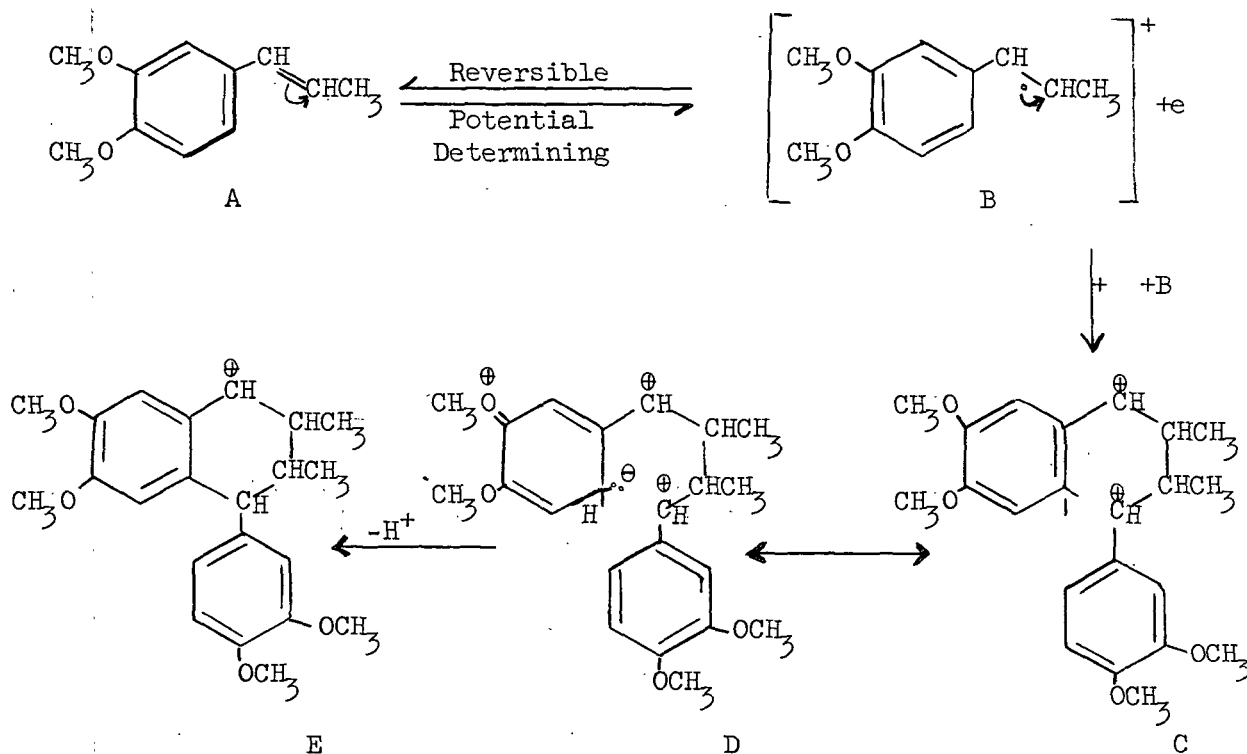


The localization of the electrons at the beta carbon is shown in the acid-catalyzed dimerization of 3,4-DMPB where proton addition to the beta carbon atom decreases the activation energy of the system sufficiently to permit chain initiation to occur (98). The importance of the contributing structure B above is shown by the ready loss of hydrogen ion from the protonated beta carbon as a result of

hyperconjugation of the C_{β} -H bonds with the electron-deficient α -carbon atom (99). Similarly, all of the chemical oxidations discussed earlier resulted in a removal of the electrons from the unsaturated side chain leading to chain cleavage or addition of nucleophiles.

A similar attack at the center of greatest electron density is expected in the electrolytic oxidation of 3,4-DMPB. Thus, Wave I of 3,4-DMPB in unbuffered acetonitrile corresponds to the removal of a single electron from the vicinity of the beta carbon atom with the formation of a highly reactive carbonium ion radical. Although such a species may stabilize in a variety of ways, e.g., dimerization, fragmentation, addition of radicals and nucleophiles, ejection of hydrogen ions, or a combination of these processes, it appears that the 3,4-DMPB carbonium ion radical stabilizes primarily by a single mechanism. This statement is made on the basis of the relatively small number of products formed in significant quantity by controlled potential electrolysis of 3,4-DMPB as shown by chromatographic investigation.

The primary oxidation product is a purple-colored material (XXIV) which was not successfully isolated in pure form but which yielded a light-colored compound upon treatment with sodium hydroxide. The infrared spectrum of the latter compound is suggestive of a substituted tetralin. The dimeric nature of the compound is also indicated by the similarity of R_f values to those of dimethyldiisoeugenol in a number of substrate-developer systems. These observations, together with the finding of 0.5 to 1.0 hydrogen ion per electron transferred in the anolyte from the controlled potential oxidation of 3,4-DMPB suggests a reaction scheme of the following type.

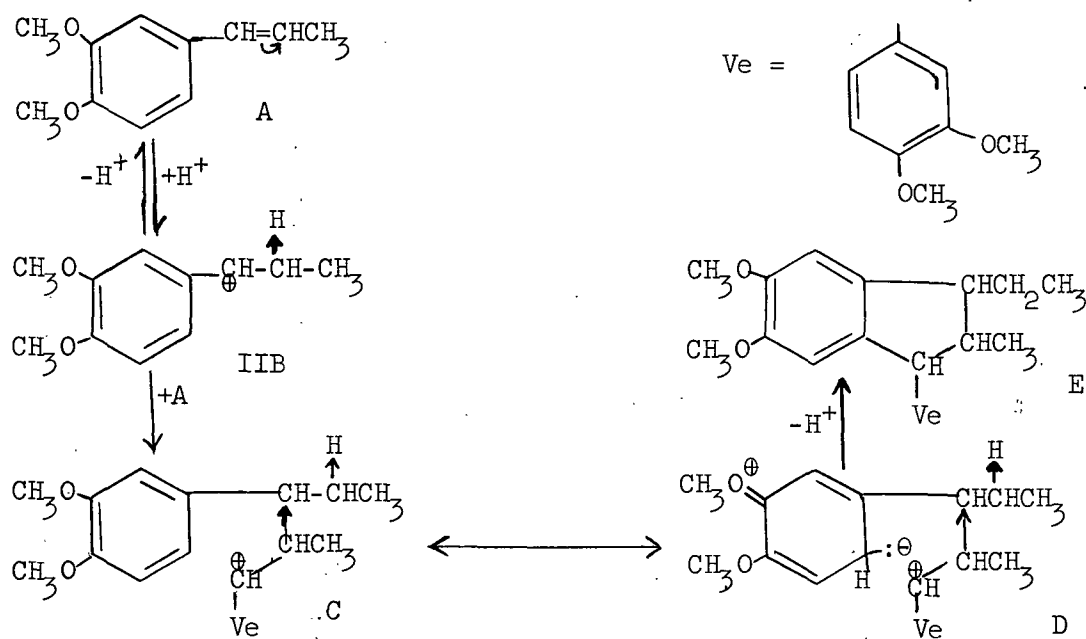


In the proposed reaction scheme the carbonium ion radical (B) formed in the electrode reaction undergoes a free radical dimerization with a second radical ion to give a divalent carbonium ion dimer (C) linked through the beta carbons of the side chain. Stabilization by ring closure with the ejection of a hydrogen ion follows essentially the same path described by Müller (96) for the acid-catalyzed dimerization of propenylphenol ethers. The monovalent carbonium ion (E) may stabilize by the addition of a nucleophilic reagent such as the perchlorate anion or by ejection of a second hydrogen ion. In the latter case the loosely held hydrogen on C₂ of the tetralin nucleus would probably be lost with the formation of a double bond between C₁ and C₂. The structure obtained would thus be the same as that of Compound XXVI except for the absence of hydroxyls and the presence of a single double bond between C₁ and C₂.

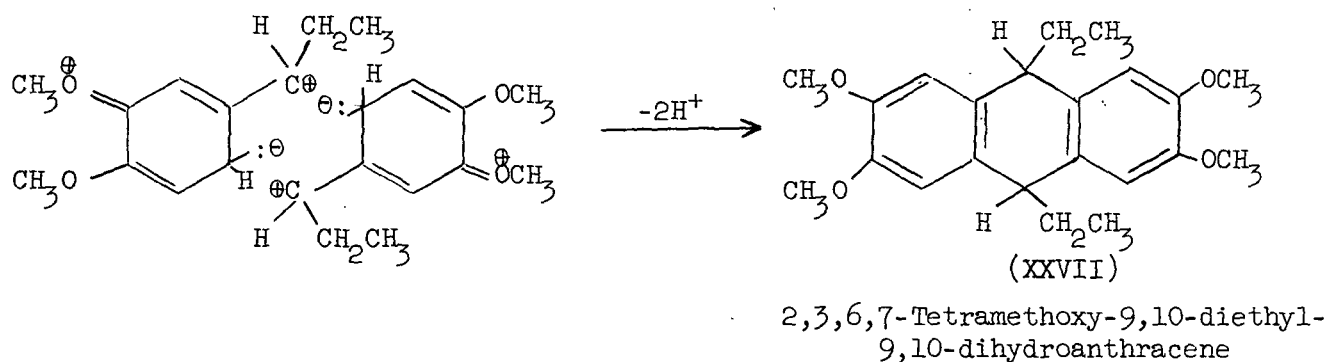
It should be emphasized that the above reaction scheme is only an attempt to suggest a possible logical mechanism consistent with the limited amount of

experimental data and the expected behavior of 3,4-DMPB based on its known reactions in other systems. Since the formation of beta-beta carbon linkages between C_6-C_3 units to yield dimers of the lignan family is of definite interest to the wood chemist, a more detailed study of this reaction would be desirable. However, it will be necessary to find a method for effectively removing the liberated hydrogen from the system without at the same time changing the nature of the primary electrode reaction.

The removal of the hydrogen ion is, of course, necessary to prevent the acid-catalyzed dimerization of 3,4-DMPB to yield dimethyldiisoeugenol. It has been shown that this product is formed in appreciable quantity in the controlled potential electrolysis of 3,4-DMPB in unbuffered acetonitrile by its isolation and identification. Its effect in causing an abnormally rapid decrease in current during the electrolysis has also been established by somewhat more detailed studies of the acid-catalyzed dimerization of 3,4-DMPB by perchloric acid in acetonitrile. The results of these studies are in agreement with the mechanism proposed by Müller (59) and others as shown in the following reactions:



Two other oxidation products were isolated in very small quantity, namely, 2,3,6,7-tetramethoxyanthraquinone (XXI) and a fluorescent, crystalline material (XXII) melting at 184-194°C. which bears a resemblance to 2,3,6,7-tetramethoxy-9-ethylanthrone (XXIII) and its carbenium salts (91). It has been shown that the acid-catalyzed dimerization of 3,4-DMPB yields small quantities of 2,3,6,7-tetramethoxy-9,10-diethyl-9,10-dihydroanthracene (XXVII) possibly by dimerization of two molecules of the protonated 3,4-DMPB (II).



Electrolytic oxidation of this compound in the presence of the small amounts of water present in even the "dry" acetonitrile may account for the finding of anthraquinone and possibly anthrone derivatives.

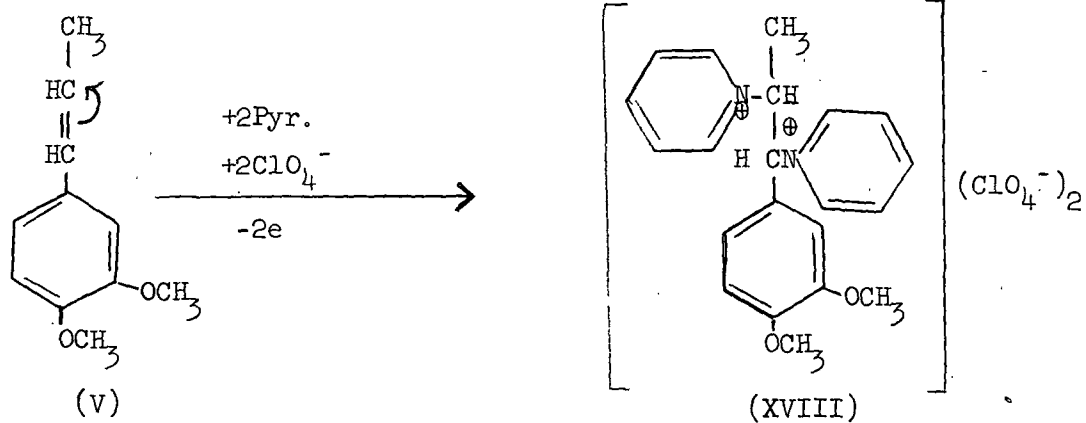
Little can be said on the basis of the experimental data obtained thus far concerning the origin and nature of the second and third voltammetric waves given by 3,4-DMPB in unbuffered acetonitrile. The $\frac{I_d}{I_p}$'s of the waves indicate one-electron processes. However, the reproducibility of the waves is poor, and, at times, the waves appear to merge into a single, drawn-out wave. It seems likely that the waves are not representative of the oxidation of a single species but rather of 3,4-DMPB itself and also various dimers and decomposition products of the primary electrode products. It has been shown, for example, that the acid-catalyzed dimer of 3,4-DMPB itself gives three well-defined waves with half-wave potentials only slightly greater than the waves shown by 3,4-DMPB. The relative contribution of these secondary products will of course depend on their rates of

formation as compared to the rate of diffusion of the primary oxidation product of 3,4-DMPB away from the surface of the electrode.

The effect of acetic acid, acetic anhydride, and water on the second and third waves also suggests a change in nature of the secondary reaction steps following the electrode reaction or in the electrode process itself. It might be expected that oxidation of 3,4-DMPB in the presence of these compounds would lead to the addition of the acetate or hydroxyl ion as obtained in chemical oxidations using oxidants such as peracetic acid or lead tetraacetate.

In the presence of pyridine, 3,4-DMPB gives a single wave corresponding to a two-electron, irreversible oxidation reaction. Controlled potential electrolysis of 3,4-DMPB in the presence of pyridine resulted in the almost quantitative formation of a dipyridinium diperchlorate of 3,4-DMPB. Although this compound itself is oxidizable below the decomposition potential of the solvent-electrolyte system, a second wave is not observable in the voltammogram of 3,4-DMPB in the presence of pyridine. This may be attributed to the formation of a film on the surface of the electrode in the presence of excess pyridine which acts as an effective barrier to the transfer of electrons.

The oxidation of 3,4-DMPB in the presence of pyridine may be pictured as a reaction involving a concerted push-pull attack by the unshared electron pair of the pyridine molecule and the positively charged electrode surface. The delocalization of the positive charge at the alpha carbon atom due to the co-ordination with pyridine results in a decrease in the potential required to remove the second electron. The divalent ion formed is stabilized by the addition of the second pyridine molecule and two perchlorate anions. The over-all reaction may be summarized as follows:



It should be noted that while the pyridine molecules have been accorded the most logical positions for addition, namely at the alpha and beta carbons of the side chain, no proof is offered that this is, in fact, the actual position of addition.

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