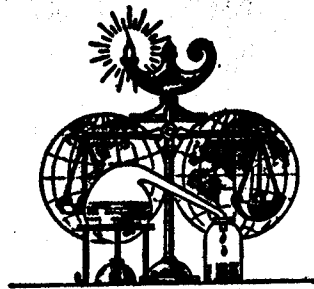


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VOL. 25 REPRINT

1971



PURE and APPLIED CHEMISTRY

*The Official Journal of the
International Union of Pure and Applied Chemistry*

CHIMIE PURE et APPLIQUÉE

*Journal officiel de
l'Union internationale de Chimie pure et appliquée*

BUTTERWORTHS
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CHEMISTRY

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Ordering information
Purchased from the publisher
London, W.C.2

Subscription information
Overseas Offices Australia:
343 Little Collins Street, Melbourne
4 Curity Avenue, Toronto 374.
35 High Street, Auckland 1.
Published quarterly, four issues per volume, four
times a year. U.K. £12.00, U.S.A. \$36.00

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THE ELECTROCHEMISTRY OF ORGANIC COMPOUNDS IN APROTIC SOLVENTS— METHODS AND APPLICATIONS

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ABSTRACT

The importance of aprotic solvents in studies of the electrochemistry of organic compounds is discussed and a general mechanism for the oxidation and reduction of aromatic hydrocarbons and related substances is presented. The effect of molecular structure on the electrochemical behaviour of organic compounds is illustrated by discussing the relationship between conformations of aryl-substituted anthracenes and dimethylaminophenyl-substituted ethylenes and their electrochemical properties. Techniques and methodology for electrochemical studies in nonaqueous solvents, including solution preparation and cell and electrode design, are briefly reviewed.

INTRODUCTION

The use of anhydrous aprotic solvents, such as N,N-dimethylformamide (DMF), acetonitrile (MeCN), and dichloromethane (CH₂Cl₂) as solvents for electrochemical studies started about fifteen years ago. Although many studies of the electrochemistry of organic compounds had been reported up to that time, most were carried out in partially or totally aqueous media. Indeed the second edition of Kolthoff and Lingane's *Polarography*¹ has a chapter of only six pages on nonaqueous solvents and in a discussion of the polarography of organic compounds characterizes most reductions of these as irreversible. Although the earliest applications of aprotic solvents were aimed at increasing the solubility of the organic compounds, pioneering studies by Wawzonek, Hoytink, Peover, and their co-workers² demonstrated that the use of these solvents simplified the electrochemical behaviour of organic substances by removing or decreasing the extent of chemical reactions coupled to the electron transfer step. Under these conditions many organic electrode reactions are electrochemically reversible so that correlations of electrode potentials with spectroscopic and molecular orbital (MO) data became possible and a molecular basis of electrochemical reactions of aromatic hydrocarbons was established. Moreover, aprotic solvents provided reduction and oxidation limits beyond those obtainable in aqueous solutions, so that a wider range of potentials became available for electrochemical studies.

In the last decade a number of new electrochemical techniques have been devised and theoretical treatments for the diagnosis of complex reaction schemes using the data obtained by these techniques have been reported. Modern instrumentation for applying these techniques, based on operational amplifier instrumentation, and more recently on direct data acquisition with digital computers, has also become available. The application of three electrode cells, particularly when used in conjunction with instrumentation employing positive feedback circuits, have made precise measurements possible, even in highly resistive organic solvents. Finally techniques of solvent purification and solution preparation using vacuum line or dry box techniques have decreased even further the effects of side reactions caused by oxygen, water, or other impurities.

This paper is concerned with a brief review of the techniques and methods of studying electrode reactions of organic compounds in aprotic media. A general mechanism for the reduction and oxidation of aromatic compounds is presented and several examples of studies from our laboratories illustrating the effect of structure and solvent on electrochemical behaviour will be described.

TECHNIQUES AND METHODS

The successful use of aprotic solvents for electrochemical studies requires high purity of both solvent and supporting electrolyte and a system for preparing and maintaining test solutions in a water and oxygen-free environment. We have found that vacuum line techniques have been especially valuable for this purpose. A schematic diagram of a typical vacuum line is shown in *Figure 1*. This line uses a mechanical vacuum pump and a three stage oil diffusion pump and is generally able to maintain a pressure of about 10^{-5} torr. The solvent is purified on a separate line, using procedures described in Mann³ with the last step usually being a vacuum distillation. The purified solvent is stored under vacuum and later transferred under vacuum to the electrochemical cell by distillation or poured into the cell under an inert atmosphere. A typical electrolysis cell of the type designed by Dr Ves Childs and C. P. Keszthelyi in our laboratories is shown in *Figure 2*. The cell is attached to the vacuum line by a vacuum stopcock-ball joint arrangement. The side-arm allows for solvent pretreatment without affecting the electrodes. The cell is first oriented with its side-arm facing downwards and the sample, solvent and supporting electrolyte are introduced. This is then degassed by the freeze-pump-thaw method by immersing the side-arm in liquid nitrogen and pumping on the solution, closing the stopcock to the cell and allowing the solution to thaw and bubble out any dissolved gas. This cycle is repeated several times. The stopcock can then be closed, the cell removed from the vacuum-line and the main cell body filled by tilting and allowing solution to flow into the auxiliary and test chambers. When a reference electrode, such as an aqueous saturated calomel electrode (S.C.E.), or a working electrode which cannot be subjected to high vacuum are employed, purified helium is led into the cell, and the electrode is then introduced while maintaining a positive helium pressure within the cell. J. T. Maloy has devised a rotating

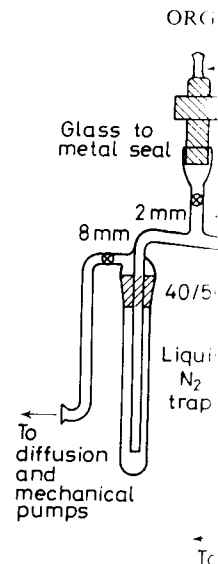


Figure 1. Vacuum line with ball joint at the right.

ring-disc electrode and which contains an atmosphere, thus eliminating oxygen.

A number of references have been published on the use of aprotic solvents³. The aqueous solution has led to few problems introduced into the test solution-supporting electrolyte determinations of potential systems whose potential electrode, such as an aqueous solution, can be employed.

A number of electrochemical observation times are rates of perturbing conditions of these experiments electro-organic chemistry of products. The time graphy, cyclic voltammetry about 10^{-3} to 10^2 seconds rotating disc electrode

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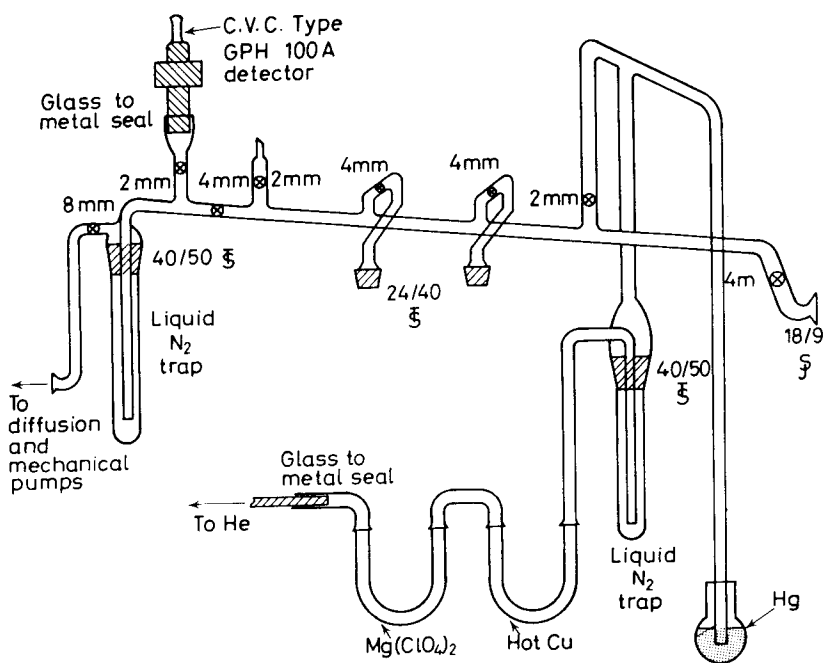


Figure 1. Vacuum line for electrochemical studies. The electrochemical cell attaches to the ball joint at the right. Purified helium can be introduced by the line at the bottom

ring-disc electrode assembly which can be used in such a closed system and which contains the entire motor and tachometer enclosed in the inert atmosphere, thus eliminating the need for a rotating seal (Figure 3).

A number of reference electrodes have been proposed for work in aprotic solvents³. The aqueous S.C.E. has probably been used most frequently, and has led to few problems when prepared with an agar salt bridge and introduced into the test solution via a second salt bridge of the appropriate solvent-supporting electrolyte system. For measurements where exact determinations of potential are not required, such as kinetic studies in systems whose potentials have already been characterized, a quasi-reference electrode, such as an unpoised silver wire immersed directly in the test solution, can be employed.

A number of electrochemical techniques are available which have different observation times and which allow measurements of different types and rates of perturbing coupled chemical reactions. The slowest measurements (10^2 to 10^4 seconds) are made with controlled potential coulometry. The conditions of these experiments most closely approximate those of preparative electro-organic chemistry and allow the preparation of rather large amounts of products. The time scale of voltammetric techniques, such as dc polarography, cyclic voltammetry, chronopotentiometry and chronocoulometry, is about 10^{-3} to 10^2 seconds. The fastest measurements are made with the rotating disc electrode (R.D.E.) and by ac polarography. The application of

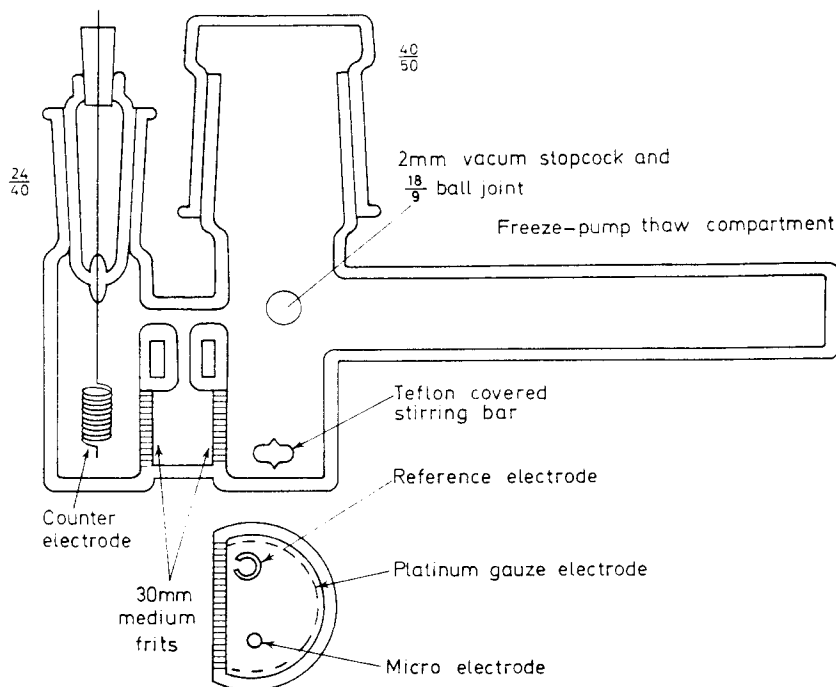


Figure 2. Electrochemical cell for studies in aprotic solvents. The cell attaches to the vacuum line by a ball joint and stopcock. The cell illustrated is for both voltammetric and large scale coulometric studies. A cell with only a single diaphragm can also be employed for voltammetry

digital simulation techniques⁴ allow many complex reaction schemes to be treated. However, distinguishing between different possible schemes requires highly precise measurements over as wide a range of observation times and solution concentrations as possible. The application of *in situ* spectroscopic techniques, such as electron spin resonance (E.S.R.) spectroscopy, often provides important information about products and intermediates.

GENERAL MECHANISMS FOR REDUCTIONS AND OXIDATIONS

The general mechanism for the reduction of an organic compound, such as an aromatic hydrocarbon, R, usually starts by the addition of one electron to the lowest vacant molecular orbital (LVMO) to form the anion radical

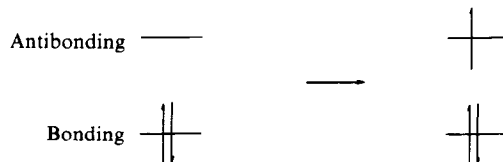


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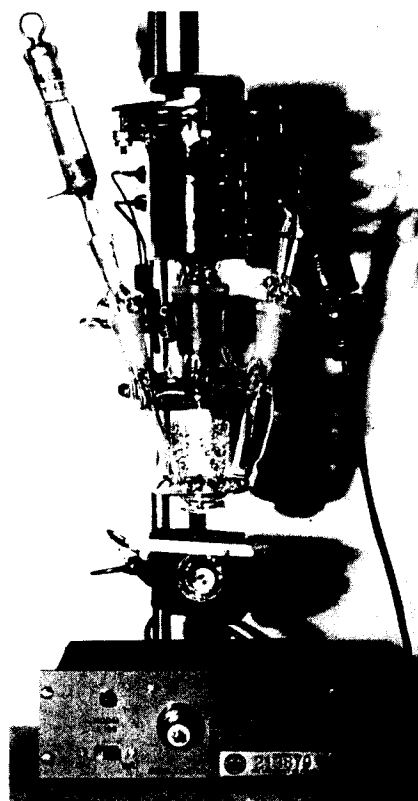
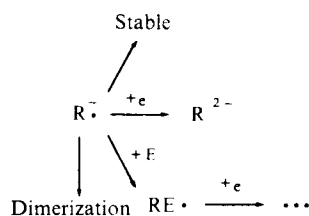


Figure 3. Rotating ring-disk electrode assembly for use in aprotic solvents and closed systems. The entire motor-tachometer assembly is enclosed in the glass envelope. The motor power supply and controller is at the bottom of the picture

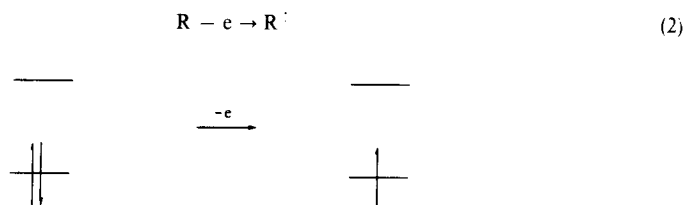
This first step is usually rapid and reversible; the potential at which the reduction occurs often correlates very well with molecular orbital calculations of the energy of the LVMO². The species R^{-•} is frequently stable, but it may also undergo several following reactions, as shown below:



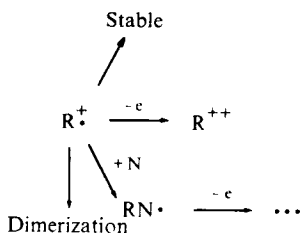
In this scheme E represents an electrophilic species, such as H⁺ or CO₂ which can attack the anion radical and produce a species which is frequently

easier to reduce than the parent, R. Under these conditions the reactions are classified as ECE reactions (electron transfer, followed by a chemical reaction, followed by a second electron transfer), and may resemble an overall two- or multi-electron transfer reaction. Dimerization is prevalent in molecules such as the substituted ethylenes and may be the prevalent path of the hydrodimerization reaction investigated by Baizer and co-workers^{5,6}.

A similar sequence can be written for oxidation reactions. In this case the cation radical is first formed by removal of an electron from the highest occupied molecular orbital (HOMO).



This is also usually a rapid reaction so that the potential at which oxidation occurs correlates well with the calculated energy of the HOMO, although the potentials measured by voltammetry are often perturbed in this case by fast following reactions of the cation radical. The reactions of the cation radical are analogous to those of $R^{\cdot-}$.



Here N represents a nucleophilic agent, such as pyridine, hydroxyl ion, cyanide ion, or acetate ion which can attack the cation radical.

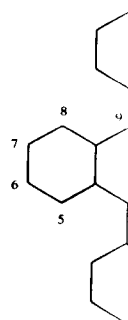
The particular aprotic solvent and supporting electrolyte used affects the nature of the overall mechanism in several ways. The overall oxidation and reduction limits are determined by the solvent system. The solvent or impurities often play the role of N or E in the above sequences. Water, which is difficult to remove in levels below 1 mM from solvents such as MeCN, probably is a common agent for the attack of cation radicals⁷. Protonation of the anion radical or dianion also often involves the solvent system or supporting electrolyte. Dimerization of the ion radicals is favoured by increases in the dielectric constant of the solvent. On the other hand formation of ion pairs between hydrocarbon ions and counterions from the supporting electrolyte is favoured by small dielectric constants. The extent of solvation of the ions affects the potentials of the corresponding electrode

reactions and indications. Solvation of the radical ions to the parent hydro

EFFECT OF STERIC

Conformations of

Since the first effect of the LVMO or the LUMO molecular orbitals is increased conjugation and raises the HOMO of the conjugated system and oxidized with ease are easier to reduce at electrolysis, is biphenyl the relationship of potentials to determine the conformation of the compounds. Consider



9,10-diphenyl

The steric interaction between the phenyl rings is quite large, so the anthracene nuclei by the angle for 9,10-DPA is relative hyperfine coupling on the molecule with values of θ . These M LVMO and HOMO 9,10-DPA were compared with ESR results (employing a scale of potentials), and

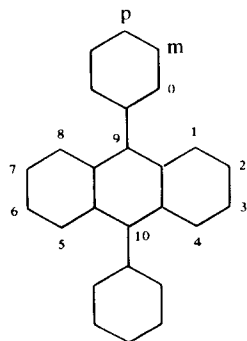
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reactions and is especially important in the formation of dianions and dications. Solvation is also a factor in the rates of electron transfer reactions of the radical ions and probably of the rate of heterogeneous electron transfer to the parent hydrocarbon.

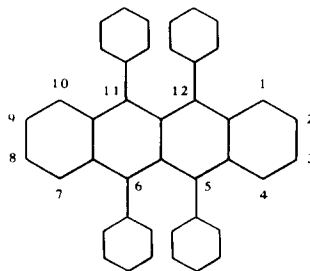
EFFECT OF STRUCTURE ON ELECTROCHEMICAL BEHAVIOUR

Conformations of molecules by electrochemistry

Since the first electron transfer step can be correlated with the position of the LVMO or the HOMO, structural changes which affect the energies of the molecular orbitals also affect the reduction and oxidation potentials. Hence increased conjugation in an aromatic hydrocarbon lowers the LVMO and raises the HOMO, so that both oxidation and reduction of a highly conjugated system occurs more readily. For example benzene is reduced and oxidized with great difficulty⁸. More conjugated hydrocarbon systems are easier to reduce or oxidize; the sequence, in order of increasing ease of electrolysis, is biphenyls, naphthalenes, anthracenes, naphthacenes, etc. This relationship of potential and conjugation has been exploited in our laboratory to determine the conformations of phenyl substituted anthracenes and related compounds. Consider, for example, 9,10-diphenylanthracene (9,10-DPA).



9,10-diphenylanthracene



5,6,11,12-tetraphenyl-naphthalene

The steric interaction between the hydrogen atoms on positions 1, 4, 5, and 8 and the hydrogen atoms on the ortho-positions of the substituted phenyl rings is quite large, so that the phenyl rings are rotated out of the plane of the anthracene nuclei by some angle θ . Previous ESR studies⁹ showed that the angle for 9,10-DPA was about 68° . This value was obtained by fitting the relative hyperfine coupling constants of hydrogen atoms on various locations on the molecule with values calculated by Hückel MO theory for different values of θ . These MO calculations also give the relative energies of the LVMO and HOMO. When the reduction and oxidation potentials of 9,10-DPA were compared to those predicted from MO theory based on the ESR results (employing anthracene and naphthalene to fix the relative scale of potentials), an excellent correlation was obtained¹⁰. This application

of electrochemical measurements for the determination of conformations was extended to a number of other related compounds; typical results are given in Table 1^{10,11}. The trends observed in the θ -value of these compounds

Table 1. Reduction potentials of phenyl-substituted anthracenes and related compounds in DMF and calculated angles, θ , between substituent group and anthracene nucleus^a

Molecule	$-E_2$ (V. vs. S.C.E.)	θ (def.)	Reference
2-phenylanthracene	1.872	25	10
1-phenyl-	1.878	53	10
9-phenyl-	1.863	68	10
9,10-diphenyl-	1.835	68	10
1,10-diphenyl-	1.787	60-70 ^b	10
1,9-diphenyl	1.846	60-70 ^c	10
9,10-dinaphthyl-	1.82	70-75	11
5,6,11,12-tetraphenylnaphthacene	1.410	60	10

^a Data for reduction of substances in DMF - 0.1 M tetra-*n*-butylammonium iodide at mercury electrode.

^b position 10.

^c position 9.

is in the expected direction; 2-phenylanthracene, which has a rather weak steric interaction (like that of biphenyl) shows the smallest θ , while the molecules with large steric interactions, such as 9,10-di(α -naphthyl)anthracene, show large values of θ . In many of the above cases the electrochemically determined θ -values were checked by ESR spectroscopy, and good agreement was found.

One vs. two electron oxidations

The question of whether the primary electron transfer involved the removal or addition of one or two electrons was the subject of some controversy in several investigations. It now appears that many apparent simultaneous two-electron transfers actually are ECE reactions. Within the framework of simple Hückel MO theory, the transfer of an electron to the anion radical or the removal of an electron from the cation radical should occur at the same potentials as those at which the ion radicals themselves are formed, since formation of the dianion or dication involves electron addition to, or removal from, the same MO. However, simple MO theory neglects the electron repulsion. Calculations which include these additional repulsion terms indicate the additional energy required to add the second electron is in the order of 5.0 eV. The difference between the first and second electron transfers is not that large, however, because the dianion and dication will be more highly solvated¹² than the radical ions, and they will also tend to form stronger ion pairs or aggregates. These effects tend to greatly decrease the overall energy required to add the second electron, and the usual separation between the first and second electron transfer steps is about 0.5 V. However, geometric changes in the molecule after the addition or removal of one and two electrons can change the orbital energies enough to make the second electron transfer occur more readily than the first. Cases such as this were

recently investigated by aminophenyl substituted the electrochemical behavior of butylammonium perchlorate (*p*-N,N-dimethylamino)

Table 2. Electrochemical data

Molecule	(substituents)	Abi
1,1	2,2	s-T
1,2	1,2	s-T
1,1,2	2	(cis O) HN
1,1,2,2	—	ON
tetra(<i>p</i> -methoxyphenyl)-ethylene	—	TA

^a The solution was CH₂Cl₂-0.2 M tetra-*n*-butylammonium perchlorate.

^b i_p = anodic peak current (μ A), v = scan rate (V/sec).

^c i_L = limiting current (μ A), C = concentration (M).

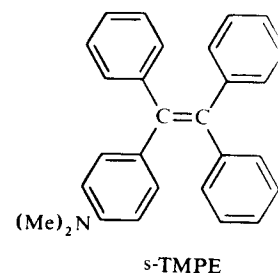
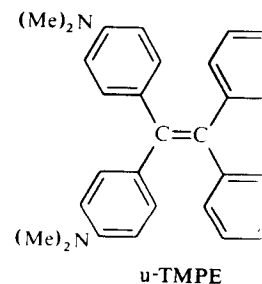
^d Slope of plot of E vs. $\log(i_L - i)$.

^e Potential controlled at least 0.2 V past i_p .

^f Slope non-linear (see Figure 6).

^g Oxidation at 0.95 V vs. S.C.E. ESR structure.

^h Oxidation at 1.2 V vs. S.C.E.



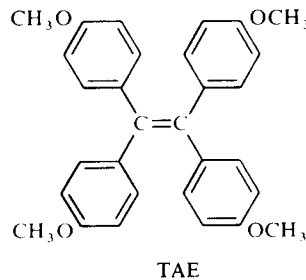
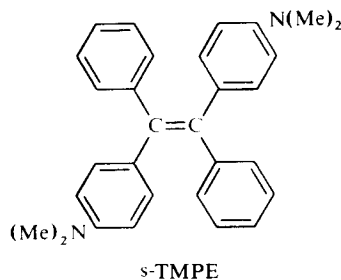
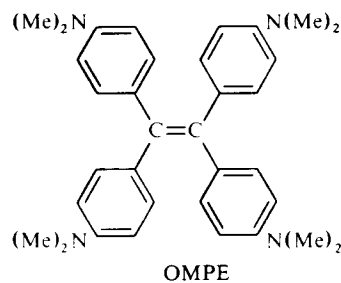
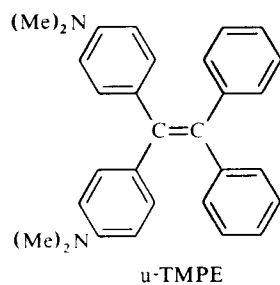
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recently investigated by John Phelps in a study of the oxidation of dimethylaminophenyl substituted ethylenes and related compounds¹³. A summary of the electrochemical behaviour of these substances in CH₂Cl₂-0.2 M tetra-*n*-butylammonium perchlorate is given in Table 2. The compound 2,2-bis-(*p*-N,N-dimethylaminophenyl)-1,1-diphenylethylene (u-TMPE) undergoes

Table 2. Electrochemical data for oxidation of some dimethylaminophenyl-substituted ethylenes^{13, a}

Molecule	(substituents)	Abbreviation	Cyclic Voltammetry		E ₁ (V. vs. S.C.E.) R.D.E.	Log Plot ^d	
			i _p /v ^{1/2} C ^b	i _L /C ^c		Slope (mV) Voltammetry	Coulometry n _{app} ^e
1,1	2,2	s-TMPE	12.8	8.6	0.578	58	0.98
			14	16.2			
1,2	1,2	s-TMPE (cis or trans)		20.4	0.44	34	2.01
1,1,2	2	HMPE	31	19.2	0.321	36	2.02
1,1,2,2	—	OMPE	32	18.0	0.160	36	2.01
tetra(<i>p</i> -methoxyphenyl)-ethylene		TAE	17	15	0.99	f	0.86 ^g 2.1 ^h

- ^a The solution was CH₂Cl₂-0.2 M tetra-*n*-butylammonium perchlorate. The electrode was platinum.
^b i_p = anodic peak current (μA), v = scan rate (V/sec), C = concentration (mM), electrode area = 0.013 cm².
^c i_L = limiting current (μA), C = concentration (mM).
^d Slope of plot of E vs. log (i_L - i).
^e Potential controlled at least 0.2 V past E₁ (except for TAE). n_{app} = number of faradays per mole.
^f Slope non-linear (see Figure 6).
^g Oxidation at 0.95 V vs. S.C.E. E.S.R. examination of solution shows intense singlet with some superimposed hyperfine structure.
^h Oxidation at 1.2 V vs. S.C.E.



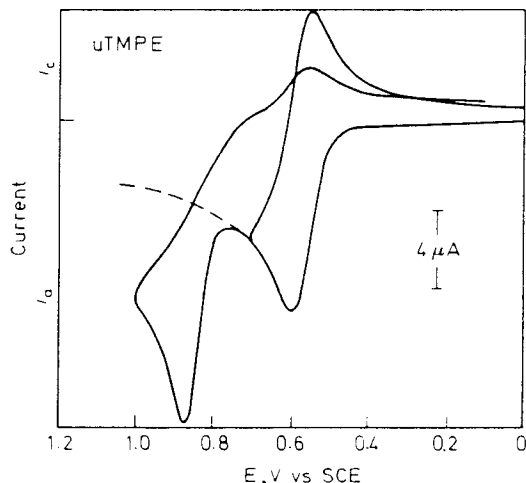


Figure 4. Cyclic voltammetric oxidation of 2,2-bis(*p*-*N,N*-dimethylaminophenyl)-1,1-diphenylethylene (u-TMPE) at platinum electrode in methylene chloride-0.2 M tetra-*n*-butylammonium perchlorate

an initial one electron oxidation step at 0.57 V. vs. S.C.E., followed by a second one electron oxidation at 0.85 V. (Figure 4). Similar behaviour is found with *N,N,N',N'*-tetramethyl-*p*-phenylenediamine. The results of a number of different electrochemical techniques, including cyclic voltammetry, chronoamperometry, rotating disc electrode voltammetry and coulometry all give unequivocal evidence for this scheme¹³. The related compounds, tetrakis(*p*-*N,N*-dimethylaminophenyl)-ethylene (OMPE), 1,1,2-

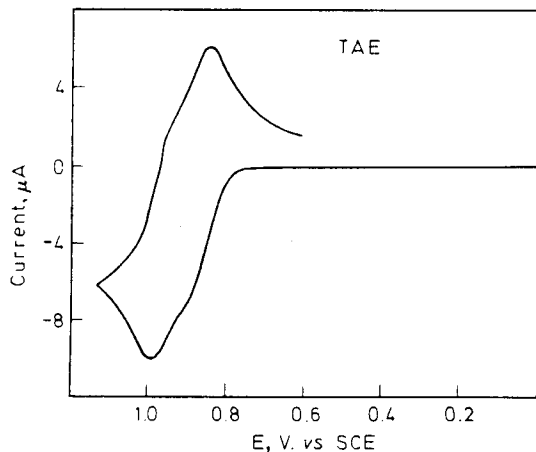


Figure 5. Cyclic voltammetric oxidation of tetrakis(*p*-methoxyphenyl)ethylene at platinum electrode in methylene chloride-0.2 M tetra-*n*-butylammonium perchlorate

tris(*p*-*N,N*-dimethylamino)-*trans*-1,2-bis(*p*-*N,N*-dimethylaminophenyl)-ethylene all show behaviour characteristic of a two electron process. For example, the limiting current is about twice that of the first electron transfer. In cyclic voltammetry for OMPE, the second voltammetric wave shows a small peak transfer, and coulometry shows a two electron process (Table 2). Interesting results for tetrakis(*p*-methoxyphenyl)-ethylene are shown in Figure 5. The curves (Figure 5) show some behaviour intermediate between that expected from theory for a two electron process (Figure 6) obtained

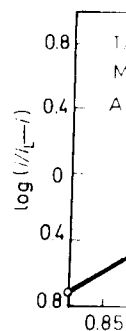


Figure 6. Logarithmic analysis of cyclic voltammograms for (*p*-methoxyphenyl)ethylene at platinum electrode

closely spaced waves and a rate constant K for the reaction

The values of K found in cyclic voltammetry are smaller for MeCN than for MeCN. The fact that the first electron transfer is a single direct two electron process and relief of steric strain in the oxidized state. Compounds related to tetrakis(*p*-methoxyphenyl)ethylene are shown in Figure 7; this steric strain because of interactions between the rings (Figure 7); this steric strain is relieved by twisting of the C-phenyl bond and by twisting of the C-phenyl bond. Goldberg have shown that the steric strain is relieved so that the molecule would

ORGANIC COMPOUNDS IN APROTIC SOLVENTS

tris(*p*-*N,N*-dimethylaminophenyl)-2-phenylethylene (HMPE), and *cis*- and *trans*-1,2-bis(*p*-*N,N*-dimethylaminophenyl)-1,2-diphenylethylene (*s*-TMPE) all show behaviour characteristic of a single two-electron oxidation step. For example, the limiting current at a rotating disc electrode for OMPE is about twice that of the first wave of *u*-TMPE, the anodic peak current in cyclic voltammetry for OMPE is about (2)³ that of *u*-TMPE, analysis of the voltammetric waves shows behaviour attributable to a reversible two electron transfer, and coulometry shows 2.0 faradays consumed per mole of OMPE (Table 2). Interesting intermediate behaviour is shown by tetrakis(*p*-methoxyphenyl)-ethylene (TAE). The results here are characteristic of two closely spaced single electron transfers. The cyclic voltammetric waves (Figure 5) show some suggestion of two waves, and the value of $i_p/v^{1/2}C$ is intermediate between that of a single step one and two electron transfer, as expected from theory¹⁴. Logarithmic analysis of the current-potential curve (Figure 6) obtained with a R.D.E. shows the curvature expected of two

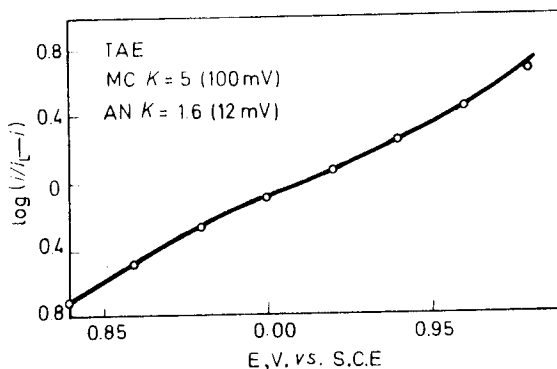
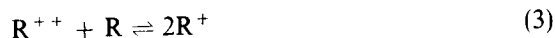
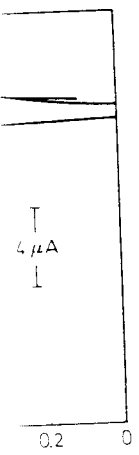


Figure 6. Logarithmic analysis of rotating disc voltammetric wave for oxidation of tetrakis-(*p*-methoxyphenyl)ethylene at platinum electrode in methylene chloride-0.2 M tetra-*n*-butylammonium perchlorate

closely spaced waves and allows determination of the equilibrium constant, K , for the reaction

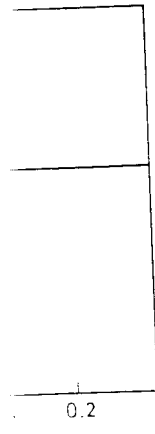


The values of K found in CH_2Cl_2 and MeCN are 55 and 1.6 respectively. The smaller value for K in MeCN is probably caused by greater solvation of the dication by MeCN. The fact that OMPE and related compounds undergo a single direct two electron step can be attributed to changes in geometry and relief of steric strain in the molecules upon oxidation to the dication. Compounds related to the tetraphenylethylenes show considerable steric strain because of interactions of hydrogen atoms on the substituent phenyl rings (Figure 7); this steric strain is relieved by rotation around the C-phenyl bond and by twisting of the C-C ethylene bond. Calculations by Dr Ira Goldberg have shown that upon oxidation of these molecules the bond order of the C-phenyl bond increases and that of the C-C ethylene bond decreases, so that the molecule would tend to twist as it oxidizes. Thus, if the parent



N,N-dimethylaminophenyl)-1,1-diphenylethylene chloride-0.2 M tetra-*n*-butyl-

vs. S.C.E., followed by a second wave (Figure 4). Similar behaviour is observed for *N,N*-dimethylamine. The results of a cyclic voltammetry including cyclic voltammetry and coulometry and this scheme¹³. The related compound is tetrakis(*p*-methoxyphenyl)-ethylene (OMPE), 1,1,2,2-



(*p*-methoxyphenyl)ethylene at platinum electrode in methylene chloride-0.2 M tetra-*n*-butylammonium perchlorate

ALLEN J. BARD

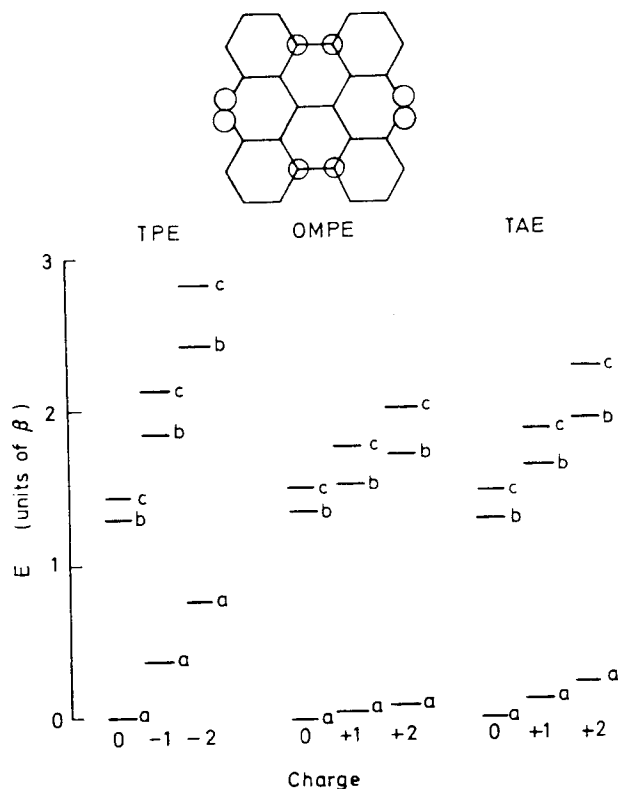


Figure 7. Top: Steric interactions in phenyl substituted ethylene molecules. Bottom: Calculated resonance energies for parent, radical ion, and dianion of tetraphenylethylene (TPE), tetrakis-(*p*-dimethylaminophenyl)ethylene (OMPE) and tetrakis-(*p*-dimethoxyphenyl)ethylene (TAE) with following conformations (a) planar; (b) angle about C-Phenyl = 56°, angle about ethylene C—C = 18°; (c) angle about C-Phenyl = 67°, angle about ethylene C—C = 0°

and radical cations are constrained to seek planarity, but the dications can twist and relieve steric strain, the HOMO may move upward in the oxidation process and removal of the second electron may be made easier. Some representative calculations illustrating these effects are shown in Figure 7. These calculations must be considered only in a qualitative sense since the actual conformations of the molecules are not known and relief of steric strain by bond bending and stretching is also possible. A very similar explanation has been invoked by Garst and co-workers¹⁵ to explain the disproportionation of the tetraphenylethylene anion radical. Additional evidence for the weakening of the C—C ethylene bond in the dication is obtained from the following experiment. The *s*-TMPE molecule can exist in two forms, *cis*- and *trans*-, which show essentially identical electrochemical behaviour, but which can be separated and yield distinct nuclear magnetic resonance spectra. Upon controlled potential oxidation of *trans*-*s*-TMPE to the dication, followed by reduction back to the parent compound, a

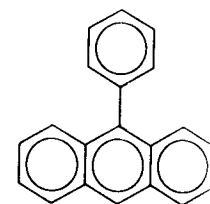
390

ORGANIC C

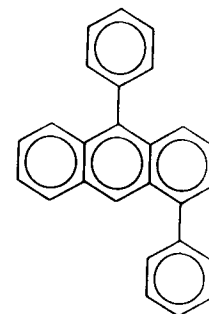
mixture of both the *cis*- and *trans*- isomers of the parent compound does not isomerize with the proposed mechanism.

Structure and reactivity of

The structure of the anion radical coupled to the first or second of a proton on a radical anion of high electron density¹⁶. The reduction potentials of anthracene are 0.045, 0.087 V vs SCE. The reduction of anthracene by phenyl-groups leads to a radical anion which is more stable. The overall path of the reduction of the species formed upon protonation of the species formed upon protonation. Note that 9,10-DPA and 9,10-DPA show a third wave, since protonation in



conjugation between the phenyl groups and the anthracene ring system. 1,10-DPA show a third wave reduced, since protonation in

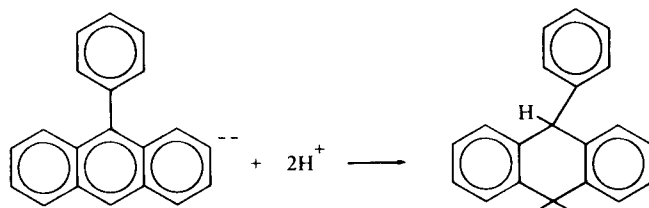


The resistance of cation radical depends upon the extent to which the phenyl groups are blocked¹⁸. Electrochemical reduction of cation radicals of substituted

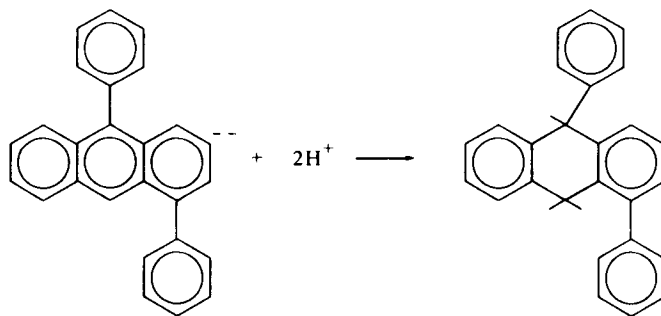
mixture of both the *cis*- and *trans*- forms was obtained. Although the parent compound does not isomerize, the dication isomerizes readily, in agreement with the proposed mechanism.

Structure and reactivity of radical ions

The structure of the aromatic species also affects the path of reactions coupled to the first or second electron transfer step. For example, the attack of a proton on a radical anion or dianion will generally occur at positions of high electron density¹⁶. The electron densities on positions 1, 2, and 9 of anthracene are 0.045, 0.087, and 0.184, respectively, hence protonation would occur in the 9 and 10 positions. For the anion radicals, blocking of these sites by phenyl-groups leads to greater stability of the ions, so that 9,10-DPA anion radical is more stable in DMF than that of anthracene. Moreover, the overall path of the reduction of these compounds depends upon the structure of the species formed upon protonation of the dianion. Cyclic voltammetric data for the reduction of several phenyl anthracenes is given in Table 3¹⁷. Note that 9,10-DPA and 9-phenylanthracene (PA) show only two reduction waves, since protonation in the 9 and 10 positions leaves a system with no



conjugation between the phenyl rings. On the other hand 1,9-DPA and 1,10-DPA show a third wave at potentials close to those where biphenyl is reduced, since protonation of the dianion leads to a biphenyl-like system.



The resistance of cation radicals from attack by nucleophilic species also depends upon the extent to which the positions of high charge density are blocked¹⁸. Electrochemical studies of the rate constants for the decay of cation radicals of substituted anthracenes in a CH₂Cl₂-0.2 M tetra-*n*-

TAE

— c
— c — b
— b
— c
— b

— a — a
— a — a
0 +1 +2

molecules. Bottom: Calculated for tetraphenylethylene (TPE), tetrakis(methoxyphenyl)ethylene (TAE) phenyl = 56°, angle about ethylene about ethylene C—C = 0°

ity, but the dications can be upward in the oxidation may be made easier. Some effects are shown in Figure 7. In qualitative sense since the known and relief of steric hindrance is possible. A very similar mechanism¹⁵ to explain the stability of the anion radical. Additional steric hindrance in the dication is observed. The TPE molecule can exist in two different electrochemical states. The oxidation of *trans*-s-TMPE is more difficult than the parent compound, a

Table 3. Cyclic voltammetric data for the reduction of several phenyl-substituted anthracenes^{17, a}

Molecule	Wave I		Wave II		Wave III	
	i_p/v^{\ddagger}	$-E_{pc}^b$	i_p/v^{\ddagger}	$-E_{pc}$	i_p/v^{\ddagger}	$-E_{pc}$
9-PA	1.90	1.96	1.76	2.56	—	—
1,9-DPA	0.28	1.93	0.30	2.40	0.27	2.79
1,10-DPA	1.04	1.79	1.20	2.37	0.56	2.65

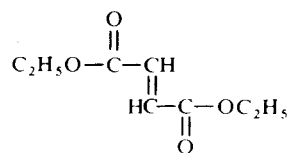
^a Reduction in DMF - 0.1 M tetra-*n*-butylammonium iodide at hanging mercury drop electrode at scan rate, v , of 0.312 V sec. i_p = peak current (μ A). Results are for different concentrations and electrode areas.

^b E_{pc} = cathodic peak potential, in V. vs. S.C.E.

butylammonium perchlorate medium shows that 9,10-DPA and 9,10-dimethylantracene form stable cation radicals. The 9,10-di(α -naphthyl)-anthracene cation radical is moderately stable¹¹, while the cation radical of anthracene is very unstable and undergoes an ECE-type reaction. Double potential step chronoamperometric measurements were used to measure the rate constants for the decay of related radical cations with intermediate stability¹³. For example, 9-PA cation radical decays with a rate constant of about 2.7 sec^{-1} . The 1,4,9-triphenylantracene cation radical in which there is no substitution on the reactive 10 position but where this position is blocked by the phenyl on the 4 position, is more stable and reacts with a rate constant of 0.19 sec^{-1} .

Hydrodimerization reactions

Finally, we might consider some recent work in our laboratory on the hydrodimerization reaction in DMF⁶. The electroreduction of diethylfumarate (DEF) at a platinum electrode was investigated using cyclic



DEF

voltammetry, double potential step chronoamperometry, chronocoulometry, and controlled potential coulometry. The mechanism of the reaction was established by comparing experimental chronoamperometric curves with theoretical curves obtained by digital simulation for different possible mechanisms leading to hydrodimers. The mechanism which fits the data best, for a large number of experiments with different DEF and water concentrations, temperature, etc., is one in which the radical anions dimerize and then protonate. The second order rate constant for this dimerization reaction increases from $37 \text{ l-mole}^{-1}\text{-sec}^{-1}$ for nominally anhydrous DMF to $145 \text{ l-mole}^{-1}\text{-sec}^{-1}$ for DMF containing 500 mM water, apparently without a change in mechanism.

The support of this (GP-6688X) and the Rob

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ACKNOWLEDGEMENT

The support of this research by the National Science Foundation (GP-6688X) and the Robert A. Welch Foundation is gratefully acknowledged.

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substituted anthracenes^{17, a}

Wave III	
$i_p/v^{\frac{1}{2}}$	$-E_{pc}$
0.27	2.79
0.56	2.65

top electrode at scan rate, v. of 0.312

9,10-DPA and 9,10-dihydro-9,10-di(α -naphthyl)-anthracene are used to measure the rate constant of the cation radical in which there are no substituents at the 1 and 8 positions where this position is substituted and reacts with a rate

constant of 1.0 x 10⁴ s⁻¹ in our laboratory on the electroreduction of diethyl-amine investigated using cyclic

voltammetry, chronocoulometry, and the mechanism of the reaction was investigated by comparing amperometric curves with theoretical curves for different possible mechanisms which fits the data at different DEF and water content. The radical anions dimerize rapidly and the rate constant for this dimerization is 1.0 x 10⁴ s⁻¹ in nominally anhydrous DMF with 100 mM water, apparently