Voltammetry: Doing Chemistry with Electrodes

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Recent years have seen an upsurge of interest in the application of electroanalytical techniques to studies of oxidation and reduction reactions of many types of compounds. The most widely used technique is cyclic voltammetry (CV), which is unmatched in its ability to provide qualitative information about the steps in a redox reaction with only a modest expenditure of time and effort in the acquisition and interpretation of data. When quantitative rate measurements are desired or information not readily obtainable by CV is required, supplementary techniques such as chronoamperometry, rotating disk, and ring–disk voltammetry and ac polarography are often employed.[1]

In this Account we will review some recent examples of the application of electroanalytical techniques with emphasis upon the types of chemical information which have been acquired, promising new solvent and electrolyte systems and the growing awareness that un-ambiguous solutions to subtle mechanistic questions require the complementary application of electrochemical and nonelectrochemical techniques.

Before embarking on this tour, it is worthwhile to consider the nature of the electrode reactions we will be considering. Electrode reactions may be classified according to the degree of interaction of reactants, intermediates, and products with the electrode surface.[2] When the interaction is very strong, the species are bonded to the surface or, as in the case of electrodeposition of metals, they may be a part of the surface such as a lattice defect. Weaker interactions such as chemisorption or physical adsorption are important in many electrode reactions, and the thermodynamics and kinetics of the adsorption processes must be considered when one attempts to characterize the reactions. In the limit of very weak interaction, the reactants, intermediates, and products are freely diffusing solution species whose properties are unaffected by the electrode. Reactants diffuse to a reaction site near the electrode where electron transfer occurs, producing an intermediate or product which diffuses away. Except in cases where heterogeneous electron-transfer rates are being measured or when participants in the reaction are involved in very fast chemical reactions in solution, the electrical double layer is without appreciable effect and the thermodynamic and kinetic data obtained are those of the ordinary solution species.

It is this weak interaction case which will be of interest here because we want to use the electrochemical data to provide new chemical information about participants in the electrode reaction. It is fortunate that in nonaqueous solvents most organic species are not adsorbed at the electrode so their reactions fit the weak interaction case rather closely. This is in marked contrast to aqueous media where adsorption is common. Even in the case of organic solvents, adsorption and other surface effects can occur, and it is essential to detect these before concluding that the chemical properties which have been measured are those of the ordinary solute species, unaffected by the electrode–solution interface.

In the voltammetric experiment the electrode has two interrelated roles: (a) by controlling the current or the electrode potential, a variable and precisely known amount of oxidation or reduction is caused to occur in a small volume of solution within about 0.1 mm of the surface; (b) the current–potential data obtained during or after step a give information about the intermediates and products formed in the electrode reaction, i.e., the electrode monitors the solution reactions. Ideally information can be obtained concerning both the standard (formal) potentials and rates of reaction of intermediates and products.

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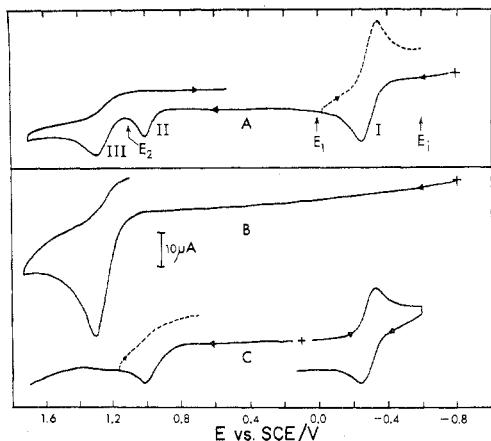
(1) Cyclic voltammetry is usually performed with a small (<1 cm²), stationary electrode immersed in an unstirred solution of ca. 1 mM reactant in a suitable solvent and electrolyte. The potential of the electrode is varied linearly with time in either the positive or negative direction until a switching potential is reached, at which time the direction of potential sweep is reversed and the potential is returned to the original value. The current is measured throughout the experiment and the resulting current–potential curve is called a voltammogram. The characteristic peaks in the voltammograms are caused by the formation of a depletion layer in solution near the electrode. The position of the peaks on the potential axis is related in a simple manner to the formal potential of the redox process, and the peak height and shape give information about the reactant concentration and number of electrons in the half-reaction. For an introduction to this and other electroanalytical techniques see R. N. Adams, "Electrochemistry at Solid Electrodes", Marcel Dekker, New York, N.Y., 1969, Chapter 3–6.

(2) H. Gerischer, *Discuss. Faraday Soc.*, 56, 7 (1973).

Figure 1. Cyclic voltammograms of 2,4,6-tri-*tert*-butylphenol in acetonitrile with 0.10 M tetraethylammonium perchlorate, glassy carbon electrode. (A) 1.00 mM 2,4,6-tri-*tert*-butylphenoxide (2). (B) 1.00 mM 2,4,6-tri-*tert*-butylphenol (1). (C) Approximately 1.0 mM 2,4,6-tri-*tert*-butylphenoxy radical (3), prepared by controlled potential electrolysis of solution used in A at 0.0 V.[3]

Studies of the First Step of Oxidation or Reduction

Voltammetric Oxidation of Phenols. The oxidation of phenols will be considered as a representative example of recent electroanalytical studies and a reference point for the discussion of other results and current research directions.

Cyclic voltammograms for oxidation of 2,4,6-tri-*tert*-butylphenol (1) are presented in Figure 1.[3] This

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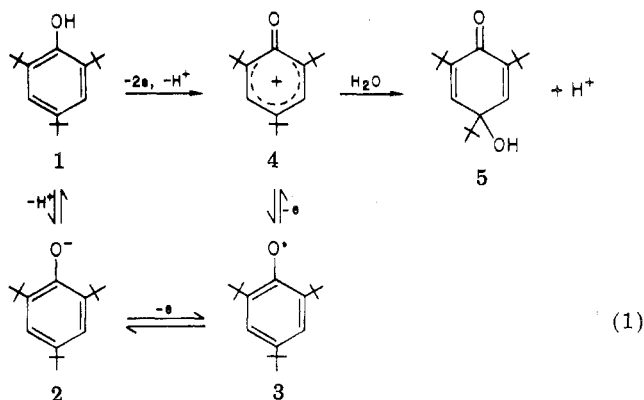
phenol was selected for initial study because its phenoxy radical, **3**, is very stable; this should lead to simplification of the electrochemical behavior. As shown in Figure 1A, when the phenol is converted to the phenoxide, **2**, by in situ treatment with tetraalkylammonium hydroxide, a reversible oxidation (peak I) to radical **3** is observed at −0.27 V vs. SCE. Reversal of the direction of potential sweep after peak I reveals the reduction peak for **3 → 2**.

Two additional oxidation peaks are observed. Peak II is due to the further oxidation of phenoxy radical **3**. This is confirmed by Figure 1C which shows cyclic voltammograms of a solution of radical **3** prepared by controlled-potential electrolysis at 0.0 V of the solution used in A. The solution of **3** shows both the reversible reduction peak **3 → 2** and irreversible oxidation peak II at +1.02 V, leaving little doubt that peak II is due to oxidation of the phenoxy radical. Peak III is due to

(3) J. A. Richards, P. E. Whitson, and D. H. Evans, *J. Electroanal. Chem.*, 63, 311 (1975).

the oxidation of the phenol **1** (formed by the processes occurring at less positive potentials), and this conclusion is supported by the voltammogram of **1** given in Figure 1B. The unusually small height of peak II, Figure 1A, will be discussed later.

The Phenoxide/Phenoxy Radical Couple. This process is a good example of a case of weak interaction of reactant and product with the electrode surface. The shape of the cyclic voltammogram and particularly the dependence of the peak potentials and peak currents on scan rate are indicative of the nature of the electrode reaction. In the present case,[3] data for scan rates over the range of 0.05–100 V/s were completely consistent with a one-electron, diffusion-controlled process with a very rapid heterogeneous electron-transfer rate constant and no significant adsorption of reactant or product.[4]

Stable Electrode Reaction Product. Phenoxy radical **3** is extremely stable, so the CV data give information about the reversible half-wave potential which is usually within a few mV of the formal potential of the couple.[6] In such cases CV is a simple and useful tool for examination of thermodynamic effects of changes in solution composition. For example, the addition of small amounts of hydroxylic cosolvents causes substantial shifts in potential due to preferential solvation of the anionic partner,[7,8] or substitution of alkali metal cations for the bulkier tetraalkylammonium ions normally used as electrolyte can result in ion pairing with the anionic partner which causes potential shifts from which ion-pair formation constants can be obtained. In addition to the oxidation of phenoxides,[9] data on ion pairing have been obtained for the reduction of quinones,[10] benzil,[11] and aromatic nitro compounds.[12]

Another useful application involves the use of CV to determine structural effects on formal redox potentials. The CV method is very rapid, and it is particularly powerful when the product of the reaction is stable on the CV time scale but not sufficiently stable to permit convenient preparation of solutions of known concentration for classical potentiometric studies. A good example of this application is the determination of the formal potentials for the oxidation of 56 tetraalkylhydrazines to their corresponding radical cations and the comparison of the data with ionization potentials derived from photoelectron spectra.[13]

Reactive Electrode Reaction Products. Phenoxy radicals undergo a number of reactions which can influence the electrochemical data. Some of these re-

(4) Though CV is quite sensitive to adsorption, an even more useful technique is chronocoulometry, which can detect as little as a few percent surface coverage of adsorbed reactant.[5]

(5) For a recent application see M. J. Hazelrigg, Jr., and A. J. Bard, *J. Electrochem. Soc.*, 122, 211 (1975).

(6) U. Svanholm and V. D. Parker, *J. Chem. Soc., Perkin Trans. 2*, 755 (1975).

(7) J. A. Richards and D. H. Evans, *J. Electroanal. Chem.*, 81, 171 (1977).

(8) B. S. Jensen and V. D. Parker, *Acta Chem. Scand., Ser. B*, 30, 749 (1976).

(9) F. Šebesta and J. Petránek, *Collect. Czech. Chem. Commun.*, 35, 2136 (1970).

(10) M. K. Kalinowski and B. Tenderende-Gumińska, *J. Electroanal. Chem.*, 55, 277 (1974).

(11) M. D. Ryan and D. H. Evans, *J. Electroanal. Chem.*, 67, 333 (1976).

(12) C. P. Andrieux and J. M. Savéant, *J. Electroanal. Chem.*, 57, 27 (1974).

(13) S. F. Nelsen, V. Peacock, and G. R. Weisman, *J. Am. Chem. Soc.*, 98, 5269 (1976).
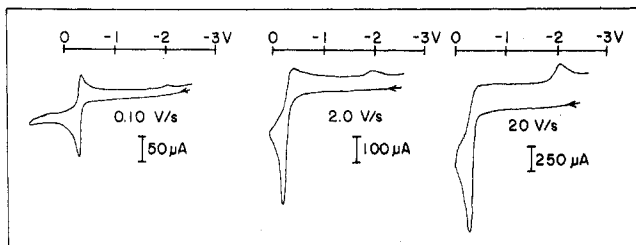
Figure 2. Cyclic voltammograms of 4.14 mM 2,6-di-*tert*-butyl-4-ethylphenoxide in acetonitrile with 0.10 M tetraethylammonium perchlorate, glassy carbon electrode.[7]

actions are too slow to affect the CV response, but they will be apparent during slower experiments such as controlled-potential electrolysis. For example, phenoxy radicals containing alkyl groups with α-hydrogen atoms such as **6** are susceptible to disproportionation to the
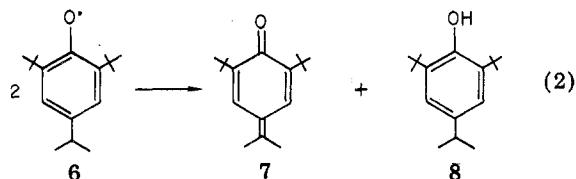
quinone methide **7** and the original phenol **8**, and this reaction becomes dominant during controlled-potential electrolysis, after which **7** and products derived from it are detected.[7]

Faster reactions will show their effects in the CV experiment. A particularly interesting example is the reversible dimerization of phenoxy radicals to give
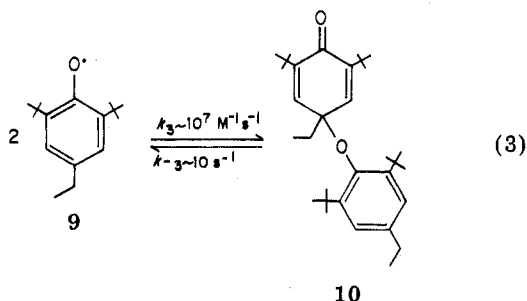

dimers which are thought to have the quinol ether structure, e.g., **10**. Cyclic voltammograms are given in Figure 2, where it may be seen that at moderate scan rates (20 V/s) the oxidation of the phenoxide at −0.3 V appears irreversible with no reduction peak for the phenoxy radical being observed. Instead a reduction peak appears at −2.0 V due to reduction of **10**. This is because the dimerization is so fast that the radicals react before they can be detected on the reverse scan.[7]

At slower scan rates, a small phenoxy radical reduction peak appears at −0.35 V, and it grows at the expense of the −2.0-V peak as the experiment is performed more and more slowly. This is because at slow scan rates there is ample time for the back-reaction to occur, namely, the dissociation of the dimer to the phenoxy radical which is removed by its reduction to phenoxide. Comparison of the data of Figure 2 with theoretical calculations based on reaction 1 gives excellent agreement,[7] and the rate constants obtained are similar to those measured in another solvent by a flash photolysis experiment.[14] This supports the notion that the kinetic parameters being measured are those of the

(14) E. J. Land and G. Porter, *Trans. Faraday Soc.*, **59**, 2016 (1963).

solution species and the CV results can give reliable chemical information about reactive intermediates.

It is far more common for the product of the initial electron transfer reaction to be involved in irreversible chemical reactions. For example, many phenoxy radicals rapidly dimerize at para or ortho positions, giving keto dimers which tautomerize, producing new electroactive species. As another example, the dibenzoylmethyl radicals **12** formed by oxidation of the
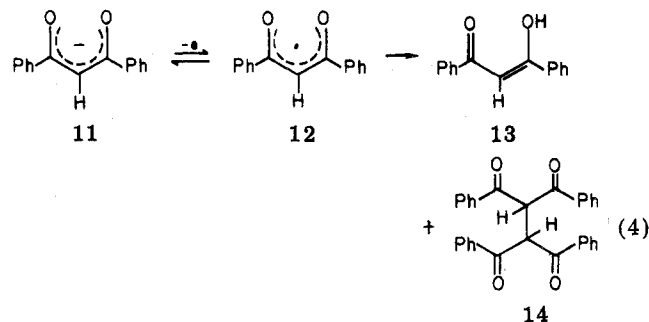
enolate of dibenzoylmethane[15] react rapidly by hydrogen atom abstraction, producing dibenzoylmethane **13**, and by dimerization, giving **14**. These irreversible reactions are very rapid, and their rates could not be measured by CV. However, **14** is susceptible to enolization and further oxidation to tetrabenzoylethylene, a product detected in fully electrolyzed solutions by CV and liquid chromatography.[15]

A reaction of particular interest in recent years has been the reductive coupling of activated olefins, **15** (X = CN, COOR, COR, Ar, etc.), a reaction which has been
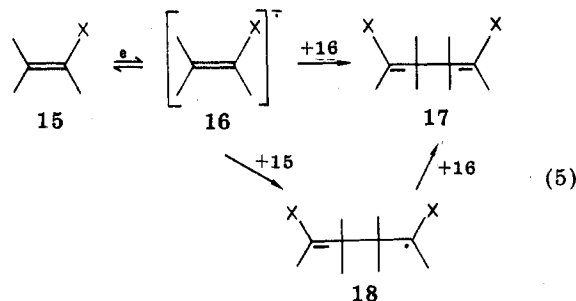
brought into prominence by the successful industrial process of the electrolytic reductive coupling of acrylonitrile to adiponitrile.[16] Two reaction pathways for the initially formed radical anions are envisioned. The first is simple dimerization, while the second involves reaction of the radical anion with the parent olefin, forming an intermediate dimer (**17**) which in turn is reduced by another molecule of radical anion or by the electrode. The latter is an example of an ECE process where a chemical step is interposed between two electron-transfer steps.[17] The rate of disappearance of **16** may be determined by voltammetry, but the theoretical responses for these two schemes are rather similar using CV or double potential step chronoamperometry,[18] so it was very difficult to prove which

(15) H. W. VandenBorn and D. H. Evans, *J. Am. Chem. Soc.*, **96**, 4296 (1974).

(16) D. Danly in "Organic Electrochemistry, An Introduction and a Guide", M. M. Baizer, Ed., Marcel Dekker, New York, N.Y., 1973, pp 936–939.

(17) The second electron transfer often occurs principally by reaction in solution rather than at the electrode.

(18) W. V. Childs, J. T. Maloy, C. P. Keszthelyi, and A. J. Bard, *J. Electrochem. Soc.*, **118**, 874 (1971).

pathway was correct. Fortunately, it has been possible to distinguish the two using special variants of rotating ring–disk voltammetry[19] and chronopotentiometry[20] in which the contribution of the ECE path (if important) could be exaggerated by generating a small amount of radical anion in the presence of much unreacted olefin. These studies, as well as concurrent studies by Lamy, Nadjo, and Savéant[21] using observed peak potential shifts in linear sweep voltammetry, have shown that the direct dimerization of radical anions predominates for a variety of activated olefins. (Actually, most of the kinetic studies have used 1,2-diactivated olefins.) Savéant and co-workers[22] have thoroughly analyzed these two reaction schemes, including the effects of solution electron transfers and protonation reactions, and have concluded that the reduction of activated olefins proceeds by radical–radical coupling under a variety of conditions. However, it is possible that the pathway which is important at the millimolar concentration levels typically employed in voltammetry may differ from the pathway at the higher substrate concentrations used in electrosynthesis. This question was recently attacked by Nadjo and Savéant,[23] who were able to employ substrate concentrations up to 0.1 M in their chronopotentiometric studies of the reductive coupling of *p*-methylbenzylidenemalononitrile in DMF. They used high electrolyte concentrations to minimize mass transport by migration. Their results indicate that radical–radical coupling continues as the dominant pathway at 0.1 M substrate concentrations. The ECE scheme may be important for other as yet unstudied substrates or experimental conditions, but so far the weight of the kinetic evidence favors a radical dimerization pathway.

The dimerization pathway persists when activated olefins are reduced in the presence of alkali metal ions. As mentioned above, ion pairing between organic anions and alkali metal ions causes a shift in the observed potentials, but in the present case, an additional effect is seen, viz., the ion pairs react more rapidly than the free radical anions (eq 6–10). Three dialkyl fumarates,

$$A + e \rightleftharpoons A^{-\cdot} \tag{6}$$

$$A^{-\cdot} + M^+ \underset{}{\overset{K_7}{\rightleftharpoons}} M^+A^{-\cdot} \tag{7}$$

$$2\,A^{-\cdot} \overset{k_8}{\longrightarrow} dimer \tag{8}$$

$$M^+A^{-\cdot} + A^{-\cdot} \overset{k_9}{\longrightarrow} dimer \tag{9}$$

$$2M^+A^{-\cdot} \overset{k_{10}}{\longrightarrow} dimer \tag{10}$$

ethyl cinnamate, and cinnamonitrile have been studied in DMF in the presence of Li$^+$, Na$^+$, and K$^+$ and for diethyl fumarate, K_7, k_8, k_9 and k_{10} have been evaluated in DMF using double potential step chronoamperometry[5] and in Me$_2$SO using CV.[24] The rate constants decrease in the order $k_{10} \gg k_9 \gg k_8$ due apparently to decreased charge repulsion in the reactions of the ion pairs.

Studies of the Second Step of Oxidation or Reduction

The products of the first step of oxidation or reduction are typically ion radicals or neutral radicals which may range from being indefinitely stable to highly reactive. If the potential is made more and more positive (or negative), a second step of oxidation (or reduction) occurs which normally produces diamagnetic ions. These ions are usually very reactive, the cations being susceptible to nucleophilic attack by trace impurities or nucleophiles intentionally added and the anions being prone to react with electrophiles, particularly proton donors.

Second Step of Phenoxide Oxidation. It has already been pointed out that peak II in Figure 1A is due to the oxidation of 2,4,6-tri-*tert*-butylphenoxy (3). CV shows the process to be irreversible even at rapid sweep rates, coulometry indicates $n = 1.1–1.3$, and the hydroxydienone 5 is obtained as the principal product.[3] This is best explained by assuming that phenoxonium ion 4 is the initial product, but that it rapidly reacts with residual water in the acetonitrile solvent. (When water is removed, some attack on solvent occurs, giving products which incorporate acetonitrile.[25])

Normally the height of the second oxidation peak should be equal to the first when measured from an extension of the currents past the first peak. Peak II in Figure 1A is much smaller than peak I, and the cause may be traced to reaction of phenoxonium ion with water, a process which frees protons which diffuse away from the electrode (cf. reaction 1). These protons neutralize incoming phenoxide, giving the phenol 1, which is not oxidizable at the potential of peak II. Hence the protons "shut off" the flux of reactant, causing the peak to be smaller than expected.

This notion was tested[3] by a double potential step experiment in which the potential was changed from $E_i = -0.60$ V to $E_1 = 0.00$ V for 2.00 s, during which time the expected current for one-electron oxidation of 2 to phenoxy radical 3 was observed. Then the potential was changed to $E_2 = +1.10$ V to cause the oxidation of 3 to phenoxonium ion 4 and thence hydroxydienone 5. The observed current–time curve is shown as the solid curve (curve A) in Figure 3. The current is very low, even falling below the one-electron level (curve B). After passing through a shallow minimum, the current increased toward the one-electron level. A theoretical curve which includes the effects of the protons generated in the second step was found to fit the experiment (curve D).

Behavior like this is frequently detected at the second step of oxidation or reduction. For example, the second step of the oxidation of tetraalkylhydrazines gives dications which rapidly deprotonate, and the protons attack incoming hydrazine giving hydrazinium ions which are not oxidized at that potential.[26] A slightly different example may be found in the reduction of triphenylcyclopropenium cation, which gives dimer at the first step of reduction (dimerization of cyclopropenyl radicals) and also dimer at the second step (attack of cyclopropenyl anion on starting material).[27,28]

(19) V. J. Puglisi and A. J. Bard, *J. Electrochem. Soc.*, **119**, 829 (1972).
(20) S. C. Rifkin and D. H. Evans, *J. Electrochem. Soc.*, **121**, 769 (1974).
(21) E. Lamy, L. Nadjo, and J. M. Savéant, *J. Electroanal. Chem.*, **42**, 189 (1973).
(22) C. P. Andrieux, L. Nadjo, and J. M. Savéant, *J. Electroanal. Chem.*, **42**, 223 (1973).
(23) L. Nadjo and J. M. Savéant, *J. Electroanal. Chem.*, **73**, 163 (1976).
(24) M. D. Ryan and D. H. Evans, *J. Electrochem. Soc.*, **121**, 881 (1974).

(25) G. Popp and N. C. Reitz, *J. Org. Chem.*, **37**, 3646 (1972).
(26) D. H. Evans, S. F. Nelsen, and P. J. Kinlen, unpublished results.
(27) R. Breslow and W. Chu, *J. Am. Chem. Soc.*, **95**, 411 (1973).
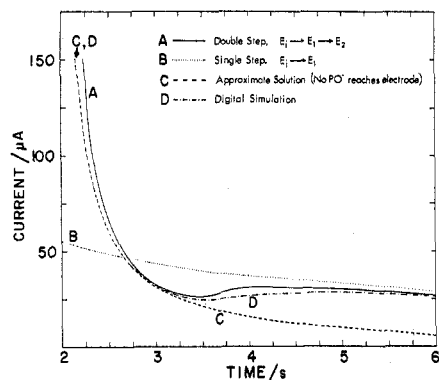(28) R. Breslow and R. F. Drury, *J. Am. Chem. Soc.*, **96**, 4702 (1974).

Figure 3. Double potential step chronoamperometry of 2,4,6-tri-*tert*-butylphenoxide (2). Conditions as in Figure 1. (A) Double potential step experiment with 5.00 mM, 2. $E_i = -0.60$ V, $E_1 = 0.00$ V, $E_2 = 1.10$ V; $t_1 = 2.00$ s; only $t > t_1$ shown; (B) single-step experiment with solution used in A; $E_i = -0.60$ V; $E_1 = 0.00$ V; only $t > 2.00$ s shown. (C) Approximate solution. (D) Digital simulation.[3]
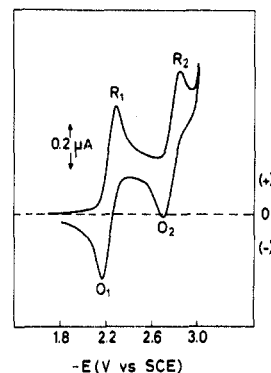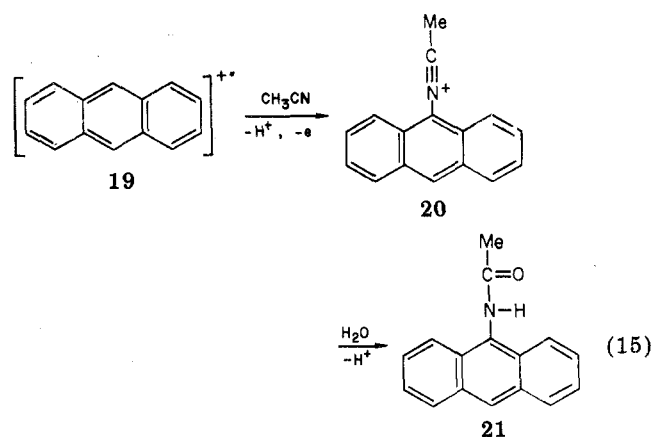

Figure 4. Cyclic voltammogram of 1.9 mM chrysene in DMF saturated with Me_4NBr at 12 °C, platinum electrode. Scan rate: 0.153 V/s.[31]

In general, the product at a second stage of electrolysis is very reactive, and its reactions can influence the voltammetric behavior in unusual and interesting ways.

Special Solvent/Supporting Electrolyte Systems for Stabilizing Two-Electron Oxidation and Reduction Products. The rapid attack of the phenoxonium ion 4 by residual water in the solvent suggests that the stability of reactive electrode reaction products could be enhanced by employing highly purified solvents. Indeed, considerable effort has been expended in the development of purification procedures for the common electrochemical solvents such as acetonitrile, *N,N*-dimethylformamide, and dimethyl sulfoxide. Still none of these has proven to be as spectacularly successful as the procedure introduced by Parker[29] in which neutral alumina is added to the cell in order to adsorb trace impurities. Typically, the solution is stirred for about 1 min, and the voltammogram is recorded about 10 s after the stirring is stopped, allowing the alumina to settle.

Using this simple procedure Parker and co-workers have shown that a variety of substrates can be oxidized in stepwise fashion first to the cation radical and then to the dication and that the dications have half-lives greater than several seconds as shown by dication → cation radical reduction peaks of theoretical height even at slow scan rates.[29]

Similar results were found for reduction reactions of nitrobenzene,[30] benzophenone,[30] and aromatic hydrocarbons.[31] As may be seen in Figure 4, reversible stepwise reduction of chrysene to its anion radical and dianion can be achieved even though the second potential is extremely negative.[31]

Armed with the formal potentials obtained in this manner, one can proceed to calculate K_d, the equilib-

$$A + e \rightleftharpoons A^{-.} \qquad E^0_1 \qquad (11)$$

$$A^{-.} + e \rightleftharpoons A^{2-} \qquad E^0_2 \qquad (12)$$

$$2A^{-.} \rightleftharpoons A^{2-} + A \qquad K_d \qquad (13)$$

$$\log K_d = \frac{nF}{2.303RT} (E^0_2 - E^0_1) \qquad (14)$$

rium constant for disproportionation of the anion radical (or cation radical). This number is of considerable interest in radical ion chemistry, and it can now be determined very readily by the voltammetric technique in a variety of solvents using various counterions, ionic strengths, and temperatures.[31] It has been shown recently that quite low concentrations ($<10^{-2}$ M) of hydroxylic solvents like methanol can increase K_d, presumably by preferential solvation of the dianions.[8]

Another promising solvent/supporting electrolyte system is liquid NH_3/KI in which reversible two-step reduction of benzophenone,[32] nitrobenzene,[33] and nitrosobenzene[33] has been observed.

In many cases, the removal of impurities by the alumina treatment is not sufficient to ensure the stability of ion radicals and doubly charged ions. For example, the cation radical of anthracene rapidly at-

tacks solvent in "superdry" acetonitrile,[34] leading eventually to *N*-(9-anthryl)acetamide (21). Solvents such as dichloromethane (with suspended alumina) or the moderately acidic medium of dichloromethane–trifluoroacetic anhydride–trifluoroacetic acid (45:5:1) are required to obtain stable solutions of anthracene radical cation, and the dication is still very unstable in these media.[35] Trifluoroacetic acid has a stabilizing effect on cation radicals and dications, and the anhydride is

(29) O. Hammerich and V. D. Parker, *Electrochim. Acta*, 18, 537 (1973).
(30) B. S. Jensen and V. D. Parker, *J. Chem. Soc., Chem. Commun.*, 367 (1974).
(31) B. S. Jensen and V. D. Parker, *J. Am. Chem. Soc.*, 97, 5211 (1975).

(32) A. Demortier and A. J. Bard, *J. Am. Chem. Soc.*, 95, 3495 (1973).
(33) W. H. Smith and A. J. Bard, *J. Am. Chem. Soc.*, 97, 5203 (1975).
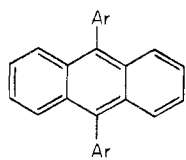(34) O. Hammerich and V. D. Parker, *J. Chem. Soc., Chem. Commun.*, 245 (1974).
(35) O. Hammerich and V. D. Parker, *J. Am. Chem. Soc.*, 96, 4289 (1974).

thought to act as a scavenger of the last traces of water in the solvent.

Using the acidic solvent mixture, reversible two-step oxidation of 9,10-di(p-anisyl)anthracene (22) could be

22, Ar = p-anisyl
23, Ar = p-tolyl
24, Ar = phenyl

observed, but the cations of 9,10-di(p-tolyl)anthracene (23) and 9,10-diphenylanthracene (24) react with trifluoroacetate. For the latter two, a more acidic medium (CH_2Cl_2–FSO_3H) and lower temperature (–34 °C) were required to see reversible cation/dication electrochemistry.[35]

The considerable stability of the dication of the dianisylanthracene is demonstrated in Figure 5 where stirred solution voltammograms are shown for various times during the coulometric oxidation. The initial solution shows two steps with half-wave potentials of +1.1 and +1.5 V for the neutral/cation and cation/dication couples, respectively. When one-electron oxidation has been accomplished (curve d, Figure 5), a solution of cation radical results which has a reduction step (+1.1 V) and an oxidation step (+1.5 V). Finally, when the oxidation to the dication is complete (curve g), its two reduction steps are obtained. The relative heights of the limiting currents show that very little dication has been lost during the electrolysis.[35]

These acidic media have been used to generate what appear to be stable protonated phenoxy radicals for an α-tocopherol model compound[36] and the methylene bridged phenolic biphenyl, **25**.[37] The reversible oxi-

$$25 \rightleftharpoons 26 \quad$$

$$\rightleftharpoons 27 \qquad (16)$$
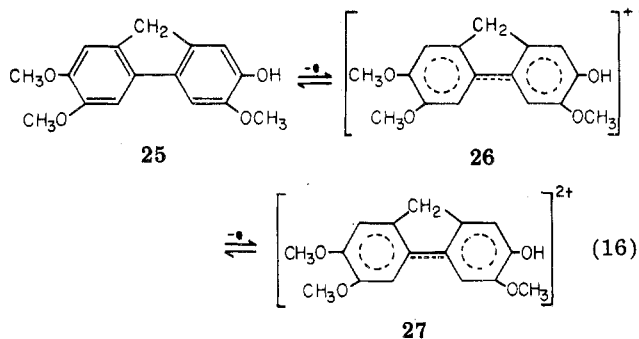
dation of simpler phenols to their cation radicals has been reported using CH_2Cl_2–FSO_3H (90:10) at –50 °C (Figure 6).[38] The reversible potential was independent of fluorosulfuric acid concentration which is consistent with the proton remaining with the radical cation as shown. The reversible potential for the **28/29** couple was +1.68 V vs. SCE.

This number is extremely important because it is the final factor needed to permit the construction of a tentative potential–pH diagram for a simple phenol

(36) U. Svanholm, K. Bechgaard, and V. D. Parker, *J. Am. Chem. Soc.*, **96**, 2409 (1974).
(37) A. Nilsson, U. Palmquist, A. Ronlán, and V. D. Parker, *J. Am. Chem. Soc.*, **97**, 3540 (1975).
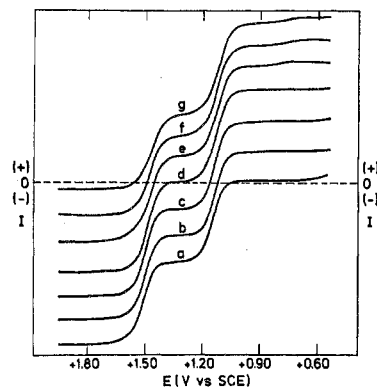(38) O. Hammerich, V. D. Parker, and A. Ronlán, *Acta Chem. Scand.*, *Ser. B*, **30**, 89 (1976).

Figure 5. Stirred solution voltammograms of 9,10-di(p-anisyl)anthracene during constant-current coulometry. Methylene chloride–trifluoroacetic anhydride–trifluoroacetic acid (45:5:1) with tetra-n-butylammonium tetrafluoroborate, platinum electrode. Time of oxidation at 25.0 mA (in min): (a) 0, (b) 1.0, (c) 2.0, (d) 3.22, (e) 4.22, (f) 5.22, (g) 6.22 (time required for one-electron oxidation, 3.22 min).[35]
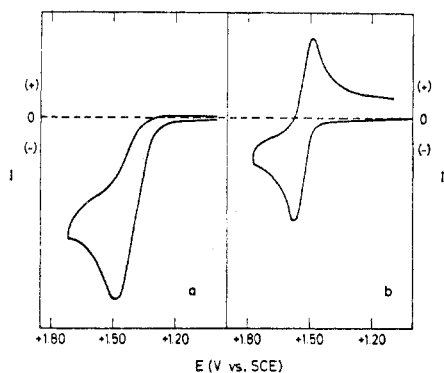

Figure 6. Cyclic voltammogram of 2 mM 4-hydroxybiphenyl in CH_2Cl_2 with 0.20 M tetra-n-butylammonium tetrafluoroborate at –50 °C and 0.086 V/s, platinum electrode. (a) In the absence of acid; (b) in the presence of 10% FSO_3H.[38]

(Figure 7). The importance of such equilibrium diagrams, which are completely analogous to those used in metal ion redox equilibria, has been emphasized by Savéant.[39] Such a diagram defines the E–pH fields in which the various phenolic species (POH, PO⁻, PO·, PO⁺ and POH⁺·) are thermodynamically capable of existence, and it provides a useful conceptual framework from which the various reactions of phenoxy radicals, phenoxonium ions, etc., can be extrapolated. For example, Figure 7 gives the approximate range of pH and potential where products derived from trialkylphenoxonium ions would be expected.

Kinetics Schemes for the Reaction of Cation Radicals with Nucleophiles. Now that procedures have been established for the electrochemical production of radical ions and doubly charged ions under conditions that the species have significant lifetimes, it becomes possible to determine how the presence of nucleophiles and electrophiles will affect the overall electrode reaction.

One of the earliest reactions studied was the anodic pyridination of 9,10-diphenylanthracene (DPA) which yields a two-electron oxidation product ($DPA \cdot Py_2^{2+}$) in which pyridine has added to the 9 and 10 positions.[40] What are the steps in the overall electrode reaction?

(39) L. Nadjo and J. M. Savéant, *J. Electroanal. Chem.*, **33**, 419 (1971).
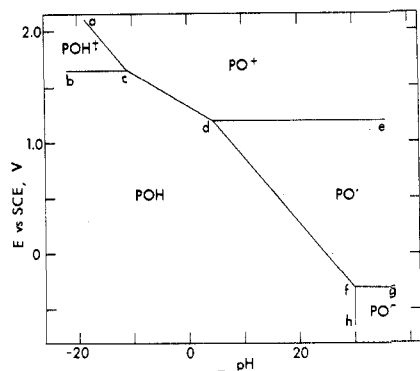(40) D. T. Shang and H. N. Blount, *J. Electroanal. Chem.*, **54**, 305 (1974).

Figure 7. Approximate pH–potential diagram for a 2,4,6-tri-alkylphenol in acetonitrile. Line segment bc is at the level of the phenol/phenol cation radical couple (POH/POH$^+$·);[38] line de is at the phenoxy radical/phenoxonium ion potential (PO·/PO$^+$);[3] line fg is the phenoxide/phenoxy couple (PO$^-$/PO·);[3] and fh is at the pK_a of the phenol in acetonitrile.[48] Line cd represents the pH dependence of the potential of the PO$^+$ + H$^+$ + 2e = POH couple; line df is for the PO· + H$^+$ + e = POH couple. Abscissa is a combined pH/acidity function scale.

Two schemes seem most probable. The first is a type of ECE process which involves initial formation of radical cation (DPA$^+$·) followed by addition of pyridine, oxidation, and, finally, addition of a second pyridine, giving DPA·Py$_2$$^{2+}$.[41]

The second scheme involves disproportionation of the radical cations giving the dication which is rapidly pyridinated. These two schemes have proven to be quite difficult to distinguish by voltammetry, but more definitive results have been obtained by supplementary application of other techniques. For example, the rate of disappearance of DPA$^+$· has been measured by visible absorption spectroscopy following electrochemical generation of the radical cation at a transparent electrode.[42] The pyridination reaction was shown to

(41) G. Manning, V. D. Parker, and R. N. Adams, *J. Am. Chem. Soc.*, **91**, 4584 (1969).

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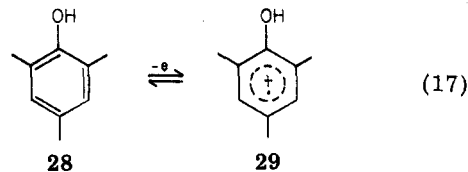
proceed via the ECE scheme. A simple and direct procedure was employed by Svanholm and Parker[43] who generated known concentrations of DPA$^+$· in superdry media using an anode of large surface area and known constant currents. They then used a rotating disk electrode to monitor the concentration of DPA$^+$· as it reacted with pyridine in homogeneous solution. Their results strongly support the ECE scheme. This technique has been applied to other anodic reactions in which even more complex rate laws have been found.[44-46] Similar ECE schemes are operative in the reduction of quinones in the presence of proton donors.[47]

The foregoing journey through recent work in electrochemistry shows that many electrode reactions fall in the class of weakly interacting systems in which the electrochemically generated intermediates diffuse into solution where they display their inherent chemical properties. Voltammetry provides thermodynamic and kinetic information concerning the species participating in the reaction, and in this way gives new insight into chemical properties.

(42) H. N. Blount, *J. Electroanal. Chem.*, **42**, 271 (1973).
(43) U. Svanholm and V. D. Parker, *Acta Chem. Scand.*, **27**, 1454 (1973).
(44) U. Svanholm, O. Hammerich, and V. D. Parker, *J. Am. Chem. Soc.*, **97**, 101 (1975).
(45) U. Svanholm and V. D. Parker, *J. Am. Chem. Soc.*, **98**, 997 (1976).
(46) U. Svanholm and V. D. Parker, *J. Am. Chem. Soc.*, **98**, 2942 (1976).
(47) R. M. Wightman, J. R. Cockrell, R. W. Murray, J. N. Burnett, and S. B. Jones, *J. Am. Chem. Soc.*, **98**, 2562 (1976).
(48) J. F. Coetzee and G. R. Padmanabhan, *J. Phys. Chem.*, **69**, 3193 (1965).

Laser Photochemistry of Selected Vibronic and Rotational States

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Many of the photochemical studies in the last several decades have dealt with the elucidation of the mechanisms which give satisfactory quantitative account of the observed final photoproducts, and some have been very successful in providing the detailed information

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about the roles each excited electronic state plays in various primary photochemical processes.[1] While the reactivity of the excited states is of general interest, the physical properties of the excited states which give rise to instability as manifested by luminescence, radiationless transition, predissociation, dissociation, molecular rearrangement, etc., are of more fundamental interest. However, less is known about these

(1) (a) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", Wiley, New York, N.Y., 1966; (b) N. J. Turro, "Molecular Photochemistry", Benjamin, New York, N.Y., 1965; (c) J. P. Simons, "Photochemistry and Spectroscopy", Wiley-Interscience, New York, N.Y., 1971.