Anodic Oxidation Pathways of Aromatic Hydrocarbons and Amines

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Inorganic electron-transfer theory has been developed elegantly by Taube, Marcus, Sutin, Vlcek, and Halpern, among others. A similar picture for organic redox systems is very sketchy, although definitive contributions have come from Hoijtink,[1] Peover,[2-4] and other groups.[5]

Hoping to establish a general pattern for aromatic systems, anodic oxidations have occupied our attentions for some 10 years. Such studies admittedly represent a restricted viewpoint, although anodic electrochemistry yields a variety of information on properties of electron-deficient species. Similar data are obtained from chemical oxidations,[6] photoejection of electrons,[7] and various mass spectrometry and particle-impact methods. Correlations of electrochemical data with this information are of interest. In fact, it is not the electrochemistry itself which is important, but that it is a very suitable means of studying the properties of these species.

Let us initially put the electrochemistry aside and predict a basic pattern of anodic behavior based upon simple organic chemistry concepts. Then we can compare this with experimental facts.

Designating any aromatic compound by Ar, we can write the initial electrochemical event

$$Ar \leftrightharpoons Ar(+) + n_1e$$
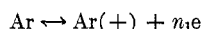
The symbolism $Ar(+)$ indicates that n_1 can be any number of electrons in general, but certainly not less than one.

The details of this reaction are fundamental in the theory of redox processes and occupy the main attention of many electrochemists. For the present discussion, the electrode reaction happens to be a convenient method of generating the electron-deficient entity, $Ar(+)$. We will concentrate on one aspect of this process, namely, n_1, the primary number of electrons transferred. Many experimental examples will suggest that almost always $n_1 = 1$. Although this is only a restatement of the Michaelis postulate, it is not universally popular, but, as we will show, that is "like it is."

Whether $Ar(+)$ is the cation radical, $Ar \cdot^+$ (if $n_1 = 1$), or another electron-deficient species, there are two situations to consider.

A. $Ar(+)$ Is Relatively Stable. Although the stability of $Ar(+)$ is only a relative parameter and will depend on the time scale of the electrochemical experiment, it is convenient to classify many $Ar(+)$ as stable. There are at least three possibilities for such stability: (a) a high degree of charge delocalization in $Ar(+)$; (b) reactive sites in $Ar(+)$ blocked; (c) $Ar(+)$ stabilized by specific functional groups. Extensive examples of the first two situations are found in hydrocarbon oxidations, and the aromatic semiquinones fit the third case. Any $Ar(+)$ is also inherently more stable in a solvent of low nucleophilicity.

B. $Ar(+)$ Undergoes Extensive Chemical Reactions. This is the common behavior of $Ar(+)$. After the primary electron transfer, one or more chemical reactions (follow-up reactions) and additional electron transfers may develop. These follow-up processes occur in two categories.

A. EC Processes. The terminology EC means the initial electron transfer (E) is followed by a chemical reaction (C). For an oxidation it is formulated

$$Ar \leftrightharpoons Ar(+) + n_1e$$

$$Ar(+) + Z \xrightarrow{k_f} P$$
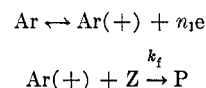
$Ar(+)$ reacts with a nucleophile, Z (frequently the solvent). (Instead of the designation N or B for nucleophile, the symbol Z is used herein since it is common in the electrochemical literature.) The product, P, is not further oxidizable at the applied potentials (or may already be in the oxidized state). In any event the net flow of current corresponds to only n_1 electrons.

B. ECE Processes. The ECE interaction of $AR(+)$ makes the anodic electrochemistry a delightful and intriguing mess. The abbreviation ECE indicates there is a chemical reaction interposed between two electron transfers. The process can be summarized as follows.

(1) G. J. Hoijtink, *Rec. Trav. Chim.*, **76**, 885 (1957).
(2) T. A. Gough and M. E. Peover, "Polarography-1964," Macmillan and Co., Ltd., London, 1966, p 1017.
(3) M. E. Peover and B. S. White, *J. Electroanal. Chem.*, **13**, 93 (1967).
(4) M. E. Peover in "Electroanalytical Chemistry," A. J. Bard, Ed., Marcel Dekker, New York, N. Y., 1967, Chapter 1.
(5) C. L. Perrin, *Progr. Phys. Org. Chem.*, **3**, 165 (1965).
(6) For reviews of chemical oxidations, see W. A. Waters, "Mechanisms of Oxidation of Organic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1964, and R. Stewart, "Oxidation Mechanisms," W. A. Benjamin, New York, N. Y., 1964.
(7) For recent studies of photooxidations with implications to electrochemistry, see H. I. Joschek and S. I. Miller, *J. Am. Chem. Soc.*, **88**, 3273 (1966).

$$Ar \rightleftharpoons Ar(+) + n_1e$$

$$Ar(+) + Z \xrightarrow{k_f} C$$

$$C \rightleftharpoons D + n_2e$$
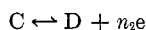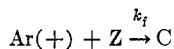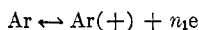
$Ar(+)$ again reacts with nucleophile, Z, but in this case an intermediate product, C, undergoes further oxidation. C generally will be more easily oxidized than the starting Ar. Hence, the applied potential is more than sufficient to carry out an additional stage of oxidation and C is transformed to D with the loss of n_2 electrons. In the limit $n_1 + n_2$ electrons are liberated. (The so-called "nuances" of the ECE process are not discussed herein. They do not alter the concept of total electron flow.)

It is surprising how widespread this ECE mechanism is in anodic oxidations. The initial oxidation products of hydrocarbons mostly interact with solvent to provide a route for ECE reactions. Hydroquinones and similar species, oxidized in the presence of amines or other electron-donating species, undergo 1,4-addition reactions and the intermediates are further oxidized via the ECE path. Z is not always a nucleophile in the usual sense. It may be another $Ar(+)$, i.e., a cation-radical dimerization occurs. Unless the dimer is seriously twisted from steric interferences, it will be easier to oxidize than the parent Ar. Many examples of these dimerizations prevail in the oxidation of aromatic hydrocarbons and amines. There are also successive electron transfers without intervening chemical steps (EE reactions). If one is fond of letter codes, over-all processes like ECCEC can be written and verified. All combinations are presumably possible, with four-letter combinations neither neglected nor preferred.

These processes are studied like any other problem in chemical kinetics. One generates the intermediate, $Ar(+)$, then provides a suitable time for its interactions. At the end of the time gate, the system is sampled for remaining concentration of $Ar(+)$ or any of the new products (P, C, or D of the previous formulations). The time gate can be adjusted by choice of the electrochemical technique which often provides the sampling procedure. In addition, one uses everything available for qualitative and quantitative sampling—electron paramagnetic resonance (epr), visible, uv, ir, and fluorescence spectroscopy, and thin layer and gas chromatography are some of the techniques which are utilized. The electroanalytical techniques themselves are well documented.[4,8-14] A detailed treatment applied to anodic oxidations will soon be available.[15] Only cyclic voltammetry is reviewed

(8) R. S. Nichol on and I. Shain, Anal. Chem., **36**, 706 (1964); **37**, 178 (1965).
(9) G. S. Alberts and I. Shain, ibid., **35**, 1859 (1963).
(10) D. Hawley and R. N. Adams, J. Electroanal. Chem., **8**, 163 (1964).
(11) R. N. Adams, ibid., **8**, 151 (1964).
(12) W. H. Reinmuth, Anal. Chem., **32**, 1514 (1960).
(13) A. C. Testa and W. H. Reinmuth, J. Am. Chem. Soc., **83**, 784 (1961); Anal. Chem., **33**, 1320 (1960).
(14) A. J. Bard and H. B. Herman in ref 2, p 373.
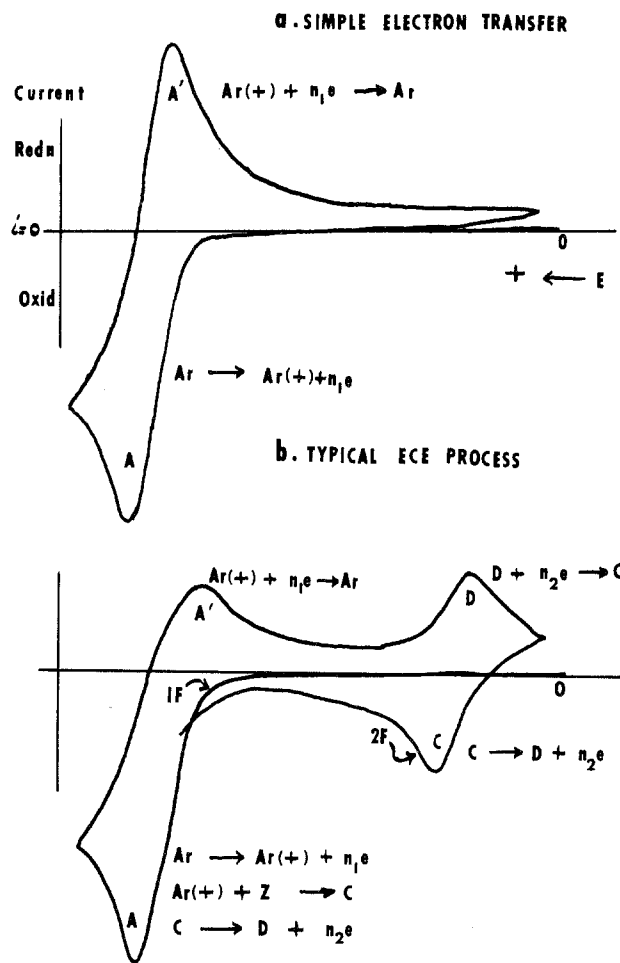(15) R. N. Adams, "Electrochemistry at Solid Electrodes," Marcel Dekker, New York, N. Y., 1969.

Figure 1. Typical cyclic polarograms for oxidation of aromatic compounds. The polarogram of part a is actually the experimental data for perylene in nitrobenzene. The points marked 0 represent the starting points of the first anodic sweeps (marked 1F). Voltages (E) and current are in arbitrary units.

briefly here since it so well illustrates the over-all nature of complex electrode reactions.

Cyclic voltammetry (CV) utilizes a triangular wave potential sweep applied to a stationary electrode in quiet solution. Sweep intervals varying from 0 to 2 V and sweep rates of 0.2–50 V/min are common. One measures the current–potential characteristics—just as in conventional polarography—only in a repetitive, cyclic fashion. The cyclic polarograms are usually traced on an XY recorder or oscilloscope. Figure 1a shows a typical response for the oxidation of an aromatic system where $Ar(+)$ is very stable. $Ar(+)$ formed at the electrode surface in the anodic sweep (peak A) is available for reduction back to Ar on the cathodic going sweep (peak A'). The peak current ratio, $i_{p,c}/i_{p,a}$, is 1, and the system will cycle repeatedly with only minor changes due to gradual adjustment of concentration gradients.

The situation is much different with a follow-up reaction, as shown in Figure 1b. Here $Ar(+)$ is partially consumed in the chemical reaction: hence $i_{p,c}/i_{p,a} \ll 1$ for peaks A, A'. If this were a typical ECE process,

some D would be formed during the first anodic sweep (marked 1F), and it would be detected as a reduction (peak D) on the reverse, cathodic sweep. The amount of C formed as a result will now be seen as a new oxidation (peak C) on the second (2F) and subsequent anodic sweeps. Note that peak C was absent on the first anodic sweep. Whenever the second and subsequent sweeps of a cyclic polarogram differ markedly from the first, a follow-up chemical reaction has occurred. The time gate for the chemical reaction is adjustable *via* sweep-rate adjustment. With this very simple experimental technique one often quickly obtains an over-all picture of the electrode process. The quantitative details can be obtained by careful CV and combinations with the other mentioned techniques.
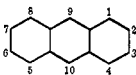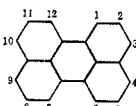
Aromatic Hydrocarbons

The extremes of stability in Ar(+) are well illustrated by unsubstituted polyacenes. Lund reported the first definitive voltammetry of aromatic hydrocarbons and indicated a primary two-electron loss.[16] Over the years, subsequent studies of $E_{1/2}$–HMO parameters,[17] controlled potential electrolyses,[18] anodic substitution,[19] and electrochemiluminescence[20] were divided in opinion between the one- or two-electron process. Perrin's review provided a strong argument in favor of the one-electron reaction.[5]

Very recently, from three independent groups, unequivocal evidence for one-electron oxidations even with unsubstituted hydrocarbons has appeared. The first, by Peover and coworkers, was in acetonitrile and showed that $i_{p,c}/i_{p,a}$ was close to unity for a variety of hydrocarbons.[2-4] Bard and coworkers also used quantitative aspects of CV, together with epr, to show stabilities of various radical cations in methylene chloride.[21] Our laboratory demonstrated one-electron oxidations *via* rotated disk electrodes and epr in nitrobenzene as solvent.[22] There now is no question about the prevalence of one-electron anodic oxidations in hydrocarbons.

A. Relatively Stable Cation Radicals. The stabilities of the hydrocarbon radical cations are qualitatively predictable by simple HMO reactivity parameters. For a cation radical, a reasonable reactivity parameter is ρ, the unpaired electron density at various atomic positions in the highest filled molecular orbital. In simple HMO calculations, $\rho = c^2$, where c is the usual atomic orbital coefficient in the highest filled molecular orbital. Values of ρ are readily calculated from standard sources.[23] As an example of stability predictions, Table I shows the ρ values for perylene and anthracene.

Table I

Unpaired Electron Distribution in Cation Radicals (Anthracene and Perylene)

	Positions[a]	ρ^b
	1 (4, 5, 8)	0.0967
	2 (3, 6, 7)	0.0484
	9 (10)	0.1936
	1 (6, 7, 12)	0.0835
	2 (5, 8, 11)	0.0130
	3 (4, 9, 10)	0.1076

[a] The first position corresponds to the listed coefficient in Coulson and Streitwieser. Those in parentheses are equivalent by symmetry. [b] $\rho = c^2$ where c is the coefficient of the highest filled atomic orbital of the hydrocarbon.

The only plausible explanation of stability for either of these radical cations would be a high degree of charge delocalization, *i.e.*, that ρ is well spread out over the molecular framework. As is well known, the 9,10 positions of anthracene are highly reactive, and this is reflected in the corresponding ρ values of Table I. The ρ values in perylene cation radical, on the other hand, are well distributed; there are no strong centers of reactivity. In accord with this, among the unsubstituted hydrocarbons, the perylene cation is quite stable by all the electrochemical and epr criteria. There is, however, almost no stability to the anthracene cation. Similarly, the tetracene cation radical, with high ρ at the 5, 6, 11, and 12 positions, is markedly unstable, although one-electron behavior is observed in nitrobenzene (with high rotation rates at a rotated disk electrode). These qualitative stability predictions have been extended to a variety of unsubstituted hydrocarbons and are in agreement with experiment.[22,24]

Blocking the reactive sites obviously produces stable radical cations. Thus, 9,10-diphenylanthracene (9,10-DPA) gives a very stable one-electron product.[3,21,22] Similarly, rubrene, which is 5,6,11,12-tetraphenyltetracene, gives a remarkably stable cation radical.[21,22] Methyl groups are effective blockers, and 9,10-dimethylanthracene (9,10-DMA) gives a moderately stable one-electron product in nitrobenzene. For instance, it shows $i_{p,c}/i_{p,a} = 0.84$ at the relatively slow cyclic sweep rate of 5 V/min.[22] In addition to the blocking effect, what appears to be extra charge delocalization in 9,10-DPA·+ (although the phenyl groups are strongly twisted out of the anthracene plane) makes it considerably more stable than 9,10-DMA·+. This is more evident in a comparison of 9-phenyl- and 9-methylanthracenes. Here, with one reactive posi-

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(17) G. J. Hoijtink, *Rec. Trav. Chim.*, **77**, 555 (1958); E. S. Pysch and N. C. Yang, *J. Am. Chem. Soc.*, **85**, 2124 (1963); W. C. Neikam and M. M. Desmond, *ibid.*, **85**, 4811 (1964); C. Parkanyi and R. Zahradnik, *Collection Czech. Chem. Commun.*, **30**, 4287 (1965); A. Stanienda, *Z. Physik. Chem.* (Frankfurt), **33**, 170 (1962).

(18) K. E. Friend and W. E. Ohnesorge, *J. Org. Chem.*, **28**, 2435 (1963).

(19) L. Eberson and K. Nyberg, *J. Am. Chem. Soc.*, **88**, 1686 (1966); *Tetrahedron Letters*, 2389 (1966).

(20) R. E. Visco and E. A. Chandross, *J. Am. Chem. Soc.*, **86**, 5350 (1964); R. E. Sioda and W. S. Koski, *ibid.*, **87**, 5573 (1965).

(21) J. Phelps, K. S. V. Santhanam, and A. J. Bard, *ibid.*, **89**, 1752 (1967).

(22) L. S. Marcoux, J. M. Fritsch, and R. N. Adams, *ibid.*, **89**, 5766 (1967); L. S. Marcoux, PhD. Thesis, University of Kansas, 1967.

(23) C. A. Coulson and A. Streitwieser, "Dictionary of Pi Electron Calculations," W. H. Freeman, San Francisco, Calif., 1965.

(24) See ref 15, Chapter 10.

tion still open, the 9-phenylanthracene radical cation is fairly stable ($i_{p,c}/i_{p,a}$ = 0.5 at 5 V/min), but the 9-methylanthracene one-electron product shows no indications of stability.

The blocking groups discussed do not in themselves make a particular hydrocarbon much easier to oxidize. Substituents like OH, NH_2, OCH_3, $N(CH_3)_2$, etc., normally make an otherwise "inert" hydrocarbon anodically electroactive. Using a wide variety of blocking groups (including this type of electroactive substituent), Zweig and coworkers demonstrated wide ranges of cation-radical stabilities.[25]

B. Highly Reactive Radical Cations. Many hydrocarbons undergo very complex anodic reactions. Completely satisfying understandings of these systems have not yet emerged, but recent results are encouraging. It is clear that the over-all processes are a "cascade" or series of ECE reactions.[3,18,21,22,26] Strong evidence (in many cases unequivocal) for an initial one-electron transfer has been presented.

The short-lived Ar·+ reacts rapidly with (1) solvent, (2) small amounts of water, (3) other solvent impurities, and (4) Ar·+ (dimerization). Despite the high solvent concentration, water (with its strong nucleophilic character) is one of the most frequent reactants. Although nonaqueous solvents used in hydrocarbon electrochemistry are highly purified, with ordinary electrochemical procedures the water content at best is ca. 4–10 mM. This is about the usual concentration of the hydrocarbon, so serious interaction is always possible. The rapid electrochemical techniques give consistent information. Controlled potential preparative work often leads to quite different results. The extent and nature of the follow-up reactions may depend on the various "impurity" concentrations and the total electrolysis time as well. Ohnesorge and coworkers found bianthrone and anthraquinone as products of exhaustive electrolysis of anthracene in acetonitrile containing various amounts of alcohol and water.[26] Using essentially vacuum-line electrolysis techniques with methylene chloride as solvent, Bard's group finds 9,10-dichloroanthracene, which indicates major solvent interaction.[27]

Some of the difficulties in this work are illustrated by very recent studies by L. Jeftic in our laboratory on benzo[a]pyrene (BP). We were particularly interested in this hydrocarbon because of recent reports of one-electron oxidations implicated in the metabolic reactions of it and other powerful carcinogens.[28] Cyclic voltammetry of BP in nitrobenzene shows a relatively short-lived one-electron intermediate with complex follow-up reactions. Controlled potential coulometry indicates a total of six electrons, and the major isolated

product is the 1,6-quinone, identifiable via uv spectral comparisons with authentic samples. (Two other isomeric quinones have been fractionated from the electrolysis mixture.) During both small- and large-scale electrolyses a film forms on the electrode. If this film is dissolved and fractionated by column chromatography, it can be shown to consist of the 1,6-quinone and significant amounts of the BP dimer.[29] The dimer is easily missed because its fluorescence is completely quenched by the quinones and without the chromatographic separation would never be observed. The relative amounts of dimer and quinones and the nature of the follow-up couples in the cyclic voltammetry are markedly dependent upon the water level of the solvent. Details of this reaction consistent with an initial one-electron transfer and a series of ECE reactions with water will soon be given.[30]

It is increasingly clear that to obtain a complete picture of the oxidation pathways of these highly reactive hydrocarbons will require careful work with particular emphasis on product identification and its relation to the voltammetry information.

C. Anodic Substitution Reactions. Anodic substitution reactions may be considered as a purposeful addition of a nucleophile, Z, to the electrogenerated Ar(+).[24] The earlier concepts of a Kolbe style reaction were eliminated by careful voltammetric studies,[31–34] most forcibly by the excellent work of Eberson and Nyberg.[19,35] There is now no question but that typical substitution reactions like acetoxylation, cyanation, methoxylation, and pyridination are reactions of Ar(+) with the corresponding nucleophiles. However, most workers have concluded Ar(+) is the dication. We have felt for some time the reaction was an ECE process with the initial stage Ar·+ reacting with the nucleophile. Just recently Parker and Manning have obtained what we believe is strong evidence that acetoxylation, pyridination, hydroxylation, methoxylation, and cyanation of hydrocarbons all operate via initial reaction with Ar·+. For instance, in the pyridination of anthracene and 9-phenylanthracene in acetonitrile, the stoichiometric effect of the pyridine concentration on the hydrocarbon peak current proves clearly that pyridine interacts with the cation radical. Although over-all two-electron reactions are frequent in anodic substitutions (and, indeed, in the pyridination of anthracene, a well-characterized dipyridyl adduct is isolated[16]), the pathway is a rapid ECE with two one-electron stages. These results will be reported in detail soon.[36]

(25) A. Zweig, A. H. Maurer, and B. G. Roberts, J. Org. Chem., **32**, 1332 (1967).

(26) E. J. Majeski, J. D. Stuart, and W. E. Ohnesorge, J. Am. Chem. Soc., **90**, 633 (1968).

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(28) J. Fried and D. E. Schumm, J. Am. Chem. Soc., **89**, 5508 (1967).

(29) M. Wilk, W. Bez, and J. Rochlitz, Tetrahedron, **22**, 2599 (1966).

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(31) S. D. Ross, M. Finkelstein, and R. C. Petersen, J. Am. Chem. Soc., **86**, 4139 (1964).

(32) F. D. Mango and W. H. Bonner, J. Org. Chem., **29**, 1367 (1964).

(33) M. Leung, J. Herz, and H. W. Salzberg, ibid., **30**, 310 (1965); H. W. Salzberg and M. Leung, ibid., **30**, 2873 (1965).

(34) V. D. Parker and B. E. Burgert, Tetrahedron Letters, 4065 (1965); 2415 (1968).

(35) L. Eberson, J. Am. Chem. Soc., **89**, 4669 (1967).

Aromatic Amines

The amines can be classified like the hydrocarbons—those with stable radical cations and those with extensive follow-up reactions. The follow-up reactions usually involve a fast ECE (the first E being the initial cation-radical formation). The chemical step is a bit more standard than in hydrocarbons owing to the amine function. It most often consists of a coupling (dimerization) to give a substituted benzidine (C–C coupling). In some cases N–C coupling occurs. The benzidines, etc., are usually more easily oxidized than parent amine, hence the over-all ECE reaction. In certain instances, the coupling is a straight EC process.

Later these oxidized products may undergo secondary chemical interactions like hydrolyses, 1,4 additions, etc. The latter sometimes are rapid and mixed with earlier ECE stages.

Absolute proof of the initial cation radical is lacking in many cases. However, all the electrochemistry as well as correlations with chemical oxidations favor the radical cation. In general the amines have been studied in both aqueous and nonaqueous media. We shall first examine the most stable one-electron compounds (not all amine systems are included in the following outline).

A. Tertiary Amines. *1. Triphenylamines.* If the phenyl groups are tri-*para*-substituted, the only reaction is the reversible one-electron transfer

$$(XC_6H_4)_3N \rightleftharpoons (XC_6H_4)_3N\cdot^+ + e$$
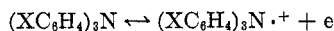
and the cation radical is very stable. Trianisylamine cation (TAA·+) is not only stable in acetonitrile and other nonaqueous media but also in 50% acetone–water buffers from pH 2 to pH 6. The epr spectra are well characterized.

With unsubstituted *para* positions there is rapid coupling to a substituted benzidine and an ECE process as, for example, with the unsubstituted triphenylamine.

$$(C_6H_5)_3N \longrightarrow (C_6H_5)_3N\cdot^+ + e$$
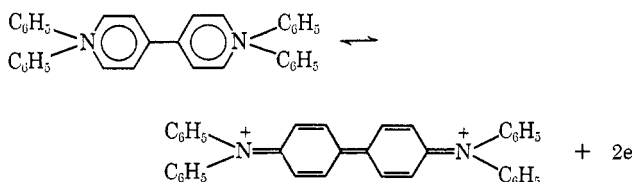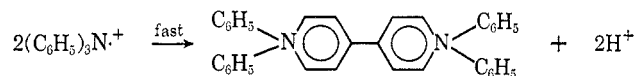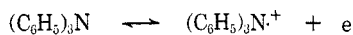
The benzidine oxidations can frequently be seen as two one-electron stages and the epr spectrum of the benzidine radical cation verified. The coupling rates depend somewhat statistically on the number of open positions but even more on specific substituents. A single methoxy group, in *p*-methoxytriphenylamine,

greatly stabilizes the monocation radical and little coupling occurs. A thorough quantitative study has been made of coupling rates as a function of substituents and unpaired electron density in the cation radical.

The triphenylamines thus have cation radicals varying from very stable to short-lived (but usually electrochemically detectable). All of the triphenylamine results have been summarized in the literature.[37-39]

2. N,N-Dialkylanilines. N,N-Dimethylaniline (DMA) was the first aromatic amine studied in depth. Cyclic voltammetry, rotated disk electrodes, visible and epr spectroscopy, and tritium tracer identification of products all verified the rapid coupling to tetramethylbenzidine and its further oxidation *via* the ECE route. The results on DMA are in accord with chemical oxidations.[40]

To date the DMA·+ has eluded detection due to the rapid coupling reaction. Other dialkylanilines react similarly to DMA. Benzidine formation also occurs in acetonitrile[39,41] and anhydrous acetic acid.[42] Emphasizing the role of the solvent, Weinberg and Brown found side-chain methoxylation occurring in methanol containing potassium hydroxide.[43] Different reactions occur in methanol with ammonium nitrate as supporting electrolyte, and Weinberg and Reddy discuss the significance of adsorption of DMA and DMA·+ in the over-all reactions.[44] A wide variety of substituted DMA's, many of which give stable cation radicals, were studied by Zweig, *et al.*,[45] and Latta and Taft.[46]

3. N-Alkyldiphenylamines. Only two such compounds apparently have been studied in any detail. Both N-methyldianisylamine and N-methyldi-*p*-toly-amine oxidize in two stages. The first stage is a clear one-electron process leading to stable cation radicals with defined epr spectra. Further oxidation yields a series of secondary follow-up processes.[47]

B. Secondary Amines. *1. N-Alkylanilines.* N-Methylaniline (MA) undergoes the same reactions as DMA—an ECE process leading to oxidized N,N'-dimethylbenzidine. An added complication over the DMA process is a secondary reaction of the fully oxidized dimethylbenzidine diquinoid compound with excess MA.[48]

(36) V. D. Parker, G. Manning, L. Jeftic, and R. N. Adams, unpublished data.

(37) E. T. Seo, R. F. Nelson, J. M. Fritsch, L. S. Marcoux, D. W. Leedy, and R. N. Adams, *J. Am. Chem. Soc.*, **88**, 3498 (1966).
(38) R. F. Nelson and R. N. Adams, *ibid.*, **90**, 3925 (1968).
(39) R. F. Nelson, Ph.D. Thesis, University of Kansas, 1967.
(40) T. Mizoguchi and R. N. Adams, *J. Am. Chem. Soc.*, **84**, 2058 (1962); Z. Galus and R. N. Adams, *ibid.*, **84**, 2061 (1962); Z. Galus, R. M. White, F. S. Rowland, and R. N. Adams, *ibid.*, **84**, 2065 (1962).
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(42) J. E. Dubois, P. C. Lacaze, and A. Aranda, *Compt. Rend.*, **260**, 3383 (1965).
(43) N. L. Weinberg and E. A. Brown, *J. Org. Chem.*, **31**, 4058 (1966).
(44) N. L. Weinberg and T. B. Reddy, *J. Am. Chem. Soc.*, **90**, 91 (1968).
(45) A. Zweig, J. E. Lancaster, M. T. Neglia, and W. H. Jura, *J. Am. Chem. Soc.*, **86**, 4130 (1964).
(46) B. M. Latta and R. W. Taft, *ibid.*, **89**, 5172 (1967).
(47) D. W. Leedy, Ph.D. Thesis, University of Kansas, 1968.
(48) Z. Galus and R. N. Adams, *J. Phys. Chem.*, **67**, 862 (1963).

2. Diphenylamines. Diphenylamines unsubstituted in the *p*-phenyl groups oxidize and undergo extensive follow-up reactions. If an initial one-electron oxidation is assumed, HMO calculations predict considerable unpaired electron density at both the *ortho* and *para* positions. One can expect coupling to ordinary benzidines, *o*-benzidines, and mixed types. In addition, N–N coupling to give tetraphenylhydrazines occurs. Nelson studied a few such systems in acetonitrile, but the full pathways are not too clear.[39]

The *para*-substituted diphenylamines give moderately stable cation radicals in acetonitrile, but these slowly decay to uncertain products. These compounds may also be studied in acetone–water mixtures. Here the oxidation is apparently a two-electron process, and the resulting quinoid structure undergoes hydrolytic cleavage to give benzoquinone and the corresponding amine.[47]

C. Primary Amines. *1. Anilines.* The electrochemical oxidation of aniline produces a species $Ar(+)$ with very little stability. Mohilner concluded the initial oxidation was a one-electron process.[49] The cation radical would have the principal structures I–III.
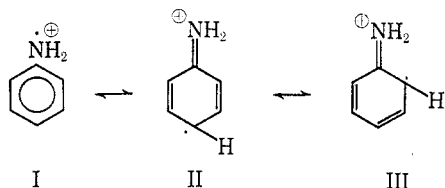
Rapid follow-up reactions consistent with structures I and II give dimeric products but little *ortho* coupling. Bacon studied the aniline oxidation from pH 0 to pH 6.5 *via* cyclic voltammetry. He found *p*-aminodiphenylamine to be the principal product (also found in strong acid[49]). With resonance forms I and II, this head-to-tail coupling can be written as
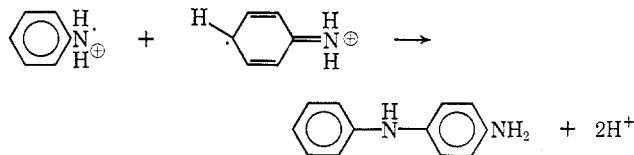
Since *p*-aminodiphenylamine is much easier to oxidize than aniline, an over-all ECE process results as
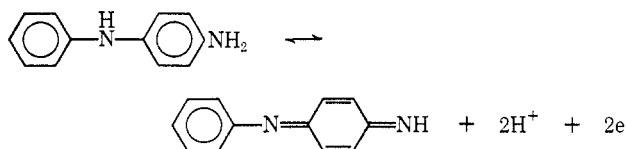
Significant amounts of benzidine are also found in the more acid range. Excellent matching of the cyclic polarograms of aniline, *p*-aminodiphenylamine, benzidine, and mixtures of all three provides striking evidence for this mixed process.[50] *para*-Substituted anilines were found to undergo head-to-tail coupling yielding the corresponding 4'-substituted *p*-aminodiphenylamine. Here the final product was already in the oxidized form, and the process is an EC reaction.[50] Wawzonek and McIntyre obtained N–N coupling in acetonitrile in the presence of pyridine with *para*-substituted anilines.[51]

2. Aminophenols, Diamines, etc. We and others have spent a great deal of time on the oxidation of aminophenols and phenylenediamines, and their electrochemistry is especially interesting. However, it is mainly concerned with hydrolysis of quinone imines (EC processes) and 1,4 additions (ECE paths) and is outside the scope of this review. The general role of quinone imine hydrolyses in the electrooxidation of amines has been discussed.[15,52]

One particular point should be noted about phenylenediamines. Maricle and coworkers studied a series of multiple N-substituted *p*-phenylenediamines in nonaqueous solvents. They presented electrochemical and epr evidence for discrete two-electron oxidations. No monocation was formed in instances where there was sufficient isolation between the phenylenediamine units.[53]

Summary

No attempt has been made to cover many aspects of the electrochemistry of hydrocarbons and amines. The excellent and comprehensive review on electrooxidation by Weinberg and Weinberg contains much additional information.[54] The present article has concentrated on the predominance of one-electron and ECE pathways in the electrode processes and their justification *via* simple physical organic principles. The general pattern is clear. Some of the details need further verification.

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(53) D. L. Maricle, W. G. Hodgson, H. Kaempfen, and J. P. Mohns, Abstract No. 200, 133rd Electrochemical Society Meeting, Boston, Mass., May 1968.

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