

Anodic Oxidation Pathways of *N*-AlkylanilinesRodney L. Hand^{1a} and Robert F. Nelson*^{1b}

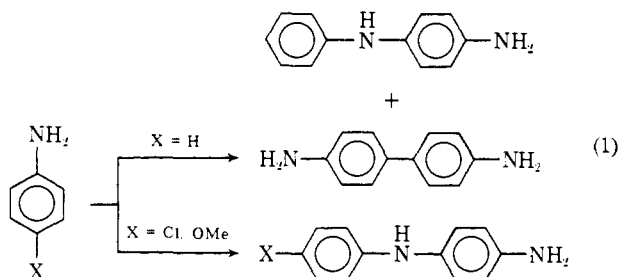
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Abstract: The anodic oxidations of aniline and *N*-alkylanilines in both aqueous and nonaqueous media produce substituted benzidines and diphenylamines by tail-to-tail and head-to-tail couplings, respectively; these are proposed to occur by discrete, parallel reaction pathways. The bulk of the alkyl group is a primary determining factor in the product distribution, but parent concentration, current density, and solution basicity can also be controlling conditions. Electrosynthesis studies show that the benzidines are best prepared in strong acid solution and the diphenylamines in nonaqueous media. In aqueous solution the diphenylamine diimine forms are successively hydrolyzed ultimately to *p*-benzoquinone under the electrolysis conditions.

In the anodic oxidations of aromatic amines, the electrogenerated cation radicals and dications first formed have been found to undergo a variety of decomposition pathways. These pathways are usually very much dependent upon the nature of the medium, primarily aqueous as compared with nonaqueous, and become less diverse as the parent molecule, aniline, is more heavily substituted; the literature has recently been reviewed and a number of generalities have emerged.²

More specifically, for aniline and a number of ring-substituted derivatives Bacon and Adams have recently found that the primary anodic decomposition modes are tail-to-tail and head-to-tail couplings to generate respectively benzidines and diphenylamines.³



In an earlier related study, Galus and Adams found that benzidine formation was a predominant pathway for the anodic oxidation of *N*-methylaniline in aqueous solutions,⁴ but they also found a secondary electrolysis product that was tentatively proposed to be a benzidine-amine adduct. With the goals of possibly relating these two works and extending our knowledge of the oxidation mechanisms of aromatic amines, we have investigated the electrochemistry of aniline and a series of *N*-alkyl derivatives (alkyl = methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, *tert*-butyl), at platinum and carbon paste working electrodes in both aqueous and nonaqueous media. The results of this study are reported herein.

Experimental Section

Instrumentation, Cells, and Electrodes. The instrument used for the electroanalytical studies was a standard operational ampli-

fier-based potentiostat/amperostat employing a three-electrode configuration. Current-voltage and current-time curves were monitored with a Hewlett-Packard 7030A X-Y recorder. Coulometric *n* values were obtained with a Wenking 68FR 0.5 fast-rise potentiostat equipped with a digital integration system and preparative electrolyses were effected with a "home-built" ± 70 V, ± 2.5 A potentiostat.⁵

For electroanalytical experiments, a one-compartment cell containing a carbon paste or platinum working electrode, platinum wire auxiliary, and aqueous sce reference was employed. Coulometric *n* values were taken in a two-compartment cell in which the carbon rod auxiliary electrode was in one compartment and the platinum gauze (MeCN) or carbon cloth (aqueous) working electrode and aqueous sce reference were in the other; the two were separated by a porous glass frit.

Preparative electrolyses were conducted in 400- and 600-ml beakers with a large porcelain cup auxiliary compartment in the center (carbon rod auxiliary electrode). The working electrode was a large graphite felt anode with a platinum foil backing. Contact was made at several points on the working electrode to minimize localized potential gradients. In some cases, the platinum foil was used by itself.

The *n* value and preparative electrolyses were terminated at the point where the electrolysis current was about 1% of the initial value. At times in preparative electrolyses low steady-state currents would occur toward the end; in these cases the experiment was concluded at this time. The magnitudes of these steady-state currents never exceeded a few per cent of the initial electrolysis current levels.

Solvents, Supporting Electrolytes, and Reagents. The acetonitrile (MeCN) was purified by drying over CaH₂ for several days followed by double distillation from P₂O₁₀ (middle 60% fraction); it was always used within 10 days of its distillation. The supporting electrolyte for MeCN oxidations was tetraethylammonium perchlorate (TEAP), obtained either commercially or by reaction between tetraethylammonium hydroxide and perchloric acid, followed by three recrystallizations from water.

Aqueous solutions were prepared from doubly distilled water and reagent grade H₂SO₄ or standard buffer reagents.

The aniline and *N*-alkylanilines were commercial products which were purified by vacuum distillation from zinc dust; they were stored in amber containers. The *N*-*tert*-butylaniline, *N,N'*-diethylbenzidine, and *N,N'*-diisopropylbenzidine were all prepared by standard literature methods. Benzidine and 4-aminodiphenylamine were commercial products that were purified by column chromatography on Woelm neutral alumina with benzene and recrystallization from benzene-ethanol.

All other materials were reagent grade and were used without further purification.

Preparative Electrolyses. Roughly 100 preparative electrolyses were run in both MeCN-TEAP and aqueous acid and buffer solutions. These electrolyses involved all of the compounds studied and were primarily concerned with variations of experimental parameters such as cell design, concentration of electroactive species, current density, electrode material, temperature, and

(1) (a) University of Idaho; (b) University of Georgia.

(2) R. F. Nelson in "Techniques of Organic Chemistry," A. Weissberger and N. L. Weinberg, Ed., Wiley, New York, N. Y., 1974, Chapter 5.

(3) J. Bacon and R. N. Adams, *J. Amer. Chem. Soc.*, **90**, 6596 (1968).

(4) Z. Galus and R. N. Adams, *J. Phys. Chem.*, **67**, 862 (1963).

(5) R. L. Hand and R. F. Nelson, *Anal. Chem.*, submitted for publication.

stirring rates. The goal of this survey was to determine the optimum conditions for generation of the benzidines and diphenylamines derived from *N*-alkylanilines, so the electrolysis conditions given below are those wherein specific product yields were maximized.

I. Electrolyses in MeCN. **A. Benzidine Maximization; Electrolysis of *N*-*tert*-Butylaniline.** The *N*-*tert*-butylaniline (500 mg) was dissolved in 150 ml of MeCN-0.1M TEAP and electrolyzed at a platinum gauze at 1.0 V. Following rereduction to -0.7 V to convert any products to the neutral reduced form and eliminate protons from the medium, cyclic voltammograms run on the solution indicated that roughly half of the *N*-*tert*-butylaniline remained (protons released in the coupling reaction render amine molecules electroinactive *via* protonation during the oxidation process) and that the concentration of *N,N'*-di-*tert*-butylbenzidine in solution was about 20% of the starting amine concentration. In addition, filtration of the solution after electrolysis yielded 53 mg of the benzidine perchlorate salt. The total yield of benzidine in solution and as the perchlorate salt was essentially quantitative in terms of oxidized amine, or about 50% overall.

B. Benzidine Maximization; Electrolysis of *N*-Ethylaniline. *N*-Ethylaniline (1.2 g) was dissolved in 15 ml of MeCN and titrated into an electrolysis vessel containing 300 ml of MeCN-0.1 M TEAP over a 3-hr period. The electrolysis was carried out at a platinum foil electrode (250 cm² area) at an oxidation potential of 1.0 V. During this time a nearly steady current of about 130 mA was sustained; toward the end of the electrolysis the current dropped to a final value of 5-6 mA. After rereduction at -0.75 V the solution was taken to dryness on a steam bath and the residue was extracted with benzene in order to separate the products of the electrolysis from the supporting electrolyte. The benzene solution was chromatographed on a 6-in. column composed of Woelm neutral alumina; unelectrolyzed parent material passed through the column with benzene elution while the benzidine adsorbed strongly. The latter was eluted with dichloromethane and the eluent was then taken to dryness. The product was recrystallized from benzene-ethanol and was positively matched with an authentic sample of *N,N'*-diethylbenzidine. Cyclic voltammograms run on the electrolysis solution before work-up showed the crude yield of *N,N'*-diethylbenzidine to be about 60-70% based on electrolyzed *N*-ethylaniline, or 30-35% overall.

A slightly higher yield of the *N,N'*-diethylbenzidine was obtained by direct electrolysis of 0.12 g of *N*-ethylaniline in 400 ml of MeCN-0.1 M TEAP at an initial electrolysis current of 300 mA in a controlled-potential oxidation at 1.0 V.

C. Diphenylamine Maximization; Electrolysis of *N*-Ethylaniline. *N*-Ethylaniline (4.0 g) was electrolyzed in 600 ml of MeCN-0.1 M TEAP at a platinum foil working electrode (250 cm² area) at a potential of 1.0 V. A current of 600 mA was maintained for 30 min and the electrolysis was then terminated well short of completion. Following rereduction at -0.75 V, cyclic voltammograms were run on the solution, indicating a yield of 450-500 mg of (presumably) *N*-ethyl-4-ethylaminodiphenylamine. This corresponds to approximately a 70% yield based on the amount of current passed. Due to the extreme ease of air oxidation and subsequent decomposition the product could not be isolated.

The cyclic voltammograms also indicated the yield of *N,N'*-diethylbenzidine to be about 15%, again based on the current passed.

A similar electrolysis on a 2.6-g sample of *N*-ethylaniline oxidized at 200 mA for 2 hr resulted in a slightly higher (75-80%) yield of the diphenylamine and a correspondingly lower amount of the benzidine.

II. Electrolyses in Aqueous Acid. **A. Benzidine Maximization; Electrolysis of *N*-Isopropylaniline.** *N*-Isopropylaniline (1.0 g) was dissolved in 600 ml of 3 M H₂SO₄ and electrolyzed at 1.0 V at a carbon cloth working electrode with a platinum foil backing (electrochemical area of roughly 400 cm²). The initial current of 2.1 A slowly dropped over a period of 40 min to a final value of 30-40 mA. Following rereduction at 0.0 V, cyclic voltammograms run on the electrolysis solution showed a large quasireversible couple attributable to quinone-hydroquinone (*vide infra*) and small anodic and cathodic peaks for *N,N'*-diisopropylbenzidine. The solution was made basic with NaOH and extracted several times with benzene. The benzene solutions were combined and taken to dryness on a steam bath. Cyclic voltammograms verified the composition of the residue as being only *N,N'*-diisopropylbenzidine, crude yield 65%. The crude material was purified by column chromatography and matched with an authentic sample for verification.

Electrolyses of 1-g samples of *N*-ethylaniline and *N*-methylaniline under the same conditions resulted in crude yields of the corresponding *N,N'*-dialkylbenzidines of 60 and 50%, respectively; in both cases the balance of the product yield was identified as a quinone-hydroquinone mixture.

B. Preparative Electrolysis of 4-Aminodiphenylamine. 4-Aminodiphenylamine (1.0 g) was dissolved in 3 M H₂SO₄ and electrolyzed at 1.0 V. The initial current of 2.0 A slowly decayed to a low steady-state value (40-50 mA), during which time the solution color changed from an intense greenish-purple to a clear yellow. The electrolysis was terminated at an *n* value of 6, and cyclic voltammograms run on the solution showed that essentially all the parent material had been consumed. The current-voltage curve was identical with that obtained from a solution of hydroquinone in 3 M H₂SO₄; no other peaks were observed. The visible spectrum of the solution showed a broad band with an absorption maximum of 435 nm; an essentially identical spectrum was obtained from electrolyzed benzidine under the same conditions.

After rereduction at 0.0 V, the acid solution was treated with NaHCO₃ to raise the pH to 5.0 and was then extracted with benzene. The benzene was taken to dryness and a black semicrystalline mass (800 mg) resulted. Vacuum sublimation yielded white crystalline material with a mp of 169-170° and an nmr spectrum in D₂O with singlet peaks at 4.6 and 6.6 ppm. The same nmr spectrum was obtained from a solution of authentic hydroquinone in D₂O; the solutions contained some *p*-benzoquinone, formed apparently by air oxidation of the hydroquinone. The melting point matched that of hydroquinone and a mixture melting point showed no depression.

A similar electrolysis of 4-isopropylaminodiphenylamine yielded the same product distribution, namely a large amount of hydroquinone and a trace of benzidine.

C. Anodic Oxidation of 4-Hydroxydiphenylamine. The 4-hydroxydiphenylamine (30 mg) was dissolved in 6 M H₂SO₄ (300 ml) and electrolyzed at 1.0 V at a carbon cloth anode. The initial current of 350 mA slowly dropped to a low steady-state value of 20-30 mA while the color changed from greenish-blue to a pale yellow. After the cessation of current flow, a visible spectrum taken on the solution showed a single broad peak with λ_{max} 435 nm; a cyclic voltammogram of the solution indicated that the major product was hydroquinone-quinone.

Results and Discussion

As stated previously, studies were conducted in both acetonitrile and in aqueous acid. Due to solubility limitations the aqueous work was restricted to pH's of 4 or less. Overall, it was found that quite similar oxidation pathways were operative for the *N*-alkylanilines in both aqueous and nonaqueous media; the differences were more quantitative than qualitative. Further qualitative discrepancies were found, however, in preparative electrolytic studies and so this section is divided into three discrete portions dealing with aqueous electroanalytical, nonaqueous electroanalytical, and preparative electrolytic results.

I. Aqueous Electroanalytical Studies. The series of cyclic voltammograms in Figure 1 indicates the varied behavior of the *N*-alkylanilines as a function of the alkyl group on the amine nitrogen. The current-voltage curve for aniline is essentially identical with those reported by Bacon and Adams;³ the reversible follow-up couple marked "2" is assigned to benzidine and the "1" couple to 4-aminodiphenylamine. This was confirmed by visible spectral curves recorded for electrolyzed solutions of aniline, benzidine, and 4-aminodiphenylamine, as shown in Figure 2. The match up for benzidine is excellent while that for 4-aminodiphenylamine is marginal; however, the absorption curves for the latter are characteristically weak and ill-defined and thus some shifting of the λ_{max} value is to be expected.

The *N*-methyl- and *N*-isopropylanilines show somewhat different behavior in two respects. It is readily

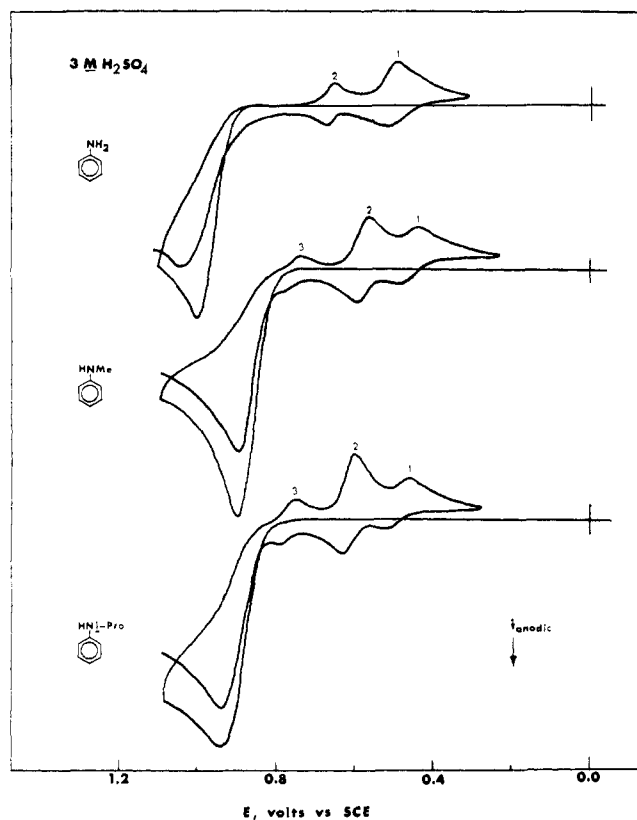


Figure 1. Cyclic voltammograms of aniline and *N*-alkylanilines in 3 *M* H_2SO_4 at carbon paste; scan rate, 100 mV sec^{-1} .

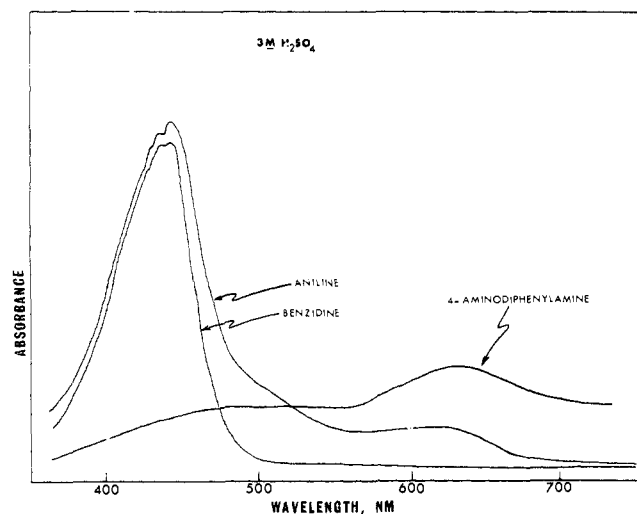


Figure 2. Visible absorption spectra of partially electrolyzed solutions in 3 *M* H_2SO_4 .

apparent from Figure 1 that the ratio of peak currents for the "1" and "2" couples shifts dramatically from aniline to *N*-isopropylaniline. For the former, the major product is 4-aminodiphenylamine, with benzidine being clearly the minor product. However, for *N*-isopropylaniline this distribution is quite the reverse and the benzidine peak is considerably larger than that for the substituted diphenylamine;⁶ the *N*-methyl-

(6) Throughout this paper, the terms "benzidine" and "diphenylamine" will be used as shorthand notation for the correspondingly substituted derivatives of the *N*-alkylanilines; thus, in the case of *N*-isopropylaniline, the term "benzidine" would actually be referring to *N,N'*-diisopropylbenzidine and the "diphenylamine" would be *N*-isopropyl-4-isopropylaminodiphenylamine.

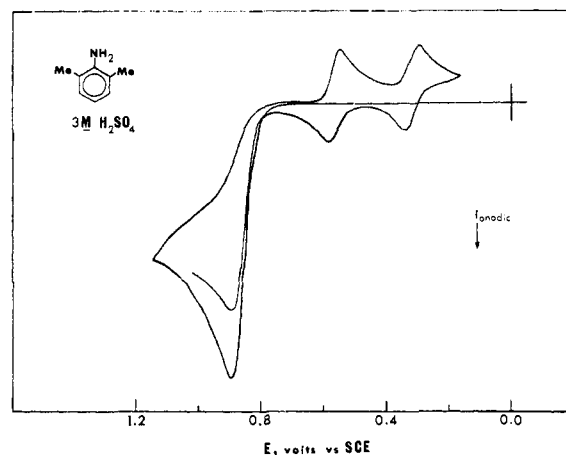


Figure 3. Cyclic voltammogram for 2,6-dimethylaniline in 3 *M* H_2SO_4 at carbon paste; scan rate, 100 mV sec^{-1} .

aniline current-voltage curve is intermediate and supports this trend.

It is not likely that the presence of an *N*-alkyl group would alter the electron distribution in the aromatic ring (HMO calculations have, in fact, verified this⁷), and so the realignment of product distribution under identical solution conditions is largely due to a steric effect. This is not surprising when one considers that head-to-tail coupling, which is the pathway for diphenylamine formation, would be highly dependent upon the bulk of the *N*-alkyl group.

A second apparent difference between aniline and the others is that the *N*-alkylanilines have a third reversible follow-up couple marked "3." This is not visible in the aniline current-voltage curve, but at high sweep rates a blown-up curve shows an analogous couple which is much less reversible than those shown for the *N*-alkylanilines. This unstable couple matches in position and reversibility the oxidation wave for 2,4'-diaminobiphenyl (the *o,p*-benzidine from aniline); in addition, the oxidation of 2,6-dimethylaniline shows no such couple under comparable conditions.

The current-voltage curve for the latter compound, shown in Figure 3, illustrates a further aspect of the steric requirements for these coupling reactions. Note that the relative amounts of benzidine and diphenylamine are considerably different than for aniline itself; for 2,6-dimethylaniline the benzidine/diphenylamine ratio is much greater. This is again consistent with steric hindrance of the amino group inhibiting the head-to-tail coupling route and thus enhancing tail-to-tail benzidine formation; since both ortho positions are substituted the *o,p*-benzidine cannot form.

The cyclic voltammetric curves, then, indicate that the product distribution depends very strongly upon the steric environment of the amino group, the benzidine/diphenylamine ratio increasing with the degree of substitution around and on this site.

The electroanalytical data for the *N*-alkylanilines in 3 *M* H_2SO_4 are shown in Table I. The electrochemical characteristics of a model two-electron compound, *N,N,N',N'*-tetramethyl-*p*-phenylenediamine, are also given for purposes of comparison. Meaningful data could not be obtained for *N-tert*-butylaniline due to the

(7) A. K. Carpenter and R. F. Nelson, unpublished data.

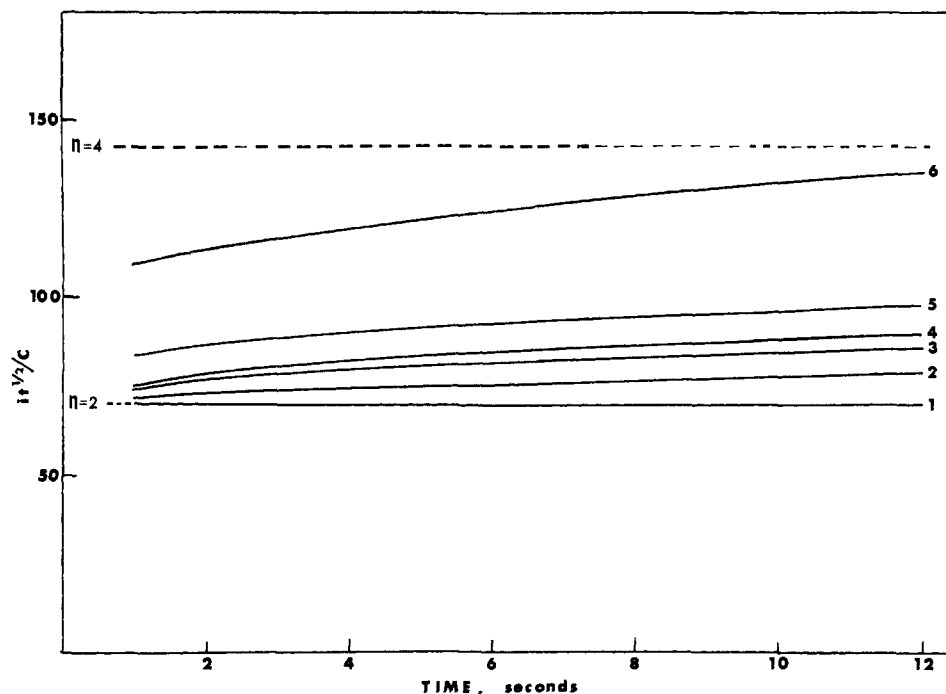

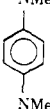


Figure 4. Chronoamperometric data taken at carbon paste for the following compounds: (1) *N,N,N',N'*-tetramethyl-*p*-phenylenediamine; (2) *N*-isopropylaniline; (3) *N*-*n*-butylaniline; (4) *N*-ethylaniline; (5) *N*-methylaniline; (6) aniline. Individual points are omitted to avoid confusion.

Table I. Electroanalytical Data for *N*-Alkylanilines in 3 *M* H_2SO_4

HNR 	R =	$E_{p/2}^a$	$i_p/V^{1/2}C^b$	$it^{1/2}/C^c$	n value ^d	
					$5 \times 10^{-4} M$	$5 \times 10^{-3} M$
H		0.96	54.8–59.3	109–135	4.0	4.0
Me		0.84	55.0–58.3 (R)	83.5–100	3.3	3.9
Et		0.86	47.3–50.0 (R)	74.7–91.5	2.9	3.4
<i>n</i> -Pr		0.85	48.8–51.7 (R)	74.3–86.4	2.8	3.3
<i>i</i> -Pr		0.89	31.3–43.2	75.0–80.3	2.3	2.6
<i>n</i> -Bu		0.85	48.3–50.2 (R)	78.7–92.2	3.0	3.4
			41.5	70.0	2.02	1.96

^a In *V* vs. *sec* at a carbon paste working electrode. ^b Data taken from linear scan chronoamperometry curves. The (R) denotes a random variation whereas in the other cases there is a regular trend toward higher values as the sweep rate is decreased. ^c Data taken from chronoamperometric current–time curves; in all cases there is a trend to higher values with increasing time. ^d Data derived from controlled-potential exhaustive electrolyses of solutions with the concentrations denoted; the values given are precise to ± 0.2 *n* value unit. ^e Model two-electron oxidation in 3 *M* H_2SO_4 .

broadness of its anodic wave and its proximity to background. The peak current and chronoamperometry data indicate that all of the anilines have *n* values of 2 at short times; these then increase beyond that as the electrochemical time gates proceed. The peak current data are generally random and run slightly above *n* = 2, with the exception of the isopropyl derivative. This latter compound has $i_p V^{-1/2} C^{-1}$ quotients substantially below the value for two electrons at high sweep rates; however, as *V* decreases the quotient increases and finally reaches the *n* = 2 value at about a 50 *mV sec*⁻¹ sweep rate. This may be due to the fact that this com-

pound has two closely spaced waves which merge to a single peak at low sweep rates.

The chronoamperometric data are more sensitive to changes in *n* values in the 1–12 sec electrolysis time gate available and again indicate a fast two-electron process with a slow increase in *n* following this. Some of the chronoamperometry data in Table I are plotted in Figure 4 to demonstrate the variation in short-time *n* values as a function of the size of the *N*-alkyl group. One sees that the *n* value for aniline is well above 2 even at *t* = 1 sec and approaches *n* = 3–4 at longer times. Conversely, the isopropyl derivative is near *n* = 2 at all times, showing only a slight increase as *t* becomes greater. For the other *N*-alkylanilines, the trend is regular in that the *n* value becomes greater and more variable as the bulk of the *N*-alkyl group diminishes. All the curves shown, however, very nearly approach *n* = 2 at short times with the exceptions of aniline and *N*-methylaniline.

The coulometric data reflect the long-term behavior of these systems and more or less verify what was seen in the short-time experiments, namely that as the bulk of the *N*-alkyl substituent diminishes the *n* value increases. There is also a significant shift toward higher *n* values at higher parent concentrations, indicative of a concentration-dependent process.

As will be seen eventually, an *n* value of 4 would correspond to exclusive formation of diphenylamine whereas quantitative benzidine production is indicated by an *n* value of 2. Thus the *n* values give a semi-quantitative evaluation of the product distributions from these electrolyses. Cyclic voltammograms were run on all of these solutions following exhaustive electrolysis and the peak currents for the benzidine and diphenylamine oxidations (the latter was actually monitored with the quinone–hydroquinone couple) generally correlated well with the *n* value data. One notable ex-

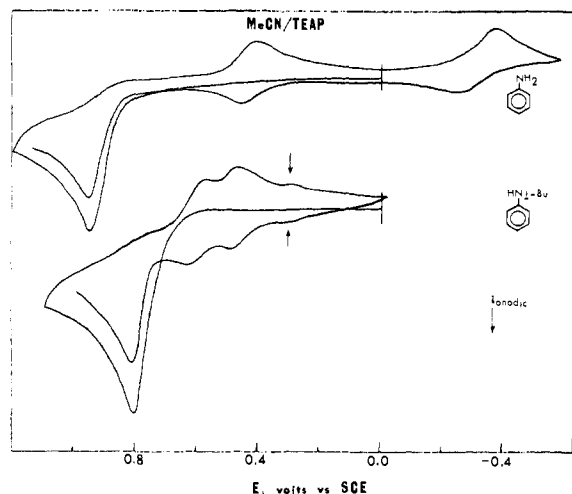


Figure 5. Cyclic voltammograms of aniline and *N-tert*-butylaniline in MeCN-0.1 *M* TEAP at platinum; scan rate, 150 mV sec⁻¹.

ception is the aniline system, which showed small amounts of benzidine present even though *n* values of 4.0 were obtained. In addition, the 5×10^{-3} *M* *N*-methylaniline solution appeared to contain about 20% benzidine, which is somewhat more than what would be expected based on the *n* value data.

The trend in *n* values over the series of compounds for a given concentration also follows the diphenylamine-benzidine distribution seen on cyclic voltammograms of unelectrolyzed solutions quite closely, *i.e.*, aniline, which forms primarily 4-aminodiphenylamine, has a high *n* value and *N*-isopropylaniline, from which the corresponding benzidine is largely generated, approaches the base *n* value of 2. These data imply that the diphenylamines formed in these systems may be decomposing to other electroactive species, while the benzidines formed are stable as the dications. In fact, coulometric data showed, for example, *n* values of 2.0–2.2 for benzidine and *N,N'*-diisopropylbenzidine and about 6 for 4-aminodiphenylamine. Thus, an *N*-alkylaniline that yields primarily the *N,N'*-dialkylbenzidine as the coupling product would have an *n* value close to 2; if the corresponding *N*-alkyl-4-alkylaminodiphenylamine were the major product the *n* value would be higher. The phenomenon of higher *n* values at higher parent concentrations implies that the product distributions are concentration dependent and thus that two parallel mechanisms may be operative in these systems. Since higher *n* values appear to be associated with diphenylamine formation, high concentrations seem to favor the latter over the corresponding benzidines.

The electroanalytical data lead to the conclusion that the electrode reactions of aniline and the *N*-alkylanilines in strong acid involve a fast two-electron process (it may also be two one-electron steps in an ECE pathway) followed by a slower decomposition reaction leading to other electroactive species in some cases. These decomposition pathways appear to involve the diphenylamines formed, while the corresponding benzidines are stable as the dications under these conditions.


II. Nonaqueous Electroanalytical Studies. All of the nonaqueous studies were conducted in MeCN-0.1 *M*

TEAP. Typical cyclic voltammograms for aniline and *N-tert*-butylaniline are shown in Figure 5; again, the trend is from diphenylamine to benzidine as the *N*-alkyl group becomes bulkier. The shift is even more marked in MeCN than in strong acid, as can be seen in Figure 5. For aniline, the only visible product is 4-aminodiphenylamine; the quasireversible couple at -0.2 to -0.4 V is due to protons liberated in the coupling reaction. All of the *N*-alkylanilines show a mixture of benzidine and diphenylamine, increasing toward the former with bulkier groups until only a small amount of diphenylamine can be seen (arrows in Figure 5) in the cyclic voltammogram for *N-tert*-butylaniline; *N,N'*-di-*tert*-butylbenzidine is by far the major product and is represented by the two reversible follow-up couples at 0.5 to 0.7 V. In preparative electrolyses, the benzidine is the only product isolated or detected in solution (see Experimental Section).

The current-voltage curves, then, are essentially identical in strong acid and MeCN, with the exceptions that they are somewhat better defined in the former medium and the product distribution appears to be greater in breadth in the latter.

The electroanalytical data for these compounds are shown in Table II. As for the strong acid systems, the

Table II. Electroanalytical Data for *N*-Alkylanilines in MeCN-TEAP

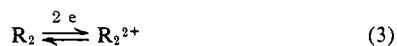
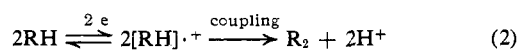
R =	$E_{p/2}^b$	$i_p/V^{1/2}C^c$	$it^{1/2}/C^d$	<i>n</i> values ^e		
				10 ⁻² <i>M</i>	10 ⁻³ <i>M</i>	10 ⁻⁴ <i>M</i>
H	0.90	31.0	56.0	1.10	1.31	1.52
Me	0.78	31.0	60.0	1.13	1.07	0.99
Et	0.77	31.5	59.5	1.03	0.92	0.92
<i>n</i> -Pr	0.76	31.3	58.5	0.93	0.92	0.90
<i>i</i> -Pr	0.78	32.5	57.5	0.99	0.97	0.94
<i>n</i> -Bu	0.76	30.0	56.0	0.99	0.94	0.92
<i>t</i> -Bu	0.79	29.5	57.5	0.95	0.93	0.94
NMe ₂ 		33.5	60.0	1.01	0.98	0.99

^a Model one-electron compound in MeCN-TEAP. ^b In V vs. sce, taken at a sweep rate of 200 mV/sec at platinum; values shift anodic with increasing scan rate. ^c Average values from linear scan voltammograms with sweep rates varied from 33.3 to 350 mV/sec. ^d Average values taken from current-time curves (1–8 sec); there is a slight increase (~5%) with increasing time. ^e Coulometric *n* values; in all cases, low steady-state currents were obtained at the end of the electrolysis (typically 1–5% of the initial current value); values are precise to ± 0.05 *n* value unit.

$E_{p/2}$ values have no great meaning since the reported numbers are considerably shifted from the true reversible $E_{p/2}$'s due to the rapid follow-up reactions involved. The trend in these values does, however, characterize the electron-donating nature of the *N*-alkyl groups, thus shifting the $E_{p/2}$'s less anodic relative to aniline, as well as the twisting effect of the bulky isopropyl and *tert*-butyl groups which moves the $E_{p/2}$ values more anodic. Again, the *N,N,N',N'*-tetramethyl-*p*-phenylenediamine is included for purposes of comparison, since its first anodic wave is a reversible one-electron process with no chemical complications in MeCN.

In contrast to the aqueous data, the peak current and chronoamperometric quotients show little variation with time (or sweep rate) and all are close to the model system one-electron standards. The n value data, taken over a two orders of magnitude concentration range, also indicate one-electron processes for these molecules and again there is a slight but consistent trend toward higher n values at higher parent concentrations, particularly in those systems in which diphenylamines are generated to an appreciable extent. The data for aniline are an exception to this in that these n values are appreciably above one and increase markedly with decreasing concentration.

The n values of unity for the other compounds is consistent with a classic ECE two-electron overall coupling reaction where one proton per parent molecule is released in the oxidation process, the coupled product is oxidized at the potential of the primary oxidation and the parent is at least a moderately strong organic base. The true n value of 2 is reduced to 1 by the fact that the liberated protons attack other parent molecules and render them electroinactive according to the general scheme



Overall, there is a transfer of four electrons with the result that four parent molecules are removed from the system.

It is noteworthy that the n values are much lower in MeCN than in strong acid, thus suggesting a difference in long-time oxidation pathways. This fact, coupled with the behavior of aniline in the nonaqueous system (which is probably about 10–20 mM in residual water), leads to the hypothesis that the decomposition reactions involving the diphenylamine coupling products may be hydrolyses. These are well documented for diphenylamines⁸ and this would also explain the n value data for aniline, since hydrolysis in MeCN electrolyses would lead to higher n values at lower parent concentrations, the water/parent amine ratio being high under these conditions. In fact, the preparative electrolytic studies described in the following section verified this hypothesis.

III. Preparative Electrolytic Studies. The electroanalytical studies indicated that the major products obtained from the anodic oxidations of aniline and the N -alkylanilines are diphenylamines and benzidines in both aqueous and nonaqueous media, the product ratio depending largely upon the bulk of the alkyl group. It was also noted that decomposition reactions predominated in systems where diphenylamines were present in appreciable amounts and led to higher n values; the data pointed to these reactions being hydrolyses. It also was shown that there is a parent concentration effect in that n values were somewhat higher at increased parent levels. Unresolved questions involved the nature of the diphenylamine decomposition products, the intermediates and pathway leading to further electroactive species, other factors affecting the

diphenylamine/benzidine product ratio and the conditions necessary for exclusive generation of one or the other of the two products.

Preparative and exhaustive electrolyses were carried out in both strong acid and MeCN with parent concentrations ranging from 10^{-4} to 10^{-1} M. In some cases, product yields were evaluated from cyclic voltammetric curves run on solutions following electrolysis and in other cases products were actually isolated. In the course of conducting over 100 preparative electrolyses, it became apparent that several factors beside the bulk of the N -alkyl group could strongly affect the product distribution, among these being parent concentration, current density (CD), and solvent basicity (or, rather, the types of bases present in solution).

The parent concentration and CD effects were observed in both strong acid and MeCN. It was found that regardless of the nature of the N -alkyl group benzidines are more likely to be formed at low concentrations (10^{-3} to 10^{-4} M) and/or at high CD's, but as the parent level rises and/or the CD is lowered the diphenylamine/benzidine ratio increases. This is shown graphically in Figure 6, which is composed of cyclic voltammograms taken on partially and completely electrolyzed solutions of varying concentrations of N -ethylaniline in MeCN. In the most dilute solution, which was electrolyzed at maximum current throughout (initial CD = 4 mA cm²) and carried to completion, the only product visible is N,N' -diethylbenzidine; no diphenylamine is observed. Curves B and C were obtained from solutions containing intermediate concentrations of N -ethylaniline, both having been electrolyzed at a CD of 2 mA cm² for 105 sec. It is apparent, although the curves are not sharply defined, that in the more dilute solution the diphenylamine/benzidine ratio is lower. Only the first benzidine wave can be seen, since the anodic current drops sharply after that due to electrolysis of excess parent. Curve D is for a more concentrated solution electrolyzed at a CD of 0.8 mA cm² for 120 min. With a low CD and high parent concentration the diphenylamine is formed almost exclusively.

Other experiments confirmed the fact that both CD and parent concentration are instrumental in the control of product distributions in these systems. Thus, when a dilute solution was electrolyzed at low CD, both benzidine and diphenylamine were generated; the same was found to be true for a concentrated solution at high CD. Cyclic voltammograms run on solutions during electrolysis also showed that as the oxidation proceeded, the relative amount of benzidine would increase. Thus, in runs where we were attempting to maximize diphenylamine production, the electrolyses were terminated well before completion, generally at the one-fourth to one-third point.

The fact that benzidines could only be generated in the absence of diphenylamines in dilute solutions posed something of a problem for their preparation on gram-quantity scales, since this would require unusually large solution volumes to keep the parent concentration below the millimolar level. Appreciable quantities of benzidines were obtained, however, by electrolyses where the parent amine was titrated into the electrolytic cell, as described in the Experimental Section for N -ethylaniline. In this way, gram quantities of the N -

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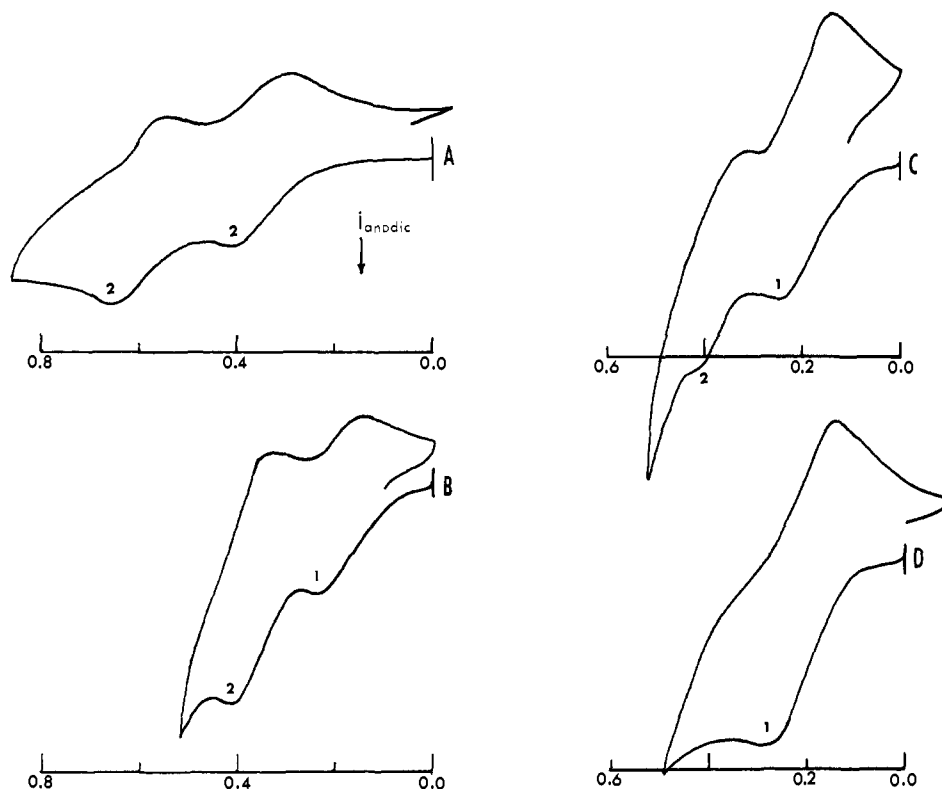


Figure 6. Cyclic voltammograms of electrolyzed solutions (volume = 300 ml) of *N*-ethylaniline in MeCN–0.1 *M* TEAP; scan rate, 100 mV sec⁻¹ for all curves. All electrolyses were done at carbon cloth with a platinum backing; electrochemical area, ca. 250 cm². The abscissa is the scan potential in V vs. sce. The peaks marked "1" are for the diphenylamine and those marked "2" are for the benzidine: curve A, 0.12 g, complete electrolysis; curve B, 0.2 g, electrolyzed at 500 mA for 105 sec; curve C, 1.0 g, electrolyzed at 500 mA for 105 sec; curve D, 2.6 g, electrolyzed at 200 mA for 120 min.

alkylanilines could be converted to the corresponding benzidines, since the CD would be maximal and the parent concentration always low.

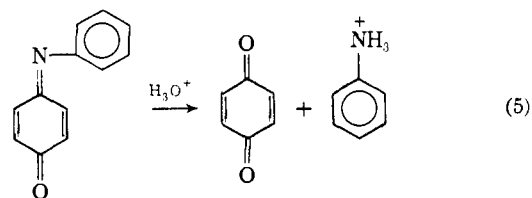
The foregoing studies, which were conducted in MeCN, showed that the nonaqueous media could be manipulated to yield either of the two products to the virtual exclusion of the other on a preparative scale. However, work-up problems are appreciable due to the presence of large amounts of parent and the ready air oxidation of the diphenylamines.

Bacon and Adams showed clearly that the relative amounts of benzidine and 4-aminodiphenylamine generated from aniline vary considerably with pH, the benzidine being the minor product at higher pH's (0–4), but growing in quantity with increasing acid strength.³ This observation was based on cyclic voltammetry data and we have found the same trend in preparative electrolyses with both aniline and the *N*-alkylanilines, although the change in product distribution is not as broad as that observed in cyclic voltammetry experiments; this is no doubt due to the different diffusion and electrolysis conditions surrounding the two techniques.

Product isolation work in aqueous solutions met with only mixed success. Since in strong acid the species being electrolyzed is the protonated amine, aqueous electrolyses have the distinct advantage of going to completion with little or no parent left in solution. The *N,N'*-dialkylbenzidines were, in fact, generated and isolated in yields of 50% or better (see Experimental Section), but no success was realized in diphenylamine maximization experiments. In solu-

tions where it was anticipated that large quantities of diphenylamines would be generated, such as aniline in 0.1 *M* H₂SO₄, cyclic voltammograms following exhaustive electrolysis showed only a single product whose redox behavior at different pH's was identical with that of quinone–hydroquinone. The latter product was further identified by isolation and matching with an authentic sample through melting point and spectral data. This product was found in *all* the *N*-alkylaniline preparative electrolyses in acid solutions run under conditions where diphenylamines would be expected to form, and so it is apparent that any general mechanism for these systems must incorporate the quinone–hydroquinone couple as an end product.

Leedy and Adams have shown that compounds such as 4-alkoxy- and 4-hydroxydiphenylamines will, in the quinoneimine forms (generated *via* two-electron oxidations of the parent molecules), be hydrolyzed and cleaved to give a mixture of *p*-benzoquinone and aniline.^{8a}

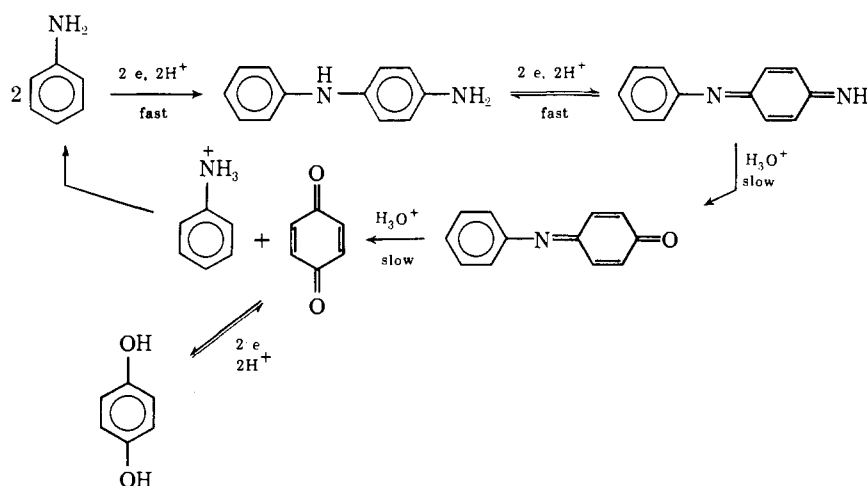


It has recently been shown that, in contrast, the oxidation of 4-aminodiphenylamine in MeCN is rather straightforward and involves mainly electron and

Table III. Some Typical Electrolysis Conditions and Corresponding Product Yields

Compd (amount, g)	Electrolysis conditions	Product(s) (% yield) ^b
Aniline (1.0) ^a	MeCN-TEAP, low CD	4-Aminodiphenylamine (40)
Aniline (1.0) ^a	0.05 M H ₂ SO ₄ , high or low CD	<i>p</i> -Benzoquinone (90-100)
Aniline (0.4) ^a	6 M H ₂ SO ₄ , high CD	<i>p</i> -Benzoquinone (80-90), benzidine (10-20)
<i>N</i> -Methylaniline (1.0) ^a	6 M H ₂ SO ₄ , high CD	<i>p</i> -Benzoquinone (50), <i>N,N'</i> -dimethylbenzidine (50)
<i>N</i> -Ethylaniline (1.2) ^a	MeCN-TEAP, parent titrated into electrolysis vessel over 3 hr, low CD	<i>N,N'</i> -Diethylbenzidine (60-70)
<i>N</i> -Ethylaniline (0.12) ^a	MeCN-TEAP, high CD	<i>N,N'</i> -Diethylbenzidine (70-80)
<i>N</i> -Ethylaniline (4.0) ^c	MeCN-TEAP, low CD	<i>N</i> -Ethyl-4-ethylaminodiphenylamine (70), <i>N,N'</i> -diethylbenzidine (15)
<i>N</i> -Ethylaniline (1.0) ^a	6 M H ₂ SO ₄ , high CD	<i>p</i> -Benzoquinone (40), <i>N,N'</i> -diethylbenzidine (60)
<i>N</i> -Isopropylaniline (1.0) ^a	3 M H ₂ SO ₄ , high CD	<i>p</i> -Benzoquinone (35), <i>N,N'</i> -diisopropylbenzidine (65)
<i>N-tert</i> -Butylaniline (0.5) ^a	MeCN-TEAP, high CD	<i>N,N'</i> -Di- <i>tert</i> -butylbenzidine (100)

^a Controlled-potential electrolysis; "high" or "low" CD designates initial value. ^b Yield based on amount of electrolyzed parent. ^c Constant-current electrolysis; terminated well short of completion.



(6)

proton transfer reactions.⁹ In aqueous solution, however, hydrolysis of the quinonediimine form could easily occur to generate the quinoneimine (the oxidized state of 4-hydroxydiphenylamine) which would then go on to the products above. In this way, starting with aniline one would have a fast two-electron process, probably *via* an ECE reaction or some nuance thereof, to generate the 4-aminodiphenylamine quinonediimine. Through successive hydrolysis steps this would be converted to a mixture of *p*-benzoquinone and aniline; since the potential would be set for the oxidation of aniline the latter would be recycled through the same process again and again. This would finally result in an *n* value of 4 (note the data in Table I) if all of the aniline were converted to *p*-benzoquinone; in fact, small amounts of benzidine are always formed (not shown below), so a slightly lower *n* value should result.

This pathway was further verified by preparative electrolyses of the 4-amino- and 4-hydroxydiphenylamines. In both cases the major product was *p*-benzoquinone, with small amounts of benzidine being detected spectroscopically (see Experimental Section) and on the cyclic voltammograms of the electrolyzed solutions; the latter product would arise from tail-to-tail coupling following the oxidation of the aniline generated by hydrolytic cleavage.

The same pathway could also apply to the *N*-alkyl-

anilines studied, with the exception that the *N,N'*-dialkylbenzidines would be generated in substantial amounts by both the primary oxidation process and by additional parent regenerated through the hydrolysis steps.

It was also found through exhaustive electrolytic studies of 4-hydroxydiphenylamine in 6 and 0.1 M H₂SO₄ that these hydrolysis reactions are markedly pH dependent, as would be anticipated, and that the rate constants, which appear to be on the order of 10⁻²-10⁻¹ sec⁻¹, increase with increasing pH. We have also qualitatively observed that as the *N*-alkyl groups become more bulky the hydrolysis rates for the corresponding diphenylamines diminish, presumably due largely to a steric effect. Unfortunately, it is also true that diphenylamine formation is enhanced at higher pH's and so it is apparent that the conditions that are optimal for diphenylamine production are also highly conducive to the decomposition reactions.

As can be seen from the preparative electrolyses described in the Experimental Section, considerable success was achieved in generating each product in substantial yield in the virtual absence of the other, this in spite of the many pitfalls described above. Benzidine yields were maximized by operating at low parent concentrations, high CD, and low solution basicity. The bulk of the *N*-alkyl group is of great importance, but this can be circumvented by careful manipulation of the above conditions. Diphenylamines were maximized

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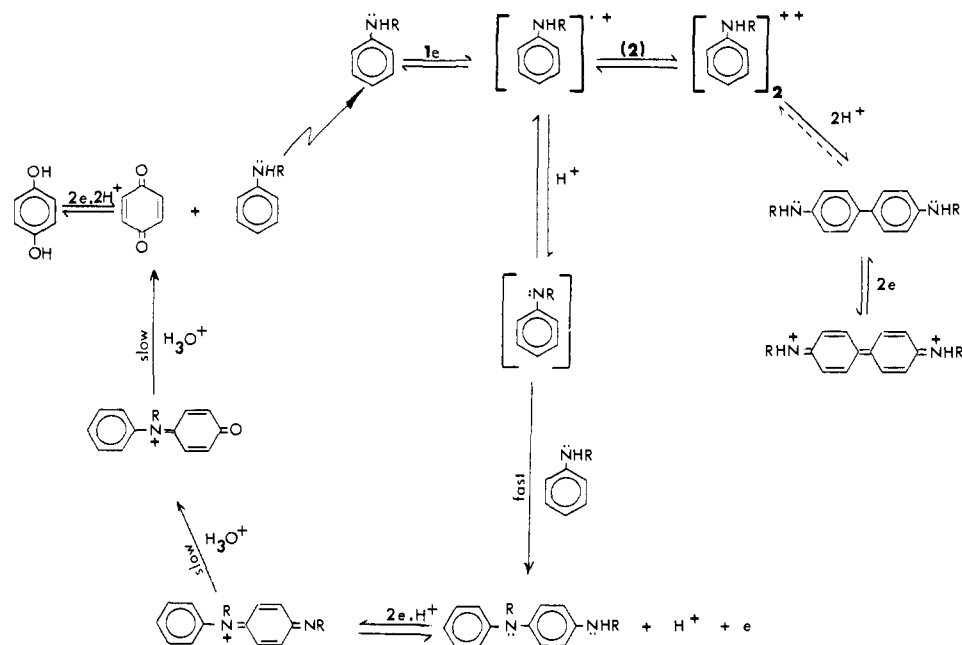


Figure 7. Proposed anodic oxidation pathway for aniline and the *N*-alkylanilines in aqueous and nonaqueous media.

under the opposite conditions, *i.e.*, high parent concentration, low CD, and high solution basicity, but isolation of these products is rendered difficult by hydrolysis reactions and facile air oxidation. Some typical electrolysis conditions and product yields are shown in Table III.

Efforts are presently under way involving diphenylamine maximization electrolyses and product isolations carried out under inert atmospheric conditions. These studies will hopefully lead to appreciable yields of these unique *N*-alkyl-4-alkylaminodiphenylamines, which may have applications as photographic developers and rubber antioxidants, since they are basically substituted *p*-phenylenediamines. To the best of our knowledge, they have not been synthesized by other means.

Conclusions

The generalized mechanism for aniline and the *N*-alkylanilines shown in Figure 7 has been distilled from the electroanalytical and preparative data discussed in the previous section. Due to the different solution conditions for strong acid and MeCN electrolyses, this general mechanism is not completely balanced with respect to protons. According to this scheme, the electrogenerated cation radical is susceptible to two competitive processes, namely dimerization and deprotonation.

The dimerization process, as depicted, is favored by a high cation radical concentration. Similar monomer-dimer equilibria have been well characterized for stable anion and cation radicals *via* epr and visible spectral data,¹⁰⁻¹⁶ and it is not unreasonable to propose such

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intermediates for systems with unstable cation radicals. In the cases of the latter, however, bond formation can occur and aromaticity can be reached by loss of two protons; the driving force for this process would depend upon the unpaired electron densities at reactive sites (such as the para ring positions) and could be either large or small. The dashed reverse arrow for the proton loss is not meant to imply that this is an equilibrium process, but that there may be some sort of acid effect not presently defined whereby systems involving such coupling reactions can be stabilized by strong acid solutions; this proposal is based on a number of spectral studies in which organic cation radicals known to undergo coupling reactions have been shown to be appreciably less reactive in solutions of strong Lewis and Brønsted acids than in more conventional media.¹⁷⁻²¹ Once formed, the benzidines undergo reversible two-electron oxidation (two one-electron steps in MeCN) to the stable diimine species.

An alternative dimerization-type pathway not shown would involve formation of a dimer cation radical by association of an amine cation radical with a parent molecule. These dimer cation radicals have been reported in spectral studies of several aromatic hydrocarbon systems²²⁻²⁶ and radical-parent interactions

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have frequently been proposed as alternatives to radical-radical couplings in electrochemical mechanisms. In these aniline systems, however, it appears that association of the electrogenerated cation radicals with the parent molecules would result in the deprotonation route discussed below being followed.

If the solution conditions are such that deprotonation of the cation radical is favored, then the alternate pathway is followed. The deprotonation is not spontaneous but must be effected by some base in the system; obviously, the stronger the base present the greater the likelihood will be that this is the preferred pathway. In our systems, the bases would probably be the parent amine in MeCN and either sulfate or bisulfate in the aqueous solutions (where essentially all the parent is protonated). Similar base-dependent processes have been previously reported for diphenylamine²⁷ and carbazole²⁸ oxidations in MeCN and so it may be that this is a general reaction pathway for anodic oxidations.

The resultant arylamino free radical is then depicted as reacting with a parent molecule to generate another intermediate, not shown, which leads to the substituted diphenylamine by loss of an electron and a proton, not necessarily in that order. This species then is oxidized to the diimine form, which may undergo the hydrolysis steps previously discussed to generate, eventually, *p*-benzoquinone and the parent amine. The latter is then recycled through the same process.

The key to the pathway which is followed in a given electrolysis appears to be the radical/parent ratio near the electrode surface. When this ratio is low the diphenylamine pathway is followed and when it is high the benzidine is the principal product. Thus, the "ideal" electrolysis conditions for diphenylamine production are high parent concentration and low CD, while the opposite conditions favor the benzidine.

This mechanism bears some resemblance to the previously reported literature on aniline oxidations in aqueous acid²⁹ and MeCN³⁰ solutions. In both cases,^{29,30} however, as well as in a number of other chemical and electrochemical oxidation studies,³¹ the oxidation pathway is depicted as going ultimately to a greenish-black substance which has been characterized as an oligomer of aniline, usually in the form of a linear octamer called emeraldine. We anticipated the formation of this substance, particularly in our strong acid electrolyses, and in fact a black precipitate with a deep green tinge was obtained from both aniline and 4-amino-diphenylamine. Isolation experiments indicated that at least a major constituent of this black precipitate is a quinone-hydroquinone mixture, known as quinhydrone. In addition, it is well known that oxidized benzidine salts (such as a dication sulfate salt) have a deep green color. Also, formation of oligomers will not give an *n* value greater than 2 unless there is considerable condensation *via* intramolecular cross-coupling reactions; *n* values of 3-4 are definitely not compatible with products such as the linear aniline octamer emeraldine.

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(31) These oxidations have been summarized in ref 2.

Therefore, we propose that the anodic oxidations of aniline and the *N*-alkylanilines lead to products composed primarily of mixture of quinone-hydroquinone and benzidine salts, the composition being contingent upon the parent molecule. This holds primarily for aqueous acid oxidations, but may also apply to MeCN electrolyses where the water level is comparable to the concentration of the amine being studied. After completing this study and having run many electrolyses under so many different conditions, it seems likely to us that the aniline electrolysis product variously characterized as "aniline black," "emeraldine," etc., is largely, if not completely, composed of the mixture cited above, *i.e.*, mainly quinhydrone with a small amount of benzidine salt.

In their previous study of the *N*-methylaniline oxidation in aqueous solutions, Galus and Adams reported that the primary electrolysis product was *N,N'*-dimethylbenzidine, but that the oxidized form of the benzidine interacted with excess *N*-methylaniline to form an adduct of unspecified structure.⁴ Their experiments and conclusions are consistent with this adduct actually being the corresponding diphenylamine from *N*-methylaniline, but we observed a persistent blue color in some of our aqueous acid benzidine maximization electrolyses where the benzidines would be in the presence of large excesses of parent. This color could not be ascribed to the various forms of the benzidines or diphenylamines expected to be generated, but no anomalous products were isolated from these blue solutions. Similar benzidine-amine adducts have also been proposed for *N,N*-dimethylaniline oxidations,^{32,33} a system where head-to-tail coupling is not a viable pathway, so this point in the Galus and Adams study must remain unresolved. While their reported benzidine-amine adduct could be the diphenylamine, namely 4-methylamino-*N*-methyldiphenylamine, it is not necessarily so. We are at present pursuing the isolation and structure elucidation of these purported adducts in hopes of clarifying this problem area.

Studies are also under way to establish the benzidine/diphenylamine ratios for ortho-, meta-, 3,5-, and 2,6-substituted anilines in order to more clearly elucidate the steric and electronic requirements of these interesting parallel reaction pathways. Preliminary results indicate that in aqueous acid solution all of the above aniline derivatives form the corresponding benzidines and diphenylamines, but the relative amounts vary considerably. It would also be anticipated, if the mechanism shown in Figure 7 is correct, that the benzidine/diphenylamine ratio would depend upon the basicity of the parent aniline (and hence the corresponding cation radical), the ratio being smaller for more acidic amines. Although it is difficult to discern electronic effects from steric factors in ring-substituted anilines, cyclic voltammetric data indicate that this is the case in aqueous acid at carbon paste. Quantitative results will be reported in future communications.³⁴

Acknowledgments. Support for this research through

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(34) NOTE ADDED IN PROOF. It should be pointed out that benzidine and several of its derivatives are known to be carcinogenic and so great care should be taken in handling these materials.

National Science Foundation Grant No. GP-31199 is gratefully acknowledged. Samples of the substituted benzidines were prepared by A. K. Carpenter and the

N-tert-butylaniline was synthesized by P. Berkenkotter. Special thanks are due to Dr. R. N. Adams and Dr. D. E. Smith for their support and encouragement.

Oxidation and Fragmentation of Some Phenyl-Substituted Alcohols and Ethers by Peroxydisulfate and Fenton's Reagent¹

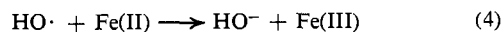
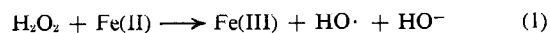
Maurice E. Snook and Gordon A. Hamilton*

Contribution from the Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802. Received July 24, 1973

Abstract: The mechanisms of the reactions of the hydroxyl radical (generated from Fenton's reagent) and the sulfate radical anion (generated thermally from $S_2O_8^{2-}$), with various phenyl-substituted alcohols have been examined in some detail. The reaction of 1-phenylalkanols ($PhCHOHR$) with $XO\cdot$ ($X = H$ or SO_3^-) at pH 1.8 yields some $PhCOR$, but benzaldehyde is the major product when R is isopropyl or *tert*-butyl and a minor product when R is ethyl. The total yield of carbonyl products is 70–100%. From competition experiments it was determined that all the 1-phenylalkanols are 5–6 times more reactive than 2-propanol toward $HO\cdot$, and $PhCHOHCH_3$ is 22 times more reactive than 2-propanol toward $SO_4^{\cdot-}$. Para-substituted 1-phenylethanols show relative reactivities toward $HO\cdot$ increasing in the sequence: $CN < Br < H < C_2H_5$. The tertiary alcohol, $PhC(CH_3)_2OH$, is more reactive toward $XO\cdot$ than 2-propanol and is converted in good yield to $PhCOCH_3$, but *tert*-butyl alcohol is relatively unreactive and gives only a small amount of acetone. Ethers of 1-phenylalkanols are also more reactive toward $XO\cdot$ than 2-propanol and yield both fragmentation and ketone products. Secondary and tertiary alcohols of structure $Ph(CH_2)_nC(OH)(CH_3)R$ show high reactivity toward $XO\cdot$ and give fragmentation products when $n = 0-2$ and $R = H$ or CH_3 ; when $n = 3$ and $R = CH_3$, however, the alcohol has a reactivity similar to *tert*-butyl alcohol. 1-Deuterio-1-phenylalkanols show the same relative reactivities toward $HO\cdot$ as their hydrogen analogs but $PhCDOHCH(CH_3)_2$ gives a higher ratio of benzaldehyde (completely $PhCDO$) to ketone than does $PhCHOHCH(CH_3)_2$. Product studies indicate that the fragmentations occur by cleavage of alkyl radicals. The electrophilic radicals ($XO\cdot$) generated by several different methods, in the presence or absence of transition metals, give essentially the same reaction characteristics. The presence of $Fe(III)$, $Cu(II)$, $Hg(II)$, or complexing agents does not affect the yields, relative reactivities, or product ratios obtained with Fenton's reagent at pH 1.8, but increasing the pH to 4.6 does; the pH effects were shown to be largely due to the phenyl-substituted alcohol acting as a catalyst for the conversion of $Fe(II)$ to $Fe(III)$ at higher pH's. The characteristics of the reaction of thermally generated $SO_4^{\cdot-}$ are unchanged from pH 1.5 to 11. The results are interpreted in terms of a mechanism involving a resonance stabilized cation radical as an intermediate in the reactions of these reactive phenyl-substituted alcohols and ethers with $XO\cdot$; the results require that the cation radical be stabilized by delocalization over the aromatic ring and oxygen functions.

Our interest in the mechanisms of biological oxidation-reduction reactions and related model systems²⁻⁴ has led us to reexamine some aspects of the oxidation of alcohols and ethers by peroxydisulfate ($S_2O_8^{2-}$) and Fenton's reagent ($Fe(II)$ and H_2O_2). Since the original report⁵ by Fenton in 1876, numerous papers concerned with the mechanism of alcohol oxidation by Fenton's reagent⁶⁻¹³ and other hydroxyl

radical systems¹⁰⁻¹⁶ have appeared. Through the efforts of these and other workers, the mechanism of oxidation of aliphatic alcohols by Fenton's reagent has been fairly well established to be that shown in eq 1-4.



Related investigations of aliphatic alcohol oxidations by $S_2O_8^{2-}$, in the presence^{6a,17} or absence¹⁸ of transition

(1) Taken in part from the Ph.D. Thesis of M. E. Snook, The Pennsylvania State University, 1971, and presented in part at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, Abstracts, No. ORGN-135.

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