Table XII. Loss of Hydride from Diborane Solution in THF in the Presence of Air at Room Temperature

	Time, hr						
	0	0.5	1.0	3.0	6.0	24.0	48.0
M in H^-	0.97	0.94	0.91	0.88[a]	0.86	0.71	0.46
% H^-	(100)	(97)	(94)	(91)	(89)	(73)	(48)

[a] The solution became slightly turbid.

posed to the dry air with constant stirring. Aliquots were removed and analyzed for residual hydride. The observed decrease in the hydride concentration is summarized in Table XII.

Procedure. All reductions were carried out under a dry nitrogen atmosphere, using hypodermic syringes to transfer solutions. In a 100-ml flask fitted with a side arm capped by a rubber septum (to permit introduction and removal of material with a hypodermic syringe) was placed 45 ml of a solution of diborane in THF (50 mg-ions of H^-). The flask was immersed into an ice bath. The reaction mixture was diluted with 5 ml of THF containing 12.5 mmol of the compound to be reduced. For the reaction of alcohols, mercaptans, amines, and acids, the reaction flask was attached to a gas meter. At different time intervals, 5-ml samples were withdrawn and quenched in glycerol–water (1:3) or in concentrated hydrochloric acid (for sulfur- and nitrogen-containing compounds). The hydrogen evolved was measured volumetrically. The reaction was continued until two or more analyses indicated a constant utilization of hydride. In the case of relatively slow reductions, the reactions were also run at 25° to establish that a definite stoichiometry could be achieved.

Reduction with Isolation of Product. In a number of cases, the reduction was carried out as described above for the established yield and stoichiometry. However, the reaction mixtures were then worked up to isolate and characterize the reduction products. Several representative examples are described to illustrate the procedures.

Reduction of *p*-Benzoquinone to Hydroquinone. To a 45-ml solution of BH_3 in THF (50 mg-ions of H^-), 1.351 g of *p*-benzoquinone (12.5 mmol) was added as a solid. After 48 hr, an uptake of 2 mg-ions of hydride per mmol of compound could be detected by hydrolyzing the milky and viscous reaction mixture with water.

The hydrolyzed material was evaporated to dryness under reduced pressure. Then 10 ml of dry methanol was added and the solution was evaporated to dryness again. This procedure was repeated for several times to remove the boric acid as methyl borate. Following this treatment, 1.36 g of a slightly colored crystalline residue was recovered. Flame analysis showed only traces of boron. (The expected amount of hydroquinone for 100% yield was 1.37 g.) The crude product was recrystallized from water and 1.12 g, a yield of 82%, of *p*-hydroquinone, mp 170–171°, was obtained.

Reduction of Azobenzene to Aniline. To a 45-ml solution of BH_3 in THF, containing 50 mg-ions of hydride, 2.28 g of azobenzene (12.5 mmoles) in 5 ml of THF was added. The reaction mixture was allowed to stand for 48 hr at 0°. Then 40 ml of the solution was hydrolyzed with 10 ml of concentrated HCl (17.2 mmol of hydrogen evolved). After removing the THF under reduced pressure, 3 *N* sodium hydroxide solution was added. The strongly basic solution was extracted with ether (3 times) and the extract dried over anhydrous magnesium sulfate. After filtration, dry hydrogen chloride was passed through for about 20 min. A white precipitate formed. After filtration, the residue, 2.21 g, was treated with alcohol and filtered again. A white crystalline residue was obtained which did not melt up to 280°. The filtrate was evaporated to dryness and yielded 1.34 g (10.3 mmol) of aniline hydrochloride, mp 180–185° (after sublimation, mp 197°); yield, 51%.

Azobenzene was treated with diborane as described above in a ratio 1 H^- to 1 azobenzene. About 50% of the pure starting material was recovered, and 25% of the aniline hydrochloride was obtained.

Reduction of Dimethyl Sulfoxide to Dimethyl Sulfide. To a 45-ml solution of BH_3 in THF, containing 50 mmol of hydride, 0.9765 g of dimethyl sulfoxide (12.5 mmol) in 5 ml of THF was added at 0°. The solution was allowed to stand at 0° for 48 hr (80% reduction).

A 5-ml sample of the reaction mixture was hydrolyzed in 3 ml of water for several hr.

Potassium carbonate, 5 g, was then added (saturation). The upper layer was checked by glpc analysis (tricresyl phosphate column, 5% on chromasorb W). The product was compared with a standard solution (2.5 mmol of dimethyl sulfide in 10 ml of THF). A 78% yield of the expected dimethyl sulfide was found (after 80% reaction by stoichiometry), corresponding to an overall yield of 97%.

Reduction of Various Representative Functional Derivatives with the Stoichiometric Amount of Hydride to Get Aldehyde. The reduction of phenyl acetate is described as representative. In a 100-ml flask were injected 3.3 ml of 2 *M* borane (20 mg-ions of H^-) solution and 11.8 ml of THF. The temperature was kept at 0°, and 5 ml of THF, containing 20 mmol of phenyl acetate (2.723 g), was added under stirring to the diborane–THF solution.

The reaction mixture was checked for aldehyde by treating 2.5-ml samples with 2,4-dinitrophenylhydrazine. The reaction was continued until no more hydrogen was evolved by hydrolysis, indicating that all of the available hydride had been utilized for reduction.

Anodic Oxidation Pathways of Aromatic Amines. IV. Diphenylamine Systems in Aqueous Acid Solution[1]

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Contribution from the Department of Chemistry, University of Kansas, Lawrence, Kansas 66044. *Received July 10, 1969*

Abstract: The overall anodic oxidation pathways of diphenylamine systems in aqueous solutions have been examined. The nature and extent of the chemical reactions which follow the electron transfers are summarized. Products of these reactions are unequivocally established by various chemical and spectrophotometric methods and some rate data are presented.

Previous studies of the anodic oxidation of tertiary amines have emphasized the role of coupled chemical reactions following the initial electron transfer. The present results, in brief, summary form, illustrate that such follow-up reactions also dominate the overall electrooxidation of diphenylamine systems.

Earlier studies of diphenylamines have been concerned with effects of structure on $E_{1/2}$, ease of oxidation, and antioxidant behavior.[2,3] Brief reports of the

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(1) Part III: J. Bacon and R. N. Adams, *J. Amer. Chem. Soc.*, **90**, 6596 (1968).

(2) F. T. Eggertsen and F. T. Weiss, *Anal. Chem.*, **28**, 1008 (1956).

(3) G. E. Panketh, *J. Appl. Chem.*, 7, 512 (1957).

oxidation of several diphenylamines in acetonitrile have appeared.[4,5] We were interested primarily in the aqueous behavior, which has not been reported previously. The solubility requirements dictated the use of acid–acetone solvents. All studies were carried out in 50% acetone–50% 1.01 *M* perchloric acid. There is no reason to believe the acetone affects the electrochemistry and the results reflect the aqueous acid behavior of this series of diphenylamines.

Experimental Section

All of the electrochemical, electron paramagnetic resonance (epr), and other spectroscopic techniques employed were conventional and have been amply described previously. Cyclic voltammetry (CV) was used for general qualitative pictures of the electrode reactions and chronoamperometry and chronopotentiometry served for quantitative measurements. Some rate measurements were also made by CV as indicated later.

A Beckman platinum button (No. 39273) was utilized as the working electrode and had a geometric area of *ca.* 0.22 cm². All potentials are in volts *vs.* aqueous sce. In the aqueous acetone system, these potentials are within 10–20 mV of their counterparts in pure aqueous acid solution. All solutions were thoroughly bubbled with nitrogen to eliminate air oxidation.

Aniline Analyses. Substituted anilines were suspected as electrolysis products and positive identification was accomplished *via* a modification of the Bratton-Marshall procedure described by Schmir and Cunningham.[6,7] This involves diazotation of the aniline solution followed by coupling with N-(1-naphthyl)ethylenediamine. Authentic aniline derivatives were coupled and the absorption maxima of the substituted azo dyes were used as standards. Electrolysis solutions, similarly treated, were compared against these standards for positive aniline identification.

Substituted Diphenylamines. A few of the diphenylamines were commercial products, but most were prepared from standard literature references. The references and preparations are available on request from the authors and have been recorded.[8] All compounds were purified *via* column chromatography and/or recrystallization before use. The compounds studied are listed in Table I. The alternate nomenclature is listed to illustrate the functionality which plays a role in their electrochemical reaction. For convenience in discussion, the compounds are given roman numeral designations.

Results

A. N-Phenyl-*p*-aminophenol-like Compounds. Compounds I through III can be considered as N-substituted *p*-aminophenols as indicated in column 4 of Table I. Their electrochemical reactions reflect this formulation.

Table I. Substituted Diphenylamines

No.	R_4	$R_{4'}$	R_N	Alternate name
I	OH	H	H	N-Phenyl-*p*-aminophenol
II	OH	OCH_3	H	N-(*p*-Methoxyphenyl)-*p*-aminophenol
III	OH	NO_2	H	N-(*p*-Nitrophenyl)-*p*-aminophenol
IV	OCH_3	H	H	N-Phenyl-*p*-anisidine
V	OCH_3	OCH_3	H	N-(*p*-Methoxyphenyl)-*p*-anisidine
VI	OCH_3	NO_2	H	N-(*p*-Nitrophenyl)-*p*-anisidine
VII	OCH_3	OCH_3	CH_3	N-Methyldi-*p*-anisylamine ·
VIII	CH_3	CH_3	CH_3	N-Methyldi-*p*-tolylamine

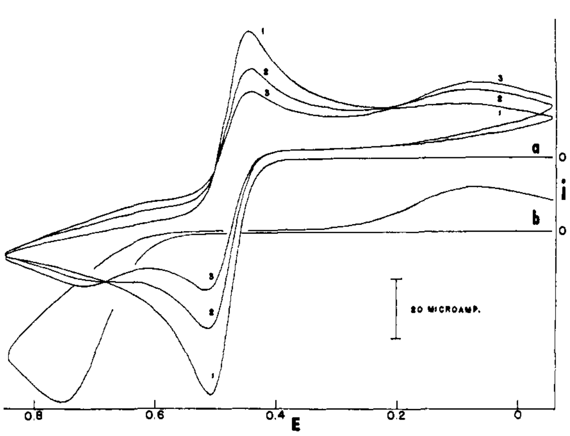
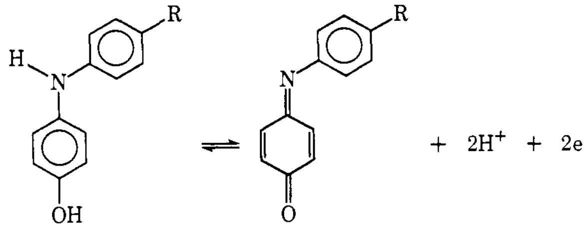


Figure 1. Cyclic voltammetry of N-phenyl-*p*-aminophenol: (a) N-phenyl-*p*-aminophenol; numbers 1, 2, and 3 denote first three cycles, respectively; (b) hydroquinone under identical conditions; Pt button electrode, sweep rate 4.17 V/min.

The overall electrochemical behavior of N-phenyl-*p*-aminophenol (I), N-(*p*-methoxyphenyl)-*p*-aminophenol (II), and N-(*p*-nitrophenyl)-*p*-aminophenol (III) is strongly dependent upon pH. This is, for the most part, due to the different degrees of stability of the quinone imines, a class of Schiff bases, formed as a result of the electron transfer process. In strong acid solutions (*ca.* 6 *M* $HClO_4$), the electron transfer process is uncomplicated in the time period of a cyclic polarogram and corresponds to the chemically reversible oxidation of the aminophenol to the corresponding N-phenyl-*p*-benzoquinone imine. However, when the acidity of the system is decreased a different electrochemical behavior is exhibited. Figure 1a shows the CV (three cycles) of I on 50% 1 *M* $HClO_4$ at a platinum electrode. On the first anodic sweep the oxidation of I to N-phenyl-*p*-benzoquinone imine is observed with $E_{p/2}$ *ca.* 0.45 V. Upon reversal of the voltage scan at 0.85 V, a new cathodic couple with E_p *ca.* 0.08 V is observed in addition to the reduction of the quinone imine. On subsequent anodic scans an additional wave is observed with E_p *ca.* 0.70 V. Also shown in Figure 1b is a cyclic polarogram of hydroquinone under identical conditions which shows typically irreversible behavior. The CV suggests that, following the initial oxidation of I, quinone is formed in a follow-up reaction. The following mechanism is postulated for the oxidation of I and its substituted derivatives



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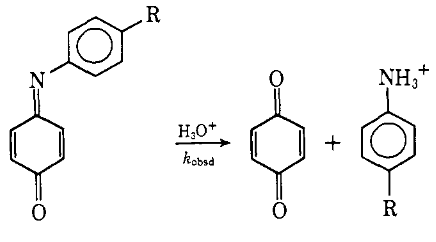

(2)

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(4) V. Dvorak, I. Nemec, and J. Zyica, *Microchem. J.*, 12, 99, 350 (1967).

(5) R. Nelson, Ph.D. Thesis, University of Kansas, 1967.

(6) A. C. Bratton and E. K. Marshall, *J. Biol. Chem.*, 128, 537 (1939).

(7) G. L. Schmir and B. A. Cunningham, *J. Amer. Chem. Soc.*, 87, 56, 92 (1965).

(8) D. W. Leedy, Ph.D. Thesis, University of Kansas, 1968.

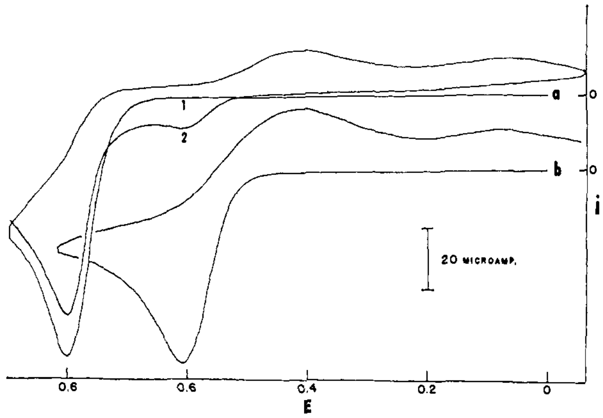


Figure 2. Cyclic voltammetry of N-substituted *p*-anisidine and corresponding *p*-aminophenol: (a) N-(*p*-nitrophenyl)-*p*-anisidine; number 1, first complete cycle; number 2, second anodic sweep; (b) N-(*p*-nitrophenyl)-*p*-aminophenol, identical conditions; Pt button electrode, sweep rate 5.0 V/min.

Although the CV is indicative of the formation of quinone, several identifications, independent of the electrochemistry, were performed to verify the overall mechanism.

a. Product Identification. Controlled potential coulometry in conjunction with electron prarmagnetic resonance (epr) spectroscopy and visible absorption methods was used to confirm that quinone and the corresponding substituted aniline were formed upon oxidation of I, II, and III in 50% acetone–50% 1 *M* $HClO_4$.

Quinone (*p*-benzoquinone) was identified as the *p*-benzosemiquinone anion radical. The experiment was performed in the following manner. A solution of the phenol (concentration *ca.* 2 m*M*) under investigation was exhaustively electrolyzed at a controlled potential such that the electron transfer process reached completion. In each case, 2.0 ± 0.2 electrons per molecule were transferred. An aliquot was then removed from the electrolysis cell and the pH rapidly adjusted to *ca.* 8–9. The solution was then transferred to the cavity of the epr spectrometer. A 5-line epr spectrum with a proton coupling constant of 2.35 G was obtained. This is unequivocal evidence of the presence of *p*-benzoquinone. The epr signal arises from air oxidation of the corresponding hydroquinone.

The substituted anilines were identified by coupling with N-(1-naphthyl)ethylenediamine as described in the Experimental Section. In each case the absorption maximum was identical with that obtained for an authentic sample of the corresponding aniline and was unique enough for positive identication.

b. Rate Measurements. The mechanism indicated in eq 1 and 2 is a typical EC mechanism, *i.e.*, a two-step process in which an electrochemically generated intermediate undergoes a subsequent chemical reaction.

Reverse current chronopotentiometry (RCC) and CV were used to determine the pseudo-first-order hydrolysis rates of the N-phenyl-*p*-benzoquinone imines formed in the anodic oxidation of I, II, and III. Rate constants obtained by both methods agreed well. For example, the rate of hydrolysis of the quinone imine generated from I as measured by RCC is 3.73×10^{-2} sec^{-1}. The value obtained by CV is 3.65×10^{-2} sec^{-1}. These rate constants were obtained in 50% acetone–50% 1.01 *M* perchloric acid. In general, rate constants obtained in this manner were reproducible within 5% and are consistent with expectations for N-substituted quinone imine hydrolyses. Table II summarizes the hydrolysis rates together with selected electrochemical parameters for the three compounds.

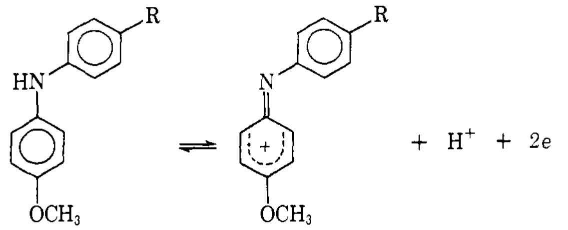
Table II. Electrochemical Parameters of Substituted N-Phenyl-*p*-aminophenols[a]

Compd	$E_{p/2}$[b]	$it^{1/2}/C$[c]	$i_p/v^{1/2}C$[d]	$k_{obsd} \times 10^2$[e]
I	0.45	46.0	32.2	3.7
II	0.49	47.2	32.0	1.0
III	0.56	44.7	34.7	6.4

[a] In 50% acetone–50% 1.01 *M* $HClO_4$. [b] In volts *vs.* sce. [c] *i* in μA, *t* in sec, *C* in m*M*. [d] i_p in μA, *v* in V/min, *C* in m*M*. [e] Units of sec^{-1}.

B. N-Phenyl-*p*-anisidine-like Compounds. Compounds IV through VI are the methyl ethers of the corresponding compounds I–III and may be considered as *p*-anisidine derivatives. The overall anodic oxidation of N-phenyl-*p*-anisidine derivatives is directly related to the electrochemical properties of their "parent" N-phenyl-*p*-aminophenols. (The behavior of the ethyl and isopropyl ethers of I was found to be identical with the methyl ether IV.)

Figure 2a shows a cyclic polarogram of VI (two anodic sweeps), representative of the N-phenyl-*p*-anisidines, in 50% acetone–50% 1 *M* $HClO_4$ at a platinum electrode. On the first anodic scan the oxidation of VI is observed with $E_{p/2}$ at 0.76 V. On the reversal at *ca.* 0.9 V, the reduction of the initial oxidation product of VI is not observed but two slight cathodic waves appear with E_p *ca.* 0.42 and 0.08 V. On the second and all additional anodic scans a new anodic wave is observed with $E_{p/2}$ *ca.* 0.56 V. The new redox systems may be identified as belonging to III (the corresponding phenol) and *p*-benzoquinone–hydroquinone resulting from the hydrolysis of the quinone imine of III. (Included in Figure 2b for com-



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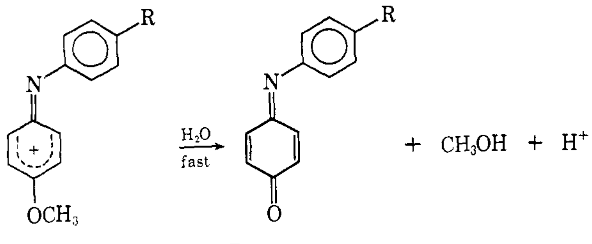

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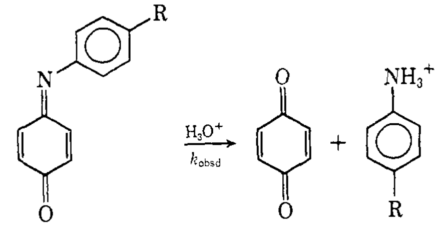

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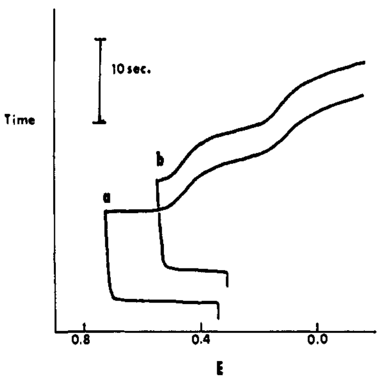

Figure 3. Reverse current chronopotentiometry comparison of N-substituted *p*-anisidine and corresponding *p*-aminophenol: (a) N-(*p*-nitrophenyl)-*p*-anisidine; (b) N-(*p*-nitrophenyl)-*p*-aminophenol; Pt button electrode, $i_r = -0.414\, i_f$.

parison is a cyclic polarogram of III under identical conditions.)

The electrochemical and chemical oxidation of alkoxy phenols has been shown to lead to the corresponding quinones.[9,10] In view of these studies, the mechanism shown below is postulated for the oxidation of IV, V, and VI. Note the second chemical step, eq 5, is identical with eq 2. This is verified by the data which follow.

Figure 3 shows the reverse current chronopotentiometry (RCC) for VI and III with the current density such that $i_c = -0.414 i_a$.[11] The first wave (see Figure 3a) involves the oxidation of VI to the alkoxy carbonium ion proposed in eq 3. Upon reversal of the current at time t_f ($t_f - \tau_f$), the potential drops rapidly to *ca.* 0.5 V where a transition time for the reduction of N-(*p*-nitrophenyl)-*p*-benzoquinone imine and a subsequent transition time for the reduction of *p*-benzoquinone resulting from the hydrolysis of the quinone imine are observed. The reverse cathodic chronopotentiometric waves of VI occur at precisely the same potentials as those observed from III (Figure 3b). If the hydrolysis of the cationic intermediate is fast as is indicated in eq 4, then the RCC measured rate of hydrolysis of N-(*p*-nitrophenyl)-*p*-benzoquinone imine as generated from either III or VI should be identical. Figure 4 summarizes the data obtained from these experiments. The dimensionless parameter kt_f is determined as a function of the rates of the reverse transition time (τ_r) to the forward electrolysis time (t_f) from working curves and is the typical final plot in RCC treatment of hydrolysis rates. As can be seen from Figure 4, the data from III and VI fall on the same line, the slope of which gives an almost identical rate constant for the hydrolysis of the quinone imine.

In addition, compounds IV, V, and VI were subjected to the product identification experiments as described for the N-phenyl-*p*-aminophenols. Coulometric oxidation of each required 2 electrons per molecule. In each case, quinone was isolated as an electrolysis product and verified by epr measurements. The suspected aniline was also detected as previously described. Analysis for methanol in the electrolysis solution was not attempted.

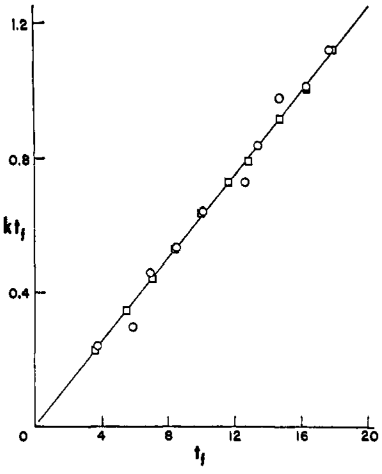

Figure 4. Hydrolysis rate plot for N-substituted quinone imines: ○, quinone imine generated from N-(*p*-nitrophenyl)-*p*-aminophenol; □, quinone imine generated from N-(*p*-nitrophenyl)-*p*-anisidine; see text.

The electrochemical parameters and hydrolysis rate constants for IV, V, and VI are summarized in Table III.

Table III. Electrochemical Parameters of Substituted N-Phenyl-*p*-anisidines[a]

Compd	$E_{p/2}$[b]	$it^{1/2}/C$[c]	$i\tau^{1/2}/C$[d]	$k_{obsd} \times 10^2$[e]
IV	0.59	51.2	67.8	4.0
V	0.5, 0.75	48.3	*f*	*f*
VI	0.76	47.1	74.8	6.3

[a] In 50% acetone–50% 1.01 *M* $HClO_4$. [b] In volts *vs.* sce. [c] *i* in μA, *t* in sec, *C* in m*M*. [d] *i* in μA, τ in sec, *C* in m*M*. [e] Units of sec^{-1}. [f] Preprotonation equilibrium splits the initial oxidation wave of III. Chronopotentiometric rate measurements under these conditions were not reproducible.

C. **N-Methyldiphenylamines.** The anodic electrochemical behavior of the N-methylated diphenylamines differs from the proton analogs in that the oxidation process occurs in two one-electron steps. Two compounds of this type were investigated, N-methyldi-*p*-anisylamine (VII) and N-methyldi-*p*-tolyamine (VIII). The second stage of oxidation of VIII occurs beyond the background limits of the acetone–acid solutions used in this study.[12] This oxidation process was observed for VII, however, and was investigated in detail.

Figure 5 shows the CV of VII, including both oxidation processes. If the sweep is limited to the first wave, *i.e.*, 0.0–+0.8 V, the electron transfer process is uncomplicated in the time period of a cyclic polarogram. The half-wave potential of 0.50 V and the separation in anodic and cathodic peak potentials is 56 mV, which is in agreement with the theoretical value for a one-electron process.[13] The $it^{1/2}/C$ value obtained from Cottrell measurements was 26.9, which is 56% of the value obtained from N-(*p*-methoxyphenyl)-*p*-anisidine (compound V). These data suggest that the initial oxidation

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(9) M. D. Hawley and R. N. Adams, *J. Electroanal. Chem.*, **8**, 163 (1964).

(10) E. Adler and R. Magnuson, *Acta Chem. Scand.*, **13**, 505 (1959); E. Adler, I. Falkehag and B. Smith, *ibid.*, **16**, 529 (1962).

(11) D. J. Macero and C. B. Anderson, *J. Electroanal. Chem.*, **6**, 221 (1963).

(12) The half-peak potential for VIII is 0.65 V. The epr spectrum observed for this species was identical with that obtained in nonaqueous media (see ref 5) although the stability was somewhat less than that of VII.

(13) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).

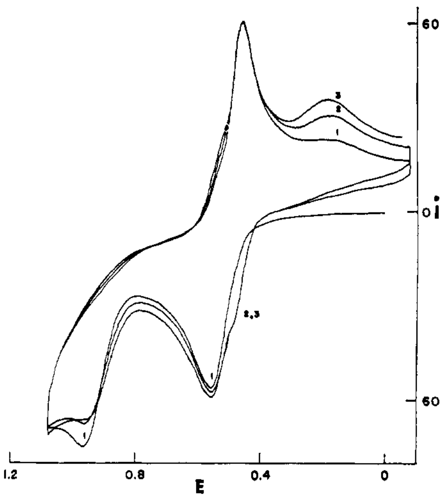
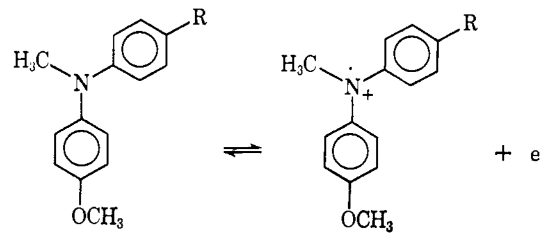


Figure 5. Cyclic voltammetry of N-methyl-*p*-anisylamine; numbers 1, 2, and 3 denote first three complete cycles; Pt button electrode, sweep rate 3.13 V/min.

process of VII is the formation of the corresponding cation radical. Epr measurements confirmed the formation of the primary cation radical.[5]

If the anodic sweep is carried out to *ca.* 1.1 V an entirely new cyclic pattern is observed. A second peak is observed at $E_{p/2}$ *ca.* 0.96 V. Upon reversal of the scan, the reduction of the two-electron oxidation product of VII is not observed, but two additional cathodic peaks are present. In analogy with the electrochemistry of the N-phenyl-*p*-anisidines discussed earlier, the cathodic process occurring at E_p *ca.* 0.46 V is the reduction of N-methyl-N-(*p*-methoxyphenyl)-*p*-benzoquinone imine. The second cathodic peak arises from the reduction of *p*-benzoquinone produced from the hydrolysis of the N-methylquinone imine. The mechanism for the oxidation of VII (eq 6–9) is consistent with the CV shown in Figure 5. Although the second stage of oxidation of VIII could not be studied due to the background limitations, it appears to behave similarly to VII.

In summary, of the three types of diphenylamines examined, the *p*-aminophenol-like compounds involve a two-electron oxidation and subsequent hydrolysis of the quinone imine analogous to all *p*-aminophenols. The follow-up reactions of the corresponding alkyl ethers initially involve alkoxy elimination—common to previous findings with *p*-alkoxyphenols—followed by quinone imine hydrolysis. Finally, the N-methyl derivatives give an initial one-electron oxidation and the primary cation radical. Further one-electron oxidation leads eventually to quinone imine hydrolysis as in the other compounds. Although the anodic electrochemistry of yet another series of diphenylamines (those which can be considered as N-phenyl-*p*-phenylenediamines) is similar, it involves enough nuances due to solvent interactions that it will be discussed in detail separately.



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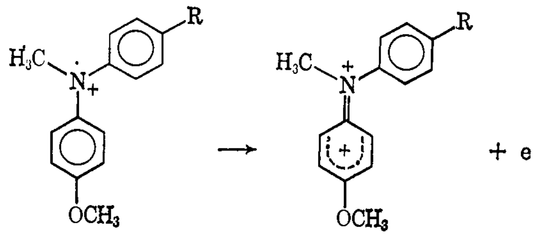

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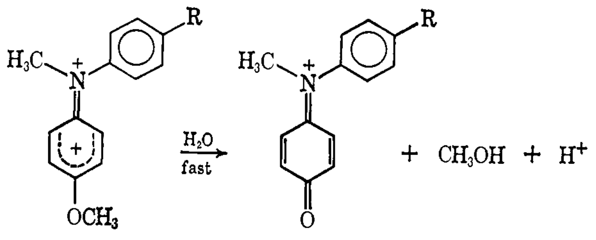

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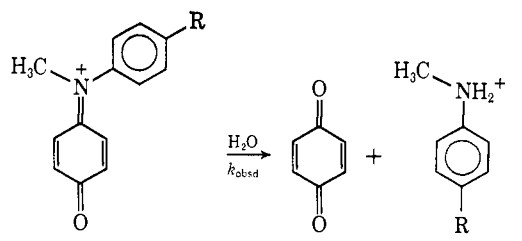

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Acknowledgment. The support of this work by the National Institutes of Health through Grant No. GM-13791 is gratefully acknowledged.