Anodic Oxidation Pathways of Aromatic Amines. Electrochemical and Electron Paramagnetic Resonance Studies

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Abstract: The anodic oxidation pathways of a variety of triphenylamines and other tertiary aromatic amines have been examined. The initial electron-transfer reaction and the identity and stability of the monocation radicals were studied by electrochemistry and epr. Rapid followup chemical reactions (coupling to give substituted benzidines) were found to be prevalent. Well-resolved epr spectra of several triphenylamine cation radicals generated electrolytically in acetonitrile are reported.

For several years studies in this laboratory have been concerned with the anodic oxidation mechanisms of aromatic systems, including individual aromatic amines.[2-5] These studies are of interest not only to organic electrochemistry but also because of correlations with chemical and biochemical oxidation–reduction systems in which aromatic amines play an important role. Waters has indicated, in his recent monograph, the paucity of information on the oxidation mechanisms of aromatic amines.[6]

Experimental measurements at solid electrode surfaces have become more reliable in the last few years. Significant advances also have been made in theoretical treatments of complex electrode processes. Techniques like rapid-scan spectrophotometry and electron paramagnetic resonance (epr) have become commonplace in electrochemical studies. With such supporting tools we felt it worthwhile to begin a thorough and extensive study of the anodic oxidation of aromatic amines. This work summarizes the results with particular emphasis on tertiary amines. The approach to these studies may be divided into two main parts. First, we have examined the nature of the primary electron-transfer processes and the identity and stability of the *initial* oxidation products. Spectrophotometric and epr identifications of radical cation intermediates were particularly useful in this phase of the work. Secondly, the chemical reactions following the electron transfers (follow-up reactions) were examined in detail, mainly by fast sweep electrochemical techniques. The results illustrate that coupled chemical reactions are very prevalent and of utmost importance in organic electrooxidations. Solubility limitations in many cases dictated the use of nonaqueous solvents. In addition, radical-ion stabilities are usually greater in nonaqueous media than in water. Hence, most of the work was done in acetonitrile and similar solvents, but extensions of the ideas to aqueous media are discussed.

All of the electrochemical and epr techniques have been reviewed adequately, and it is assumed that the reader is familiar with these methods. Specific references to individual techniques are given in the Experimental Section. Details of the methods are discussed in the text only insofar as they are pertinent to the present study. Since most of the epr spectra involved are being reported for the first time, they are discussed in required detail in part B.

Experimental Section

Single-sweep and cyclic voltammetry were used extensively in this study and the instrumentation and theory have been described.[7-9] For rapid-sweep work, the triangular wave from a Hewlett–Packard Model 202A function generator was fed to the potentiostat portion of the cyclic voltammetry (cv) instrument. The output was displayed on a Tektronix 535A oscilloscope with type D plug-in amplifier. Pictures were recorded with a Dumont 2614 oscillograph camera with a Type-2620 Polaroid attachment. For slower sweep rates, a Moseley Model 3S X–Y recorder was used. The chronopotentiometric measurements were conventional.

The electrochemical studies were carried out in a one-compartment cell with a Vycor bridge separating the saturated calomel reference electrode (sce) from the bulk solution. A Beckman platinum button (No. 39273) was the working electrode. A platinum foil served as auxiliary electrode and was spatially removed far enough from the working electrode to avoid mixing of electrolysis products.

Large-scale controlled potential electrolyses for spectrophotometry were carried out with a controlled-potential coulometer.[10] In this case the cell contents, after electrolysis, were transferred by gravity flow to the optical cell of a Cary Model 14 spectrophotometer. For transient optical spectra, a platinum gauze was placed directly in the optical path, and the controlled potential electrolysis was carried out *in situ*.

Epr spectra of electrolysis products were determined by both external and internal generation techniques which have been reviewed.[11] In general, parent amine concentrations of 1 to 5 × 10^{-4} M gave the best resolved epr spectra *via* external generation techniques. The cation radicals of N,N-dimethyl-*p*-toluidine and N,N-dimethyl-*p*-aminophenol were quite unstable, and 10^{-2} M solutions were electrolyzed externally and passed rapidly to the epr cavity.

The acetonitrile (MeCN) was purified by drying with calcium hydride followed by two distillations from phosphorus pentoxide and a third distillation from calcium hydride. In all distillations only the middle 60% fraction was collected. The supporting

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[1] (a) TRW Systems, Redondo Beach, Calif.; (b) Monsanto Research Center, St. Louis, Mo.

[2] T. Mizoguchi and R. N. Adams, *J. Am. Chem. Soc.*, **84**, 2058 (1962).

[3] Z. Galus and R. N. Adams, *ibid.*, **84**, 2061 (1962).

[4] Z. Galus, R. M. White, F. S. Rowland, and R. N. Adams, *ibid.*, **84**, 2065 (1962).

[5] D. M. Mohilner, R. N. Adams, and W. J. Argersinger, *ibid.*, **84**, 3618 (1962).

[6] W. A. Waters, "Mechanisms of Oxidation of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1964, pp 148, 149.

[7] Z. Galus, H. Y. Lee, and R. N. Adams, *J. Electroanal. Chem.*, **5**, 17 (1963).

[8] J. R. Alden, J. Q. Chambers, and R. N. Adams, *ibid.*, **5**, 152 (1963).

[9] R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964); **37**, 178 (1965).

[10] M. T. Kelly, N. C. Jones, and D. J. Fisher, *ibid.*, **31**, 488 (1959).

[11] R. N. Adams, *J. Electroanal. Chem.*, **8**, 151 (1964).

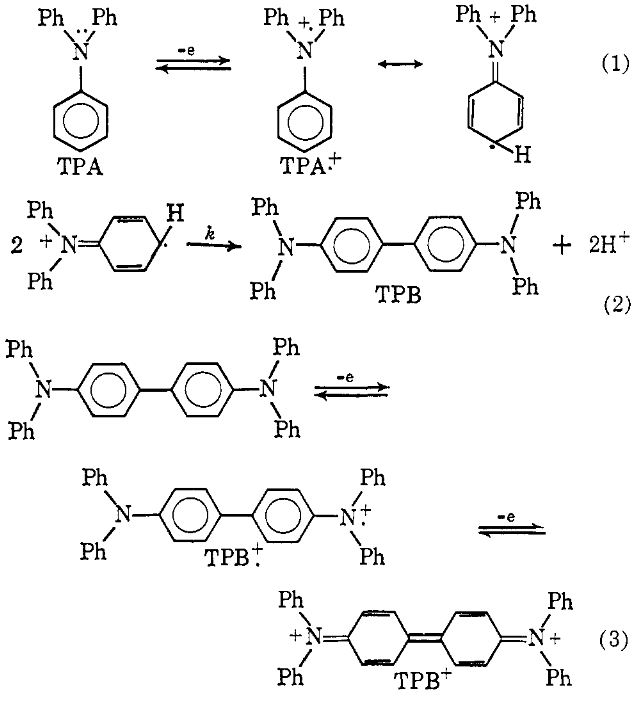
electrolyte was 0.1 *M* tetraethylammonium perchlorate (TEAP) for all studies unless otherwise noted. All potentials are in volts referred to the aqueous sce.

Water was triply distilled with the first two distillations, being from potassium permanganate and sulfuric acid, respectively. Reagent grade acetone was refluxed with potassium permanganate and distilled. Britton and Robinson buffers were prepared by conventional methods. The pH's listed are "apparent values."

Most of the triarylamines were prepared by standard literature methods. They were purified by chromatographic techniques. Complete references on individual preparations are available on request.

Results and Discussion

A. Electrochemical Studies. The anodic oxidation of triphenylamine (TPA) in MeCN is discussed first in some detail. The behavior of various tertiary amines can then be compared to the TPA results. TPA is oxidized at *ca.* +0.98 v *vs.* sce to an unstable monocation radical, TPA·+. The cation dimerizes (couples) or reacts with parent rapidly to form tetraphenylbenzidine (TPB). This is accompanied by the loss of two protons per dimer, but it has not been ascertained if the proton loss occurs before or after coupling. The chemical follow-up reaction product, TPB, is more easily oxidized than the starting TPA and undergoes further oxidation at the applied potential. This occurs in two, discrete one-electron steps to give the TPB·+ and finally the quinoidal dication TPB^{2+}. The over-all reaction scheme is



The process cited above was verified by a number of independent means. (Actually the possibility exists that the coupling is between the monocation and an unoxidized molecule rather than dimerization of two cation radicals. We cannot distinguish between these processes.) Generally speaking, this process is of the ece type (*e*lectron transfer–*c*hemical reaction–*e*lectron transfer). (Actually, since TPB is more easily oxidized than TPA, it is possible to have chemical oxidation of TPB by TPA·+ which constitutes an ecc process—an electron transfer followed by two chemical steps.[12] The net electrochemical effect is the same. The small but real differences which are evident in the quantitative measurements are of little consequence to the general arguments presented herein.) The ece process has been treated thoroughly by Nicholson and Shain for both linear (single) sweep and cyclic voltammetry.[9] For the single sweep peak polarograms of TPA, one would expect to find a small shift of the anodic peak potential, $E_{\mathrm{p_a}}$, to less positive potentials as the potential sweep rate decreases.[9] This was indeed found; as the sweep rate decreased from 15.64 to 0.76 v/min, $E_{\mathrm{p_a}}$ shifted cathodically by *ca.* 60 mv.

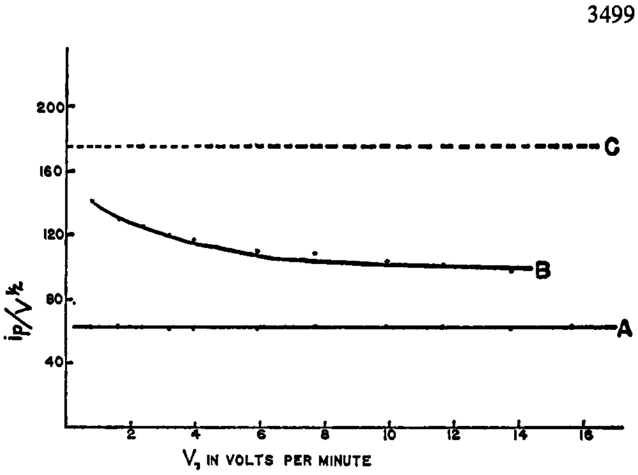


Figure 1. Peak current *vs.* scan rate behavior for various triarylamine oxidations: (A) oxidation of 2.00×10^{-3} *M* *p*-trianisylamine; (B) oxidation of 2.00×10^{-3} *M* triphenylamine; (C) theoretical line for two-electron oxidation, calculated for line A (medium: 0.1 *M* TEAP/MeCN, platinum button electrode).

The variation of peak current, i_p, as a function of V, the potential sweep rate, is more informative with regard to the follow-up process. If one plots $i_p/V^{1/2}$ *vs.* increasing V (or $V^{1/2}$), a horizontal straight line is obtained if there are no coupled chemical reactions. The actual data for TPA are seen as line B of Figure 1, compared to the theoretical horizontal lines for one- or two-electron processes (no chemical complications). Actually, the bottom horizontal line (A) in Figure 1 is the experimental data for the oxidation of tri-*p*-anisylamine where the monocation radical is completely stable; *i.e.*, it oxidation is a simple one-electron process with no chemical reactions. The shape of the TPA line is that predicted by Nicholson and Shain for the ece process and also is what one expects intuitively. At rapid sweep rates, the effect of the follow-up chemical reaction is minimized and the over-all behavior tends toward that of a simple one-electron oxidation. As the sweep rate decreases, the benzidine oxidation contributes a greater amount to the total peak current, and there is a trend toward an observed two-electron oxidation. Assuming that the diffusion coefficients of tri-*p*-anisylamine and TPA are approximately the same, it can be seen in Figure 1 the TPA approaches the one- and two-electron cases at the extremes of sweep rate.

The presence of the tetraphenylbenzidine in the oxidized TPA system can be seen by cyclic voltammetry. Two oxidation and reduction peaks appear at potentials slightly cathodic to the main TPA oxidation peak. (The second anodic peak is obscured by the main oxidation wave, but both cathodic peaks are seen clearly.) These oxidation–reduction couples are evi-

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[12] M. D. Hawley and S. Feldberg, Abstracts, Winter Meeting of the American Chemical Society, Phoenix, Ariz., Jan 1966, Abstract B 26.

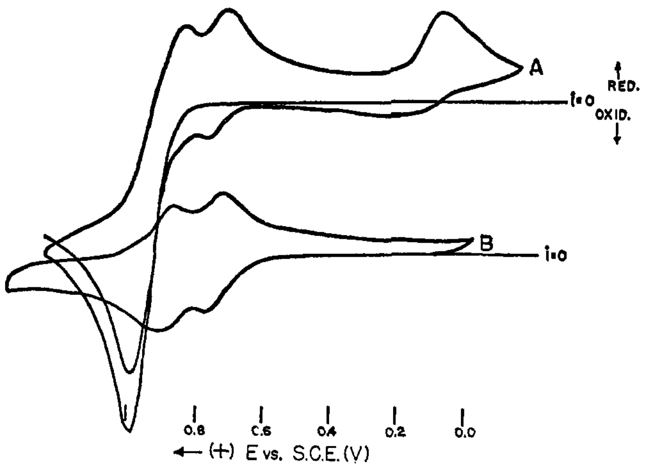

Figure 2. Cyclic polarograms of TPA and TPB: (A) 2.00×10^{-3} *M* TPA, (B) saturated solution (*ca.* 5×10^{-4} *M*) of TPB (medium: 0.1 *M* TEAP/MeCN, platinum button electrode, scan rate 7.8 v/min for both curves).

dent *only after the first anodic sweep;* hence they are generated *via* chemical reaction following the initial oxidation of TPA. This is seen in the cyclic polarograms of Figure 2. The cyclic polarograms of an authentic sample of TPB matched these oxidation–reduction systems very well. The peak at *ca.* 0.0 v in Figure 2 is due to reduction of protons released in the coupling reaction.

More positive identification of TPB in oxidized TPA solutions is obtained *via* epr spectra. Solutions of both compounds, anodically oxidized at *ca.* +1.0 v within the microwave cavity, give identical epr spectra. These spectra are poorly resolved in MeCN. The spectrum consists of five major groups with a total spectral width of *ca.* 32 gauss. Slightly better defined spectra are obtained in dimethylformamide and propylene carbonate. The epr spectrum from a 10^{-3} *M* solution of TPB in N,N-dimethylformamide, using exhaustive external generation and a flow system, is far better resolved. The large number of small proton splittings makes resolution very difficult, and a complete analysis of the spectrum has not been accomplished. It can be determined, with certainty, that the major five-line hyperfine interaction is due to two equivalent N^{14} nuclei with $a_N = 5.3 \pm 0.25$ gauss. Since both oxidized TPA and TPB give the same substituted benzidine cation radical (a TPA cation radical would have only one N^{14} interaction and hence a major triplet splitting), the epr spectra provide convincing proof of the proposed electrode process.

There is one other electrochemical study which verifies the previous data. Reverse current chronopotentiometry was carried out with unequal current densities arranged such that both forward and reverse transition times (τ_f and τ_r, respectively) would be equal in the absence of any complications. With TPA oxidations, the value of τ_f/τ_r was 2.00. This is the expected value if there is quantitative conversion of TPA to TPB^{2+}. Thus conversion of TPA to TPB^{2+} is a four-electron process (two electrons per mole of TPA). However, on the current reversal, TPB^{2+} consumes only two electrons in going to TPB; hence $\tau_f/\tau_r = 2.00$. The forward and reverse chronopotentiograms were consistent with the cv results, *i.e.*, only one oxidation wave, but two cathodic waves at slightly more cathodic potentials.

Although its existence is fleeting, the triphenylamine cation radical, $TPA\cdot^{+}$ can be seen with very rapid sweep cv and oscillographic recording. It is also possible to identify the $TPA\cdot^{+}$ by rapid optical spectroscopy. (It may appear strange that $TPA\cdot^{+}$ can be seen optically but not *via* epr, since one is accustomed to thinking of the high sensitivity of the latter technique for detecting radical species. However, observation of $TPA\cdot^{+}$ by epr is hampered not only by the short lifetime involved, but also by the concurrent growth of a large epr signal from the far more stable benzidine radical ion. We did not attempt rapid flow epr detection of $TPA\cdot^{+}$.) External electrolysis at +1.15 v of solutions of both TPA and TPB (gravity transfer to a Cary spectrophotometer) gave identical optical spectra. This was a single, broad band with λ_{max} at 480 mμ. This band is apparently due to $TPB\cdot^{+}$ which is in agreement with the findings of Hasegawa[13] and Hall.[14] When the controlled potential electrolysis is carried out directly in the optical cell and the spectrum recorded during the first few seconds of electrolysis, a band is seen at 640 mμ. This may be attributed to $TPA\cdot^{+}$. Lewis and Lipkin found λ_{max} at 655 mμ for $TPA\cdot^{+}$ formed by photooxidation of TPA in rigid media.[15] Dollish and Hall also observed a band (λ_{max} at 660 mμ) when TPA was adsorbed on silica–alumina.[14] Finally, Stamires and Turkevich reported λ_{max} 650 mμ for TPA–iodine mixtures in chloroform, and epr spectra for $TPA\cdot^{+}$ adsorbed on zeolites.[16] Thus, there is real evidence for the electrochemical formation of the transient monocation $TPA\cdot^{+}$.

The opposite extreme in monocation radical stability is obtained in the oxidation of trianisylamine (TAA). The $TAA\cdot^{+}$ is extremely stable, not only in MeCN but even in 50% acetone–water buffers from pH 2 to 6. The cv in all media indicates a perfectly reversible one-electron transfer. Further, in the aqueous media, the oxidation is pH independent as would be predicted for a simple electron transfer.

Table I summarizes the amines studied, their relative ease of oxidation in terms of $E_{p/2}$, and relative stability of their monocation radicals as determined by the ratio of cathodic-to-anodic peak current. All of the tri(*para*-substituted) compounds II–V give very stable monocation radicals in MeCN. In addition, it was possible to obtain stable radical cations for compounds II, III, IX–XI in the acetone–water buffer system.

Coupling is the predominate reaction pathway for the unstable cation radicals (compounds I, XII–XVIII). It should be emphasized that *p*-benzidine formation has been proven unequivocally for only compounds I, XVII, and XVIII. There is no question that very similar coupling reactions occur for the other compounds, but authentic samples of these benzidines were not available for comparison studies. It must be admitted that the coupling reactions in these cases could produce *o*-benzidines or -diphenylines. It can be stated with certainty that the coupled products from compounds VI–VIII are dimeric. Like the TPA system, their oxidations produce epr spectra with five major splittings, showing the presence of two equivalent N^{14} nuclei.

(13) H. Hasegawa, *J. Phys. Chem.*, **66**, 834 (1962).
(14) F. R. Dollish and W. K. Hall, *ibid.*, **69**, 2124 (1965).
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(16) D. N. Stamires and J. Turkevich, *ibid.*, **85**, 2554 (1963).

Table I. Electrochemical Characteristics of Tertiary Aromatic Amines

	Substituted triphenylamine,[a] $NR_1R_2R_3$			$E_{p/2}$, V *vs.* sce			
No.	R_1	R_2	R_3	Aqueous[b]	MeCN	Monocation radical stability	i_{pc}/i_{pa}
I	C_6H_5	C_6H_5	C_6H_5	...	+0.92	Very unstable	..
II	$C_6H_4OCH_3$	$C_6H_4OCH_3$	$C_6H_4OCH_3$	+0.48	0.52	Very stable	1.00
III	$C_6H_4CH_3$	$C_6H_4CH_3$	$C_6H_4CH_3$	+0.76[c]	0.75	Very stable	1.00
IV	C_6H_4Cl	C_6H_4Cl	C_6H_4Cl	...	1.04	Very stable	1.00
V	C_6H_4Br	C_6H_4Br	C_6H_4Br	...	1.05	Very stable	1.00
VI	C_6H_5	$C_6H_4OCH_3$	$C_6H_4OCH_3$	...	0.63	Very stable[d]	1.00
VII	C_6H_5	C_6H_5	$C_6H_4OCH_3$	...	0.76[c]	Quite stable	0.98
VIII	CH_3	C_6H_5	$C_6H_4OCH_3$	...	0.77	Fairly stable	0.86
IX	CH_3	$C_6H_4OCH_3$	$C_6H_4OCH_3$	+0.49	0.65	Quite stable[e]	1.00
X	CH_3	CH_3	$C_6H_4OCH_3$	+0.62	0.49	Fairly stable	0.94
XI	CH_3	$C_6H_4CH_3$	$C_6H_4CH_3$	+0.67	0.60	Fairly stable	0.94
XII	CH_3	CH_3	$C_6H_4CH_3$	...	0.65	Quite unstable	0.31
XIII	C_6H_5	$C_6H_4NO_2$	$C_6H_4NO_2$	...	1.34	Highly unstable	...
XIV	C_6H_5	C_6H_5	$C_6H_4NO_2$	...	1.15	Highly unstable	...
XV	CH_3	CH_3	$C_6H_4NO_2$	...	1.19	Highly unstable	0.3
XVI	CH_3	CH_3	C_6H_4Cl	...	0.84	Highly unstable	0.29
XVII	CH_3	C_6H_5	C_6H_5	...	0.84	Highly unstable	...
XVIII	CH_3	CH_3	C_6H_5	...	0.71	Highly unstable	...

[a] R_1, R_2, and R_3 are total substituent groups on amine N; all substituents on phenyl groups are *para*. [b] 50% by volume acetone–aqueous buffer solution. [c] Approximate value due to concurrent background oxidation. [d] Negligible decay of epr signal. [e] Very slow decay of epr signals.

The final oxidation products of compounds XII and XV are not known. Here *p*-benzidine formation obviously cannot take place without some group elimination. The cv shows a rather poorly defined but obviously reversible system more anodic than the primary oxidation wave, but nothing is known of the species responsible thus far.

A priori one might expect a statistically predictable inhibition of coupling by blocking either one or two of the *p*-aryl positions with some functional group (neglecting strong substituent effects). This was attempted with several partially *para*-substituted triphenylamines, but it was found that substituent effects cannot be ignored; indeed they are surprisingly large.

The relative rates of the coupling reactions can be studied in a qualitative sense *via* chronopotentiometry by plotting $i_0\tau^{1/2}$ *vs.* increasing i_0 over at least a twofold range of current density. For no coupling, one should obtain a horizontal straight line corresponding to a one-electron process (monocation radical formation only). For extremely rapid coupling, one obtains again a horizontal line, but corresponding to a two-electron over-all process. For most coupling rates, a sloping line tending toward the one-electron process at high current densities would be expected (the analysis is similar to that discussed earlier for $i_pV^{1/2}$ *vs.* *V*; here, as current density increases, there is less time available for follow-up chemical reactions, and results tend toward the initial one-electron process).

If the coupling rates are within the range of experimental detection, the magnitude of the $i_0\tau^{1/2}$ product can be taken as a measure of the relative coupling rates, assuming the diffusion coefficients are similar (it has been found that they are indeed identical within ±20%).

The tri-*p*-anisylamine molecule was taken as a standard for a one-electron (no coupling) process. Its $i_0\tau^{1/2}$ product is essentially constant over a wide current range (line A in Figure 3). As expected, the line for TPA oxidation is considerably above this (B), indicating the presence of the follow-up chemical reaction.

Now, by blocking one of the *para* sites in TPA, one would expect the coupling reaction to be slowed down if coupling is the result of a bimolecular collision process. Theoretically, the number of collisions resulting in reactions should be diminished by blocking some of the "active" *para* sites. Experimentally, one sees a different picture, as shown in Figure 3.

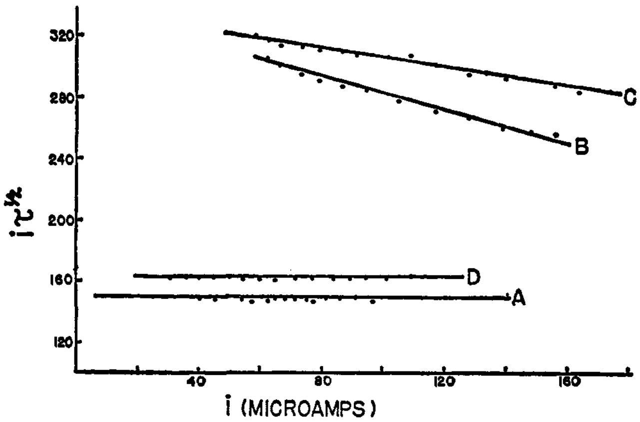


Figure 3. Chronopotentiometric study of relative coupling rates: (A) *p*-trianisylamine, (B) triphenylamine, (C) 4-nitrotriphenylamine, (D) 4-methoxytriphenylamine (medium: 0.1 *M* TEAP/MeCN, all solutions 2.00 × 10^{-3} *M* in amine).

Line C is plotted from the data for 4-nitrotriphenylamine and line D for 4-methoxytriphenylamine. It is obvious that, though both are monosubstituted triphenylamines, their behaviors vary considerably. According to the data, there is almost no coupling reaction for 4-methoxy-TPA upon oxidation to the monocation. A plot of $i_p/V^{1/2}$ also gives a horizontal straight line, and a rather stable monocation species can be generated external to the epr cell and a well-resolved epr spectrum was obtained.

From the chronopotentiometry data, it is apparent that the coupling reaction of 4-nitro-TPA is much accelerated relative to TPA. Reverse-current chrono (τ_f/τ_r = 2.00), epr (five major groups with a spectral with of $\sim$33 gauss), and cyclic voltammetry all verify that coupling does occur. As is the case with 4-methoxy-TPA, it has not been proven unequivocally that a *p*-benzidine is formed. Quantitative studies of coupling

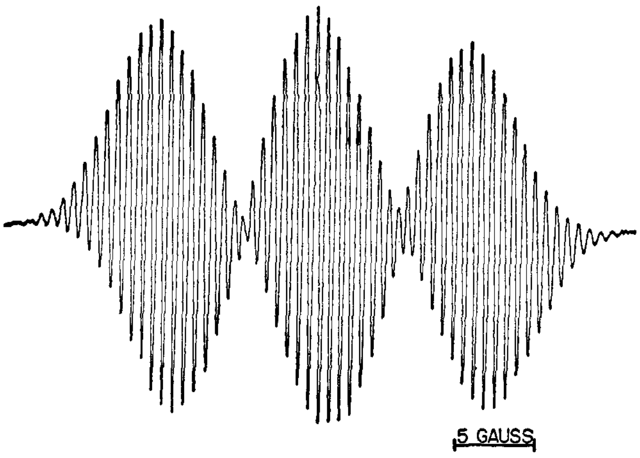


Figure 4. Epr spectrum of electrolytically generated tri-*p*-anisylamine cation radical. External generation from 2 × 10^{-4} *M* solution of amine in 0.1 *M* TEAP/MeCN, original recording.

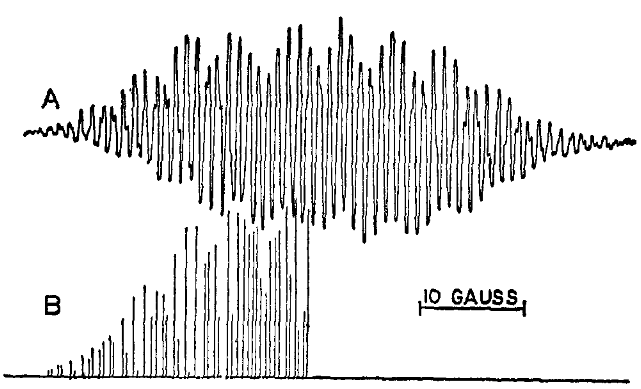
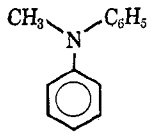


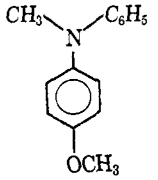
Figure 5. Epr spectrum of electrolytically generated tri-*p*-tolylamine cation radical: (A) external generation from 2 × 10^{-4} *M* solution of amine in 0.1 *M* TEAP/MeCN, retraced from original recording; (B)s tick diagram drawn from computer-plotted spectrum (one-half of spectrum).

rates and product formation from a variety of triphenylamines with substituents of varying electronegativities are in progress.

Methoxy groups show an extreme tendency to stabilize the cation radicals and prevent coupling. The most dramatic example is furnished by the comparison of compounds XVII and VIII of Table I. When XVII is oxidized the N,N′-dimethyl-N,N′-diphenylbenzidine is formed readily. The oxidation of VIII leads instead to a very stable monocation radical. Statistically, with the blocked *para* position in VIII, one would expect lesser coupling than with XVII, but the greatly enhanced cation radical stability is unexpected.



XVII



VIII

The anodic oxidation of N,N-dimethylaniline (DMA) to the corresponding tetramethylbenzidine was studied previously in aqueous media.[2-4] The *over-all* reaction is identical with those of the triarylamines to which DMA bears an obvious relationship. The previous studies proposed a mechanism whereby DMA was oxidized to a dication and this species attacked a parent DMA to give the benzidine. The dication picture was favored since electrochemical, spectrophotometric, and epr measurements all failed to show any evidence of the monocation radical. Further, the electrochemical reaction was found to be first order in DMA. The main oxidation peak was taken as totally irreversible, and from an analysis of the peak shape, βn_a was found to be *ca.* 1.1. Assuming *ca.* 0.5 as a reasonable value for the anodic transfer coefficient, β, it was deduced that n_a was most likely 2 electrons; hence a DMA^{2+} species was indicated.

It is now quite clear from the theoretical treatments of Nicholson and Shain[9] that our previous analysis of the peak polarogram for βn_a values is incorrect. The peak polarogram for a reversible electron transfer followed by a rapid, irreversible, chemical reaction has a wave shape which is *of the same form as that for an irreversible electron transfer.* However, it is the effect of the fast chemical reaction which gives rise to this behavior, and one cannot analyze this wave shape in terms of a slow electron-transfer process for βn_a. In light of this we have attempted again, using fast cv and optical spectrophotometry, to detect the DMA cation radical in both aqueous and nonaqueous media. None of these attempts were successful. Since even $TPA\cdot^+$ was difficult to detect, it is not surprising that the fast coupling reaction to give tetramethylbenzidine renders the $DMA\cdot^+$ too short lived for detection by these means. By analogy to the relative stability to the triarylamine monocation radicals, it seems now more reasonable that $DMA\cdot^+$ is the initial anodic oxidation product of DMA.

B. Epr Studies. Figure 4 shows the epr spectrum of the very stable tri-*p*-anisylamine cation. Experimental and computer-plotted spectra (using the experimental coupling constants of Table II) agree perfectly. The N^{14} triplet hyperfine interaction (*ca.* 9 gauss) is clearly evident. The only previous report of the tri-*p*-anisylamine cation in solution is that of Walter, *et al.*, who reported a N^{14} coupling of 10 ± 1 gauss in tetrachloroethane.[17] In some of the other epr spectra, this N^{14} splitting is not particularly dominant. Figure 5 shows the spectrum of the tri-*p*-tolylamine radical where the N^{14} triplet is no longer immediately evident. These spectra are quite difficult to interpret owing to the large number of small coupling constants. Singular interpretations were obtained by confirmation with computed spectra. A large number of spectra were computed from the possible combinations of plausible coupling constants and line widths. That computed spectrum fitting the experimental one best was taken as the most reliable choice. Where unequivocal interpretations could not be made (*i.e.*, *ortho vs. meta* ring protons), they were assigned in accord with Hückel molecular orbital calculations. Parameters for these calculations were: $h_N = 1.0$ and $k_{C-N} = 0.8$ for the nitrogens,[18,19] $h_O = 2.0$ and $k_{C-O} = 0.8$ for the methoxy substituents,[20]

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and $h_{\text{C-ring}} = -0.3$ for the methyl substituents.[21] Table II lists the coupling constant data. Where applicable, the numerical designations used in Table I identify the compounds. For the tri-*p*-chlorotriphenylamine cation the natural abundance and distribution of the Cl^{35} and Cl^{37} isotopes had to be considered. The interpretation was made on the basis that the coupling constants for the two isotopes were in the ratio of their nuclear magnetic moments. The spectrum computed with the distribution and coupling constants shown in Table II coincides with the experimental spectrum.

Table II. Coupling Constants[a] of Tertiary Aromatic Amine Cation Radicals

Cation radical	a_N	$a_{H(NR)}$	$a_{H(ortho)}$	$a_{H(meta)}$	$a_{H(para)}$
II	8.97	...	1.22	0.61	0.61[b]
III	9.45	...	2.06	1.03	3.89[c]
IV	9.52	...	1.12	0.56	1.72[d]
					1.43[e]
IX	9.77	10.27[c]	2.42	0.48	0.97[b]
	(9.67)[f]	(10.31)	(2.41)	(0.49)	(0.97)
XI	10.65	11.83[c]	2.90	1.24	5.31[c]
X	10.00	10.40[c]	4.25	1.82	1.85[b]
XII	11.06	12.20[c]	5.30	1.35	10.00[c]

[a] Coupling constants in MeCN, 0.1 *M* TEAP, in gauss. The estimated precision of coupling constants is *ca.* 1% or better for a_N and $a_{H(NR)}$ and varies between 1–5% for the various ring and methyl protons. [b] Methoxy protons. [c] Methyl protons. [d] Cl^{35} isotope. [e] Cl^{37} isotope. [f] Values in parentheses for compound IX are for 50% acetone–water buffer. The coupling constants were pH independent.

Although the cation radical of the bromo derivative (compound V) is quite stable, only a very broadened three-line epr spectrum could be obtained. Since the Br^{79} and Br^{81} isotopes are present in equal abundance and both have spin $^3/_2$ and possess large nuclear quadrupole moments, this broadening is not too surprising. No further attempts at interpretation were made.

The stability of the radical ions follows a generally predictable pattern. The tri-*p*-anisylamine and tri-*p*-tolylamine cations were extremely stable and their epr spectra showed practically no intensity decrease with time. Replacement of *para*-substituted phenyl groups with methyls tends to destabilize the radical ions probably owing to less delocalization. Even so, the cation radicals of N-methyl-di-*p*-anisylamine (IX) and N-methyl-di-*p*-tolylamine (XI) are relatively stable. Replacment of two phenyl groups with methyls (corresponding to *para*-substituted N,N-dimethylanilines) causes serious destabilization of the radical cations. Of the compounds studied only N,N-dimethyl-*p*-anisidine (X) gave a reasonably stable cation. Although the N,N-dimethyl-*p*-toluidine cation was very short-lived, reasonably interpretable spectra were obtained with care. Weak, but resolvable, spectra were obtained for the N,N-dimethylanilines where the *para* substituent was OH, N=O, NO_2, CN, and CHO, but no signal was obtained for the corresponding chloro derivative. The spectra of the *p*-nitro and *p*-aldehyde derivatives have been reported in aqueous media *via* Ce(IV) oxidation by Waters and co-workers.[22,23]

The epr spectra of the cation radicals which were stable in the acetone–water system were essentially identical with those obtained in MeCN. In Table II, the coupling constants for compound IX are compared in the two media. Previous studies have shown only insignificant solvent effects on coupling constants for diamine cation radicals.

All of the epr spectra, for which data are reported in Table II were obtained by the external generation method with exhaustive electrolysis. In this case homogeneous electron exchange with the parent is eliminated. In internal generation in MeCN, significant line broadening due to electron exchange was observed with the various amines.

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