

ELECTROCHEMICAL OXIDATION PATHWAYS OF SUBSTITUTED DIMETHYLANILINES

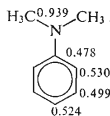
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The electrochemical oxidations of *N,N*-dimethylaniline and several ring-substituted dimethylanilines in non-aqueous media are reported. A number of different products were formed, including *N,N,N',N'*-tetramethylbenzidine, 4,4'-methylenebis (dimethylaniline), crystal violet dye and the leuco form contingent upon concentration, solvent conditions and electrolysis time. The *N,N*-dimethyl-*p*-anisidine underwent attack on the cation radical by small amounts of water in the acetonitrile to form the phenoxy analog. *N,N*-Dimethyl-*p*-toluidine and other *para*-alkyl substituted anilines lose a proton from the cation radical to form a benzylic free radical; these then couple to form substituted bibenzyls. Other derivatives such as *p*-dimethylaminobenzaldehyde, *p*-dimethylaminobenzoic acid, *p*-iodo-, *p*-bromo-, and *p*-chloro *N,N*-dimethylanilines were found to undergo group elimination upon electrochemical oxidation with subsequent formation of *N,N,N',N'*-tetramethylbenzidine. The *p*-iodo- and *p*-bromo *N,N*-dimethylanilines at higher concentrations appear to follow the same mechanistic pathway as *N,N*-dimethylaniline itself.

The electrochemical oxidation of *N,N*-dimethylaniline (*I*) has commanded considerable interest in years past, as has oxidation by chemical means. A large number of products were obtained by oxidation under varying conditions¹⁻⁹. These are mainly products of coupling reactions, but substitution can also occur under certain conditions, either on the aromatic ring¹⁰⁻¹² or on the *N*-methyl groups^{13,14}. Because of the variation in products obtained from *I*, it is apparent that *I* is an extremely reactive molecule. Consequently, a program to study the oxidation pathways of *I* and its substituted derivatives under various solvent conditions was undertaken and is reported herein.



I

In addition to the literature data cited above, a cursory inspection of the simple Hückel molecular orbital calculations (using $h_N = 1.0$, $k_{C-N} = 0.8$), shown below, convinces one that indeed *I* has several reactive sites available for coupling upon electrochemical oxidation (the numbers shown represent the sum of the squares of the atomic orbital coefficients for all the occupied orbitals for each position — the numbers should not be given a great deal of weight in themselves, but are of significance relative to one another in that they are indicative of relative electron densities). Almost every position is potentially quite reactive, including the N-methyl groups. Calculations did not include these groups, but from the very high electron density on the amine nitrogen one could also anticipate a high reactivity for the methyl groups. N,N-Dimethylaniline is itself very unstable when oxidized to the cation radical, but it was hoped that ring substitution would stabilize the cation radical somewhat. This hope was realized to some extent, but it was found that even the ring-substituted derivatives had relatively unstable cation radicals that decomposed by a variety of pathways.

EXPERIMENTAL

Methods

The basic instrument for these studies, a multi-purpose electrochemical scanner, has been previously described¹⁵. Current-voltage curves were recorded with a Hewlett-Packard 7030 A X-Y recorder and Tektronix 564 B storage oscilloscope. Rapid cyclic voltammetry experiments were carried out using the above-mentioned electrochemical scanner in conjunction with a Hewlett-Packard 3300 A function generator and 3302 A trigger/phase lock plug-in unit. Large-scale coulometry and 'n-value' determinations were accomplished using a Wenking 61 RH fast-rise potentiostat and a digital output assembly¹⁶. A gating counter was added to effect more careful scrutiny of the course of electrolysis. Visible absorption spectra were recorded using a Cary 14 spectrometer and a cell specially designed for *in situ* electrolyses¹⁵. The EPR spectra were obtained with a Varian E-3 EPR spectrometer and *in situ* electrolysis cell. Low-temperature studies were effected with a "home-built" unit in which air was passed through a cold trap and into the spectrometer cavity; to avoid frosting, the cavity was encased in a specially built plastic cover.

The purification of acetonitrile and tetraethylammonium perchlorate has been previously described¹⁷; for aqueous studies McIlvain buffers were employed¹⁷. Current-voltage curves were taken at both platinum and carbon paste working electrodes; a large platinum gauze was employed for preparative scale electrolyses. All potentials reported are *vs.* an aqueous s.c.e. reference electrode. The method employed for isolation of electrolysis products has also been described previously¹⁸.

Chemicals

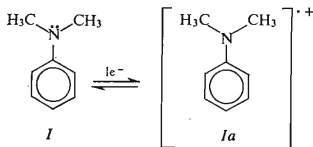
All the substituted dimethylanilines used, whether prepared synthetically or obtained commercially, were purified before use. The purification of *I* and all its suspected electrolysis products has been presented¹⁸. N,N-Dimethyl-*p*-anisidine was prepared from trimethyl phosphate and *p*-anisidine¹⁹. The product was isolated by steam distillation and recrystallized from methanol, m.p. 46–47°C (lit.²⁰ 48°C). N,N-Dimethyl-*p*-aminophenol was prepared from *p*-aminophenol and

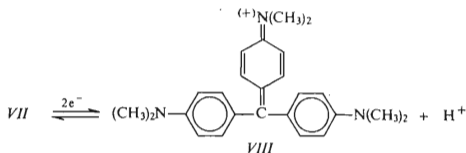
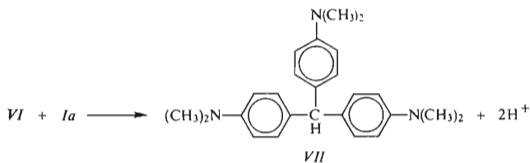
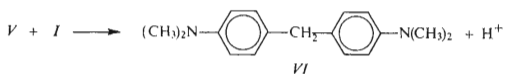
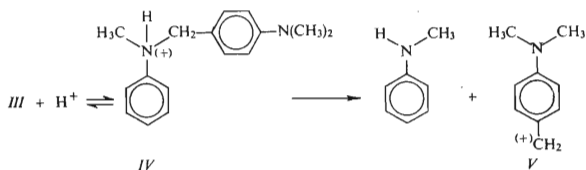
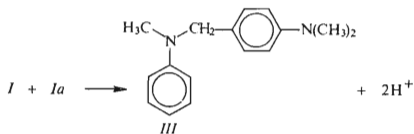
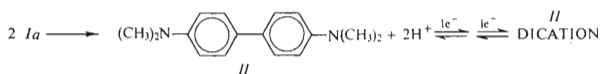
methyl iodide by the procedure of Zandstra and Evleth²¹. The compound readily air oxidizes, so it must be prepared shortly before use. The *p*-alkyl dimethylanilines were prepared by methylation of the corresponding *p*-alkylanilines; similarly, N,N,N',N'-tetramethyl- α,α' -bi-*p*-toluidine was prepared from α,α' -bi-*p*-toulidine¹⁷. The *p*-*t*-butyl-N,N-dimethylaniline was prepared by nitration of *t*-butylbenzene. The *ortho* and *para* isomers were separated on a spinning band column; the purity of the *p*-*t*-butylnitrobenzene was checked by NMR (Perkin-Elmer R 20 spectrometer) and EPR spectroscopy. The corresponding aniline was generated by a Sn-HCl reduction and methylation yielded the *p*-*t*-butyl-N,N-dimethylaniline.

The *p*-iodo derivative was prepared by a standard procedure²²; all the other halogenated N,N-dimethylanilines were synthesized by methylation of the corresponding haloanilines, followed by purification by column chromatography using hexane and Woelm neutral alumina or by vacuum distillation. The completeness of the methylation process was verified by infrared spectroscopy (Perkin-Elmer 621 spectrometer). All of the other substituted N,N-dimethylanilines mentioned herein were obtained as commercial samples or by methylation of the corresponding anilines. In all cases, melting points were compared with literature values and purities were verified spectroscopically.

RESULTS AND DISCUSSION

As a point of reference and comparison, the electrochemistry of N,N-dimethylaniline (*I*) itself was studied under various conditions. Generally, it was found that the products formed depend primarily upon concentration of *I* but also upon such variables as electrolysis time and solvent composition¹⁸. In Scheme 1 the general reaction course in acetonitrile is shown. Obviously, a variety of products form; at low *I* concentrations ($10^{-3}F$) benzidine formation predominates, but as one increases the amount of parent dimethylaniline (*I*) other products are found. At about $10^{-2}F$ *I*, a primary electrolysis product is 4,4'-methylenebis(dimethylaniline) (*VI*) and at $10^{-1}F$ *I*, crystal violet dye *VIII* is formed in large amounts, along with the leuco form *VII*. Also, for a given intermediate or high concentration, prolonged electrolysis (*i.e.*, working at lower current densities) leads to a higher yield of crystal violet dye *VIII* and its leuco form *VII* (ref.¹⁸). However, at all concentrations small amounts of *II* are formed, apparently by a parallel reaction pathway. This mechanism is analogous to one proposed²³ for chemical oxidation of *I*, the only difference being the last step, formation of *VII* and *VIII*. Although the proposed mechanism shows attack of a dimethylaniline cation radical on a molecule of *VI*, it may in fact be the reverse, *i.e.*, attack of a *VI* cation radical on excess *I*. Chemical oxidation studies





SCHEME 1

tend to verify this as the mechanistic pathway²⁴; this study is particularly pertinent, since one-electron oxidants, copper(II) and chloranil, were employed. Based on kinetic data, they chose the reaction between oxidized VI and I parent as being the proper pathway. However, the irreversibility of the first oxidation step of VI (as determined from cyclic voltammograms) and the fact that it is oxidized at almost the same potential as I itself precludes positive verification of this being the electrochemical oxidation pathway. Consequently, one could not, say, oxidize VII in the presence of I and try to observe crystal violet (VIII) formation.

One could conceivably stabilize the Ia cation either by blocking reactive coupling sites or by increasing the electronic delocalization in the molecule. The latter has been shown to be effective in that increasing radical stability is achieved by successively replacing methyl groups on I with phenyl groups. Thus, increasing cation radical stability is observed as one goes from N,N-dimethylaniline (I) to N-methyldiphenylamine to triphenylamine²⁵. The former method, *viz.*, substituent blocking, was investigated in a number of ways.

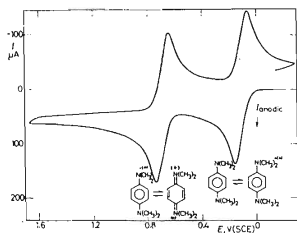


FIG. 1

Cyclic Voltammogram of $1 \cdot 10^{-3} F$ Wurster's Blue in Acetonitrile — 0.1F Tetraethylammonium Perchlorate at Platinum; Sweep Rate = 8.0 V/min

Anodic processes are as shown; cathodic processes are the reverse.

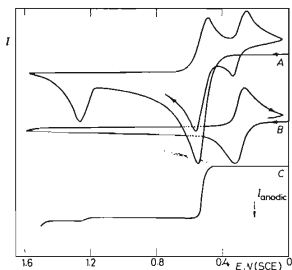


FIG. 2

Voltammograms

Curve A: Cyclic voltammogram of $2 \cdot 10^{-3} F$ N,N-dimethyl-*p*-anisidine in acetonitrile-0.1F tetraethylammonium perchlorate at platinum; sweep rate = 10.0 V/min. Curve B: Cyclic voltammogram of $8 \cdot 10^{-4} F$ N,N-dimethyl-*p*-aminophenol, same conditions as for curve A. Curve C: Rotating disk voltammogram of $1 \cdot 10^{-3} F$ N,N-dimethyl-*p*-anisidine in acetonitrile-tetraethylammonium perchlorate at platinum, rotation rate = 2.000 r.p.m.

The electrochemical oxidation of a series of *N,N*-dialkylanilines, where the alkyl group was ethyl, *n*-butyl, *sec*-butyl and *n*-decyl, yielded results somewhat different from those for *I*. At all concentrations only the corresponding tetraalkylbenzidines could be isolated from electrolysis mixtures; yields were typically 30–40%. However, none of the other corresponding products could be found, indicating that the lability of the methyl group is marked in comparison with the other alkyl groups on the amine nitrogen. Since they are all fairly similar electronically the differences in reactivity may be due to steric effects.

In the reaction Scheme 1, it is apparent that the ring carbon *para* to the dimethylamino group must be unsubstituted for formation of VIII and VI. It was anticipated that *para*-substituted *N,N*-dimethylanilines would be considerably more stable than the parent *I* when oxidized due to blocking of this most active coupling site. This was based on the previous data as well as the known stabilities of two *para*-substituted *N,N*-dimethylanilines *viz.*, *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (Wurster's blue) and *N,N*-dimethyl-*p*-phenylenediamine (Wurster's red). These molecules, particularly Wurster's blue, have been used as model systems for biological studies requiring a reversible, one-electron redox system, most notably in the pioneering work of Michaelis²⁶; more recent studies involving electrolytic generation of the cation radicals of these molecules have verified their marked stability^{27,28}. The stabilization is no doubt achieved due to the strong delocalizing power of the additional amino or dimethylamino group as compared to *I*. These derivatives are so stable, in fact, that even the dications are relatively unreactive, as shown by the cyclic voltammogram in Fig. 1. The highly conjugated quinone diimine dications do, however, decompose slowly *via* as yet undetermined pathways²⁹.

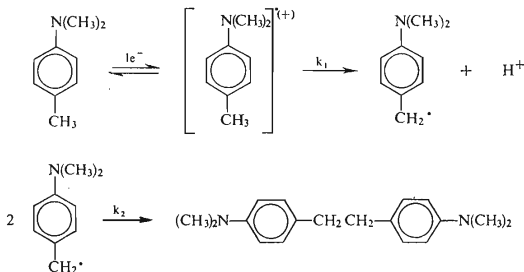
The alkoxy derivatives were found to exhibit somewhat different behavior. Although the cation radicals are quite stable, slow decomposition ensues *via* attack of small amounts of water in the acetonitrile. Thus, *N,N*-dimethyl-*p*-anisidine and *N,N*-dimethyl-*p*-phenetidine (the methoxy and ethoxy analogs, respectively), when oxidized electrochemically in acetonitrile containing roughly 10 milliformal residual water, form relatively stable cation radicals that decompose slowly to the phenoxy analog. This was determined by matching of cyclic voltammograms and visible and UV absorption spectra obtained *in situ* as shown in Fig. 2 and 3 respectively. One anomaly that persists is the nature of the second oxidation wave of the anisidine and phenetidine. In Fig. 2 it is quite small relative to the first oxidation peak but it increases markedly with increasing scan rate, hence it is not a strictly diffusion-controlled process such as oxidation to the dication as in the Wurster's blue system. These data are characteristic of a system where there is a fast follow-up chemical reaction following the second charge transfer step; as one scans more rapidly the chemical reaction is minimized. This latter assertion is refuted, however, by the rotating disk voltammogram (Fig. 3, curve C) that only shows a single major oxidation process for the anisidine; a small wave is seen at more anodic potentials, but the height varies

only slightly with rotation rate up to 10000 r.p.m. It can be seen from Fig. 2, curve B that the anomalous wave is not due to the phenoxy product formed since it exhibits only a single one-electron wave out to +2.0 volts *vs.* S.C.E.

The hydrolysis mechanism has been well documented for alkoxy aromatics such as *p*-methoxyphenol³⁰ and *p*-methoxydiphenylamines³¹, but these studies were in aqueous media. The fact that trace amounts of water in the acetonitrile would effect hydrolysis implies a high charge density on the ring carbon *para* to the dimethylamino group; Hückel calculations verify this qualitatively.

The oxidation of *N,N*-dimethyl-*p*-aminophenol is also interesting in that it undergoes an apparently uncomplicated one-electron oxidation to form the cation radical. However, EPR studies of electrolytically oxidized solutions indicate that the cation radical is quite unstable; the EPR spectrum is obtained only with great difficulty and the ensuing decomposition is rapid, even at low temperatures. Exhaustive oxidation of a milliformal solution of the phenol in acetonitrile followed by re-reduction restored the system to its original state, so overall the redox process is reversible. Apparently, no gross, irreversible chemical decomposition of the cation radical occurs, but rather the overall redox process involves only proton and electron transfers. A reasonable mechanistic pathway would consist of the primary oxidation involving loss of an electron and a proton to form a phenoxy free radical. These may dimerize in solution to form a peroxy-type compound. Upon re-reduction, this dimer would pick up two electrons and two protons to form the parent phenol once again. Although this explanation is consistent with the EPR and electrochemical data it should be emphasized that it is speculative at best.

It was anticipated that *para*-alkyl-*N,N*-dimethylaniline cation radicals would not undergo hydrolysis and hence would be more suitable as examples of inert blocking groups lending enhanced stability. Therefore, a series of *para*-alkyl-*N,N*-dimethylanilines, where the alkyl group was methyl, ethyl, *n*-butyl, *sec*-butyl, and *n*-decyl, were synthesized and their electrochemical behavior investigated. The methyl derivative, *N,N*-dimethyl-*p*-toluidine, will be discussed; it is representative of the series



in that the electrochemical data on the others are similar. By comparison with the aforementioned derivatives, it was thought the alkyl analogs would have less stable cation radicals, but the marked instability encountered in fact was unexpected¹⁷. It was found that, in fact, this instability is not unreasonable since the cation radical of *N,N*-dimethyl-*p*-toluidine can lose a proton to form a benzyl-type free radical. These can then couple to form a bibenzyl, as shown below¹⁷. This general pathway occurs for all the *p*-alkyl DMA's mentioned above; this is not surprising since they all have a labile proton on the alpha-carbon of the alkyl side chain.

Kinetic studies were hampered by the fact that the protons liberated in the coupling reaction tended to protonate both the parent amines and the coupled products; hence, accurate values of neither k_1 nor k_2 could be obtained. It was ascertained, however, that the coupling reaction involving k_2 is more likely the rate-determining step. This was accomplished by running cyclic voltammograms on solutions of *N,N*-dimethylaniline-*p*-toluidine at concentrations of 10^{-3} and 10^{-4} F. As can be

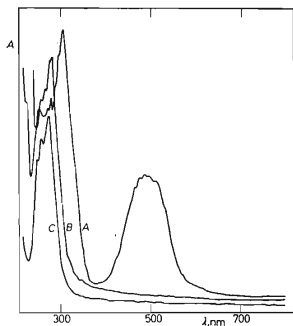


FIG. 3

Visible Absorption Spectra in Acetonitrile

Curve A: Partially electrolyzed solution of *N,N*-dimethyl-*p*-anisidine; oxidation potential is +1.0 V. vs. S.C.E. The broad band centered about 500 nm is the primary cation radical. Curve B: Totally electrolyzed solution of *N,N*-dimethyl-*p*-anisidine. Curve C: Solution of *N,N*-dimethyl-*p*-aminophenol electrolyzed at +1.0 V. vs. S.C.E.

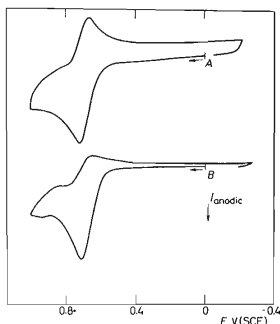


FIG. 4

Cyclic Voltammograms of *N,N*-Dimethyl-*p*-toluidine at Varying Concentrations in Acetonitrile-0.1 F Tetraethylammonium Perchlorate; for Both Curves the Sweep Rate = 3.0 V/min

Curve A: $1.0 \cdot 10^{-4}$ F, curve B: $1.0 \cdot 10^{-3}$ F.

seen in Fig. 4, there is considerably more reverse current following the initial oxidation at $10^{-4}F$, indicating that stability of the cation radical is dependent upon concentration.

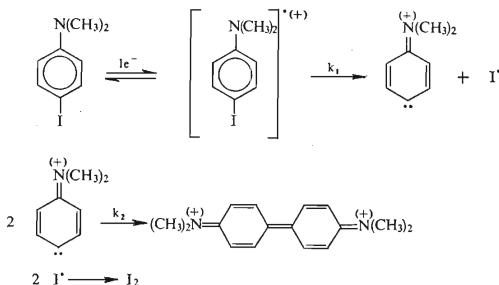
These compounds were also studied in aqueous media from pH 3.0 to 9.0 and the same general behavior was observed, *i.e.*, bibenzyl formation and a cation radical intermediate.

In order to eliminate the possibility of benzyl free radical formation and subsequent coupling, the electrochemical oxidation pathways of *p*-*t*-butyl- and *p*-triphenylmethyl-*N,N*-dimethylanilines were studied. Since the alkyl groups here do not have a proton on the alpha carbon it was hoped that markedly enhanced radical stability would be realized. This was found to be the case; the primary cation radicals, formed by one-electron oxidation of the parent amine, were considerably more stable than was the case for the other *p*-alkyl derivatives. However, these radicals did decompose also at a moderate rate to form, as yet, undetermined products.

Since halogens are generally good leaving groups, the *parahaloDMA*'s were studied also. Variable behavior was found for these compounds. Generally, this behavior ranged from total and rapid halogen elimination for *p*-iodoDMA to a complete absence of elimination for *p*-fluoroDMA.

Fig. 5, curve A shows the cyclic voltammogram obtained for *p*-iodoDMA in acetonitrile at platinum. One sees an irreversible oxidation wave with $E_p = 0.9$ V.; upon scan reversal three cathodic waves are found, all of which are reversible. At high scan rates (100–1000 V/min) the initial oxidation wave becomes more and more reversible, *i.e.*, i_{pc}/i_{pa} approaches unity, and at 1500 V/min one sees only a single reversible one-step oxidation-reduction process over the voltage range 0 to 1.2 volts.

Coulometry of 10^{-3} and $10^{-4}F$ solutions of *p*-iodoDMA gave *n*-values of 1.03 and 0.98, respectively, so it is apparent that the primary oxidation is a one-electron process. If elimination were occurring, one would expect iodine and TMB as the electrolysis products. In fact, a mixture of I_2 and TMB in acetonitrile gives curve B



in Fig. 5; the match-up with the follow-up systems in curve A is striking. In light of the products formed, one can propose the following mechanism for the electrochemical oxidation of *p*-iodoDMA in acetonitrile:

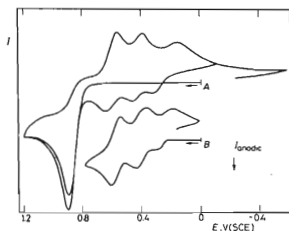


FIG. 5

Cyclic Voltammograms

Curve A: $2 \cdot 10^{-3} F$ *p*-iodo-*N,N*-dimethylaniline in acetonitrile-0.1*F* tetraethylammonium perchlorate at platinum; sweep rate = 8.0 V/min. Curve B: a mixture of *N,N,N',N'*-tetramethylbenzidine (II) and I_2 , same conditions.

Again, one has the possibility of either first- or second-order rate control. From cyclic voltammograms run at 0.5, 2.0 and 4.0 m*F*, it was found that the ratio of i_{pc}/i_{pa} changed very little with varying concentration, indicative of a follow-up

TABLE I

Determination of First-Order Rate Constants for Halogen Elimination from *p*-Bromo- and *p*-Iodo-*N,N*-Dimethylaniline

Compound $p-(CH_3)_2NC_6H_4X$	Concentration m <i>F</i>	k^a , s ⁻¹
X = Br	0.5	1.08 ± 0.21^b
		1.30 ± 0.20^c
	2.0	1.05 ± 0.25^b
X = I	4.25	1.28 ± 0.30^c
	1.80	6.16 ± 0.95^b
		7.71 ± 1.40^c
	0.65	6.59 ± 1.50^b

^a Solvent was acetonitrile-0.1*F* TEAP, temperature $25 \pm 1^\circ C$; ^b $i_{rev}/i_{for} = 0.414$; ^c $i_{rev}/i_{for} = 0.225$.

reaction adhering to first-order kinetics. A small decrease in i_{pc}/i_{pa} at higher concentration is indicative of chemical complications other than elimination and coupling.

Identical electrochemical behavior was observed for *p*-bromoDMA, except that the primary cation radical is more stable than is that of the iodo derivative. Reverse-current chronopotentiometry was used to determine the first-order rate constants for these systems. Table I shows that the compounds adhere to first-order kinetics over a fairly wide range of concentrations. The variation in the k values is slight and is a strong, though not prohibitive, argument for the proposed mechanism. Because of the high reactivity of carbene intermediates, it is reasonable that the elimination step would be rate-controlling; subsequent coupling of the free carbenes is probably diffusion-controlled, or close to it.

The postulation of the quinoidal-type carbene intermediate is rather unusual for an electrochemical oxidation, but it is difficult to propose an alternate mechanism considering the data presented. However, similar carbene-type intermediates have been proposed for the decompositions of some quinone azines^{32,33}, and *p*-bromophenols³⁴. In these cases also the resulting products were *para*-coupled diquinoidal compounds.

At higher concentrations (10^{-2} to $10^{-1}F$), the *p*-bromo- and *p*-iodoDMA follow the same mechanistic pathways as DMA itself, *i.e.*, formation of MBDMA at intermediate concentrations and crystal violet dye at high concentrations. In addition, the *p*-bromoDMA gave a high yield (approx. 40%) of *p*-bromo-*N*-methylaniline upon electrolysis of a $10^{-1}F$ solution in acetonitrile; this in addition to a small amount of MBDMA and about 30% crystal violet dye. The *p*-bromo-*N*-methylaniline may be a by-product of crystal violet formation, as shown in the mechanism in Fig. 1, or it may be formed by a parallel reaction pathway; the surprisingly high yield suggests the latter.

The *p*-chloroDMA was found to eliminate chlorine to only a minor extent in dilute solution ($10^{-3}F$) to form TMB; the major decomposition pathway of the cation radical is as yet undetermined. No elimination occurs upon oxidation of *p*-fluoroDMA; the cation radical is quite stable and decomposes only slowly. In the case of this compound and the chloro analog concentration studies show that the decomposition pathway follows second-order kinetics; coupling through the amino methyl groups to form substituted ethylenediamines is suspected but as yet unconfirmed.

Two other derivatives were found to undergo partial elimination to form TMB-*p*-dimethylaminobenzaldehyde and *p*-dimethylaminobenzoic acid. Other derivatives such as *p*-dimethylaminobenzonitrile and *N,N*-dimethyl-*p*-nitroaniline do not undergo any *para* group elimination, but their cation radicals are only moderately stable; at present, little can be said regarding their decomposition pathway(s).

In an effort to determine the role the *ortho* ring positions play, if any, in the decomposition pathways of substituted DMA cation radicals, several 2,4,6-trisubstituted DMA's were studied electrochemically, *viz.*, *N,N*,2,4,6-pentamethylaniline, 2,4,6-

trichloro-N,N-dimethylaniline and 2,4,6-tribromo-N,N-dimethylaniline. However, the electrochemistry of these compounds indicates that the *ortho* substituents twist the dimethylamino group to such an extent that the cation radicals are destabilized and their decomposition pathways are more like those of aliphatic amines^{3,5}. Apparently, the stability of the various cation radicals depends on electronic delocalization into the aromatic ring to a significant degree. Hence, the cyclic voltammogram of *p*-chloro-N,N-dimethylaniline is completely reversible at 50 V/min, while that of 2,4,6-trichloroderivative is almost completely irreversible at this scan rate, indicating that the cation radical of the latter compound is considerable less stable than that of the former.

CONCLUSIONS

Although these studies are somewhat incomplete, a clear picture of the decomposition pathways of substituted N,N-dimethylanilines can be discerned. As has been shown, N,N-dimethylaniline (*I*) itself is extremely reactive, the key positions in the molecule being the methyl groups and the ring position *para* to the dimethylamino group. When the methyls are replaced with other, less labile alkyl groups, the only detectable radical decomposition pathway is *via para-para* ring coupling. Substitution of „inert” blocking groups at the *para* ring position is less successful in simplifying the electrochemistry of *I*. For these molecules there seems to be a series of decomposition pathways that can be followed; for each molecule the favored route appears to depend upon the nature of the *para* substituent.

The least stable radicals were those of *p*-bromo-, *p*-iodo-N,N-dimethylanilines and *p*-dimethylaminobenzoic acid, all of which underwent group elimination. Decomposition of the *para*-substituent can also occur, as in the case of the *p*-alkyl derivatives, or substitution can take place as for N,N-dimethyl-*p*-anisidine going to N,N-dimethyl-*p*-aminophenol.

If none of these reactions take place the cation radical is fairly stable, the ensuing decomposition is relatively slow and the products formed are as yet undetermined. Since the *para*-substituents are, indeed, inert in these molecules it would seem that the next most reactive site, the methyls of the dimethylamino group, are involved. This would lead to substituted diphenylethylenediamines as oxidation products of *para*-substituted N,N-dimethylanilines where the substituent group does not lead to decomposition by other, more facile pathways.

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