[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF KANSAS, LAWRENCE, KANSAS]

Anodic Oxidation Studies of N,N-Dimethylaniline. I. Voltammetric and Spectroscopic Investigations at Platinum Electrodes

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The anodic oxidation of N,N-dimethylaniline at a platinum electrode in acidic buffers was examined by conventional and cyclic voltammetry, Tafel plot measurements, *in situ* spectrophotometric and electron paramagnetic resonance techniques. The oxidation was shown to lead to the formation of N,N,N',N'-tetramethylbenzidine and its oxidized quinoid as principal products. A general mechanism scheme for the oxidation is presented.

Introduction

Valid mechanism studies of organic oxidations at solid electrodes are quite complex and the correct interpretation of data is difficult for several reasons. Using platinum or gold electrodes, concurrent oxidation of the electrode surface may well occur in the range of potentials involved. The role of surface oxides in an over-all electrode reaction, while receiving much attention at present, is by no means fully understood. Thus, the evaluation of kinetic parameters for a solid electrode reaction, *i.e.*, n_a, K^0 and i_0 (exchange current) should be viewed with caution since at least it must be granted that the true surface oxide conditions on noble metal electrodes are rarely known with certainty.

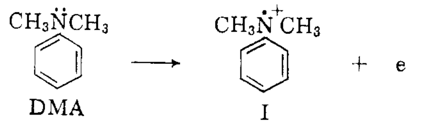
Since the *complete* elucidation of even a simple electrode reaction is a difficult task, one often must be content with the determination of one or more of the kinetic parameters, or perhaps merely the over-all number of electrons transferred (n_T). Conventionally, the latter quantity is derived from one of the forms of a limiting current equation (*e.g.*, Ilkovic equation for the DME), assuming all other quantities in the equation are known or measurable. Here, with organic electrooxidations, there are at least two pitfalls: The possibilities of follow-up chemical reactions after the primary electrode process are wide-spread and the limiting current may not be at all representative of the initial electrochemical process. Furthermore, the value of the diffusion coefficient (D) needed to evaluate n_T is rarely known in the medium of interest. Recent determinations of D values show that the use of infinite dilution or totally estimated values involves considerable doubt.[2-4] The use of electrochemical methods to evaluate D when n_T is unknown can lead to considerable uncertainty.

Using the points mentioned above as guiding principles, a concerted effect has been in progress in this Laboratory for some time to study the mechanism of anodic oxidations of aromatic molecules, primarily amines. The approach has been to apply to a given electroactive system a wide variety of electrochemical techniques, coupled with *in situ* absorption spectroscopy and examination of products using high activity tritium labeled compounds. The electrochemical data has been viewed initially with extreme scepticism until spectral and tracer identification of products gave results which could be legitimately interpreted through the electrochemistry. Since chemical interaction of the initial electrolysis products was known to be prevalent and to proceed in a complex fashion, large scale electrolyses could have given erroneous results, although Geske and co-workers have recently given interpretations of controlled potential electrolyses involving subsequent chemical reactions.[5] Using the tracer technique, product identification was carried out under very low level conditions corresponding to the small currents and times employed in several polarograms or chronopotentiograms. Part 1 of this series concerns the electrochemical reaction at Pt electrodes and Parts 2 and 3 deal with carbon paste electrodes and tritium tracer studies.

Based on preliminary work, the following process suggested itself for the over-all electrochemical oxidation at about pH 2–3. Two alternate charge transfer processes have to be postulated.

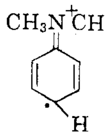
Reaction Scheme.—The initial charge transfer step is probably preceded by the rapid acid dissociation of dimethylanilinium ion to the free base, DMA, although this reaction has not been substantiated in the present studies.

Charge transfer reaction

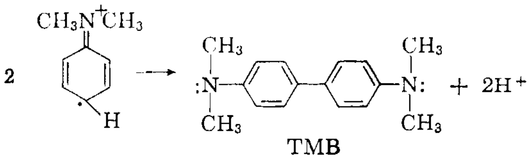


(1)

The free radical I can be written in a variety of equivalent resonance forms of which structure II with the unpaired electron on the *para* position is probably an important contribution. Now coupling of two DMA free radicals can occur to give tetramethylbenzidine (TMB) as



II



(2)

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[1] Dept. of Chemistry, Kyoto University, Kyoto, Japan.

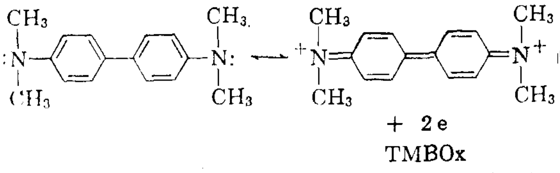
[2] M. V. Stackelberg, M. Pilgrim and V. Toome, *Z. Elektrochem.*, **57**, 342 (1953).

[3] C. L. Rulfs, *J. Am. Chem. Soc.*, **76**, 2071 (1954).

[4] D. J. Macero and C. L. Rulfs, *ibid.*, **81**, 2942 (1959).

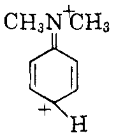
[5] (a) D. H. Geske and A. J. Bard, *J. Phys. Chem.*, **63**, 1057 (1959). (b) D. H. Geske, *ibid.*, **63**, 1062 (1959).

The TMB is then further oxidized *via* a 2-electron transfer (which may involve 1-electron intermediate stages) giving the quinone diimine (TMBOx)



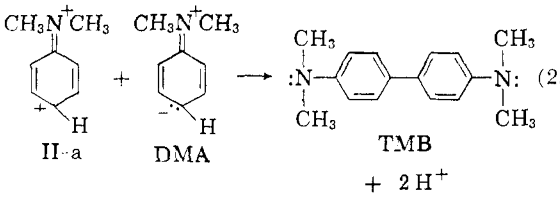
(3)

An alternate electron transfer reaction is the removal of 2 electrons leading to the intermediate II-a



II-a

This species can now react with a molecule of unoxidized DMA to give rise to TMB as



(2A)

The further oxidation of TMB to TMBOx is the same as before so that either electron transfer reaction leads to the same final product. The formation of the dipositive species II-a, while probably energetically more difficult, is strongly supported by the electrochemical evidence. On the other hand, dimethylanilino free radical ions have been postulated in the oxidation of DMA by peroxidase,[6] by iodosobenzene acetate,[7] and in the oxidation of malachite green.[8] In each case TMB or the corresponding diimine TMBOx was formed.

The results have been condensed as much as possible without, it is hoped, sacrificing interpretation of the data. Only where the techniques differ from conventional electrochemical practice are experimental details given.

A. Conventional Voltammetry of DMA.—The polarographic behavior was investigated at a stationary platinum wire electrode (StPtW) from *p*H 2–9 using Britton and Robinson buffers with essentially constant ionic strength maintained by 1 *M* sodium sulfate. In quiet solution, at voltage scan rates of 200 mv./min., peak polarograms were obtained as expected. The usual variation of $E_{p/2}$ *vs.* pH was observed with a sharp break about pH 4.9 corresponding approximately to the pK_a of dimethylanilinium ion. The peak current was essentially independent of pH up to about pH 4. Between pH 4–8 it increased almost linearly with an overall increase of about 30%.

The voltammetry of TMB shows it to be considerably *more easily* oxidized than the parent DMA. In the pH range 1–4 the $E_{p/2}$ of TMB is several tenths of a volt less anodic than that of DMA. (Hence the unoxidized TMB cannot be expected as a final product.) Beyond pH 4, TMB is only slightly soluble in the buffer systems.

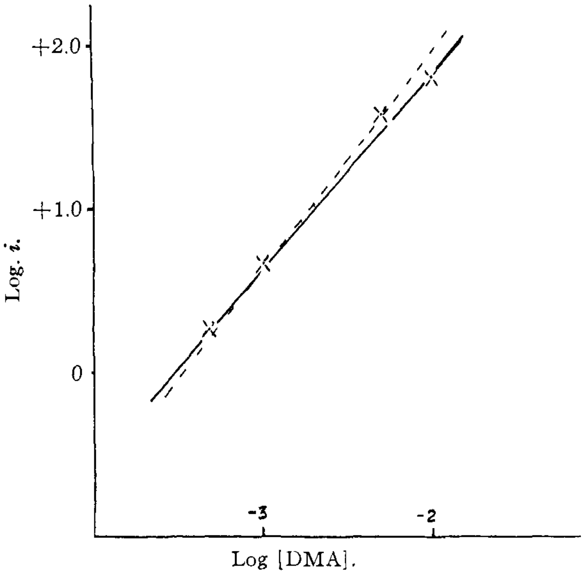


Fig. 1.—Reaction order for DMA oxidation: solid line, slope = 1.1; dotted line, slope = 1.3; current units, microamperes.

B. Tafel Plot Measurements.—The classical method of electrochemical kinetics involves the measurement of log $i - E$ curves under conditions of very rapid mass transport so that the electron transfer process is rate controlling. This technique is admirably suited to relatively slow reactions whereas more sophisticated relaxation methods may be needed for rapid processes. From the slope of the straight line portion of the log $i - E$ curve, one easily calculates the product βn_a the product of the anodic transfer coefficient (β) by the number of electrons in the rate controlling step. Details of Tafel plots and other forms of the pertinent equations are given by Delahay.[9] Further, from a series of Tafel plots taken with varying bulk concentration of electroactive species (C^b_{red}) one can measure log i at a constant E_{app}. A plot of log i *vs.* log C^b_{red} gives a straight line whose slope indicates the exponent or order of the electrochemical reaction with respect to C_{red}. This technique has been used widely by Vetter.[10]

Tafel measurements were carried out using a Pt wire electrode with very efficient stirring. The electrode had 4 stirrer blades mounted just above the wire and was similar to the wire convection electrode of Kolthoff and Jordan.[11] Linear Tafel regions were obtained for all concentrations of DMA.

Figure 1 shows the plot of log i *vs.* log C_{DMA} obtained. The value of log i was measured in all cases at + 0.63 v. *vs.* s.c.e. The experimental

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(6) F. T. Naylor and B. C. Saunders, *J. Chem. Soc.*, 3519 (1950).

(7) J. Mitchell and K. H. Pausacker, *Austral. J. Chem.*, **10**, 460 (1957).

(8) V. Hanousek and M. Matrka, *Coll. Czech. Chem. Comm.*, **24**, 16 (1959).

(9) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishing Co., New York, N. Y., 1954.

(10) K. J. Vetter, *Z. Elektrochem.*, **59**, 596 (1955); K. J. Vetter, in "Transactions of the Symposium on Electrode Processes," John Wiley and Sons. Inc., New York, N. Y., 1961.

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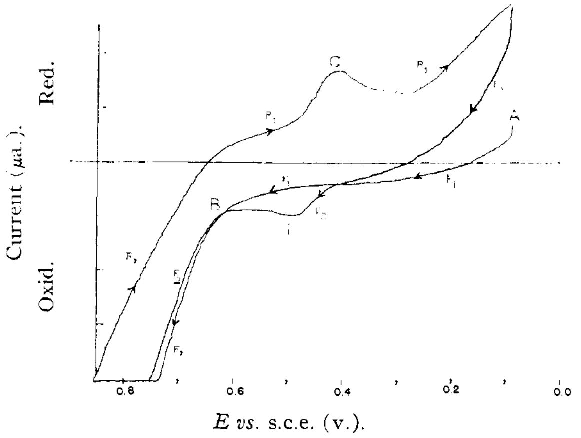

Fig. 2.—Cyclic polarograms of DMA.

slope is between 1.1 and 1.3 pointing to an order or molecularity of unity for DMA.

The value of βn_a obtained from each Tafel plot varied somewhat with DMA concentration. Over the DMA concentration range 10^{-4} to $10^{-2}M$, the mean value of βn_a was 1.23. Since n_a must be a small and integral number, it can hardly be 1 or β is greater than unity. This is untenable since the transfer coefficient is a fraction of the over-all potential contributing to the anodic reaction. Thus n_a must be at least 2 although higher integers are not excluded. The Tafel plot data thus point toward a DMA molecularity of 1 with 2 electrons transferred in the rate controlling step. This dictates the dipositive species II-a as the primary intermediate rather than the DMA free radical. Further substantiation of the 2-electron transfer derived from rotating disk experiments is found in Part 2.

C. Cyclic Voltammetry.—In the cyclic voltammetry method as used by Kemula and co-workers,[12] a moderately slow triangular voltage sweep is applied to the voltammetric cell. A typical application to solid electrode systems has recently been given.[13] In the present case a triangular sweep varying between about + 0.1 and + 0.9 v. *vs.* s.c.e. was applied to a Pt wire electrode and the s.c.e. The sweep rate was *ca.* 0.9 v./min. The current was measured as an *iR* drop across a decade box and applied to the y-axis of a Moseley Model 3 Autograph. The applied voltage to the cell was monitored with a Leeds and Northrup 7664 pH meter whose output fed the x-axis of the recorder. Figure 2 shows 2 cycles of the resulting polarograms. Starting at point A, the first anodic sweep F_1 shows only residual current up to point B (*ca.* + 0.6 v.) where the oxidation of DMA begins. This continues till + 0.9 v. when the applied voltage reverses and the reverse cathodic sweep (R_1) is observed. At point C on R_1 a cathodic peak polarogram ($E_{p/2}$ *ca.* + 0.45 v.) is observed. After R_1 reverses at + 0.1 v. the anodic sweep F_2 begins. This time an anodic peak with $E_{p/2}$ = + 0.45 v. is observed. Subsequent scans repeat this pattern. The almost reversible electroactive system appearing at + 0.45 v. is identical with that obtained from cyclic scans of solutions of TMB only. This is very convincing evidence for the postulated follow-up chemical reaction.

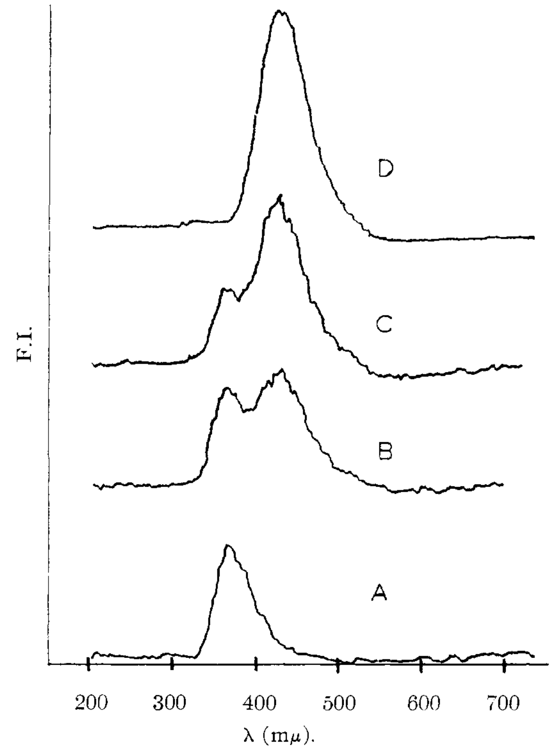

Fig. 3.—Fluorescence spectra of oxidized DMA and TMB: A, DMA, no oxidation; B, DMA, 3 minutes oxidation at +0.8 v.; C, DMA, 5 minutes oxidation at +0.8 v.; D, TMB, 5 minutes oxidation at +0.8 v. . All in pH 2.5 buffer.

D. Spectrophotometric Identification of Electrode Products.—A polarographic cell was inserted directly in the cell of a rapid scan spectrophotometer (American Optical Company). The Pt working electrode was a foil arranged to be parallel to the light beam. Photographs were made of the oscilloscope traces before and during electrolysis of both DMA and TMB solutions in pH 2.5 buffer. Both solutions showed practically no visible absorption prior to electrolysis but strong absorption at about 545 mμ after about 3–5 minutes oxidation at *ca.* 1 ma. of current. The complete spectra were almost identical and there is strong evidence that DMA and TMB give the same oxidation product.

Since visible spectra of highly conjugated molecules are hardly specific, the corresponding fluorescence spectra were examined. Although the fluorescence spectra were not obtained using the *in situ* technique, they were observed within a few minutes after generation. The spectra were taken with a Aminco–Bowman instrument using an activation wave length of 262–263 mμ for both DMA and TMB. In Fig. 3, Curve A is the fluorescence spectrum of DMA in pH 2.5 buffer before electrolysis, showing a fluorescence peak at *ca.* 365 mμ. Upon oxidation at a small Pt wire using an applied voltage of + 0.8 v. *vs.* s.c.e. for 3 minutes Curve B results. After 5 minutes oxi-

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(12) W. Kemula and Z. Kublik, *Nature*, **182**, 793 (1958); *Bull. Acad. Pol. Sci.*, **6**, 653 (1958); *Roczniki Chem.*, **32**, 941 (1958).

(13) C. Olson, H. Y. Lee and R. N. Adams, *J. Electroanal. Chem.*, **2**, 396 (1961).

dation curve C shows the new fluorescence peak at about 430 mμ increases with time of electrolysis. Finally Curve D shows this peak is identical with that obtained by similar electrolysis of TMB alone. Further spectral substantiation of the formation of TMBOx during electrooxidation of DMA is hardly necessary.

E. Electron Paramagnetic Resonance Studies.—It should be possible to observe relatively long-lived free radical intermediates in the DMA oxidation by carrying out the electrolysis in the microwave cavity of an e.p.r. spectrometer. The *in situ* generation technique has been developed to a high degree by Maki and Geske.[14–16] Application of the technique to studies of aqueous solution electrochemistry has recently been given.[17]

Using $10^{-3}M$ DMA solutions in pH 2.4 buffers only very weak, broad, resonance signals are obtained which can in no way be interpreted as due to the presence of dimethylanilino free radical ions. At high pH indications are one or more radical ion species develop which change with time of electrolysis. The interpretation of the hyperfine interactions of these spectra are consistent with the presence of the tetramethylbenzidine positive ion. Full interpretation of the e.p.r. results must await further study, but it is safe to conclude that the results are consistent with the idea that the initial charge transfer does not produce dimethylanilino radicals, or if it does, the lifetime of this species is too short to be detected by standard electrochemistry or e.p.r. spectroscopy under the conditions employed herein.

Summary.—By a variety of electrochemical and supporting techniques, the oxidation of N,N-dimethylaniline at pH 2–3 has been shown to lead to N,N,N′,N′-tetramethylbenzidine and its oxidized quinoid form as principal products.

Acknowledgments.—We are indebted to Doris Carter for carrying out the fluorescence measurements reported. This work was supported by the Atomic Energy Commission through contract AT-(11-1)-686 and this support is gratefully acknowledged.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KANSAS, LAWRENCE, KANSAS]

Anodic Oxidation Studies of N,N-Dimethylaniline. II. Stationary and Rotated Disk Studies at Inert Electrodes

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The oxidation of N,N-dimethylaniline was studied at carbon paste electrodes and found to be consistent with the previous data obtained at platinum surfaces. Using cyclic voltammetry, the follow-up chemical reaction producing tetramethylbenzidine was examined in detail. It was shown that a further reaction of dimethylaniline and tetramethylbenzidine occurs and becomes important in alkaline media. Very convincing evidence of the existence of tetramethylbenzidine as an intermediate in the over-all process was obtained using the rotating ring-disk electrode technique.

In Part I of this series, emphasis was placed on the use of electrochemical and spectrophotometric techniques to identify the final products of DMA oxidation at platinum electrodes. The work described herein concerns some less conventional electrochemical methods at carbon paste electrodes to substantiate the intermediate electrochemical and follow-up chemical steps in the over-all electrode process. Considerable evidence has been gathered that carbon paste electrode surfaces do not undergo oxidation during anodic reactions. Hence, the possible role of surface oxides in the DMA oxidation can be established more closely.

Experimental

Carbon paste (CE-NjP) and platinum (Pt) electrodes were used. The surface area of the CE-NjP was 0.40 cm.^{2} Details on the preparation and usage of these electrodes have been given.[1,2] The rotating disk electrode was a carbon–Nujol paste (designated CE-NjP-RD) of 0.1 cm.^{2} area. It was arranged for rotation speeds from 3 to 30 rev./sec. The rotation speeds were controlled with a feedback network and were calibrated with a stroboscope attachment. The rotation speeds were held constant within ± 1%. A "double disk" (ring-disk) rotating electrode, fashioned of carbon paste after the design of Levich[3] was also used. Construction details of the double disk and the utility of carbon paste rotated disk electrodes have been given recently.[4]

Most of the voltammetry was carried out with a controlled potential polarograph of the operational amplifier type. Both single sweep and cyclic voltammetry were used with potential sweep rates from 0.5 to 2.0 v./min. Measurements were carried out at 25 ± 0.1° unless otherwise noted.

Results

A. Cyclic Voltammetry at Carbon Paste Electrodes.—The cyclic voltammetry was examined over a wide range of *p*H (from 3 M H_2SO_4 to *p*H 10 buffer). At about pH 2–4, the results were very similar to that given in Part 1 for Pt electrodes, *i.e.*, after the first anodic scan an almost reversible redox system appeared at *ca.* + 0.4 v. *vs.* s.c.e. which can be identified with the system TMB–TMBOx.

In a more basic medium (pH > 5) two redox systems were obtained (again, the *first* anodic scan shows only a single peak current due to DMA oxidation). In pH 6.0 buffer these systems appeared at about + 0.4 and + 0.2 v. *vs.* s.c.e.

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