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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(17) L. H. Piette, P. Ludwig and R. N. Adams, *ibid.*, **83**, 3909 (1961).

[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

BY Z. GALUS AND R. N. ADAMS

RECEIVED NOVEMBER 6, 1961

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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(1) R. N. Adams, *Anal. Chem.*, **30**, 1576 (1958).

(2) C. Olson and R. N. Adams, *Anal. Chim. Acta*, **22**, 582 (1960).

(3) V. G. Levich, "Fiziko-Khimcheskaya Gidrodinamika" (Physico-Chemical Hydrodynamics, Gosudarstvennoe Izdetelstvo Fiziko-Matematicheskoi Literatury, Moscow, 1959.

(4) Z. Galus, C. Olson, H. Y. Lee and R. N. Adams, *Anal. Chem.*, **34**, 164 (1962).

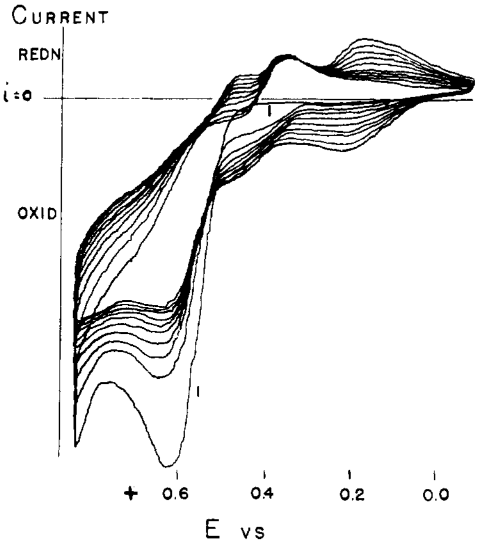
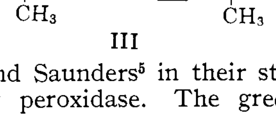


Fig. 1.—Cyclic voltammetry of DMA at stationary carbon paste electrode; *p*H 6.0, scan rate *ca.* 1 v./min.

This is seen in Fig. 1 which represents 10 cyclic scans of 1.0×10^{-3} *M* DMA at pH 6.1. The redox system at about + 0.2 v. is seen to increase with the successive cyclic excursions of the potential. The TMB–TMBOx system at about + 0.4 v. and the anodic DMA wave at + 0.6 v. decrease in peak current with number of cyclic scans.

As indicated in Part 1, there is little doubt that the redox system at + 0.4 v. is that of TMB–TMBOx. The "extra" system at about + 0.2 v., which forms most rapidly at high pH, is more difficult to identify in an absolute sense. That it is, however, a secondary reaction product between the excess DMA and TMBOx can be shown by the following experiments. TMBOx was prepared by chemical oxidation of TMB with lead dioxide and isolated as the perchlorate. A solution of this TMBOx was made up in pH 4 buffer and divided into two parts. To one solution, DMA was added and, after about 40 minutes standing, cyclic polarograms were run on both solutions. In the solution containing just TMBOx, only the usual cathodic–anodic waves at + 0.4 v. corresponding to TMB–TMBOx were found. In the solution mixed with DMA, the additional anodic–cathodic system at *ca.* + 0.2 v. was also detected. (The anodic sweep of the cyclic polarograms was only allowed to go to + 0.5 v. in this case and DMA itself was not electrochemically oxidized during these runs.)

Of considerable interest in these particular experiments are the colors of the two solutions. The solution containing only TMBOx developed a green color whereas the solution of TMBOx plus DMA was pale blue. The green color has been connected with the TMB radical ion:



III

by Naylor and Saunders[5] in their study of DMA oxidation by peroxidase. The green color was found in DMA oxidation in basic media by these workers, and indeed, a solution of TMBOx (yellow) could be transformed to the green color and finally back to the fully reduced TMB by the action of dilute sodium hydroxide. When the green solution was treated with DMA, a blue solution resulted. The color reactions seen in the present electrolysis studies bear a remarkable similarity to those observed by Naylor and Saunders. It is proposed that the secondary coupling reaction of DMA, resulting in the electroactive system at + 0.2 v., occurs by reaction of DMA with Species III, the radical ion of TMB. This reaction is relatively slow but is favored at pH > 4 since in more acid solution the possible protonation of III leads to less resonance stabilization for the radical.[5] While it is impossible from the present data to give the structure of this coupling product, tritium tracer studies in Part 3 support the contention that the reaction is one involving the *para* position of DMA.

B. Peak Polarograms and Kinetic Parameters for DMA and TMB.—The half-peak potentials ($E_{p/2}$) of DMA at carbon paste electrodes varied with pH in the same manner as at Pt. It was also found that $E_{p/2}$ varied considerably with scan rate, which is typical of an irreversible electrode reaction. However, the slopes of the peak polarograms were essentially independent of scan rate in solution of pH<4. This is shown in the last column of Table I where the slope is expressed as the difference between the peak and half-peak potential ($E_p - E_{p/2}$). Some temperature variation studies are included in Table I. The slopes of the peak polarograms are used in the next section to derive the kinetic parameter βn_a.

Table I

Peak Polarogram Behavior of DMA at Carbon Paste Electrodes

Scan rate, *V* (v./sec.)	pH	Temp. (°C.)	$E_{p/2}$ (v. *vs.* s.c.e.)	$E_p - E_{p/2}$ (mv.)
8.33×10^{-4}	2.4	25.0	0.652	43.6
3.33×10^{-3}	2.4	25.0	.699	47.3
8.33×10^{-3}	2.4	25.0	.670	45.4
1.67×10^{-2}	2.4	25.0	.682	43.6
3.33×10^{-2}	2.4	25.0	.680	47.2
8.33×10^{-3}	2.2	41.9	.662 ± 0.001[a]	46.6
8.33×10^{-3}	2.2	55.9	.638 ± 0.001[a]	45.1

[a] Indicates typical reproducibility of runs. [b] DMA concentration 10^{-3} *M* in all cases.

If the charge transfer process is preceded by a slow chemical step, the quantity ($i_p/V^{1/2}$) should vary with the scan rate *V* at constant electrode area, pH, and DMA concentration. If however, precursor reactions are absent or too rapid to be detected by this means, ($i_p/V^{1/2}$) is independent of $V^{1/2}$. The latter is the case for DMA oxidation in *p*H 2–4 buffers at carbon paste electrodes where ($i_p/V^{1/2}$) was found essentially constant over a range of scan rates from 0.096 to 1.94 volts/minute. The value of i_p increases linearly with $V^{1/2}$ of course.

The influence of the electrode material on the nature of the oxidation was examined by comparing peak polarograms at Pt and carbon paste electrodes. Table II shows the behavior of DMA is quite

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

TABLE II

COMPARISON OF PEAK VOLTAMMETRY AT Pt AND CARBON PASTE ELECTRODES

Scan rate, V (v./sec.)	$E_{p/2}$ (v. *vs.* s.c.e.) Pt	CE-NjP	$E_p - E_{p/2}$ (mv.) Pt	CE-NjP
3.33×10^{-3}	0.690	0.684	47.9	43.7
8.33×10^{-3}	.694	.697	49.3	45.3
1.67×10^{-2}	.697	.698	48.2	43.9
3.33×10^{-2}	.710	.703	51.0	42.9

[a] All at pH 2.2, 0.09 N H_2SO_4, 1 M Na_2SO_4 buffer.

similar at the two electrodes. The slopes of the polarograms are a bit greater at Pt. Also, the quantity $i_p/V^{1/2}$ is not independent of V at Pt electrodes but decreases with increasing scan rates. This same effect was noted in chronopotentiometry at Pt foils where $i_0\tau^{1/2}$ showed a marked decrease with increasing current density. A completely satisfactory explanation of this effect is not available.

The evaluation of the product βn_a (the anodic transfer coefficient, β, by the number of electron, n_a, in the rate controlling step) was obtained from the slopes of the peak polarograms. For a totally irreversible system, one has the relation[6]

$$(E_p - E_{p/2})_{\text{Irr}} = 1.85\,\frac{RT}{\beta n_a F} \qquad (1)$$

Since the quantity $(E_p - E_{p/2})$ was independent of V over a wide range of scan rates, the process can be assumed to fit the totally irreversible situation. In Table III are collected the values of βn_a so obtained. The product βn_a is evidently constant over a wide range of scan rates and shows only a slight tendency to increase at higher temperatures.

TABLE III

KINETIC PARAMETERS FOR DMA OXIDATION AT CARBON PASTE ELECTRODES

Scan rate, V (v./sec.)	pH	Temp. (°C.)	βn_a	log K_b
8.33×10^{-4}	2.4	25.0	1.10	−19.6
3.33×10^{-3}	2.4	25.0	1.02	−20.0
8.33×10^{-3}	2.4	25.0	1.06	−19.8
1.67×10^{-2}	2.4	25.0	1.10	−19.8
3.33×10^{-2}	2.4	25.0	1.02	−19.9
8.33×10^{-3}	2.2	24.2	1.03	−20.9
8.33×10^{-3}	2.2	41.9	1.09	−19.3
8.33×10^{-3}	2.2	55.9	1.16	−18.1

A simple transformation of the equation of Matsuda and Ayabe to conform to anodic reactions allows the calculation of $k_b{}^0$ from

$$E_{p(\text{Irr})} = \frac{RT}{\beta n_a F}\left[0.78 - \ln\frac{k_b{}^0 f_{\text{red}}}{D_{\text{red}}{}^{1/2}} + \frac{1}{2}\ln\frac{\beta n_a F V}{RT}\right] \qquad (2)$$

where $k_b{}^0$ = rate constant at $E = 0$ referred to standard hydrogen electrode, f_{red} = activity coefficient of DMA, and the other symbols have their usual significance. For the calculations the diffusion coefficient of DMA was taken as 0.47×10^{-5} cm.^{2}/sec. and a mean value of $\beta n_a = 1.06$ was used. The values of $k_b{}^0$ are summarized in Table III.

From the slope of a plot of log $k_b{}^0$ *vs.* $1/T$ an apparent heat of activation for the reaction was found to be 42.0 kcal./mole.

The TMB–TMBOx system behaves essentially reversibly at all but the highest scan rates used. For reactions controlled only by linear diffusion, the difference between peak and half-peak potentials according to Matsuda and Ayabe[6] is

$$(E_p - E_{p/2})_{\text{rev.}} = \frac{0.057}{n}\ \text{v.} \qquad (3)$$

The validity of this equation for anodic reactions at solid electrodes (B_4C) has been verified.[7] A difference of *ca.* 30 mv. was found for the TMB oxidation which agrees well with a 2-electron oxidation process. Further, it can be noted that the difference between the cathodic and anodic peak potentials of a reversible system is given by[6,7]

$$E_p(\text{anodic}) - E_p(\text{cathodic}) = \frac{0.058}{n}\ \text{v.} \qquad (4)$$

In the cyclic scans of TMB–TMBOx, this difference of about 30 mv. again correlates with a reversible redox system. At the highest cyclic scan rates, the difference increases but this is expected. The conditions upon which equation 4 is based assume a uniform concentration of either Ox or Red prior to initiation of the voltage scan. With rapid cyclic scans this uniform concentration is not obtained of course. Also, at high scan rates some degree of change transfer control may become apparent.

Knowing the value of βn_a for DMA it is possible to calculate the diffusion coefficient of DMA from the peak current equation for a totally irreversible process given by

$$i_p(\text{irr}) = Kn(\beta n_a)^{1/2}AD^{1/2}C^bV^{1/2} \qquad (5)$$

With the peak current expressed in microamperes, the value of K is 3.00×10^5.[6,8] Table IV contains the D values of DMA determined in several background media. The values of βn_a were determined in each medium.

TABLE IV

DIFFUSION COEFFICIENTS OF DMA IN VARIOUS MEDIA

Background solution	$D \times 10^5$ cm.^{2}/sec.[a]
pH 2.4 Buffer	0.47
0.5 N H_2SO_4	.54$_3$
0.09 N H_2SO_4, 1 M Na_2SO_4	.47$_5$
3 N H_2SO_4	.46$_0$
6 N H_2SO_4	.33$_5$

[a] At 25.0°. [b] Britton and Robinson buffer.

C. Rotated Disk Studies.—The limiting current i_{lim} at a rotated disk electrode where the current is entirely controlled by mass transport is given by[3,8]

$$i_{\text{lim}} = 0.62\, nFA\ C^bD^{2/3}\nu^{-1/6}\omega^{1/2} \qquad (6)$$

where

i_{lim} = limiting current in amperes
C^b = bulk concentration in mole/cm.^{3}
ν = kinematic viscosity of the solution in cm.^{2}/sec.
ω = angular velocity of the disk given by $\omega = 2\pi N$ where N = revolutions/sec.

Equation 6 predicts a linear plot of i_{lim} *vs.* $N^{1/2}$, and this has been verified at the carbon paste disk

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(6) H. Matsuda and Y. Ayabe, *Z. Elektrochem.*, **59**, 494 (1955).

(7) T. R. Mueller and R. N. Adams, *Anal. Chim. Acta.*, **25**, 482 (1961).

(8) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, New York, N. Y., 1954, p. 126.

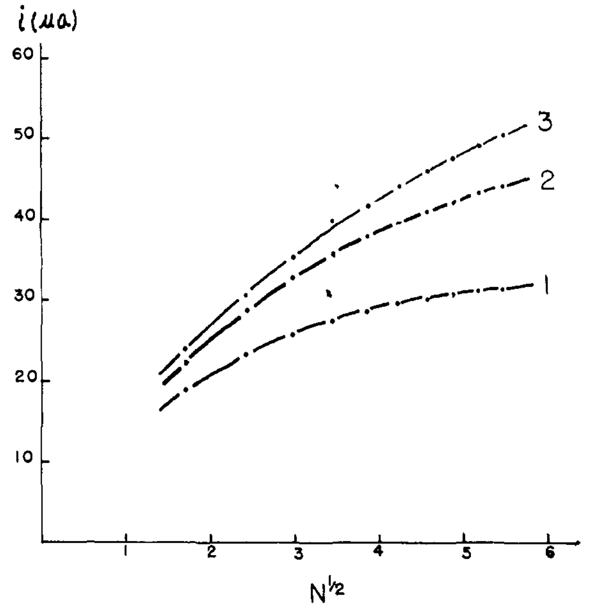

Fig. 2.—Current *vs.* rotation speed for DMA at rotated disk electrode.

for such reactions as the oxidation of *o*-dianisidine in acid solution.[4] For reactions involving both mass and electron transfer (irreversible reactions) Levich has derived the expression

$$i = \frac{nFADC^{\mathrm{b}}}{1.61\left(\frac{D}{\nu}\right)^{1/3}\left(\frac{\nu}{\omega}\right)^{1/2} + \frac{D}{K_{\mathrm{r}}}} \tag{7}$$

where K_{r} is "constant of reaction" which is closely related to the heterogeneous rate constant for the charge transfer process; units are cm./sec. and the other symbols have the significance given before. When K_{r} is very large, *i.e.*, when the charge transfer is rapid, it is clear, that equation 7 reduces to the case of a mass transport controlled process given by equation 6. The curves of i *vs.* $N^{1/2}$ for DMA oxidation shown in Fig. 2 are of the form of equation 7, *i.e.*, at low values of E_{app}, current is essentially independent of $\omega^{1/2}$ (or $N^{1/2}$). Even at + 1.0 v., the pure linear dependence on $\omega^{1/}$ is not realized; the current is dependent on both mass and electron transfer.

From the data of Fig. 2 the order of the electrochemical reaction can be found from expressions derived by Levich

$$m \ln\left[\frac{1 - \frac{i_1\delta_1}{C^{\mathrm{b}}D}}{1 - \frac{i_2\delta_2}{C^{\mathrm{b}}D}}\right] = \ln\frac{j_1}{j_2} \tag{8}$$

where m = order of reaction

$$j = 0.62\, D^{2/3}\, \nu^{-1/6}\omega^{1/2}C^{\mathrm{b}} \tag{9}$$

$$\delta = 1.61\, D^{1/2}\, \nu^{1/6}\omega^{-1/2} \tag{10}$$

The "flux" j is evidently i/nFA as seen from equation 6. The thickness of the diffusion layer δ is obtained from the known D values and the kinematic viscosity of the solution.

The δ values were evaluated at N = 9 and 27 revolutions/sec. using D_{DMA} = 0.46 cm.^{2}/sec. and N = 0.01 cm.^{2}/sec. for 3NH$_2$SO$_4$. The corresponding values of δ were 1.68 × 10^{-3} cm. (N = 9 rev./sec.) and 0.966 × 10^{-3} cm. (N = 27 rev./sec.). The values of j at 9 and 27 rev./sec. were determined knowing the electrode area and substitution of the various values in equation 8 gave the order, m. For curve 2 of Fig. 2, m = 0.87 and for Curve 3, the value 0.98 was obtained. Thus, the rotated disk studies at carbon paste agree remarkably well with Tafel measurements on platinum and substantiate the reaction order of unity for DMA in acidic solution.

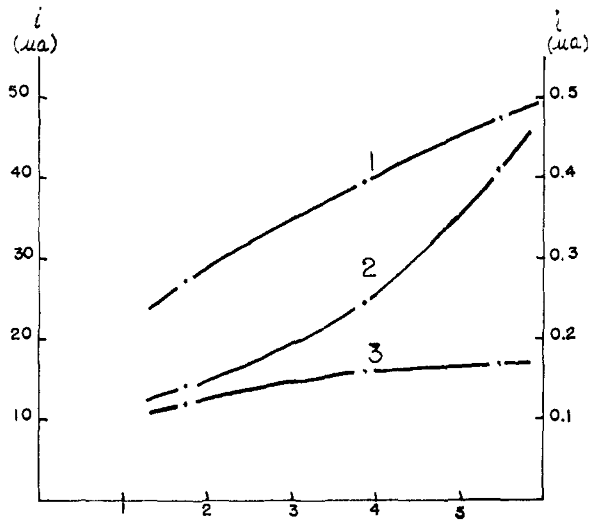

Fig. 3.—Current-rotation relation for DMA at double disk electrode: curve 1, current at inner disk, $E_{\mathrm{app.}}$ = +0.85 v.; curve 2, current at outer ring ($E_{\mathrm{app.}}$ = +0.6 v.) when oxidation of DMA occurring at inner disk ($E_{\mathrm{app.}}$ = +0.85 v.); curve 3, residual current at outer ring ($E_{\mathrm{app.}}$ = 0.6 v.) with no electrolysis at inner disk (open circuit).

The rotated double-disk electrode provides the most convincing evidence to prove the contention that TMB, since it is oxidizable at potentials considerably less positive than the parent DMA, is never observed as the final oxidation product, but instead is further oxidized to TMBOx at ordinary electrodes.

The i_{Lim} *vs.* $N^{1/2}$ behavior of 2 × 10^{-3} M DMA in 0.1 N sulfuric acid was examined at the double-disk electrode. The results are presented in Fig. 3. Curve 1 is the current at the inner disk with a potential of + 0.85 v. applied. This curve is identical with that obtained with an ordinary (single) disk electrode of the same geometry. Curve 3 shows that only a low residual current flows at the outer ring with an E_{app} of +0.6 v. on the outer ring which *is sufficient to oxidize TMB but not DMA* under the solution conditions. Now, curve 2 shows the current at the outer ring (+0.6 v.) when +0.85 v is applied to the inner disk and the oxidation of DMA is occurring at the inner surface. Two things are evident: (1) the current at the outer ring is small and hardly greater than the residual current at low rotation speeds; (2) the outer ring current increases markedly as rotation velocity increases.

These results are readily interpreted. The outer disk current can represent only TMB oxidation, since E_{app} is only + 0.6 v. The chemical reaction producing TMB which follows the primary electrode process is rapid and at low rotation velocities, the TMB is simply further oxidized at the inner electrode and is indistinguishable in the over-all current. Only a very little TMB is swept to the outer ring at low rotation velocities. At higher rotation speeds, the rate of the chemical reaction and the mass transfer outward are competitive and the TMB–TMBOx current is obtainable at the outer electrode. These results are most gratifying in terms of the postulated reaction scheme and suggest the use of double disk techniques in complex organic electrode reactions will be most advantageous. The complete theory and quantitative treatment of double disk electrodes have been given.[9,10]

Summary.—Primarily through the use of cyclic voltammetry and rotated disk electrodes, it has been established that the charge transfer reaction in the oxidation of DMA in acidic media involves a 2-electron removal from a single molecule of DMA. Further, the existence of TMB as an intermediate in the over-all electrode process has been proven with a double disk technique.

Acknowledgment.—This work was supported through the Atomic Energy Commission through contract AT (11-1)-686 and this support is gratefully acknowledged.

[9] B. Levich and Ju. Ivanov, *Compt. Rend. Acad. Sci. U.R.S.S.*, **126**, 1029 (1959).

[10] A. Frumkin, L. Nekrasov, B. Levich and Ju. Ivanov, *J. Electronanal. Chem.*, **1**, 84 (1959)

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

Anodic Oxidation Studies of N,N-Dimethylaniline. III. Tritium Tracer Studies of Electrolysis Products

BY Z. GALUS, R. M. WHITE,[1] F. S. ROWLAND AND R. N. ADAMS

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Tritium tracer studies have permitted the isolation of products from the anodic oxidation of N,N-dimethylaniline (DMA) during electrolysis approximating normal polarographic conditions. The total number of electrons transferred per molecule of DMA in the non-volatile residue (*ca.* 10 micrograms) is 2.0 ± 0.2 at *p*H 3–4. The number of electrons is higher at *p*H 6.8 because of further chemical reaction of excess DMA with the oxidized form of tetramethylbenzidine. About 20% of the DMA molecules in the non-volatile residue had not lost the hydrogen in the *para* position, indicating the presence of products other than *para*, *para*-tetramethylbenzidine.

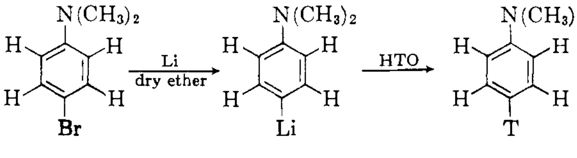
Introduction

One of the most direct and fundamental methods for studying electrochemical reactions is the identification of products. If such product identification is carried out on a macro scale, using controlled potential electrolysis, considerable quantities of products from follow-up chemical reactions may form and these may undergo further electrochemical reaction. Since follow-up chemical reactions were known to prevail in the anodic oxidation of N,N-dimethylaniline (DMA), tritium labeled DMA of high specific radioactivity was used in the present study to help identify electrode products resulting from the current passed during one or two polarograms or chronopotentiograms.

Experimental

Preparation and measurement of tritiated molecules. A. Generally Labeled N,N-Dimethylaniline (TDMA).—Tritium was introduced into N,N-dimethylaniline by exposure to T_2 gas for about one week (New England Nuclear Corp.). The crude TDMA was initially distilled under reduced pressure and then purified as the picrate. Successive recrystallizations gave a compound that was both chemically and radiochemically pure, as shown by the constant specific radioactivity of the picrate. The specific activity of the purified TDMA was 4.16 × 10^6 dpm./mg. This method of tritiation produces tritiated material that is labeled in every position, although not in uniform specific radioactivity. No degradations were performed to determine the intramolecular distribution of radioactivity, but similar tritiations generally introduce more tritum activity into the aromatic positions than in methyl groups.

B. N,N-Dimethylaniline Specifically Labeled in the *para* Position.—The specifically *para* labeled compound (*p*-TDMA) was made by the following series of reactions



The starting *p*-bromo-DMA was prepared in 70–85% yield after the method of Kosolapoff[2] and was recrystallized from ethanol–water until the correct m.p. of 55° was obtained. It is important to purify the compound well at this stage, since it is necessary that it be free of *ortho* and *meta* bromo isomers before preparing the lithium derivative.

The *p*-lithium–DMA was readily obtained by treatment of the dry *p*-bromo-DMA with lithium metal in anhydrous ether in a nitrogen atmosphere, following the method of Gilman, Zoellner and Selby.[3] After the lithium reaction was complete, the excess metal was removed and tritiated water HTO, added dropwise to keep the hydrolysis reaction under control. At completion, the lithium hydroxide was filtered off and ether removed, leaving crude *p*-TDMA in 50–60% yield. The crude was steam distilled from strong base solution, dried over KOH and then purified by vacuum distillation. Several cycles of picrate formation, hydrolysis back to free base, distillation, picrate formation, etc., were used to obtain a pure product.

The specific radioactivity of the final *p*-TDMA was 3.64 × 10^5 dpm./mg. The specificity of the labeling process was checked by converting an aliquot of the purified material back to the *p*-bromo-DMA, with the loss of more than 99.5% of the tritium radioactivity.

C. Generally Labeled Tetramethylbenzidine (TMB).—Tritium-labeled tetramethylbenzidine was produced by neutron irradiation of a mixture of lithium carbonate and tetramethylbenzidine. It was purified by recrystallization to a constant specific activity of 9.0 × 10^5 dpm./mg.

D. Measurement of Tritium Radioactivity.—All samples containing tritium activity were either crystalline solids or semi-crystalline evaporated residues from the electrochemi-

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[1] Department of Chemistry, Jacksonville University, Jacksonville, Florida.

[2] M. Kosolapoff, *J. Am. Chem. Soc.*, **75**, 3596 (1953).

[3] H. Gilman, E. Zoellner and W. Selby, *ibid.*, **55**, 1252 (1933).