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

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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.

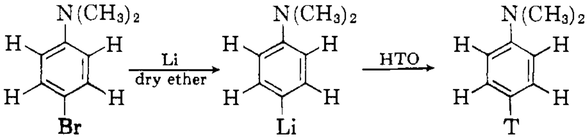
Introduction

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).

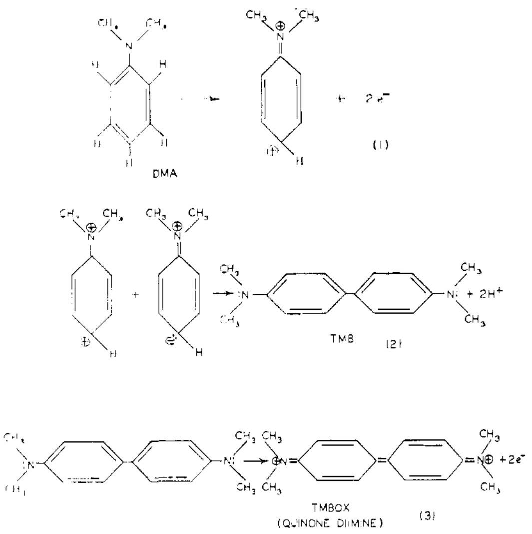

Fig. 1.—Reaction scheme for DMA oxidation.

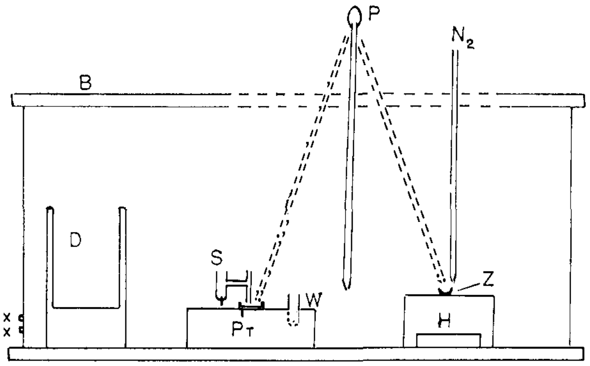

Fig. 2.—Apparatus for electrolysis and evaporation of tritiated DMA: **B**, glass balance case arranged for nitrogen atmosphere chamber; D, Dewar for initial flooding of chamber *via* addition of liquid nitrogen; H, hot-plate with adjustable temperature; P, transfer pipet; S, saturated calomel reference electrode; Pt, platinum working electrode; W, air free rinse water for quantitative transfer; X, electrical connections to S and PT; Z, zinc boat.

cal solutions. The tritium in each of these samples was converted to gas by the zinc fusion technique and assayed by gas proportional counting. In this technique, the solid sample in a zinc boat is sealed in a combustion tube with powdered zinc, nickelic oxide and a small quantity of paraffin wax. After heating at 700° for 4 hr., the combustion tube is transferred to a vacuum line, opened by cracking a break-tip, and an aliquot of the gaseous contents is transferred to a 100 cc. silver-walled glass gas proportional counter. The combustion technique insures that the tritum is quantitatively present in the gas phase as HT or CH_3T, with traces of higher hydrocarbons. Forty cm. of propane are added to the proportional counter for the assay in order to insure good counting characteristics of the gas mixture.

The absolute specific radioactivity is estimated to be accurate to about ± 5%. However, the data are quoted to three places to facilitate comparisons of the ratios of activity. The largest source of error in the absolute measurement is in the fraction of the total gas sample in the active volume of the counter (including end-effects in counter operation). Since this factor is the same for all measurements, the ratio of radioactivities is more accurately measured than the absolute value and is estimated as about ± 1%. Other errors in the measurement scatter more widely and cause the lesser accuracy of the calculations of n_T. Further details of the counting technique can be found in the literature.[4]

Electrolysis and separation of products.—The fundamental problem in the present study was the electrolysis of solutions *ca.* 10^{-3} *M* in TDMA (for very short times and employing microampere current levels) followed by separation of the tritium containing products from the large excess of TDMA. Fortunately, it was found that DMA could be volatilized from weakly acidic solution by gentle heating (less than 100°) without removing any TMBOx, the latter being the expected main product containing the tritium activity, as shown in Fig. 1.[5] Since the amount of product from the electrolysis was comparable to or less than the amount formed by air oxidation of DMA during the heating operation, it was necessary to carry out the entire electrolysis and volatilization under a nitrogen atmosphere. This was accomplished on the apparatus of Fig. 2, a dismantled glass balance case

The electrolysis vessel itself was of "bathtub" shape and consisted of a rectangular rim of paraffin wax about 1/4'' high built up on a 2 cm.^{2} platinum foil—the electrode formed the bottom of the vessel. The vessel held *ca.* 1 ml. of solution and the tip of the s.c.e. salt bridge made contact with the surface of the solution. Leads to the polarograph or constant current source were led outside through a small opening in the case. The volume of the electrolysis cell was kept as small as possible to minimize the amount of solution (and of active DMA) for evaporation.

Inside the case were a small Dewar for liquid nitrogen which provided an initial flooding of the space with nitrogen, a hot-plate for evaporation of the sample and a small cell of deaerated, distilled water for quantitative transfer of sample to the zinc boat. Through the rubber dam cloth on top were inserted a capillary pipet and a tube for directing a stream of nitrogen on the boat.

The procedure consisted of first flooding the chamber with nitrogen, then filling the electrolysis vessel with a known volume, usually 0.50 ml., of TDMA solution (all solutions containing DMA were made from carefully deaerated solutions and all precautions were taken to minimize air oxidation prior to electrolysis). Following the short period of electrolysis, a quantitative transfer of the contents of the electrolysis vessel was made *via* pipet to the zinc boat used in the counting technique. Since the volume of this boat was small, the transfer was accomplished in stages. With the temperature of evaporation about 60–70° and the nitrogen stream on the liquid surface in the boat, this evaporation and transfer require about 45 minutes. The zinc boat was then stored in a desiccator until ready to be counted.

Results

A. Total Electrons Transferred (n_T) in DMA Oxidation.

—The procedure carried out in these experiments measures the amount of radioactivity fixed in non-volatile combination after electrolysis under controlled conditions. This non-volatile activity can be used to calculate the number of molecules of starting DMA fixed in the residue, and thereby the number of electrons required per molecule in the oxidation, if the radioactivity does not escape from the residue by volatilization of the product or by isotopic exchange with the solvent. Since the expected non-volatile product is tetramethylbenzidine, experiments were carried out to show that no appreciable radioactivity was lost from labeled TMB kept in the solution during the electrolysis under typical conditions of non-radioactive DMA. The results of six such test electrolyses shown in Table I indicate a loss of the order of 10% of the radioactivity under these circumstances. This loss seems to be slightly smaller at the lower temperatures. The nature of this loss has not been determined.

The amounts of non-volatile radioactivity found in a series of typical electrolysis experiments carried

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[4] K. Wilzbach, L. Kaplan and W. G. Brown, *Science*, **118**, 522 (1953); F. S. Rowland, J. K. Lee and R. M. White, Oklahoma Conference on Radiosotopes in Agriculture, TID-7578, p. 39 (1959).

[5] See papers I and II of this series.

TABLE I

NON-VOLATILE TRITIUM ACTIVITY IN *p*H 2.1 BUFFER REMAINING AFTER ELECTROLYSIS AND EVAPORATION OF SOLUTION CONTAINING TRITIATED TETRAMETHYLBENZIDINE AND UNLABELED DIMETHYLANILINE[a]

Temp. of evap. (°C.)	Fraction of activity recovered after electrolysis and evaporation
55	0.95
60	.93
65	.91
75	.87
85	.92
95	.91

[a] Current = 30.2 μamp., time of electrolysis = 240 sec. for all runs.

out with generally-labeled DMA are given in Table II. Eight runs carried out as blanks, with no electrolysis, are also included. These runs give an estimate of the amount of air oxidation occurring during electrolysis, despite the experimental precautions taken.

TABLE II

ELECTROLYSIS OF GENERALLY TRTIUM-LABELED N,N-DIMETHYLANILINE

Temp. (°C.)[a]	*p*H	Current (μamp.)	Electrolysis time (sec.)	Non-volatile radioactivity dpm. × 10^{-3}	n_T
70	3.0	0	0	1.1	..
70	3.0	0	0	1.2	..
70	3.0	0	0	0.3	..
70	3.0	29.94	480	29.3	2.1
70	3.0	29.94	480	32.5	1.9
70	3.0	29.94	480	33.5	1.9
60	4.0	0	0	0.6	..
60	4.0	30.00	480	34.9	1.9
60	4.0	30.00	480	34.3	1.9
70	4.0	0	0	0.4	..
70	4.0	0	0	0.4	..
70	4.0	0	0	0.3	..
70	4.0	30.05	480	32.6	1.9
70	4.0	30.05	480	33.7	1.8
70	4.0	29.94	480	29.6	2.1
70	4.0	29.94	480	31.4	2.0
60	6.8	0	0	0.5	..
60	6.8	30.00	480	18.6	3.5(3.8)
60	6.8	30.00	480	19.6	3.4(3.6)
60	6.8	30.00	480	16.7	4.0(4.2)

[a] Temperature of evaporation as measured by thermometer near zinc boat.

The last column of Table II contains values of n_T, the total number of electrons transferred per molecule of DMA in the non-volatile residue. These values can be calculated directly from the known current and the specific activity of the original DMA by the formula

$$n_T = \frac{itAM}{1000\ FA_p}$$

where i = current, μamp.
t = time of electrolysis in sec.
F = 96,500
A = specific activity of DMA in dpm./mg.
A_p = activity of product, dpm.
M = mol. wt. of DMA

The only appreciable uncertainties in this calculation arise from the measurement and significance of the non-volatile radioactivity. The observed non-volatile activities used in the calculation of n_T have all been diminished by 0.6 × 10^3 dpm. to allow for air oxidation, and then increased by 7% at 60° or 12% at 70° to compensate for electrolysis-evaporation loss as in Table I. In addition, since one hydrogen atom from the original TDMA is lost in oxidizing to labeled TMB, the specific radioactivity of the TDMA residue is lower than that of the original molecule. An approximate estimate of this correction factor has been made by assuming uniform labeling (plus no isotope effects in the reactions) and multiplying the observed residue activity by 11/10. A more precise estimate of this correction factor does not seem worthwhile in view of the other corrections already involved and the complexities introduced by non *para–para* coupling (see below). The over-all accuracy in the n_T measurements with these correction factors is estimated to be ± 10%.

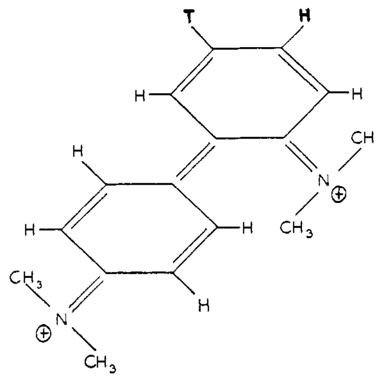

Fig. 3.—*Ortho–para* coupling product in DMA oxidation.

The values of n_T for pH < 4 are all quite close to the value of 2 electrons per molecule of DMA, as expected for the electrolysis mechanism shown in Fig. 1. The current–time integrals of the runs in Table II are somewhat greater than that of an ordinary single polarogram but are in the correct range. A few runs were made at current levels of 520μ amp. for only 36 sec., using TMDA of much lower specific radioactivity. The counting accuracy of these experiments was not as favorable but also gave values consistent with $n_T \cong 2 \pm 0.5$. The use of the radioactive tracer technique thus gives an essentially "chemical" check of the over-all electrode reaction with approximately 10 μgrams of product. The apparent increase of n_T at pH 6.8 is shown in section C to be the result of further chemical reaction of TMBOx and excess DMA.

B. Oxidation of *para*-Tritiated N,N-Dimethylaniline.—It has been previously assumed in the discussion that the chemical reaction following electrolysis formed only TMB, *i.e.* the reaction was a *para–para* reaction of two DMA species. While *meta* interactions are unlikely, it is clear that some *ortho* interactions should be considered. Thus, in addition to TMB, an *ortho–para* coupled product as in Fig. 3 should be possible.

If the electrolysis is carried out with specifically-labeled *p*-TDMA, the molecule shown in Fig. 3 would retain tritum activity, whereas both *para* tritium atoms are eliminated in the formation of TMB and no activity should be found in the product. The electrolysis experiments were carried out as described previously, and the results are seen in Table III.

Since the specific radioactivity of the *p*-TDMA was approximately one factor of ten lower than that of the generally labeled TDMA, the numbers in column 6 of Tables II and III should be directly comparable. It is clear that much less radioactivity is found in the non-volatile residue when *p*-TDMA is used in the electrolysis, confirming that the main product has lost the tritium atoms from both *para* positions, as expected for TMBOx. However, the residue is radioactive, indicating that some of the non-volatile molecules have not lost both of the *para* tritium atoms in the coupling reaction. Assuming that n_T is 2 at pH 3.9 and 12% loss at 80°, the fraction of N,N-dimethylaniline molecules retaining the *para* tritium atom in the residue is shown in the last column of Table III. The electrolyses carried out at pH 6.2 again show less radioactivity than the corresponding runs at the more acid pH. No retention of tritium is shown for this pH because of the uncertainty in choosing a value of n_T for the calculation.

TABLE III

ELECTROLYSIS OF SPECIFICALLY LABELED *p-t*-N,N-DIMETHYLANILINE

Temp. (°C.)[a]	*p*H	Current (μamp.)	Electrolysis time (sec.)	Non-volatile radioactivity dpm. × 10^{-2}	% DMA molecules retaining tritium in residue
80	3.9	0	0	0.1 ± 0.1	..
80	3.9	0	0	.1	..
80	3.9	0	0	.0	..
80	3.9	30.2	480	6.2	21
80	3.9	30.2	480	6.0	20
80	3.9	30.2	480	6.0	20
80	3.9	30.2	720	9.5	21
80	3.9	30.2	720	8.5	19
60	6.2	0	0	0.1	..
60	6.2	30.2	480	4.2	[a]
60	6.2	30.2	720	5.2	[a]
80	6.2	0	0	0.1	..
80	6.2	0	0	.2	..
80	6.2	30.2	300	.9	..
80	6.2	30.2	300	1.6	[a]
80	6.2	30.2	600	4.4	[a]
80	6.2	30.2	600	4.8	[a]

[a] Not calculated because of uncertainty in proper choice choice of n_T.

C. Interaction of TMBOx and DMA.—From Table II it can be seen that n_T increases to between 3 and 4 above pH 6. This result can be interpreted in two ways: (a) the change is real and the electrode process now involves approximately twice as many electrons, or (b) the tracer technique gives a false value of n_T at higher pH. If the former is true, then the limiting currents should increase accordingly. No such radical shifts in i_p, i_{Lim} or $\tau^{1/2}$ were obtained (See Parts 1 and 2). However, as shown in Part 2, a new redox system appears at the higher *p*H which was clearly shown to be a coupling product of TMBOx and DMA. For the reasons previously given, this reaction is believed to proceed *via* interaction of the radical ion of TMB and DMA. Since this product oxidizes at an even lesser positive potential than either DMA or TMB, its oxidation will proceed at potentials sufficient for the DMA reaction and consume electrons. It is not unreasonable to assume that n_T will appear higher than 2 when evaluated by the tracer method. The significance of these values of n_T in the region of pH 6 is lessened, however, since the correction factors have been applied on the basis of experiments made with TMBOx, and these are probably not correct for the molecules formed by the further interaction of TMBOx and DMA. If it is assumed that there is no electrolysis-evaporation loss in this pH range, the values of n_T shown in parentheses in Table II are obtained.

Further information about the nature of this reaction was obtained by experiments involving unlabeled TMBOx and *p*-TDMA. TMBOx isolated as the perchlorate after lead peroxide oxidation of DMA, was prepared in pH 6.5 buffer. The green color, apparently that of TMB^+, appeared. An excess of *p*-TDMA was then added and the mixed solution allowed to stand for ten minutes. Both visual observation of a color change from green to blue and cyclic voltammetry demonstrated that an interaction had taken place between the TMBOx and the *p*-TMDA. However, in three separate experiments, no tritium radioactivity appeared in the non-volatile residue left behind after evaporation of the solution and assay for tritium. Since this interaction results in no perceptible incorporation of tritium in the product, the reaction must be one involving the *para* position of DMA. It is not useful to speculate further on the structure of the product found.

Summary.—In Part 1 of this series it was established that the principal reaction in the electrolysis of DMA in acidic solution is the formation of TMBOx. The charge transfer process was shown to be the loss of 2 electrons from a molecule of DMA by cyclic voltammetry and rotating disk techniques in Part 2. Kinetic parameters of the electrode reaction are entirely consistent with this mechanism. The chemical follow-up step is the reaction of a molecule of oxidized DMA with the parent DMA to give TMB. The existence of TMB as an intermediate was proven by the use of a double disk rotating electrode. In Part 3, the total number of electrons transferred was shown to be consistent with this picture by using tracer electrolysis techniques. The further complicating reactions of TMBOx and DMA were partly elucidated by the use of specifically labeled DMA. It was also shown that a small amount of *ortho*-coupling of DMA exists in the chemical reaction following electron transfer. The DMA oxidation was carried out at both platinum and other inert electrodes whose surfaces do not undergo concurrent oxidation. Since the results were essentially independent of the electrode, it is believed that surface oxides play little or no part in this anodic reaction.

Acknowledgments.—Some of the early tracer experiments were carried out by T. Mizoguchi. The support of this work by the A.E.C. through contracts AT-(11-)-686 and AT-(11-1)-407 is gratefully acknowledged.