Anodic Oxidation of *N*,*N*-Dimethyl-*m*-toluidine at a Platinum Electrode in an Acetonitrile Solution

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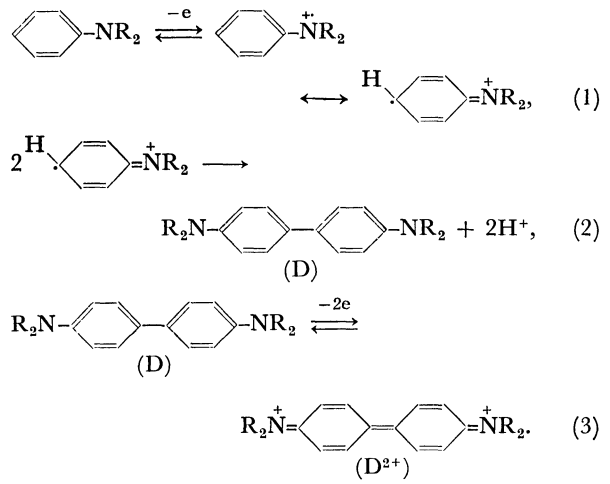
The electrochemical behavior of *N*,*N*-dimethyl-*m*-toluidine (DMMT) in an acetonitrile solution at a Pt electrode was investigated. By controlled-potential oxidation at 0.65 V (*vs.* Ag/0.01 mol dm^{-3} AgClO$_4$), the dihydro compound (**I-a**), which had been considered to be an intermediate in the reaction forming benzidine, was probably obtained. **I-a** was gradually converted to *N*,*N*,*N'*,*N'*-tetramethyl-2,2'-dimethylbenzidine (TMMB) in the solution within several hours. **I-a** was easily converted to TMMB by the cathodic re-reduction at -0.9 V or by adding either pyridine or water; this reaction pathway is useful for the synthesis of TMMB. Preliminary mechanistic information on the anodic oxidation of DMMT is also given by cyclic and ring-disk electrode voltammetry, current-reversal chronopotentiometry, and controlled-potential coulometry. The proposed reactions are: $A - e \rightarrow A^{+\cdot}$, $A^{+\cdot} + A \xrightarrow{k} A\text{-}A^{+\cdot}$, and $A\text{-}A^{+\cdot} - e \rightarrow DH_2^{2+}$, where A and $A^{+\cdot}$ are, respectively, DMMT and its cation radical, DH_2^{2+} is the dihydro compound (**I-a**), and *k* is the rate constant of the coupling reaction (*ca.* 5×10^3 dm^3 mol^{-1} s^{-1}). TMMB is formed by: $DH_2^{2+} + 2e(\text{or } 2Py) \rightarrow D + H_2(\text{or } 2PyH^+)$, where D is TMMB and Py is pyridine.

N,*N*-dialkyl-substituted aromatic amines show very similar behavior to each other on the anodic oxidation in a nonaqueous solution. In the case of *N*,*N*-dimethylaniline (DMA),[1] the primary electrode reaction is a one-electron transfer to form a cation radical which then couples to form *N*,*N*,*N'*,*N'*-tetramethylbenzidine (TMB) with simultaneous loss of protons. TMB thus formed is more readily oxidized than the starting amine and is converted to the diquinoid structure (TMB^{2+}). Thus, a general reaction scheme is

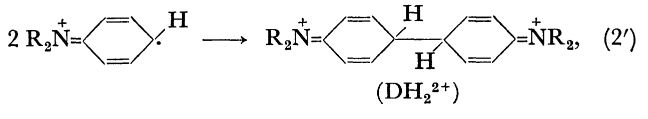


(1)

(2)

(3)

In the coupling reaction (Eq. 2), the dihydro compound (DH$_2$$^{2+}$) is considered to be an intermediate,[2]



(2')

and D is formed by loss of protons from DH$_2$$^{2+}$.

The same reactions as Eqs. 1—3 were proposed for DMA also in AlCl$_3$–NaCl melts.[3] However, an intermediate such as DH$_2$$^{2+}$ is usually unstable and has not yet been isolated. Furthermore, some coupling reactions other than Eq. 2 are possible, but the mechanism has usually not been clarified.

The aims of this paper are to describe the interesting fact that a DH$_2$$^{2+}$-like compound was formed by the anodic oxidation of *N*,*N*-dimethyl-*m*-toluidine (DMMT), to give preliminary information on the mechanism of this electrode reaction, and also to describe the fact that *N*,*N*,*N'*,*N'*-tetramethyl-2,2'-dimethylbenzidine (TMMB) was easily synthesized by the re-reduction of the oxidation product of DMMT or by adding a base to the product.

DMMT was adopted for the present study because (i) the ring-substituted methyl group makes the cation radical stable, and thus the coupling reaction may be easily examined, (ii) the low basicity of DMMT[4] compared to its isomers may decrease the complication of the oxidation pathway due to protonation of the parent molecule, and (iii) no study has been reported on the anodic oxidation of DMMT in a nonaqueous solution.

Experimental

DMMT (analytical GR grade) was used as received. Sodium perchlorate (analytical EP grade) was recrystallized twice from ethanol, dried overnight under a reduced pressure (3 mmHg, 1 mmHg≈133.3 Pa), and stored over silica gel. Acetonitrile (MeCN) was purified by distillation from P$_2$O$_5$, from K$_2$CO$_3$, and then three times by slow fractional distillation. The water content of the MeCN (0.18 wt%) was determined by the Karl-Fischer titration.

Cyclic voltammograms were measured at a Pt disk electrode (1.96×10^{-3} cm^2) sealed in a soft glass using a set of Yanaco P8 polarographs. The working electrode was polished with an oilstone before each measurement. The counter electrode was an Hg pool (*ca.* 3 cm^2). A Ag/0.01 mol dm^{-3} AgClO$_4$ couple in MeCN, which was connected to the test solution with a 1 mol dm^{-3} NaClO$_4$ agar bridge, was used as a reference electrode. All potentials appearing in this paper are referred to this electrode (whose potential was 0.19 V *vs.* SCE).

Macro-scale electrolyses were carried out using a Nikko Keisoku NPGS 301 potentiostat. A two-compartment cell with a fine glass frit was used. The anode electrolyte was usually 200 ml in volume. The working and the counter electrodes were planar Pt. During electrolysis, cyclic voltammograms of the solution were measured at suitable times to check the changes of the composition of the solution. Low concentrations of DMMT ($<$10 mmol dm^{-3}) were used because a benzidine-type product was generally formed predominantly at a low concentration of a starting amine.[5] After exhaustive oxidation at 0.65 V (*vs.* Ag/Ag$^+$), the product I was obtained as follows: After evaporation of the solvent and then addition of 100 ml of aqueous 0.2 mol dm^{-3} $HClO_4$ to remove the supporting electrolyte, I was extracted with benzene and was obtained by evaporation of the benzene. When the supporting electrolyte was removed by water with no perchloric acid, the same product as II described below was obtained. Since the product I was gradually converted to product II in the test solution within several hours and its stability depended sensitively upon the concentration of water contained in the solution, repeated trials for obtaining I were made to get reproducible data. The product II, which was produced by re-reduction at −0.9 V of the solution obtained by exhaustive oxidation at 0.65 V, was obtained by the same method as that used for the product I except for the use of water to remove the supporting electrolyte. To check the purity of the products, they were chromatographed on both an alumina (Wako B-10F) and a silica gel (Wako B-10) with benzene, and the chromatograms obtained were developed with iodine. For both products, three spots due to products I and II, and DMMT which remained unreacted, were detected. Thus, I obtained here contained II (typically about 10—20 %) and a small amount (less than 5 %) of DMMT, while II obtained here contained only a small amount of DMMT and a trace amount of I. For both products I and II without further purification, IR (in KBr wafer using a Hitachi 125 G spectrophotometer), NMR (in $CDCl_3$ using a Hitachi R-24 at 60 MHz), and mass (at 75 eV using a JOEL JMS D-100) spectra were measured. A UV spectrum of the test solution was measured by a Hitachi 200-10 spectrophotometer.

Other electrochemical measurements for rotating ring-disk electrode (RRDE) voltammetry and current-reversal chronopotentiometry (CRC) were carried out by using commercially available apparatuses constructed by Nikko Keisoku. All experiments were carried out at 25±0.3 °C.

Results and Discussion

The cyclic voltammogram of DMMT exhibited one anodic wave (Ia) having a peak potential (E_p) of 0.45 V (Fig. 1a), and no other appreciable wave was observed near this peak. To obtain the oxidation product, controlled-potential electrolysis at 0.65 V was carried out. During electrolysis the height of the wave Ia decreased and a new irreversible reduction wave (IIc) appeared at $E_p = -0.83$ V (Fig. 1b). Since no wave was observed at the potential near 0.45 V, TMMB was not produced because TMMB, if formed, must be oxidized at a somewhat less anodic potential than that for the wave of DMMT. The vicinity of the anode was colored pink, which might be due to the formation of the cation radical of DMMT, and the bulk solution became green. By coulometry for a 5 mmol dm^{-3} DMMT solution, 0.97 electrons/molecule of DMMT were consumed and the product I was obtained.

Controlled-potential re-reduction at −0.9 V was carried out consecutively after exhaustive oxidation at 0.65 V. 0. 9 electrons/molecule of DMMT were consumed to make the reduction wave IIc on the voltammogram of the solution disappear; the solution turned dark brown and this color no longer changed to green by the anodic re-oxidation. The cyclic voltammogram of the solution obtained by the re-reduction showed one reversible wave (IIIa/IIIc) at a somewhat less anodic ($E_p = 0.42$ V for IIIa) potential than that for DMMT (Fig. 1c). This suggests that TMMB is produced by the re-reduction of the product I. In confirmation of this consideration product II was isolated after exhaustive re-reduction of I. Both products I and II thus obtained were analyzed to determine their structures, and the characteristics of the analytical data are summarized in

Table 1. Analytical data on the products (I and II) and DMMT

Compound	I	II	DMMT
IR[a] (KBr) (cm^{-1})	1687 (νC=N), 1120 (ClO_4^-), 1607, 1491 (Ring νC=C), 2800—3000 (Me νC–H)	1610, 1498 (Ring νC=C), 1350, (1228) (Ar. *t*-amine νC–N), 815, 808, 832 (1,2,4-trisubstituted benzene δC–H), 2800—3000 (Me νC–H)	1607, 1500 (Ring νC=C), 1350, (1230) (Ar. *t*-amine νC–N), 767, 692 (1,3-disubstituted benzene δC–H), 2800—3000 (Me νC–H)
UV_{max} (MeCN) (nm) (log ε)	255 (<3), 300 (<2.6)	265 (4.36), 300 (3.8—3.9 shoulder)	255 (4.19), 300 (3.34)
NMR[b] ($CDCl_3$) δ (ppm)	2.08 (3H, s, Me), 3.08 (6H, s, Me_2N), 6.8—7.3 (3-4H, m, Ar–H)	2.04 (3H, s, Me), 2.92 (6H, s, Me_2N), 6.5—7.3 (3H, m, Ar–H)	2.30 (3H, s, Me), 2.83 (6H, s, Me_2N), 6.5—7.3 (4H, m, Ar–H)
MS[c] (75 eV) *m/e* (rel intensity)	269.5 (17.9), 268.5 (51.6), 267.5 (14.7), 254.5 (9.5), 253.5 (12.1), 209 (10.5), 135 (67.4), 134 (100), 121 (25.3), 120 (32.6), 119 (29.5), 118 (23.2), 91 (34.7)	269 (21.2), 268.5 (100), 267.5 (24.1), 253 (16.6), 252 (11.2), 209 (10.7), 157 (20.2), 133 (31.6)	135 (66.3), 134 (100), 121 (10.0), 120 (13.7), 119 (12.1), 118 (8.4), 91 (19.5), 77 (9.5), 69 (13.2), 65 (10.5)
Elemental analysis Found (%) (Calcd)	C: 50.413 (46.055)[d] H: 5.631 (5.543) N: 6.100 (5.970) Others: 37.856 (42.431)	80.207 (80.471)[e] 8.696 (8.941) 9.673 (10.439) 1.424 (—)	—

a) Absorption bands are listed in the order of their strength except for those in the parentheses. ν= stretching, δ=bending, t=tertiary, Ar=aromatic, and Me=methyl. b) TMS was used as the internal standard. s=singlet and m=multiplet. c) Only main peaks are listed. d) Calcd for **I-a**. e) Calcd for TMMB.

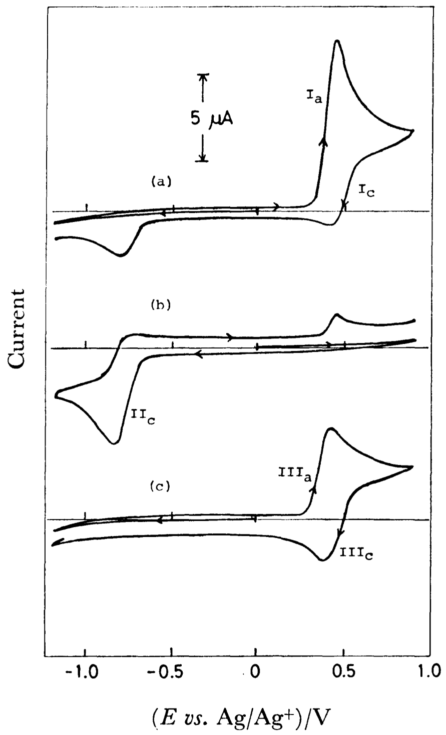
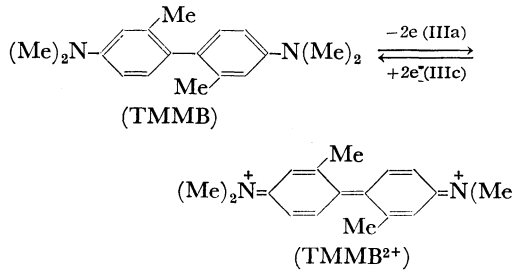


Fig. 1. Cyclic voltammograms of 5 mM DMMT in MeCN-0.4 M $NaClO_4$. Scan rate: 0.5 V s^{-1}. The direction of the potential scan is shown by arrows on the voltammograms.
a) Before controlled-potential electrolysis, b) after exhaustive oxidation at 0.65 V, and c) after exhaustive re-reduction at −0.9 V.

Table 1.

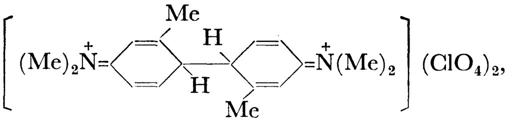
Re-reduction Product II. Comparing the analytical data on II with those on DMMT, we easily find that II is TMMB, as was suggested by the cyclic voltammetric behavior. The reasons for the conclusion that II is identical with TMMB are as follows. a) The IR data on II show that (i) C–N stretching absorption of the tertiary aromatic amine at 1350 cm^{-1} remains and (ii) absorption due to C–H bending of the 1,3-substituted aromatic ring at 692 and 767 cm^{-1} observed for DMMT changes to those of the 1,2,4-substituted one at 808, 815, and 832 cm^{-1}. b) The NMR data on II indicate that (i) since the peak of methyl protons on the ring shifts to a higher field ($\delta=2.04$ for II and $\delta=2.30$ for DMMT), a shift which probably results from the ring-current effect, the methyl group is not coplanar to the ring and thus a 2,2′-dimethylbiphenyl-type structure is suggested, and (ii) the number of aromatic protons reduces to three-fourths of that of DMMT. c) In the mass spectrum, the parent ion peak of TMMB is observed (Found: *m*/*e* 268.5, Calcd for TMMB: M, 268.4) and the fragmentation is also reasonably explained. d) The UV spectrum of II is similar to that of 2,2′-dimethylbenzidine[6] (the red-shift of λ_{max} for II is explained in terms of the replacement of H atoms on nitrogen with methyl groups). e) The electrochemical data are also consistent with the conclusion of the formation of TMMB, and the reaction for the wave IIIa/IIIc is



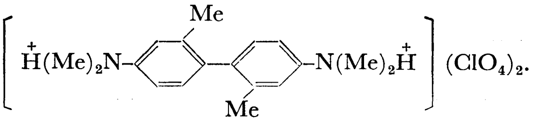
(4)

Furthermore, anodic oxidation of II gave a blue solution having absorption maxima at 378 and 680 nm, a result which is similar to that reported for the oxidation of 3,3′-dimethylbenzidine.[7] Thus, TMMB was formed either by the re-reduction or by adding a base after exhaustive oxidation of DMMT in MeCN. This simple method is useful for the synthesis of TMMB in the yield of 80—90%.

Oxidation Product I. Some remarkable differences in the analytical data on I from those on DMMT and TMMB are observed. However, since TMMB is easily produced by the reduction of I or by adding pyridine (or a base) to I, the structure of I must be similar to that of II. The strong absorption at 1120 cm^{-1} in the IR spectrum shows that I forms a salt with a perchlorate anion; the NMR data also support this conclusion because the electron density near *N*,*N*-dimethyl protons of I ($\delta=3.08$) is lower than those of DMMT ($\delta=2.83$) and TMMB ($\delta=2.92$). The methyl-proton peak of I shifts to a higher field ($\delta=2.08$) than that of DMMT ($\delta=2.30$), as is observed for TMMB ($\delta=2.04$), a fact which indicates that the structure of I is similar to that of TMMB. These results and the fact that no strong UV absorption of I was observed suggest the following two possible structures:



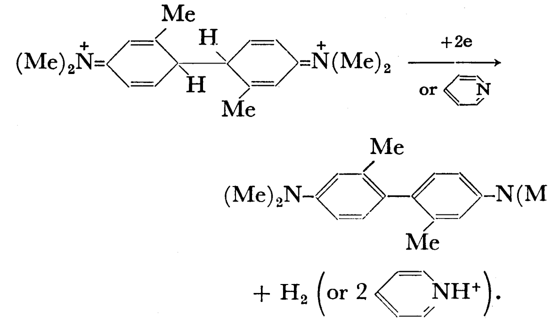
(I-a)



(I-b)

Thus, to determine the structure of I, we tried to distinguish between **I-a** and **I-b** by measuring the number of aromatic protons by integration of the NMR spectrum, but no reproducible result was obtained (the number of protons was 3—4). No appreciable absorption was observed for an N–H proton. However, the structure **I-b** is rejected because (i) in the IR spectrum of I, the C=C ring stretching absorption at 1491 and 1607 cm^{-1} is reduced and the C=N stretching absorption at 1687 cm^{-1} appears, and (ii) in the mass spectrum of I, the peaks at *m*/*e*=134 and 135 have larger intensity than that of the parent ion peak, a fact which shows that I has an unstable structure which can be split easily into two halves. On the other hand, the largest-intensity peak of **I-b** may be the parent ion peak, as is observed for TMMB. Thus, product I is determined to be the dihydro compound (**I-a**).

I-a was easily converted, as is expected from its structure, to TMMB by cathodic reduction or by adding pyridine (or a base):



(5)

Oxidation Mechanism. To obtain mechanistic information on the formation of the dihydro compound (**I-a**), some preliminary experiments were carried out. By cyclic voltammetry, the ratio of the anodic peak current of the wave Ia to the square root of the scan rate, $i_{pa}/v^{1/2}$, decreased with increasing scan rate, and the ratio of the cathodic reversal current (i_{pc}) to i_{pa}, i_{pc}/i_{pa}, decreased with an increase in the concentration of DMMT (Table 2). These results are explained in terms of the reactions in which a second-order chemical reaction is involved between two charge-transfer reactions (so-called an ECE mechanism). Usually two possible types of coupling reactions are considered. One is dimerization of intermediates and the other is the coupling of an intermediate with a parent molecule. These two mechanisms are distinguishable by both RRDE voltammetry[8,9] and CRC.[10] Thus, RRDE voltammetry was first applied to obtain precise information. On the basis of Bard's method, the kinetic collection efficiency, $N_k(=-i_r/i_d$ where i_r and i_d are the ring and the disk currents, respectively), was measured as a function of the disk current, CONI ($=i_d/i_{d,l}$ where $i_{d,l}$ is a limiting disk current for the oxidation of DMMT). The N_k values decreased with increasing 1-CONI (Fig. 2). This trend shows[8] that the intermediate generated by the first charge-transfer reacts with the parent molecule and is further oxidized to form the dimer:

$$A - e \rightleftarrows A^{+}, \qquad (6)$$

$$A^{+} + A \xrightarrow{k} A\text{-}A^{+}, \qquad (7)$$

$$A\text{-}A^{+} - e \rightleftarrows DH_2^{2+}, \qquad (8)$$

where A and A^{+} are DMMT and its cation radical and DH_2^{2+} is the dihydro compound (**I-a**).

TABLE 2. CYCLIC VOLTAMMETRIC DATA FOR OXIDATION OF DMMT IN MeCN- 0.4 M $NaClO_4$
(1 M=1 mol dm^{-3})

Concn of DMMT (C) mM	Scan rate (v) V s^{-1}	i_{pa} μA	$i_{pa}/v^{1/2}C$ μA V$^{-1/2}$ s$^{1/2}$ mM^{-1}	i_{pc}/i_{pa}
1.0	0.05	0.82	3.67	—
	0.1	1.18	3.73	—
	0.25	1.70	3.40	—
	0.5	2.32	3.28	0.48
	1.0	2.78	2.78	0.53
2.0	0.05	1.58	3.53	—
	0.1	2.16	3.42	—
	0.25	3.12	3.12	—
	0.5	3.96	2.80	0.42
	1.0	4.88	2.44	0.55
4.0	0.25	6.40	3.20	—
	0.5	7.80	2.76	0.39
	1.0	10.1	2.53	0.52
7.0	0.25	11.4	3.26	—
	0.5	13.5	2.73	0.39
	1.0	15.4	2.20	0.52
10.0	0.25	13.9	2.78	—
	0.5	18.6	2.63	0.39
	1.0	23.9	2.39	0.45

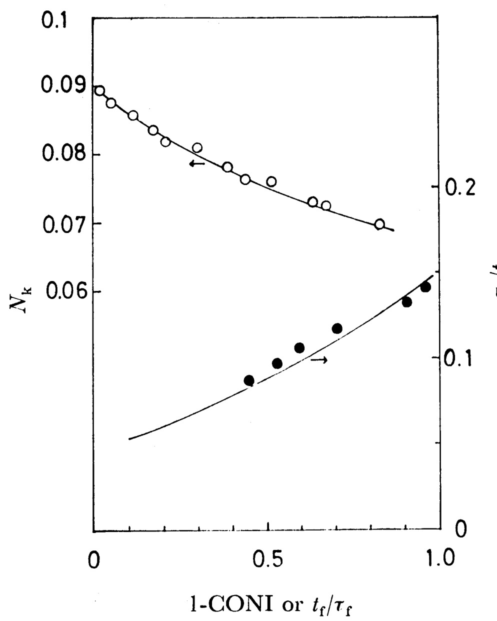


Fig. 2. Collection efficiency (N_k) *vs.* 1-CONI and τ_r/t_f *vs.* t_f/τ_r for oxidation of 1 mM DMMT in MeCN-0.1 M $NaClO_4$. Points are experimental data. For RRDE voltammetry the ring electrode was maintained at 0 V and the rotation rate of the electrode was 105 rad s^{-1}. For CRC the ratio of reverse to forward currents was 1/2 and t_f=1.0 s. Solid lines are simulated results corresponding to the rate constant of 5×10^3 M^{-1} s^{-1} (for RRDE) and 7×10^3 M^{-1} s^{-1} (for CRC) for Eqs. 6—8.

To give further support for this mechanism, CRC using the method developed by Evans[10] was also applied. The plots of τ_r/t_f *vs.* t_f/τ_f, where τ_f and τ_r are the forward and the reverse transition times, respectively, and t_f is the forward electrolysis time, showed an upward trend in τ_r/t_f values with increasing t_f/τ_f (Fig. 2); this trend also indicates[10] the above reaction pathway (Eqs. 6—8). By using a digital simulation method the rate constant for the coupling reaction (Eq. 7) was estimated to be approximately 5×10^3 dm^3 mol^{-1} s^{-1} (Fig. 2). To obtain an accurate value of k and more precise mechanistic information, the details of the kinetics of the reaction are being investigated by CRC and RRDE voltammetry and will be reported later.

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References

1) R. N. Adams, "Electrochemistry at Solid Electrodes," Mercel Dekker, Inc., New York (1969), p. 351, and references cited therein.

2) S. D. Ross, M. Finkelstein, and E. J. Rudd, "Anodic Oxidation," Academic Press, Inc., New York (1975), pp. 203—207.

3) H. L. Jones and R. A. Osteryoung, *J. Electroanal. Chem. Interfacial Electrochem.*, **49**, 281 (1974).

4) R. A. Benkeser and H. R. Krysiak, *J. Am. Chem. Soc.*, **75**, 2421 (1953); N. F. Hall and M. R. Sprinkle, *ibid.*, **54**, 3469 (1932).

5) R. Hand and R. F. Nelson, *J. Electrochem. Soc.*, **117**, 1353 (1970).

6) R. B. Carlin and R. C. Odioso, *J. Am. Chem. Soc.*, **76**, 2345 (1954).

7) J. W. Strojek and T. Kuwana, *J. Am. Chem. Soc.*, **90**, 1353 (1968); H. N. Blount and T. Kuwana, *ibid.*, **92**, 5773 (1970).

8) U. J. Puglisi and A. J. Bard, *J. Electrochem. Soc.*, **119**, 829, 833 (1972).

9) T. H. Teharani, L. A. Tinker, and A. J. Bard, *J. Electroanal. Chem. Interfacial Electrochem.*, **90**, 117 (1978), and references therein.

10) S. C. Rifkin and D. H. Evans, *J. Electrochem. Soc.*, **121**, 769 (1974).