

using the program UCLATO1.²³ The analysis was quite successful, with over 90% of the magnitudes, on the average, of the anisotropic thermal parameters β_{ij} being expressible as rigid body translation and libration. Table VIII gives the results of the rigid body analysis.

TABLE VIII
RESULTS OF RIGID BODY THERMAL ANALYSIS

The translational tensor T and its estimated standard deviation

$$\begin{pmatrix} 0.0316 & -0.0025 & 0.0000 \\ & 0.0308 & .0000 \\ & & .0422 \end{pmatrix} \begin{pmatrix} 0.0014 & 0.0016 & 0.0000 \\ & 0.0021 & .0000 \\ & & .0012 \end{pmatrix}$$

Principal axes of T (Å.) and their direction cosines relative to the cartesian coordinate system defined in Table V

0.205	0.000	0.000	1.000
.184	.758	-.652	0.000
.170	.652	.758	0.000

The librational tensor ω and its estimated standard deviation (sq. radians)

$$\begin{pmatrix} 0.0076 & 0.0031 & 0.0000 \\ & 0.0038 & .0000 \\ & & .0079 \end{pmatrix} \begin{pmatrix} 0.0004 & 0.0003 & 0.0000 \\ & 0.0003 & .0000 \\ & & .0007 \end{pmatrix}$$

Principal axes of ω and their direction cosines (degrees)

5.5	-0.872	-0.489	0.000
5.1	.000	.000	1.000
2.6	-.489	.872	0.000

The rigid body translations are not markedly anisotropic. The largest amplitude, 0.205 Å., is in the direction of the hydrogen-bonded chain. The next largest amplitude, 0.184 Å., is very roughly perpendicular to the molecular plane. The smallest amplitude, 0.170 Å., is roughly in the molecular plane and perpendicular to the hydrogen-bonded chain.

The smallest rigid body librational axis, 2.6°, is very nearly perpendicular to the molecular plane. The other two librational axes, of amplitudes 5.1 and 5.5°, are very nearly in the molecular plane and parallel to the hydrogen-bonded chain, respectively. The smaller

(23) P. Gantzel, C. Coulter, and K. Trueblood, IBM 709 or 7090 Program UCLATO1, private communication.

libration around the axis perpendicular to the molecular plane is consistent with the tight packing along the hydrogen-bonded chains discussed under closest intermolecular approaches above.

The rigid body libration causes a shift in the apparent atomic centers toward the center of rotation (here assumed to be the center of mass of the molecule with all atoms equally weighted). Corrected atomic positions were obtained by the method of Cruickshank,²⁴ and all intramolecular distances and angles were recalculated (see Table IV). The magnitude of the librational correction for the intramolecular distances varied from 0.003 to 0.013 Å.

Discussion

Both hydrogen bonds in this structure are at critical distances where it cannot be said with certainty that the hydrogens should be centered in a symmetrical single potential well, or distributed over a double potential well,²⁵ and, as has been noted,^{20,21} this question cannot be settled using ordinary methods of X-ray diffraction, and probably not by neutron diffraction.²⁶

One of the significant features of this structure determination is that it demonstrates that with careful (but not excessively time-consuming) attention to gathering and treatment of the X-ray data, and sufficient computer capacity, structures are obtainable where bond distances are reliable to about 0.01 Å. (The difficulties in attaining such accuracies have been pointed out by Cruickshank.²⁷) This makes possible the discrimination between single and double potential wells for hydrogen bonds by the presence or absence of the abnormal isotope effect²⁸ as suggested by Rundle.²⁹

Acknowledgments.—The authors are indebted to Prof. Shigeru Oae, who correctly prophesied that this compound would have a strong intramolecular hydrogen bond and led us to undertake the problem.

(24) D. Cruickshank, *Acta Cryst.*, **14**, 896 (1961).

(25) R. Blinc, D. Hadzi, and A. Novak, *Z. Elektrochem.*, **64**, 567 (1960).

(26) S. Peterson and H. Levy, *J. Chem. Phys.*, **29**, 948 (1958).

(27) D. Cruickshank, *Acta Cryst.*, **13**, 774 (1960).

(28) J. Robertson and A. Ubbelohde, *Nature*, **139**, 504 (1937).

(29) R. Rundle, paper to be published in *J. Phys. Radium* as part of the International Symposium on Neutron Diffraction, Grenoble, 1963.

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The Anodic Oxidation of Triphenylmethane Dyes

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The anodic oxidation pathways of several typical triphenylmethane dyes have been examined in acidic buffers. The oxidation of crystal violet and malachite green leads to the formation of the oxidized form of N,N,N',N'-tetramethylbenzidine. This was shown to be an unusual reaction in which the central carbon residue is ejected followed by intracoupling to give the benzidine derivative. The role of hydrated forms of the dyes in these reactions was studied.

A previous communication reported the unusual electrochemical reaction of crystal violet and related triphenylmethane dyes which yield the diquinoid of N,N,N',N'-tetramethylbenzidine (TMBOx) upon oxidation in acidic, aqueous buffers.¹ Previous workers have established that the chemical oxidation of triphenylmethane dyes of this type lead to TMBOx.²⁻⁴

(1) Z. Galus and R. N. Adams, *J. Am. Chem. Soc.*, **84**, 3207 (1962).

The surprising points about the electrochemical oxidation are that the anodic reaction apparently proceeds *via* ejection of an integral unit of the central carbon attached to a phenyl group. Also, apparently only the hydrated form of the dye yields TMBOx.

(2) J. Knop, *Z. anal. Chem.*, **85**, 253 (1931).

(3) F. Kehrmann, G. Roy, and M. Ramm, *Helv. Chim. Acta*, **5**, 153 (1922).

(4) V. Hanousek and M. Matrka, *Collection Czech. Chem. Commun.*, **24**, 16 (1959).

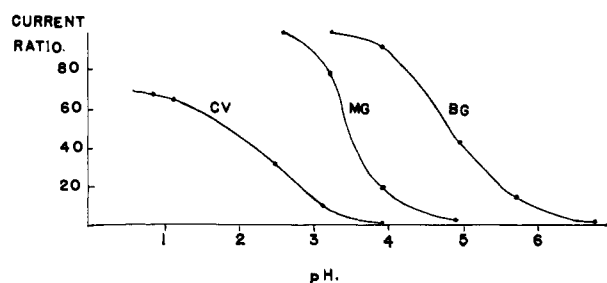


Fig. 1.—Ratio of peak currents vs. pH (see text).

Experimental

Carbon paste and platinum electrodes were used. The surface areas were 0.3 cm.² for the carbon-Nujol paste and 0.88 cm.² for the platinum. A rotated disk electrode (r.d.e.) of carbon paste was also used which had a surface area of 0.18 cm.². The preparation of electrodes and the technique of the cyclic voltammetry and r.d.e. experiments have been described previously.⁵

Crystal violet (CV), malachite green (MG), brilliant green (BG), and ethyl violet (EV) were commercial du Pont dye samples which were recrystallized from water. The *p,p'*-methylenebis(*N,N*-dimethylaniline) (MBis) was recrystallized from ethanol and melted at 91.5°. Britton and Robinson buffers were prepared from reagent grade chemicals and contained 1 *N* sodium sulfate to swamp ionic strength effects. All potentials were measured vs. s.c.e.

Results and Discussion

The anodic behavior of all the compounds is similar at carbon paste and platinum electrodes although they tend to oxidize with more difficulty at the carbon paste; CV, MG, and BG all showed two primary oxidation peaks. As the pH increased, the first peak (at lesser positive potential) decreased in height while the second peak increased. This is shown in Fig. 1 as the % ratio of peak currents $i_{(1)}/(i_{(1)} + i_{(2)})$. With increasing pH both waves, when present, were shifted toward more cathodic potentials.

That TMBOx is formed following the primary oxidation of CV is shown in the cyclic polarograms of Fig. 2. On the first anodic sweep, marked 1F, the first anodic reaction is that of peak A around +0.8 v. which is the primary oxidation wave of CV. The second peak, B, is also observed in this strong acid medium. On the reverse cathodic going sweep a reduction wave is obtained at C'. On all subsequent sweeps the reversible oxidation-reduction system, C, C' at ca. +0.55 v. develops. The half-peak ($E_{p/2}$) potentials of this system are within 2 mv. of that of *N,N,N',N'*-tetramethylbenzidine (TMB) and its fully oxidized diquinoid TMBOx. It is to be noted that the TMB oxidation-reduction couple results from oxidation of the dyestuff since no evidence of its presence is observed on the first anodic sweep. In a similar fashion it can be shown that TMB-TMBOx is formed from MG and MBis. In the case of the ethylated dyes BG and EV, the tetraethylbenzidine system is formed in an analogous fashion.

To support this purely electrochemical evidence, CV, MG, and MBis were oxidized in 1 *M* sulfuric acid with lead dioxide. Here the chemical oxidation of CV and MG is known to lead to TMBOx. To the brown solutions obtained by the lead dioxide treatment, perchloric acid was added. The resulting precipitates were dissolved and the cyclic voltammetry of these solutions showed TMB-TMBOx polarograms identical

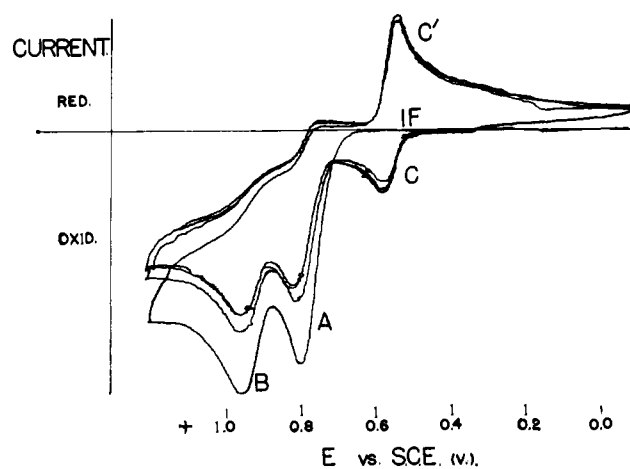


Fig. 2.—Cyclic polarograms of crystal violet.

with those obtained by direct anodic oxidation of the dyes. Other portions of these precipitates were dissolved in buffer solution with 50% acetone (apparent pH 3.8). Partial reduction of the dication TMBOx gave e.p.r. spectra consistent with that of the tetramethylbenzidine cation radical.⁵ Thus, beyond doubt, TMB is formed in a chemical reaction following the anodic oxidation of these compounds.

Two possible routes exist for the formation of TMB. First, 1 molecule of TMB may arise by oxidation of 2 dye molecules, each losing a *N,N*-dimethylphenyl fragment, followed by a chemical coupling reaction. The second possibility is that 1 dye molecule loses the central (methyl) carbon-phenyl unit and the remaining 2 *N*-substituted phenyl groups couple intra to give TMB.

To solve this question the voltammetry of MG was compared with that of *N,N*-dimethylaniline (DMA). Previous work has established that DMA yields TMBOx upon anodic oxidation.⁵ Peak polarograms of MG and DMA were recorded and at a potential 100 mv. more anodic than the primary oxidation wave the sweep was reversed. The reduction current for TMBOx was measured for both systems. Using equal starting concentrations of DMA and MG, the TMBOx current from MG was 1.8 times greater than that from DMA (all other experimental conditions held constant). Since it was previously shown that 2 moles of DMA yield 1 mole of TMBOx, the present results indicate a 1 mole of MG produces 1 mole of TMBOx. Similar results were obtained with CV and MBis. Although this comparison of peak currents is open to some question, we feel certain it is reliable. If, contrary to our conclusions, 2 moles of dye was required to produce 1 of TMB, there are no obvious experimental reasons why the current for TMB should be almost twice as great as would be predicted.

It is true that the present data can be said to prove only that the stoichiometry is 1 mole of TMBOx formed per mole of CV, MG, etc. However, the chemical oxidation studies of Hanousek and Matrka were very definitive. They carried out three experiments designed to prove the intracoupling argument. In the first they oxidized an unsymmetrical homolog of MG (*i.e.*, one phenyl containing dimethylamino, the other diethylamino) and identified the major product as *N,N*-dimethyl-*N',N'*-diethylbenzidine. Not even traces of the symmetrical tetraethyl- or tetramethylbenzidines were found which could have come from the

(5) Z. Galus and R. N. Adams, *J. Am. Chem. Soc.*, **84**, 2061 (1962).

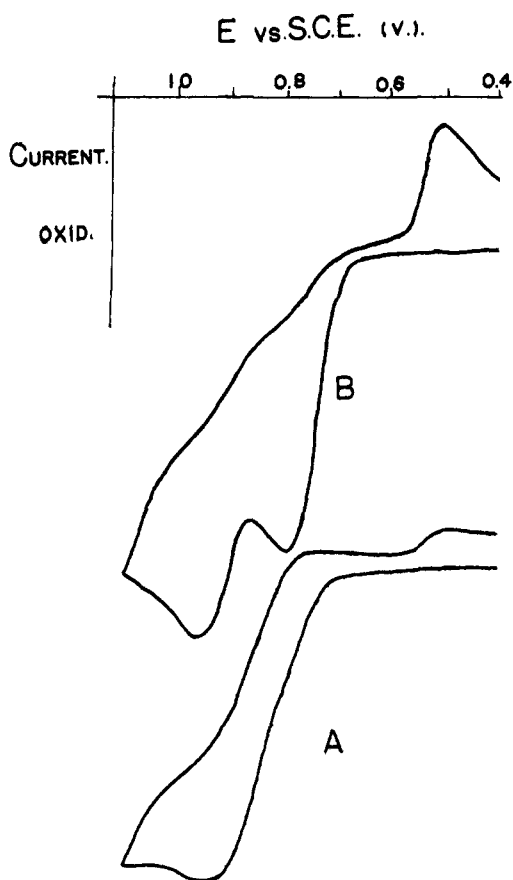


Fig. 3.—Time dependence of cyclic polarograms of crystal violet in acid solution: A, taken immediately after acidification; B, 10 min. after acidification.

intercoupling. In the second experiment, they oxidized an equimolar mixture of MG and brilliant green (the ethyl homolog) and obtained only tetramethyl- and tetraethylbenzidines with no mixed products from intercoupling. Finally, by oxidizing an equimolar mixture of dimethyl- and diethylaniline, they obtained both symmetrical products, tetramethyl- and tetraethylbenzidine as well as the mixed *N,N*-dimethyl-*N',N'*-diethylbenzidine. Hence, the chemical oxidation is unequivocally an intracoupling process. The electrochemical process is normally considered to be a milder form of oxidation than the chemical process. With the limiting current information supplanting this picture it seems most reasonable that the electrode reaction follows the same path and that the intracoupling occurs. The recent studies of Eastman, Engelsma, and Calvin showed CV could be formed by oxidation of dimethylaniline with chloranil.⁶ Here the central carbon of the CV must originate from a methyl carbon of dimethylaniline. This central carbon of a triphenylmethane dye (and related compounds like MBis) is apparently a remarkably mobile portion of a complex molecule. The present results together with those of Calvin and co-workers are interesting in terms of models to compare with some of the exceedingly intricate oxidation-reductions transformations which must occur in biochemical systems.

The next problem in this investigation was to consider the nature of the second oxidation peak. Cyclic voltammetry was carried out on CV in 1 *N* sulfuric acid—

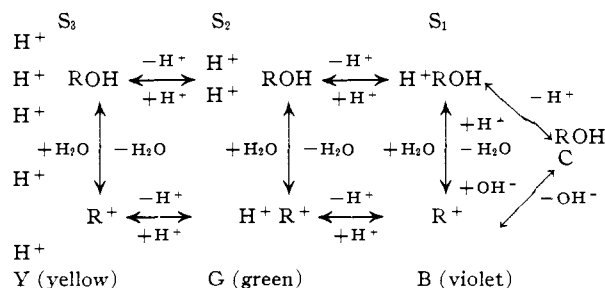
1 *N* sodium sulfate buffers in the following fashion: (1) An anodic sweep was carried to a point 10 mv. more positive than the first anodic peak. The sweep was then reversed and the corresponding reduction current for TMBOx measured.

(2) The anodic sweep was run as before but stopped and held at a potential less anodic than the foot of the second peak for a fixed time. The time interval was just that which would have been required to sweep farther past the second anodic peak and return. After holding the fixed potential for this interval, the sweep was reversed and the reduction current for TMBOx recorded as before. In both experiments the current for TMBOx was almost identical. This shows that TMBOx is apparently not formed in the anodic reaction of the second peak but arises from only the first peak.

This conclusion was substantiated in another way. With CV in pH 4 buffer, the first peak is almost non-existent (see Fig. 1). In this case the cyclic voltammetry of CV shows almost no indication of the oxidation-reduction system TMB-TMBOx.

As can be seen in Fig. 1, the second peak is formed at high pH. It is well known that triphenylmethane dyes exist in acid solutions in protonated forms. For example, with CV a violet color is observed at high pH and is due to the unprotonated dye. As acidity is increased the color changes to blue, then to green, and finally yellow as the result of continuing protonation of the dimethylamino sites. In acid solution, the dyes also undergo hydration reactions. As was shown by Cigen, the protonation reactions are rapid but the hydrations are quite slow.⁷

In its simplest form the protonation and hydration reactions of CV can be illustrated by the scheme given by Cigen, where R represents the triphenylmethyl nucleus $[(CH_3)_2NC_6H_4]_3C-$



The forms B, G, and Y (nomenclature of Cigen) are the easily observed colors upon successive protonation of the dimethylaniline groups. The forms S_3 , S_2 , S_1 , and C are all colorless, C being the so-called carbinol base of the dyestuff. All of the proton transfer reactions are, as usual, very rapid, but the interconversions involving the hydrations are measurably slow. Of particular interest to the present problem is the form Y and its hydrated analog S_3 . In strong acid Y predominates but, according to Cigen, the equilibrium constant for formation of the colorless hydrated form S_3 is relatively large. Thus, $[S_3]_\alpha/[Y]_\alpha \cong 79$. (The α indicates measurements made at sufficiently long time for the slow interconversion to be complete; see ref. 7.) Nevertheless the rate of formation of S_3 is quite slow.

We observed these slow hydration reactions in the following manner. A solution of CV in pH 7 buffer (at

(6) J. W. Eastman, G. Engelsma, and M. Calvin, *J. Am. Chem. Soc.*, **84**, 1139 (1962).

(7) R. Cigen, *Acta Chem. Scand.*, **12**, 1456 (1958).

this pH the dye exists completely unhydrated) was added to 1 *N* sulfuric acid and the cyclic voltammetry was recorded as quickly as possible after mixing. Only a single cycle was carried out, *i.e.*, one "forward" anodic sweep and the reverse cathodic sweep. As seen in Fig. 3A, the main oxidation consists almost entirely of the second peak. In connection with this, the cathodic current for TMBOx at *ca.* +0.5 v. is quite small. (Since these are single cycle runs no corresponding anodic reoxidation of TMB appears at +0.5 v.—it would appear on the second and subsequent sweeps.)

When this same operation was carried out 10 min. after mixing the CV with the sulfuric acid, the results were as seen in Fig. 3B. Now two anodic peaks are seen and the TMBOx current at +0.5 v. is considerably larger. (It should be noted that the electrode was not in contact with the solution during the 10 min. period but was immersed just prior to recording curve 3B. This rules out the possibility that a slow adsorption occurs on the electrode surface and that the first peak is a more easily oxidized sorbed species.) These experiments show that CV exists in strong acid solution in two forms and the formation of the species responsible for the first anodic peak is slow. Taking into account the work of Cigen it is reasonable to assume that the first anodic peak of CV is due to an oxidation of the protonated and hydrated form. This oxidation leads to the formation of TMBOx. The second anodic peak is due to the oxidation of the unhydrated form of the dye. Only the first peak leads directly to TMBOx formation.

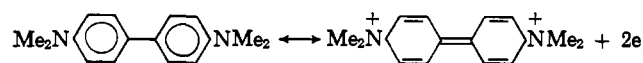
These experimental facts lead us to an interesting paradox. Two assumptions have served as guides in many studies of anodic oxidations of aromatic amines. The first is that the site of electron abstraction is the amino function. This has never been proved and, indeed, it may defy experimental proof, but from an intuitive viewpoint it seems entirely acceptable. Thus, in the case of aniline, abstraction of electrons from the amine function in preference to the π -system seems perfectly logical. Secondly, it is assumed that the non-protonated form of the amine is the easier of the two conjugate acid-base species to oxidize. If, following the first assumption, electrons are to be abstracted from an amine function, this process certainly will be facilitated by having an unshared pair on the nitrogen. Indeed, if the amine is protonated, one expects a dissociation prior to electron transfer. Such precursor reactions are rapid, but recently Mark and Anson definitely demonstrated their existence in the oxidation of some phenylenediamines and related compounds *via* chronopotentiometry at platinum electrodes.⁸

Now, the paradox is that the present results indicate the protonated hydrated form of CV (which leads to TMBOx) is *easier to oxidize than the nonprotonated form* (*i.e.*, the slowly formed species gives the first peak at lesser anodic potentials). If this is so and the CV dimethylamino groups are all protonated, we would expect still to find evidence of a precursor proton dissociation. However a plot of $i\tau^{1/2}$ vs. i over about the same range of currents used by Mark and Anson failed to show any decrease of $i\tau^{1/2}$. This study was made at platinum electrodes since there is some doubt about the reliability of carbon paste for this particular meas-

urement. Since the evidence is that the dimethylamine groups in CV are fully protonated, yet no proton dissociation prior to oxidation can be detected, one could conclude that the protonated dimethylamine group, contrary to previous beliefs, is the actual species undergoing electron transfer. This we find difficult to believe and are more willing to accept an alternate hypothesis, namely, that in strong acid solution, the most easily oxidized portion of CV is the central carbonol group. This would be consistent with the fact that when some of the amine protons are removed at pH 4 and higher, very little TMBOx results from anodic oxidation; *i.e.*, the over-all oxidation mechanism apparently changes. To attempt to pinpoint the site of electron transfer like this is necessarily difficult and these conclusions must be regarded as tentative. Further studies of similar systems are planned to substantiate these ideas.

Table I summarizes the electrochemical information for the compounds examined. It can be observed that the second anodic peak for those compounds with only two *N*-methylated groups is obtained only at higher pH's (compare Fig. 1). The slopes of the first anodic wave ($E_p - E_{p/2}$) are similar for all compounds studied. From these, the product βn_a (product of the anodic transfer coefficient by the number of electrons in the rate-determining electrochemical step) can be evaluated. The value, varying between 0.77 and 0.78 for all compounds, suggests $n_a = 2$ electrons.

On the basis of these studies we propose the initial charge transfer step is a 2-electron transfer. Hanousek and Matrka preferred a 1-electron process in the chemical oxidation of MG and similar dyes. They also proposed a series of rearrangements following the oxidation step which involved the formation of a cyclopropane ring system involving the "central" carbon and two phenyl groups. Upon reaction with water this intermediate split to form TMB and the corresponding carboxylic acid. Our electrochemical studies do not detect such subtle intermediates and one can only say that, following the charge transfer step, a series of chemical interactions occurs whereby TMB is formed by intracoupling of two dimethylanilino groups. Since it is clear that TMB (or its ethyl derivatives in the case of the ethylated dyes) undergoes oxidation at far less anodic potentials (*ca.* +0.5 v.) than the primary dye oxidation (*ca.* +0.8 v.), TMB is immediately oxidized at the electrode surface to TMBOx and is the



final product of the electrolysis. This picture is in agreement with the experimental facts. By the transfer of a total of 4 electrons, 1 mole of dye leads to 1 mole of TMBOx (or the tetraethyl derivative). Table II shows an evaluation of the total number of electrons transferred for the compounds studied. This was determined by comparing the limiting current at a r.d.e. for each compound with that of an equimolar amount of TMB. The latter is clearly a 2-electron oxidation. The currents in Table II are normalized to a value for TMB = 1. Only in the case of BG is the experimental value considerably lower than $n = 4$. With the unknown differences in diffusion coefficients and the fact that purity criteria for the dyes are lacking, we feel

(8) H. B. Mark and F. C. Anson, *Anal. Chem.*, **35**, 722 (1963).

TABLE I
 OXIDATION OF TRIPHENYLMETHANE DYES AT PLATINUM^a

Compound	Structure	$E_{p/2}$ 1st peak	2nd peak	$(E - E_{p/2})^b$ mv	β_{n_a}	Secondary oxidation-reduction system formed
Crystal violet		0.632	0.886	63	0.77	TMB/TMBOx
Malachite green		0.690	...	61	0.78	TMB/TMBOx
<i>p,p'</i> -Methylenebis-(<i>N,N</i> -dimethylaniline)		0.775	...	62	0.78	TMB/TMBOx
Ethyl violet		0.796	0.954	66	0.73	TEB/TEBOx ^c
Brilliant green		0.798	...	67	0.72	TEB/TEBOx

^a Background electrolyte 1 *N* H₂SO₄ + 1 *N* Na₂SO₄, scan rate 1 v./min.; potentials in v. *vs.* s.c.e. ^b Slope of first anodic wave. ^c TEB = tetraethylbenzidine.

confident that the results support a 4-electron over-all oxidation.

 TABLE II
 TOTAL ELECTRONS TRANSFERRED *via* LIMITING CURRENTS
 AT R.D.E.^a

Compound	Current (TMB current = 1)	<i>T</i>
TMB	1.00	2.0
CV	1.89	3.8
MG	1.75	3.5
BG	1.58	3.2
MBis	1.85	3.7

^a Rotation speed 6 rev./sec.; concentration of all compounds 1.0 × 10⁻⁴ *M*; background electrolyte 1 *N* H₂SO₄.

A thorough examination of the oxidation of the leuco dyes was not made, but leuco crystal violet (LCV) was investigated in some detail. It is most surprising that the oxidation mode of LCV in aqueous media bears little resemblance to the oxidation of the dyestuff.

In 1 *M* sulfuric acid the slope of the anodic wave of LCV at a carbon paste or platinum r.d.e. as indicated by $(E_{3/4} - E_{1/4})$, is 0.057 v. This suggests a reversible 1-electron transfer and, indeed, Allen and Powell⁹ reported the oxidation at a r.p.e. in 1 *M* HCl to be a reversible 1-electron process leading to the free radical. This, however, is untenable in light of further voltammetric studies. If one compares the limiting current for equimolar concentrations of LCV and the compound MBis (previously shown to be a 4-electron oxida-

tion), the apparent *n*-value for LCV is between 4 and 5 electrons. Further, no evidence of any radical ion intermediates are seen if LCV is oxidized electrochemically in the cavity of an e.p.r. spectrometer in aqueous media. Voltammetric studies in aqueous media are complicated by absorption and film formation on the electrode surface and the apparent *n*-values cited above are to be viewed with caution. Further study is necessary to give a complete picture of the oxidation of LCV in acidic, aqueous solution, but it is safe to say it does not proceed mainly *via* oxidation to CV followed by further conversion to TMBOx. Similar results with adsorption complications have been found by Reddy.¹⁰

On the other hand, in nonaqueous solvents like acetonitrile and acetone, LCV gives two anodic peaks at a stationary platinum electrode. In acetonitrile, the $E_{p/2}$ values are +0.51 and +0.87 v. *vs.* s.c.e. In acetone, the oxidation is a bit more difficult with $E_{p/2}$'s of +0.67 and 1.07 v. *vs.* s.c.e.

In acetonitrile the first peak at 0.51 v. corresponds to oxidation to CV. This was shown by carrying out the oxidation directly in a rapid scan spectrophotometer. The visible absorption spectrum after a few minutes generation at the first peak potential (*ca.* +0.7 v.) was identical with that of a solution of CV itself in acetonitrile. The second peak of LCV in acetonitrile appears also to be a 2-electron process, but nothing is known of the product.

(9) M. J. Allen and V. J. Powell, *Trans. Faraday Soc.*, **50**, 1244 (1954).

(10) T. B. Reddy, Abstracts, Electrochemistry Society Fall Meeting, New York, N. Y., Sept., 1963.

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Electron Spin Resonance Studies of Aromatic Polynitro Compounds¹

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The three nitromesitylenes and two nitrodurenes have been reduced electrolytically in *N,N*-dimethylformamide solutions and their electron spin resonance spectra studied. Some spectra were also observed in dimethyl sulfoxide solutions. The e.s.r. spectra were obtained in conjunction with conventional and alternating current polarographic investigations. Different spectra were obtained at the successively higher polarographic waves. The first polarographic wave for each compound was found to be reversible and, except for trinitromesitylene, the expected number of nitrogen splittings were observed. At successively higher waves for all the compounds, a nitrogen splitting disappeared from the spectrum and the polarographic wave was irreversible. No interpretable e.s.r. spectra were obtained at polarographic waves above those for which only one nitrogen splitting remained in the spectrum. The radicals produced at the higher waves were not identical with the radicals of the parent compound with the same number of nitrogen splittings; e.g., the radical at the second wave of dinitromesitylene, which shows the splittings from only one nitrogen nucleus, is different from the radical generated at the first polarographic wave of mononitromesitylene. The two radicals with spectra containing two nitrogen splittings exhibited the alternating line width phenomenon to a marked extent.

I. Introduction

In recent electron spin resonance studies of a number of aromatic polynitro compounds, Ward^{3,4} observed that the radicals produced by alkali metal reduction exhibit hyperfine splittings from only one nitrogen nucleus. In the *m*-dinitrobenzene anion, he found two nitrogen splittings, but one was thirty times larger than the other.⁵ These results were explained in terms of a tightly bound ion-pair complex between the alkali metal cation and the nitro group of the anion radical. Effects such as this are not observed, however, when the dinitrobenzene anions are generated by electrolytic reduction with bulky tetraalkylammonium ions as supporting electrolytes.⁶

During the course of an investigation into the alternating line width phenomenon in nitro compounds,⁷ we were led to an examination, using electrolytic techniques, of the nitromesitylenes. These were also found by Ward to lead to only one nitrogen splitting. Our results indicated that several nitrogen splittings could be observed, but that different spectra were obtained at different polarographic waves. A detailed study has therefore been made of the three nitromesitylenes and two nitrodurenes. Electron spin resonance spectra were examined at successive polarographic waves, and conventional and alternating current polarographic studies were used in conjunction with the e.s.r. investigation.

II. Experimental

Electron spin resonance measurements were performed at X-band frequencies using a spectrometer previously described.⁸ Radicals were produced by electrolytic reduction in a cell out-

side the cavity of the spectrometer under conditions which allowed control of the potential and essentially complete reduction.⁹ The techniques as well as the factors that determine the sharpness of the lines in the spectrum have been discussed in detail elsewhere.⁹

N,N-Dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were used as solvents. Tetra-*n*-propylammonium perchlorate (TNPAP) and, in some instances, tetra-*n*-butylammonium perchlorate (TNBAP) were used as the supporting electrolyte. The concentrations of the reducible material ranged from 5 to 0.5 mM, and the solutions were 0.1 M in supporting electrolyte. In some experiments, but not all, lowering of the concentration below 1 to 2 mM improved the sharpness of the lines of the spectrum. Radicals which were quite stable at concentrations of a few millimolar became unstable at the lower concentrations. This instability was presumably caused by impurities in the solutions and/or on the walls of the electrolytic cell, e.s.r. sample tube, and interconnecting tubing. Reduction potentials were measured with respect to a silver-silver perchlorate electrode.⁹ It should be noted that the potentials of this electrode tend to drift with time, and therefore we have taken care, whenever comparative determinations of potential were important, to perform them on the same day. No attempt has been made, however, to relate the potentials to an absolute scale.

Conventional oscillographic studies were undertaken using equipment described elsewhere.¹⁰ Solutions for polarographic investigations were approximately 1 mM in reducible material, and nitrogen was bubbled through them to remove oxygen. The measurements were made at room temperature without temperature control.

A macroelectrolysis was carried out for one compound, trinitromesitylene. A thermostated electrolytic cell equipped with a stirrer was employed that had a flat, square, platinum anode 1 cm.² in area. The cathode was a mercury pool which was also approximately 1 cm.² in area. A constant potential electrolysis was carried out using the Ag-AgClO₄ electrode to establish the reference potential.

Trinitromesitylene was obtained from K and K Laboratories, Inc. (m.p. 235–236°, lit.¹¹ 236°). Dinitromesitylene (m.p. 85–86°, lit.¹¹ 86°) and nitromesitylene (m.p. 45–46°, lit.¹¹ 45.5°) were obtained from Eastman Organic Chemicals. Dinitrodurene was prepared according to the procedure of Smith and Dobrovolsky¹² (m.p. 211–212° uncor., lit.¹² 207–208°). Nitrodurene was made by the method of Smith and Taylor¹³ (m.p. 113–114°, lit.¹³

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(2) Socony-Mobil Predoctoral Fellow, 1961–1962.

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