VOLTAMMETRIC OXIDATION OF TRIPHENYL-METHANE DYES AT PLATINUM IN LIQUID SULPHUR DIOXIDE*

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Abstract—The electrochemical oxidation-reduction behaviour at the platinum electrode in liquid sulphur dioxide of four triphenylmethane dyes (crystal violet, ethyl violet, malachite green and brilliant green), the leuco form of one (leuco crystal violet), a possible oxidation product (N,N,N',N'-tetramethylbenzidine), and potassium salts of the anions present in the dyes (chloride and bisulphate) has been investigated using voltammographic (polarographic) and cyclic voltammetric techniques. The oxidation of the dyes in liquid sulphur dioxide is quite different from that observed in acidic aqueous solution.

Voltammography revealed no cathodic waves before solution discharge at −0·2 to −0·4 V. All the compounds give well-defined anodic waves. Each dye gives one anodic wave corresponding to oxidation of the organic cation or carbonium ion produced on dissociation and one or two waves corresponding to oxidation of its anion.

The cyclic voltammetric patterns are much more complex. Each of the dyes shows a one-electron redox wave, which is probably due to oxidation of the carbonium ion to a free radical via attack on a lone electron pair on one nitrogen, followed by reduction of the free radical.

Résumé—Recherches par voltamétrie cyclique et polarographie du comportement redox sur électrode Pt poli dans SO₂ liquide de 4 colorants de triphénylméthane (violet cristallisé, violet d'éthyle, vert malachite, vert brillant), la leuco-forme du premier, un produit d'oxydation possible (N,N,N',N'-tétraméthylbenzidine) et des sels de potassium des anions présents (chlorure et bisulfate). Ce comportement en SO₂ liquide est très différent de celui observé en solution aqueuse acide. La polarographie ne manifeste pas de vague cathodique avant −0,2 à 0,4 V. Tous les composés manifestent des vagues anodiques bien définies. Chaque colorant manifeste une vague d'oxydation du cation organique ou de l'ion carbonium engendré par dissociation et une ou deux vagues d'oxydation de son anion. Les résultats de voltamétrie cyclique sont plus complexes: chaque colorant manifeste une vague redox à un électron, probablement due à l'oxydation en radical libre de l'ion carbonium et qui est suivie par la réduction du radical libre.

Zusammenfassung—Es wurde das elektrochemische Oxidations/Reduktions-Verhalten von vier Triphenylmethanfarbstoffen (Kristallviolett, Äthylviolett, Malachitgrün und Billiantgrün) an der Platin-Elektrode in flüssigem Schwefeldioxyd mittels polarographischer und zyklischer voltametrischer Methoden untersucht. Des weiteren wurde die Leuko-Form eines der Farbstoffe (Leukokristall-violett), ein mögliches Oxidationsprodukt (N,N,N',N'-Tetramethylbenzidin), und die Kaliumsalze der in den Farbstoffen vorhandenen Anionen in die Untersuchung mit einbezogen. Die Oxidation der Farbstoffe verläuft in flüssigem Schwefeldioxyd vollständig anders als in saurer, wässeriger Lösung. Es werden polarographisch vor der kathodischen Reduktion der Lösung bei −0,2 bis −0,4 V keine Wellen beobachtet. Alle Verbindungen geben jedoch gut definierte anodische Stufe. Jeder Farbstoff zeigt sowohl eine anodische Stufe, welche der Oxidation des durch Dissoziation entstandenen organischen Kations oder des Karbonium-Ions entspricht, als auch eine oder zwei Stufen, welche der Oxidation seines Anions zuzuschreiben sind. Die Bilder, welche sich bei der zyklischen Voltametrie ergeben, sind bedeutend komplexer. Jeder der Farbstoffe zeigt eine ein-Elektronenstufe, welche wahrscheinlich der Oxidation des Karbonium-Ions zu einem freien Radikal über den Angriff an einem einsamen Elektronenpaar eines Stickstoffatoms zuzuschreiben ist, und welcher die Reduktionswelle des freien Radikals folgt.

INTRODUCTION

GALUS and Adams[1] reported that the electrochemical oxidation of crystal violet and three related triphenylmethane dyes in acidic aqueous buffered solution,[1,2] similar to the chemical oxidation of triphenylmethane dyes of this type,[3–5] leads to the formation of compounds of the type of the diquinoid of N,N,N',N'-tetramethylbenzidine (TMBOX). The latter results from the ejection of the central carbon residue from the

* Manuscript received 3 May 1965.

triphenylmethyl moiety followed by intramolecular coupling of the two phenyl frag-
ments. Cyclic voltammetry in acidic buffers[1] revealed that only oxidation of the
protonated and hydrated dye results in the intramolecular coupling reaction to yield
TMBOX.

The electrochemical behaviour at the platinum electrode of the four triphenyl-
methane dyes, tetramethylbenzidine, and the leuco form of crystal violet has now been
investigated in the nonprotonic medium, anhydrous liquid sulphur dioxide, using
voltammographic and cyclic voltammetric techniques. The electrochemical behaviour
of these compounds in sulphur dioxide is significantly different from that in aqueous
media.

The structures and commonly used abbreviations for the compounds involved are
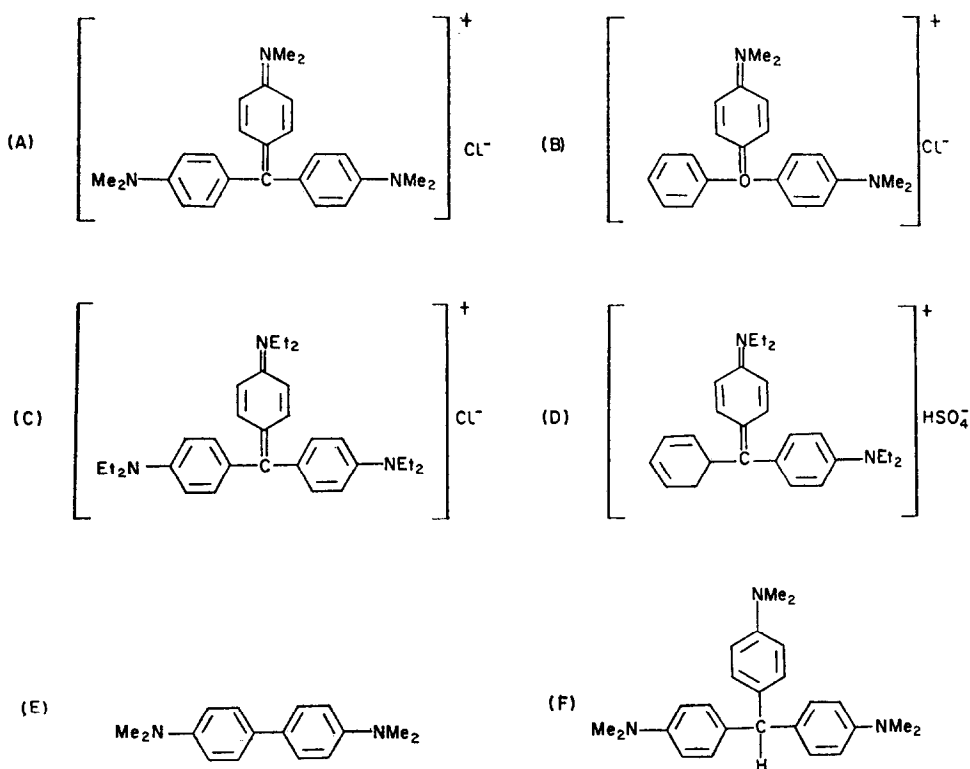given in Fig. 1.

Fig. 1. Structure of the triphenylmethane dyes and related compounds.
(A) crystal violet (CV); (B) malachite green (MG); (C) ethyl violet (EV); (D) brilliant
green (BG); (E) tetramethylbenzidine (TMB); (F) leuco crystal violet (LCV).

EXPERIMENTAL TECHNIQUE

Chemicals

Crystal violet (CV), malachite green (MG) and ethyl violet (EV) were obtained
from the National Aniline Division of Allied Chemical Corp. as chloride salts;
brilliant green (BG) (a bisulphate salt) was a National Aniline & Chemical Co. dye.
These dyes were recrystallized from water. Leuco crystal violet (LCV) and N,N,N',N'-
tetramethylbenzidine (TMB) were Eastman white label grade.

Anhydrous grade sulphur dioxide (Matheson; stated purity: 99·98%) was treated to remove H_2O, SO_3 and non-condensable gases as previously described.[6]

Apparatus

The electrolytic cell previously described[6] was used for both voltammographic and cyclic voltammetric measurements; this cell contained a platinum disk indicating electrode (0·5 mm dia.), a Ag/AgBr helix reference electrode (0·4 mm dia. and 150 mm long), and similar disk platinum electrode (for short-circuiting between the two platinum electrodes) and Ag/AgBr electrode (as a third working electrode for iR drop compensation).
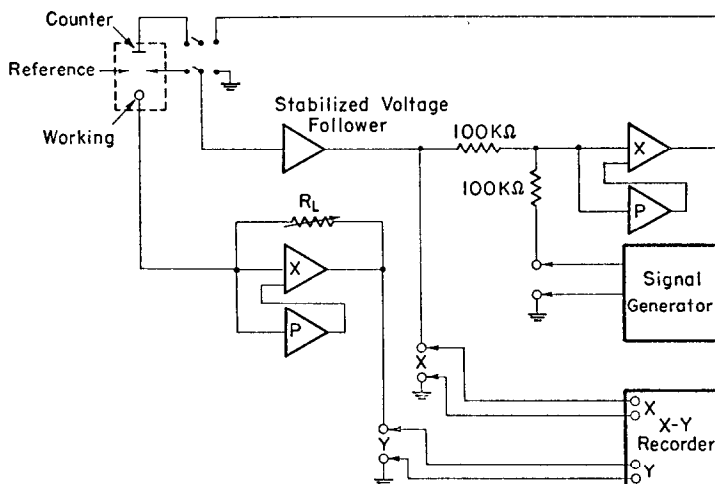

FIG. 2. Schematic diagram of cyclic voltammetry unit.
The triangles are Philbrick operational amplifiers: X, K2-XA; P, K2-P; unmarked, K2-XA with K2-P as stabilizer. Counter, Reference and Working refer to the two Ag/AgBr and one platinum electrode, respectively.

Current/potential curves were recorded by a modified Sargent Model FS polarograph,[6] using the Sargent Model A resistance (iR-drop) compensator.

Solution resistance was measured with a Jones-type conductivity bridge.

Cyclic voltammetry (Fig. 2) was carried out by a unit that used the triangular wave form of 0·01 to 1200 c/s generated by a Hewlett-Packard Model 202A low frequency function generator. The cathode follower and iR-drop compensator were an operational amplifier unit constructed as described by Underkofler and Shain.[7] The Moseley Autograf X-Y recorder used was capable of following up to frequencies of 0·1 c/s. All wave forms were calibrated by means of a Tektronix Model 502 oscilloscope.

Procedures

The gas-handling procedures for purifying and charging sulphur dioxide into the cell have been described.[6,8] The cell was immersed in a propanol-CO_2 bath, controlled to $-20 \pm 0.5°C$ by adding a small piece of solid CO_2 before each run. Both voltammography and cyclic voltammetry were undertaken in the absence of a background electrolyte.

The general procedures for obtaining voltammograms have been described.[6]

The span (amplitude), initial and final potential, and frequency of the triangular wave used in cyclic voltammetry were set via the amplitude, dc level and frequency controls, respectively, of the function generator. The exact values of the amplitude, and initial and final potentials, were determined by means of the calibrated Tektronix oscilloscope.

After the initial settings were made, the circuit was connected as shown in Fig. 2 except for the cell. The initial application of the wave to the cell was accompanied by a potential excursion, which went off scale, of approximately 20 s duration. The voltammograms immediately following this excursion were characterized by changing peak currents presumably due to the establishment of the diffusion layer. All voltammograms were recorded after a minimum of three cycles, each of 100 s duration. The voltage and current sensitivities were adjusted via the controls on the X-Y recorder and the current-calibrating resistor R_L.

RESULTS AND DISCUSSION

Typical experimental results are summarized in Tables 1 and 2; typical voltammograms and cyclic voltammograms are shown in Fig. 3 and Figs. 4 to 8, respectively. All values of $E_{p/2}$ and $E_{h/2}$ cited in the text are the averages of two or more voltammograms. All potentials cited are vs the Ag/AgBr electrode and are presumably corrected for iR drop. Background electrolytes were not present in these experiments, since solutes fully satisfactory as background electrolytes in liquid sulphur dioxide have not yet been found.

Voltammographic Behaviour

Generally, the voltammograms or polarograms obtained were satisfactory with well-defined waves (Fig. 3).

The polarographic patterns of the four dyes, LCV and TMB on negative polarization exhibit no waves before the cathodic solution discharge potentials, which are generally in the range of -0.2 to -0.4 V.

The polarograms of the dyes on positive polarization generally show two or three anodic waves. These are composite polarograms due to the oxidation of both the organic cation or carbonium ion produced by each dye on dissociation and its corresponding anion. The half-height potential, $E_{h/2}$, of the first wave, which may be assigned to the carbonium ion, is in each case within the range of 0.75–0.88 V; that of the second wave, which is due to the oxidation of chloride ion in the case of MG, CV and EV and bisulphate ion in the case of BG, is within 1.11–1.22 V. The bisulphate ion in the case of BG exhibits an additional wave at 1.43 V. Although the half-height potential of the first wave of the four dyes are all relatively close together, the dyes having three aminophenyl groups (CV and EV) show considerably higher currents than do the corresponding compounds having two aminophenyl groups and one unsubstituted phenyl group (MG and BG). This would seem to indicate a greater degree of oxidation of the trisubstituted as compared to the disubstituted triphenylmethane dyes.

The potentials of the two LCV anodic waves do not correspond to those of the CV waves.

TABLE 1. VOLTAMMETRY OF TRIPHENYLMETHANE DYES AT PLATINUM IN SULPHUR DIOXIDE[a]

Compound[c]	Conc. mM	Cathodic discharge V	Wave I $E_{h/2}$ V	Wave I i_t μA	Wave I i_t/C	Wave I Slope[b] mV	Wave II $E_{h/2}$ V	Wave II i_t μA	Wave II i_t/C	Wave II Slope[b] mV	Discharge potential V	Solution resistance KΩ
CV	0·11	−0·37	0·86	0·02	0·18	9					1·5	140
	1·68	−0·33	0·88	0·38	0·23	85					2·4	50
(Cl⁻)	0·11		1·11	0·06	0·55	126						
	1·68		1·17	0·84	0·50	90					1·9	50
MG	1·90	−0·26	0·75	0·12	0·06	96						
(Cl⁻)			1·21	0·01	0·01							
EV	0·60	−0·13	0·86	0·09	0·15	89					2·0	100
	1·30	−0·24	0·87	0·28	0·22	60					2·0	70
(Cl⁻)	0·60		1·18	0·30	0·50	105						
	1·30		1·22	0·60	0·46	98						
BG	2·12	−0·23	0·83	0·19	0·09	62	1·43	0·34	0·16	100	2·3	50
(HSO₄⁻)			1·12	0·29	0·14	65	1·56	0·09	0·07	179		
LCV	1·26	−0·34	1·05	0·23	0·18	265	0·75	0·15	0·09	125	2·2	160
TMB	1·70	−0·19	0·49	0·07	0·04	61	1·31	0·39	0·23	248		
KCl	0·91	−4·8	1·12	0·59	0·65		III				4·1	

[a] All half-height and discharge potentials are vs the Ag/AgBr reference electrode at −20 + 0·5°C. The platinum electrode area was 0·196 mm². The scan rate was 0·004 V/s.

[b] This slope is that for a plot of log $[i/(i_t − i)]$ vs E.

[c] In the case of each of the four dyes, the data are first given for the waves, which can be assigned to the organic cation; this is followed by the wave pattern believed due to the anion of the dye, which is indicated in parentheses. The data are the averages of two or more voltammograms at each concentration.

TABLE 2. CYCLIC VOLTAMMETRY OF TRIPHENYLMETHANE DYES AT PLATINUM IN SULPHUR DIOXIDE SOLUTION[a]

		Cathodic pattern				Anodic pattern					
		Peak (or Wave) I			Discharge potential V	Peak (or Wave) I			Peak II		
Compound[b]	Concn. mM	$E_{p/2}$ V	i_p μA	i_p/C		$E_{p/2}$ V	i_p μA	i_p/C	$E_{p/2}$ V	i_p μA	i_p/C
CV (Cl⁻)	1·35	0·50	0·87	0·64	−0·39	1·34	0·70	0·52	2·56	3·72	2·76
						1·75	1·14	0·84			
MG (Cl⁻)	1·46	0·76	0·06	0·04		0·75	0·31	0·21	2·26	0·1	0·1
EV (Cl⁻)	1·41	0·82	0·06	0·04	−0·28	1·35	0·05	0·04			
		0·48	0·44	0·31		1·17	0·42	0·30			
BG (HSO₄⁻)	1·41	0·72	0·25	0·18	−0·15	1·69	2·34	1·66	2·43	0·62	0·44
		0·43	0·99	0·70		1·38	1·55	1·10	0·98	0·26	0·18
						0·55	—	—	III 1·62	1·46	1·04
									IV 1·95	0·18	0·13
KHSO₄	Satd	0·62	0·01			0·53	0·02		0·93	0·04	0·04
KCl	1·39	0·52	0·08	0·06		0·56	0·06	0·04	III 1·48	0·03	—
									1·38	1·49	1·07
									III 1·76	0·08	0·06
TMB	1·70					1·32	0·36	0·21			
LCV	1·26				0·03	1·17	0·43	0·34	2·10	0·19	0·15

[a] All potential measurements are vs the Ag/AgBr reference electrode at −20 ± 0·5°C. The platinum electrode area was 0·196 mm². The scan rate was 0·03–0·08 V/s.

[b] In the case of each of the four dyes, the data are first given for the waves, which can be assigned to the organic cation; this is followed by the wave pattern believed due to the anion of the dye, which is indicated in parentheses. The data are the averages of two or more voltammograms for that potential span which gave the largest number of waves.
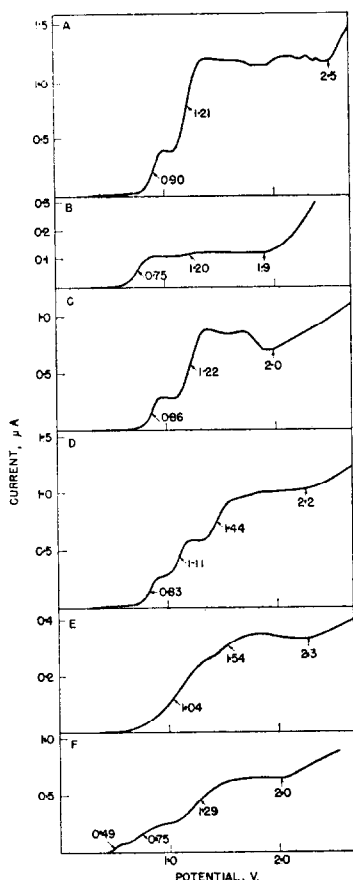
FIG. 3. Voltammograms (polarograms) showing the anodic patterns observed at a platinum electrode for sulphur dioxide solutions.

A, crystal violet (1·68 mM), B, malachite green (1·90 mM), C, ethyl violet (1·30 mM), D, brilliant green (2·12 mM), E, leuco crystal violet (1·26 mM), and F, N,N,N′,N′-tetramethylbenzidine (1·70 mM).
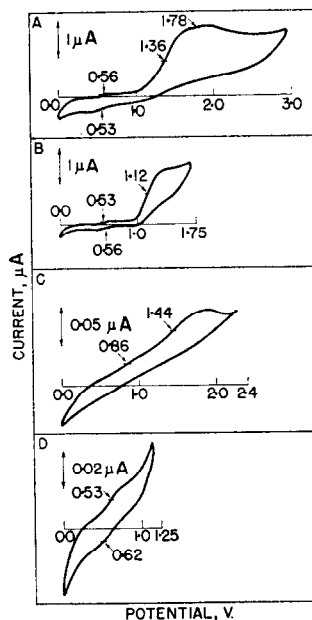
FIG. 4. Cyclic voltammograms (scan rate, V/s, in parentheses) at a platinum electrode for sulphur dioxide solutions.

A, potassium chloride, 1·39 mM, (0·06); B, potassium chloride, 1·39 mM, (0·035); C, potassium bisulphate, saturated, (0·048); D, potassium bisulphate, saturated, (0·025). Potential range scanned is indicated by the potential axis shown.

TMB exhibits three oxidation waves, whose half-height potentials are quite different from those of the four dyes.

CYCLIC VOLTAMMETRY OF TRIPHENYLMETHANE DYES

The anions of the dyes used show characteristic redox patterns. Crystal violet, ethyl violet and malachite green are chloride salts; brilliant green is a bisulphate salt.

In the subsequent discussions of the wave patterns of individual compounds, the potentials given refer to the half-height potentials.

Chloride, introduced as potassium chloride, is characterized by three oxidation waves at 0·56, 1·38 and 1·76 V, and one reduction wave at 0·52 V (Fig. 4, A, B). On scanning with limitation of the potential range or span covered, the second and third oxidation waves show no sign of reversibility; the first oxidation wave, however,

is reversible. Its redox couple is shown in all voltammograms, *ie* spans of 0–3, 0–1·75, 0–1·5 and 0·3–0·8 V. The current produced is very small relative to the second or main wave, and may be due to a capacitive effect resulting from film formation or a change in sign of the ions associated with the double layer of the platinum electrode.

The change of $E_{h/2}$ for the second wave with change in span magnitude is of significance. For a span of 0–3 V, it is 1·38 V; for spans of 0–1·75 and 0–1·5 V, it is 1·12 V. The latter value is close to that obtained in slow-scan voltammetry.
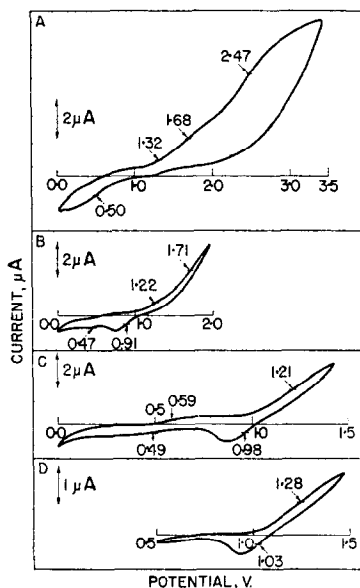

FIG. 5. Cyclic voltammograms of 1·35 mM crystal violet at a platinum electrode in sulphur dioxide solutions.
Scan rate, V/s: A, 0·07; B, 0·04; C, 0·03; D, 0·02. Potential range scanned is indicated by the potential axis shown.

Voltammograms of bisulphate (Fig. 4, C, D), introduced as potassium bisulphate, are difficult to interpret due to the limited concentration ($KHSO_4$ is only slightly soluble in SO_2). For a potential span of 0·0–3·0 V, oxidation waves appear at 0·93 and 1·48 V; the presence of the first wave is quite doubtful, but the second is well-defined with good peak formation. When the potential span is limited to 0·0 to +1·25 V, a redox couple is observed with an anodic wave at 0·53 V and a cathodic wave at 0·62 V.

Since the correlation of potentials for the inorganic chloride and bisulphate salts with those for the dyes having the same anion is not good, it is evident that ion aggregation such as ion pairing has a definite effect on the $E_{h/2}$ values observed. The oxidation potential of either chloride or bisulphate would change depending on the nature of its counter ion in an ion pair and on the stability of the ion pair.

In the ensuing discussion of the electrolytic behaviour of the triphenylmethane dyes investigated, an attempt will be made to assign the waves observed to their likely origins.

Crystal violet

The CV pattern (Fig. 5, A) (0·0 to +3·5 V scan) is characterized by poorly defined oxidation waves at 1·34, 1·75 and 2·56 V and one similar reduction wave at 0·50 V.

On the basis of $E_{h/2}$ values, the reduction wave can be assigned to chloride ion; the corresponding oxidation wave is poorly defined and no attempt was made to assign an $E_{h/2}$ value to it.

A second reduction peak is observed at 0·90 V, when the third oxidation wave is eliminated by limiting the potential span (Fig. 5, B); its height remains essentially constant over prolonged periods of electrolysis. Upon elimination of the second oxidation wave (Fig. 5, C), the reduction peak height at 0·90 V increases with time of electrolysis; a small oxidation pre-wave also appears at 0·59 V.

On scanning from 0·5 to 1·5 V (Fig. 5, D), an oxidation wave appears at 1·28 V and a reduction wave at 1·03 V, which appear to constitute a near-reversible redox couple. Since chloride itself shows no degree of reversibility for its second and third oxidation waves, it may be assumed that this couple involves the carbonium ion and is due to the formation of a free radical in the process corresponding to the first CV oxidation wave.

The second CV oxidation wave is irreversible and can be assigned to the oxidation of chloride. The oxidation at 2·56 V probably involves the ion aggregate.

Malachite green

The MG pattern is characterized by three oxidation waves at 0·75, 1·35 and 2·26 V and one reduction wave at 0·76 V (Fig. 6, A). The current for all waves is approximately an order of magnitude lower than that observed for the other three dyes. The
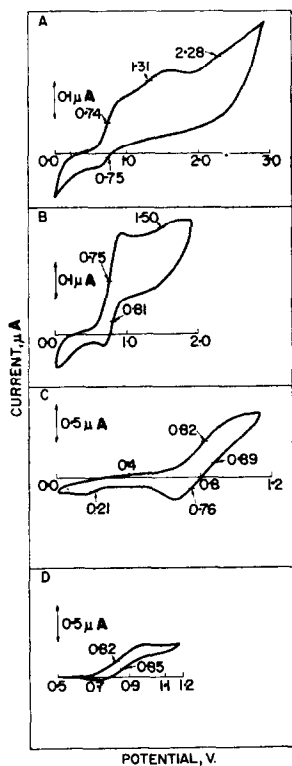

FIG. 6. Cyclic voltammograms of 1·46 mM malachite green at a platinum electrode in sulphur dioxide solution.
Scan rate, V/s: A, 0·06; B, 0·04; C, 0·024; D, 0·014. Potential range scanned is indicated by the potential axis shown.

test solution was stirred before electrolysis to effect solution of the dye, but the deep green (almost black) colour of the solution made it impossible to detect undissolved dye. Similar low currents were obtained with conventional slow-scan voltammetry.

Elimination of the third MG oxidation wave (Fig. 6, B) by span limitation reduces the second oxidation wave from 0·09 μA to 0·01 μA. The reduction wave at 0·76 V, which appears on the reverse sweep, shows no increase with respect to cathodic current component but a definite increase with respect to anodic current component. The wave patterns obtained on scans of 0–3 and 0–2 V decrease in height with time of electrolysis; this, presumably, could be due to film formation on the platinum electrode. Runs made on different test solutions of the dye show patterns with considerable shifts in potential; patterns on a single test solution, however, show very good reproducibility.

Elimination of the second oxidation wave (Fig. 6, C), which is probably chloride ion, by span limitation results in a pattern with one oxidation wave at 0·79 V and two reduction waves at 0·72 and 0·24 V. The reduction at 0·24 V increases with time. The 0·72 V reduction wave does not increase with time for a 0–1·0 V scan, but does for a 0–1·2 V scan. The pattern on elimination of the wave at 0·24 V (Fig. 6, D; scan of 0·5–1·2 V) shows a reversible couple (oxidation at 0·84 V; reduction at 0·86 V). A frequency study of the latter couple was undertaken, using a scan of 0·5 to 1·2 V; a plot of (i_a/i_c) vs frequency is composed of two straight lines with a small change in slope. The anodic current produced on the reverse sweep, ie 1·2–0·5 V, remains close to a value of 0·3 μA for frequencies less than 0·15 c/s. It would seem that this current should increase correspondingly to the increase observed for the oxidation peak on the 0·5 to 1·2 V sweep, since the anodic current on the reverse sweep is attributed to the further oxidation of the compound.

The reversible couple may be due to a free radical produced in the first MG oxidation step.

Ethyl violet

The EV pattern (Fig. 7, A) is characterized by three oxidation waves at 0·59, 1·17 and 1·69 V, and two reduction waves at 0·82 and 0·48 V; all are ill-defined. The oxidation at 0·59 V and the reduction at 0·48 V appear to correspond to the chloride redox couple. The oxidation at 1·69 V can also be assigned to chloride. The reduction wave at 0·82 V, which is small but detectable, may possibly correspond to the reduction of a free radical produced in the oxidation at 1·17 V. Since elimination of the third oxidation wave was not undertaken, a more positive statement cannot be made.

Brilliant green

The BG pattern is complex, involving six oxidation waves at 0·55, 0·98, 1·38, 1·62, 1·95 and 2·43 V, and two reduction waves at 0·72 and 0·43 V (Fig. 8, A). The oxidation at 0·55 V and reduction at 0·43 V may be assigned to the bisulphate ion. Since the oxidation waves at 1·95 and 0·98 V are too small for meaningful measurement, their significance is doubtful.

The oxidation waves at 1·38 and 1·62 V are separated by a very small inflexion, which can be overlooked; proof of the existence of two separate waves is presented in studies entailing elimination of the oxidation wave at 1·62 V.

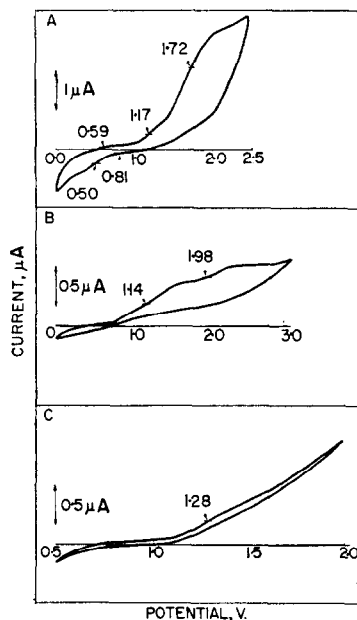Upon elimination of the 2·43-V oxidation wave (Fig. 8, B) by span limitation, the

FIG. 7. Cyclic voltammograms (scan rate, V/s, in parentheses) at a platinum electrode for sulphur dioxide solutions.
A, ethyl violet, 1·41 mM, (0·05); B, leuco crystal violet, 1·26 mM, (0·06); C, tetra-methylbenzidine, 1·70 mM, (0·04). Potential range scanned is indicated by the potential axis shown.
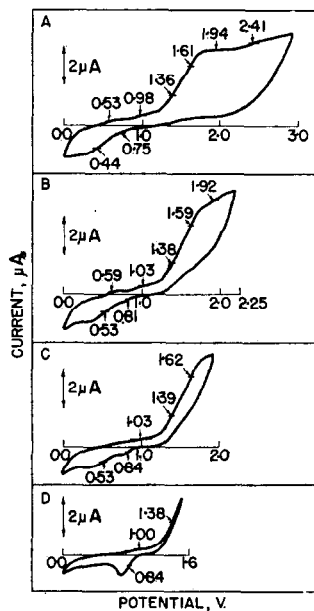

FIG. 8. Cyclic voltammograms of 1·41 mM brilliant green at a platinum electrode in sulphur dioxide solution.
Scan rate, V/s: A, 0·06; B, 0·05; C, 0·04; D, 0·032. Potential range scanned is indicated by the potential axis shown.

reduction waves at 0·43 and 0·72 V shift to 0·53 and 0·81 V, and the oxidation wave at 1·95 V increases in magnitude. Elimination of the 1·95-V oxidation wave (Fig. 8, C) has little or no effect on the voltammetric pattern.

On elimination of the 1·62-V wave (Fig. 8, D), the reduction peak at 0·81 V increases in height with time of electrolysis and shifts to 0·85 V. The pattern for a scan of 0–1·6 V includes three oxidation waves at 0·53 (bisulphate), 1·00 (very small) and 1·38 V, and two reduction waves at 0·86 and 0·41 V (bisulphate). The bisulphate waves are hardly noticeable. The potentials of 1·38 (oxidation) and 0·86 V (reduction) are believed to be due to a redox couple, which obviously shows a considerable degree of irreversibility.

Summary of cyclic voltammographic behaviour

The data clearly indicate the presence of a redox couple in the oxidation of each of the four dyes.

In the case of MG (0·75 V), the presence of a reversible couple is certain. The BG and CV voltammograms are suggestive of the existence of such a couple, which has an associated degree of irreversibility, *ie* for CV, 1·28 V (oxidation) and 1·03 V (reduction) (0·5–1·5 V span); similarly, for BG, 1·38 V (oxidation) and 0·86 V (reduction) (0–1·6 V span), and 1·38 and 0·72 V (0–3 V span); EV shows waves at 1·17 V (oxidation) and 0·82 V (reduction) (0–2·5 V span).

The $E_{h/2}$ values for the individual couples have a low level of confidence associated with them due in all likelihood to the relatively poor reproducibility of the platinum electrode in cyclic voltammetry. Specifically, cyclic voltammograms taken for one sample on a given day are reproducible. A run made on a newly prepared solution on another day may show differences in $E_{h/2}$ and i_t values. As a result, any trends shown by the $E_{h/2}$ and/or i_t values for the four dyes may be fortuitous. These comments regarding reproducibility refer specifically to fast-scan cyclic voltammetry and do not apply to slow-scan voltammetry. The latter method has proved to be a dependable tool for electrochemical studies in sulphur dioxide.

Cyclic voltammetric patterns of TMB (Fig. 7, C) exhibit only an anodic wave, although in a few cases a cathodic wave (0·96 V) appeared, which showed a degree of reversibility with the anodic wave at 1·05 V. The currents were 0·37 and 0·33 μA, corresponding to i_t/C values of 0·22 and 0·19 for the cathodic and anodic waves.

In the case of LVC (Fig. 7, B), the cyclic voltammetric pattern shows two anodic waves at 1·17 and 2·10 V. Slow-scan voltammetry has shown that these waves cannot be related to those obtained for the four dyes (*cf* discussion of voltammetric behaviour).

INTERPRETATION OF THE WAVES

The electrochemical oxidation of the four triphenylmethane dyes investigated in the present study has been reported[1] to involve in aqueous acidic, buffered solution the formation of the diquinoid (TMBOX) of N,N,N′,N′-tetramethylbenzidine (TMB) from the oxidation of the protonated, hydrated forms of the dyes. Consequently, the electrochemical oxidation of the dyes in an anhydrous non-protonic solvent such as sulphur dioxide would naturally not be expected to involve the formation of TMB or TMBOX. In fact, the polarographic and cyclic voltammetric behaviour of TMB is sufficiently different from those of the four triphenylmethane

dyes to support the argument that the TMB–TMBOX system is not involved in the oxidation of the dyes in liquid sulphur dioxide.

On normal dc, essentially constant-potential polarography or voltammetry, the four triphenylmethane dyes exhibit one anodic wave associated with the carbonium ion, but no cathodic waves except for the solution discharge. The relatively close relationship in the half-height potentials of the oxidation wave for all of the dyes indicates that similar oxidation reactions are involved in their electrochemical oxidation.

The two dyes (CV and EV) having p-amino substituents on all three phenyl groups have values of i_l/C of ca 0·20. The corresponding values for the dyes having p-amino substituents on two phenyl groups (BG and MG) are 0·09 and 0·06. These values are for a gross electrode area of 0·196 mm² and should be multiplied by 5·1 to get the current in $\mu A/mm^2$ per mM concentration.

Inspection of the i_l/C data in Table 1 and of the literature data on the chemical and electrochemical oxidation of triphenylmethane dyes in aqueous media tend to support the notion that a value of i_l/C of ca 0·20 represents a one-electron transfer. This is the value observed for the oxidation wave in the case of the two compounds (CV and EV), which give the best patterns, and for the one major wave in the case of each of the other two compounds (LCV and TMB) studied in the present investigation.

Plots of log $[i/(i_l - i)]$ vs E for the anodic waves are linear for at least half of the complete wave; the slopes of the linear portions are given in Table 1. The calculated slope for a reversible one-electron process at −20° is 50 mV. The slopes for CV and EV are relatively similar: 82 and 75 mV; this relationship and the similarity of the half-height potentials and i_l/C values definitely indicate that similar reactions in respect to mechanism and degree of reversibility or rate are involved in the oxidation of CV and EV.

The slopes for MG (96 mV), BG (62 mV) and TMB (61 and 125 mV) oxidation are rather different from those of CV and EV.

The slopes for the LCV oxidation (265 and 179 mV) differ markedly from those for its oxidation in aqueous acidic medium and for the oxidation of CV, the other dyes and TMB in liquid sulphur dioxide. Allen and Powell[9] reported a value of 67 mV at 29·9° for the oxidation of LCV at a rotating platinum electrode at pH 1·1, which they assumed to indicate a one-electron change to a free radical (the theoretical slope for a one-electron process is 60 mV).

Although the course of the oxidation of the dyes and the other compounds in liquid sulphur dioxide cannot be definitely determined from the present data, the first wave in the case of the four dyes, LCV and TMB does appear to involve a one-electron process.

It is difficult to suggest a cause for the relatively low values of the cathodic discharge potentials except in terms of the reduction of a salt-solvent complex as suggested for liquid sulphur dioxide solutions of the quaternary ammonium halides, which have cathodic discharge potentials within the range of −0·3 to −0·6 V.[6]

The anodic discharge potentials, which for the dyes cluster around 2 V, are somewhat less positive than those observed for solutions of the quaternary ammonium salts.[6]

Although there is no direct agreement between the potentials of the polarographic

and cyclic voltammetric oxidation waves, the tendency toward oxidation in both approaches appears to be parallel.

Possible mechanism

The structural changes on oxidation of the triphenylmethane dyes investigated have not yet been clearly elucidated even for aqueous solution except for the oxidation of the protonated, hydrated dye forms, involving the ejection of central carbon residue followed by intramolecular coupling to yield TMB.[1,2]

However, Michaelis *et al*[10,11] showed that organic dyestuffs in general undergo a two-step oxidation in aqueous solution; the first leads to a half-oxidized form (the semiquinoid form) and the second to a further oxidized or quinoid form. Allen and Powell[9] suggested a one-electron oxidation of LCV to a rather stable triphenylmethane-type free radical at pH 1·1, at which pH all of the nitrogen was considered to form ammonium ion-type species, in which nitrogen can keep its lower oxidation state. Under less acidic conditions, the unshared pair of electrons on one of the nitrogens is more easily lost to form the quinoid form.

In anhydrous, non-protonic sulphur dioxide solution, the stability of the unshared lone electron pair on each nitrogen of the dyes is not clearly known. It would be reasonable to postulate that a lone electron pair on one nitrogen is attacked during oxidation to yield a free radical via a one-electron process and to assume a form equivalent to the semiquinone. There is considerable experimental evidence to support such a mechanism, *eg* the relatively close relationship between half-height potentials, current densities and wave slopes for the various dyes, and the reversibility of the oxidation process.

The difference in the half-height potentials between the dyes and TMB can then be attributed to the difference in their structures. Furthermore, if the first step in the oxidation of LCV involves attack on the central carbon, as Allen and Powell[9] postulated, as contrasted with the dyes and TMB for which attack on the nitrogen atoms is assumed, the higher half-height potential of LCV and the unusually high slope of its first wave would be understandable.

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