Electrochemical Synthesis of Heterocyclic Compounds. Part 6.[1] The Redox Behaviour of the Formazan–Tetrazolium Salt System in Acetonitrile

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The synthesis in quantitative yield of 2,3,5-triaryltetrazolium salts by anodic oxidation of formazans is described. The redox behaviour of the 1,3,5-triphenylformazan–2,3,5-triphenyltetrazolium perchlorate system was studied in detail using electroanalytical techniques. It is concluded that two-electron oxidative cyclisation of formazan to tetrazolium salt occurs through an e-c-P-e-(d) mechanism, using the nomenclature of Andrieux and Savéant. The reduction of the tetrazolium salt to the formazan goes by opposite mechanistic pathways (e-P-c-e) to those for the electrochemical oxidation of formazan.

THE oxidation of formazans provides the only synthetically useful route to tetrazolium salts and reduction is the most characteristic reaction of tetrazolium salts. The oxidizing agents used in the preparation of tetrazolium salts include lead tetra-acetate, mercuric oxide, nitric acid, halogeno-amides, and t-butyl hypochlorite.[2,3] The pathways leading from formazan to tetrazolium salts using bromine as oxidizing agent have been discussed in a recent communication.[4] The reducing agents which have been widely used for the conversion of tetrazolium salts into formazans include ascorbic acid, ammonium sulphide, sodium amalgam, and sodium dithionite.[2,3] Tetrazolium salts, which are used as biological staining agents, are generally colourless and may be reduced *in situ* to the highly coloured formazans.[5]

The electrochemical oxidation of 1,3,5-triphenylformazan to 2,3,5-triphenyltetrazolium perchlorate was reported by Lund many years ago.[6] We have also shown [7] recently that the anodic oxidative cyclisation of 3-aroyl-1,5-diarylformazans represents a useful synthetic route to the corresponding tetrazolium salts. Polarographical studies have concentrated on the reduction of tetrazolium salts.[6,8] It has been shown that the reduction mechanism is dependent upon the pH of the solution. Polarography has contributed little to the question of intermediates between tetrazolium salts and formazans.

Details of the electrochemical investigation of the oxidation of 1,3,5-triphenylformazan and the reduction of 2,3,5-triphenyltetrazolium perchlorate are presented herein.

RESULTS AND DISCUSSION

Electrochemical Synthesis of 2,3,5-Triaryltetrazolium Salts.—Voltammetric and preparative data for the anodic oxidation of several 1,3,5-triarylformazans are given in the Table. The ease of oxidation was found to be dependent on the nature of the substituents in the aryl group and on the supporting electrolyte used. All formazans showed two waves in acetonitrile–tetraethylamonium salt solution. The first wave can be attributed to the oxidation of the parent molecule and the second presumably to the formazan protonated by the protons liberated along the first wave. The current functions, $i_L/w^{1/2}C$, obtained with a rotating disc electrode, were constant for rotation rates in the range 300—3 000 r.p.m. Electrochemical oxidation of 1,3,5-triarylformazans at controlled potentials in acetonitrile with tetraethylammonium salts as supporting electrolytes gave high yields of tetrazolium salts.

Coulometry at the applied potential showed that the overall electrode reaction was a two-electron oxidation in all cases examined. The oxidation products were the expected 2,3,5-triaryltetrazolium salts, as confirmed by elemental analysis and i.r. spectra.

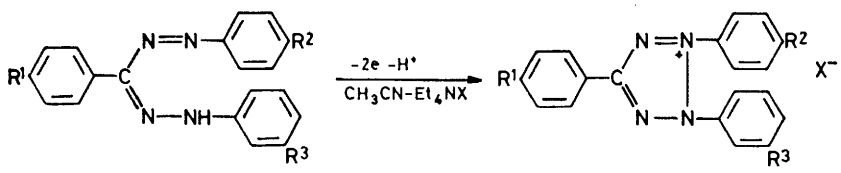
The i.r. spectra of these tetrazolium salts exhibit a characteristic and very strong band at 1 060—1 200 cm^{-1} due to the presence of various anions (ClO_4^-, BF_4^-, and p-TsO^-). The tetrazolium salts obtained were reduced to the original formazans by alkaline ascorbate solution.[9] The electrochemical synthesis of tetrazolium salts can also be performed by means of constant current electrolysis (*ca.* 7 mA cm^{-2}) using a divided cell and tetraethylammonium salt–acetonitrile as a solvent-supporting electrolyte system. The decolouration of the solution indicates the end point of the reaction.

Oxidation of 1,3,5-Triphenylformazan to 2,3,5-Triphenyltetrazolium Perchlorate.—The mechanism of the oxidation of 1,3,5-triphenylformazan was studied in detail. The electrochemical studies were conducted using acetonitrile–0.1M-tetraethylammonium perchlorate solutions. A three compartment cell was employed; the platinum anode and cathode were separated by a glass frit. A saturated calomel electrode (s.c.e.) was used as a reference electrode.

Coulometry at +1.1 and 1.6 V, corresponding to the first and second plateaux of the current–potential curve [Figure 1(a)] show that the overall electrode reaction is a two-electron oxidation. As shown in the Table 2,3,5-triphenyltetrazolium perchlorate was isolated in quantitative yield.

Typical cyclic voltammograms for oxidation and reduction of 1,3,5-triphenylformazan and for the reduction of 2,3,5-triphenyltetrazolium perchlorate are shown in Figure 1. Cyclic voltammogram of 1,3,5-triphenylformazan exhibit two anodic waves at 0.93 and 1.4 V [Figure 1(a)]. No evidence of reversibility was seen for sweep rates from 0.02 to 50 V s^{-1}. The

Electroanalytical and preparative data



Formazan	$E_{1/2}$ (V *vs.* s.c.e.) wave I	wave II	Applied potential (V *vs.* s.c.e.)	Tetrazolium salt X	M.p. (°C) (decomp.)	Yield of tetrazolium salt (%)	Analysis (%) found (required) C	H	N	$\nu_{max.}$/cm^{-1}
$R^1 = R^2 = R^3 = H$	0.91	1.47	1.2	ClO_4	274—276 *	100	57.2 57.25	3.8 3.7	14.05 14.05	3 070, 1 605, 1 530, 1 485, 1 455, 1 300, 1 090, 1 000, 930, 775, 730, 690, 625
$R^1 = R^2 = R^3 = H$	0.89	1.46	1.2	BF_4	218—220	97	59.1 59.2	3.9 3.85	14.5 14.4	3 070, 1 610, 1 530, 1 455, 1 060, 930, 775, 730, 690
$R^1 = R^2 = R^3 = H$	0.78	1.56	1.1	p-TsO	220—222	90	66.35 66.0	4.7 4.7	11.9 11.65	3 060, 1 610, 1 530, 1 485, 1 455, 1 200, 1 120, 1 035, 1 015, 1 000, 820, 775, 730, 695, 680
$R^1 = CH_3, R^2 = R^3 = H$	0.86	1.40	1.2	ClO_4	>320	100	58.15 57.9	4.15 4.1	13.55 13.8	3 000, 1 610, 1 460, 1 419, 1 090, 825, 800, 770, 625
$R^1 = NO_2, R^2 = R^3 = H$	1.04	1.53	1.3	ClO_4	137—139	96	51.4 51.2	3.2 3.25	15.8 15.55	3 090, 1 600, 1 525, 1 460, 1 350, 1 090, 1 000, 855, 765, 730, 690
$R^1 = R^3 = H, R^2 = CH_3$	0.87	1.39	1.1	ClO_4	309—311	100	58.15 58.2	4.15 4.1	13.55 13.6	3 060, 1 610, 1 530, 1 490, 1 455, 1 090, 825, 770, 735, 690
$R^1 = CH_3, R^2 = H, R^3 = CH_3$	0.83	1.37	1.1	ClO_4	>320	95	56.95 57.0	4.3 4.1	12.65 12.85	3 080, 1 605, 1 540, 1 490, 1 460, 1 250, 1 090, 860, 830, 770, 750, 690, 625
$R^1 = R^2 = H, R^2 = CH_3$	0.88	1.42	1.2	ClO_4	>320	100	58.15 58.2	4.15 4.15	13.55 13.6	3 060, 1 610, 1 530, 1 490, 1 460, 1 090, 1 000, 825, 775, 735, 690, 625

* Lit.,[2] 269—270°; lit.,[6] 241°.

irreversibility in the sweep range studied can be explained by a fast chemical reaction which follows electron transfer.[10] No variation of the current function, $i_P/v^{1/2}C$, with sweep rate in the range 0.02—50 V s^{-1} was observed. The first peak corresponds to the oxidation of the parent molecule and the second peak to 1,3,5-triphenylformazan protonated by protons liberated along the first wave. Sweep reversal from the anodic to the cathodic side causes the appearance of two reduction peaks; one at −0.42 V corresponding to the reduction of 2,3,5-triphenyltetrazolium perchlorate formed as a product and the second at −0.76 V corresponding presumably to the reduction of 1,3,5-triphenylformazan, as can be seen in curves (a) and (b). Upon reversal of the scan direction after the first peak the same two reduction peaks were observed.

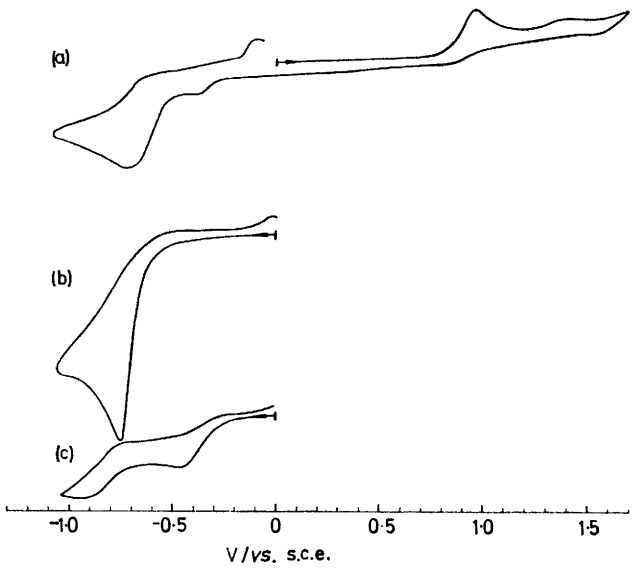


FIGURE 1 Cyclic voltammograms of 1mM solution in 0.1M-Et_4NClO_4–CH_3CN at a platinum electrode with scan rate 0.1 V s^{-1}: (a) 1,3,5-triphenylformazan; (b) 1,3,5-triphenylformazan; (c) 2,3,5-triphenyltetrazolium perchlorate

The conclusions about the nature of the anodic peaks were substantiated by further voltammetric studies at a rotating disc electrode. The results of rotating disc voltammetry are shown in Figure 2. The curve in Figure 2(a) shows two well defined waves with half-wave potentials 0.91 and 1.47 V, respectively, for the oxidation of 1,3,5-triphenylformazan in acetonitrile. The current functions, $i_L/w^{1/2}C$, obtained by rotating disc electrode voltammetry, were constant with rotation rates (from 100 to 3 000 r.p.m.) for both waves. A comparison of the values of the current functions with that obtained for ferrocene, a compound known to undergo reversible one-electron oxidation, showed that the sum of these two

anodic waves corresponds to the transfer of two electrons. The reduction of the number of the electrons for the first wave to a value less than two through protonation of the parent molecule by protons liberated in anodic oxidation can be explained by reactions (1) and (2). Results

$$RH \underset{}{\overset{-2e}{\rightleftharpoons}} R^+ + H^+ \quad (1)$$

$$RH + H^+ \rightleftharpoons RH_2^+ \quad (2)$$

obtained upon the addition of 4-cyanopyridine [Figure 2(b)] confirm the role of the parent molecule in the chemical step. After addition of 4-cyanopyridine as base the second wave disappeared and the first wave increased with a half-wave potential which shifted to cathodic side ($E_{1/2}$ 0.87 V). The increase of the first wave indicates that 4-cyanopyridine replaces 1,3,5-triphenylformazan consumption at the chemical step level. The current function, $i_L/w^{1/2}C$, obtained in the presence of 4-cyanopyridine was constant with rotation rates in the range from 100 to 3 000 r.p.m. and showed two-electron behaviour.

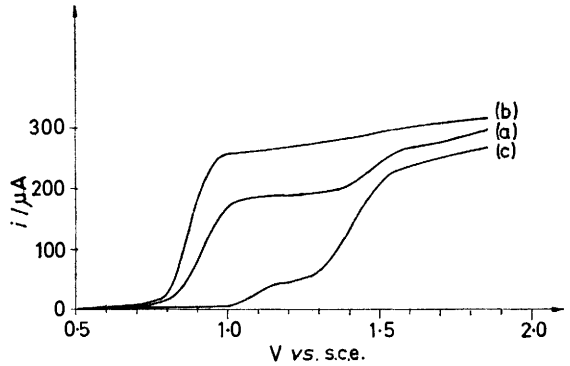


FIGURE 2 RDE voltammograms of 1mM solution in 0.1M-Et_4NClO_4–CH_3CN at a rotation rate of 1 400 r.p.m.: (a) 1,3,5,-triphenylformazan; (b) 1,3,5-triphenylformazan plus 1 equiv. 4-cyanopyridine; (c) 1,3,5-triphenylformazan plus 1 equiv. $HClO_4$

If the voltammetric studies at a rotating disc electrode are performed in the presence of perchloric acid [Figure 2(c)] the first wave is decreased and second wave increased. Thus, the experiments described confirm that the first wave represents oxidation of the parent formazan and second oxidation of protonated formazan.

To obtain more information on the oxidation of 1,3,5-triphenylformazan rotating ring–disc electrode (RRDE) studies were performed. A typical RRDE voltammogram for a solution of 1,3,5-triphenylformazan in acetonitrile containing tetraethylammonium perchlorate is shown in Figure 3.

The potential of the ring was held constant at −0.4 V where tetrazolium salts are electroactive, the potential of the disc was varied linearly, and the current–potential curve was recorded. The ring current increase results from reduction of the tetrazolium salt being formed at the disc electrode. When the potential of the ring was held at a more positive potential (+0.7 V) no ring current was observed. Consistent with these results there is no build-up of relatively long lived intermediates in the conversion of formazan into tetrazolium salts.

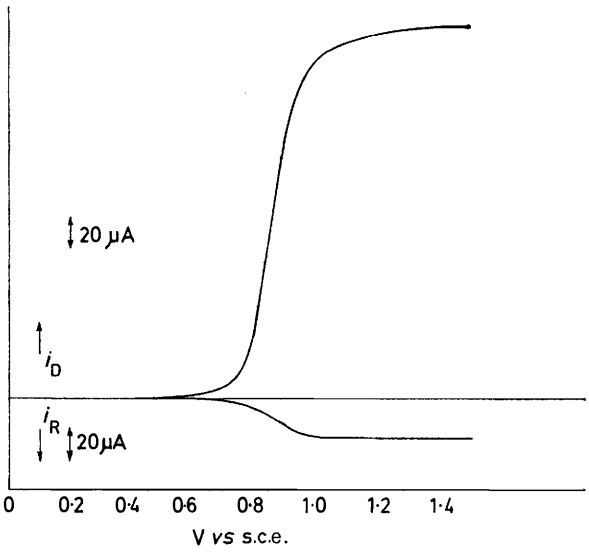


FIGURE 3 RRDE voltammograms of 1mM-1,3,5-triphenylformazan in 0.1M-Et_4NClO_4–CH_3CN solution at a rotation rate of 1 500 r.p.m.

This is also substantiated by the fact that cyclic voltammetry failed to show any reduction peaks due to primary electrode products. The collection efficiency, $N = i_R/i_D$, obtained for acetonitrile solution had a value of 0.13 and remained constant with a change of the rotation rate of the electrode in the range 300—3 000 r.p.m. When an equimolar amount of 4-cyanopyridine was added as base the collection efficiency increased to 0.17 but remained constant with the change of the rotation rate of the electrode.

The results indicate that intramolecular oxidative cyclisation of 1,3,5-triphenylformazan to 2,3,5-triphenyltetrazolium perchlorate occurs through very rapid reactions following electron transfer. The formation of 2,3,5-triphenyltetrazolium perchlorate can be explained on the basis of a theory for cyclisation reactions propounded by Andrieux and Savéant.[11] Oxidative cyclisation of 1,3,5-triphenylformazan to 2,3,5-triphenyltetrazolium perchlorate corresponds to an

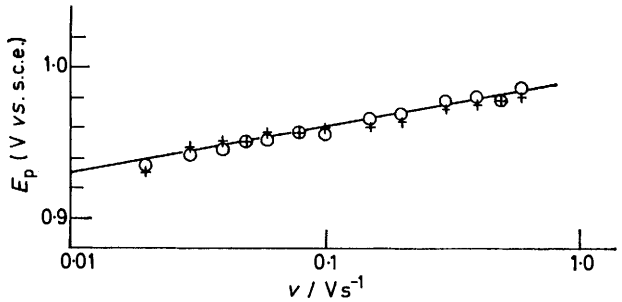
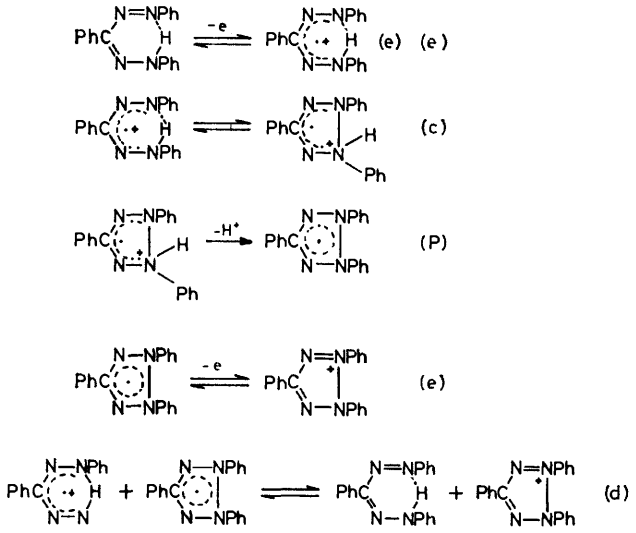


FIGURE 4 Peak potential *versus* sweep rate and initial concentration of 1,3,5-triphenylformazan in 0.1M-Et_4NClO_4–CH_3CN solution initial concentration: (○) 0.3 mM; (+) 1mM

overall two-electron exchange and loss of one proton along a single wave. In order to discriminate among the

various possible mechanisms of oxidative cyclization, E_p–log v and E_p–log C variations were examined. The results are shown in Figure 4.

It is seen that the rate of variation of E_p with log v is 30 mV per decade of sweep rate and that there is no variation of the peak potential with the concentration of 1,3,5-triphenylformazan. According to the diagnostic criteria previously established four possible mechanistic schemes are possible: e-C-e-p-p, e-C-d-p-p, e-c-P-e-p and e-c-P-d-p (the capital letter designates the rate-determining step). If cyclisation is the rate-determining step the resulting e-C-e-p-p and e-C-d-p-p mechanisms would not imply variation of E_p with concentration of the base. However, we have observed the 35 mV shift of E_p cathodically in the presence of an equimolar quantity of 4-cyanopyridine. That the cyclisation process is fast is confirmed by the absence of cathodic wave in cyclic voltammetry at 50 V s^{-1} and by the RRDE experiments.



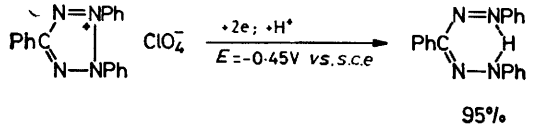
SCHEME 1

These observations rule out the first two mechanisms. The remaining possibilities are e-c-P-e-p and e-c-P-d-p.

Our final conclusion is therefore that the mechanism of intramolecular oxidative cyclisation of 1,3,5-triphenylformazan to 2,3,5-triphenyltetrazolium perchlorate involves cyclisation of the initial radical-cation and deprotonation as the rate-determining step. The mechanism is represented in Scheme 1.

The two-electron oxidation product, 2,3,5-triphenyltetrazolium perchlorate, is formed through oxidation of the parent 1,3,5-triphenylformazan to a radical-cation (step e) which then cyclises (step c). The deprotonation of the cyclic radical-cation leading to the tetrazolinyl radical (step p) is the rate-determining step. It is difficult to decide whether the second electron is transferred through direct electron transfer (step e) or through solution electron transfer (step d). The feasibility of step (d) is given support by Maender and Russell [12] who found by means of e.s.r. that a mixture of formazan and tetrazolium salt gave rise to a paramagnetic product.

Reduction of 2,3,5-Triphenyltetrazolium Perchlorate to 1,3,5-Triphenylformazan.—The preparative reduction of



SCHEME 2

2,3,5-triphenyltetrazolium perchlorate has been performed at the first peak potential of the voltammogram shown in Figure 1(c) using CH_3CN–0.1M-Et_4NClO_4 medium in a divided cell at the Pt cathode.

The reduction of the tetrazolium salt was carried out at −0.45 V until the current had decayed to 3% of its original value. Coulometry at this potential resulted in an exchange of two electrons per molecule of starting material. After electrolysis, 1,3,5-triphenylformazan was isolated in 95% yield and the structure was confirmed by comparison of m.p. and i.r. and n.m.r. spectra with those of an authentic sample.

Slow cyclic voltammetry (from 0.02 to 0.8 V s^{-1}) run in the potential range from 0 to −0.6 V at a platinum cathode in acetonitrile purified by the usual procedure [13] [Figure 5(a)] showed one irreversible wave. Peak potentials of this wave shift cathodically with increasing sweep rate. By carrying out cyclic voltammetry in the presence of activated alumina, according to Parker's method,[14] the voltammogram showed [Figure 5(b)] that

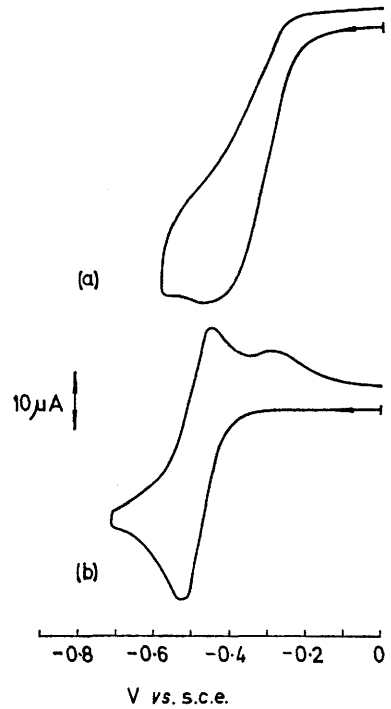


FIGURE 5 Cyclic voltammograms of 1mM-2,3,5-triphenyltetrazolium perchlorate in 0.1M-Et_4NClO_4–CH_3CN solution at a platinum bead electrode; scan rate 0.2 V s^{-1}. Solution conditions: (a) CH_3CN, (b) CH_3CN plus activated alumina present

the tetrazolinyl radical was stable during the time scale of the experiment. Differences in voltammetric peak

potentials measured under reversible and irreversible conditions are due to the occurrence of a chemical reaction coupled to electron transfer.[10] The cyclic voltametric parameters for the reduction wave of 2,3,5-triphenyltetrazolium perchlorate, *i.e.* peak current ratio (i_{pa}/i_{pc} *ca.* 0.9) determined by the method of Nicholson,[15] peak potential separation ($E_{pc} - E_{pa}$) of *ca.* 60 mV, and constant current function ($i_p/v^{1/2}C$) with sweep rate [Figure 6(b)] show that this wave is a reversible one-electron process leading to tetrazolinyl radical which is a stable species in dry acetonitrile.

The variation of the current function, $i_p/v^{1/2}C$, with sweep rate is shown in Figure 6. The shape of the curve for the irreversible wave [Figure 6(a)] is, according to theory,[10] that predicted for an e.c.e. process. At faster sweep rates the effect of the chemical step is minimised and the overall behaviour tends to be controlled by the initial electron-transfer step. At low sweep rates there is time for a reducible product to be formed at the electrode which, upon reduction, causes the current function to increase showing two-electron behaviour. The current function obtained with a rotating disc electrode, $i_L/w^{1/2}$ C, under the same solution conditions is in accord with the cyclic voltammetry experiments. The current function obtained by cyclic voltammetry in the presence of alumina [Figure 6(b)] was constant with the change of the sweep rate corresponding to one-electron behaviour.

The data available are limited but do allow a mechanistic hypothesis to be formulated as shown in Scheme 3.

Coulometry at a controlled potential and product characterization for the preparative electrolysis show that the conversion of tetrazolium salt to formazan is a two-electron reduction. According to the cyclic voltammetry results, using generally an accepted interpretation, two electrons and one proton were transferred through an e.c.e. sequence. The mechanism for this reaction includes, first, electron transfer leading to the tetrazolinyl radical (step e) which is then protonated by water present (step p) giving rise to a cyclic radical-cation. Protonation seems to be the rate-determining step for the overall reaction. Analysis by the method of Hagan *et al.*[16] showed that concentration of water in the cell was 1—5mM. By carrying out cyclic voltammetry in the presence of activated alumina, *i.e.* in ' super-dry acetonitrile ', protonation was prevented and the current function showed reversible one-electron behaviour. The cleavage–cyclisation reaction of the radical-cation (step c) is proposed as the fast reaction. The radical-cation formed is reduced by a second electron-transfer at the applied potential to 1,3,5-triphenylformazan. Solution transfer (step d) as discussed above, is a reasonable reaction (see Scheme 1).

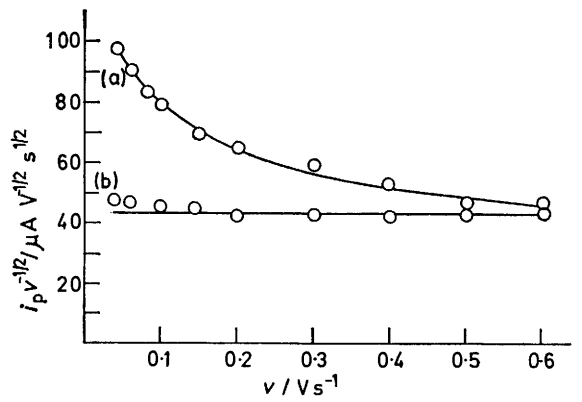
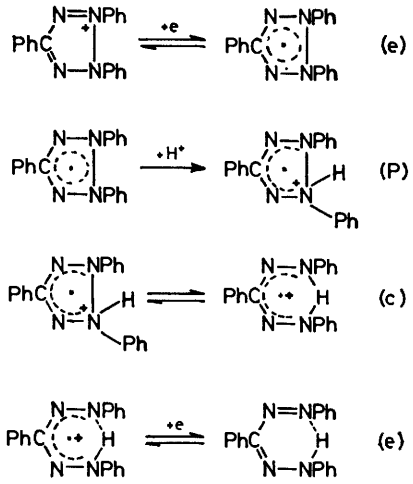


FIGURE 6 Dependence of $i_p/v^{1/2}$ on v in reduction of 1mM-2,3,5-triphenyltetrazolium perchlorate at a platinum bead electrode: (a) 0.1M-Et_4NClO_4–CH_3CN; (b) 0.1M-Et_4NClO_4–CH_3CN plus activated alumina present



SCHEME 3

In conclusion we can say that the reduction of 2,3,5-tetrazolium perchlorate to 1,3,5-triphenylformazan occurs by opposite mechanistic pathways from those for the electrochemical oxidation of 1,3,5-triphenylformazan to 2,3,5-triphenyltetrazolium perchlorate.

EXPERIMENTAL

Materials.—Acetonitrile (Merck) was purified by refluxing over potassium permanganate for 1 h, followed by distillation over P_2O_5.[13] Tetraethylammonium perchlorate (Eastman) was recrystallized twice from water, then dried in an oven at 110° and kept in a desiccator over P_2O_5. Tetraethylammonium tetrafluoroborate was prepared from tetraethylammonium bromide and sodium tetrafluoroborate.[13] Tetraethylammonium toluene-*p*-sulphonate (Aldrich) was recrystallised three times from acetone and dried in a vacuum oven.

The triarylformazans were prepared by treating the appropriate hydrazone with the appropriate diazonium salt in the presence of pyridine.[17] All aldehydes, arylhydrazines, and arylamines used were commercially available. The 1,3,5-triarylformazans had the following m.p.s and analytical data upon recrystallization from aqueous ethanol: 1,3,5-triphenyl, m.p. 177—178° (lit.,[4] 178°); 1,5-diphenyl-3-*p*-tolyl, m.p. 169—170° (lit.,[4] 170°); 1,5-diphenyl-3-*p*-nitro, m.p. 204—206° (lit.,[17] 204°), 1,3-diphenyl-5-*p*-tolyl, m.p. 155—156° (lit.,[18] 155.5°); 1,3-*diphenyl*-5-m-*tolyl*, m.p. 149—150° (Found: C, 76.1; H, 5.7; N, 17.5. $C_{20}H_{18}N_4$ requires C, 76.45; H, 5.75; N; 17.85%); 1-*phenyl*-3-p-*tolyl*-5-m-*methoxyphenyl*, m.p. 129—

130° (Found: C, 73.5; H, 5.65; N, 16.5. $C_{21}H_{20}N_4O$ requires C, 73.25; H, 5.8; N, 16.25%).

Apparatus.—A three compartment cell was used in all voltammetric experiments with the platinum anode and cathode separated by a glass frit. The Luggin capillary was mounted on a syringe barrel so that the position of the tip with respect to the working electrode was easily adjusted. The apparatus used for cyclic voltammetry was a multipurpose controlled potential unit designed in our laboratory according to instructions kindly given to us by Professor V. D. Parker. The current–potential curves were monitored with Hewlett–Packard 7004BX-Y recorder or Tele-equipment oscilloscope type D 53. For rotating disc electrode studies, a Tacussel rotating electrode type EDI was employed. Precise control of the rotation speed was ensured by an independent servo control electronic unit, type Assevitex 3000. For RRDE studies, a Tacussel Bipad bipotentiostat, model Bipad 2, and rotating ring-disc electrode, type EAD 3000, was employed. A Wenking function generator provided a direct current potential ramp for RRDE experiments recorded on an X–Y recorder. Preparative controlled potential electrolyses were carried out by means of an Amel model 550-SU potentiostat using the divided electrolytic cell previously described.[7]

I.r. spectra were recorded on a Perkin–Elmer 377 Infracord spectrophotometer, using KBr pellets. M.p.s were determined on a Kofler microapparatus.

General Procedure for Preparative Oxidation of 1,3,5-*Triarylformazans.*—1,3,5-Triarylformazan (0.2—0.6 g) was added to the anodic compartment of the cell filled with a 0.1M solution of Et_4NX ($X^- = ClO_4^-$, BF_4^-, or p-TsO^-) in acetonitrile (100 ml). The potential was maintained at a fixed value (see Table) with initial currents generally 150—350 mA. Electrolysis was usually discontinued when the current dropped to 3—7 mA which generally took 1—2 h. The anolyte was evaporated to *ca.* 10 ml and water (100 ml) was added to precipitate the tetrazolium salt. The crude products, obtained in quantitative yield, were recrystallised from 96% ethanol, giving analytically pure samples.

General Procedure for Preparative Reduction of 2,3,5-*Triphenyltetrazolium Perchlorate.*—2,3,5-Triphenyltetrazolium perchlorate (0.3 g) was added to the cathodic compartment of the cell filled with 0.1M-Et_4NClO_4–CH_3CN solution. The potential was maintained at −0.45 V *versus* s.c.e. with an initial current of *ca.* 60 mA. Electrolysis was discontinued when the current dropped to *ca.* 2 mA which took 1 h. The catholyte was evaporated to *ca.* 20 ml and water (100 ml) was added. 1,3,5-Triphenylformazan precipitated and was collected by filtration (0.21 g, 95%). Recrystallisation from aqueous ethanol yielded pure product with the same m.p., 176—178°, and i.r. spectrum as an authentic sample.[4]

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