Tetrahedron Vol. 30, pp. 2911 to 2917. Pergamon Press 1974. Printed in Great Britain

ELECTROCHEMICAL SYNTHESES OF HETEROCYCLIC COMPOUNDS—I

INTRAMOLECULAR ELECTROCHEMICAL CYCLIZATION OF FORMAZANS TO TETRAZOLIUM SALTS

M. Laćan, I. Taboković* and Ž. Čeković
Faculty of Technology, University of Zagreb, Zagreb

and

Faculty of Sciences, University of Belgrade, Belgrade, Yugoslavia

(*Received in the UK* 8 *February* 1974; *Accepted for publication* 20 *March* 1974)

Abstract—A novel way of tetrazolium salt preparation by anodic oxidation of formazan is described. Products were obtained in good yields and purity. The mechanism of oxidation was deduced from voltammetric data and by coulometry at controlled potential. Two main pathways were identified, one leading via radical-cation and dication to ring closure by nucleophilic addition, the other involves disproportionation of the radical-cation to dication plus original formazan. Oxidability of differently substituted 3-aroyl-1,5-diarylformazans depends on the electron-withdrawing powers of substituted rings.

Syntheses of tetrazolium salts from formazans using various oxidants have been reported by several authors. The oxidizing agents used in these preparations include yellow mercury (II) oxide,[1] lead tetraacetate,[2] hydrogen peroxide in hydrochloric acid with added vanadium pentoxide,[3] nitric acid,[4] t-butyl hypochlorite,[5] N-bromo and N-chlorosuccinimides, N-chloroacetamide, and N-bromophthalimide.[6,7] This paper describes a novel way of formazan oxidation, by anodic current, and discusses possible electrochemical reaction mechanisms involved in these oxidations. Several 3-aroyl-1,5-diarylformazans have thus been oxidized to corresponding tetrazolium salts.

RESULTS†

Electrolysis at controled potential. Electrochemical oxidation of formazans at a platinum anode by controled-potential electrolysis (+ 2 V, and + 1·5 V, respectively) in acetonitrile, with tetraethylammonium perchlorate or tetraethylammonium tetrafluoroborate as supporting electrolytes, gave large yields of tetrazolium salts. Results of these experiments are summarized in Table 1. The overall electrochemical reaction was a two-electron type oxidation since coulometric determination of electron turnover gave 2·0 ± 0·1 electrons transferred per molecule of formazan, irrespective of the actual potential level. Oxidation products had the expected structures of 3-aroyl-1,5-diaryltetrazolium salts, as was confirmed by elemental analysis and IR spectrophotometry. IR spectra of these tetrazolium salts exhibit strong bands at the following wavenumbers (cm^{-1}): 1650–1700 ($\bar{\nu}_{C=O}$), 1500–1510 ($\bar{\nu}_{C=N}$), 1400–1410 ($\bar{\nu}_{N=N}$), 1230–1245 ($\bar{\nu}_{C_{\varphi}-N}$), 1050–1090 ($\bar{\nu}_{ClO_4^-}$ or $\bar{\nu}_{BF_4}$), and 830–840 ($\bar{\nu}_{N-N}$). Tetrazolium salts obtained in these experiments could be reduced back to the original formazans by alkaline ascorbate solution;[10] IR spectra and m.ps of the resulting products were identical with those of authentic samples.[11]

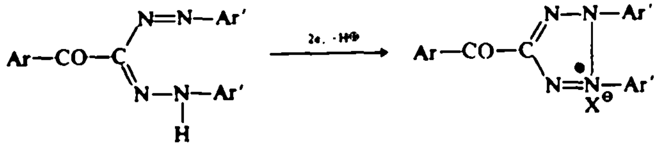
Voltammetry. Fig 1 shows the current-voltage curve obtained when oxidizing 3-thenoyl-1,5-diphenylformazan in acetonitrile containing 0·1 M tetraethylammonium perchlorate at a rotating Pt-anode. This curve possesses two well defined waves with half-wave potentials at + 1·28 and + 1·75 V, respectively. The limiting currents of either wave are linearly dependent on formazan concentration within a range from $4 \cdot 10^{-5}$ to 10^{-3} M, and their temperature coefficients were about 1% per °C in the interval from 20 to 35°C, as should be expected for diffusion-controled limiting currents. Plotting potential differences, ΔE, taken from Fig 1, *vs* $\log[(i_L - i)/i]$ from the same figure gave straight lines for each wave, indicating irreversibility for either process. These lines had slopes of 105 mV and 103 mV, respectively.

Figure 2 shows some results obtained with a rotating electrode, *viz* the relationship between $i_L/\omega^{1/2}C$ *vs* $\omega^{1/2}$ (where i_L means the limiting current

---

†All voltages are given with reference to the saturated calomel electrode.

Table 1. Electrochemical synthesis of tetrazolium salts by oxidation of formazans



Ar	Ar′	$X^{\ominus}$	Yield %	M.p. (°C) decamp.	Analysis found (required) C	H	N	S	IR cm⁻¹
C_4H_3S-	C_6H_5-	$ClO_4^{\ominus}$	95	264–266	49·59 (49·94)	3·31 (3·00)	13·01 (12·94)	7·01 (7·39)	3430, 1650, 1510, 1410, 1250, 1095, 840
C_4H_3S-	p-CH_3-C_6H_4-	$ClO_4^{\ominus}$	84	265–268	52·27 (52·06)	3·56 (3·68)	12·07 (12·15)	7·29 (6·94)	3420, 1650, 1500, 1410, 1245, 1090, 840
C_4H_3S-	C_6H_5-	$BF_4^{\ominus}$	83	235–238	51·51 (51·44)	3·20 (3·09)	13·61 (13·33)	7·70 (7·62)	3240, 1660, 1510, 1410, 1245, 1055, 840
C_6H_5-	p-CH_3-C_6H_4-	$ClO_4^{\ominus}$	91	294–296	52·27 (52·06)	3·56 (3·68)	12·07 (12·15)	7·29 (6·94)	3420, 1650, 1500, 1410, 1245, 1090, 840

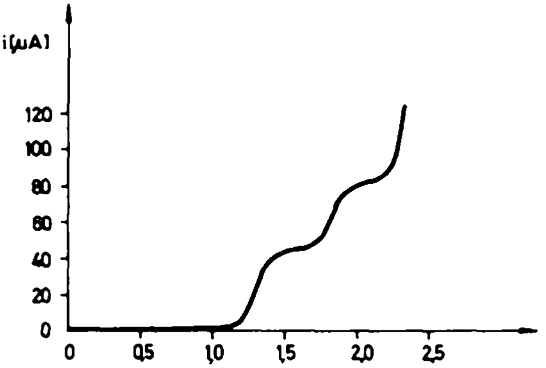


Fig 1. Current-potential curve obtained with 5×10^{-4} M 3-thenoyl-1,5-diphenylformazan oxidized at a rotating platinum electrode. 0·1 M $(C_2H_5)_4NClO_4$ in CH_3CN; 125 rad s^{-1}; 1 V min^{-1}.

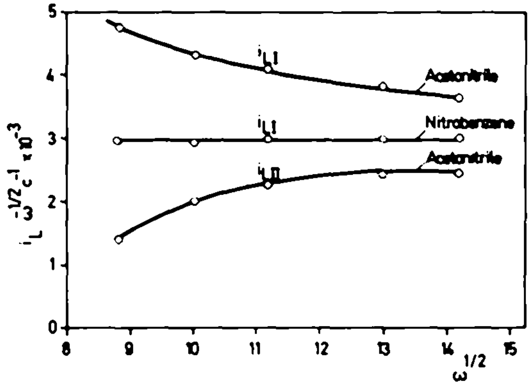


Fig 2. Relationship of $i_L/C\omega^{1/2}$ and $\omega^{1/2}$ in oxidation of 1×10^{-3} M 3-thenoyl-1,5-diphenylformazan at potentials corresponding to the first and second plateaus of the curve in Fig. 1. Pt-anode; 0·1 M $(C_2H_5)_4NClO_4$ in CH_3CN or Ph-NO_2 1 V min^{-1}.

corresponding to a wave, ω is the angular velocity of the electrode, and C is the formazan concentration). In these, experiments oxidations were carried out in two different solvents, acetonitrile and nitrobenzene. In acetonitrile the variable $i_L/\omega^{1/2}C$ decreases for the first anodic wave, while that for the second wave increases with $\omega^{1/2}$. In nitrobenzene $i_L/\omega^{1/2}C$ is independent of $\omega^{1/2}$.

Cyclic voltammetry. The cyclic voltammogram given in Fig 3 was obtained by anodic oxidation of 3-thenoyl-1,5-diphenylformazan in the acetonitrile–tetraethylammonium perchlorate system. Two irreversible oxidation peaks (O_1 and O_2) can be recognized at + 1·3 V, and + 1·87 V, respectively. Sweep reversal from anodic to cathodic causes the appearance of two reduction peaks, one at − 0·3 V (R_1, corresponding to O_1), and the other at + 0·3 V, corresponding to O_2. The sweep covered a range from zero to + 2 V, rates varying from 0·1 to 30 volts per second, but the general shape of voltamograms never changed with sweep rate. The current function $i_p/V^{1/2}$ (i_p means peak current) depended, however, on sweep rates, and this dependence is shown in Fig 4 for the first (curve I) and the second (curve II) wave. A ten-fold increase in sweep rate resulted additionally in 40 to 60-mV shifts of peak potentials anodically.

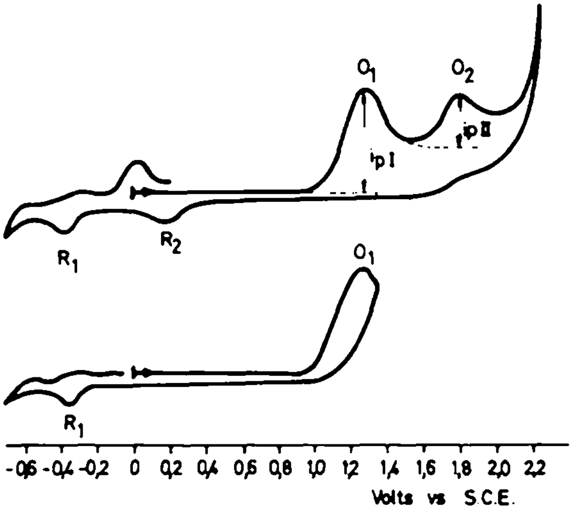


Fig 3. Cyclic voltammogram with 3 - thenoyl - 1,5 - diphenylformazan. Pt-anode; 0·1 M $(C_2H_5)_4NClO_4$ in CH_3CN; 0·1 V s^{-1}.

Influence of formazan structure on oxidability. All but one of the formazans, oxidized electrochemically, gave two well-defined polarographic waves; the exception was 3-thenoyl-1,5-*bis*(4'-nitrophenyl)formazan with only one wave. On the voltammograms showing two waves different behavior of limiting currents was observed in dependence of aryl ring substitution. The first wave's height increases, that of the second wave decreases with a rise of the ring's electron-withdrawing power (Table 2). The minimum ratio of limiting currents, $i_{L,I}/i_{L,II}$ = 1·14, was obtained with 4-methoxy, and the maximum, 3·72, with 4-chlorosubstituted aryls. Dependence of oxidability on ring substitution is further demonstrated by both waves' giving straight-line plots of half-wave potentials *vs* Brown's substituent constants. Structural changes in the 3-aroyl group also influences the oxidability of formazans, as shown by differences in the half-wave potentials between 3-benzoyl-1,5-ditolylformazan ($E_{1/2}$, 0·97 and 1·4 V, respectively) and 3-thenoyl-1,5-ditolylformazan ($E_{1/2}$, 1·15 and 1·62, respectively).

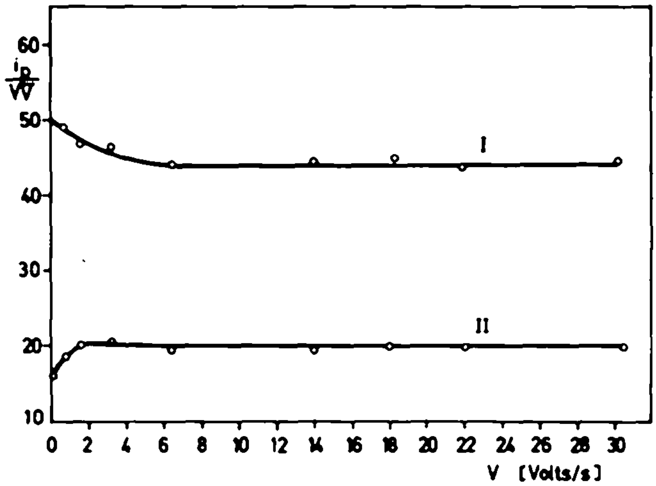


Fig 4. Dependence of $i_p/V^{1/2}$ on V in oxidation of 1×10^{-3} M 3 - thenoyl - 1,5 - diphenylformazan at a stationary platinum anode. 0·1 M $(C_2H_5)_4NClO_4$ in CH_3CN.

Table 2. Results of voltammetry of substitued 3-tenoyl-1,5-diarylformazanes in acetonitrile containing 0·1 M Et_4NClO_4; concentration of formazane: 5×10^{-4} M; 125 rad·s^{-1}

	First wave		Second wave		
Substituent	$E_{1/2}$[V]	$i_{L,I}$[μA]	$E_{1/2}$[V]	$i_{L,II}$[μA]	$i_{L,I}/i_{L,II}$
p-OCH_3	0·97	20	1·35	17·5	1·14
p-CH_3	1·15	22	1·62	16·2	1·36
H	1·28	22	1·75	13·4	1·64
p-Cl	1·35	26	1·77	7	3·72
p-NO_2	1·65	28	—	—	—

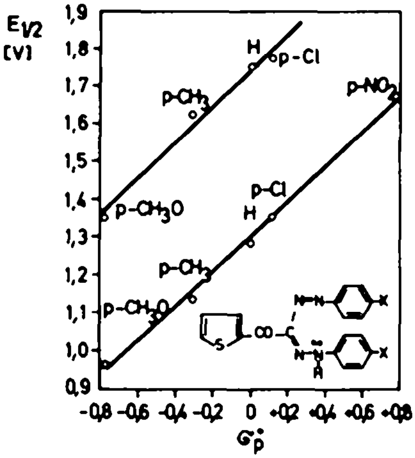


Fig 5. Relationship of half-wave potentials and Brown's substituent constants for some 3 - thenoyl - 1,5 - diaryl - formazans.

DISCUSSION

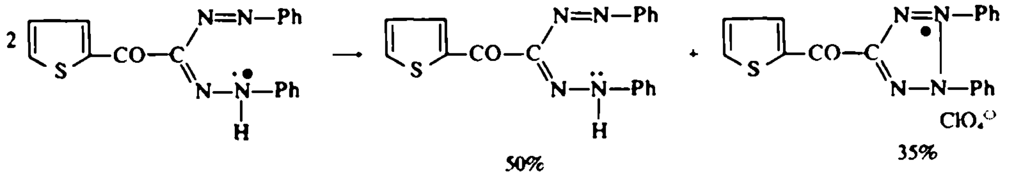
Quite obviously, electrochemical oxidation of formazans is a particularly advantageous preparative route to tetrazolium salts, giving high yields (80–95%) of relatively pure and easily separable products. Tetrazolium salts widely differing in anions can be prepared by merely using a supporting electrolyte carrying the desired anion, provided this electrolyte possesses an oxidation potential higher than that of the formazan. Tetrazolium perchlorates, tetrafluoroborates, acetates, nitrates, hexafluoroplatinates, chlorides, etc can be obtained in this manner.

The mechanism of formazan oxidation has hitherto received only casual attention. Ashley *et al*,[12] for instance, have suggested that oxidation with lead tetraacetate proceeds *via* tetrazolinyl radicals, and this view seems to be supported by experimental evidence contributed by Maender and Russell[8] who reported the detection by ESR spectrometry of free-radical formation during formazan oxidation with air in presence of t-butoxide. Conversely, ESR-detection of free-radical formation was also reported in reduction of tetrazolium salts.[8,13,14] One should also recall that stable tetrazolinyl radicals have been obtained from certain formazans by homolytic bond fission.[7,9]

In principle, three basic pathways are open to a two-electron oxidation of a formazan to the corresponding tetrazolium salt. Firstly, the formazan anion may be oxidized to a radical[8] which is then oxidized further to the tetrazolium salt: this pathway represents an EE mechanism. Alternatively, the formazan may be primarily oxidized to a radical-cation, then deprotonized to a simple radical, and subsequently oxidized to a cation; the latter stabilizes by ion-pair interaction with an anion, to give the tetrazolium salt. This sequence is equivalent to an ECE mechanism. Finally, the formazan might again be oxidized first to a radical-cation, but instead of being immediately deprotonized, oxidizes further to a dication, and this species undergoes deprotonation followed by intramolecular nucleophilic addition to the electron-deficient nitrogen atom with ring closure: along this pathway the tetrazolium salt is formed by an EEC mechanism.

One can eliminate the first pathway considering a formazan anion cannot exist, as an electroactive species, in neutral or acidic media. The primary one-electron oxidation product of formazan must, therefore, be the radical-cation. In deciding the further fate of the radical-cation, however, let us remember that although most anodic substitution or addition reactions actually follow ECE-type mechanisms,[15] which would favour pathway two, EEC[16] and mixed mechanisms[17,18] are possible, and these would lead over pathway three.

Coulometry at + 2·0 V, corresponding to the second plateau of the current-potential curve in Fig 1 identifies the overall electrode reaction as a two-electron oxidation. Yields up to 95% in oxidation product can be obtained at this potential. But even at the potential of the lower plateau, + 1·5 V, the oxidation is almost quantitative (up to 90%), and the coulometrically determined electron turnover is equal to that at + 2·0 V. Interruption of the electrolysis after having transferred 1·1 electrons per molecule of formazan left 50% of the latter unchanged, and resulted in 35% of the theoretical yield of tetrazolium salt (*cf* Experimental). Reaction Scheme 1 offers an interpretation of this result, assuming a disproportionation of the primarily formed radical-cation (TDF$^{+\cdot}$) into the initial formazan (TDF) and the dication (TDF^{++}). The latter undergoes the two final steps of the EEC pathway giv-

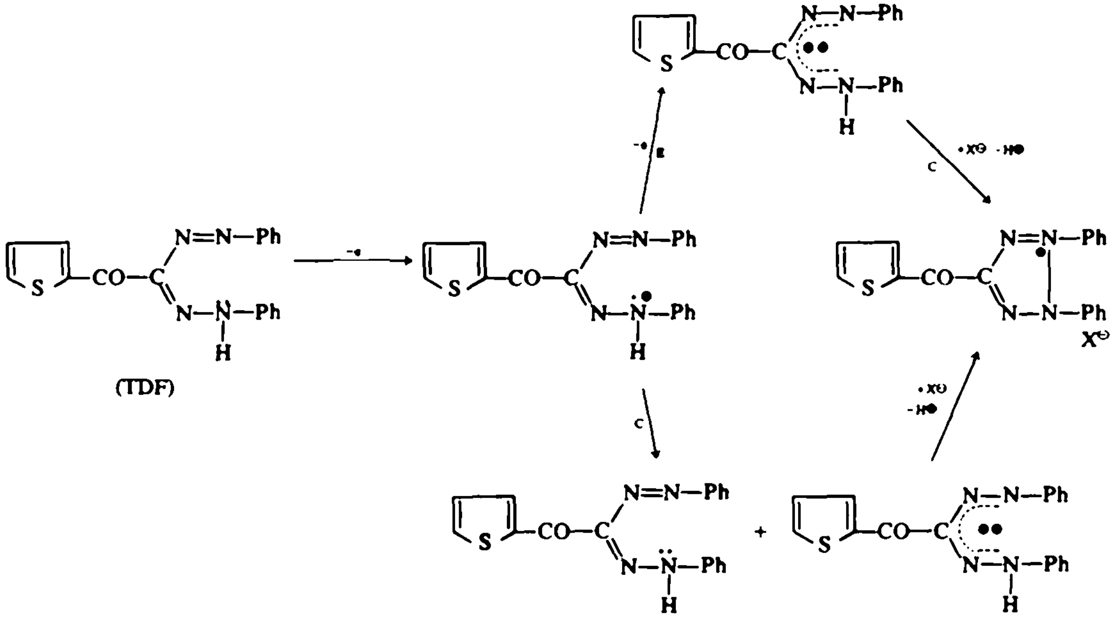


SCHEME 1.

ing the final oxidation product. Similar disproportionation reactions have been reported earlier for other electrochemical oxidations, *viz* those of tetraphenylethylene,[17] 1,1-dimethylaminoethylene,[19] as well as for the anodic hydroxylation of phenothiazine.[20]

The relationship of limiting currents, as measured on a typical polarogram (that for TDF, Fig 1), in which the first wave has a higher limiting current than the second, can be satisfactorilly explained by the assumed disproportionation reaction. Since this disproportionation yields a product immediately oxidizable at the anode—TDF, contributing an increment to the limiting current of the first anodic wave, this current eventually rises above the limiting current of the second wave. The results of rotating-electrode voltammetry can also be interpreted by the disproportionation of the radical-cation. Here the variable $i_{L_I}/C\omega^{1/2}$ decreases monotonously with $\omega^{1/2}$ during oxidation in acetonitrile, while $i_{L_{II}}/C\omega^{1/2}$ simultaneously increases, and the two variables never assume equal values, because no amount of increase in angular velocity can overcome the effect of the disproportionation reaction. In contrast, $i_L/C\omega^{1/2}$ for the first anodic wave obtained in nitrobenzene is independent of $\omega^{1/2}$, suggesting that TDF$^{\cdot}$ does not undergo disproportionation in this solvent. As a matter of fact, this radical-cation proved to be more stable in nitrobenzene than in acetonitrile.[21] All results from rotating-electrode experiments agree well with argument put forward by Adams *et al.*[21,22]

Irreversibility of electrochemical formazan oxidations can be deduced both from rotating-electrode and from cyclic voltammetry. In the cyclic voltammetry experiments sweep reversal failed to produce reversible peaks, while logarithmic replot of data from rotating-electrode voltammograms gave straight-line relationships. Either wave corresponds, therefore, to an irreversible electrode process. The first peak at + 1·3 V on the cyclic voltammogram in Fig 3 indicates radical-cation formation, and the latter can be reduced, by sweep reversal, at − 0·3 V, but is otherwise stable enough to persist through a relatively large increase in potential of 500 mV, i.e. up to + 1·8 V, where oxidation to the dication stage occurs.



SCHEME 2.

Shain and Nicholson[23,24] have demonstrated that the type of dependence of current function $i_p/V^{1/2}$ on sweep rate (V t^{-1}) is characteristic of the electrode reaction mechanism. In our experiments the current function for the first wave decreases, while that for the second wave increases with increasing sweep rate, in the range below 4 V s^{-1}. Over the remaining range, up to 30 V s^{-1}, the current functions for either wave remained constant. These results, as well as the 40–60 mV anodic shift of peak potentials with increasing sweep rate, suggest two consecutive irreversible reactions ocurring at larger sweep rates, namely

$$\mathrm{TDF} \xrightarrow[+1\cdot3\,\mathrm{V}]{e^-} \mathrm{TDF}^{\cdot} \xrightarrow[+1\cdot8\,\mathrm{V}]{e^-} \mathrm{TDF}^{\cdot\cdot},$$

while disproportionation might be operating at slower sweep rates:

$$2\,\mathrm{TDF}^{\cdot} \longrightarrow \mathrm{TDF} + \mathrm{TDF}^{\cdot\cdot}.$$

In summary, the mechanism of the two-electron oxidation starting from TDF is presented in reaction Scheme 2. The initial step consists in an irreversible one-electron oxidation producing a radical-cation. The latter is either oxidized to the next stage—a dication—by another E-process, or it undergoes disproportionation to the original formazan plus the dication. These two alternative C-pathways may work in concert or in competition.* Subsequently the dication loses a proton, whereupon a nucleophilic addition takes place at the electron-deficient nitrogen atom, and the adduct is finally stabilized by ion-pair interaction with the anion from supporting electrolyte.

Since the half-wave potentials of both waves showing in Fig 5 are linearly related to Brown's δ_p^+ substituent constants, one may assume that *p*-substitution tends to stabilize the positively charged species, i.e. the radical-cation and the dication. On the other hand, increase in limiting current rations with strengthening of electron-withdrawing power in substituted aryl rings clearly shows that this structural feature favors the radical-cation disproportionation reaction.

The present results are, of course, obtained with formazan anodic oxidations, but there is no reason why homogenous reactions of a similar type should greatly differ in mechanism. An inquiry into this question would well be worth while.

EXPERIMENTAL

Apparatus. IR spectra were recorded with a Perkin-Elmer Infracord 137 spectrophotometer, using KBr pellets. M.ps were determined on a Kofler microstage: uncorrected values are reported.

Rotating-electrode voltammetric measurements were made in a three-electrode cell with a spherical Pt anode, 0·15 cm in diam, fused to a glass holder; a piece of Pt wire served as the cathode, and a saturated-calomel reference electrode was provided. The anode was thoroughly cleaned before each series of experiments by immersion in conc HNO_3 first, then in conc H_2SO_4; it was rinsed repeatedly with distilled water, and finally conditioned by a rinse with acetonitrile. An operation-amplifier based function generator was utilized to produce the ramp potential. Voltammograms were recorded with a Hewlett-Packard 7004 B X-Y recorder, or displayed on the screen of a Hewlett-Packard 130C Cathode Ray Oscilloscope. Rotating-electrode voltammetry was carried out with an Amel Model 550-SU recording polarograph.

Preparative electrolyses were made in a jacketed, water-cooled cell divided by a sintered-glass diaphragm into anode and cathode compartments. The anode was made from Pt-wire gauze (5 × 3 cm), and the cathode was a small piece of Ni sheet. A saturated-calomel reference electrode was connected to the anode compartment through a Luggin capillary. The amount of current transported during constant-potential oxidation was determined in each instance by either graphical integration of current-time curves, or by comparison of weights of cut-out profiles obtained in an actual experiment and in one-electron oxidation of ferrocene at the same concentration. Constance of potential in controled-potential electrolysis was warranted by an operation-amplifier based potentiostat.

Temp control was maintained in all experiments: voltammetric measurements were made at 25 ± 0·1°C, and electrolyses were carried out within 18 and 20°C.

Chemicals. 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.[23] Acetonitrile was purified by refluxing over potassium permanganate for 1 h, followed by distillation over P_2O_5.[24] Nitrobenzene was redistilled twice under reduced pressure. Formazans were prepared by reacting aryl diazonium salts with 1,6-diaryl-1,3,4,6-hexanetetrones.[11]

General procedures in preparing 3-thenoyl-1,5-diaryltetrazolium salts. Four fifths of a 0·3 M solution of tetraethylammonium perchlorate or tetrafluoroborate in acetonitrile (100 ml) was placed in the anode compartment of the electrolysis cell, and the remaining one-fifth was filled into the cathode compartment. Then 0·78–1·2 g of 3-thenoyl-1,5-diaryl-formazan was added to the anolyte and allowed to dissolve. Electrolysis was conducted for about 2 h at + 2·0 V. During this period the current dropped to its base value (about 15 mA), and the color of the soln changed from the initial dark red to blue-violet, and finally turned light brown. After reducing the volume to about 10 ml, 100 ml water was added to precipitate the tetrazolium salt, yields varied from 80–95%). The crude products were recrystallized from 96% EtOH, giving analytically pure samples in form of light yellow crystals.

Oxidation of 3-thenoyl-1,5-diphenylformazan at controlled potential with transfer of 1·1 equivalents of electrons. 0·4 g 3-thenoyl-1,5-diphenylformazan was dissolved in 80 ml 0·3 M tetraethylammonium perchlorate soln in acetonitrile, and electrolysed for 35 min at + 1·5 V. At this point current had dropped to 30 mA (approximately 10% of its initial value), and coulometric monitoring of electron turnover indicated a transfer of n = 1·1 electrons per molecule of formazan. The resulting blue-violet soln was left at room temp for another h, then 100 ml water was added. 0·2 g (50% theor) of unchanged 3-thenoyl-1,5-diphenylformazan separated and was collected by filtration. Recrystallization from EtOH yielded the pure substance, as confirmed by an identical IR spectrum, as well as m.p. 172–174°C,[11] as the original formazan. The filtrate was evaporated to 50 ml and chilled. 3-Thenoyl-1,5-diphenyltetrazolium perchlorate separated (0·18 g: 35% theor.), showing an identical IR spectrum and the same m.p. (264–266°C) as an authentic sample.

Oxidation of 3-thenoyl-1,5-diphenylformazan at controlled potential with transfer of 2 equivalents of electrons. 0·334 g 3-Thenoyl-1,5-diphenylformazan was dissolved in 80 ml of the tetraethylammonium perchlorate solution and electrolysed for 110 min at + 1·5 V. This operation reduced the current to its base value, and coulometry indicated a transfer of 1·9 to 2·0 electrons per molecule of

---

*Theoretically one must consider a further possibility, represented by another C-reaction in form of a radical-cation deprotonation. The resulting tetrazolinyl radical might be expected to possess sufficient stability for enabling ESR-detection. However, an ESR spectrum recorded after completion of the electrolysis failed to confirm the presence of the radical in question.

formazan. After evaporation and addition of water, the 3-thenoyl-1,5-diphenyltetrazolium perchlorate was obtained in a 90% yield (0·386 g). The product had the correct m.p. and gave the characteristic IR absorption spectrum.

Acknowledgement—Discussions with Drs. Lj. Jeftić and Ž. Fuks are gratefully acknowledged.

REFERENCES

[1] H. V. Pechman and P. Runge, *Ber. Dtsch. Chem. Ges.* **27**, 2920 (1894)
[2] R. Kuhn and D. Jerchel, *Chem. Ber.* **74**, 941 (1951)
[3] W. Reid, *Angew. Chem.* **64**, 391 (1952)
[4] F. Fichter and E. Schiess, *Ber. Dtsch. Chem. Ges.* **33**, 747 (1900)
[5] F. R. Benson, E. A. Otten and R. E. Schachat, *J. Am. Chem. Soc.* **76**, 1695 (1954)
[6] R. Kuhn and W. Münzing, *Chem. Ber.* **86**, 858 (1953)
[7] F. A. Neugebauer, *Tetrahedron* **26**, 4843 (1970)
[8] O. W. Maender and G. A. Russell, *J. Org. Chem.* **31**, 442 (1966)
[9] F. A. Neugebauer, *Tetrahedron Letters* No. 17, 2129 (1968)
[10] R. Kuhn, H. M. Weitz, *Chem. Ber.* **86**, 1199 (1953)
[11] M. Laćan, Dj. Šehović and M. Kuleš, *Croat, Chem. Acta* in print
[12] J. N. Ashley, B. M. Davis, A. W. Nineham and R. Slack, *J. Chem. Soc.* 3881 (1953)
[13] R. T. Lofberg, *Nature.* **206**, 503 (1965)
[14] Y. Deguchi and Y. Takagi, *Tetrahedron Letters.* 3179 (1967)
[15] G. Manning, V. D. Parker and R. N. Adams, *J. Am. Chem. Soc.* **91**, 4584 (1969)
[16] V. D. Parker, *Chem. Comunn.* 848 (1969)
[17] J. D. Stuart and W. E. Ohnesorge, *J. Am. Chem. Soc.* **93**, 4531 (1971)
[18] Lj. Jeftić and R. N. Adams, *Ibid.* **92**, 1332 (1970)
[19] K. Kuwata and D. H. Geske, *Ibid.* **86**, 2101 (1964)
[20a] H. J. Shine and Y. Murata, *Ibid.* **91**, 1872 (1969); [b] Y. Murata and H. J. Shine, *J. Org. Chem.* **34**, 3368 (1969)
[21] P. A. Malachesky, L. S. Marcoux and R. N. Adams, *J. Phys. Chem.* **70**, 4068 (1966)
[22] J. S. Marcoux, J. M. Fritsch and R. N. Adams, *J. Am. Chem. Soc.* **89**, 5766 (1967)
[23] R. S. Nicholson and I. Shain, *Analit. Chem.* **16**, 706 (1964)
[24] R. S. Nicholson and I. Shain, *Ibid.* **37**, 178 (1965)
[25] J. F. O'Donnel, J. T. Ayres and C. K. Mann, *Ibid.* **37**, 1162 (1965)
[26] D. Clark, M. Fleischmann and D. Pletcher, *J. Electroanal. Chem.* **36**, 137 (1972)