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Electrochemical Reduction Mechanism of Organic Sulphides. Diphenylmethyl *p*-Nitrophenyl Sulphide

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The electrochemical reduction mechanism of diphenylmethyl *p*-nitrophenyl sulphide (DNPS) in dimethylformamide has been investigated by direct current polarography, potential sweep voltammetry, controlled potential electrolysis, and e.s.r. spectrometry. This compound presents several kinetic reduction waves, the first of which corresponds to a reversible one-electron transfer, leading to the radical anions of DNPS, as revealed by the e.s.r. spectrum of the solution electrolysed *intra muros* at low temperature. These radical anions undergo irreversible first-order decay, with fission of the activated C–S bond, giving rise to an e.c.e. electrode reaction. The nature and yields of the electrolysis products and the coulometric results indicate that DNPS radical anions dissociate into *p*-nitrothiophenolate anions and diphenylmethyl radicals. The latter decay through two fast parallel reactions: electrode reduction to diphenylmethane at the formation potential and dimerization to tetraphenylethane, while *p*-nitrothiophenolate anions undergo a further reversible one-electron transfer at more negative potential (second reduction step) with formation of relatively stable radical dianions. The rate constant for the dissociation of the DNPS radical anions, which is the rate-determining step of the overall electrode process, has been evaluated by kinetic analysis of the voltammetric results. The third reduction step corresponds to a direct two-electron transfer of DNPS, leading to unstable dianions which undergo a very fast dissociation into *p*-nitrothiophenolate anions and diphenylmethyl carbanions. The intermediate formation of the latter is confirmed by the presence, among the electrolysis products, of the adducts of their nucleophilic attack on DNPS.

RELATIVELY little information is available on the electrode reaction mechanism of organic sulphides. Gerdil[1] reported that sulphides of general formula Ph–S–R (R = aryl or alkyl) are polarographically reduced in anhydrous dimethylformamide (DMF) at negative potentials, the electrode process involving an irreversible two-electron transfer and fission of the R–S bond. Farnia *et al.*[2] have shown that the same type of behaviour, with fission of the C–S bond, holds for several substituted aryl diarylmethyl sulphides $X^1C_6H_4(X^2C_6H_4)$-CH–SC_6H_4Y.

The electrode reaction mechanism proposed postulates the intermediate formation, through a one-electron transfer, of the radical anion of the depolariser. This species is assumed to decay through two alternative paths involving either the proton assisted addition of a second electron and/or its homolytic fission to thiophenolate anion and a neutral radical reducible at the potential of formation. However, owing to the presumably high reactivity of the primary radical anion, direct evidence for its formation could not be provided and the relative importance of the two decay paths could not be evaluated. The study of the decay mechanism of the primary radical anion and its influence on the electrochemical behaviour of organic sulphides seemed therefore to deserve further attention. For this purpose we have considered diphenylmethyl *p*-nitrophenyl sulphide in which the characteristics of the nitro-substituent in the *para*-position ought to displace the reduction potentials towards more positive values and enhance the stability of the primary radical.

EXPERIMENTAL

Materials.—Commercial grade DMF was dried over K_2CO_3 and fractionally distilled under reduced pressure; the middle fraction was collected and stored under nitrogen.

Diphenylmethyl *p*-nitrophenyl sulphide (DNPS) was prepared from diphenylmethanol and *p*-nitrothiophenol according to the method reported for the preparation of sulphides[3] and crystallized from ethanol, m.p. 128—129 °C. Tetrabutylammonium *p*-nitrothiophenolate (NTP) was obtained by lyophilisation of an aqueous solution of *p*-nitrothiophenol neutralized with tetrabutylammonium hydroxide. *p*-Nitrotriphenylmethane (NTPM) was prepared according to Ungnade and Crandall,[4] purified by chromatography on a silica gel column, using a light petroleum–benzene eluting phase and crystallized from

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[1] R. Gerdil, *J. Chem. Soc.* (*B*), 1966, 1071.

[2] G. Farnia, A. Ceccon, and P. Cesselli, *J.C.S. Perkin II*, 1972, 1016.

[3] C. Finzi and V. Bellavita, *Gazzetta*, 1932, **62**, 699.

[4] H. E. Ungnade and E. W. Crandall, *J. Amer. Chem. Soc.*, 1949, **71**, 2209.

light petroleum, m.p. 90—91 °C. Tetrabutylammonium perchlorate used as background electrolyte, diphenylmethane (DPM), tetraphenylethane (TPE), and all other products used were reagent grade chemicals.

Apparatus and Procedure.—Polarographic and potential sweep volammetric measurements were carried out with an AMEL model 448, three electrode apparatus. An Ag–AgCl–tetramethylammonium chloride saturated solution in acetonitrile was used as reference electrode, a platinum foil as counter-electrode, and a hanging mercury drop electrode or a dropping mercury electrode with mechanical control of the drop-time as indicating electrode. Controlled potential electrolysis and coulometric measurements were performed with an AMEL potentiostat model 557 equipped with a current integrator model 558.

E.s.r. spectra were recorded at different temperatures, on a Varian E3 spectrometer; the radicals were produced electrolytically either directly within the e.s.r. cavity or in an external cell from which the electrolysed solution was transferred into the cavity.

NTP was quantitatively determined directly in the electrolysed solution either polarographically or through its visible absorption spectrum, λ 510 nm (ε 25 000) recorded with an Unicam SP 800 spectrometer. DPM was determined by g.l.c. on a Carbowax 400 (60—80 mesh) on 15% Chromosorb PDMCS 1/8 in × 10 ft column with a Varian 1200 chromatograph. For the determination of TPE and NTPM the electrolysed solution was first treated with trifluoroacetic acid and then vacuum distilled. After repeated extractions with water to eliminate the background electrolyte, the residue was fractioned by column chromatography (silica gel with light petroleum–benzene as eluting phase) and the fractions vacuum distilled. TPE was then crystallised from a benzene–methyl alcohol solution, m.p. 213—215 °C. The i.r. spectrum of this product was identical with that of an authentic sample. NTPM was crystallised from light petroleum and determined by polarography.

RESULTS

Polarography and Potential Sweep Voltammetry.—The polarographic pattern of DNPS is rather complex and markedly dependent on experimental parameters such as temperature T and drop time t as illustrated in Figures 1 and 2.

None of the waves is diffusion controlled. The relative half-wave potentials ($E_{\frac{1}{2}}$) are listed in Table 1. The most significative indications as to the electrode reaction mechanism are provided by the drop-time dependence of the limiting current j of wave II (see Figure 3). In fact the slope of the log j–log t straight line changes from 0.17 at 25 °C, when the wave itself is almost fully developed, to 1.17 at −22 °C, when the wave height is *ca.* 15% that of wave I. Variations of the depolariser concentration do not appear to alter these data significantly.

It can be easily recognised that the slopes for wave II fit well the values characteristic of a first order e.c.e. mechanism of the type $\mathrm{O} \underset{}{\overset{ne}{\rightleftarrows}} \mathrm{R} \xrightarrow{k} \mathrm{O'} \underset{}{\overset{ne}{\rightleftarrows}} \mathrm{R}$, the product of the first electron transfer R being irreversibly transformed into the species O′, reducible at more negative potentials. In fact, in the semi-infinite linear diffusion approach, the value of j for the reduction of the species O′ is given by $j = qt^{1/6}[1 - \mathrm{expt}(-kt)]$, q being a factor independent of k and t.[5] For values of kt sufficiently high, $j \propto t^{1/6}$, as for the diffusion controlled process. In contrast for low values of kt, $j \propto t^{7/6}$ which is typical for the e.c.e. mechanism mentioned above.[6,7]

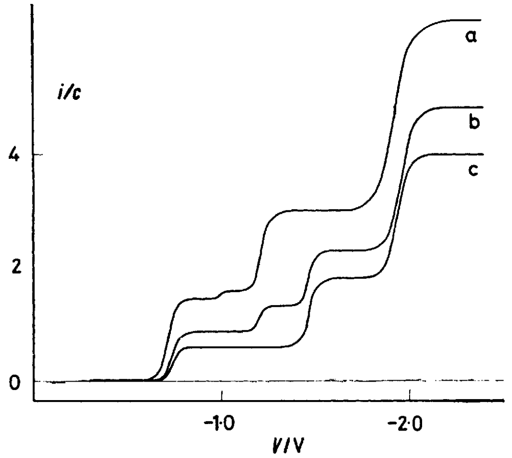

FIGURE 1 Direct current polarograms of DNPS: c, 5 × 10^{-4}M; t, 3 s; T, a, 25 °C; b, −1 °C; c, −24 °C

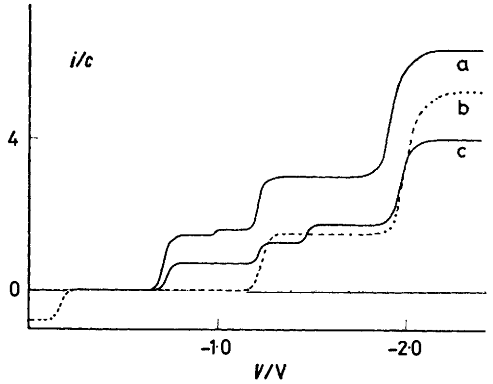

FIGURE 2 Direct current polarograms of DNPS: c, 5 × 10^{-4}M; T, 25 °C; a, t, 3 s; b, polarogram recorded after exhaustive electrolysis at wave I potentials; t 3 s; c, t 0.5 s

TABLE 1

Polarographic reduction potentials

	$E_{\frac{1}{2}}$/V [a]				
Compound	Wave I	Wave Ia	Wave II	Wave III	Wave IV
$Ph_2CH{-}S{-}C_6H_4NO_2$	−0.72	−0.99	−1.22	−1.47 [b]	−1.92
$[Ph_2CH]^{\cdot}$	−0.78 [c]				
$[S{-}C_6H_4NO_2]^-$ [d]			−1.23		−2.00
$Ph_2CH{-}C_6H_4NO_2$	−0.80				−1.85

General conditions: c 5 × 10^{-4}M; T 25 ± 0.1 °C; drop-time 3 s.

[a] *versus* Ag–AgCl–tetramethylammonium chloride saturated electrode. [b] Drop-time 0.5 s. [c] Obtained by polarographic reduction of diphenylmethyl bromide according to ref. 9. [d] Also presents an anodic wave with $E_{\frac{1}{2}}$ −0.16 V.

At relatively high temperatures ($T > 15$ °C) a new wave (Ia) is observed, increasing the depolariser concentration c. This wave, whose height becomes at most half that of wave I, is also kinetic in character. If phenol is added, wave I increases at the expense of wave Ia and for a phenol

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[5] G. Albert and I. Shain, *Analyt. Chem.*, 1963, **35**, 1859.

[6] J. M. Saveant, *Electrochim. Acta*, 1967, **12**, 753.

[7] J. M. Saveant, *Bull. Soc. chim. France*, 1967, 471.

to depolariser concentration ratio of 0.5 : 1 a single wave is again obtained. Wave IV is present in all conditions and its variations with the experimental parameters do not appear to be inter-related with those of the other waves.

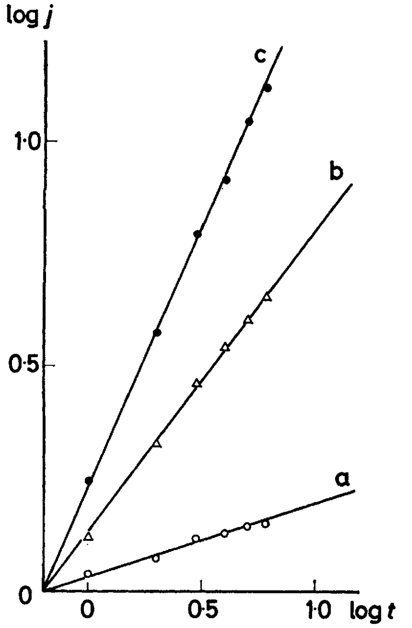

FIGURE 3 log plot of the wave II limiting current (j) against drop-time t: c, 5×10^{-4}M; T, a, 25 °C; b, 5 °C; c, -22 °C. The lines are arbitrarily shifted along the ordinates

The behaviour of DNPS in potential sweep voltammetry parallels that observed in polarography; however in this case more detailed information can be obtained, owing to the wide variability of the sweep rate v and to the anodic peaks formed by cyclic voltammetry. In fact four reduction peaks are normally observed by single cathodic scan but, by cyclic voltammetry, two peaks appear on the anodic branch, apparently corresponding to peaks I and II respectively (see Figure 4); the potential difference ΔE_p between the cathodic and the related anodic peak is *ca.* 60 mV at 20 °C, as expected for a reversible one-electron transfer. However the anodic peak I, which is hardly noticeable for $v < 1.5$ V s^{-1} at 20 °C, increases with either increasing v or decreasing T. The ratio between the anodic and the cathodic peak currents $(i_{ap}/i_{cp})_I$ is reported as a function of v, at different values of T, in Figure 5, together with the current function $(i_{cp})_I/v^{\frac{1}{2}}c$. The peak potential $(E_{cp})_I$ is practically independent of c in the range explored (5×10^{-5}—5×10^{-4}M) and is also independent of v whenever the corresponding anodic peak is present; however when, with decreasing v, the anodic peak disappears, $(E_{cp})_I$ shifts towards more positive values of *ca.* 29 mV per log v unit, at 20 °C (see Figure 6).

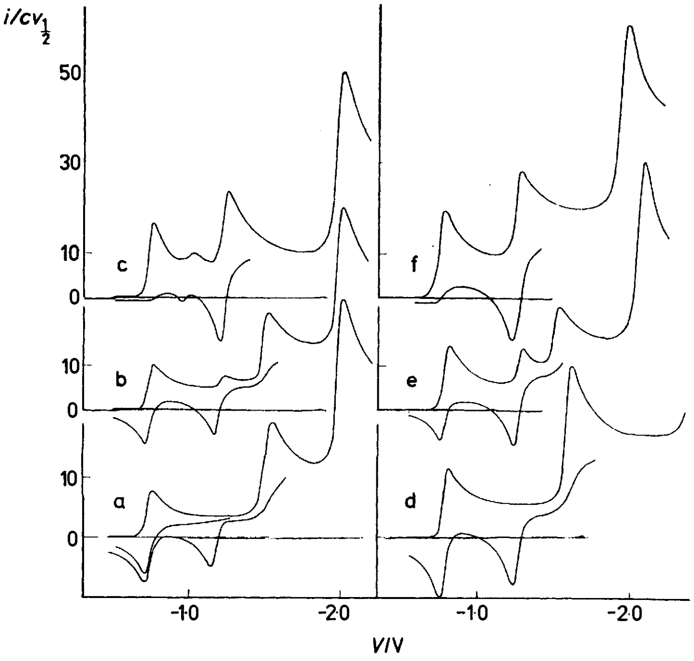

FIGURE 4 Potential sweep voltammetry of DNPS: c, 5×10^{-4}M; v, 1 V s^{-1} for a—c; T, a, -24 °C; b, 1 °C; c, 40 °C; T 20 °C for d—f; v, d, 100 V s^{-1}; e, 2.5 V s^{-1}; f, 0.04 V s^{-1}

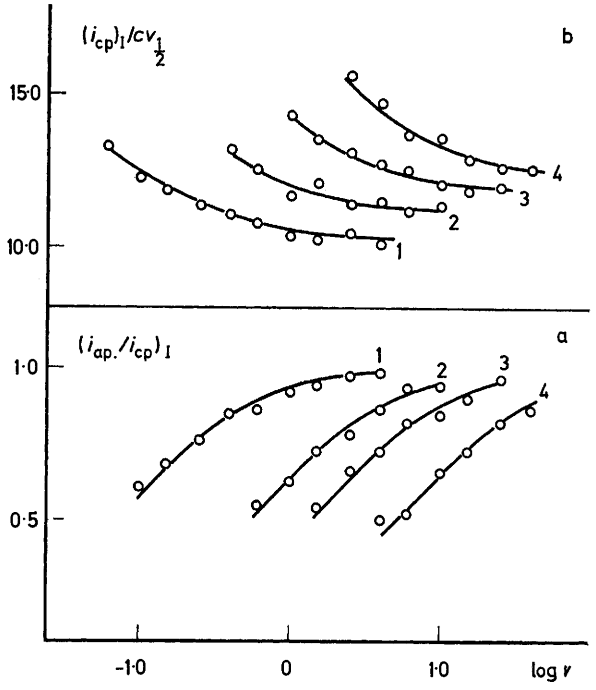

FIGURE 5 a, Sweep rate dependence of the ratio of the anodic to cathodic peak currents for peak I; b, sweep rate dependence of the peak current function for cathodic peak I; c, 1×10^{-4}M; T, 1, 1 °C; 2, 13.5 °C; 3, 23 °C; 4, 34 °C

Both peaks II and III vary markedly with T and v, as illustrated in Figure 4. In Figure 7 the dependence of $(i_{cp})_{II}$ on v is reported, together with the ratio $(i_{cp})_{II} : (i_{cp})_I$. Although the determination of $(i_{cp})_{II}$ is rather approximate, since it is measured with respect to the extension of the descending part of peak I, considered as a base line, these results show a behaviour which is typical of the e.c.e. mechanism mentioned above.[6-8]

Also in potential sweep voltammetry a new peak (Ia) intermediate between I and II is observed, at higher values of T and c and the lower value of v (see Figure 4). This peak appears to be associated with an anodic partner, the ΔE_p value being higher than 60 mV and variable with

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[8] R. S. Nicholson and I. Shain, *Analyt. Chem.*, 1965, **37**, 178.

v and c. The effect of phenol addition is similar to that observed in polarography: peak I increases at the expense of Ia, while the anodic peak corresponding to the latter *decreases*.

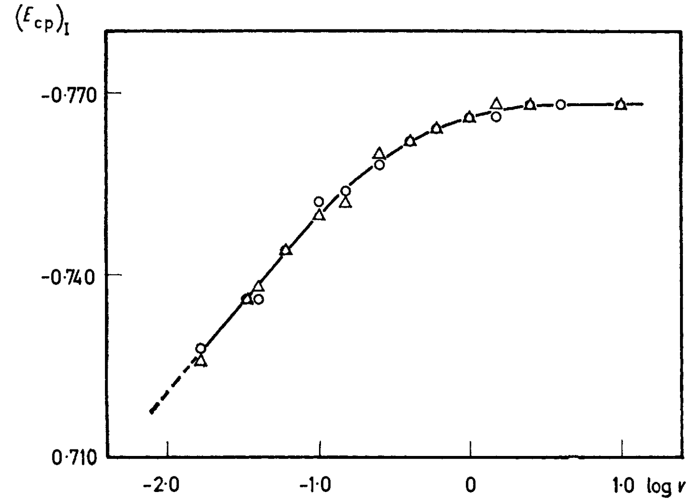

FIGURE 6 Sweep rate dependence of the cathodic peak I potential: T, 20 °C; c, ○ 5×10^{-5}M; △ 5×10^{-4}M

Peak IV, which is present in all conditions, although not very reproducible, is irreversible and appears to correspond to a many-electron process.

Controlled Potential Electrolysis and E.s.r. Spectra.—Macroscale electrolysis performed at potentials of wave I of DNPS causes a simultaneous decrease of waves I and III, which eventually disappear, while wave II increases up to a height comparable with that of wave I before electrolysis and a new anodic wave is observed at −0.16 V. The coulometric n values (Faradays per mole of DNPS) obtained by current integration and the yields of the various electrolysis products are reported in Table 2. It should be noted that addition of a radical scavenger (styrene) or of a proton donor (phenol) affects significantly both the yields and the coulometric n values.

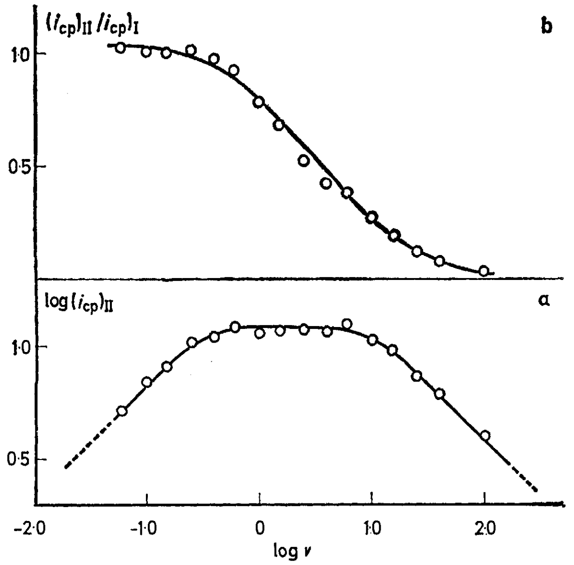

FIGURE 7 a, log plot of the peak II current against sweep rate; b, sweep rate dependence of cathodic peak I to cathodic peak II current ratio; c, 5×10^{-4}M; T, 25 °C

TABLE 2

Electrolysis products

Reduction potential (V)	Coulometric n value [a]	Yield [b]			
		NTP	TPE	DPM	NTPM
−0.80	1.2	100	60—70	20—30	
−0.80 [c]	1.0	100	30—35	Trace	
−0.80 [d]	2.0	100	Trace	80—90	
−1.30	1.2	100	60—70	20—30	
−1.60	1.1	70 [e]	30—40	15—20	20—30
Reaction DPM⁻ + DNPS		40 [e]	40		30

c 2×10^{-2}M; T 20 °C.

[a] Number of Faradays per mole of DNPS. Electrolysis carried out up to suppression of wave I. [b] Yield is referred to mole % DNPS converted into products. [c] In the presence of styrene (4×10^{-1}M). [d] In the presence of phenol (8×10^{-2}M). [e] Other possible sulphur-containing products have not been determined.

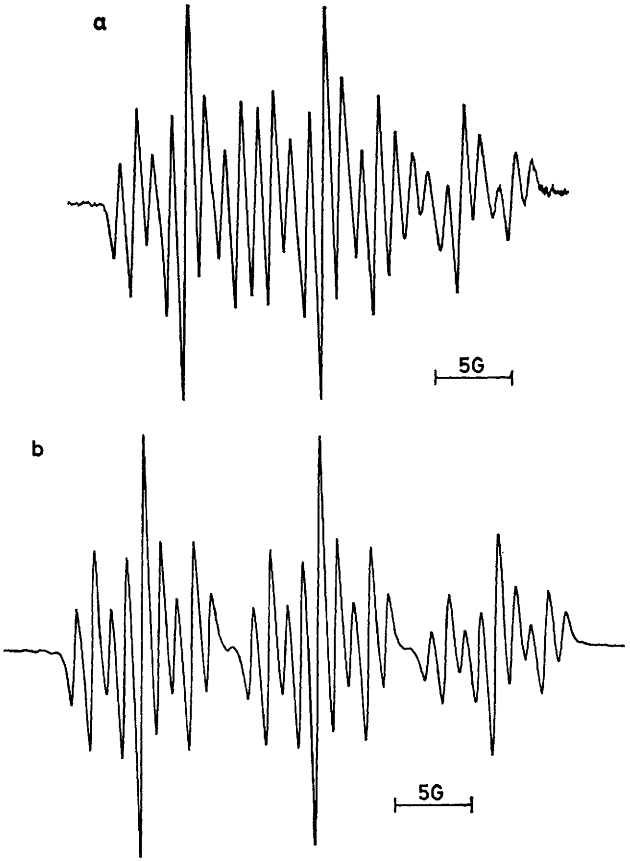

FIGURE 8 E.s.r. spectra obtained by electrolysis of DNPS: a, within the cavity at −30 °C; b, at wave II potentials, after disappearance of wave I

Additional information as to the intermediates of the electrode process is provided by the e.s.r. spectra recorded during electrolysis. The spectrum of Figure 8a can be obtained by reduction of DNPS at any potential corresponding to waves I—III, as long as wave I is still present. It can be detected, however, only when electrolysis is performed at a low temperature (−20 °C) directly within the e.s.r. cavity. This spectrum shows a hyperfine structure which is interpretable as due to the interaction of the unpaired electron with a nitrogen nucleus and two pairs of equivalent protons. The values of the coupling constants and *g* factor are listed in Table 3.

Effects of electrolysis performed at potentials of wave II are qualitatively and quantitatively similar to those observed by reduction at wave I potentials (see Table 2). However if electrolysis is continued after waves I and III have disappeared, the cathodic wave II is progressively transformed into a reversible cathodic–anodic wave at the same potential. If the solution is then transferred into the e.s.r. cavity, the spectrum of Figure 8b can be recorded. This spectrum, which is stable at room temperature, presents a hyperfine structure deriving from the interaction of the unpaired electron with the same set of nuclei of the spectrum of Figure 8a, but with different values of the nitrogen coupling constant and *g* factor (see Table 3).

TABLE 3

Hyperfine splitting constants (G) and *g* factors

Radical-ion	a_N	a_H^{ortho}	a_H^{meta}	a_{CH_3}	Δa_N	g
$[Ph_2CHSC_6H_4NO_2]^{-\cdot}$	9.06	3.50	1.06		2.91	2.004 87
$[SC_6H_4NO_2]^{\cdot 2-}$	11.97	3.37	1.19			2.005 68
$[CH_3OC_6H_4NO_2]^{-\cdot}$ [a]	11.57	3.43	1.11	0.30	2.23	
$[OC_6H_4NO_2]^{\cdot 2-}$ [b]	13.80	3.14	0.72			
$[O_2NC_6H_4SC_6H_4NO_2]^{-\cdot}$ [c]	8.80	3.32	0.99			

[a] Ref. 14. [b] Ref. 15. [c] Ref. 10.

Also, electrolysis at potentials of wave III causes at first a decrease of both waves I and III; when the latter have disappeared wave II is still present although its limiting current is lower than the corresponding one after electrolysis at the potentials of wave I or II. Beside the usual products a new nitro-derivative, NTPM, is found by reduction at -1.60 V.

Characterisation of the Electrolysis Products.—Since NTP is the main reduction product of DNPS, some checks have been performed on this compound, for the sake of comparison. NTP displays three polarographic waves the first of which is an anodic one; the relative $E_{\frac{1}{2}}$ values are listed in Table 1. The first reduction wave, which has the same $E_{\frac{1}{2}}$ of wave II of DNPS is shown, by logarithmic analysis, to correspond to a reversible one-electron transfer. Two reduction peaks are observed in potential sweep voltammetry the first of which shows a corresponding anodic peak at a potential *ca.* 60 mV less negative, in agreement with the reversible character of the charge transfer process.

During macroscale electrolysis performed at potentials corresponding to the plateau of the first reduction wave, the latter is progressively transformed into a reversible cathodic–anodic wave. If the electrolysed solution is then transferred into the e.s.r. cavity a stable spectrum is recorded which is coincident with that obtained by reduction of the species corresponding to wave II of DNPS after waves I and III have disappeared (Figure 8b). This spectrum is therefore clearly attributable to the *p*-nitrothiophenolate radical dianion.

The presence of DPM and TPE among the electrolysis products, suggests the formation of diphenylmethyl radicals as unstable intermediates. According to Matsui *et al.*, polarography of diphenylmethyl bromide in DMF provides the reduction potential of diphenylmethyl radicals, which are formed in a fast reaction between the depolariser and the mercury of the cathode.[9] We have checked the value of $E_{\frac{1}{2}}$ for the reduction of diphenylmethyl radicals under our experimental conditions; it is only slightly more negative than that of wave I of DNPS (see Table 1).

NTPM found among the electrolysis products at the potentials of wave III is likely to derive from the interaction of the DPM carbanion, which is a possible intermediate, and DNPS. To check this point we have prepared a solution of the carbanion by reaction of DPM with an equimolecular amount of butyl-lithium, in anhydrous tetrahydrofuran. This solution was slowly added to an equimolecular amount of DNPS in DMF. All operations were carried out under an inert atmosphere. At the end the reaction mixture was treated as described above for the determination of TPE and NTPM. The corresponding yields are reported in Table 2.

The polarographic behaviour of NTPM is typical of nitro-derivatives in aprotic media. It presents in fact a reversible one-electron wave (see Table 1) leading to the radical anion of the depolariser and a second multi-electron wave at more negative potentials corresponding to the reduction of the nitro- to the amino-group, through a complex reaction path. Neutralisation of the acidic proton of NTPM with a strong base (DMF solution of tetrabutylammonium hydroxide) causes disappearance of the first wave and reduction of the resulting anion directly at the second wave potential.

DISCUSSION

The results indicate that, under suitable experimental conditions (low *T* and high *v*), the first step in the reduction of DNPS is a diffusion controlled, reversible, one electron transfer. The corresponding product ought to be the radical anion of DNPS [reaction (1)] to

$$Ph_2CH\text{-}S\text{-}C_6H_4NO_2 + e \rightleftharpoons [Ph_2CH\text{-}S\text{-}C_6H_4NO_2]^{-\cdot} \quad (1)$$

which the e.s.r. spectrum of Figure 8a can be reasonably attributed, though only the splittings due to the C_6H_4-NO_2 group are observable. The absence of the splittings corresponding to the interaction of the unpaired electron with the protons of the diphenylmethyl group can in fact be accounted for by the lack of conjugation across the C–S bond, as already observed for the radical anion of bis-*p*-nitrophenyl sulphide.[10] This radical shows, moreover, a value of the nitrogen coupling constant comparable with that of the spectrum of Figure 8a (see Table 3).

All experimental evidence (in particular the variations of the anodic peak I with *T* and *v* and the instability of the e.s.r. spectrum even at low *T*) indicates that the radical anion of DNPS decays rapidly. Considering the nature and yields of the electrolysis products, the decay mechanism (2) can be assumed.

$$[Ph_2CH\text{-}S\text{-}C_6H_4NO_2]^{-\cdot} \xrightarrow{k} [Ph_2CH]^{\cdot} + |S\text{-}C_6H_4NO_2]^{-} \quad (2)$$

In fact, beside NTP, which is obtained in quantitative yield, both other products, TPE and DPM, are likely to derive from the diphenylmethyl radicals through at least

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[9] Y. Matsui, T. Soga, and Y. Dake, *Bull. Chem. Soc. Japan*, 1971, **44**, 513.

[10] J. E. Harriman and A. H. Maki, *J. Chem. Phys.*, 1963, **39**, 778.

two alternative paths. The fraction of the radicals formed close to the electrode should be reduced [reaction (3)] at the present potential (see Table 2), the resulting

$$[Ph_2CH]^{\cdot} + e \longrightarrow [Ph_2CH]^- \qquad (3)$$

carbanion being a base strong enough to be protonated by some acidic impurity of the solution. The diphenylmethyl radicals formed far from the electrode should undergo a fast dimerisation (4). Reaction (3) would

$$2[Ph_2CH]^{\cdot} \longrightarrow Ph_2CH\text{-}CHPh_2 \qquad (4)$$

account for the coulometric value $n = 1.2$ corresponding to the low yield (20%) of DPM.

In the presence of excess of styrene, the main reaction path should become the addition of diphenylmethyl radicals to this scavenger; in fact the yield of TPE decreases significantly, that of DPM falls practically to zero, and $n = 1$.

The alternative to the radical fission (2), involving the DPM carbanion and the *p*-nitrothiophenol radical can be reasonably excluded, since it would justify neither the nature of the electrolysis products nor, in particular, the quantitative yield of NTP, even in the presence of styrene, towards which thiyl radicals are known to be very reactive.

Although the mechanism involving reactions (1)—(4) is likely to predominate in aprotic conditions, the very high yield of DPM, the absence of TPE, and the coulometric n value observed in the presence of phenol are probably better explained by a reaction path, which is characteristic of the reduction of nitro-derivatives in the presence of proton donors, *i.e.* protonation of the radical anion to neutral radical and reduction of the latter at the potential of formation; the resulting anion should then decompose to give the overall process (5).

$$[Ph_2CH\text{-}S\text{-}C_6H_4NO_2]^{-\cdot} \xrightarrow[\text{donor}]{\text{proton}}$$

$$[Ph_2CH\text{-}S\text{-}C_6H_4NO_2H]^{\cdot} \xrightarrow{e} Ph_2CH_2 + [S\text{-}C_6H_4NO_2]^- \qquad (5)$$

This reaction is likely to occur, in part, in the absence of added proton donors, owing to acidic impurities in the solution. In particular, DNPS itself can act as a proton donor, owing to the acidic properties of the hydrogen atom of the diphenylmethyl group,[2] by the autoprotonation mechanism already verified for nitro-derivatives with acidic functions.[11,12] The conjugated base of DNPS, formed in this reaction, is reduced at potentials more negative than DNPS itself, owing to coulombic repulsion, giving rise to wave Ia. This is in agreement with the kinetic character of the wave, which is present only at the highest values of T and c, suggesting that the depolariser responsible for it is formed in a relatively slow second-order reaction. Also the effects of a weak proton donor such as phenol, which causes an increase of wave I at the expense of wave Ia, supports this hypothesis.

In order to evaluate the kinetic constant for the rate-determining step of the anion radical decay, the kinetic analysis has been carried out on the basis of the voltammetric results. The rate constants k have been determined from the ratio $(i_{ap} : i_{cp})_I$ at different values of v, with the aid of a plot of the theoretical data published by Nicholson and Shain.[13] It must be noted, however, that in the region of v where the ratios $(i_{ap} : i_{cp})_I$ diminish, the cathodic current function $(i_{cp})_I/cv^{\frac{1}{2}}$ increases significantly. This is to be attributed to the influence of reactions (3) and (5) on the cathodic current. For this reason in the calculation of k, instead of the actual value of $(i_{cp})_I$, use has been made of the peak current function extrapolated from those values of v at which no complications arise. With this correction the ratio $(i_{ap} : i_{cp})_I$ is independent of the depolariser concentration, at a fixed v value, as expected for first-order decay. This is also in agreement with the concentration independence of $(E_{cp})_I$ and with the slope of its variation with v $[\Delta(E_{cp})_I/\Delta \log v = 29 \text{ mV}]$. The rate constants calculated at several temperatures and concentrations are reported in Table 3. The Arrhenius plot of Figure 9 allowed us to calculate the activation energy for the process, 21 kcal mol^{-1}.

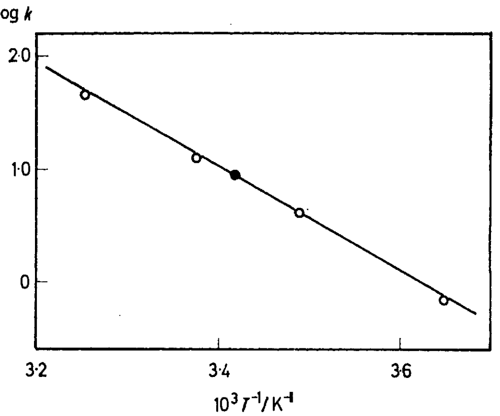

FIGURE 9 Arrhenius plot of the rate constant of DNPS radical anion decay: c, ○, 5×10^{-4}M; ● average value for three different concentrations (see Table 4)

TABLE 4

Rate constants k of DNPS radical anion decay

T/°C	1.0	13.5	23.1	34.2	19.5		
10^4[DNPS]/M	5.0	5.0	5.0	5.0	0.52	1.0	3.7
k/s^{-1} [a]	0.7	4.0	12.4	45.1	8.5	9.4	9.1

$\Delta E^{\ddagger}$ 21 kcal mol^{-1}

[a] Rate constants are reproducible to within ±10%.

Wave II is evidently due to the reduction of NTP formed according to reaction (2). In fact this wave is missing in conditions such that the primary anion radical does not decay appreciably and the polarogram obtained after exhaustive electrolysis at the potentials of wave I is practically coincident with that of a standard solution

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[11] G. Farnia, G. Mengoli, and E. Vianello, *J. Electroanalyt. Chem.*, 1974, **50**, 73.

[12] G. Farnia, A. Roque da Silva, and E. Vianello, *J. Electroanalyt. Chem.*, 1974, **57**, 191.

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of NTP anion. The electrode process implies a reversible, one-electron transfer with formation of the stable radical dianion responsible for the e.s.r. spectrum of Figure 8b [reaction (6)]. It should be recalled that the

$$[\mathrm{S{-}C_6H_4NO_2}]^- + \mathrm{e} \rightleftharpoons [\mathrm{S{-}C_6H_4NO_2}]^{2-\cdot} \qquad (6)$$

hyperfine structure of this radical is similar to that of the DNPS radical anion, but with a larger value of the nitrogen coupling constant, which gives better resolution of the spectrum. A similar difference between the nitrogen coupling constants has already been observed for *p*-nitroanisole anion radical and *p*-nitrophenolate dianion radical[14,15] (see Table 3).

Further support for the attribution of the e.s.r. spectra is provided by the value of the g factor, which is larger for the radical dianion of NTP. It is known that the main contribution to g in these radicals derives from the spin density on the sulphur atom since it has a large spin–orbit coupling constant. An increase in g is expected by the mixing of excited configurations involving the excitation of lone pair electrons to the singly occupied π orbital. Since the radical dianion of NTP has two lone pairs on sulphur instead of one as in the DNPS radical anion the effect should be larger. This discussion follows that of Norman to explain the g factors of oxygen-containing free radicals.[16]

The large $E_{\frac{1}{2}}$ difference between the reversible redox processes (1) and (6) indicate that the redox equilibrium (7) should be strongly displaced towards the right. The

$$[\mathrm{S{-}C_6H_4NO_2}]^{2-\cdot} + \mathrm{Ph_2CH{-}S{-}C_6H_4NO_2} \overset{K}{\rightleftharpoons} [\mathrm{S{-}C_6H_4NO_2}]^- + [\mathrm{Ph_2CH{-}S{-}C_6H_4NO_2}]^{-\cdot} \qquad (7)$$

equilibrium constant is in fact very high, $K = \exp F\Delta E_{\frac{1}{2}}/RT = 2.8 \times 10^8$; furthermore the radical anion of DNPS is continuously removed, owing to reaction (2). Reaction (7) accounts for the fact that electrolysis at potentials of wave II causes the latter to decrease only after wave I has disappeared, *i.e.* after DNPS has been consumed. It also clears up why the e.s.r. spectrum of the DNPS radical anion is recorded first, while that of the NTP radical dianion appears only after prolonged electrolysis at wave II potentials.

Wave III can be reasonably ascribed to the reduction (8) of the DNPS radical anion, *i.e.* to a two-electron transfer to DNPS.

$$[\mathrm{Ph_2CH{-}S{-}C_6H_4NO_2}]^{-\cdot} + \mathrm{e} \longrightarrow [\mathrm{Ph_2CH{-}S{-}C_6H_4NO_2}]^{2-} \qquad (8)$$

However the dianion thus formed should be very rapidly inactivated, as suggested by the irreversibility of peak III even at the lowest temperatures and highest sweep rates. Among the various conceivable decay paths for the dianion (protonation, nucleophilic attack, dissociation) reaction (9) can be tentatively considered, since it rationalises at least the experimental facts observed at low temperature. In fact the formation of NTP and its further reduction according to (6) accounts

$$[\mathrm{Ph_2CH{-}S{-}C_6H_4NO_2}]^{2-} \xrightarrow{\text{fast}} [\mathrm{Ph_2CH}]^- + [\mathrm{S{-}C_6H_4NO_2}]^- \qquad (9)$$

for the presence of the anodic peak II in conditions such that the corresponding cathodic peak is absent, provided the switching potential lies in the potential region of peak III (see Figures 4a and d). Furthermore if reaction (7) is taken into account, one can understand why the e.s.r. spectrum of Figure 8a can be recorded by low temperature reduction even at wave III potentials.

The nature and yields of the macroscale reduction products indicate however that a more complex mechanism underlies wave III, at least at room temperature and/or in the time scale of mass electrolysis. Comparison of the results reported in the last two lines of Table 2 suggests that the DPM carbanion formed in reaction (9) should be in part protonated to DPM and in part it should attack DNPS through at least two parallel nucleophilic reactions (10) and (11) accounting for the formation of TPE and NTPM. The anion of NTPM is

$$[\mathrm{Ph_2CH}]^- + \mathrm{Ph_2CH{-}S{-}C_6H_4NO_2} \longrightarrow \mathrm{Ph_2CH{-}CHPh_2} + [\mathrm{S{-}C_6H_4NO_2}]^- \qquad (10)$$

$$[\mathrm{Ph_2CH}]^- + \mathrm{Ph_2CH{-}S{-}C_6H_4NO_2} \longrightarrow [\mathrm{Ph_2C{-}C_6H_4NO_2}]^- + \mathrm{HS{-}CHPh_2} \qquad (11)$$

considered in reaction (11), rather than the anion of diphenylmethanethiol, because the latter is certainly a weaker acid. This is also in agreement with unreduced NTPM being found among the electrolysis products, owing to the very negative reduction potential of the corresponding anion (see Table 1).

It is easily verified that the overall electrode process occurring at wave III potentials involves three electrons per molecule of DNPS, if only reactions (1), (8), (9), and (6) need to be taken into account (low temperature), whereas two electrons at maximum are required if reactions (10) and (11) must also be considered. For the overall process at wave II potentials the corresponding values are one and two electrons respectively, when reactions (2) and (6) need to be considered together with (1). Therefore at low temperature, wave II is missing and wave III is almost double in height with respect to the one-electron wave I (see Figure 1); on the other hand, when the temperature is high enough for reactions (2), (10), and (11) to be fast on the drop-time scale, the overall electrode process involves two electrons per DNPS molecule either at wave II or at wave III potentials, so that wave III becomes indistinguishable (see Figure 1). The same is true for potential sweep voltammetry, except that in this case similar effects can also be obtained by varying v (see Figure 4d).

It should finally be noted that reactions (10) and (11) could occur also at wave I potentials, owing to reactions (2) and (3). In this case however dissociation of the

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[16] R. O. C. Norman and R. J. Pritchett, *Chem. and Ind.*, 1965, **11**, 2040.

electron transfer product yields diphenylmethyl radicals, which are known to dimerise rapidly,[9] while DPM carbanions correspond to that fraction of radicals which undergoes a further electron transfer. This and the absence of NTPM from the electrolysis products indicate that the contribution of reactions (10) and (11) to the overall process underlying wave I is to be considered negligible.

Wave IV has not been investigated in detail, since it is clearly due to the reduction of the nitro-group. Whenever enough protons are available, such a reduction proceeds to give the corresponding amino-derivative.

The kinetic results reported, as far as the nature and fate of the intermediates is concerned, show that, however complex the reduction mechanism of DNPs may be, the decay of the primary radical anion is the rate-determining step. Further investigations are needed, however, to verify whether the mechanism proposed can be generalised to organic sulphides, owing to the role that different substituents may play.

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