

Substituent Effect on Polarographic Reduction of Aryl Diphenylmethyl Sulphides in *NN*-Dimethylformamide

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Aryl diphenylmethyl sulphides, $\text{XC}_6\text{H}_4(\text{X}'\text{C}_6\text{H}_4)\text{CH}-\text{S}\cdot\text{C}_6\text{H}_4\text{Y}$, are reduced polarographically in *NN*-dimethylformamide in an irreversible two-electron process with fission of the C-S bond. The interpretation of the polarogram is complicated by a reaction of the reduced species with the unreduced depolarizer (autoprotonation effect). The extent of this effect varies with the substituents and can be eliminated by addition of phenol. The polar effects of substituents X and Y as measured by Hammett σ constants are correlated with the half-wave potentials, giving two distinct correlations with different ρ values. Analysis of this substituent effect has allowed us to show how the C-S bond is modified in its charge character at the transition state thereby defining the actual reaction site. The suggested mechanism for the reduction is supported by controlled-potential electrolysis and e.s.r. experiments.

ELECTROCHEMICAL fission of the activated C-S bond is of considerable interest especially for sulphones and sulphonium salts.¹ However the information available on C-S fission in sulphides is scarce. Gerdil² found that diphenyl, Ph-S-Ph, and alkyl phenyl, R-S-Ph, sulphides are reduced in dimethylformamide in a single two-electron polarographic wave with fission of Ph-S and R-S bonds respectively. The Taft-Hammett relationship was found to be valid for most of the alkyl phenyl sulphides with a positive ρ value of +0.268 V. The postulated mechanism involves the formation of a hypothetical intermediate, the anion radical, which follows different paths yielding the products, hydrocarbon and thiophenol.

In this work we have investigated the polarographic reduction of substituted diphenylmethyl phenyl sulphides, $\text{XC}_6\text{H}_4(\text{X}'\text{C}_6\text{H}_4)\text{CH}-\text{S}\cdot\text{C}_6\text{H}_4\text{Y}$, in dimethylformamide. The polarographic technique was coupled with e.s.r. spectroscopy and macroscale electrolysis.

There are a number of reasons which make this class of compound, displaying well-defined and reproducible waves, convenient for a polarographic study. From their effect on the half-wave potential substituents on both halves of the molecule, X and Y, should tell us how the C-S bond is modified in its charge character at the transition state, thus defining the actual reaction site. Moreover, on some of the same substrates, one of us³ has been able to measure the rates of hydrogen-deuterium exchange, a reaction which involves a transition state with a high carbanion character. Thus if the transition state of reduction resembles that of exchange, the half-wave potentials should be connected with the rates of exchange and the substituent effects should be analogous. Finally, we noted the interpretation given by Gerdil on the negative value of the Hammett reaction constant ρ found only for isopropyl and *t*-butyl phenyl sulphides. He stated that 'when secondary or tertiary alkyl groups are present the rate-determining step might depend on a pre-dissociation of

the bond.' This process should ionize the bond in an $\text{S}_{\text{N}}1$ fashion, *i.e.*, $\text{R}^+ - \text{SPh}$, in these substrates. Diphenylmethyl phenyl sulphides, owing to the ability of diphenylmethyl moiety to stabilize a positive charge, should furnish evidence for such a mechanism, if it exists.

EXPERIMENTAL

Materials.—Reagent-grade dimethylformamide was dried (K_2CO_3) and fractionally distilled under reduced pressure, the middle fraction being collected. The solvent was stored under nitrogen.

Tetraethylammonium perchlorate was vacuum-dried and stored in a vacuum desiccator.

Aryl diphenylmethyl sulphides were prepared from the appropriate substituted diphenylmethanols and thiophenols in acetic acid with sulphuric acid.⁴ They were crystallized from ethanol twice. Phenyl triphenylmethyl sulphide was prepared by the same procedure. The yields were always >70%. The purity was checked with n.m.r. spectroscopy. M.p.s and elemental analyses^{5,6} are in Table 1.

Apparatus and Procedure.—Polarographic measurements were taken with a polarograph consisting of a conventional d.c. polarizing unit and a current Lange recorder equipped with a Multiflex galvanometer. The drop time of the dropping mercury electrode was regulated by means of a magnetic hammer triggered by a solid state timer. A Heyrovsky cell *versus* mercury pool was used as the reference electrode. The supporting electrolyte was tetraethylammonium perchlorate (0.1M) and the concentration of the depolarizer $1.0 \times 10^{-3}\text{M}$. The solutions were deaerated with nitrogen and the polarograms recorded at $25 \pm 0.1^\circ\text{C}$. The $E_{\frac{1}{2}}$ of each compound was averaged from at least three measurements and the value of the half-wave potential of the parent sulphide, $E_{\frac{1}{2}}^0$, was checked before each series of runs.

Potential-sweep chronoamperometric curves (p.s.c.) were recorded by means of an Amel model 448 instrument.

Controlled-potential electrolyses were carried out with an Amel 557 potentiostat. The cell was similar to that previously described⁷ except for some modifications neces-

¹ H. Lund, *Acta Chem. Scand.*, 1960, **14**, 1927; P. Zuman and Sue-yuon Tang, *Coll. Czech. Chem. Comm.*, 1963, **28**, 829; O. Manousek, O. Exner, and P. Zuman, *ibid.*, 1968, **33**, 310; 1968, **33**, 322.

² R. Gerdil, *J. Chem. Soc. (B)*, 1966, 1071.

³ A. Cecon, to be published.

⁴ C. Finzi and V. Bellavita, *Gazzetta*, 1932, **62**, 699.

⁵ J. E. Cranham, D. Greenwood, and H. A. Stevenson, *J. Sci. Food Agric.*, 1958, **9**, 147.

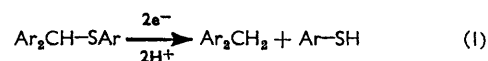
⁶ I. I. Lapkin and N. I. Panova, *Zhur. obshchei Khim.*, 1962, **32**, 745.

⁷ G. Farnia, G. Mengoli, and E. Vianello, *Ricerca sci.*, 1967, **37**, 668.

sary for use of aprotic solvent. Solutions were 5×10^{-3} M sulphide and 0.1M supporting electrolyte. The end of the electrolysis was monitored polarographically. When it was possible to follow the decay of radical intermediates, samples of electrolysed solutions were quickly transferred through a suitable outlet into an e.s.r. cell, thus allowing the recording of the intensity of the signal with time at a constant magnetic field. Usually the electrolysis was conducted directly in the cavity. The spectra were recorded with an E3 Varian spectrometer.

In order to identify the products of the electrolysis the solutions were subjected to g.l.c. Quantitative estimation

to reaction (1). There is considerable evidence suggesting that the reduction wave is due to a two-electron



process, though this is not unambiguously settled. We have examined the polarographic behaviour of 4-biphenyl(phenyl)methane in dimethylformamide. The polarogram showed a single reduction wave at -2.37 V, which corresponds exactly to the $E_{\frac{1}{2}}$ of the second wave

TABLE 1

Physical characteristics of aryl diphenylmethyl sulphides, $\text{XC}_6\text{H}_4(\text{X}'\text{C}_6\text{H}_4)\text{CH-S-C}_6\text{H}_4\text{Y}$

X	X'	Y	M.p./°C ^a	Found (%)				Required (%)			
				C	H	S	Cl	C	H	S	Cl
H	H	H	78.5 ^b	81.85	5.95	11.6		82.55	5.85	11.6	
4-Cl	4-Cl	H	69—70 ^c	67.0	3.95	9.35	20.2	66.1	4.1	9.3	20.6
4-Cl	H	H	57	73.2	5.1	10.3	11.25	73.4	4.9	10.3	11.4
3-Cl	H	H	Oil ^d	74.1	4.75	10.2	11.3	73.4	4.9	10.3	11.4
4-Ph	H	H	128—129	85.35	5.7	9.2		85.2	5.7	9.1	
3-OMe	H	H	Oil ^e	78.9	5.95	10.1		78.4	5.9	10.45	
4-Me	H	H	48—49	83.35	6.3	10.85		82.65	6.25	11.05	
3,4-Me ₂	H	H	68—69	82.5	6.55	10.4		82.85	6.6	10.55	
4-OMe	4-OMe	H	88—89	75.05	5.95	9.3		74.95	6.0	9.55	
H	H	4-Cl	100—101	74.15	5.1	10.25	11.45	73.4	4.9	10.3	11.4
H	H	3-Cl	90	73.1	4.95	10.3	11.35	73.4	4.9	10.3	11.4
H	H	4-F	66.5—67 ^f	77.15	5.15	11.2		77.5	5.15	10.9	
H	H	4-Me	67 ^g	83.2	6.25	11.15		82.65	6.25	11.05	
H	H	4-OMe	91	77.5	5.75	10.5		78.4	5.9	10.45	
Phenyl triphenylmethyl sulphide			106—107 ^h	85.15	5.70	9.2		85.2	5.7	9.1	

^a Uncorrected. ^b Lit.,⁴ 78 °C. ^c Lit.,⁵ 72 °C. ^d The crude product was extracted from the reaction mixture with ether; the ether evaporated and the oil distilled at 200 °C and 5 mmHg. ^e The crude product extracted with ether and the solvent evaporated. ^f Lit.,⁵ 101—102 °C. ^g Lit.,⁵ 65 °C. ^h Lit.,⁴ 66 °C. ⁱ Lit.,⁴ 106—107 °C.

of the yield was made by comparison of the areas below the chromatographic peaks by use of internal standard. Authentic samples of the products were available. The results of replicate experiments were reproducible within 2%.

RESULTS AND DISCUSSION

The half-wave potentials and the αn_a values of substituted diphenylmethyl phenyl sulphides are listed in Table 2.

All sulphides displayed a single well defined wave except (II)—(V) which showed an additional second wave at more negative potentials (see Table 2). In cyclic voltammetry experiments, peaks corresponding to polarographic waves were observed in the reduction sweep; only sulphide (V) showed an oxidation peak in correspondence to the second wave. It appears that the reduction is an irreversible process. The results of controlled-potential electrolysis are instructive with regard to the overall chemical change. Exhaustive controlled-potential electrolysis carried out at the potential corresponding to the top of the first wave on (I), and (III), gave equivalent amounts of thiophenol and hydrocarbon so that the polarographic wave can be related to an overall two-electron process according

of the analogous sulphide (V) (see below). In cyclic voltammetry it was possible to register an oxidation

TABLE 2

Half-wave potentials and αn_a values of substituted diphenylmethyl phenyl sulphides, $\text{XC}_6\text{H}_4(\text{X}'\text{C}_6\text{H}_4)\text{CH-S-C}_6\text{H}_4\text{Y}$, in dimethylformamide

Compound	X	X'	Y	$(-E_{\frac{1}{2}})$	$(-E_{\frac{1}{2}})$	αn_a
				$\pm 0.003/\text{V}^a$ (First wave)	$\pm 0.003/\text{V}^a$ (Second wave)	
(I)	H	H	H	2.001		0.41
(II)	4-Cl	4-Cl	H	1.895	2.315	0.50
(III)	4-Cl	H	H	1.938	2.354	0.45
(IV)	3-Cl	H	H	1.923	2.342	0.47
(V)	4-Ph	H	H	1.802	2.371	0.63
(VI)	3-OMe	H	H	1.971		0.47
(VII)	4-Me	H	H	2.022		0.43
(VIII)	3,4-Me ₂	H	H	2.029		0.44
(IX)	4-OMe	4-OMe	H	2.105		0.51
(X)	H	H	4-Cl	1.912		0.46
(XI)	H	H	3-Cl	1.842		0.44
(XII)	H	H	4-F	1.958		0.43
(XIII)	H	H	4-Me	2.061		0.44
(XIV)	H	H	4-Me	2.089		0.50
(XV)	Phenyl triphenylmethyl sulphide			1.930		

^a Against mercury pool.

peak whose potential is 60 mV more positive than that of reduction. Moreover, when the electrolysed solution

of the hydrocarbon was allowed to flow through the e.s.r. cell the spectrum of Figure 4 is observed. This spectrum shows a rather complex hyperfine structure which is difficult to analyse in terms of splitting constants. However, it can very likely be attributed to the radical anion of 4-biphenyl(phenyl)methane. Thus this hydrocarbon in dimethylformamide gives only one wave of height equivalent to the addition of one electron with limiting current $I_d = 0.62$ (mA l mol⁻¹ mg⁻² s^{1/2}). The behaviour is not very different from that found for biphenyl and other hydrocarbons which in the absence of proton donors are reduced in a one-electron process.⁸ Now, if we take the value of I_d as corresponding to a one-electron addition the first waves of the sulphides (I)–(XV) can be divided into two classes: (a) compounds (IX) and (XV) with $I_d = 1.23$, a value

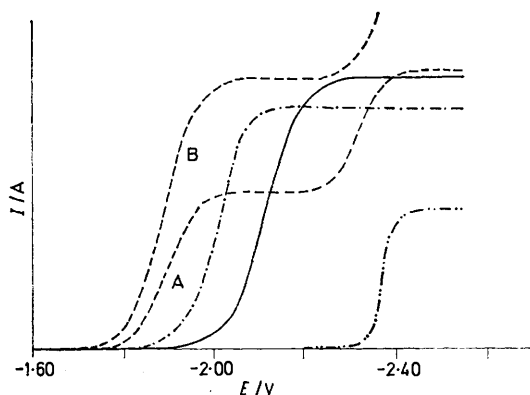


FIGURE 1 Schematic polarographic curves: (— · —) unsubstituted sulphide (I); (—) 4,4'-dimethoxy (IX); and (— · —) 4,4'-dichloro (II); A, without phenol; B, in the presence of phenol; (— · —) 4-biphenyl(phenyl)methane

approximately equivalent to the addition of two electrons; this limiting current is practically unaffected by addition of phenol in a molar ratio phenol:substrate > 1; and (b) all other compounds with I_d lower (10–40%) than that of compounds of class (a). The lowest value was exhibited by compound (II) whose limiting current is 0.78 mA. For these compounds addition of phenol increases the limiting current up to the value of class (a). The polarograms of three typical substrates and of 4-biphenyl(phenyl)methane are reported in Figure 1. So for compounds (IX) and (XV) and for all others in the presence of phenol we confidently assume that the first wave is associated with a two-electron transfer.

Under aprotic conditions for compounds of class (b), a reasonable interpretation of the change of the height of polarographic waves with the nature of the depolarizer is that the depolarizer itself can act as a proton donor towards some intermediate reduced species (auto-protonation effect), thereby decreasing the concentration

of depolarizer available for reduction. This competing reaction makes it difficult to measure the number of electrons involved and this difficulty is reflected in the diffusion current. The addition of phenol eliminates any concurrent reactions. The extent of this phenomenon could depend on the acidity of the methine proton; in effect, one can observe that compounds with no α -protons (XV) or with a weakly acidic α -proton (IX) do not display the phenomenon while it is observed with compound (II) where two *p*-chloro-substituents make the proton rather acidic. This explanation, which has been already invoked for other reduction processes in dipolar aprotic solvents when depolarizers with acidic hydrogen atoms were involved,^{9,10} is at variance with that given by Gerdil,² who interpreted the behaviour of some sulphides such as (phenylthio)-acetic acid whose limiting current is reduced to a half with respect to that of the parent sulphide Ph-S-Ph as evidence of an overall one-electron process. From the preceding discussion, it should be clear that even under aprotic conditions we associate the first polarographic wave of all sulphides with a two-electron process. In most cases, however, the depolarizer is not quantitatively involved in the electrochemical process since its conjugate base cannot be reduced at the same potential.

The question remains if one or two electrons are implicated in the slow step of reduction. The results of the substituent effect suggest that the rate-determining step involves the addition of one electron. To correlate in a free-energy diagram the half-wave potentials with some property of substituents, one should ascertain that the same electrochemical mechanism is operative for all compounds of the series. This is supported by the following facts: (a) the αn_d values (Table 2) calculated from the logarithmic analysis of the waves are similar (*ca.* 0.5) for all members and practically unaffected by the presence of phenol; (b) the diffusion nature of the current was obtained from the usual curves $\log I$ against $\log v$, where $v = dV/dt$; (c) the half-wave potential of each compound does not change whether or not phenol is present.

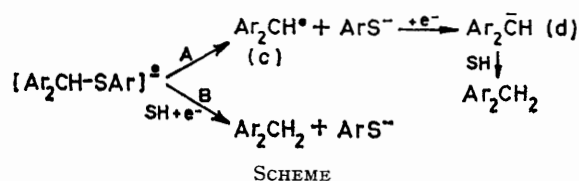
When $E_{1/2}$ values are plotted against σ (Figure 2) it appears that, depending on substituents X or Y, two distinct correlations are obtained, substituents on the diphenylmethyl skeleton giving a line whose slope, $\rho_x = +0.203 \pm 0.008$ V (correlation coefficient $r = 0.995$), is notably lower than that of the line obtained with substituents on the thiophenyl ring, $\rho_y = +0.386 \pm 0.009$ V ($r = 0.996$). Thus, for both classes of substituent, electron-donating groups make the half-wave potential more negative while electron-attracting groups make the sulphide easier to reduce, the effect being much greater for substituents on the thiophenyl ring. If two electrons instead of one were involved in the slow step of reduction with consequent formation of a diphenylmethyl carbanion and a thiophenoxide anion,

⁸ P. H. Given and M. E. Peover, *J. Chem. Soc.*, 1960, 385.

⁹ G. Farnia and E. Vianello, *Chimica e Industria*, 1967, 49, 971, 1101; G. Farnia, A. Romanin, G. Capobianco, and F. Torzo, *J. Electroanalyt. Chem.*, 1971, 33, 3144.

¹⁰ J. Janata, J. Gendell, R. G. Lawton, and H. B. Mark, jun., *J. Amer. Chem. Soc.*, 1968, 90, 5226.

methyl radical is at least 1 V less negative¹⁶ than the $E_{\frac{1}{2}}$ of the corresponding sulphide (XV).] Alternatively, the anion radical captures one proton and one electron giving rise to the hydrocarbon and thiophenoxide



anion. In path B the proton source (besides the solvent) may be the depolarizer itself. The predominance of route A or B depends on the acidity of the α -hydrogen atoms of the depolarizer and the presence of phenol.

Indirect evidence in favour of the Scheme has been obtained from macroscale electrolysis and from e.s.r. spectroscopy. In the potential-controlled electrolyses the dimethylformamide solutions became intensely coloured, the colour persisting for several minutes after the end of the electrolysis. The colour should be attributed to the carbanion (d) which is slowly protonated by solvent (diphenylmethyl salts are intensely coloured).¹⁷ No spectrum, in fact, was registered when the coloured solutions were transferred into the e.s.r. cavity, showing that the colour cannot be due to radical species. Moreover, it is significant that the presence of phenol hindered the formation of any colour.

On the other hand, when the electrolysis was carried out on compounds (I), (III), and (IV) directly in the

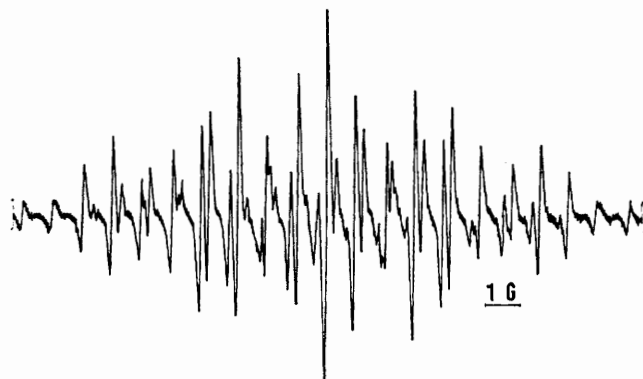


FIGURE 3 E.s.r. spectrum of the radical anion produced by electrolysis in dimethylformamide of compounds (I), (III), and (IV)

e.s.r. cell, we were unsuccessful in obtaining the spectrum of the neutral radical (c) but we did observe in each case the spectrum reported in Figure 3. This spectrum can be interpreted only if one assumes the interaction

¹⁶ G. Kothe, W. Summermann, H. Baumgartel, and H. Zinnermann, *Tetrahedron Letters*, 1969, **26**, 2185.

¹⁷ W. K. McEwen, *J. Amer. Chem. Soc.*, 1936, **58**, 1124; R. Weack and M. A. Doran, *ibid.*, 1963, **85**, 1651.

of an odd electron with three sets of equivalent protons having coupling constants 3.06 G (2 protons), 2.56 G (4 protons), and 0.82 G (4 protons). These coupling constants are consistent with those of the ketyl radical of benzophenone.¹⁸ The presence of ketyl radical, though in hardly detectable concentration, is likely to be ascribed to the oxidation of the diphenylmethyl radical (c) by traces of oxygen in the solution. Evidently a very small amount of the radical can be trapped by traces of oxygen instead of being reduced to carbanion. It is striking that the presence of carbonyl species is a common feature when fission of an R-S bond is produced photolytically in compounds where R is benzyl or diphenylmethyl.¹⁹ The fact that the 4-chloro-substituted compound (III) displays the same spectrum as the

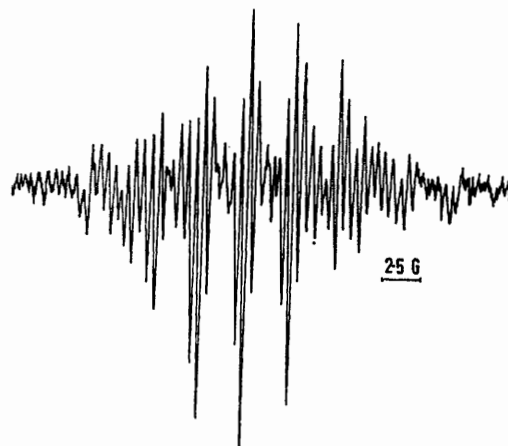


FIGURE 4 E.s.r. spectrum of the radical anion produced by electrolysis of 4-biphenyl(phenyl)methane

unsubstituted one is in agreement with recent results on the polarographic reduction of 4-chlorobenzophenone, where heterolytic decomposition of the radical anion to a chloride ion and a neutral radical was found.²⁰

Finally the appearance of the spectrum of the unsubstituted benzophenone radical anion when the 3-chloro-derivative (IV) is submitted to electrolysis can be explained by a reductive cleavage of the substituent. In fact, the working potential corresponds to the value of the second wave of 3-chlorobenzophenone.

Second Wave.—The second wave of sulphide (V) displays characteristics which are quite close to those of 4-biphenyl(phenyl)methane. In fact, it is reversible and has the same $E_{\frac{1}{2}}$. Moreover after exhaustive electrolysis of (V) at the first-wave potential, the wave remains unchanged and if one continues the electrolysis at more negative potentials, it is possible to register the spectrum of Figure 4. The wave corresponds to

¹⁸ P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, 1962, **37**, 2811.

¹⁹ U. Mazzucato, G. Beggiato, and G. Favero, *Tetrahedron Letters*, 1966, 5455; G. Favero and U. Mazzucato, *Photochem. Photobiol.*, 1967, **6**, 589.

²⁰ L. Nadjo and J. M. Saveant, *J. Electroanal. Chem.*, 1971, **30**, 41.

the reduction of the hydrocarbon to its anion radical. The second wave of sulphides (II), (III), and (IV), which is irreversible as shown by p.s.c. analysis, should correspond to the electrochemical cleavage of C-Cl bond to give diphenylmethane and chloride ion. This step, in fact, is still present after electrolysis at the first wave potential is completed and its $E_{1/2}$ is equal to the $E_{1/2}$ of 4-chlorophenyl(phenyl)methane. G.l.c. ana-

lysis of the electrolysed solutions at the potential of the second wave established that halogenated diphenylmethane, the product of the electrolysis of the first wave, is completely transformed into unsubstituted diphenylmethane.

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