Single-electronic Cleavage of a Carbon–Sulphur Bond in the Cathodic Reduction of 2,3-Bis(phenylsulphonyl)-1,4-dimethylbenzene in Dimethyl Sulphoxide

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2,3-Bis(phenylsulphonyl)-1,4-dimethylbenzene, dissolved in dimethyl sulphoxide, undergoes a one-electron single reduction wave at −1.6 V with respect to Ag–Ag$^+$ (0.01M). The reduction was studied by differential pulse polarography, cyclic voltammetry, and controlled-potential electrolysis. Fast chemical steps follow the initial reduction and the isolated products are 1,4-dimethyldibenzothiophene 5,5-dioxide and 1,4-dimethyl-2-(phenylsulphonyl)benzene. In some experiments small percentages of 5a,9a-dihydro-1,4-dimethyldibenzothiophene 5,5-dioxide are also obtained. The results argue in support of the electron-transfer mechanism previously proposed for the photoinduced reactions of the same substrate with sodium arenethiolates in dimethyl sulphoxide.

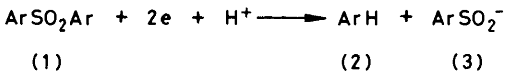
Several studies[1] on the electrochemical behaviour of diaryl sulphones show that their cathodic reduction involves a two-electron fission of the carbon–sulphur bond leading to arene and arenesulphinate anion [equation (1)]. Two distinct mechanisms have been proposed for this electrode process and the prevalence of one over the other appears to depend mainly on the kind of solvent used.

In dipolar aprotic solvents (Scheme 1), two one-electron reduction waves have been in general observed by polarography. The first electron uptake corresponds to the reversible formation of the radical anion (4), which then is reduced at a more negative potential to the corresponding dianion (5). Protonation of (5), more or less contemporaneous with the acquisition of the second electron, gives rise to the C–S bond cleavage with formation of the final products (2) and (3) (e.e.c. mechanism).

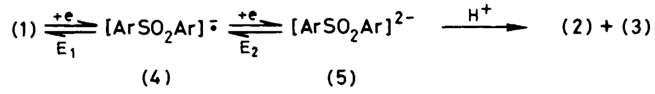
On the other hand, a two-electron single reduction wave has been observed in media with higher proton disposibility. In these cases, it has been proposed (Scheme 2) that the proton transfer occurs to the less basic radical anion (4). The resulting neutral radical (6) is reduced at the same potential and consequent fragmentation into the final products (2) and (3) occurs (e.c.e. mechanism).

The electrochemical behaviour of diaryl sulphones is in agreement with the results obtained by Rossi and Bunnett[2] in the reaction of diphenyl sulphone with solvated electrons in liquid ammonia. Under these conditions, phenyl anion, which gives benzene as final reaction product, has been proposed as the immediate product of cleavage either according to path A or B of Scheme 3. Actually there was no experimental evidence that the radical anion (8) could decay by furnishing phenyl radical and benzenesulphinate anion as in the alternative path C of Scheme 3.

The results found by some of us[3] for the photostimulated reactions of 2,3-bis(phenylsulphonyl)-1,4-dimethylbenzene (9) with sodium arenethiolates in dimethyl sulphoxide were in contrast to all the above findings. The collected data, in fact, were interpreted on the basis of a preliminary single-electron transfer (s.e.t.) from the arenethiolate anion to (9), to give the radical anion (10), which fragments into the intermediate σ radical (11) and benzenesulphinate (Scheme 4). The successive transformation of (11) gives rise to the formation of a mixture of the substitution product (12), the cyclization product (14), and the reduction product (15).

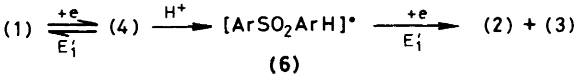


$$\underset{(1)}{ArSO_2Ar} + 2e + H^+ \longrightarrow \underset{(2)}{ArH} + \underset{(3)}{ArSO_2^-} \quad (1)$$



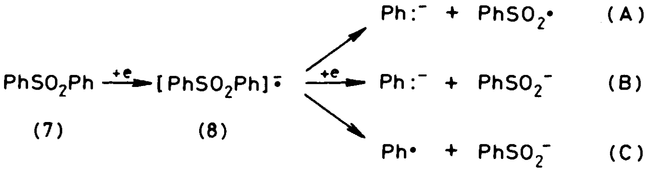
$$(1) \underset{E_1}{\overset{+e}{\rightleftharpoons}} \underset{(4)}{[ArSO_2Ar]^{\cdot-}} \underset{E_2}{\overset{+e}{\rightleftharpoons}} \underset{(5)}{[ArSO_2Ar]^{2-}} \xrightarrow{H^+} (2) + (3)$$

Scheme 1.



$$(1) \underset{E_1'}{\overset{+e}{\rightleftharpoons}} (4) \xrightarrow{H^+} \underset{(6)}{[ArSO_2ArH]^{\cdot}} \underset{E_1'}{\xrightarrow{+e}} (2) + (3)$$

Scheme 2.



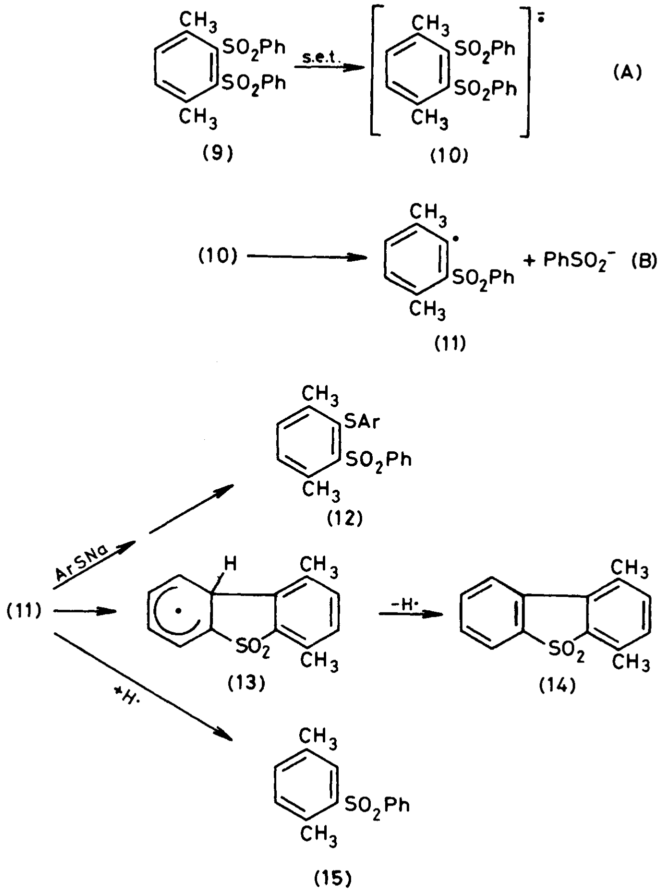
Scheme 3.

On the basis of these considerations, an investigation of the cathodic reduction of (9) appeared to be required in order to confirm the proposed mechanism.

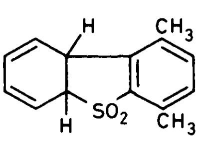
Results and Discussion

Differential pulse polarography (d.p.p.) of the bis-sulphone (9) (substrate concentration *ca.* 10^{-3}M in dimethyl sulphoxide containing tetra-n-butylammonium fluoroborate as supporting electrolyte) carried out with a platinum cathode and at room temperature (20 ± 0.1 °C) displayed four reduction current maxima with peak potentials at −1.62, −2.02, −2.36, and −2.59 V [*versus* Ag–Ag$^+$ (0.01M)].

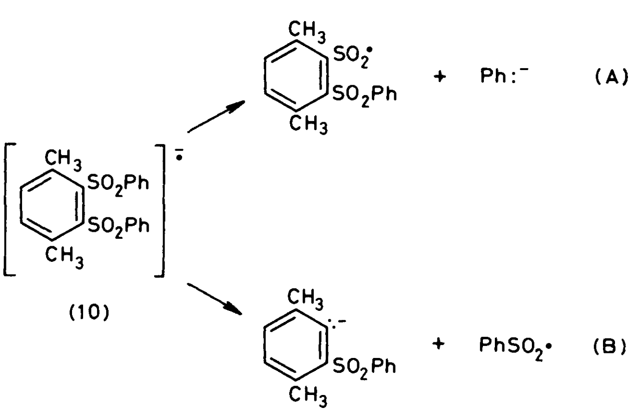
An independent d.p.p. experiment performed on the dibenzothiophene derivative (14) showed two reduction peaks at −2.01 and −2.59 V. The second and fourth reduction steps



Scheme 4.



(16)



Scheme 5.

observed in the experiment carried out on (9) could be, therefore, reasonably attributed to the formation of this compound during the electrolytic reduction of (9). In a similar manner the third reduction peak observed for (9) could be attributed to the monosulphone (15).

Fast linear sweep and cyclic voltammetric analyses of the same solution were in agreement with the above results. Moreover, experiments carried out in the potential range corresponding to the first voltammetric peak (-1.5 to -1.9 V) showed that there was no tendency toward chemical reversibility when raising the sweep rate up to the maximum allowed by the instrument (100 V s^{-1}). Conversely, the polarographic study of (9) at a dropping mercury electrode (d.m.e.) showed for the first electrode process a behaviour similar to an electrochemically reversible one. Surprisingly enough by plotting $E_{d.m.e.}$ against log $[(i_d - i)/i]$ a straight line was in fact obtained (r 0.9998) and the slope observed (52 mV at 20 °C) was very close to the value of 58 mV expected for a reversible one-electron addition. The above results suggest that the electrode process is complicated by very fast chemical events which follow the initial reduction step. Further investigation with the aid of other voltammetric diagnostic criteria appears to be therefore necessary in order to elucidate the electrode mechanism completely.

Controlled-potential electrolyses (c.p.e.) of (9) were carried out at a potential corresponding to the plateau of the first polarographic wave (-1.7 V). Several independent experiments, performed on different amounts of (9), indicated that the charge consumption was 0.99 ± 0.04 F mol^{-1}. Chemical analyses of the electrolysis products, performed by conventional work-up (fully described in the Experimental section), led to the isolation of 1,4-dimethyldibenzothiophene 5,5-dioxide (14) (71%) and of 1,4-dimethyl-2-(phenylsulphonyl)-benzene (15) (23%). It is worth noting that these relative yields of (14) and (15) are very similar to those obtained[3] in the photostimulated reactions of (9) with sodium arenethiolates in dimethyl sulphoxide. The structures of the two electrolysis products were confirmed by comparison with authentic samples (mixed m.p.s, t.l.c., and ^1H n.m.r. spectra) prepared as previously reported by us.[3]

In some c.p.e. experiments the yield of (14) slightly decreased and 5a,9a-dihydro-1,4-dimethyldibenzothiophene 5,5-dioxide (16) was isolated in 5—8% yield. The assignment of structure (16) was done on the basis of elemental analysis and ^1H n.m.r. spectra.

The obtained electrochemical and chemical data show that products (14) and (15) arise from the electrolytic reduction of (9) corresponding to the first voltammetric wave. Considering that both the coulometric and polarographic measurements indicate that one electron per molecule of substrate is consumed in the first reduction step, the most rational way to explain these results is again that shown in Scheme 4. Even if no direct attempt has been made to detect the radical anion (10) (*e.g.* by e.s.r. spectroscopy), the formation of radical anions in the electrochemical reduction of aromatic sulphones is well documented.[1]

To our knowledge the reported behaviour of (9) represents the first example of one-electron C–S bond cleavage occurring on aromatic sulphones (e.c. mechanism).

Fragmentation of (10) according to equation (B) of Scheme 4, instead of the alternative ways shown in Scheme 5, is, in our opinion, supported by the following facts: (*a*) the formation of compound (14) which can be reasonably conceived to occur only *via* intramolecular free-radical substitution from (11); (*b*) the isolation in some c.p.e. experiments of the dihydro-derivative (16), which can be envisaged to arise from disproportionation[4] of the intermediate cyclohexadienyl radical (13) leading to (14); (*c*) the lack, in the catholyte, of any appreciable (g.l.c.) amount of benzene which would arise from protonation of the phenyl anion generated by path (A) of Scheme 5.

To shed more light on the behaviour of aromatic sulphones in electron-transfer reactions, further electroanalytical and photochemical studies are in progress.

Experimental

^{1}H N.m.r. spectra were taken on a Varian FT 80 spectrometer using Me_4Si as an internal standard. G.l.c. analyses were carried out on a Carlo Erba Fractovap 4160 chromatograph equipped with an OV 1 capillary column and a flame-ionization detector. Polarographic measurements were carried out at room temperature (20 ± 0.1 °C) on a Tacussel pulse polarograph model PRG 4 equipped with a potentiostat model PRT 30-01 which is controlled by a command signal furnished and programmed by a pulse control unit model UAP 4. The electrochemical cell was a Tacussel assembly model CPRA. Current–potential and current–time curves were recorded on a Linseis *X–Y* recorder model LY 1800.

All potentials reported in this paper are referred to the $Ag-Ag^+$ (0.01M) reference electrode in the solvent used (double-junction type).

Materials.—The supporting electrolyte, tetra-n-butylammonium fluoroborate (TBAF), was a Fluka AG reagent and was used without further purification. Spectroscopic grade dimethyl sulphoxide, distilled under reduced pressure over calcium hydride, was stored over molecular sieves (type 4A). Cell solutions were deoxygenated by using high purity argon which was previously passed through columns of granular silica gel.

2,3-Bis(phenylsulphonyl)-1,4-dimethylbenzene (9), 1,4-dimethyldibenzothiophene 5,5-dioxide (14), and 1,4-dimethyl-2-(phenylsulphonyl)benzene (15) were prepared as already reported.[3]

Constant-potential Electrolysis of (9) *and Determination of the Reaction Products.*—Preparative-scale reductions of (9) were carried out at −1.7 V. Compound (9) was dissolved in anhydrous dimethyl sulphoxide [150 ml per mmol of (9)] containing 0.1M-TBAF as supporting electrolyte. The solution was placed in the cathode compartment of a H-type electrolysis vessel fitted with a mercury pool cathode, a salt bridge connection to an $Ag-Ag^+$ (0.01M) electrode, and an argon inlet. The anode compartment contained 0.1M electrolyte in dimethyl sulphoxide and a platinum anode. Reduction was continued, under magnetic stirring, until the current fell to a negligibly low value. In order to correct for the background current, the quantity of electricity given by the reduction of (9) (0.99 ± 0.04 F mol^{-1}) was determined by the method of plotting the charge as a function of time and extrapolating the linear portion back to zero time.

The catholyte was then poured into brine and extracted with ether. The ether extract was washed with brine, dried (Na_2SO_4), and the solvent removed on a rotoevaporator under reduced pressure. The residue, dissolved in dichloromethane, was chromatographed on a silica gel column using dichloromethane as eluant. After the first fractions containing traces of an unidentified product, 1,4-dimethyl-2-(phenylsulphonyl)benzene (15) was obtained in 23% average yield, m.p. 111 °C (from EtOH) (lit.,[5] 111—112 °C). The ^{1}H n.m.r. spectrum was identical with that of an authentic sample. The successive fractions eluted from the column gave 1,4-dimethyldibenzothiophene 5,5-dioxide (14) (71% average yield) which was identified by ^{1}H n.m.r. spectroscopy and mixed m.p. with an authentic sample.

In some experiments 5a,9a-*dihydro*-1,4-*dimethyldibenzothiophene* 5,5-*dioxide* (16) (5—8%) was collected from the column after (15) and (14). Compound (16) had m.p. 172 °C (from EtOH), δ_H ($CDCl_3$) 7.20 (2 H, AB pattern, *J* 7.7 Hz, H-2 and -3), 6.44 (1 H, dd, *J* 5.1 and 10.6 Hz, H-7), 6.01 (2 H, m, H-5a and -9a), 5.61 (1 H, d, *J* 10.6 Hz, H-6), 4.47 (1 H, d, *J* 10.8 Hz, H-9), 4.17 (1 H, dd, *J* 5.1 and 10.8 Hz, H-8), 2.62 (3 H, s, CH_3), and 2.39 (3 H, s, CH_3) (Found: C, 68.3; H, 5.8; S, 13.0. $C_{14}H_{14}O_2S$ requires C, 68.3; H, 5.7; S, 13.0%).

Qualitative g.l.c. analysis of the reaction mixture was also carried out in order to verify the possible formation of benzene. For this purpose the catholyte (30 ml) was poured into brine and extracted with n-pentane (4 × 5 ml). The pentane extract was washed with brine, dried over molecular sieves (type 4A), and analysed by g.l.c. Blank experiments showed that $<5\%$ of benzene in the reaction mixture could be detected by this procedure.

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