# Electrochemical Reactions. Part 22.[1] Intramolecular Trapping of Radical Intermediates in the Reduction of Arylsulphones

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The cyclic sulphone (1) gives a radical ion which is stable in dimethylformamide on the time scale of cyclic volt-ammetry and the *ortho*-substituted diarylsulphone (3) shows only irreversible electrochemical behaviour. Either sulphone at the potential of the first reduction wave gave products which indicate decomposition of the radical anion by cleavage of a carbon–sulphur bond to form an aryl radical and sulphinate ion. The isolated products result from intramolecular trapping of the aryl radical intermediate.

DIARYL and aryl alkyl sulphones can be reduced at a mercury cathode in both methanol and dimethylform-amide solution. The polarographic half-wave potentials for these processes are in the region of $-2.0$ to $-2.3$ V *vs.* s.c.e.[2-4] In protic solvents the direction of cleavage of aryl alkyl sulphones depends upon the electron-withdrawing properties of substituents on the aryl ring. Sulphones bearing no strongly electron-withdrawing substituents afforded the arylsulphinic acid and hydro-carbons derived from the alkyl group R, principally RH but also present were ethane in the case of R = Me and ethylene in the case of R = Et.[5] Cleavage was con-sidered to occur by the steps:

$$ArSO_2R + e \longrightarrow ArSO_2^- + R^\circ$$
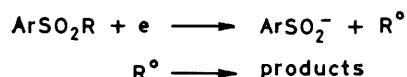
$$R^\circ \longrightarrow products$$

When the aryl group bears a strongly electron-with-drawing substituent the products are the alkylsulphinic acid and Ar-H. A reaction scheme was proposed [3] for the addition of two electrons and a proton in fast, consecutive steps to the aryl ring followed by cleavage of the carbon–sulphur bond:
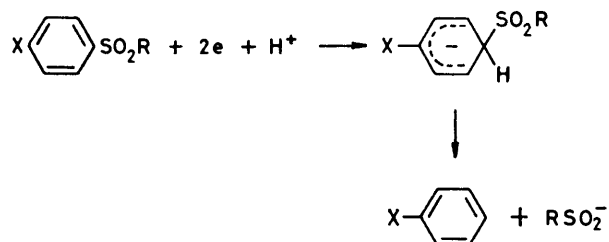


Cyclic voltammetry of diphenyl sulphone in methanol shows only one irreversible cathodic peak ($E_p$ $-207$ V *vs.* AgCl electrode) and in dimethylformamide two cathodic peaks ($E_p$ $-2.19$ and $-2.65$ V *vs.* AgCl electrode).[4] In dimethylformamide, the first peak is reversible and the radical anion formed at this potential can be detected by e.s.r. measurements.[6] The second peak is irreversible and corresponds to addition of a second electron to form the dianion which decomposes. Diaryl sulphones with *meta*- and *para*-alkyl, $CO_2Me$, $CONH_2$, or CN substituents show similar behaviour. Diaryl sulphones with two or more *ortho*-substituents on one or both aryl rings show two irreversible cathodic peaks in aprotic solvents,[4] and the radical anions of such sulphones have not been detected. A parallel to these observations is known for

the stability of radical anions derived from nitroaryl halides.[7] Substituents *ortho*- to the halogen greatly increase the rate of carbon–halogen bond cleavage in these radical-anions. Cleavage of diphenyl sulphones is thought [4,8] to follow an ECE mechanism in protic

$$PhSO_2Ph + e \longrightarrow radical\ ion$$
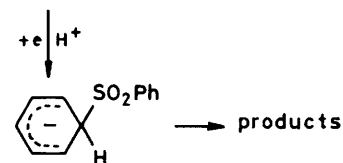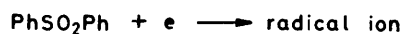


solvents (above) and an EEC mechanism for cyclic voltammetry in aprotic solvents at fast sweep rates:

$$PhSO_2Ph + e \rightleftharpoons radical\ ion$$



$$dianion \xrightarrow{H^+} C_6H_6 + PhSO_2^-$$
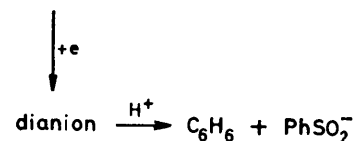
At slow sweep rates in dimethylformamide, the first peak looses its reversible character. It was suggested [4] that this is because the rate of protonation of the radical anion by traces of water becomes important so that the reaction follows an ECE route as in protic solvents.
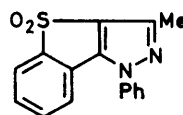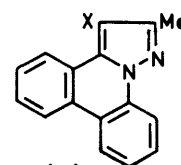


(1)          (2)

Cleavage of the diphenyl sulphone radical anion to benzene sulphinate ion and phenyl radical, followed by further reduction and protonation of the radical to give benzene has not been considered as a possible pathway in these reactions. There is however some evidence in the literature in favour of phenyl radical intermediates. Biphenyl has been isolated in low yield from reduction of diphenyl sulphone at a mercury cathode.[5] More significantly, reduction of the cyclic sulphone (1) with sodium and ethanol gives a good yield of the sodium sulphinate (2; X = $SO_2^-Na^+$). This loses sulphur dioxide on acidification to give (2; X = H) which is

referred to as ' product A ' by Barry and McClelland.[9] 3-Methyl-1,5-diphenylpyrazole is probably also formed in this reaction since its reduction product, the $\Delta^2$-pyrazoline, was isolated. Reduction of (1) with sodium amalgam and ethanol gave 3-methyl-1,5-diphenyl-pyrazole as the only isolated product. The formation of (2; X = $SO_2^-Na^+$) can be rationalised by assuming that addition of an electron to (1) causes cleavage of a carbon–sulphur bond to give sulphinate ion and a σ-radical. The radical centre then undergoes intra-molecular radical substitution on the adjacent benzene ring. We have previously shown that related intra-molecular substitution reactions of radicals derived by reduction of aryl halides in aprotic solvents proceed in good yields in spite of competition from other reactions of the radical centre.[10] Cyclic voltammetry of (1) in dimethylformamide showed the reversible addition of one electron at slow sweep rates and an irreversible reaction at more negative potentials. A preparative-scale reaction at the potential required to form the radical anion effected the conversion of (1) into (2; X = $SO_2^-$) so this radical anion is not stable on a relatively long time scale. The product was isolated as (2; X = H).

A second example of trapping of some reactive inter-mediate by an intramolecular process was provided from reduction of the sulphone (3). Cyclic voltammetry of (3) in dimethylformamide indicates two irreversible electron-addition steps in agreement with the behaviour of other ortho-substituted diaryl sulphones. This sul-phone shows two N–CH$_3$ resonances in the n.m.r. spectrum (ratio 88 : 12) due to restricted rotation about the amide bonds. The resonance at lower field is due to a syn-arrangement of aryl groups and for N-methyl-benzanilides bearing one ortho-substituent, the major rotamer at equilibrium has this syn-arrangement of aryl groups.[10] Three isomers of (3), due to this restricted rotation, are possible. The major component of this equilibrium mixture will have the syn,syn-arrangement of rotamers and this gives rise to the lower field resonance only. The next favoured isomer will have the syn,anti-arrangement and gives rise to two N-CH$_3$ resonances. The syn : anti ratio at equilibrium for one amide group is sufficiently large for the anti,anti-form of (3) to be present in negligible amount. Thus (3) contains 76% syn,syn-form and 24% syn,anti-form, the latter contributing equally to both N-CH$_3$ resonances.

Reduction of (3) in dimethylformamide at a mercury cathode afforded sulphinic acid, which was removed, and a mixture of (4; X = H), (6), and (7) which was sepa-rated by a combination of t.l.c. and fractional crystallis-ation. The yields of these products were determined by analysis of the mixture using n.m.r. spectroscopy and these yields were compared in Table 1 with those obtained by reduction of the 2-halogeno-N-methylbenzanilide (4; X = Br and I).

Reduction of aryl halides gives rise to the aryl radical and a halogen ion and radicals like (5) are known[10] to cyclise as shown giving (6) and (7). Some of the syn-radical (5) and all of the corresponding anti-radical

undergoes addition of an electron and a proton to give (4; X = H) or its anti-rotamer.



(3)

(4)

(5)

(6)        (7)
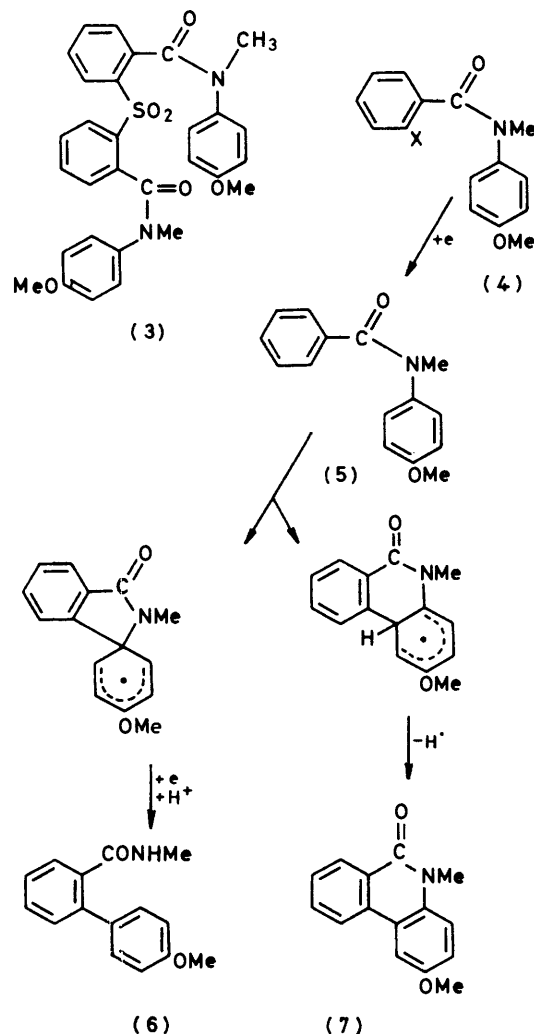
Since the same products are obtained by reduction of the sulphone (3), intramolecular trapping of some reactive intermediate also occurs in this reaction. The reactive

TABLE 1

Relative yields of products after reduction in dimethylformamide at a Hg cathode

| Compound | Solvent | V vs. s.c.e. | Relative yields [a] | | |
| --- | --- | --- | --- | --- | --- |
| | | | (4; X = H) | (6) | (7) |
| (3) | DMF | −2.0 | 22 | 50 | 28 |
| (4; X = Br) | DMF | −1.9 | 33 | 23 | 44 |
| (4; X = I) | DMF | −1.6 | 47 | 25 | 28 |
| (3) | Water | −1.9 | 26 | 63 | 11 |

[a] After removal of sulphinic acids where necessary, only starting material and these products were detected.

intermediate is unlikely to be a carbanion since nucleo-philic substitution on an unactivated benzene ring is very unlikely. The intermediate which is trapped must be either the radical anion of (3) or the σ-radical (5). In the case of the conversion of the cyclic sulphone (1) into (2, X = $SO_2^-$) the reactive intermediate which is trapped

cannot be the radical anion since the geometry of the system does not allow such a reaction to give the observed product. Assuming that the reactive intermediate is of the same type in both these examples, it can only be the σ-radical Thus reduction of (3) involves cleavage of the radical ion to (5) and a sulphinic acid.

We have found two examples of diaryl sulphone radical anions which decompose in dimethylformamide to give an aryl radical and aryl sulphinate ion, one at a rate too slow and the other too fast to measure by cyclic voltammetry. This route for the decomposition of diaryl sulphone radical anions in aprotic solvents is probably very general.

Reduction of (1) in methanol by sodium also gives (2, $X = SO_2^-Na^+$) so that radical intermediates are also involved in this reaction. Reduction of the sulphone (3) in methanol at a mercury cathode gave a low yield of (4), (6), and (7), identified by n.m.r. spectroscopy. Even in protic solvents decomposition of the radical anion to aryl radicals competes with protonation as a step in the reductive cleavage of diaryl sulphones.

EXPERIMENTAL

Dimethylformamide was purified by successive shaking with anhydrous $CaSO_4$ and $CuSO_4$ and then distillation under a nitrogen atmosphere at 14 mmHg. Potentials were measured with respect to a saturated calomel electrode. The AgAgCl, KCl sat. electrode used by Horner has potential $-0.045\ 5$ V $vs.$ s.c.e.[11]

*Di*-[N-(4-*methoxyphenyl*)-2-*carboxamidophenyl*] *Sulphone.* —Di-(2-carboxyphenyl) sulphone [12] (5.0 g) was converted into the acid chloride using thionyl chloride. The crude acid chloride was added to 4-methoxyaniline (5.0 g, 2.4 mol) in anhydrous pyridine (30 ml) and the mixture added, after 2 h, to an excess of dilute hydrochloric acid. The precipitated *amide* crystallised from aqueous ethanol as needles (7.0 g), m.p. 130—131 °C (Found: C, 64.9; H, 4.6; N, 5.6; S, 6.3. $C_{28}H_{24}N_2O_6S$ requires C, 65.1; H, 4.7; N, 5.4; S, 6.2%).

*Di*-[N-*methyl*-N(4-*methoxyphenyl*)-2-*carboxamidophenyl*)] *Sulphone* (3).—Dimethyl sulphate (3 ml, *ca.* 6 mole) was added slowly to a refluxing solution of the above amide (1.5 g) in acetone (20 ml) and aqueous 10% sodium hydroxide (20 ml). After 2 h, the mixture was poured into water, the product isolated with ether, dried $(Na_2SO_4)$, and chromatographed over neutral alumina, with ether as eluant. Evaporation of the solvent left the N-*methylamide* (3) as a gum which crystallised after some time and was recrystallised from diethyl ether–light petroleum (b.p. 40—60 °C) as octahedra, m.p. 70—71 °C (Found: C, 66.0; H, 5.3; N, 5.2; S, 5.8. $C_{30}H_{28}N_2O_6S$ requires C, 66.2; H, 5.2; N, 5.1; S, 5.9%). The n.m.r. spectrum showed signals due to $CH_3$ as one pair of large peaks δ 3.65 ($OCH_3$) and 3.42 ($NCH_3$) and one pair of smaller peaks $v$ 3.79 ($OCH_3$) and 3.12 ($NCH_3$) in a ratio of 88 : 12.

*Cyclic Voltammetry.*—The working electrode was a mercury-coated platinum sphere (0.15-cm diameter), solvent dimethylformamide 0.1M-tetrapropylammonium perchlorate, substrate concentration $10^{-3}$ M. The cyclic sulphone (1) showed two cathodic peaks $E_{P1} - 1.805$ V, $E_{P1} - 2.34$ V at scan rate 0.10 V s$^{-1}$; the second peak was irreversible. When the scan was limited to $-2.0$ V, the first peak showed

reversible behaviour with $E_{pc} - 1.805$ V, $E_{pa} - 1.745$ V, $i_{pa}/i_{pc}$ 0.95. The sulphone (3) showed two irreversible cathodic peaks $E_{P1} - 2.29$ V, $E_{P2} - 2.60$ V at scan rate 0.10 V s$^{-1}$.

*Reduction of the Cyclic Sulphone* (1).—The sulphone (1) [9] (0.20 g) in dimethylformamide (10 ml) containing tetrapropylammonium perchlorate (0.1M) was reduced at a mercury cathode (potential $-1.8$ V $vs.$ s.c.e.). The reaction mixture was poured into water, acidified, and the precipitate of (2, $X = SO_2H$) collected and refluxed with 2M-sulphuric acid for 30 min. Dilution with water precipitated 2-methylpyrazolo[1,5-*f*]phenanthridine (0.13 g) which crystallised from ethanol as needles, m.p. 120—121 °C (lit.,[9] m.p. 122—124 °C), $M^+$ 232.

*Reduction of the Sulphone* (3).—The sulphone (3) (0.10 g) in dimethylformamide (15 ml) containing 0.1M-tetrapropylammonium perchlorate was reduced at a mercury cathode (potential $-2.0$ V $vs.$ s.c.e.). Reaction was complete in 6 h and the mixture was diluted with 0.1M-sodium hydroxide. The precipitated yellow gum was collected using chloroform, dissolved in acetone (50 ml), and set aside for a few hours with an excess of potassium permanganate to oxidise any sulphinic acid. Water was then added, the mixture decolourised by passage of sulphur dioxide, and the product extracted with diethyl ether; the extract was dried $(Na_2SO_4)$ and the solvent removed. The residual oil was examined by n.m.r. spectroscopy. Preparative t.l.c. on

TABLE 2

N.m.r. spectra of reaction products $(CDCl_3)$

| Compound | $OCH_3$ δ | $NCH_3$ δ |
|---|---|---|
| (4; X = H) | 3.74 | 3.45 |
| (6) | 3.86 | 2.58 [a] |
| (7) | 3.94 | 3.81 |

[a] Doublet, $J = 5$ Hz.

silica gel, with benzene–chloroform (1 : 1) as eluant, afforded a major fraction which could be separated into two components by crystallisation from chloroform–ether. The least-soluble component was 3-methoxy-5-methylphenanthridone, m.p. 160—161 °C (lit.,[10,13] m.p. 161 °C), and the more-soluble component 4'-methoxy-N-methylbiphenyl-2-carboxamide, m.p. 134—135 °C (lit.,[10,14] m.p. 133—134 °C).

In order to compare product yields, 2-bromo-and 2-iodo-4'-methoxy-N-methylbenzanilide were reduced at a mercury cathode in dimethylformamide, and the products isolated and analysed by n.m.r. spectroscopy (see Table 1) as described previously.[10]

In another experiment, the amide (3) was reduced in methanol saturated with tetrapropylammonium perchlorate at a mercury cathode (potential $-1.9$ V) for 6 h. Work-up as described above including oxidation with potassium permanganate gave starting material and the relative yields of other products indicated in Table 1.

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