Cathodic Behaviour of Vinylic Sulfones in Weakly Acidic Media

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Four vinylic sulfones, namely, (E)-2-phenyl-vinyl phenyl sulfone, (E)-1-methyl-2-phenyl-vinyl phenyl sulfone, (Z)-1,2-diphenylvinyl phenyl sulfone, and 2,2-diphenylvinyl phenyl sulfone, and the cyclic unsaturated sulfone benzo[b]thiophene-1,1-dioxide have been reduced at a mercury cathode in N,N-dimethyl-formamide solution. The four open-chain compounds yield the corresponding olefins and benzenesulfinate ion (in one case some saturation of the double bond was also observed). The cyclic sulfone is hydrogenated, forms a hydrodimer, or polymerizes, depending on the acidity of the medium.

Polarography and cyclic voltammetry show that with one exception, the reduction potential is shifted in the anodic direction as the acidity of the solvent increases, phenol being used as the proton donor. From the electroanalytical data and the preparative results, a detailed mechanism for the cathodic cleavage is presented.

The electrochemical reduction of sulfones is characterized by cleavage of a carbon-sulfur bond rather than reduction of the sulfonyl group. For example, alkyl aryl sulfones are split at a mercury cathode to yield alkanes and arenesulfinate ions.[1,2] In their extensive study of sulfones, Horner and Neumann [1] included allyl phenyl sulfone, which was found to yield propene and benzenesulfinate ion. Hydrogenation of the allylic double bond was not observed. On the other hand, if a carbon-carbon double bond is conjugated with a sulfonyl group, cathodic reduction of the double bond seems to take place. Phenyl vinyl sulfone is thus converted to ethyl phenyl sulfone,[3] and methyl vinyl sulfone similarly is supposed to yield ethyl methyl sulfone.[4] However, other workers report that methyl vinyl sulfone may be cathodically cleaved to ethene and methanesulfinate ion,[5] the evidence being, however, indirect.

A non-electrochemical cleavage of some phenyl substituted vinyl aryl sulfones with aluminium amalgam in water-containing tetrahydrofuran has been reported by Pascali and Umani-Ronchi.[6] Under their conditions, olefins were exclusively produced.

Since *a priori* different reaction modes are possible, we considered it worth-while to make an electrochemical study of substituted vinyl phenyl sulfones. They might be cathodically cleaved to yield olefins, or the double bond might become saturated. A third possibility is hydrodimerization, an electrochemical reac-
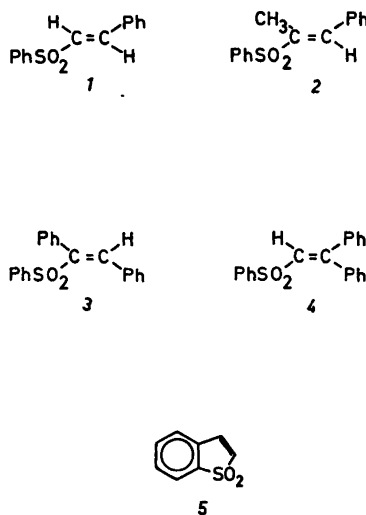

Fig. 1. Unsaturated sulfones investigated in this work.

Table 1. Polarographic and coulometric data for sulfones studied in this work.

Compound	Conc. ×10³/M	$E_{1/2}$/V [a] [i_d/μA]			$E_{1/2}$/V [b] [i_d/μA]		Coulometry F mol⁻¹ (at potential V) a	b
PhSO₂CH=CHPh (1)	1.00	−1.15 [2.7]	−1.63 [2.0]	−1.91 [3.8]	−1.05 [4.5]	−1.87 [4.0]	2.1 (−1.4)	2.1 (−1.4)
PhSO₂CMe=CHPh (2)	1.55	−1.48 [5.0]	−1.70 [3.0]	−2.25 [2.0]	−1.41 [9.0]	−2.17 [4.0]	1.9 (−1.6)	2.1 (−1.5)
PhSO₂CPh=CHPh (3)	1.30	−1.20 [6.0]	−1.60 [4.0]		−1.20 [12]	−1.60 [10]	2.7 (−1.4)	2.3 (−1.4)
PhSO₂CH=CPh₂ (4)	1.30	−1.19 [7.0]	−1.85 [5.0]		−0.98 [7.0]	−1.91 [5.5]	2.3 (−1.45)	2.1 (−1.25)
Benzo[b]thiophene-1,1-dioxide (5)	2.40	−1.07 [7.0]	−1.59 [5.5]	−2.1 [7.5]	−1.02 [16]	−1.97 [10]	1.0 (−1.3)	2.2 (−1.3)

[a] In 0.1 M tetraethylammonium perchlorate (TEAP) in DMF. Potential *vs.* Ag,AgI/0.1 M TBAI in DMF.
[b] In 0.1 M TEAP in DMF. Phenol present in a concentration 4−5 times that of the substrate. Potential *vs.* Ag,AgI/0.1 M TBAI in DMF.

Table 2. Cyclic voltammetry cathodic peak potentials (E_{pc}) for the vinylic sulfones, saturated analogs, and unsaturated hydrocarbons studied in this work. Sweep rate 80 mV s⁻¹.

Compound	E_{pc}/V [a] Unsat. sulfone				E_{pc}/V [a] Sat. sulfone [b]	E_{pc}/V [a] Unsat. hydrocarbon [c]	
PhSO₂CH=CHPh (1)	−1.23	−1.77	−2.06		−1.76	−2.12	
PhSO₂CMe=CHPh (2)	−1.42	−1.83	−2.21		−1.75	−2.20	
PhSO₂CPh=CHPh (3)	−1.25	−1.59	−1.71	−2.09	−1.67	−1.72	−2.08
PhSO₂CH=CPh₂ (4)	−1.23	−1.49	−1.99		−1.75	−1.97	
Benzo[b]thiophene-1,1-dioxide (5)	−1.15	−1.80	−2.03		−1.90	−	

[a] Potential *vs.* Ag,AgI/0.1 M TBAI in DMF. [b] Obtained through cat. hydrogenation of the vinylic double bond of the corresponding unsat. sulfone. [c] Derived from *1−4* through replacement of PhSO₂ by H. For their origin, see the text.

tion which has in fact been observed for methyl vinyl sulfone in an attempted mixed coupling reaction.[5]

The present paper deals with the cathodic behaviour of some α,β-unsaturated sulfones. They are shown in Fig. 1 and will be referred to as *1 − 5*. These compounds have been studied with conventional polarography, cyclic voltammetry at a hanging mercury drop electrode, microcoulometry, and gram-scale electrolysis followed by product identification. All experiments have been made in *N,N*-dimethylformamide (DMF), and the cathode material has been mercury.

RESULTS

Polarography. The results are summarized in Table 1. In the absence of a proton donor, sulfones *1, 2,* and *5* give three waves, and *3* and *4* give two. It is obvious that the first step (reversible) is much less cathodic than the reduction wave for simple aromatic sulfones under similar experimental conditions. For example, methyl phenyl sulfone exhibits a wave (irreversible) at −1.73 V.[7] In the presence of phenol as proton donor, the polarograms are simpler; only two waves are visible. The height of the first one is about twice that of the first wave in aprotic medium (except for *4*) and its half-wave potential has moved to a less cathodic potential (except for *3*).
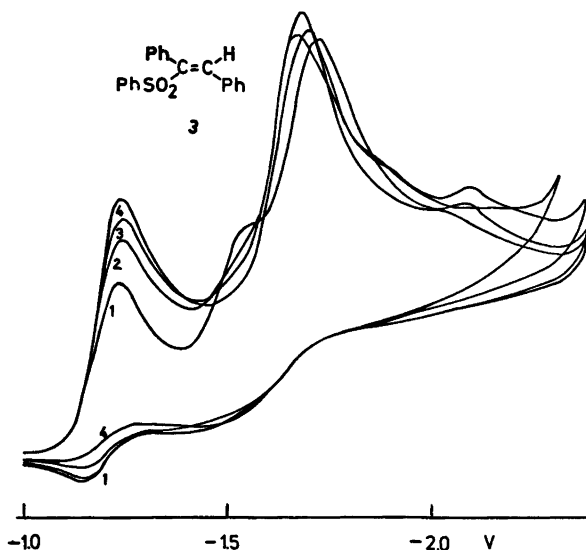
Fig. 2. Cyclic voltammograms of (Z)-1,2-diphenylvinyl phenyl sulfone in DMF. Sweep rate 600 mV s⁻¹, substrate conc. 10^{-3} M. Phenol/substrate ratio 0, 1, 2, and 4 for traces 1, 2, 3, and 4, respectively. Potential *vs.* Ag,AgI/0.1 M TBAI in DMF.

Cyclic voltammetry. The peak potentials are given in Table 2. The behaviour of two representative substrates, *3* and *4*, upon addition of increasing amounts of phenol, is depicted in Figs. 2 and 3. In the absence of phenol (trace 1), three peaks are obtained on the forward sweep. Addition of phenol causes the first peak to increase at the expense of the second one. When the concentration of phenol is four times that of the substrate, two peaks of similar height are obtained (trace 4). The first step, which is totally reversible in the absence of phenol, is then irreversible. The reversibility is separately demonstrated in Fig. 4 for substrate *3*. The influence of phenol on the peak potentials of the first step is shown in Fig. 5. It is important to note the invariance of $E_{1/2}$ for sulfone *3*.
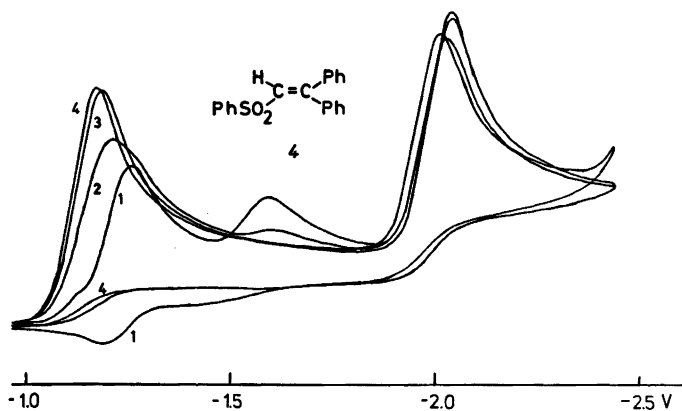

Fig. 3. Cyclic voltammograms of 2,2-diphenylvinyl phenyl sulfone in DMF. Sweep rate 600 mV s⁻¹, substrate conc. 10^{-3} M. Phenol/substrate ratio 0, 0.5, 1.5, and 4 for traces 1, 2, 3, and 4, respectively. Potential *vs.* Ag,AgI/0.1 M TBAI in DMF.
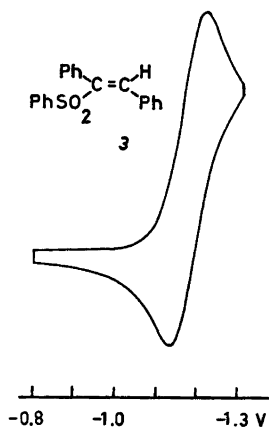
Fig. 4. Cyclic voltammogram of (Z)-1,2-diphenylvinyl phenyl sulfone in aprotic DMF. Sweep rate 250 mV s⁻¹, substrate conc. 10⁻³ M. Potential vs. Ag,AgI/0.1 M TBAI in DMF.
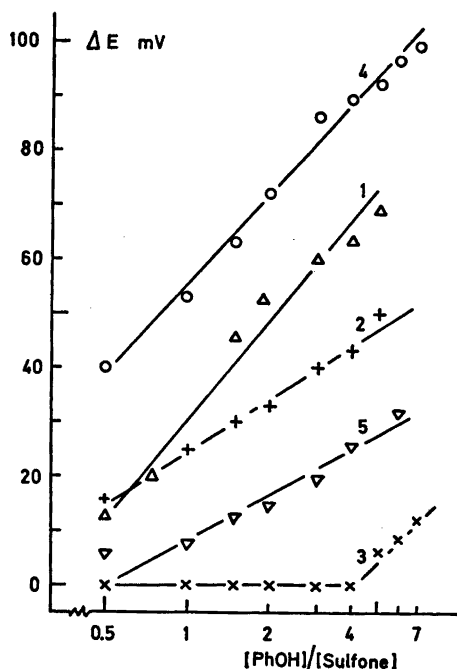

Fig. 5. Shift in potential of the first peak (relative to the aprotic value) in cyclic voltammetry as a function of phenol concentration

The unsaturated hydrocarbons corresponding to 1−4, in which the benzenesulfonyl group is replaced by a hydrogen atom, were separately

investigated under the same conditions as the sulfones. The results are given in Table 2. The peak potentials are seen to correspond to the third peak in the voltammograms of the unsaturated sulfones, suggesting that the latter yield the unsaturated hydrocarbons at the cathode.

Coulometry. Runs at the potential of the first polarographic plateau show that 2 electrons per molecule are consumed in protic media (Table 1). In aprotic medium, this number is 1 for sulfone 5 but about 2 for all others.

Preparative electrolyses. Table 3 shows the conditions of electrolysis and the compounds isolated from each experiment. It should be noted that the yields of products represent lower limits because of workup losses. Remarkably, two runs gave almost quantitative yield.

A positive identification of benzenesulfinate ion was made in one case (compound 3, run with phenol) through conversion to methyl phenyl sulfone.[1,7] In the other runs with 1−4, benzenesulfinate ion was left unidentified.

DISCUSSION

Obviously, the electrochemical reduction of 1−4 leads to unsaturated hydrocarbon in a two-electron process both in aprotic and phenol-containing DMF. A comparable amount of saturated hydrocarbon is also obtained with 3. When the rate of protonation of the radical anion is low (voltammetry in carefully dried DMF), two one-electron steps are observed before hydrocarbon reduction. The dianion formed in the second step can undergo β-elimination followed by protonation to give sulfinate ion and unsaturated hydrocarbon, or it can be protonated (3) to give the mono-anion corresponding to the saturated sulfone.

In phenol-containing DMF, the change in height and position of the first peak in the voltammograms is interpreted in terms of an ECE mechanism. The C reaction is protonation of the radical anion of the substrate. Increasing the phenol concentration causes the peak potential to shift in the anodic direction, except for 3. This behaviour is well-known for many other activated olefins, e.g., aromatic ethylenic ketones.[8]

The unsaturated hydrocarbons resulting from cleavage of 1−4 are further reduced between

*Table 3.* Preparative electrolyses of unsaturated sulfones.

Substrate	Cathode potential[a] V	Phenol/substrate initial molar ratio	Coulometry F mol⁻¹	Products (% yield)
1	−1.1	3.2	1.87	Polystyrene (43)
2	−1.4	4.1	1.95	*trans-β*-Methylstyrene (54)
3	−1.5	5.1	3.6[b]	*trans*-Stilbene (15)
				Bibenzyl (24)
3	−1.5	0	1.63	*trans*-Stilbene (25)
				cis-Stilbene (5)
				Bibenzyl (20)
4	−1.4	6.8	2.3[b]	1,1-Diphenylethene (98)
5	−1.0	5[c]	2.67	Dihydro-5 (98)
5	−1.3	3.0	1.2	Hydrodimer of 5 (12)
5	−1.3	0	0.43	Unidentified polymer

[a] *vs.* Ag,AgI/0.1 M TBAI, DMF. [b] Run was interrupted after passage of this charge. [c] Acetic acid instead of phenol.

−1.7 and −2.2 V in a two-electron process. The radical anions of the hydrocarbons are protonated fast even in the absence of phenol, except that of *3*, which forms stilbene. The radical anion of stilbene is long-lived in dry DMF.

The mechanism found in this work for the cathodic cleavage of the α,β-unsaturated sulfones is different from that of the cleavage of alkyl phenyl sulfones or allyl phenyl sulfone, even though the net outcome is the same. The detailed path is shown in Scheme 1. In the absence of a proton donor, the radical anion is stable and may be further reduced to a dianion at more negative potential, as in a cyclic voltammetry experiment. With increasing proton availability, protonation of the radical anion followed by a second electron transfer occurs to produce an organic anion. Depending on the nature and positions of the substituents at the double bond, protonation will take place at the α or β carbon with respect to the sulfonyl group. In the former case, a β-benzenesulfonyl radical is formed, which after reduction to carbanion undergoes β-elimination (left route in Scheme 1) to yield unsaturated hydrocarbon.
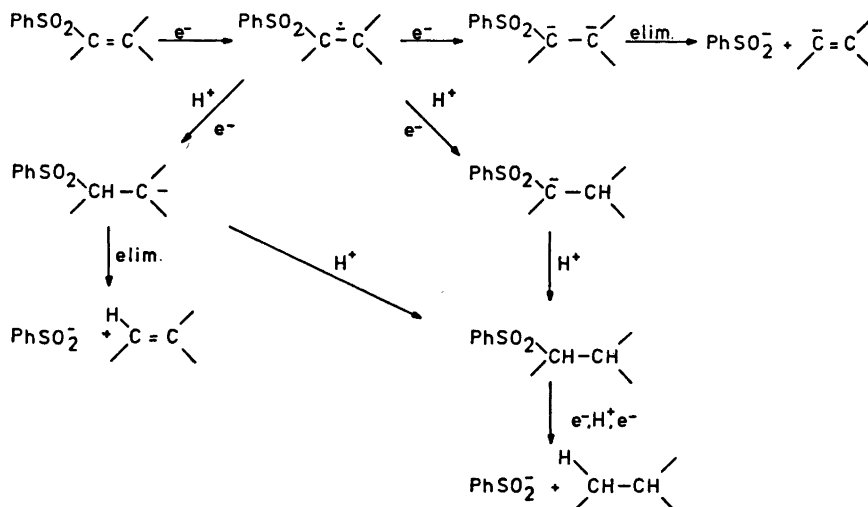
Scheme 1. Mechanism of cleavage of substituted vinyl sulfones in DMF.

On the other hand, if protonation gives an α-benzenesulfonyl radical, this will after reduction to carbanion become protonated to the saturated sulfone (right route in Scheme 1). The latter mode is observed for 3. The possibility that the saturated sulfone undergoes a base-catalyzed β-elimination at the cathode to give unsaturated hydrocarbon will be discussed below.

The cyclic sulfone 5 does not undergo elimination of sulfinate ion in a ring-opening reaction. The reason for this is that the double bond activating the sulfonyl group is also an *ortho* substituent to the same group. After electron transfer to the double bond, the sulfinate ion would be a poor leaving group because of its excess of negative charge.

With sulfone 3, some formation of dihydro-3 has also been observed.[10] In fact, 3 behaves rather differently compared to 1, 2, and 4. The proton donor concentration has a negligible influence on the peak potential of the first step. This suggests that delocalisation of the anionic charge by the substituents at the double bond is excellent. The stability of the anion radical may allow some homogeneous electron exchange with saturated sulfone,[11] at least in weakly acidic media. In this way, one can explain the formation of bibenzyl from dihydro-3 rather than *via* hydrogenation of stilbenes, which would be prohibitively slow at the potential actually employed.

Concerning the stereochemistry, only *trans*-stilbene is formed from 3 in the presence of phenol. The starting material is *trans* with respect to the two phenyl groups,[12] and the elimination step is fast enough to preserve the stereochemistry. In aprotic medium, some *cis*-stilbene is also formed. We may assume that the intermediate anion has a longer life-time so that its geometry partially changes. The resulting anion can give both *cis* and *trans* stilbene through elimination of benzenesulfinate ion.

In conclusion, the present investigation has shown that some substituted vinylic sulfones undergo cleavage at a mercury cathode to yield unsaturated hydrocarbons. Nevertheless, the electrochemical characteristics of the reaction (potential influenced by the acidity of the medium) are typical of hydrogenation reactions of activated olefins.

EXPERIMENTAL

Syntheses. (*E*)-2-Phenylvinyl phenyl sulfone (1, Fig. 1) was prepared from benzaldehyde and methyl phenyl sulfone according to Field.[13] Yield 33 %, m.p. 72−73 °C, lit.[13] 74−75 °C. The ^{1}H NMR spectrum at 60 MHz showed two peaks belonging to an AB pattern at δ 6.65 and 6.92 (CDCl₃), together 1 H. A complex pattern at δ 7.1−8.0, 11 H, contained the other half of the AB pattern and the aromatic proton signals. The coupling constant, 16.2 Hz, established the *E* configuration.

(*E*)-1-Methyl-2-phenylvinyl phenyl sulfone (2) was prepared in analogy with (1) from benzaldehyde and ethyl phenyl sulfone. Yield 13 %, m.p. 92−93 °C, lit.[14] 90 °C.

(*Z*)-1,2-Diphenylvinyl phenyl sulfone (3) was similarly prepared from benzaldehyde and benzyl phenyl sulfone. Yield 44 %, m.p. 187−188 °C, lit.[12] 183 °C.

2,2-Diphenylvinyl phenyl sulfone (4) was prepared from benzophenone and methyl sulfone following the general procedure.[13] Yield 69 %, m.p. 113−114 °C, lit.[15] 114−115 °C.

Benzo[*b*]thiophene-1,1-dioxide (5) was available from previous work.[7]

The ^{1}H NMR spectra of 2−5 were in agreement with those reported in the literature.[13−15]

For comparison purposes, compounds 1−5 were converted to their saturated analogs by catalytic hydrogenation at atmospheric or slightly elevated pressure, using 10 % palladium on charcoal as catalyst and ethanol containing a trace of conc. hydrochloric acid, as solvent.

The unsaturated hydrocarbons derived from 1−4 through replacement of PhSO₂ by H were available in the laboratory (styrene, and *trans*-stilbene), prepared independently through electrolysis of cinnamyl alcohol,[16] (β-methyl styrene), or obtained from a preparative electrolytic reduction of 4 (1,1-diphenyl ethene).

Polarography and cyclic voltammetry. The DMF used for the electroanalytical work was purified as described earlier.[7] Tetrabutylammonium iodide (TBAI) was from Fluka AG, polarography grade. A Tacussel Tipol three-electrode polarograph was used with a sweep rate of 2.5 mV s⁻¹. The supporting salt concentration was 0.15 M, and that of the substrate, 5 × 10⁻³ M. The reference electrode was Ag,AgI/0.1 M TBAI in DMF. Cyclic voltammograms on a hanging mercury drop were recorded using the same solvent and substrate concentration. A standard instrumentation from Tacussel was used. The voltammograms were either registered on a storage oscilloscope and photographed, or on a Houston XY recorder.

Coulometry. A 0.1 M solution of tetraethylammonium perchlorate in DMF was used as supporting electrolyte. The mercury cathode, about 7 cm², was agitated by a magnetic stirring bar, and the platinum anode was separated *via* a glass frit. The catholyte was purged with

nitrogen. The potentiostat and coulometer were a Tacussel type ASA 4SHT and IG4 10A, respectively. Runs were made on 20 – 30 mg of substrate. To the runs with a proton donor, a 3 – 5-fold molar excess of phenol was added. The initial current was about 30 mA. The run was stopped when the decay of current was more than 95 %.

Macroelectrolyses. Potentiostatic conditions were used for all macroelectrolyses. An H-type cell with the cathode and anode compartments separated by two glass frits was employed. The supporting electrolyte was 0.15 M TBAI in DMF. A Tacussel potentiostat with current integrator was used. The catholyte was purged with nitrogen. In each run, about 1 g of substrate was taken into work. After electrolysis, the catholyte was diluted with a ten- to twentyfold amount of water and extracted with ether. This was washed with water, dried over anhydrous sodium sulfate, filtered and evaporated. The residue was analyzed with GLC and ¹H NMR spectroscopy.

In one experiment, the catholyte was extracted with hexane and the extract was analyzed for electrolysis products. An excess of methyl iodide was then added to the DMF phase, which was heated to 50 °C for 3 h in order to convert the benzenesulfinate ion to methyl phenyl sulfone. The DMF solution was diluted with water and extracted with ether as above.

The compounds isolated from the different runs (Table 3) were easily identified through comparison, with authentic samples and/or literature data.

The electrolysis of *5* in aprotic DMF gave a dark green catholyte, which on workup yielded an unidentifiable, polymeric product. In the presence of phenol, a run with 1.5 g of *5* gave 180 mg of white crystals. These were sparingly soluble in most solvents and had a melting point above 300 °C. A mass spectral analysis (AEI 902 instrument) gave the molecular weight 334, indicating that a hydrodimer of *5* had been formed. We are not sure of its structure, but *a priori*, β,β-coupling is most likely.[5]

The low electricity consumption in the run of *3* in aprotic DMF probably depends on the substrate being destroyed by base, generated at the cathode. It could be demonstrated in a test experiment that sodium hydroxide in DMF decomposes *3* on heating.

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