

## On the Unexpected Cathodic Electrodimerization of Phenyl Vinyl Sulphone in slightly Protic Media: the Formation of 1,4-Bisphenylsulphonylbut-2-ene

N. Djeghidjeh and J. Simonet\*

Laboratoire d'Electrochimie, U.A. 439, Université de Rennes I, Campus de Beaulieu, 35042 - Rennes Cédex, France

Phenyl vinyl sulphone exhibits unusual cathodic behaviour in organic media containing a small excess of a proton donor such as acetic acid or phenol; both the saturated sulphone and an unsaturated dimer are isolated, the formation of which may be explained by hydrogen atom transfer between the organic free radicals formed at the interface.

Aromatic sulphones  $\text{ArSO}_2\text{R}$  are known<sup>1</sup> to be cleaved selectively by cathodic means by a two-electron process to lead to the arylsulphinic acid in high yield together with the remainder as  $\text{RH}$ . Even when  $\text{R}$  is unsaturated, cleavage reactions are also observed. If the sulphonyl moiety is located in an allylic or propenyl position the cleavage of the transient anion radical produced in the first electron transfer may be accelerated.<sup>2</sup> The overall reaction may however be a single electron process, since the free radical formed in the sulphone scission is often electron rich and consequently not very reactive electrochemically. When an unsaturated bond is vicinal to the sulphonyl group cleavage reactions are still observed.<sup>3</sup> In fact there are only a few examples known where the reaction of double bonds activated by a sulphonyl group can be compared with that of alkenes substituted by  $\alpha$  electron-withdrawing groups. Therefore, rare cathodic saturation reactions have been reported for sulphones.<sup>4</sup>

We now draw attention to the behaviour of phenyl vinyl sulphone which contrasts with that observed for a wide range of sulphones. In the aprotic solvent dimethylformamide cathodic cleavage rapidly leads to the formation of the vinyl radical as an intermediate.<sup>5</sup>

In contrast, addition of a relatively small amount of a proton donor leads to a drastic change in the reactivity. Thus, the reaction of (1) under these conditions proceeds as in equation (1).

In several experiments<sup>†</sup> (acetic acid or phenol, as proton donor) the relative proportions of (2) and (3) were always about 2 : 1. The *trans*-disulphone (3) is hitherto unknown. It is

<sup>†</sup> The formation of the disulphone is exemplified by the following procedure. The disulphone (1) ( $2 \times 10^{-2}$  mol  $\text{dm}^{-3}$ ; 168 mg) and phenol (0.1 mol  $\text{dm}^{-3}$ ; 470 mg) were added to the catholyte (50 ml) of a divided cell. The electrolyte was dimethylformamide of purum quality containing 0.1 mol  $\text{dm}^{-3}$   $\text{Bu}_4\text{NBF}_4$ , with a slowly stirred mercury pool (area 3  $\text{cm}^2$ ) as cathode, and a glassy carbon counter electrode. The applied potential necessary to reduce (1) was  $-1.40$  V vs.  $\text{Ag}/\text{AgI}/\text{I}^-$  (0.1 mol  $\text{dm}^{-3}$ ) reference. The electrolysis was conducted under high purity argon atmosphere carefully free of oxygen. After complete electrolysis, the catholyte was treated with aqueous sodium hydroxide and extracted with methylene chloride and ether. The organic phase gave 140 mg of the crude product, from which were isolated (2) (60 mg) and (3) (60 mg); compound (3): m.p. 126–127 °C,  $m/z$  336;  $^1\text{H}$  n.m.r. ( $\text{CCl}_4$ )  $\delta$  2.50 (4H), 4.35 (2H), and 7.80 (10H).

- 1 L. Horner and H. Nickel. *Chem. Ber.*, 1956, **86**, 1681; J. Simonet and G. Jeminet, *Bull. Soc. Chim. Fr.*, 1971, 2754.
- 2 J. Y. Pape and J. Simonet, *Electrochim. Acta*, 1978, **23**, 445.
- 3 K. Ankner, B. Lamm, and J. Simonet, *Acta Chem. Scand., Sect. B*, 1977, **31**, 742.
- 4 B. A. Arbuzov and E. A. Berdnikov, *Dokl. Akad. Nauk SSSR*, 1966, **171**, 860.
- 5 N. Djeghidjeh, J. Simonet, and G. Mousset, to be published.