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

N. Djeghidjegh 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 $ArSO_2R$ are known[1] to be cleaved selectively by cathodic means by a two-electron process to lead to the arylsulphinate in high yield together with the remainder as RH. Even when R is unsaturated, cleavage reactions are also observed. If the sulphonyl moiety is located in an allylic or propynylic position the cleavage of the transient anion radical produced in the first electron transfer may be accelerated.[2] 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.[3] 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 α electron-withdrawing groups. Therefore, rare cathodic saturation reactions have been reported for sulphones.[4]

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.[5]

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† (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

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† The formation of the disulphone is exemplified by the following procedure. The disulphone (**1**) (2×10^{-2} mol dm^{-3}; 168 mg) and phenol (0.1 mol 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 dm^{-3} Bu_4NBF_4, with a slowly stirred mercury pool (area 3 cm^2) as cathode, and a glassy carbon counter electrode. The applied potential necessary to reduce (**1**) was -1.40 V *vs.* Ag/AgI/I$^-$ (0.1 mol 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}H n.m.r. (CCl_4) δ 2.50 (4H), 4.35 (2H), and 7.80 (10H).

$$\underset{(\mathbf{1})}{3\mathrm{PhSO_2{-}CH{=}CH_2}} \xrightarrow[\text{conversion}]{\text{cathodic}} \underset{(\mathbf{2})}{\mathrm{PhSO_2{-}CH_2Me}} + \underset{(\mathbf{3})}{\mathrm{PhSO_2{-}CH_2{-}CH{=}CH{-}CH_2{-}SO_2Ph}} \qquad (1)$$

$$3\,(\mathbf{1}) \xrightarrow{3e^-,\ 3H^+} 3\ \mathrm{PhSO_2{-}CH_2{-}CH_2^{\bullet}} \qquad (2)$$

$$\mathrm{PhSO_2{-}CH_2{-}CH_2^{\bullet}} + (\mathbf{1}) \longrightarrow \mathrm{PhSO_2{-}CH_2{-}CH_2{-}CH_2{-}\dot{C}H{-}SO_2Ph} \qquad (3)$$

$$\mathrm{PhSO_2{-}CH_2{-}CH_2^{\bullet}} + \mathrm{PhSO_2{-}CH_2{-}CH_2{-}CH_2{-}\dot{C}H{-}SO_2Ph} \longrightarrow \mathrm{PhSO_2{-}CH_2{-}Me} + \underset{(\mathbf{4})}{\mathrm{PhSO_2{-}CH_2{-}CH_2{-}\,CH{=}CH{-}SO_2Ph}} \qquad (4)$$

$$(\mathbf{4}) \xrightarrow{e^-,\ H^+} \mathrm{PhSO_2{-}CH_2{-}CH_2{-}\dot{C}H{-}CH_2SO_2Ph} \qquad (5)$$

$$\mathrm{PhSO_2{-}CH_2{-}CH_2{-}\dot{C}H{-}CH_2SO_2Ph} + \mathrm{PhSO_2{-}CH_2{-}CH_2^{\bullet}} \longrightarrow \mathrm{PhSO_2{-}CH_2Me} + \mathrm{PhSO_2{-}CH_2{-}CH{=}CH{-}CH_2{-}SO_2Ph} \qquad (6)$$

formed rapidly from (**1**) in protic solvents (demonstrated from voltammetric curves). Moreover it was checked that 1,4-bisphenylsulphonylbutane treated in strongly basic solution in the presence of oxygen does not lead to (**3**). Coulometric experiments demonstrated also that the overall conversion required 0.87 ± 0.06 mol of electron per mol of (**1**). Consequently the formation of (**3**) from (**1**) could arise *via* a rather complex mechanism involving free radical addition to the substrate and internal hydrogen atom transfers [equations (2)—(6)].

Such a mechanism presupposes that free radicals (monomer and dimers produced in protic solution) react rapidly at the mercury interface and consequently hydrogen atom transfer from the solvent remains of low importance. It has been checked that an ethylenic sulphone such as (**4**) is reduced in protic solutions in the same potential range as (**1**). Moreover, the isolation of the disulphone (**3**) is due to the fact that its reduction potential (not shifted in protic solution) is about 0.15 V more cathodic than that of (**1**) [the two-electron reduction of (**3**) leads to but-2-ene]. Therefore, the proposed scheme needs 4 electrons for 4 mol of (**1**). Only traces of the saturated dimer are isolated. It could result from coupling of the primary free radicals or saturation of some of the disulphone (**4**).

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