

An electrosynthesis of sulphones

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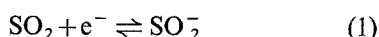
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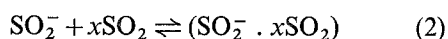
The cathodic reduction of SO_2 , dissolved in aprotic solvents, to the anion radical SO_2^- in the presence of organic halides RX results in the formation of organic sulphones $\text{R-SO}_2\text{-R}$ at appreciable current yields. With dihalides, polymeric sulphones or, as in the case of *o*-xylylenedibromide, inner sulphinic esters (sultines) are formed, the latter being easily convertible to the corresponding cyclic sulphones.

1. Introduction

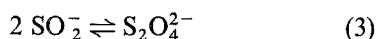
The electrochemical reduction of sulphur dioxide in aprotic solvents has been investigated previously by several workers with different techniques [1-4]. One electron is transferred at the electrode, producing the anion radical



in a quasi-reversible reaction. Subsequent chemical reactions are involved, viz. the formation of complex ions with SO_2 molecules



as well as dimerization



The polarographic half-wave potential [2] in acetonitrile (AN) was reported as -0.88 V (versus aqueous SCE). The voltammetric half-wave potential at a rotating platinum electrode [3] in dimethylsulphoxide (DMSO) varied, according to the concentration, between -0.40 and -0.43 V (versus $\text{Ag}|10^{-3} \text{ M AgCl}_2|0.1 \text{ M LiCl}$ in DMSO). Cyclic voltammograms at gold electrodes [4] in dimethylformamide (DMF) exhibited a cathodic peak potential of -0.84 V and corresponding anodic peak potentials, on scan reversal, of -0.74 and -0.25 V (versus aqueous SCE), these peaks being attributed to the oxidation of the free SO_2^- and the complex ion formed according to Equation (2), respectively.

The strong colours of the solutions upon reduction were attributed to the complex ion, in agreement with studies on the reduction of SO_2 by sodium amalgam in DMF [5]. The simultaneous presence of both the free and the complex ion radical was in accordance with an electron spin resonance (e.s.r.) investigation [6] of the electrochemically generated radical which showed two independent e.s.r. spectral lines at different g values. The blue radical exhibits considerable stability. Half-lives vary according to the conditions; in DMF, values of 100 h (at low excess concentrations of SO_2 and an initial concentration of $5 \times 10^{-3} \text{ M SO}_2^-$) for a second order disproportionation [5] and of 45 min for a first order decay [6] have been reported. The decrease of reversibility of the reaction shown in Equation (1) observed upon electrolysis in DMSO [3] was attributed to the covering of the electrode with the dithionite formed according to Equation (3), the dimer being favoured at increased concentrations of SO_2 .

The aim of the present work was to find out whether the nucleophilic properties due to the negative charge of the SO_2^- radical would provide a species which is reactive towards suitable organic compounds. In preliminary experiments on a preparative scale in DMF and AN it was observed that SO_2^- , while originally exhibiting a considerable stability and being easily recognized by its blue colour and by its e.s.r. line, did not accumulate in the bulk in the

presence of organic halides and other types of organic compounds like aldehydes. It was expected that the SO_2 group would be introduced into the organic compound via a nucleophilic substitution and that these reactions would result in the electrosynthesis of sulphones.

2. Experimental

2.1. Apparatus and solutions

Voltammetric curves were obtained at a 0.1 cm^2 glassy carbon cathode using a Wenking PCA 72 m potentiostat, a Wenking VSG 72 scan generator and a Hewlett-Packard model 7001 m XY-recorder. Preparative scale reductions were carried out in a jacketed H-cell divided by means of an Amfion A-100 or C-311 ion-exchange membrane and fitted with a magnetic stirrer. The working electrode here was a platinum sheet of 13 cm^2 (although glassy carbon, mercury, silver, and gold cathodes can be used as well); the counter electrode was glassy carbon. Potentiostatic and galvanostatic runs were controlled by the Wenking potentiostat (and occasionally, a Tacussel ASA 100 potentiostat), a Wenking SSI 70 current integrator and during potentiostatic experiments, a laboratory-made instrument for periodic voltage reversal. For both voltammetric and preparative experiments, an $\text{Ag}|\text{AgCl}|\text{sat. LiCl}$ electrode in AN served as reference.

e.s.r. measurements were carried out with an AEG spectrometer model 20 XT.

0.2 M tetraethylammonium bromide (TEAB) in AN or DMF was usually employed as the electrolyte. The solvents were spectroscopic grade and were dried prior to use with molecular sieve 3 \AA . Solutions were carefully deoxygenated and experiments were carried out under a nitrogen atmosphere to exclude oxygen.

2.2. Procedures

Preparative potentiostatic runs were conducted in the following manner: after deoxygenation, the electrolyte (100 ml) was pre-electrolysed at -1.0 V ;^{*} the initial current of about 20 mA

^{*} All potential values versus the reference electrode indicated above.

slowly decreased to about 10 mA within 30 min, corresponding to about 1 mA background current at -0.7 V (which is on the plateau of the SO_2 reduction wave). Then 5 ml of a 5 M SO_2 stock solution in AN or DMF were added to the catholyte and the solution electrolysed at -0.7 V until the integrator showed a total charge of 20 C and the blue colour of the radical was clearly visible. Then 0.02 moles of the organic halide RX were added and the electrolysis continued at -0.7 V until a total charge of 2000 C was passed (corresponding to one electron per molecule of RX and a theoretical consumption of 80% of the initial amount of SO_2). Severe fouling of the working electrode during these experiments was partially overcome by periodic switching to an anodic potential for short times (usually $+1.0 \text{ V}$ for 1 s at 60 s intervals).

Fouling of the working electrode was completely avoided by applying less negative potentials than those of the limiting plateau and, simultaneously, maintaining an excess concentration of SO_2 in the solution. (The success of these provisions may be explained by the fact, that SO_2^- is immediately complexed at the electrode under these conditions according to Equation (2) and that the complex ion is less reactive in giving polymeric products than the uncomplexed SO_2^- .) These conditions were favourably established by periodically replenishing the reactants and applying the galvanostatic mode of electrolysis. The procedure ran as follows.

Pre-electrolysis of 100 ml electrolyte was carried out at 20 mA for 30 min. Then 10 ml of 5 M SO_2 solution and 0.02 moles of RX were added. Electrolysis was carried out at 300 or 500 mA, respectively, for different runs. At these currents, the potential remains in the rising part of the reduction wave and is, therefore, less negative than during the potentiostatic reductions. After each passage of 1000 C, the SO_2 and RX were replenished and the electrolysis continued until the assigned amount of charge, a maximum of 10 000 C, was applied. In order to minimize the probability of side-reactions, the temperature was chosen in such a way that the blue colouration due to the radical never accumulated visibly in the bulk but was

restricted, if at all visible, to a thin layer adjacent to the electrode.

After the electrolysis was finished, the solvent was evaporated from the catholyte. The residue was treated with chloroform in order to separate the organic products from the supporting electrolyte. Isolation and purification of the products was carried out by conventional recrystallization and chromatographic separation. The products were identified by comparison with authentic material and/or n.m.r. u.v., i.r. and mass spectroscopy.

3. Results

Fig. 1 shows cyclic voltammetric curves for the reduction of SO_2 in AN, in the absence and presence of allyl bromide. The reduction and reoxidation peaks in the absence of allyl bromide

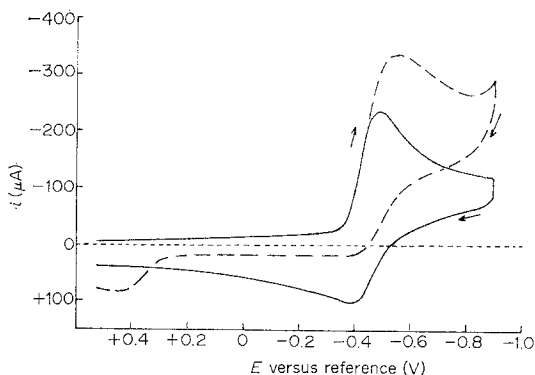


Fig. 1. Cyclic voltammetry of 0.006 M SO_2 in AN (0.2 M TEAB) at glassy carbon. Reference electrode: $\text{Ag}|\text{AgCl}|\text{LiCl}(\text{AN})$. Sweep rate: 0.2 V s^{-1} —: in absence, - - -: in presence of 0.23 M allyl bromide.

correspond to the quasi-reversible character of the reaction Equation (1). On addition of allyl bromide, the cathodic peak increases, while the reoxidation peak disappears. If the curve is recorded in a perchlorate instead of a bromide electrolyte, an oxidation peak is observed on the reversal scan due to bromide ions eliminated from the allyl bromide.

In the absence of allyl bromide, the cathodic peak of the SO_2 reduction is at more negative potentials in a bromide than in a perchlorate electrolyte; also, the u.v. absorption maximum of SO_2 solutions in AN exhibits a shift from 283 nm to 319 nm on addition of bromide. Both effects suggest the formation of a complex ion SO_2Br^- .

If the blue solution of the SO_2^- anion radical forming upon preparative electrolysis of SO_2 in AN is separated from the electrolysis cell, a 'titration' can be carried out with the organic halide RX using the blue colour as an indicator. One mole of RX is consumed by one mole of SO_2^- according to these experiments. While the e.s.r. line of SO_2^- can easily be observed, we have not yet succeeded in obtaining e.s.r. evidence of radical intermediates of the reaction between SO_2^- and RX.

The results of large-scale potentiostatic electrolyses under various conditions are summarized in Table 1. As stated above, however, potentiostatic reductions are not suitable for electrosynthesis, because fouling of the cathode (probably by polymeric products) cause an early decrease of current densities.

Table 1. Results of potentiostatic reduction of SO_2 in presence of RX

RX	Electrode	Temp. °C	Solvent	c.d. ^a mA cm^{-2}	yield ^b (%)	Product ^c
$\text{C}_6\text{H}_5\text{-CH}_2\text{Br}$	Pt	35-45	AN	20	50 ^d	I
$\text{C}_6\text{H}_5\text{-CH}_2\text{Br}$	Pt	40-45	AN	10	70 ^d	I
$\text{C}_6\text{H}_5\text{-CH}_2\text{Br}$	Pt	20-25	DMF	15	70	I
$\text{C}_6\text{H}_5\text{-CH}_2\text{Br}$	Hg	40-45	AN	20	70	I
(p)Br- $\text{C}_6\text{H}_4\text{-CH}_2\text{Br}$	Pt	35-45	AN	10	73	II
$\text{CH}_2 = \text{CH-CH}_2\text{Br}$	Pt	35-45	AN	25	64	III
CH_3I	Pt	39-41	AN	25	58	IV

^a Initial values quickly decreasing due to electrode fouling.

^b Yields refer to the amount of RX added.

^c See Table 3.

^d Different results in two runs.

Table 2. Results of galvanostatic reduction of SO_2 in presence of RX in AN at platinum cathodes

RX	Temp. °C	<i>c.d.</i>		Product ^b
		$mA\ cm^{-2}$	yield ^a (%)	
$C_6H_5-CH_2Cl$	58–60	23	55	I
<i>p</i> -xylylene-dibromide	39–41	38.5	86	V ^c
<i>o</i> -xylylene-dibromide	39–41	38.5	71	VI, VII ^d
$(C_6H_5)_2CHCl$	39–41	38.5	41	VIII
$H_3C-OOC-CH_2Cl$	44–46	23	52	IX
$C_6H_5-CO-CH_2Br$	39–41	38.5	57	X
$CH_2 = CH-CH_2Br$	39–41	38.5	64	III
$CH_2 = CH-CH_2 Br$	39–41	65	88	III
<i>n</i> - C_4H_9Br	80–82	38.5	74	XI

^a Current yields.

^b See Table 3.

^c Product is polysulphone.

^d Product consists of 95% sultine (VI) and 3% sulphone (VII).

The results of galvanostatic reductions, which are summarized in Table 2, were obtained at larger initial concentrations of SO_2 allowing for larger current densities, even though the electrode potential was at less negative values and fouling of the cathode was avoided.

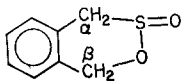
Whereas no dithionite (which might be

responsible for the incomplete yields) was found at the end of the electrolyses, organic side-products were often observed in very small amounts upon analysis of the products of these experiments, but no attempt has been made to identify them.

All the runs summarized in Table 2 were

Table 3. Properties of the products from the preparative runs (cf. Tables 1 and 2)

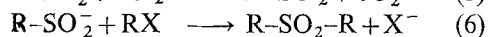
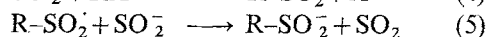
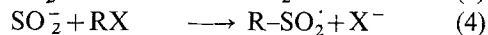
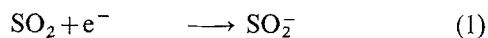
I Dibenzylsulphone:	m.p. 151–152°C from ethanol (Lit. 155°C [7])
II 4,4'-Dibromdibenzylsulphone:	m.p. 263–264 °C from acetic acid (Lit. 261–262°C [8])
III Diallylsulphone:	b.p. 137–139°C/18 mm (Lit. 88–90°C/0.4 mm [13]) GC: 5% SE-30 at 160–185°C with <i>p</i> -bromochlorobenzene as internal standard
IV Dimethylsulphone:	m.p. 108–109°C from benzene/petrolether (Lit. 110° [7]); GC: 6% cyclohexanedimethanolsuccinate at 130°C with anisaldehyde as internal standard
V <i>p</i> -Polyxylylene-sulphone:	non-melting up to 360°C (Lit. [9])
VI 1-Oxa-2-thiatetrahydronaphtalene-S-oxide:	m.p. 29–31°C by sublimation i.r. (CDCl ₃): 1115 cm ⁻¹ (SO) n.m.r. (CDCl ₃ /TMS): δ 3.46 (1 H), δ 4.20 (1 H) $J_{\alpha\alpha}$ 15 Hz, δ 4.90 (1 H), δ 5.30 (1 H) $J_{\beta\beta}$ 13 Hz, δ 7.1–7.3 (4 H) MS: M ⁺ 168, 105, 104, 103, 91
VII Benz(c)dihydrothiophene-1, 1-dioxide:	m.p. 147–148°C by sublimation (Lit. 150°C [10])
VIII Dibenzylhydrilulphone:	m.p. 187–188°C from benzene/petrolether (Lit. 185–186°C [11])
IX 1,1-Dicarbomethoxydimethylsulphone:	m.p. 112–113°C from ethanol/water (Lit. 115–116°C [12])
X Diphenacylsulphone:	m.p. 121–122°C from ethanol i.r. (CDCl ₃): 1325, 1120 cm ⁻¹ (SO ₂), 1682 cm ⁻¹ (CO); n.m.r. (CDCl ₃ /TMS): δ 5.03 (4 H), δ 7.3–8.0 (10 H); MS: M ⁺ 302, 238
XI Di- <i>n</i> -butylsulphone:	m.p. 44°C (Lit. 46°C [7]); GC: 5% SE-30 at 140° with <i>p</i> -bromochlorobenzene as internal standard



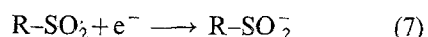
performed with TEAB as supporting electrolyte. If the bromide was replaced by perchlorate, then the reaction of SO_2^- with RX was slower and more elevated temperatures had to be applied in order to stop the blue colour accumulating in the bulk.

4. Discussion

Cyclic voltammetry, the 'titration' experiments and the fact that the main product is the corresponding sulphone, suggest the following mechanism:



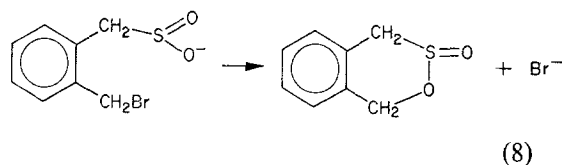
Equations (4) and (6) are normal nucleophilic substitutions. Since the blue colour due to a stationary concentration of SO_2^- was observed even in the presence of an excess of RX , if the temperatures were chosen somewhat lower than those listed in Table 2, and since no intermediate radical R-SO_2 was observed in the e.s.r. experiments, Equation (4) seems to be the slowest step in this sequence. Though the direct reduction of R-SO_2 at the electrode is probably fast at the prevailing conditions,



the reaction proceeds more probably through the homogeneous electron transfer, Equation (5), especially since it takes place also during the 'titration' experiment. The increased peak height in Fig. 1 in the presence of the organic halide is, therefore, due to the regeneration of SO_2 as shown in Equation (5).

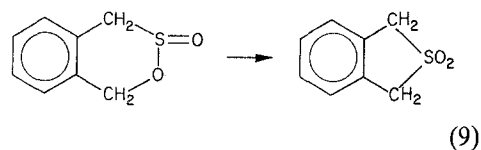
Which electrochemical process is responsible for the anodic peak which is observed in Fig. 1 at rather positive potentials, has not been studied so far. It may be due either to a reversal of Equation (7), because part of the anion R-SO_2^- has not yet reacted at that time according to Equation (6), or to the oxidation of products from the reduction of allyl bromide starting at the end of the cathodic scan.

In the case of *o*-xylylene dibromide, the intramolecular elimination reaction



obviously proceeds faster than the encounter with another RX molecule; cyclization is in favour of the six-membered ring and the sultine is the main product instead of the sulphone.

The sultine, however, is easily converted to the sulphone by treatment with silica gel in ethanol:



Though no dithionite was found as a product of the electrolyses, dimerization of SO_2^- and some subsequent reaction of the dithionite (possibly with residual water in the solution) may be responsible for the incomplete yields.

Wellisch *et al.* [9] and Matsuo *et al.* [14] have previously attempted to prepare such sulphones from the reaction of organic halides with sodium dithionite. Although these authors did not consider the possibility, it seems rather likely that the anion radical SO_2^- , forming upon dissociation of the dithionite, is the active species also in this chemical reaction. The yields, however, obtained by this method, were very low (10–15%) as compared with the promising yields obtained with the electro-synthesis presented in this work.

In other chemical routes starting with the halides RX , which are frequently employed in the preparation of sulphones, the sulphide is produced in a first step. The sulphide is subsequently converted to the sulphone by catalytic oxidation or with the consumption of oxidizing agents such as hydrogen peroxide or nitric acid. Compared with these methods, the electro-synthesis has the advantages of a one-step method and of yielding the product in a comparatively pure form.

Further work is in progress with the aim of optimizing the experimental conditions so as to increase the current densities and the yields and to provide an economical method for the separation of the product from the electrolyte.

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