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Electrosynthesis of sulphones: coupled cathodic-anodic process

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A continuous process for the electrosynthesis of sulphones by cathodic reduction of sulphur dioxide in the presence of organic halides has been investigated. The organic halide, consumed in the cathode process, is regenerated at the anode side and the halogen is hence recycled. As a model process, the synthesis of dipropyl sulphone via propyl bromide has been investigated; SO_2 and propyl alcohol are the starting materials. The alcohol, simultaneously serving as the anolyte solvent, reduces bromine to give hydrobromic acid which, in turn, regenerates the organic halide by reaction with further alcohol. The cathodic and anodic yields are both promising.

1. Introduction

A possible electrosynthesis of sulphones by cathodic reduction of sulphur dioxide in aprotic solvents, e.g. dimethylformamide or acetonitrile, in the presence of organic halides has been reported in earlier papers [1–4]. Cyclic voltammetry and preparative studies of the reaction between the anion radical $SO_2^{\overline{\cdot}}$ formed at the cathode and organic halides [1] as well as kinetic studies of this reaction using e.s.r. spectroscopy [5, 6] suggested a mechanism in which the primary electron transfer is followed by a comparatively slow nucleophilic substitution reaction:

$$SO_2^{\overline{\cdot}} + RX \longrightarrow R{-}SO_2^{\cdot} + X^- \qquad (1)$$

The mechanism originally proposed [1] has meanwhile been confirmed [7]. The cathodic overall reaction is

$$2RX + SO_2 + 2e \longrightarrow R{-}SO_2{-}R + 2X^- \qquad (2)$$

Sulphones have been obtained in over 80% current yield. Beside simple symmetric, cyclic and polymeric sulphones, non-symmetric compounds $R{-}SO_2{-}R'$ can be synthesized with good yields and high purity [2].

In the presence of excess SO_2, the primary reduction product, the anion radical $SO_2^{\overline{\cdot}}$, is in equilibrium with a dimeric ion radical [8] which gives the solution a greenish-blue to deep blue colour:

$$SO_2^{\overline{\cdot}} + SO_2 \rightleftharpoons S_2O_4^{\overline{\cdot}} \qquad (3)$$

Because the monomeric ion radical is highly reactive and may disable the electrode by the formation of non-conducting layers, electrolysis is best carried out at current densities lower than the transport-limiting values. The dimeric ion radical is less reactive and Reaction 1 takes place via the monomeric species.

We have previously reported a continuously operating laboratory plant for the electrosynthesis of sulphones [3, 4]. That work included the separation of the product from the catholyte circuit by extraction and the use, in the anode compartment, of the halide ions generated in Reaction 2. The cell was divided by an anion exchange membrane, and tetra-alkylammonium halide served as the supporting electrolyte. To avoid the formation of the trihalide X_3^- which reduces the electrolytic conductivity and makes it difficult to recover the halogen, it was necessary to add a substrate which reacts immediately with the halogen formed at the anode. In the first studies, olefins (ethylene) were used as the substrate. While the formation of trihalide is avoided, the dihalo compound generated will in general not be the organic halide used in the cathodic process.The compound may be use-

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ful, but in general not at the same rate and not at the same place.

It was therefore the aim of the present work to conduct the reactions at the anode in such a way that the compound RX used at the cathode is regenerated and the halogen cycled.

During preliminary experiments the same composition of electrolyte (acetonitrile with tetraalkylammonium bromide) was used as the anolyte and the catholyte; sulphur dioxide as well as the alcohol ROH (in this case propyl alcohol) corresponding to the alkyl halide sought were added to the anolyte. Bromine (or tribromide, respectively) formed at the anode is then reduced by SO_2 forming hydrobromic acid which then reacts with ROH to give RX, while water used for the first step is regenerated:

$$Br_2 + SO_2 + 2H_2O \longrightarrow 2HBr + H_2SO_4 \quad (4)$$

$$2HBr + 2ROH \longrightarrow 2RBr + 2H_2O \quad (5)$$

$$\overline{Br_2 + SO_2 + 2ROH \longrightarrow 2RBr + H_2SO_4} \quad (6)$$

In these experiments, sulphuric acid was removed by reaction with calcium oxide and the resulting water by treating with molecular sieves. The removal of proton donors like sulphuric acid and water before recirculating the electrolyte into the anode compartment is necessary to prevent protons getting into the cathode compartment in spite of the anion exchange membrane, and, by causing side reactions of $SO_2^{\cdot -}$ [9], decrease the sulphone yield. However, the current yield of propyl bromide was limited to about 40% under these conditions. Although no optimization of the process has been tried, a substantial improvement was not likely to be achievable. Moreover, the unfavourable formation of tribromide could not be avoided, because Reaction 4 proceeds too slowly in acetonitrile as solvent.

In the investigations described in this paper, the alcohol ROH has been used as the solvent. This makes the addition of a reductant for bromine unnecessary. Moreover, there is no formation of trihalide since the reaction between bromine and the alcohol is sufficiently fast. Propyl alcohol has been applied as a model compound so that propyl bromide is the intermediate and dipropyl sulphone is the final product.

2. Experimental

2.1. *Apparatus and solutions*

A divided cell consisting of two circular glass shells, 6 mm deep and with a diameter of 154 mm (Fig. 1) was constructed. For inlet, outlet, etc., a number of threadscrew necks were located near to the edges of the half cells. Electrodes with an area of 0.785 dm^2 were fixed to the bottom of the shells by layers of silicon rubber and connected to leads through the centre of the shell walls. The cathode was made from stainless steel, the anode from glassy carbon. Anode and cathode chambers were separated by an anion exchange membrane type Permion 1025 (RAI Research Corporation); perforated PTFE foils served as supports for the membrane and prevented it from bending and laying onto one of the electrodes. With a silicon rubber ring as packing between the edges of the two halves, the cell was clamped together by plastic rings connected with screws. The space between both electrodes was then 9–10 mm. Electrolyses were carried out galvanostatically at currents considerably less than the transport-limited current in

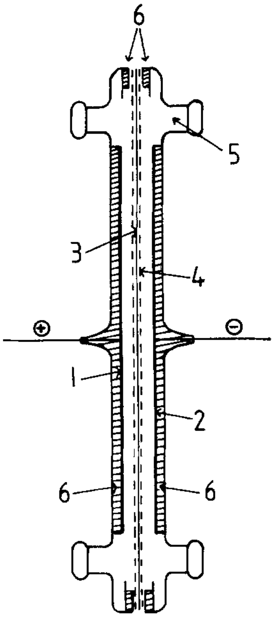

Fig. 1. Electrolysis cell (sectional view). 1, Anode; 2, cathode; 3, anion exchange membrane; 4, perforated PTFE foil (membrane support); 5, threadscrew necks; 6, silicon rubber packings.

order to avoid side products and electrode fouling [1].

The solvent for the circulating catholyte was a mixture of acetonitrile and *n*-propyl bromide containing 0.2 M tetra-ethylammonium bromide (TEAB) and saturated with sulphur dioxide (about 1.7 M SO_2 at 65° C). The circulating anolyte was a solution of 0.4 M TEAB in *n*-propanol. The catholyte was carefully deaerated with nitrogen before electrolysis; sulphur dioxide was dried by treating with P_2O_5. Chemicals were reagent grade. The temperature of the electrolytes was maintained in the range 60–70° C by a thermostat; at elevated current densities this temperature resulted from Joule heating.

Quantitative analysis by gas chromatography was made on a 10% carbowax-20 M column with *p*-chlorobenzaldehyde as internal standard. Products were identified by n.m.r., infra-red and mass spectrometry.

Current-voltage curves were obtained with a small stationary platinum electrode (0.66 cm^2) in unstirred solution and an aqueous saturated calomel reference electrode and were recorded on the 'Electrochemistry System Model 170' (PAR).

2.2. *Procedure*

The laboratory device is shown schematically in Fig. 2.

Both catholyte and anolyte were circulated at a rate of about 7.6 $cm^3 min^{-1}$ by means of peristaltic pumps (14 in Fig. 2). The total volumes circulating were about 500 cm^3 for the anolyte and 1000 cm^3 for the catholyte.

After leaving the cathode chamber (1), the catholyte passed through a reactor (2) where it was refluxed to complete the volume reaction. The solution was cooled (3) and passed through a counter-current liquid/liquid extraction column (4) to separate the product from the electrolyte; the solvent was a mixture of petroleum ether and benzene (volume ratio 4:1). Isolation of the sulphone was then completed using a rotary evaporator (5). Before flowing back to the electrolysis cell, the catholyte was supplied with the active materials (6/7 propyl bromide: 8 SO_2).

The anolyte from the anode chamber (9) passed a reactor (10) in which the synthesis of *n*-propyl bromide was completed and this product was separated by distillation with a fractionating

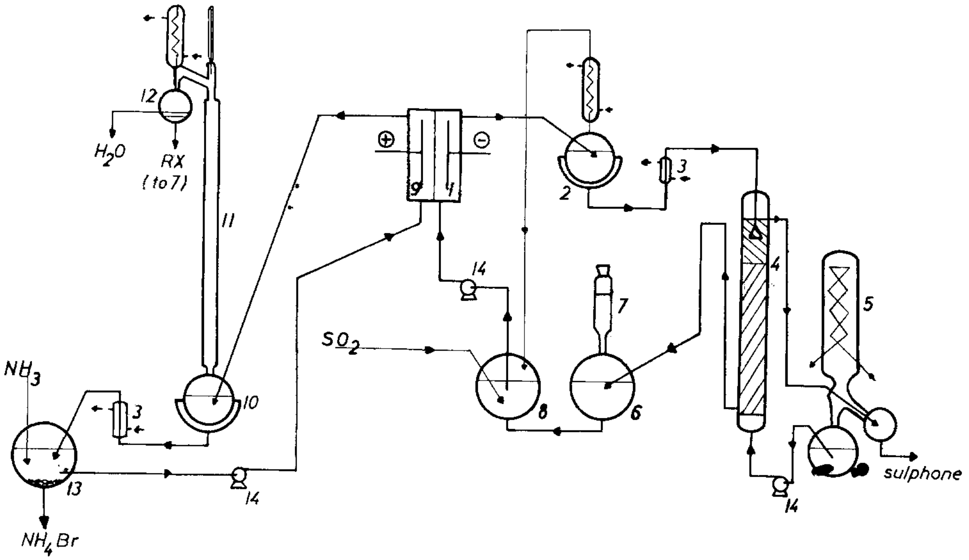

Fig. 2. Scheme of laboratory device for continuous operation. 1, Cathode compartment; 2, reaction vessel (500 ml) with heater; 3, cooler; 4, liquid/liquid extraction column (internal diameter 30 mm, height 500 mm); 5, rotary evaporator; 6, flask (500 ml) for RX dosage; 7, dropping funnel with RX; 8, flask (1000 ml) for saturation with SO_2; 9, anode compartment; 10, reaction vessel (500 ml) with heater; 11 fractionating column (height 300 mm) filled with Fenske rings; 12, collecting flask for RX (and water); 13, flask (500 ml) for precipitating ammonium bromide; 14, peristaltic pumps.

column (11). From the flask (12), the product was transferred to the catholyte circuit via the dropping funnel (7). Ammonia could be introduced into another reactor (13), in order to separate unreacted hydrobromic acid in the form of insoluble ammonium bromide.

3. Results

The sulphone current yield depended on the composition of the catholyte solvent; best results were obtained at 40–70 vol% *n*-propyl bromide. In a typical run, the composition was 1 : 1 acetonitrile/propyl bromide and the other constituents of the catholyte and the anolyte composition were as indicated in Section 2.1; at a temperature of 63° C in the electrolysis cell, a current density of 4.6 A dm^{-2} was applied requiring a cell voltage of about 10 V. After continuous operation for 2.5 h (charge 32 400 C), current yields of 53% di-*n*-propyl sulphone and 73% *n*-propyl bromide were obtained from the catholyte and anolyte circuits, respectively. No optimization has been made with respect to the operating conditions (e.g., temperature, current density, composition of the solution, rate of circulation). It has been shown however, in separate experiments, that the sulphone yield can be increased to at least 75%.

The incomplete conversion to the sulphone results equally from the formation of *n*-propylsulphinic acid *n*-propyl ester (detected by gas chromatography/mass spectroscopy, infra-red spectroscopy, n.m.r.), from the formation of inorganic products like dithionite or thiosulphate and secondary products as well as undefined sulphur-containing organic substances. Though dithionite has not been detected in the catholyte, it is a regular product of the reduction of SO_2 resulting from dimerization of the anion radical $SO_2^{\overline{\cdot}}$ [10–12].

Under the conditions employed the formation of propylbromide takes place to a considerable extent in the anode compartment. Propanol is therefore a suitable medium for the nucleophilic substitution reaction and, moreover, is capable of reducing the anodically formed bromine so that no additional reductant (like SO_2) is required.

If acetonitrile is used as the anolyte solvent, then the solution becomes deep red to brown during the electrolysis. With propanol, only a slight coloration is observed after a long period; brownish-red streaks are only observed close to the anode if there is poor stirring of the electrolyte. For evaluating the reaction mechanism, current potential curves have been measured at the small platinum electrode (see Fig. 3). The presence of a current peak at about 1.0 V upon addition of bromide to a tetraethylammonium perchlorate electrolyte and the early final current rise in the case of TEAB as supporting electrolyte show that bromide is oxidized at the anode and not propanol. Moreover, the presence of only one peak as compared with two peaks in acetonitrile [13] shows that there is little complexing between Br_2 and Br^- to give Br_3^- in propanol. Hence, anodically formed bromine reacts rapidly with propanol to give propionaldehyde and hydrobromic acid. The latter reacts by nucleophilic substitution with the solvent to give propyl bromide:

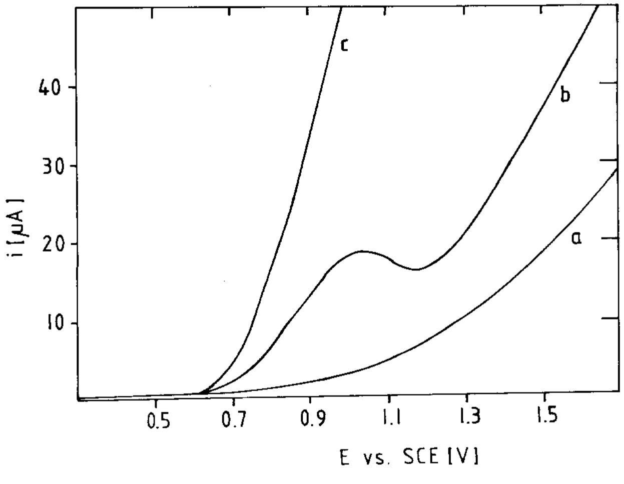

Fig. 3. Voltammetric curves in propanol at a stationary Pt electrode with different supporting electrolytes (scan rate 10 mV s^{-1}). (a) 0.1 M tetraethylammonium perchlorate (TEAP); (b) 0.1 M TEAP + 0.001 M TEAB; (c) 0.1 M TEAB.

give propyl bromide:

$$2Br^- \longrightarrow Br_2 + 2e \quad (7)$$

$$PrOH + Br_2 \longrightarrow C_2H_5CHO + 2HBr \quad (8)$$

$$2HBr + 2PrOH \longrightarrow 2PrBr + 2H_2O \quad (9)$$

Propionaldehyde reacts with propanol to give the corresponding semi-acetal and/or acetal. While no unfavourable influence of the aldehyde or the acetals on the synthesis reaction has been observed during the course of the electrolysis, an accumulation of water formed according to Equation 9 must be avoided because of the reason given in the introduction. Part of the water (about 25%) could be separated together with propyl bromide by distillation (11/12 in Fig. 2) because of the boiling point behaviour of the system propanol/water (azeotropic mixture with 28% water). Moreover, water can be removed by treating the solution with drying agents, e.g. with calcium oxide (dried at 90° C) or with a molecular sieve of 0.4 nm.

A small amount of the anodically formed bromine (about 10%) disappears by side reactions, for example the bromination of propionaldehyde [14]. Apart from these reactions, the incomplete yield (73%) of propyl bromide mentioned above is due to the incomplete conversion of hydrobromic acid. Hence, the yield can certainly be improved considerably.

Preliminary experiments with the divided electrolysis cell but without circulation of the anolyte and catholyte have shown that other alcohols can be used as solvents for the anolyte with the corresponding alkyl bromide being formed. Thus, current yields of 53% 2-bromopropane, 46% 1-bromo-butane and 40% 2-bromobutane have been obtained from isopropanol, *n*-butanol and 2-butanol, respectively. *t*-Butanol could only be used in a mixture with another solvent such as dimethylformamide because, otherwise, the conductivity is too low. Even with a second solvent, the yield of *t*-butyl bromide is very low (at most 5%) because the nucleophilic substitution reaction is sterically hindered. Instead, iso-butene is probably formed initially. *t*-Butyl bromide is, for the same reason, unsuitable for the electrosynthesis of the corresponding sulphone [7].

4. Conclusions

The present results show that the alkyl bromide reacted at the cathode side can be regenerated at the anode if the corresponding alcohol is used as the anolyte solvent. The alkyl bromide is easily separated from the anolyte by distillation. Moreover, the cell voltage is considerably lower with an alcohol than with aprotic solvents such as acetonitrile or dimethylformamide.

The yields obtained, though promising, require optimization. Since the less than 100% yield at the anode is due to incomplete conversion of hydrobromic acid, the choice of better operating conditions should lead to yields > 90%. Moreover, the sulphone formation can certainly be improved. Additional studies are also necessary to show whether the side product alkylsulphinic acid alkyl ester can be converted, by suitable treatment, into the isomeric sulphone, cf. the conversion of the sultine resulting from *o*-xylylene dibromide to the cyclic sulphone [1].

The aldehyde formed according to Equation 8, although boiling at lower temperatures than the alcohol and the alkyl bromide, cannot be removed from the circuit by distillation because of the formation of acetals exhibiting higher boiling points. During continuous operation it will therefore be necessary to keep the concentrations of aldehyde and/or acetal low by drawing off part of the anolyte, continuously or batchwise. Further studies are necessary to show whether the water content can also be kept sufficiently low by this means and by the partial removal of water during the separation of alkyl bromide by distillation, so that additional treatment with drawing agents becomes unnecessary.

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