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The electrochemical reduction of 2,5-dichlorobenzenesulphonyl chloride and the corresponding disulphide

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The electrochemical reduction of 2,5-dichlorobenzenesulphonyl chloride to the corresponding thiol proceeds at high material and current efficiencies (90–100%) on a lead cathode in organic and aqueous organic solvents. Sulpholane/hydrochloric acid or ethanol/sulphuric acid electrolytes appear suitable media for the reaction. Disintegration of the lead cathode was observed in the presence of chloride ions upon prolonged operation but this may be avoided using an alternative electrochemical/chemical process based on the reaction between the thiol and the sulphonyl chloride to produce disulphide. The disulphide may then be reduced electrochemically to the thiol, the latter being used for recycle. This route is also an effective means to circumvent the hydrolysis of the starting material to the corresponding sulphonic acid, which is reduced only with great difficulty, and its formation constitutes an inefficiency in the total process and introduces a by-product that increases process costs.

1. Introduction

A study of the electrochemical reduction of aromatic sulphonyl chlorides, specifically 2,5-dichlorobenzenesulphonyl chloride, was undertaken to assess the potential of such a process as an alternative to the method of thiol production via reduction with zinc [1]. Zinc is a relatively expensive reducing agent, and hence an electrochemical process might offer economic benefits. Zinc salts are also a potential source of heavy metal ion pollution and constitute a disposal problem; an electrochemical process would not suffer from such a drawback.

Our studies were directed towards devising an efficient electrochemical process for thiol production, utilizing solid electrodes. The reduction of 2,5-dichlorobenzenesulphonyl chloride, and that of the intermediate reduction products, to the thiol was studied under a variety of electrolytic conditions and in greater detail than was done previously [2–10].

2. Experimental

Potential sweep studies of 2,5-dichlorobenzenesulphonyl chloride and its reduction intermediates were performed using the cell and equipment described elsewhere [11]. Synthetic work was carried out by electrolysis at constant current [11]. Cation exchange membrane (Ionics 61 DYG067) was employed to prevent Cl^- transfer to the anolyte, and subsequent discharge of chlorine. Commercial solvents were used without further purification. No special precautions were taken to eliminate water since water will be present in a practical process in any event (formed as a by-product).

In a typical experiment the catholyte was prepared by dissolving 25 g of 2,5-dichlorobenzenesulphonyl chloride in 250 ml of 0·5 M aqueous HCl in sulpholane. The desired cell temperature was maintained by circulation of the anolyte and catholyte. The reservoir was heated by heating mantle. Approximately constant reactant concentration was maintained in some experiments by

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periodic addition of 2,5-dichlorobenzenesulphonyl chloride (3·0 g every 0·075 F). Product distribution during a run was monitored by periodic sampling and subsequent glc analysis. A 2ft × 1/3 in glass column packed with 18 in of 10% Silicone Gum SE-52 on Diatoport, followed by 6% of 5% Silicone Gum X-E-60 on Haloport E was used (100–240°C/15°/min; held at limit 7 min). Material yields and current efficiencies were determined by product isolation and purification at the end of selected experiments. To isolate the product the catholyte was cooled to room temperature after passage of up to 7 F. Upon cooling, the catholyte separated into two layers with the lower layer containing most (greater than 90%) of the thiol and disulphide and some sulpholane. In some instances thiol was separated by steam distillation.

3. Results

3.1. *Preliminary evaluation of electrolyte and electrode materials*

Methanol and ethanol, as well as sulpholane (tetramethylene sulphone) are good solvents for electrochemistry and the solubility of the sulphonyl chloride and the disulphide are at least 5 wt%. Dimethyl sulphoxide enters into oxidation/reduction reactions with the disulphide. Addition of water to organic solvents decreases the solubilities of RSO_2Cl and RSSR. Sulphuric acid as an electrolyte exhibits a salting-out effect, while addition of HCl has a salting-in effect. Our attempts to use aqueous emulsions of the sulphonyl chloride were unsuccessful since we were unable to produce relatively stable oil in water emulsions.

Several electrode materials were evaluated for possible use and their effects on the overall reduction rate were assessed before studying the reaction in greater detail.

Potentiodynamic studies in this work, supplemented by electrolysis data indicated that low, intermediate and high hydrogen overpotential metals should be considered from the viewpoint of total process optimization. Metals selected for further study included lead (and lead–antimony), nickel and platinum.

3.2. *Potentiodynamic measurements*

Out of the large number of potentiodynamic measurements performed only a few illustrating the most important features of these reactions will be discussed here. The current–potential curves for Pb in ethanolic H_2SO_4 supporting electrolyte show the absence of current flow until the potential of hydrogen evolution is reached. Addition of RSO_2Cl (8×10^{-2} M) results in two peaks prior to H_2 evolution indicating a two-step reduction, as evident from Fig. 1a.

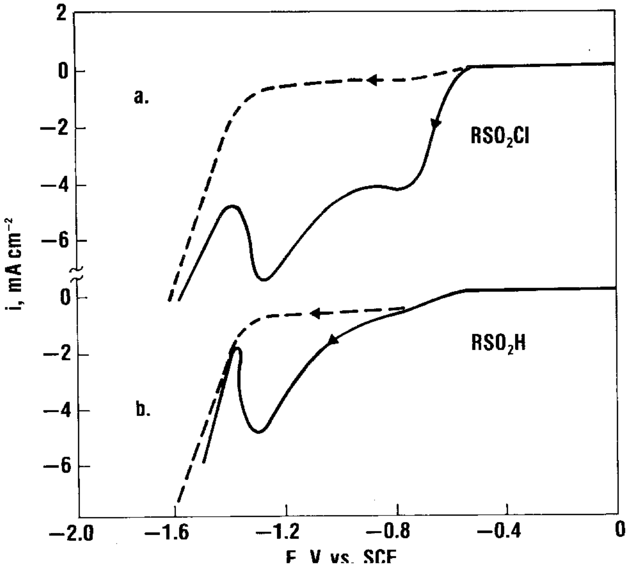

Fig. 1. Current–potential curves for RSO_2Cl and RSO_2H reductions on lead in 25 vol% concentrated H_2SO_4 in ethanol: (a) – – – pure electrolyte, —— 8×10^{-2} M RSO_2Cl; (b) – – – pure electrolyte, —— 10^{-1} M RSO_2H. Sweep rate, 50 mV s^{-1}; temperature 25° C.

Table 1. Sequence of reactions

$2RSO_2Cl + 4H^+ + 4e \longrightarrow 2RSO_2H + 2HCl$	(1)
$2RSO_2H + 2H^+ + 2e \longrightarrow RSO_2SR + 2H_2O$	(2)
$RSO_2SR + 4H^+ + 4e \longrightarrow RSSR + 2H_2O$	(3)
$RSSR + 2H^+ + 2e \longrightarrow 2RSH$	(4)
$RSO_2Cl + 6H^+ + 6e \longrightarrow RSH + HCl + 2H_2O$	(5)

Starting with RSO_2H instead of RSO_2Cl, only one peak is observed, as shown in Fig. 1b. This peak coincides with the second peak in the reduction of RSO_2Cl indicating that the first peak must be due to reduction of RSO_2Cl to RSO_2H.

Fig. 2a shows no reaction taking place prior to hydrogen evolution when RSO_2SR was introduced into the electrolyte. Introduction of RSSR, resulted in a very high current approximately at the same potential at which the first step in the reduction of RSO_2Cl takes place as seen in Fig. 2b. These two steps would be seen as a single peak in the overall reduction of RSO_2Cl to RSH.

3.3. *Constant current electrolysis*

The potential sweep measurements yielded no information on the formation and reduction of RSO_2SR. Under constant current conditions, however, the reduction of RSO_2Cl takes place in four consecutive steps [2–10] via three stable intermediates, including RSO_2SR. The sequence of these reactions is given in Table 1.

Each of the intermediates can be isolated. Product distribution ratios depend on the electrolytic conditions employed. Some of these results are given in Table 2 which illustrates the effect of both solvent and temperature upon product distribution. The current efficiency is that for the combined products. That for any given product can be obtained from the total current efficiency and product distribution. The current inefficiency is mainly due to hydrogen evolution. The latter was generally small and measured only in long-term experiments. The above results were obtained in short-term experiments with cells operating for a few hours converting some 10–30 g of starting material in a batch-wise operation; i.e., reactant concentration was not maintained constant. Conditions needed for efficient reduction and high yield of thiol are illustrated in Table 3. Long-term experiments (16–20 h) converting some 200 g of 2,5-dichlorobenzenesulphonyl chloride (kept at approximately constant concentration by periodic additions) were carried out utilizing lead electrodes in aqueous HCl/sulpholane electrolyte. They confirmed results obtained on a smaller scale. Substantial disintegration of lead electrodes was, however, observed. During prolonged electrolysis the lead electrode formed a 'mud' on its surface. On closer observation, this happened invariably whenever sufficient charge was passed to convert part of the initial RSO_2Cl to RSSR, and on further reduction of RSSR to thiol. To confirm this observation, the reduction of RSSR was performed under the same conditions. The black

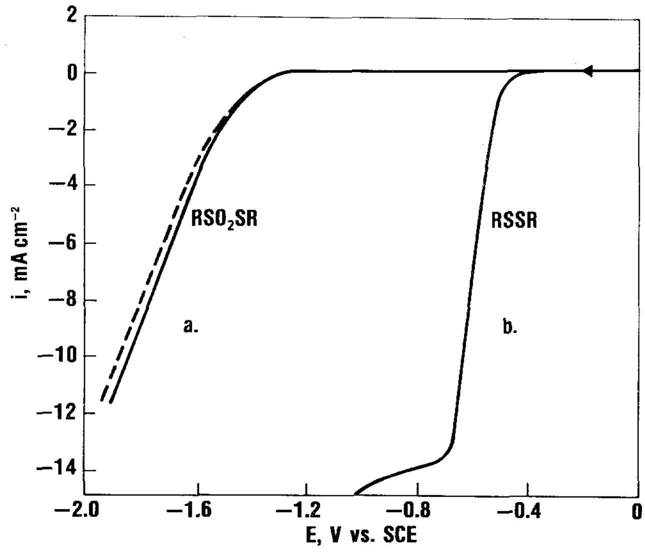

Fig. 2. Current–potential curves for RSO_2SR and RSSR reduction on lead in 25 vol% concentrated H_2SO_4 in ethanol: (a) – – – pure electrolyte, —— 5×10^{-2} M RSO_2SR; (b) —— 5×10^{-2} M RSSR. Sweep rate, 50 mV s^{-1}; temperature 25° C (a), and 80° C (b).

Table 2. Electrolysis of 2,5-dichlorobenzenesulphonyl chloride under various electrolytic conditions

					Yield (%)				
Electrode	*Electrolyte*	*Current density* (mA cm^{-2})	*Temperature* (° C)	*Current efficiency (%)*	RSO_2H	RSO_2SR	*RSSR*	*RSH*	*By-product* RSO_3H
Pb	10% HCl/MeOH	100	75	95	ND*	ND	5	80	ND
	10% HCl/EtOH	150	75	85	ND	ND	5	80	ND
	20% aqueous HCl/sulpholane†	50	45	80	ND	–	90	8	ND
		100	45	90	ND	10	70	–	
		100	75	85	ND	–	25	55	5–10%
		100	95	80	ND	ND	10	75	
Ni	20% aqueous HCl/sulpholane†	50	45	90	45	25	30	–	–
		100	45	90	2	75	20	–	–
		100	75	90	ND	50	50	–	ND
Pt	20% aqueous HCl/sulpholane†	50	45	90	60	40	–	–	–

* Not determined

† Concentrated HCl used.

Table 3. Current efficiency for reduction of RSO_2Cl for some typical conditions

cathode	lead
current density	100 mA cm^{-2}
catholyte	10% HCl/ethanol or 20% aqueous HCl/sulpholane
temperature	> 75° C
reactant concentration	10 wt%
current efficiency	90%
electrode area	up to 80 cm^2

deposit started to form on the lead cathode at the beginning of the electrolysis.

3.4. *Chemical reaction between RSO_2Cl and RSH*

It was discovered during the early phases of this work that the sulphonyl chloride and the thiol react to form corresponding disulphides according to

$$RSO_2Cl + 5RSH \rightarrow 3RSSR + HCl + 2H_2O.$$

Further study of this novel reaction, in order to assess its utility to prevent hydrolysis of sulphonyl halide and to evaluate this reaction as a potential method for Cl^- elimination from the catholyte to prevent electrode disintegration, revealed that it proceeded rapidly and quantitatively in solvents such as methanol and sulpholane in less than 2 h at 125° C (or boiling point temperature of low boiling solvents) [12]. When the thiol is present in less than the stoichiometric amounts, RSO_2Cl remains rather than yielding a mixture of different reduction products. This permits combination of a chemical/electrochemical process using RSSR and an electrolyte devoid of chloride thereby eliminating disintegration of lead.

Table 4. Conditions favourable for the electrolytic reduction of disulphide

catholyte	20 vol% concentrated H_2SO_4 in ethanol
disulphide concentration	10 wt%
electrode material	lead
current density	100 mA cm^{-2}
current efficiency	90 + %
material yield	100%
electrode size	80 cm^2

Table 5. Reduction of disulphide in different solvents

Solvent	*Electrolyte*	*Solubility (wt%)*	*Current efficiency (%)*
sulpholane	HCl	10	80–95*
sulpholane	H_2SO_4	5	30
ethanol	H_2SO_4	10	90–100

* Lead cathode corrodes.

3.5. *Electrochemical reduction of disulphides*

The solvent system found most suitable from the viewpoint of starting material and product solubility, conductivity and current efficiency was ethanol; suitable reaction conditions for this system are presented in Table 4. The current efficiency was determined on the basis of a material balance by analysis of products and also by product isolation, and by measurement of the evolved H_2. A similar experiment using sulpholane as solvent had a current efficiency of only 30%. The difference in efficiencies is due to the difference in solubility of the disulphide in ethanol and sulpholane (Table 5). The difference between HCl/sulpholane and H_2SO_4/sulpholane is evident from Table 5 and is probably not due solely to the difference in solubility. While the sulphuric acid system dissolves less disulphide, 5 wt% is the equivalent of 0·2 M which in a flowing system is more than adequate to support 100 mA cm^{-2}. It would seem that there must be a specific interaction with the sulpholane/HCl system to provide high efficiencies in that electrolyte. The lead electrode in H_2SO_4 electrolyte did not exhibit any disintegration phenomena such as observed in the reduction of disulphide in the presence of chloride ions, or earlier in the reduction of RSO_2Cl upon prolonged electrolysis.

4. Discussion

The electrochemical reduction of benzenesulphonyl chloride and the substituted derivatives (not 2,5-dichlorobenzenesulphonyl chloride) has been studied previously [2–10]. Only part of the published material was directly relevant to synthetic applications. In this respect, Nichols work is particularly worthy of attention [13]. Thiol yields

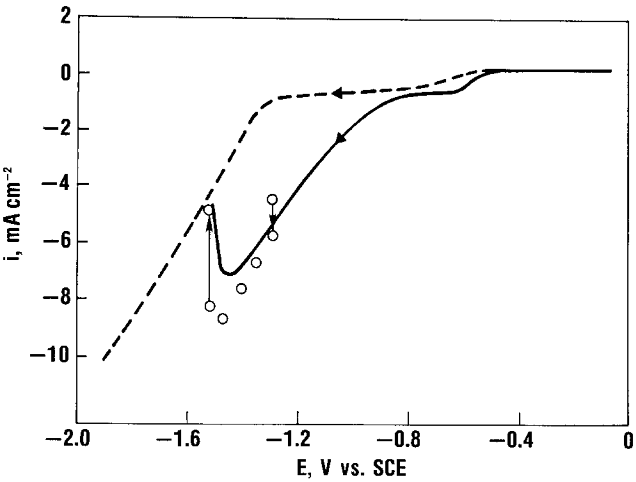

Fig. 3. Influence of competitive adsorption of hydrogen on RSO_2H reduction on lead in 25 vol% concentrated H_2SO_4 in ethanol. – – – pure electrolyte, —— 10^{-1} M RSO_2H, ○ 10^{-1} M RSO_2H under quasi-steady-state conditions. Sweep rate, 50 mV s^{-1}; temperature 25° C.

of 98% with 80% current efficiency were reported, starting with benzenesulphonyl chloride. A mercury electrode was used with 25% H_2SO_4 in ethanol as electrolyte. The electrochemical reduction of benzenesulphonyl chloride evidently proceeds through the same steps and the same intermediates, as the chemical reaction [14], namely, sulphinic acid (RSO_2H), thiosulphate (RSO_2SR) and disulphide (RSSR).

There are only a few papers available [9, 10] dealing with the detailed electrode kinetics and mechanisms of these reactions, which involve large numbers of intermediates and are complex. Our findings do not necessarily support some of the previously derived conclusions. This may be partially due to the difference in the electrolytic conditions under which the reactions were studied. The literature data also indicate that there are a number of possible chemical side reactions involving benzenesulphonyl chlorides and some of the intermediates [15–20]. One reaction of particular concern is the hydrolysis of RSO_2Cl, since RSO_3H, once formed, is difficult to reduce. Since water is the by-product in the reduction of sulphonyl chloride some degree of hydrolysis must always be anticipated.

It is evident from our potentiodynamic measurements that RSO_2Cl is reduced to RSO_2H, and RSSR to RSH via direct electron transfer rather than reduction via adsorbed hydrogen since both reductions take place at potentials far removed from the H_2 evolution potential. The mechanism for the reduction of RSO_2H becomes somewhat clarified only through comparison of potentiodynamic and quasi-steady-state measurements* since the reduction takes place at potentials close to H_2 evolution and the reduction via adsorbed hydrogen could be expected (Fig. 3). Quasi-steady-state data, however, clearly show that the current corresponding to RSO_2H reduction decreases on approaching hydrogen evolution potential. The minimum observed in this case is thus not solely due to the mass transfer. It appears that increased hydrogen adsorption competes with the adsorbed RSO_2H species and as the hydrogen evolution potential is approached causes a decrease in the rate of reduction of RSO_2H. An additional possibility is that one or more of the intermediate species are subject to the potential-dependent adsorption behaviour of organic molecules. In any event, RSO_2H reduction apparently also proceeds via direct electron transfer. This experiment is thus a classical example of the importance of competitive adsorption in electrode reactions where direct electron transfer is involved.

While potential sweep measurements do not show the reduction of RSO_2SR, the electrolyses clearly show that RSO_2SR once formed is further reduced to RSSR and RSH. The reduction may therefore proceed via evolved hydrogen, although other chemical reactions may be involved. It should be noted, however, that in the potentiodynamic experiments only RSO_2SR was added to the electrolyte. This curve might well be altered substantially in the presence of other sulphur species

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* Potential kept at certain values, indicated by dots on Fig. 3 for 1–5 min.

and thus should not be necessarily taken to represent the *i–E* curve for reduction of RSO_2SR during a preparative experiment.

The results obtained under steady-state conditions undoubtedly show that the main product from the reduction of RSO_2Cl and the reducibility of practically all components are influenced by solvent, temperature and electrode material, as shown in Table 2. Alcoholic solutions, as well as higher temperatures, favour thiol formation regardless of electrode material. This is believed to be true mainly due to the increased solubility of RSSR under these conditions. In addition, the higher temperatures may influence the product distribution via competing chemical reactions whose rates would be increased with temperature. This may be particularly true in the case of RSO_2Cl/RSH interaction (once RSH is formed), which leads to the RSSR formation, as already mentioned. The reduction of RSSR to RSH proceeds at higher rates, and lower potentials than other intermediates (RSO_2H and RSO_2SR). Constant current electrolysis generally afforded material yields exceeding 80% for the formation of RSH and/or RSSR in alcohols and sulpholane when using a lead cathode. No substantial build-up of either RSO_2H or RSO_2SR was ever observed (Table 2). Current efficiencies reported in Table 2 correspond roughly to 50% conversion. Water was required in sulpholane solutions to provide sufficient conductivity (HCl does not dissociate in sulpholane). Sulphonic acid formed via hydrolysis of RSO_2Cl was detected among products in aqueous HCl/sulpholane. The amount is estimated to be 5–10%.

Results obtained with Ni electrodes show increased yields of RSO_2H, RSO_2SR and RSSR at the expense of RSH. No thiol was formed at temperatures up to 75°C. We have found, however, that RSSR and RSH are major products at 95° C even on Ni. The latter results are not included in Table 2 since electrodes made of pure Ni are not sufficiently stable at 95° C. Inert Ni alloys or suitable stainless steel should be employed instead. Influence of temperature on product distribution ratios proved to be qualitatively the same as in the experiments with lead electrodes. Some influence of current density is also seen.

Build-up of RSO_2H observed at 45° C and low current density when using Ni cathodes supports our results obtained with the potentiodynamic technique which indicate a sharp decrease in the rate of RSO_2H reduction when hydrogen evolution becomes predominant. More importantly, no RSO_3H was detected among products in this case. Thus RSO_2Cl losses via hydrolysis are prevented. This explains the higher total material yields obtained with Ni electrodes. Total current efficiencies, quite surprisingly, compare favourably with lead electrodes in spite of the fact that H_2 evolution occurs at much lower potentials on nickel.

Preliminary scale-up results on lead confirmed those obtained earlier on a smaller scale, i.e., high efficiencies for thiol formation obtained using an 80 cm^2 electrode under the conditions given in Table 3. However, long-term operation, exceeding 0·1 A h cm^{-2} again caused disintegration of the lead electrode.

The metallic component of the ‘mud’ on the electrode is lead; some lead chloride is found as a precipitate in the electrolyte. The degradation behaviour only occurs when both chloride ions and a sulphur species are more reduced than the disulphide, i.e., RSH are in contact with the electrode. Disintegration of the cathode has been reported during hydrogen evolution on lead, antimony and tin and it has been suggested that in this instance it is due to hydride formation [21, 22]. Various lead–antimony alloys were also subject to cathodic disintegration in our experiments. Disintegration was not observed in sulphate electrolytes.

Removal of chloride from the electrolyte can be accomplished by reacting the RSO_2Cl with RSH and separating RSSR from the aqueous HCl solution (by filtration). Disulphide is then used as a reactant for subsequent reduction. The losses of RSO_2Cl due to hydrolysis are also prevented by this chemical/electrochemical process.

Earlier studies [2–7, 23, 24] as well as our present work have shown that the disulphides are generally easily reducible. The data in Table 5 show the effectiveness of an electrolytic process for the reduction of disulphide to thiols where the solvent provides adequate solubility for the reactant. Ethanol is such a solvent and the conductivity of ethanol–sulphuric acid solution is high. A limited search and evaluation of other, non-flammable solvents was made, but the ultimate results were not satisfactory.

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