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High current density organic electrosynthesis via metal powders in multiphase systems

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A procedure for the high current density (> 0.5 A cm^{-2}) reduction of organic compounds is described. The reactions employ an emulsion of aqueous zinc chloride (4 M) and the organic substrate and occur via the intermediate formation of zinc powder at the cathode. A high current density and the *in situ* reaction of the powder ensure that the metal has a high surface area, free of oxidized films: it is therefore very reactive. Two reactions, the dechlorination of 1,2,2′-trichloroethane and the reduction of nitrobenzenes, are used as examples.

1. Introduction

One reason why electro-organic processes have not become common is the low maximum current density which can be achieved for many electrode reactions in one-phase systems. Indeed, to reach a current density in the range 0.1–1.0 A cm^{-2}, common for inorganic processes (e.g. Cl_2/NaOH production, Al and Cu extraction), it is necessary for the electroactive species to be soluble to the extent of 5–50% and even when the electrolysis medium may be selected to permit such a concentration, there is a penalty: the product is usually also highly soluble and therefore difficult to extract.

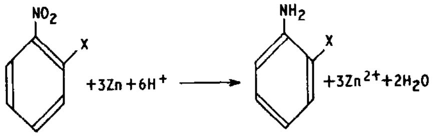
The use of multiphase systems offers an escape from these difficulties and this paper discusses the use of a three-phase system, water/organic substrate/metal powder, for carrying out reductions. The cathode reaction is the deposition of a metal, e.g.

$$Zn^{2+} + 2e \rightarrow Zn$$

from a concentrated solution of its salt and the reduction occurs by a chemical reaction between the metal and the organic substrate in an emulsion in the cathode compartment. Two reactions

$$CH_2Cl\text{–}CHCl_2 + Zn \rightarrow CH_2 = CHCl + Zn^{2+} + 2Cl^- \quad (1)$$

and



(2)

where X = H or F, will be used to illustrate the principle. It can be seen that the zinc ion is a catalyst in the reduction sequence and this method of processing has the advantage that the overall processes may be carried out at very high current density although the organic substrates are almost insoluble in the aqueous medium. The metal may be deposited with a high current efficiency even at high current density. Indeed, the use of a high current density is advantageous since it results in the formation of a metal powder of small particle size and hence high surface area which enhances its chemical reactivity. Moreover, if the metal powder is used *in situ*, its surface will be free of oxidized films and this will also make it reactive compared to zinc from a bottle. The electrolysis conditions must be chosen so that the rate of reaction between the zinc powder and the organic compounds is fast.

Earlier workers [1, 2] have proposed the use of zinc metal as an intermediate in indirect cathodic dehalogenation reactions but without apparently realising the advantage in current density which may be attained. Such indirect cathodic reductions of nitrobenzenes have not been described

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previously although the electrolytic reduction in homogeneous solution is a well-known process [3]. At very high current densities, the zinc formed should have properties close to those formed by the reaction of potassium with anhydrous zinc chloride in tetrahydrofuran [4].

2. Experiment

The electrolyses were carried out in a two-electrode beaker cell. The cathode was an aluminium disc with its top and bottom faces covered with epoxy resin so that only the edge (0.6 cm^2) was exposed to the electrolyte. The disc was rotated with a Servomex MC 43 motor and control unit. This cathode was placed inside a 50 cm^3 porous pot and the anode was a series of graphite or zinc plates placed around the outside of the porous pot. The cell had a jacket through which water from a thermostat could be circulated.

All chemicals were the highest quality grade available but were used without purification. The catholytes were, however, deoxygenated with a stream of oxygen-free nitrogen (BOC Ltd) before and during the electrolyses. The current was controlled using a modified Chemical Electronics 70 V/2 A potentiostat and charges were measured with an electronic integrator.

The current efficiency for zinc powder formation was determined by weighing the metal in the cathode compartment after it had been washed and dried. The organic analyses were carried out by g.l.c. using standard solutions of both starting materials and products; product identification was confirmed by g.l.c.–mass spectroscopy.

Vinyl chloride was a gas under the electrolysis conditions and it was condensed in two cold traps containing chloroform placed in the outlet stream from the cathode compartment atmosphere. The major products from the nitrobenzene reductions were soluble in the aqueous acid medium. Hence, after the electrolyses, the aqueous portions of the catholyte were made alkaline and the resulting solutions and precipitate [$Zn(OH)_2$] were extracted with ether.

3. Results and discussion

In a preliminary series of experiments, the current efficiency for the deposition of zinc from aqueous zinc chloride (4 M) was investigated and it was confirmed (see Table 1) that it was approximately 90% even at a current density of 1 A cm^{-2}. At the end of the electrolyses (after the passage of the charge to form 1 g Zn metal) the zinc was present either as particles, free in solution, or as a loose deposit on the cathode. Since some of the reductions would benefit from the presence of protons, the depositions were repeated in aqueous zinc chloride containing hydrochloric acid (1 M) and it can also be seen in Table 1 that this concentration of acid had little adverse effect on the current efficiency for zinc deposition.

The experiments with the nitrobenzenes were carried out at ambient temperature where the chemical reaction between the zinc powder (the zinc metal adhered to the cathode less when there was an emulsion in the cathode compartment) and the organic compound was rapid, although during the electrolysis zinc could be seen in the catholyte. The current density used was 0.5 A cm^{-2}, chosen only because higher currents produced experi-

Table 1. Current efficiency for the deposition of zinc at a rotating (1000 r.p.m.) aluminium cylinder (0.6 cm^2). $Q = 0.015$ F, temperature = 293 K

Electrolyte		*Current density* (A cm^{-2})	*Current efficiency* (%)
[$ZnCl_2$] (M)	*[HCl]* (M)		
4	0[†]	0.1	93
		0.5	91
		1.0	87
4	1	0.1	89
		0.5	88
		1.0	86

[†] Solution pH = 2.5.

Table 2. Preparative electrolyses. Rotating Al cathode in aqueous $ZnCl_2$ (4 M) + HCl with organic substrates present as a second phase. The ratio H_2O/nitrobenzenes was 13/1 and that of $H_2O/CH_2Cl–CHCl_2$ was 7/3. $I = 0.5\ A\ cm^{-2}$; $Q = 0.012\ F$

Experiment	*Substrate*	*Initial [HCl]* (M)	*T*(K)	*Product*	*Current efficiency*(%)	*Organic efficiency*(%)
1	$C_6H_5NO_2$	1.0	293	$C_6H_5NH_2$	62	44
2		0.5†			76	95
3		0.1†			90	98
4		0.1			64	57
5	o-F–$C_6H_4NO_2$	0.1†	293	o-F–$C_6H_4NH_2$	86	98
6	$CH_2Cl–CHCl_2$	0	331	$CH_2=CHCl$	84	–

† When [HCl] had dropped to a half the initial value, concentrated HCl was added to return [HCl] to the initial value.

mental problems with the equipment. The major product from the reduction of nitrobenzene was always aniline although the selectivity depended on the acid concentration (see Table 2). The optimum acid concentration was about 0.1 M; with higher concentrations, some *p*-aminophenol was observed while at higher pH coupled products were probably formed. Moreover, since the overall reduction of nitrobenzene to aniline consumes protons (6 mol H^+ to 1 mol $C_6H_5NO_2$), it is essential to ensure that the acid concentration remains at the desired level and in some experiments this was done by stepwise addition of concentrated hydrochloric acid. In these conditions the yield of aniline from nitrobenzene is good and the yield of *o*-fluoroaniline from *o*-fluoronitrobenzene is similar.

The electrolytic dechlorination of 1, 1, 2-trichloroethane was carried out at 58° C, both to increase the rate of the chemical step and to ensure that the product, vinyl chloride, was a gas and, therefore, could be readily isolated. In these conditions, the yield of vinyl chloride was also high, see Table 2, and, in fact, the current yield of vinyl chloride was independent of current density in the range 50–500 mA cm^{-2}. The advantage of electrolytic zinc could be demonstrated in this reaction; the analogous chemical reactions using zinc powder and zinc granules gave yields of vinyl chloride of only 30 and 0.5% after an hour of reaction at the same temperature. It might also be noted that the electrolytic route permits recovery of chlorine gas via the anode reaction.

In conclusion it may be noted that the results in Table 2 fully justify our expectations concerning this type of indirect electrolytic reduction. Electrolyses can be carried out at high current densities (the limit should be well above 0.5 A cm^{-2}) and give good yields of product. Moreover, the approach should be applicable to a wide range of reductions with appropriate control of the reaction conditions.

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