# A High Current Density Electrosynthesis of Amines from Nitro Compounds Using Metal Powders as Intermediates

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Copper, iron, tin and zinc powders may each be formed in very good yield in acidic aqueous solution by electrolysis at high current density (0.5 A cm^{-2}) of a solution of their metal salts (0.4−1.0 M) in an appropriate electrolyte. It is further shown that a range of nitro compounds may be reduced to the corresponding amines by electrolysis at 0.5 A cm^{-2} of an emulsion of the nitro compound, or its solution in an inert solvent, with the aqueous medium for deposition of the metal powder (typical ratio of water to organic 4:1). Tin and zinc are the best metals for this reaction when the organic and current yields can exceed 90 %.

In industry the reduction of aromatic nitro compounds to amines is carried out either catalytically or using metal/acid reductions. The latter are more suited to medium and small scale processes but lead to large volumes of effluent containing heavy metal ions. Both types of reaction have been extensively reviewed.[1,2,3] The electrolytic reduction of nitro compounds has also been extensively discussed as an alternative route[4,5] but, in general, suffers from problems of selectivity and insufficient current density. As a result, a number of indirect cathodic reductions, e.g. with titanium ions as redox catalysts,[6] have been proposed. In this paper we discuss the optimisation of a reaction route where the electrode process is the formation of metal powder, i.e. the reaction sequence is

$$M^{2+}+2e \rightarrow M$$
$$3M+6H^{+}+C_6H_5NO_2 \rightarrow$$
$$3M^{2+}+2H_2O+C_6H_5NH_2$$
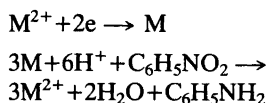
where M^{2+} is Cu^{2+}, Fe^{2+}, Sn^{2+} or Zn^{2+}. An earlier preliminary communication[7] has reported that this reaction route is possible at high current density and gives good selectivity. Moreover, the metal ion is recycled continuously so that the reaction need lead to no effluent containing heavy metal ions.

RESULTS AND DISCUSSION

Selection of the metal intermediate. Four metals, copper, iron, tin and zinc were considered as the intermediate for the high current density electrochemical, reduction of nitro compounds to amines. The metals cover a spectrum of reducing ability, their standard electrode potentials in non-complexing media spanning the range from +0.03 to −0.78 V vs. NHE (see Table 1). In order to be suitable intermediates for the desired reaction, it was necessary to find conditions where the powders could be deposited with good efficiency at high current density from an acid electrolyte since the reduction of the nitro compounds consumed 6 H^{+}/molecule and requires a low pH for a good yield.

Hence, several electrolytes were investigated for each metal. Those found suitable are listed in Table 1 which further reports the potentials where deposition commences in each electrolyte and also the current efficiencies for metal powder formation at 0.5 A cm^{-2} for three concentrations of the metal ions. Finally, Table 1 reports yields of aniline from nitrobenzene from experiments where an emulsion of 50 cm^3 of aqueous electrolyte and 10 cm^3 of nitrobenzene were electrolysed at a rotating C or Al cylinder; the electrolyses

Table 1. A comparison of metal powder intermediates for the reduction of nitrobenzene to aniline.

Electrolyte	E_e° vs. NHE/V [a]	E_{dep} vs. NHE/V [b]	Current efficiency [c] $M^{2+}+2e\rightarrow M$ at various $[M^{2+}]/\%$			Current efficiency [c,d] $C_6H_5NO_2\rightarrow$ $C_6H_5NH_2$
			1 M	0.4 M	0.1 M	
$ZnSO_4+H_2SO_4$ (1 M)	-0.76	-0.90	83	52	14	49 (74 [e,f])
$ZnCl_2+HCl$ (0.1 M)	-0.76	-0.78	90	98	21	93 [f]
$SnCl_2+HCl$ (1 M)	-0.14	-0.28	92	98	83	96
$CuSO_4+H_2SO_4$ (1 M)	$+0.03$	$+0.03$	94	91	23	16
$FeCl_2+HCl$ (0.01 M)+ NaCl (0.7 M)	-0.44	-0.75	89	95	94	low (80 [g])

[a] Standard potentials for the M^{2+}/M couple in non-complexing media. [b] Potential where metal deposition commences. [c] Current density 0.5 A cm^{-2}; charge for formation 1 g of M passed. [d] For conditions, see text. [e] With 0.1 M H_2So_4. [f] Acid added in aliquots during electrolysis. [g] Metal powder formed then nitrobenzene and 1 M HCl added and the emulsion refluxed.

were carried out at 0.5 A cm^{-2} until the charge for deposition of 1 g metal had been passed and were carried out at room temperature.

Comparison of the data shows it was possible to find conditions where deposition of each metal powder was possible with high current efficiency even when the metal ion concentration was as low as 0.4 M. Zinc and tin were, however, the better metals for this organic reaction. The conversion of nitrobenzene is low when the intermediate is copper and, indeed, at the end of the electrolysis, considerable metal powder was visible in the electrolyte. It was also not possible to find a very acidic electrolyte where iron powder was formed efficiently (iron is a good hydrogen evolution catalyst) and the electrolyte selected only gave a very low yield of aniline. Iron powder is, however, widely used in industry for the chemical reduction of nitrobenzenes but generally the reaction is carried out under reflux in more acid solution. Hence a further experiment was attempted where the iron powder was first formed by electrolysis and then 1 M HCl and nitrobenzene were added and the emulsion refluxed; the yield then increased to 80 %.

While both zinc and tin were used in later experiments, the latter is clearly the superior choice. Zinc requires the acid concentration to be controlled within a limit and, consequently, during the reduction of nitro compounds, aliquots of acid must be added during electrolysis. In contrast, tin power formation was satisfactory even from 0.1 M $SnCl_2+1.0$ M HCl. Moreover, tin deposition occurs at least 0.5 V less negative

than zinc deposition and, in an industrial cell, this would lead to a significant reduction in energy consumption.

Selection of other reaction conditions. A number of other experimental parameters, namely cathode material, cathode current density, stirring of the emulsion, the concentration of metal ion, the use of an inert solvent for the nitro compound (so that solid substrates could be used) and temperature, were considered.

The cathode cylinder must be stable both during electrolysis and on open-circuit and it was thought that a metal with an oxide coating would aid release of the intermediate metal powder. Even so, it was considered initially that several materials would be suitable; aluminium, steel and graphite were selected for trials. Some problems were, however, encountered; for example, an aluminium electrode was found to react chemically with Sn^{2+} (2 Al+3 $Sn^{2+}\rightarrow2$ Al^{3+}+3 Sn) in an $SnCl_2$/HCl solution while adhesion of zinc to graphite was good. Hence, in general, a graphite cathode was used for reaction with Sn^{2+} and aluminium for reactions with Zn^{2+}.

Electrolyses were carried out at 0.5, 1.0, 2.0 and 5.0 A cm^{-2} using nitrobenzene as the substrate and the 0.4 M $SnCl_2+1.0$ M HCl solution; in all experiments, the yield of aniline was above 95 %. In most electrolyses 0.5 A cm^{-2} was used for experimental convenience. All electrolyses used a rotating cathode to promote the release of metal powder from the cathode surface into the catholyte and to produce a dispersion of nitrobenzene in the aqueous elec-

trolyte. Most experiments used a rotating cylinder cathode. Although the rate of rotation of the cylinder did not change the current efficiency for metal deposition, it did affect the coupled chemical reaction. In experiments using 0.4 M $SnCl_2+1$ M HCl as the electrolyte, the yield of aniline from nitrobenzene was 17, 76 and 98 % when the rotation rates were 100, 500 and 1000 r.p.m.; the rest of the charge was accounted for by unreacted metal in the electrolyte at the end of the reaction. At the present time, it is not clear whether this effect is due to metal particle size or the state of dispersion of the emulsion.

In general, it was considered that the concentration of metal ion in solution should be as low as possible, both for economic reasons and because it simplifies the extraction of product when this requires neutralisation of the acidic medium. It is clear from the experiments in Table 1 that 0.4 M metal ion is sufficient to give an almost quantitative yield of metal powder. Also the yield of aniline from nitrobenzene was good and hence it can be concluded that the 4 M $ZnCl_2$ used in an earlier report [7] is quite unnecessary. In the next section, the reduction of a range of nitrobenzenes is reported and some of these were

Table 2. Effect of composition of the organic phase on the efficiency of nitrobenzene reduction. Electrolysis used 40 cm^3 of 0.4 M $SnCl_2+1$ M HCl and 10 cm^3 of organic phase, 0.5 A cm^{-2}, a carbon cathode and room temperature. Electrolysis terminated after charge for formation of 1 g Sn.

Organic phase $C_6H_5CH_3$/cm^3 + $C_6H_5NO_2$/cm^3		Current efficiency $C_6H_5NO_2 \rightarrow C_6H_5NH_2$/%
0	10	96
2.5	7.5	96
5.0	5.0	87
7.5	2.5	68

solids and needed to be introduced into the cell as solutions. To test the effect of an inert organic solvent, electrolyses were carried out where the organic phase was various mixtures of nitrobenzene and toluene, as the inert solvent, see Table 2. These experiments show that dissolution of the nitro compound in an inert solvent is possible but the concentration of the nitro com-

Table 3. Preparative electrolyses of nitro compounds with Zn and Sn as intermediates. Electrolyses at 0.5 A cm^{-2} to charge for 1 g of metal. Total catholyte volume approximately 50 cm^3.

Nitro compound	Conditions	Isolated yields of corresponding amine/% Current	Organic [c]
(a) 0.4 M $SnCl_2+1$ M HCl			
$C_6H_5NO_2$	liquid (6.6 g)	96	89
$2\text{-}F\text{-}C_6H_4NO_2$	liquid (6.6 g)	96	89
$2\text{-}Br\text{-}C_6H_4NO_2$	6 g in 10 cm^3 C_6H_6	Ratio $C_6H_5NH_2$: $2\text{-}Br\text{-}C_6H_4NH_2$ 21:79 [b]	
$2\text{-}Cl\text{-}C_6H_4NO_2$	8 g in 30 cm^3 $CHCl_3$ 70 °C	96	–
$2\text{-}CH_3O\text{-}C_6H_4NO_2$	liquid (5 g)	99	82
$4\text{-}HO\text{-}C_6H_4NO_2$	6 g in 10 cm^3 $C_2H_5OC_2H_5$	89	80
$4\text{-}CN\text{-}C_6H_4NO_2$	7 g in 20 cm^3 C_6H_6	30	80
$3\text{-}CN\text{-}C_6H_4NO_2$	7 g in 30 cm^3 C_6H_6, 70 °C	75	88
$2,5\text{-}Cl_2\text{-}C_6H_3NO_2$	9 g in 20 cm^3 C_6H_6 70 °C	31	90
$(CH_3)_3CNO_2$	5 g in 20 cm^3 C_6H_6	48	90
$C_{10}H_7NO_2$	6 g in 20 cm^3 C_6H_6	91	79
(b) 0.4 M $ZnCl_2+0.1$ M HCl [a]			
$C_6H_5NO_2$	liquid (6 g)	93	89
$2\text{-}F\text{-}C_6H_4NO_2$	liquid (6.6 g)	92	90
$2\text{-}Br\text{-}C_6H_4NO_2$	6 g in 10 cm^3 C_6H_6	Ratio $C_6H_5NH_2$: $2\text{-}Br\text{-}C_6H_4NH_2$ 8:92 [b]	

[a] HCl added in aliquots during electrolysis to maintain constant concentration. [b] GLC yield only. [c] Based on nitrobenzene not recovered.

pound should be high. In later experiments, benzene, diethyl ether and chloroform were used interchangably with toluene as the inert solvent.

The cell was fitted with a steam coil for carrying out electrolyses above room temperature. Experiments were carried out at higher temperature only when reaction did not take place at 20 °C, and in this study, this was only the case for some chlorinated derivatives (see later). The use of high temperature did not, however, present any special problems.

The reduction of substituted nitrobenzenes. Table 3 reports the isolated yields of amines from the reduction with tin of eleven nitro compounds and with zinc of three nitro compounds. It can be seen that it is possible to define conditions where the organic yields for all reactions are very good. In the cases where the current efficiency is poor, this is likely to be due to poor kinetics of the metal–nitrobenzene reaction. Certainly the current efficiency for the two chlorinated derivatives improved on increasing the temperature of electrolysis. Also with the cyanocompounds there were solubility limitations which restricted the maximum concentration of the nitro compounds in the organic phase (see Table 2); there was no reduction of the cyano group. With 2-bromonitrobenzene, and in contrast to the 2-chloro and 2-fluorocompounds, there was some cleavage of the carbon–bromine bond but this side reaction was less important using zinc than where the intermediate was tin.

The procedure reported here would seem to be a useful laboratory method for the conversion of nitro compounds to amines and it also has considerable promise as an industrial process. It gives good yields and works well for a range of structures. Moreover, from the industrial viewpoint, it has the advantages that it is successful at very high current density, in principle leads to no heavy metal effluent and that the cell could be used for a variety of reactions.

Mechanism. It has been suggested [2] that the mechanism for metal/acid reduction of nitro compounds parallels strongly that for the cathodic reaction, *i.e.* the reduction occurs in 2e steps with phenylhydroxylamine as a well-defined intermediate. In these experiments, there was, however, no evidence of intermediate reduction products even though the electrolyses were carried out with a substantial excess of nitro compounds in the catholyte. This would suggest that the initial reduction of the nitro compound is the rate determining step. Moreover, metal powder was commonly present in small amounts at the end of the electrolysis and this would suggest that the reaction is not very fast.

The basic nature of the mechanism in the three phase (water, organic phase and metal powder) system is not clear. It is even uncertain as to whether the reaction occurs at the metal/organic interface, at a three phase interface or by dissolution of the nitro compound in the aqueous solution. Some competitive experiments were carried out; equimolar amounts of two nitro compounds were electrolysed simultaneously. The results are reported in Table 4 but are both surprising and inconclusive. For example, the *o*-fluoro and *o*-methoxy compounds seem to reduce at an identical rate to the parent compound while *o*-chloronitrobenzene is reduced much more slowly than nitrobenzene.

Table 4. 6 g of nitrobenzene and the equivalent weight of substituted compound were dissolved in an organic solvent and the emulsion of the organic phase with 30−40 cm³ of 0.4 M $SnCl_2$+1 M HCl was electrolysed at 0.5 A cm^{-2}. Charge for 1 g Sn was passed. Room temperature.

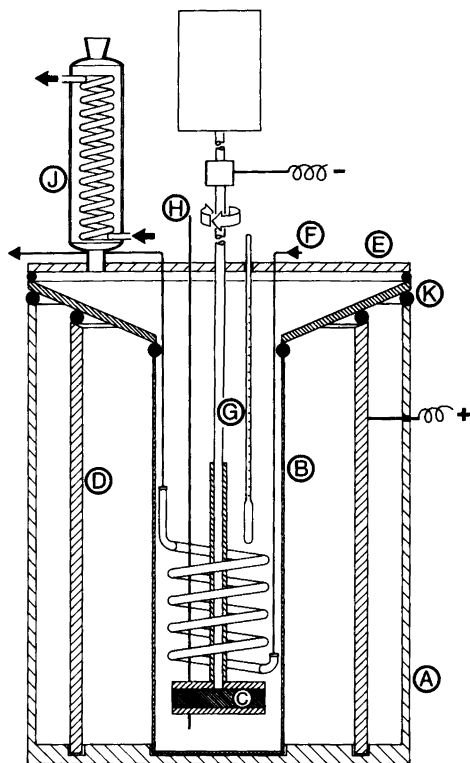| Other nitro compound	Solvent	Current yields of amines/%	
		Aniline	Other amine
$2\text{-F}-C_6H_4NO_2$	C_6H_6 (10 cm³)	44 [a]	48 [a]
$2\text{-Cl}-C_6H_4NO_2$	C_6H_6 (20 cm³)	90 [a]	6 [a]
$2\text{-CH}_3O-C_6H_4NO_2$	C_6H_6 (10 cm³)	45 [b]	45 [b]
$4\text{-HO}-C_6H_4NO_2$	$C_2H_5OC_2H_5$ (10 cm³)	47 [b]	46 [b]
$4\text{-CN}-C_6H_4NO_2$	C_6H_6 (20 cm³)	60 [b]	30 [b]
$C_{10}H_7NO_2$	C_6H_6 (20 cm³)	52 [b]	41 [b]

[a] Isolated yield. [b] GLC yield.

Fig. 1. Design of cell. A, polypropylene cell body; B, porous pot; C, rotating cylinder cathode; D, carbon tube anode; E, cell top; F, steam coil; G, thermometer; H, nitrogen inlet; J, condenser; K, O-rings.

EXPERIMENTAL

The electrolyses were carried out in the cell shown in Fig. 1. The cell body (A) was made of polypropylene and the catholyte compartment is the inside of a porous pot (B), type celloton V10 supplied by Doulton Industrial Products Ltd. and with dimensions 4.5 cm internal diameter and height 15 cm. Moreover the cell was sealed with 0-rings so that the anolyte and catholyte compartments were completely separated. The metals were deposited onto a rotating cylinder of carbon or aluminium (C) whose upper and low surfaces were masked with PTFE. The anode (D) was a carbon tube, internal diameter 8 cm, with holes drilled at the top to allow release of the gas formed at the anode. The cell top (E) was fitted with a steam coil (F), thermometer (G), nitrogen inlet (H) and condenser (J). The catholyte was an emulsion of the aqueous electrolyte and the organic phase stirred by the rotating cathode,

while the anolyte was the same aqueous electrolyte. The constant current was supplied by a Sorensen Power Supply, type SRC 60−35 and charge was measured with a laboratory-built integrator.

Electrodeposition of metals. Iron, copper and zinc metals were deposited from their respective salt solutions on an aluminium cathode while tin was deposited on a carbon cathode. Charge was passed to deposit 1 g of the metal, which was washed thoroughly with water and dried in an oven before being weighed.

Reduction of nitro compounds. Appropriate amounts of nitro compounds either dissolved in a minimum amount of solvent or as neat liquids were mixed with aqueous electrolyte in the porous pot. Before electrodeposition of metals, the catholyte was saturated with nitrogen. After the charge had been passed, the stirring was continued for a further 20 mins. The remaining metal in the porous pot, if any, was washed and isolated before any neutral organic products were extracted with ether (30 cm^3×3) from the aqueous electrolyte. The aqueous phase was then neutralised with K$_2$CO$_3$ and saturated with sodium chloride before further extraction with ether (20 cm^3×3). The solution was dried over magnesium sulfate before evaporation of ether. The products were purified by passing them through a short column of silica gel using an appropriate solvent. The purity and identity (by comparison of retention times with authentic samples or by GLC-MS spectroscopy) of the products were checked by GLC and quantitative analyses were by weight following evaporation of the solvent.

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