

# *Electroreduction of benzonitrile*

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Benzylamine is used as a photographic fixing agent, as a corrosion inhibitor and also as a raw material for the preparation of powerful explosives which are easy to handle. The conventional method adopted for the preparation of benzylamine is the catalytic hydrogenation of benzonitrile in absolute ethanol under high pressure. In the present communication, a novel electrolytic reduction technique for the conversion of benzonitrile to benzylamine, using a palladium black deposited on graphite cathode, is described. Galvanostatic polarization studies, using both a stationary and a rotating cylindrical palladium black deposited cathode, revealed that there is considerable depolarization only in a very low current density regions. The identity of benzylamine has been confirmed by NMR, mass spectral and infrared data. Carbon, hydrogen and nitrogen analysis also support the identity of benzylamine. This simple electrochemical reduction technique opens up a new route for the reduction of cyanide groups to the primary amine groups.

## 1. Introduction

Benzylamine is an aromatic primary amine which is widely used in the organic chemical industry. Among its many uses, its corrosion inhibitive property and its role as a photographic fixing agent are worth mentioning [1,2].

At present the primary amines are prepared from nitriles [3]. Nitriles may be reduced catalytically, with sodium in alcoholic medium and also with lithium aluminium hydride [4]. The yields of primary amines are less satisfactory in the reduction methods using  $\text{LiAlH}_4$  and sodium in alcoholic medium. Moreover, the re-use of  $\text{LiAlH}_4$ , which is very costly, is ruled out. Therefore a catalytic reduction technique using noble metals as catalyst is preferred. A simple liquid phase catalytic reduction leads to the formation of secondary amines and other products and hence an acidic or ammonia medium is preferred to minimize the formation of secondary amines [5,6,7]. There are some disadvantages in the catalytic reduction of nitriles to primary amines: (1) The formation of side products cannot be completely ruled out. (2) An absolute ethanolic medium is necessary which is costly. (3) The catalyst palladium adsorbed on carbon has to be freshly

prepared just before the experiment to avoid catalytic poisoning [5]. (4) Re-use of the catalyst requires elaborate purification and in this there is some loss of the precious catalyst. (5) Electrolytically pure hydrogen is necessary [5] to prevent the premature deactivation of the catalyst as a result of catalytic poisoning by impure hydrogen. (6) High pressure generating equipment is necessary.

Attempts have also been made to avoid the formation of secondary and tertiary amines by carrying out the reduction of nitriles catalytically using platinum oxide as catalyst and acetic anhydride as solvent [3]. The acylated primary amine formed is then hydrolyzed to the free base. But the method involves an additional step of alkali hydrolysis which brings down the yield.

Hence in the present approach a simpler technique, which involves a combination of *in situ* electrochemical generation of pure hydrogen and its adsorption on a thinly deposited palladium black cathode acting as the catalyst, is adopted. This electroreduction technique has opened up a simple and new route for the preparation of primary amines in high yields from nitriles. Conditions are being standardized for the reduction of various aromatic, aliphatic and heterocyclic nitriles to their primary amino compounds in this

laboratory. A higher amperage cell for the production of primary amines from the nitriles has already been designed. A patent specification on the electroreduction of aromatic and aliphatic nitriles has been filed [8]. In this communication, the reduction of benzonitrile to benzylamine is described in detail.

## 2. Results and discussion

### 2.1. Preparation of palladium black cathode on a graphite plate (stationary condition)

350 ml of aqueous HCl (3N) containing 0.35 g of palladium chloride and 1.75 g ammonium chloride was used as the catholyte. 75 ml of aqueous HCl (3N) was used as the anolyte contained in a ceramic porous pot. The anode is a graphite plate of 0.3 dm<sup>2</sup> area. A graphite plate of 1.0 dm<sup>2</sup> area was used as the cathode on which palladium black was deposited. The catholyte was gently agitated using a glass stirrer. The current density employed for the deposition was very low. The temperature of the catholyte was maintained around 30°C. Deposition was continued until the catholyte became colourless. After the deposition the deposited palladium black cathode was dried and the deposit was found to be adherent.

### 2.2. Preparation of palladium black cathode on a rotating cylindrical graphite rod

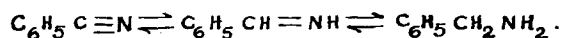
The same procedure as mentioned above is adopted. The cylindrical rod was slowly rotated using a fractional horsepower motor. The deposit of palladium black was found to be adherent in this case also.

### 2.3. Galvanostatic polarization measurements

2.3.1. *Under stationary conditions.* In an ethanolic hydrochloric acid solution as the catholyte, cathode potential measurements were carried out using deposited palladium black cathodes with and without benzonitrile. Saturated calomel was used as the reference electrode. Aqueous HCl was used as the anolyte and a graphite rod as the anode. A porous ceramic pot was used as the diaphragm. Fig. 1 gives

a plot of electrode potential (mV) versus current density in a semi-logarithmic form. From the graph it is obvious that there is considerable depolarization at low current densities. At higher current densities there is practically no depolarization and much hydrogen evolution is observed.

2.3.2. *Under rotating conditions.* Galvanostatic polarization studies were carried out with the conditions the same as in the case of a stationary cathode. Fig. 2 gives a plot of electrode potential (mV) versus current density in a semi-logarithmic form. Here also, there is considerable depolarization only at lower current densities; at higher current densities hydrogen evolution is observed.



### 2.4. Reduction of benzonitrile under stationary conditions

4 ml of benzonitrile was dissolved in a catholyte of 350 ml ethanolic HCl (3N). 75 ml of aqueous HCl (3N) was used as the anolyte. A graphite plate (0.3 dm<sup>2</sup>) was used as the anode within a porous ceramic pot. Deposited palladium black on graphite (effective area 0.5 dm<sup>2</sup>) was used as the cathode. The catholyte was gently agitated by a glass stirrer. The temperature of the catholyte was maintained around 15–25°C. A current of 2 A to give a current density of 4 A dm<sup>-2</sup> at a cell voltage of 3.5 was employed. As the yield of the benzylamine hydrochloride was found to be poor after the passage of the theoretical charge corresponding to the 4 Faraday reaction, the electrolysis was continued. On vacuum distillation the catholyte gave a yield of 4.8 g of benzylamine hydrochloride (yield efficiency 85%). The current efficiency was 60%. The pale yellow solid obtained in this way was recrystallized from rectified spirit as colourless needles melting at 248°C.

A number of such reduction experiments under similar conditions were carried out at different current densities ranging from 1–8 A dm<sup>-2</sup>. In all these cases, more than the required theoretical current was passed to obtain a good yield of benzylamine hydrochloride. Table 1 gives an idea of the yield efficiency and current efficiency at different current density regions.

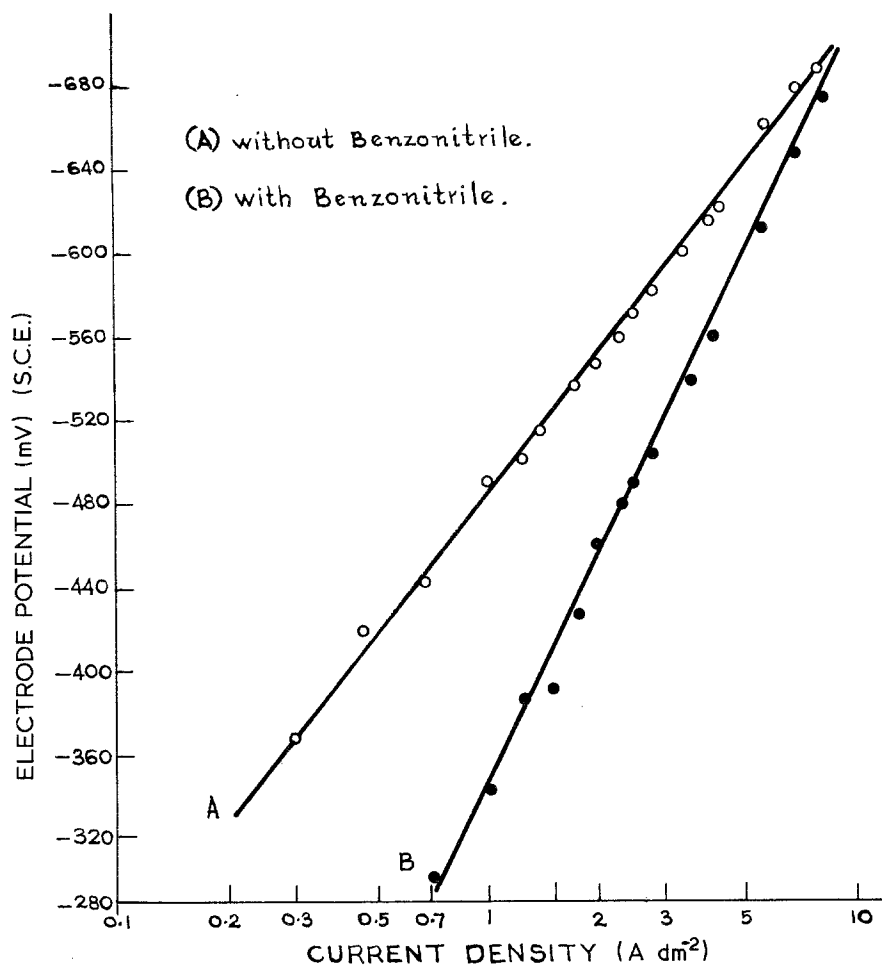


Fig. 1. Galvanostatic polarization study using deposited palladium black cathode (stationary condition).

Table 1. Reduction of benzonitrile under stationary condition

Experiment no.	Current density employed (A dm <sup>-2</sup> )	% yield of benzylamine hydrochloride	Current efficiency %
1	1	78	65
2	2	80	65
3	3	80	60
4	4	85	60
5	5	85	50
6	6	83	40
7	7	82	40
8	8	75	30

Table 2. Reduction of benzonitrile under rotating conditions

Experiment no.	Current density employed (A dm <sup>-2</sup> )	% yield of benzylamine hydrochloride	Current efficiency %
1	1	75	65
2	2	80	65
3	3	80	60
4	4	85	60
5	5	85	50
6	6	85	40
7	7	80	40
8	8	80	30

### 2.5. Reduction of benzonitrile at rotating electrodes

4 ml of benzonitrile were dissolved in a catholyte

of 350 ml ethanolic HCl (3N). Rotating cylindrical deposited palladium black on graphite cathodes were used (effective area is 0.5 dm<sup>2</sup>). The other conditions employed

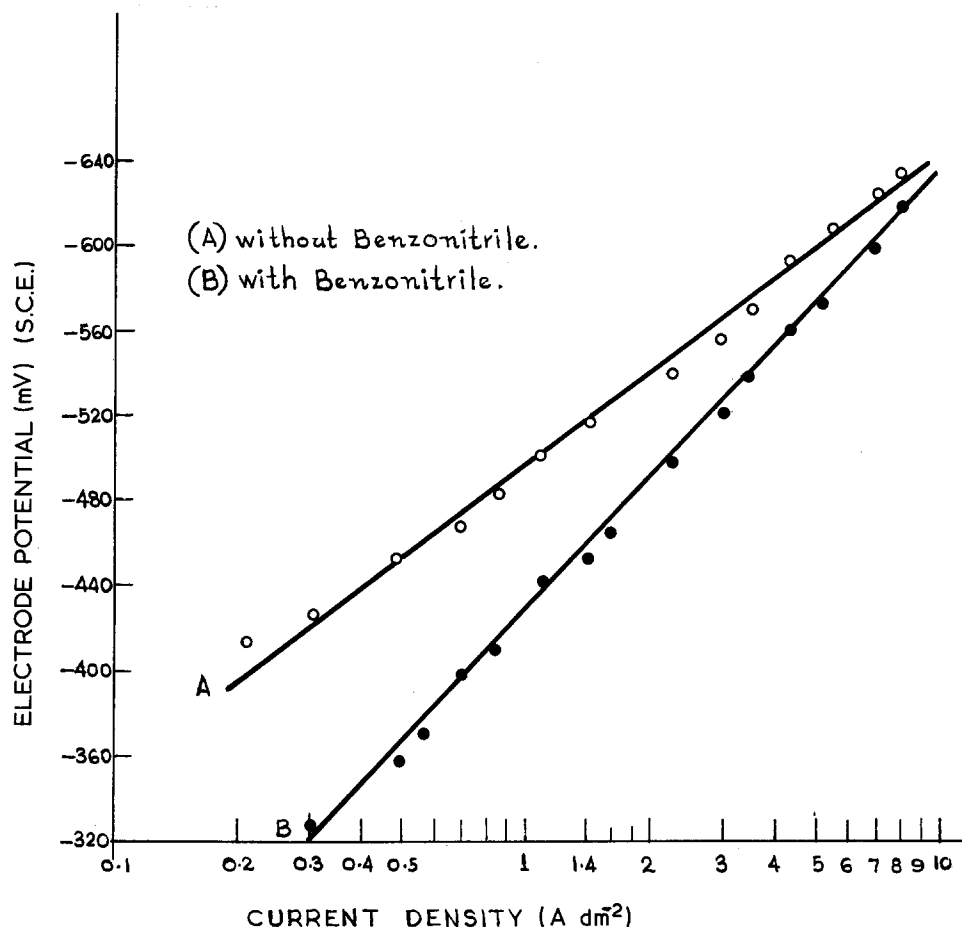


Fig. 2. Galvanostatic polarization study using rotating cylindrical deposited palladium black cathode.

were the same as those used with the stationary cathode. A current of 2.0 A to give a current density of 4 A dm<sup>-2</sup> at a cell voltage of 3.4 was employed. It was necessary to pass more than the theoretical charge to obtain a good yield efficiency. The yield of benzylamine hydrochloride here was also found to be around 85%. The current efficiency was found to be 60%.

A number of reduction experiments were carried out at different current densities ranging from 1 – 8 A dm<sup>-2</sup>. In all these experiments, more than the required theoretical charge was passed to obtain a good yield efficiency. Table 2 gives an idea of the yield efficiency and current efficiency at different current densities.

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