

Electrolytic Reduction of Nitriles. Part I

By

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The electrolytic reduction of nitriles was once undertaken by Felix B. Ahrens¹, who succeeded in isolating the corresponding primary amines but only with a very poor yield. To investigate the problem much more fully it was attempted to reduce benzonitrile, tolunitrile and benzylocyanide electrolytically under various conditions and to seek the best method by which they could be transformed into the corresponding amines.

Generally speaking, as nitriles are reducible only with great difficulty, their hydrolysis sometimes takes place far more easily than their reduction, and this makes the current efficiency for forming amines very low. Such a property predominates more in aliphatic nitriles than in the aromatic, so that benzylocyanide can hardly be reduced in an alkaline solution, unless the alkali is kept exceedingly dilute. An alcoholic solution consisting of 40 c.c. of 15% ammonium sulphate solution and 40 c.c. of 95% alcohol, when made slightly alkaline by the addition of 3 c.c. of 6N-ammonia, was found to give comparatively better results. An acid solution neither concentrated nor in a dilute state gave good results. The aromatic nitriles such as benzonitrile and tolunitrile, however, are reduced with more ease both in an alkaline and in an acid solution, though in 10% caustic soda solution they undergo hydrolysis partly.

¹ Zeit. Elektrochem., **3**, 99 (1896)

Experimental

1 Reduction of benzonitrile

About 3 grams of benzonitrile were added to the cathode solution consisting of 40 c.c. of 10% sulphuric acid and 40 c.c. of 95% alcohol. The solution was electrolysed in a porous cell with a lead cathode of about 30 sq. cm, which was carefully prepared by changing its surface first into the peroxide and then into the metallic form of spongy structure. The temperature of the bath was maintained at 25°-30° C. After passing a current of 0.45 amperes (current density, 0.015) for 14 hours the cathode solution was nearly neutralized with caustic soda, filtered and evaporated in a water bath to drive off alcohol. It was then made strongly alkaline by adding caustic soda and treated with ether so as to extract benzylamine. When the ether was evaporated from the ether extract after dehydration, a yellowish oil boiling at 183° C. was isolated. It had a strongly alkaline reaction and changed into the carbonate on absorbing carbon dioxide from the air, so that its isolation from the cathode solution must be conducted as promptly as possible, otherwise the amine changes into the carbonate having a white crystalline form and melting at 114°. It was confirmed to be benzylamine by transforming it into its hydrochloride and platinum double salt on the one hand, and by analysing it on the other. The nitrogen content was determined by Kjeldahl's method as follows:

0.2216 gm. substance gave 0.0217 gm. nitrogen

N = 9.82% (calc. 9.75%)

The electrolysis was also conducted with an alkaline solution consisting of 3 grams of benzonitrile in 40 c.c. of 10% caustic soda solution mixed with 40 c.c. of 95% alcohol. When electrolysis was over the cathode solution was made slightly acidic by adding dilute sulphuric acid, filtered and evaporated in a water bath. Now caustic soda was added to make it strongly alkaline and repeatedly extracted with ether, which was found to have dissolved benzamide besides benzylamine. After being dehydrated with anhydrous sodium sulphate, the ether extract was treated with dry hydrochloric acid gas, when the amine separated out as the hydrochloride. The hydrochloride was filtered, and from the ethereal filtrate benzamide was isolated as a white crystalline substance melting at 127°. It was analysed by Kjeldahl's method with the following result:

0.2170 gm. substance gave 0.0245 gm. nitrogen

N = 11.30% (calc. for benzamide, 11.57%)

The alkaline solution from which benzylamine and benzamide were extracted with ether was also found to contain some benzoic acid. The acid was isolated from the solution by acidifying it with dilute hydrochloric acid, and examined closely.

On the assumption that hydrolysis of the nitrile would be greatly suppressed by the use of a neutral electrolyte, to the cathode solution, prepared by dissolving 3 grams of benzonitrile in 40 c.c. of alcohol was added 40 c.c. of 15% ammonium sulphate solution and it was then electrolysed by passing a current of 0.017 amp/cm² for 14 hours at 27°-31°. As is shown in the following table, the yield of benzylamine was greater than that obtained in electrolysis either of an acid or of an alkaline solution.

Electrolyte	Yield of benzylamine, %
15% (NH ₄) ₂ SO ₄	49.50
10% H ₂ SO ₄	27.49
5% H ₂ SO ₄	24.03
10% NaOH	30.73
5% NaOH	27.00

2 Reduction of benzylcyanide

Electrolytic reduction of benzylcyanide was undertaken just in an analogous manner to the case of benzonitrile. From a sulphuric acid solution only a very small quantity of the corresponding amine was obtained as its hydrochloride, melting at 213°. From a dilute alkaline solution, however, none at all was produced, and phenylacetamide melting at 152°-153° and phenylacetic acid were obtained instead of it. Phenylacetamide was confirmed by analysis and also from its property of changing into phenylacetic acid on hydrolysis.

0.2103 gm. substance gave 0.0213 gm. nitrogen

N = 10.15% (calc. 10.37%)

Phenylacetic acid was volumetrically confirmed by titrating it with $\frac{1}{10}$ N-NaOH solution.

By using a neutral solution containing ammonium sulphate phenylethylamine was produced with a yield of 13%. It was found to boil at 198° and to be so strongly alkaline as to change into the carbonate in air. Its hydrochloride melting at 216° was analysed by Kjeldahl's method.

0.1298 gm. hydrochloride gave 0.0117 gm. nitrogen

N = 8.61% (calc. 8.91%)

The yield of phenylethylamine obtained by electrolysing a solution containing 3 grams of nitrile, 40 c.c. of alcohol and also 40 c.c. of the solution described in the following table, with a current of 0.015 ampere/cm² for 14 hours is here given :—

Electrolyte	Phenylethylamine, %
10% (NH ₄) ₂ SO ₄	13.05
10% H ₂ SO ₄	2.40
5% H ₂ SO ₄	2.11
15% HCl	1.90
10% NaOH	0.

Lead amalgam, zinc amalgam, mercury and platinum were also used as the cathode, but none of them surpassed lead in reduction efficiency.

3 Reduction of paratolunitrile

The cathodic behaviour of paratolunitrile was very much like that of benzonitrile previously described. The best result was obtained by using a 10-15% ammonium sulphate solution containing about 3 c.c. of 6N-ammonia as the cathode solution. Nearly 57% of the nitrile was changed into p-tolubenzylamine when electrolysis was continued for 14 hours with a current of 0.0175 amp/cm² at 30°. p-Tolubenzylamine was obtained as a colourless liquid boiling at 193° and having a strongly alkaline reaction. It absorbed carbon dioxide from the air and changed into the carbonate melting at 116°. Its hydrochloride melting at 232° was analysed.

0.2735 gm. hydrochloride gave 0.0226 gm. nitrogen
N = 8.26% (calc. 8.91%)

In a 10% sulphuric acid solution reduction of p-tolunitrile took place only in a very small degree, but was not accompanied by hydrolysis, while in a 10% caustic soda solution the reduction and hydrolysis took place side by side and produced p-toluamide together with p-tolubenzylamine. p-Toluamide was obtained as a crystalline substance melting at 151°. For confirmation it was analysed with the following result :

0.1935 gm. substance gave 0.0213 gm. nitrogen,
N = 11.01% (calc. 11.38%)

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