

# The Electrolytic Reduction of *o*-Nitrobenzene Azophenol

By

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It is already known that *o*-nitrobenzeneazophenol changes into phenolphentriazol<sup>1</sup> when electrolytically reduced in an alkaline solution with an electrode having a moderate reducing power, such as nickel. In this reduction the azo-group and the nitro-group may be regarded as undergoing reduction first and then interacting with each other so as to form the triazol. The present work was carried out to learn the conditions under which the nitro-group only is reduced to the amido-group and the azo-group is left unaffected.

As is well known, copper has a specific action of catalytically reducing the nitro-group to the amido-group, so copper was first chosen as the cathode, and an alkaline solution of *o*-nitrobenzeneazophenol was electrolysed with it. The cathode solution containing 2 grams of the azophenol in 150 c.c. of 4% caustic soda solution was electrolysed for 2½ hours by passing a current of 2 amperes at 30°. After the electrolysis was over, the solution was neutralised with sulphuric acid, evaporated nearly to dryness and then treated with ether to extract the azophenol that remained unchanged. On recrystallising the residue from boiling dilute alcohol, dark brown needle crystals were obtained with a yield of about 60%. They melted at 221–222° and showed all the properties of phenolphentriazol.

An acidic solution was next tried by using an alcoholic solution which contained 2 grams of *o*-nitrobenzeneazophenol in 200 c.c. of alcohol acidified with 30 c.c. of 10% sulphuric acid. A current of

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1 K. Elbs u. Keipler: J. prak. Chem., **67**, 580 (1903)

4.5-5.5 amperes was passed for 3 hours at 70-75°. During the electrolysis, the colour of the cathode solution gradually changed from red to dark brown, dark blue, yellow and finally to pink. The current was cut, and the solution was evaporated to drive off alcohol, when the *o*-nitrobenzeneazophenol that still remained unchanged crystallised out. It was filtered, and on cooling the filtrate a substance crystallising in scaly form was precipitated. As this substance was soon perceived to be the sulphate of some organic base, its concentrated aqueous solution was treated with barium carbonate, and the free base thus isolated was recrystallised from water as a dark brown crystal. The yield was found to be about 10%. It melted at 183-184° and dissolved easily in acetone, ether and alcohol, but with difficulty in benzene. It was amphoteric, dissolving in hydrochloric acid with a magenta colour, in conc. sulphuric acid with a dark green colour and in alkali with a dark brown colour. These properties all well agree with those of *o*-amidobenzeneazophenol.

The electrolysis was repeated under the same conditions, except that the current strength was decreased to 2-5 amperes and as a consequence the temperature was lowered to 40-50°. In this case the sulphate of *o*-amidobenzeneazophenol was produced only in very small quantity yielding phenolphentriazol as the chief reduction product.

It thus became apparent that the electrolytic reduction of *o*-nitrobenzeneazophenol into the corresponding amidocompound at a copper cathode could be brought about only by using an alcoholic sulphuric acid solution as the cathode solution and maintaining both current density and temperature high.

Next, lead was chosen as the cathode as having strong reducing power, and the electrolysis in the alkaline and acid solutions was studied. Two grams of *o*-nitrobenzeneazophenol were dissolved in 150 c.c. of 4% caustic soda solution, and the solution was electrolysed with a lead cathode of about 105 sq. cm. by passing a current of 2 amperes at 18° a little longer than 2 hours. After the electrolysis the cathode solution was neutralised with sulphuric acid and treated with ether in order to dissolve unchanged *o*-nitrobenzeneazophenol. The residue obtained by evaporating the solution nearly to dryness was extracted with absolute alcohol, and the alcoholic extract was recrystallized from water. Thus *o*-amidobenzeneazophenol melting at 183-184° was obtained with a yield of 25%.

A quite unexpected result was obtained when the electrolysis was

conducted with a current of greater strength (3.5-4 amperes) at a higher temperature (60-70°) keeping the other conditions just the same as in the previous experiment. After the current had been passed for nearly 1½ hours the dark coloured cathode solution was neutralised with sulphuric acid, and a gelatinous precipitate thus separated out was purified by crystallising it from hot alcohol. Greyish needle crystals showing all the properties of phenolphentriazol were isolated with a yield of about 50%. This result is just contrary to that obtained with a copper electrode in an acid solution.

The reduction experiment was also carried out in an acid solution containing 3 gr. of *o*-nitrobenzeneazophenol in the mixture of 200 c.c. of alcohol and 40 c.c. of 10% sulphuric acid. A lead plate of about 130 sq. cm. was taken as the cathode and a current of 2 amperes was passed at 21° for 4 hours. As the electrolysis went on some glittering crystals, which were afterwards identified to be *o*-amidobenzeneazophenol sulphate, begun to separate out in the solution. The yield was 25%. The yield could be raised to 45% by increasing the current strength to 3.5 amperes and at the same time raising the temperature to 60-70°.

Finally, to find the catalytic influence of copper and tin on this reduction, two experiments with the acid solution were conducted. To the cathode solution consisting of 2 grams of *o*-nitrobenzeneazophenol, 40 c.c. of 10% sulphuric acid, 150 c.c. of alcohol and 1 gram of crystalline copper sulphate were added, and this solution was electrolyzed with a current of 3 amperes at 50-60° for about 2 hours. The cathode solution gradually changed to a yellow colour, and some copper was seen floating on it.

The solution being treated in the manner described before, *o*-amidobenzeneazophenol was obtained with a yield of 50%. The remarkable catalytic action of copper on the reduction of *o*-nitrobenzeneazophenol will be clear if we compare the above result with that in the electrolysis conducted with a lead or copper electrode. The catalytic action exerted by tin was found to be still greater. In the experiment which was conducted exactly in the same way as in the above, except that 1 gram of SnCl<sub>2</sub>·2H<sub>2</sub>O was substituted for the copper salt, the yield of *o*-amidobenzeneazophenol was found to be as high as 75%.

It was also observed, from the colour change of the cathode solution, that the electricity required for the reduction of 2 grams of the azophenol was 6.4 ampere-hours when copper was used as the

catalyst, while only 4.5 ampere-hours were sufficient when tin was substituted for copper.

### Summary

1 Electrolytic reduction of *o*-nitrobenzeneazophenol was studied with the object of obtaining the corresponding amido-compound with the best yield.

2 Both alkaline and acid solutions were electrolyzed copper and lead being used as the cathode, and the conditions favourable for producing amidobenzeneazophenol were sought.

3 As a result of the research, an acidic cathode solution to which some stannous chloride has been added was found to give the best yield, when it is electrolyzed with a lead cathode at about 50–60°.

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