THE ELECTROLYTIC PREPARATION
OF
P-AMINO PHENOL

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CONTENTS

	Page
Introduction	1
Materials and Apparatus	4
Procedure	5
Discussion	9
Conclusion	14

Introduction:

A natural classification of the methods for preparing p-amino phenol is that of the electrolytic and non-electrolytic. The non-electrolytic methods are numerous and from them the commercial methods have been chosen almost entirely. They are: (1) By the reduction of p-nitro phenol with tin and hydrochloric acid, (2) By the reduction of p-nitro phenol with sodium sulfite, (3) By the molecular rearrangement of B-phenylhydroxylamine heated in a sulfuric acid solution, (4) By the reduction of p-nitro phenol in ammonia solution with hydrogen sulfide, and (5) By the reduction of nitrobenzene with zinc in concentrated sulfuric acid solution. The first two of these methods are the ones most often used commercially.

Of the electrolytic methods, two are outstanding, they are: (1) the reduction of p-nitro phenol and (2) the reduction of nitrobenzene according to the Haber scheme which involves the molecular rearrangement of B-phenylhydroxylamine in an acid solution. Both of these reductions are usually carried out in a sulfuric acid solution. The p-nitro phenol can be successfully reduced by either of such widely different electrodes as platinum or lead.[1] [2]

Platinum because of its low overvoltage and inertness in concentrated sulfuric acid has been found to be the best

1. C. J. Thatcher: U. S. 1, 501, 472
2. J. [illegible] & C. [illegible]: J. Phys. Chem. 27, 652-73.

electrode to use when this compound is prepared by the electrolytic reduction of nitrobenzene.

It is upon the reduction of nitrobenzene that the greatest efforts of producing p-amino phenol have been concentrated. This is so because, apart from its scientific interest, of the cheapness of nitrobenzene as a raw material. As yet a method which can compete with the non-electrochemical methods has not been described. There are many reasons for this.

Altho, some work[1] has been done on the reduction of nitrobenzene in dilute sulfuric acid solution it has been found necessary to carry out the reduction in concentrated sulfuric acid: partly because the rearrangement velocity is increased at higher concentrations and partly because nitrobenzene is insoluble in sulfuric acid concentrated less than 88%. The use of such a concentrated acid results in the formation of large quantities of p-amino phenol sulfonic acid, an undesirable by-product.

After reduction the spent acid has to be reconcentrated and this has proven to be an important item in the operating cost of this method.[2]

At the end of electrolysis it takes from one to two days for the p-amino phenol sulfate to separate out so that it can be filtered. In addition to this there are two more

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1. Hale: The Manufacture of Chemicals by Electrolysis, 1919

2. McDaniel, Schneider, & Ballard: Transactions of the American Electrochemical Society 39:411 (1921)

recrystallizations, each requiring a day, before the pure product can be obtained.

In order to keep down the formation of aniline the current density has to be kept down to 3-5 amp./sq.dcm., resulting in a slow rate of electrolysis.

The use of platinum electrodes, altho the platinum is not lost in the process, its original cost must be taken into consideration. Caesar[1] claims to have obtained a chemical efficiency as high as 40% with copper as a cathode instead of platinum, but we have not been able to repeat his results.

The maximum chemical efficiency for the reduction of nitrobenzene has usually been reported around 40-50% based on nitrobenzene. With p-nitro phenol the efficiency is around 60%.

In the present work an attempt has been made to surmount these difficulties by carrying out the electrolysis with the nitrobenzene suspended in dilute sulfuric acid.

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1. David Caesar: Transactions of the American Electrochemical Society 52:95 (1927)

Materials and Apparatus

The materials used in the problem were: Nitrobenzene, technical, e.p. sulfuric acid, Sp. Gr. 1.84, commercial and e.p. hydrochloric acid, woodworker's glue, and distilled water.

The nitrobenzene was purified by distilling and reserving that portion which had a constant boiling point.

A porous cup was used which had a height of 18 cm. and a diameter of 8 cm. Several hours before using, it was filled with sulfuric acid and set aside to allow the acid to permeate all the pores of the cup.

Platinum and lead sheets were used as anodes.

Platinum sheet, monel metal, nickel and copper gauzes were used as cathodes.

The source of current was a low voltage d.c. generator.

The current used was measured with a mechanical ampere hour meter.

The cell was set into a steam heated water bath to regulate the temperature.

Procedure:

In order to prepare a stable emulsion of nitrobenzene in dilute sulfuric acid it was found necessary to prepare a sulfuric acid solution which had a specific gravity the same as the nitrobenzene ±.003, which was usually around 1.198. Sulfuric acid of this density has a concentration of about 27% by weight.

Into 500 c.c. of this dilute acid about 10 c.c. of glue were dissolved. The glue could be dissolved more quickly by warming the acid slightly. The nitrobenzene was then added and the whole system vigorously stirred until a creamy white emulsion was obtained. The emulsion was then put into the cell and heated to about 50°C. when the current was turned on. The temperature was allowed to rise to the operating temperature. To help keep the nitrobenzene emulsified it was necessary to use a mechanical stirrer.

Twenty per cent more current than theoretical was passed. At the end of electrolysis the electrolyte was set on a steam bath and evaporated to one-fourth of the original volume. To this was then added 200 c.c. of commercial hydrochloric acid and the solution was then again heated for a period of from thirty minutes to an hour. This served to chlorinate the p-amino phenol. Upon setting the solution in an ice box over night the p-amino phenol hydrochloride crystallized out. The crystals were then filtered and dried before proceeding with the purification.

The dried crystals were then dissolved in the least amount of water. To prevent the oxydation of the product back to nitrosobenzene 2 gms. of sodium acid sulfite were added. The solution was then brought to boiling and to it 5 gms. of animal charcoal were added. After 20 minutes of boiling the solution was filtered. If the filtrate was dark wine colored or darker it was again boiled with charcoal. But, and as was more often the case, if the filtrate was clear or light yellow colored it was allowed to cool to room temperature; and then to this an equal volume of c.p. hydrochloric was added. The pure crystals of p-amino phenol hydrochloride were then allowed to settle out over night in an ice box.

The product was identified by chemical tests and with melting point determinations.

Cathode: Nickel

Catholyte: Emulsion of 120 gms. nitrobenzene

500 c.c. of 27% H_2SO_4

Trial	C.D., Amp./Dcm.^{2}	Temp. Deg. C	Theoretical Current Passed	Chemical Yield
1	2.5	50	115%	16.3%
2	2.5	90	100	24.6
3	5	60	100	27
4	4.5	60	130	34
5	5	78	100	34
6	6	75	115	36.2
7	6	80	135	35.4
8	7	85	115	36.9
9	7	85-90	100	34
10	8	86-90	135	36.9
11	10	78	115	56.7
12	16	94	155	35.4
13	4-12	90	130	42.5

Cathode: Copper

Catholyte: Emulsion of 120 gms. nitrobenzene in
500 c.c. of 27% H_2SO_4

Trial	C.D., $\frac{\text{Amp.}}{\text{dcm.}^2}$	Temp. Deg. C	Theoretical Current Passed	Chemical Yield	Remarks
1	5	70	120%	32.6%	
2	5	85	120	27.7	
3	7	80	110	23.8	
4	8	90-94	130	36.9	
5	12.5	55	120	44	
6	12.5	75	115	42.5	
7	12.5	85-88	120	42.5	
8	12	90	120	41.8	
9	12.5	90	120	57	
10	13	106	120	12	
11	16	94	120	49.6	
12	12	55-75	150	8.5	
13	14	65	155	24.8	
14	12	85-90	100	35.4	+ $\frac{1}{2}$ gm. Cu powder
15	12.5	75-78	155	36.2	+ $\frac{1}{2}$ gm. Cu powder
16	12.5	85	120	32	+ $\frac{1}{2}$ gm. $NiSO_4$
17	12.5	85	120	15.6	500 cc. of 55% H_2SO_4
18	10	87	130	43	1000 " " 27% "

Discussion:

Preliminary runs were made with cathodes of platinum sheet, monel metal, nickel and copper gauzes and with lead sheet to determine what electrodes were suitable for the reduction of the emulsified nitrobenzene. No p-amino phenol was obtained at a platinum electrode; monel metal gave a negligible amount. Aniline was largely formed when lead was used as a cathode. P-amino phenol, however, was immediately obtained when nickel and copper gauzes were used as cathodes. For an anode lead and platinum sheet were used.

During the electrolysis the color of the emulsion varied from a light grey at the beginning to a rose color during the middle of the run, but at the end of the run the solution invariably had a coffee brown color. At the end of the run no unreduced nitrobenzene could be detected.

The reduction was always smooth and there was little gassing until within the time that 80% of the theoretical current has been passed. Gassing and a little frothing then commenced and continued until the theoretical amount of current had been passed. The frothing then decreased, but the evolution of hydrogen continued. At a platinum electrode the frothing and gassing started almost immediately. This occurred because, due to the low overvoltage of platinum the hydrogen was liberated at such a low pressure that it could not reduce the nitrobenzene contained in its protective film of glue - therefore the hydrogen was liberated.

In contrast with all the previous work done on the reduction of nitrobenzene[1] current densities as low as 4-5 amps/sq.dcm. were unsatisfactory. For both the nickel and copper cathodes the best results were obtained when the current density was between 10 and 16 amps./sq.dcm.

The best temperature conditions are between 75-90°C. At temperature lower than 70°C the rearrangement of the phenylhydroxylamine does not take place so readily[2]; while at a temperature above 90°C the catholyte evaporates too much. Nor is it advisable to add water to the emulsion to keep it dilute since this increase gassing and frothing.

To study the effect of relatively more concentrated, but still quite dilute acid, several runs were made with emulsions of nitrobenzene in 55% sulfuric acid. The yields were very low partly because the emulsion was very unstable and partly because p-amino phenol sulfonic acid was formed. During the regular runs with the 27% acid, at the most only traces of the sulfonic acid salt were detected.

There was a decrease in yield when copper powder or nickel sulfide were used as hydrogen carriers.

Passing more than 10% of the theoretical current did not improve the chemical efficiency. This was to be expected from a consideration of the amount of gassing which took

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[1] Brockman: Electro-organic Chemistry, Chaps. IX & X.

[2] Report: Osaka Industrial Research Laboratory
Japan 5 No. 13 1-21 (1924)

place at the time when the theoretical amount of current had been passed.

In trial No. 18 with the copper cathode, a suspension was made with 100 gms. of nitrobenzene in 1000 c.c. of 27% acid, rather than in 500 c.c. as was done in all the other trials. A fairly good yield was obtained; and it may be that emulsifying the nitrobenzene in a large volume of acid will give better results.

The lead anode was very satisfactory. There was not much lead sulfate formed and what little there was could be quickly removed by allowing it to settle out. The anolyte could then be used over again.

There was little corrosion of either the electrodes or apparatus.

The yields given in the table are the chemical efficiency for p-amino phenol hydrochloride based on the nitrobenzene used and are exclusive of what was left in the mother liquor.

The copper gauze was found to be a better cathode than the nickel gauze.

The p-amino phenol hydrochloride could be immediately obtained with a high purity. The melting point was usually around 305°.

The advantages of preparing p-amino phenol by this method over any other electrolytic methods are numerous:

1. The yields are high - 57% chemical efficiency.

2. Low concentrations of sulfuric acid are used.

3. Both for the cathode and anode cheap electrodes may be used: a nickel or copper cathode and a lead anode, rather than platinum electrodes.

4. Only a little more than the theoretical amount of current need be passed, and not half again or twice as much as is necessary when concentrated sulfuric acid is used.

5. Little corrosion of either the electrodes or apparatus.

6. The operating voltage is low (from 4-5 volts.)

7. The recovery of the product has been shortened by a day.

Finally, the following procedure is recommended for a class room experiment.

Prepare an emulsion of nitrobenzene in dilute sulfuric acid in the following manner. Dilute c.p. sulfuric acid until it has the same specific gravity as the nitrobenzene ±.003. Into 300 c.c. of the dilute acid dissolve 10 c.c. of glue. Add 40 gms. of nitrobenzene to the prepared acid and shake vigorously for several minutes until a creamy white emulsion is obtained. In the meantime have a porous cup prepared by allowing sulfuric acid of the same density to permeate thru it.

Electrolyse the emulsion at a copper gauze cathode and a lead anode with a cathodic current density at 10-12 amps. per sq. dcm. Pass 10% more current than the theoretical amount.

The temperature will adjust from the heat of the reaction. It should be between 75-80°C. The solution must be agitated at all times during electrolysis.

At the end of the run boil the solution to one-fourth its original volume on the steam bath. Add 100 c.c. of commercial hydrochloric acid and continued boiling for another 20 minutes. After cooling to room temperature place the solution in the ice box over night. The crystals of p-amino phenol are then filtered and dried.

The product is then purified by dissolving it in the least volume of water and adding 2 gms. of sodium acid sulfite and 4 gms. of animal charcoal. Boil for 20 minutes and filter. If the solution is clear or light yellow colored allow it to cool to room temperature and then add an equal volume of c.p. hydrochloric acid to it. If the filtrate is dark colored reboil it with animal charcoal.

The pure crystals of p-amino phenol hydrochloride are then allowed to crystalize out at 0°C.

Filter, dry and weigh the product.

Conclusion:

Large yields of p-amino phenol have been obtained by electrolyzing an emulsion of nitrobenzene in dilute sulfuric acid by the same density as the nitrobenzene; between a cathode of nickel or copper gauze and an anode of platinum or lead.

Schuch

Electrolytic preparation of P-amino phenol.

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