THE PREPARATION OF p-AMINOPHENOL FROM NITROBENZENE

Thesis for the Degree of M. S.

Ernest P. Jensen

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amino phenol

THE PREPARATION OF
p-AMINOPHENOL
FROM
NITROBENZENE

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Ernest P. Jensen
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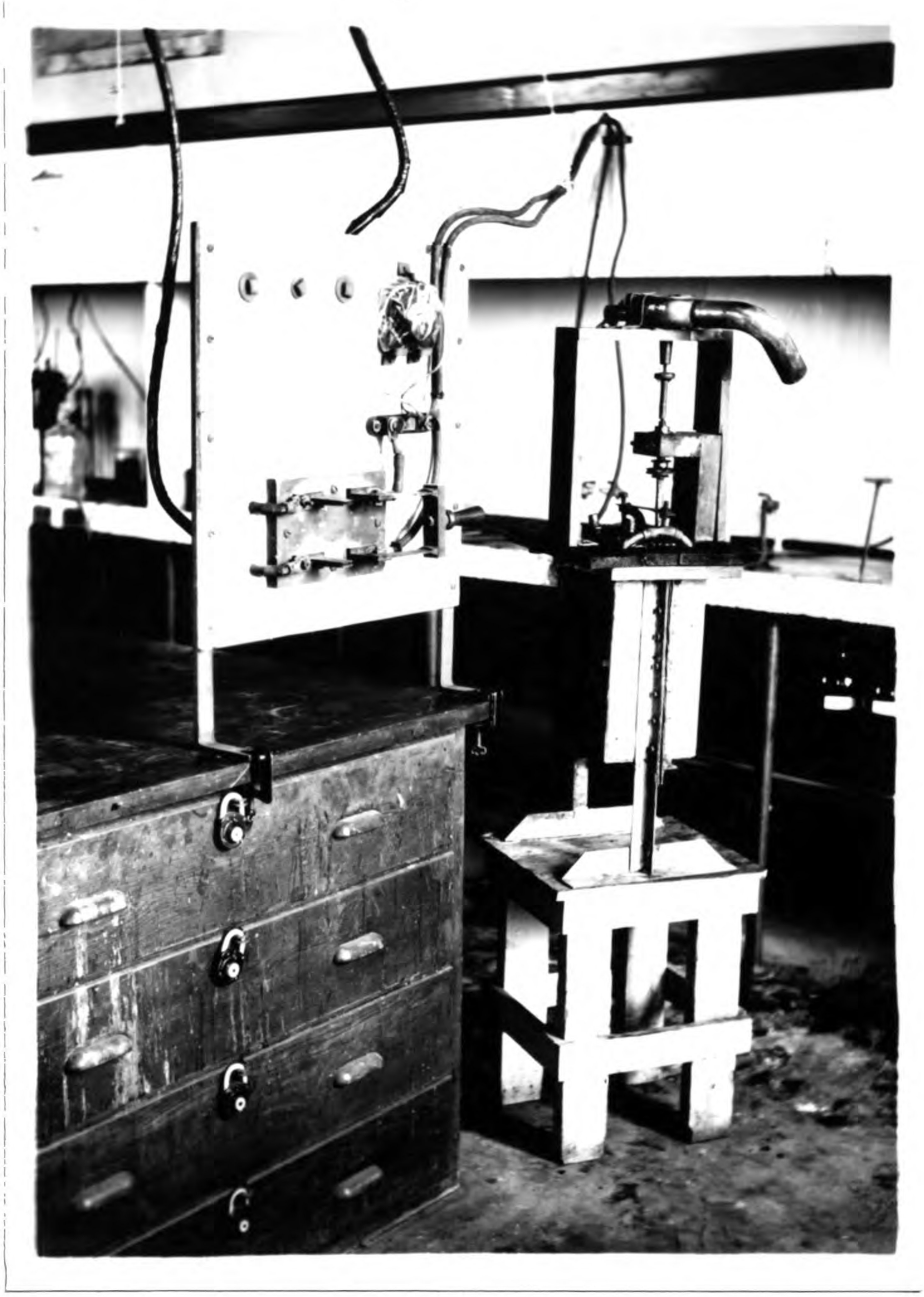

INTRODUCTION

In the electrolytic reduction of nitrobenzene in acid solution, the following compounds are formed in order: nitrosobenzene, beta-phenylhydroxylamine and aniline (Brockman - Electro-Organic Chemistry - John Wiley - (1926) page 303). Nitrobenzene is a poor depolarizer in acid solution but as soon as the reduction is started, nitrosobenzene is formed. This is a good depolarizer and is readily reduced to beta-phenylhydroxylamine. Further reduction produces aniline but if the reduction is stopped at this point, beta-phenylhydroxylamine undergoes an intramolecular rearrangement to form p-aminophenol. This rearrangement takes place readily in sulphuric acid. The rearrangement, however, is not a simple interchanging of the hydrogen atom in the para position of the ring with the hydroxyl on the nitrogen atom. Instead, beta-arylhydroxylamine (HNC_6H_4HOH) is formed and this rearranges, the hydrogen attached to the same carbon as the hydroxyl going to the nitrogen to form an amino group.

The methods of preparation of p-aminophenol may be divided into two general classes; chemical and electrochemical.

Para-nitrophenol may be reduced to p-aminophenol by the action of tin and hydrochloric acid or by iron and acetic acid. In alkaline solution it is reduced by sodium hyposulphite. p-Nitrosophenol may be reduced by sodium sulphide.

A process that has been used by manufacturers in this country is to diazotize aniline and couple it with phenol to form p-hydroxyazobenzene (Warner and Brown - J. Phys. Chem. <u>37</u>, 653-73 (1927)). This is then reduced to p-aminophenol and aniline. The aniline may then be distilled off and recovered while the p-aminophenol is crystallized out of the remaining solution.

Nitrobenzene may be reduced to p-aminophenol by zinc dust and sulphuric acid at 50°-80°C.

Komatsu and Amatatsu (C. A. <u>25</u>, 500 (1931)), in an investigation of the catalytic hydrogenation of various aromatic nitro compounds, found that p-nitrophenol shaken in an autoclave with a reduced nickel catalyst in an atmosphere of hydrogen under a pressure of 50 to 100 atmospheres and temperature of 100°C yielded p-aminophenol quantitatively.

Among the electrochemical methods of preparation is the oxidation of aniline in concentrated sulphuric acid at a platinum anode (Brockman - Electro-Organic Chemistry - John Wiley and Sons, Inc. (1926)). However, the conductivity of the solution is very poor and too much energy is required. The presence of concentrated sulphuric acid protects the p-aminophenol from further oxidation but if water is present the aminophenol reacts with the excess aniline to form p-aminohydroxydiphenylamine which is further oxidized to aniline black.

J. Warner and O. Brown (J. Phys. Chem. <u>37</u>, 652-73 (1937)) succeeded in reducing p-nitrophenol in a solution of caustic soda at a lead cathode with very high efficiencies.

McDaniel, Schneider and Ballard (Trans. of Am. Electrochem. Soc. <u>39</u>, 441 (1921)) attempted to prepare p-aminophenol by the reduction of nitrobenzene in concentrated sulphuric acid at a platinum cathode. This was done during the World War as an emergency measure and was found to be too costly to compete with chemical methods. The current yield was around 25% while the chemical yield was only 40-50%. The cost of the platinum electrodes was not the prohibitive cost since they could be used almost indefinitely but rather the cost of the sulphuric acid which could not be recovered was excessive. The temperature of the solution had to be kept at 30°C to prevent the formation of the sulphonic acid derivative which is of no value as a photographic developer.

When nitrobenzene is reduced in sulphuric acid, the reaction goes as far as the formation of phenylhydroxylamine, when an intramolecular rearrangement takes place to form p-aminophenol. This rearrangement is a well known phenomenon taking place in mineral acids (Cohen - Theoretical Organic Chemistry - MacMillan (1928)).

Practically all the work on the reduction of nitrobenzene in sulphuric acid has been done using the concentrated acid. This is due to the fact that the necessary rearrangement of phenylhydroxylamine takes place much faster in the concentrated than the dilute acid. Also, nitrobenzene is insoluble in acid less than 88% H_2SO_4 by weight which gives rise to the problem of keeping the nitrobenzene in a stable emulsion in more dilute acid. This problem is well met by the use of wood-workers glue as an emulsifying agent.

An investigation of the reduction of nitrobenzene in dilute sulphuric acid of the same specific gravity as nitrobenzene was made by Adam F. Schuch (The Electrolytic Preparation of p-Aminophenol (1931)) in this laboratory. He used platinum and lead sheets as anodes and platinum sheet, monel metal, nickel and copper gauzes as cathodes. He found that an anode of lead sheet and cathode of copper gauze gave the best yields.

This work has been done to carry out the reduction on a commercial scale and to improve on the yield. Runs were made varying the temperature, current density, the percent of theoretical current passed and the amount of nitrobenzene in the emulsion.

The product was identified by melting point tests and a sample dried in an electric oven at 100°C for 24 hours was found to have a melting point of 307°C. Before drying in the oven, the compound decomposed at about 260°C. The International Critical Tables (Vol. I, page 200) give the melting point of p-aminophenol hydrochloride as 306°C at which point the compound decomposes. It is soluble 14 g/100c.c. while the free base is soluble 1.1 g/100c.c. (Handbook of Chemistry and Physics, 17th Ed., page 380) of water at 0°C.

The photographs found in this work were developed with a solution made from some of the p-aminophenol hydrochloride produced in the experiments. The formula used is as follows (Jones - Photographic Sensitometry - Eastman Kodak Company):

Sodium Sulfite (anhydrous)	50g.
Sodium Carbonate (anhydrous)	50g.
p-Aminophenol hydrochloride	7.25g.

Dissolve in order and add a small amount of sodium hydroxide to dissolve the p-aminophenol. Add water to make 1000c.c.

APPARATUS AND MATERIALS

The cell used for all the runs made is shown in the drawings, figure 1 and figure 2. It consisted of a lead tank 7 1/8" x 9 5/8" x 14 1/4" made in two parts held together by bolts. The joint thus formed between the two sides was kept from leaking by using a rubber gasket. A diaphragm of plywood was used for most of the runs and this and this was sealed into the joint, where the two sections of the cell bolted together. by pouring sulphur around the edges. This served to hold the diaphragm in place as well as to prevent leakage from one compartment to the other. The plywood was found to work very well if the right kind was used. Three-ply wood, three sixteenths of an inch thick with a basswood center, was found to be very good. This did not warp enough to cause any trouble and stood up for more than 125 hours of actual use when runs were being made.

Figure 1 shows a side view of the cell as it looked when it was assembled. The top of the cell was fitted with a wooden top with a framework which supported a water motor (7). The water motor was connected directly to a stirrer (6) which was

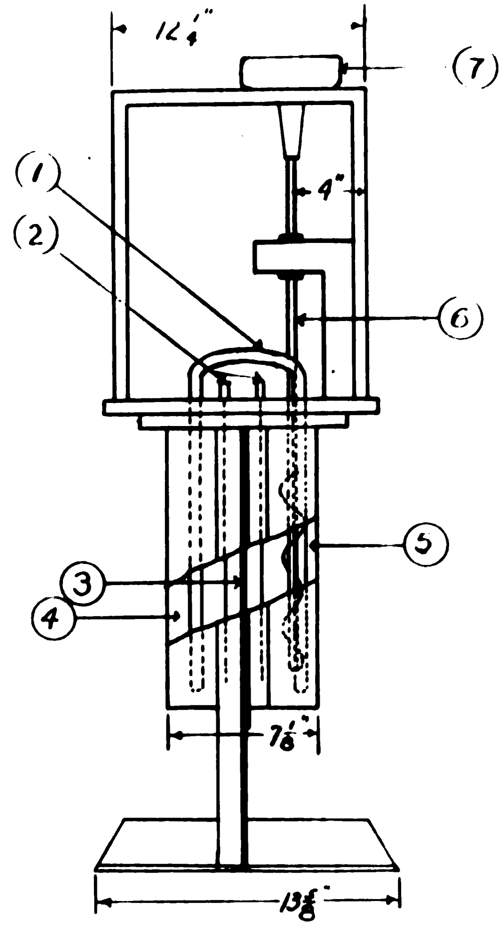

Fig. 1

made of a brass rod covered with lead. A sheath was made by wrapping a strip of lead around the brass rod and welding the joint. The stirrer extended down into the cathode compartment (5) and kept the catholyte stirred thus maintaining a good emulsion throughout the run. The cathode was made of copper gauze and had an area of 5.8 sq. dm. This was placed between the stirrer and the diaphragm (3). The anode compartment (4) contained sulphuric acid of the same specific gravity as nitrobenzene (sp. gr. 1.2). The terminals for the anode and cathode (2) were brought out at the top and extended a little above the wooden cover. The temperature within the cell was controlled by running water or steam through coils (1) which extended down into each compartment.

The materials used were as follows:

Nitrobenzene - commercial.
Sulphuric acid - c.p. sp. gr. 1.84
Sodium chloride - commercial.
Sodium bisulphite.
Hydrochloric acid - c.p.
Woodworkers glue.
Distilled water.

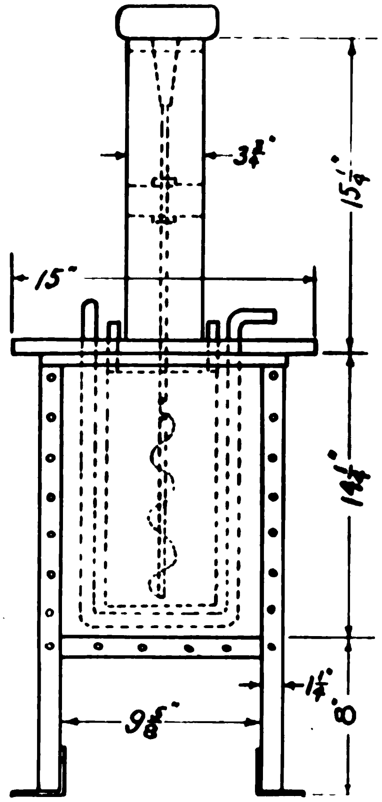

Fig. 2

Electrodes:

cathode - copper gauze.

anode - lead sheet.

PROCEDURE

Sulphuric acid was diluted with distilled water to about 30% H_2SO_4 by weight and the acid cooled to room temperature. This acid is a little more concentrated than is desired but as soon as the solution was cooled, a 100c.c. sample was taken. A few cubic centimeters of nitrobenzene was added to this sample and shaken. Water was added to the sample until the droplets of nitrobenzene just hung in the liquid and did not settle out at the top or bottom. Then an amount of water proportional to the number of cubic centimeters required to adjust 100c.c. was added to the main portion. After a thorough mixing another test sample was taken and the specific gravity tested again in the same manner. Further adjustments were made if necessary. This method was found to be superior to using a hydrometer.

The cathode solution was prepared by placing the proper amount of dilute sulphuric acid in the cathode compartment. Then about 50c.c. of wood-workers glue was added and stirred until dissolved. The required amount of nitrobenzene was then added and this was beaten into a creamy emulsion by vigorous agitation for about ? minutes. During this time the temperature was adjusted to the proper value by running steam through the coils.

The anode solution consisted of sulphuric acid of the same specific gravity as used in the catholyte. This was placed in the anode compartment at the same time the cathode compartment was filled.

The current was then turned on and the run started. When the runs were made at 40°C, trouble was encountered due to foaming at the start but this was overcome by heating the solution to about 60°C for about twenty minutes after which the temperature was readjusted to its proper value.

When the run was finished, the catholyte and anolyte were siphoned into separate jars. The catholyte was purified and the p-aminophenol extracted while the lead sulphate formed in the anolyte was allowed to settle out. The anolyte was used over again. The cell was cleaned and rinsed out with distilled water after each run.

Several methods of purification were tried. The solution was neutralized with sodium hydroxide and the free base filtered out on a suction filter. The free base was then boiled with hydrochloric acid to give the hydrochloride salt. This method was undesirable because of the cost and also because a slight excess of sodium hydroxide redissolved the free base forming sodium para-aminophenolate, $NaOC_6H_4NH_2$.

The product was evaporated to one-fourth its volume on the steam bath and hydrochloric acid added. This was not only slow but uncertain and sulphonic acids were apt to be formed.

The catholyte was neutralized with sodium carbonate to give the free base. In this case as well as with sodium hydroxide, tarry substances were formed which made the purification of the free base difficult. The free base was not redissolved when sodium carbonate was used.

The best method, however, was to use sodium chloride (Kirkhgof and Suirkin - C. A. <u>26</u>, 1957 (1932)). The cathode solution was heated almost to boiling in a four liter beaker and sodium chloride added. Two hundred grams of sodium chloride were added for each liter of solution. The solution was then covered with an evaporating dish and boiled for two hours. In boiling, the sodium chloride reacted with the sulphuric acid to form hydrochloric acid. When the solution was cooled in ice water, the crystals of p-aminophenol hydrochloride separated out along with some sodium chloride which did not react. During the boiling, the volume of the solution was decreased to about two-thirds the original volume.

The crude product which was always black in color, was filtered out on a suction filter and the filtrate discarded. On further boiling with more sodium chloride, no more p-aminophenol hydrochloride came out. Sodium chloride throws out p-aminophenol hydrochloride quantitatively as was proved by tests made on a sample of the purified product. When a saturated salt solution was added to a solution saturated with p-aminophenol hydrochloride, all the p-aminophenol hydrochloride was thrown out immediately.

The crude product was then dissolved in the least amount of hot water and 100c.c. of c.p. hydrochloric acid added. Sodium bisulphite was then added to the extent of 50 grams per liter. This was to prevent the oxidation and to decrease the solubility of p-aminophenol hydrochloride. The solution was then boiled slowly with charcoal (Norite A) for twenty minutes to decolorize the solution. About thirty grams of Norite A was usually sufficient although more was required in some cases. After twenty minutes of slow boiling, the solution was filtered hot. The filtrate should be clear or light yellow. If the solution was light yellow (caused by the oxidation of p-aminophenol) it could be cleared up at this point simply by adding a little more sodium bisulphite. Hydrochloric acid c.p. was then added to the hot solution until the precipitate which formed just dissolved. About 100c.c. per liter was all that was required. The clear solution was set in a pan of ice water to crystallize. Three or four hours were all that were required for the crystallization. The crystals of p-aminophenol hydrochloride were filtered, dried in an evaporating dish on a steam bath and weighed.

Brown and Warner (Trans. Am. Electrochem. Soc. 41, 325 (1922)) give a method of titrating for the amount of p-aminophenol. The solution is acidified with hydrochloric acid and the amine is diazotized with standard sodium nitrite according to the reaction:

$$HOC_6H_4NH_2 \quad NaNO_2 \quad 2HCl =$$
$$HOC_6H_4N{=}NCl \quad 2H_2O \quad NaCl$$

Sodium nitrite was added until a blue color was indicated on starch iodide paper.

This, however, failed to indicate an endpoint because of phenylhydroxylamine in the sample. According to Cohen (Theoretical Organic Chemistry - MacMillan (1928)), phenylhydroxylamine separates iodine from potassium iodide and dilute sulphuric acid. This would give the characteristic blue color with starch and in all trials, the test showed blue before and during the time sodium nitrite was added. No endpoint could be observed.

EXPERIMENTAL DATA

Series A

1200g. nitrobenzene in 5 liters H_2SO_4 sp. gr. 1.2

Theoretical yield of p-aminophenol hydrochloride =1420g.

Theoretical number of ampere hours = 1046

Run	Amp. hrs.	% Amp. hrs.	EMF volts	C.D. $\frac{\text{amp.}}{\text{dm}^2}$	Temp.	Yield	Chem. eff.	C. eff.
1	1150	110%	3.5	7.4	70° C	0g.	0%	0%
2	1150	110%	3.5	11	80°	190	13.4	12.2
3	1150	110%	3.6	11	60°	276	19.4	17.6
4.	1150	110%	3.4	11	40°	439	31	28.2
5	1150	110%	3.4	11	50°	552	38.9	35.4
6	1150	110%	3.5	11	75°	562	39.6	36.
7**	1120	107%	3.5	9.65	40°	537	37.8	34.4
8**	1550	148%	3.1	8.6	40°	843	59.5	40.2
9**	1060	102%	4.0	15.9	40°	638	45	44.
10**	1070	102%	3.2	17.6	70°	378*	53.2	52.2
11	1250	120%	3.3	17.2	70°	305*	43	35.8
12	1074	103%	3.3	15,2	85°	326*	46	44.6

* Only half of the total catholyte was purified. Therefore multiply these weights by two.

** Cell lined with sulphur.

Series B

1800g. nitrobenzene in 4.5 liters H_2SO_4 sp. gr. 1.2

Theoretical yield of p-aminophenol hydrochloride =2130g.

Theoretical number of ampere hours = 1569

Run	Amp. hrs.	% Amp. hrs.	EMF volts	C.D. $\frac{\text{Amp.}}{\text{dm}^2}$	Temp.	Yield*	Chem. eff.	C. eff.
1	1724	110%	3.7	15.5	40° C	262.5g.	24.6%	22.4%
2	1726	110%	3.8	15.9	60°	425	39.9	36.3
3	1584	101%	3.8	16.5	80°	415	39	38.6
4	2354	150%	4.3	16.5	40°	298	28	18.7
5	1726	110%	4.2	9.65	40°	436	41	37.2
6	1726	110%	3.1	10.3	60°	386	36.2	32.9
7	1520	97%	2.7	10.7	80°	453	42.6	43.9
8	2110	135%	3.1	9.5	40°	475	44.6	33.

* Only half of the total catholyte was purified. Therefore multiply these weights by two.

Series C

600g. nitrobenzene in 5.5 liters H_2SO_4 sp. gr. 1.2

Theoretical yield of p-aminophenol hydrochloride = 710g.

Theoretical number of ampere hours = 523

Run	Amp. hrs.	% Amp. hrs.	EMF volts	C.D. $\frac{\text{amp.}}{\text{dm}^2}$	Temp.	Yield*	Chem. eff.	C. eff.
1	576	110%	3.8	15.5	40°C	57g.	16.1%	14.6%
2	575	110%	3.5	16.2	60°	186	52.5	47.7
3	575	110%	3.4	17.9	80°	170	47.9	43.5
4	785	150%	4.4	16.7	40°	0	0	0
5	575	110%	6.	8.	40°	78	22.	20.
6	575	110%	2.8	10.3	60°	162	45.6	41.5
7	575	110%	3.4	9.3	80°	171	48.2	43.8
8	785	150%	3.5	9.15	40°	169	47.6	31.8

* Only half of the total catholyte was purified. Therefore multiply these weights by two.

DISCUSSION OF DATA

The first six runs of series A were made with a diaphragm of asbestos paper using a perforated lead sheet for a support. This, however, was found to be too porous for the cathode and anode portions diffused into each other. Then too, the metal partition acted as an electrode which made an anode in the cathode compartment. A diaphragm of three-sixteenths inch plywood with a basswood center was then used and the results found to be quite satisfactory. One of these diaphragms lasted more than 125 hours of actual working time and the two solutions did not mix. This type of diaphragm was used for the remainder of the runs.

Runs 7 to 10 inclusive were made with the cell lined with sulphur. This lining was made by pouring molten sulphur over the inside surfaces of the cell. The reason for doing this was to determine whether or not the sides of the cell were acting as electrodes. The fact that the yields did not increase proved that this belief was false. The sulphur was therefore removed from the cell and the remainder of the runs were made without any lining.

Series B was made using a larger amount of nitrobenzene in the solution and varying the temperature, current density, and the amount of current passed. This series of runs was not very satisfactory due to the fact that it was difficult to maintain a good emulsion. A good deal of unreduced nitrobenzene was left in the solution and the product was very oily and difficult to purify.

Series C was made using a smaller amount of nitrobenzene in the emulsion and varying the temperature, current density and the amount of current passed. In the case of run number 4, the catholyte contained a large amount of an unidentified green oily substance. No p-aminophenol hydrochloride was obtained from this run. In all other cases, however, the emulsion held very well and these runs were the easiest of any to purify. Runs 1 and 5 also contained a good deal of the green oily substance but not enough to interfere with the purification.

In most cases, the runs started out with a grey color. This soon turned to a light purple which became darker and finally turned black.

The runs at 80°C always foamed as soon as the theoretical amount of current had been passed. This could be stopped for a short time by adding a few grams of nitrobenzene or a little glue. However, the foaming started again within a short time and it was impossible to run the cell any longer. The froth was very stiff and would stand up out of the cell several inches.

The anolyte could be used for six to eight runs before it became dark colored. The darkening did not take place until the diaphragm was almost worn out.

At low temperatures, a lower current density seems to be more favorable. In run number 8 where the yield was 59.5%, the temperature was 40°C and the current density was 8.6 amperes per sq. dm. At higher temperatures, a higher current density works better (see runs 10 series A and 2 series C). This is probably because the speed of the rearrangement of phenylhydroxylamine is faster at the higher temperature.

The most favorable temperatures for the operation of the cell seem to be from 40° to 70°C.

The highest current efficiency was obtained in run 10 series A. In this trial, only 2% excess current was passed and the current efficiency was 53.2%.

It is believed that the yield of p-aminophenol obtained by reduction in dilute acid is bound to be low because of the fact that the speed of the rearrangement of phenylhydroxylamine is too slow to prevent the reduction of some of this compound to aniline. The formation of aniline is confirmed by the fact that large amounts of aniline hydrochloride were found in the solution after the p-aminophenol had been extracted.

SUMMARY

1. p-Aminophenol may be produced electrolytically on a commercial scale using an emulsion of nitrobenzene in dilute sulphuric acid of the same specific gravity as nitrobenzene.

2. A cathode of copper gauze and an anode of sheet lead are suitable electrodes.

3. The most favorable temperature 40° to 70°C.

4. No great excess of current need be passed.

5. The efficiencies are high - 59%.

6. A diaphragm of ply-wood, three-sixteenths of an inch thick with a basswood center is suitable.

7. The operating voltage with such a diaphragm is low - 3 to 4 volts.

8. The method of purification with sodium chloride is fast, cheap and gives the highest yields.

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