REDUCTION OF ORTHO-NITRO-BENZOIC ACID TO ANTHRANILIC ACID

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Reduction of Ortho-Nitro-Benzolic Acid to Anthranilic Acid

A Thesis

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ACKNOWLEDGMENT.

Realizing that our work has only touched on this important problem and hoping that it will be solved in the near future by more competent scholars of chemistry, we wish to express our appreciation for the time and effort given us by Professor Harry McCormack, head of the Chemical Engineering Department, Armour Institute of Technology, Chicago, Illinois.
INTRODUCTION

Reduction is the name usually given to a reaction in which oxygen is withdrawn from, or hydrogen added to a compound. In certain cases both of these processes occur.

In a preliminary study of reducing agents we find that reduction can be accomplished in a number of ways:— Nascent hydrogen in acid, neutral and alkaline solution is the most common, although it has not met with great success as a reducing agent for organic compounds. Sodium and sodium amalgam are very efficient and may be applied conveniently. Metallic tin and stannous chloride are also used extensively. Zinc and zinc dust can be used in either acid or alkaline solutions, and at times if necessary in neutral solutions.

It is well known that reduction converts $\text{NO}_2$ into $\text{NH}_2$. The agents mostly employed for the reduction of nitro compounds are tin and hydrochloric acid. The advantage of these bodies is the ease of separating the tin by hydrogen sulphide; in the solution there remains only the chloride of the amino compounds. The amines with a
basic character are precipitated from their acid solutions by ammonia; amino-phenols, by sodium carbonate; amino-carboxylic acids, by sodium acetate.

**THEORY OF THE PROCEDURE.**

The reduction of the ortho-nitro-benzoic acid is the removal of the oxygen in the nitro group and the substitution of hydrogen in its place to form the amino group. The structural formula of the basic reaction is as follows:

\[
\begin{array}{c}
C=O-H \\
\text{N}=O
\end{array}
\]

\[\rightarrow\]

\[
\begin{array}{c}
C=O-H \\
\text{N}=H
\end{array}
\]

To accomplish such a reduction reaction, it is necessary to use some metal which on addition to potassium hydroxide will liberate nascent hydrogen. We found that various metals were capable of such action.

The second reaction in this work would be the removal of the metal from the solution. From the properties of the reduced solution and also
of the metal, we found the sulphides were insoluble in alkaline solution, and also that the reduced ortho-nitro-benzoic acid was soluble even in the presence of the sulphide. The metal sulphide precipitate filtered leaves the reduced ortho-nitro-benzoic acid in solution.

The third reaction in this work is to obtain some kind of solution in which the reduced ortho-nitro-benzoic acid is less soluble than that of the material used to precipitate it.

A salt of copper seems to be the most adaptable to this purpose for two reasons:— One that the reduced ortho-nitro-benzoic acid is less soluble in such a solution than is the salt of copper, and second that the copper can be removed from the solution by the addition of H₂S, forming an insoluble precipitate of copper sulphide which can be filtered off. This should leave the reduced ortho-nitro-benzoic acid, or the ortho-amino-benzoic acid, or better named Anthranilic acid in a solution in which it can be recrystallized.
Anthranilic acid can be recrystallized from water solution, and its purity determined by its properties and its melting point.

Anthranilic acid is soluble in ether, alcohol, and water, to the greatest extent in the former which is the only solvent from which it will crystallize in long needles, the other solvents yielding a granular product. It crystallizes in leaflets which melt at 144-50°C. The aqueous solution shows a blue fluorescence and tastes sweet.

Our problem is to find a cheaper and more easily conductable method for the production of synthetic indigo from ortho-nitro-toluol. The process has already been carried to ortho-nitro-benzoic acid by the oxidation of ortho-nitro-toluol. Our work in the main is to reduce this ortho-nitro-benzoic acid to ortho-amino-benzoic acid by a simple and inexpensive procedure. The anthranilic acid can then be easily converted into indigo blue.
The reactions are as follows:

\[
\text{o-nitrotoluol} \xrightarrow{\text{KMnO}_4} \text{o-nitrobenzoic acid} \xrightarrow{H^+} \text{anthranilic acid} \]

\[
\text{Indigo-Blue.}
\]

At the present time processes for synthetic indigo have, by the application of scientific knowledge and of untiring efforts, been worked out by German chemists, by which it is possible to produce indigo blue on a large scale and at a small profit.
The process is carried out, as is indicated by the equations.

\[
\text{NaOH} \quad \text{Air}
\]

This would not be a satisfactory process in this country for the reason that the materials used are expensive and the process requires skilled labor and considerable time.

The nitro-compounds are reduced by nascent hydrogen in acid, alkaline and neutral solutions. For the reduction of each nitro group six atoms of
nascent hydrogen are necessary and the reaction may be expressed as follows:

$$XNO_2 + 6H \rightarrow XNH_2 + 2H_2O$$

The amine produced combines with excess of acid to form a salt, e.g. $XNH_2HCl$, from which the amine is obtained by the addition of an excess of caustic alkali. Tin and hydrochloric acid are usually employed, the metal being first converted into stannous and then into stannic chloride. The complete reaction is as follows:

$$2XNO_2 + 3Sn + 14HCl \rightarrow 2(X\cdot NH_2\cdot HCl) + 3SnCl_4 + 4H_2O$$

The hydrochloride of the amine combines with the stannic chloride, forming a stannichloride $(RNH_2HCl)_2SnCl_4$. Various methods are adopted in order to obtain the free amine from the acid mixture. In this case it is necessary to precipitate the tin from the diluted acid solution by means of hydrogen sulphide. The stannous or stannic sulphide is separated by filtration, the amine hydrochloride subsequently decomposed with alkali, and the free amine extracted with ether.

The objection to this method we found was the fact that the ortho-nitro-benzoic acid was only
slightly soluble in acid solution and therefore a corresponding low yield of anthranilic acid could be obtained.

Alkaline solution also favors reduction, and since the ortho-nitro-benzoic acid is soluble in such solutions, it was used.

**APPARATUS**

Mechanical stirrers were used to keep the solution of ortho-nitro-benzoic acid, potassium hydroxide, and the metal in constant agitation.

For the evaporation of the reduced solution of ortho-nitro-benzoic acid, to concentrate and crystallize the ortho-amino-benzoic acid, a vacuum drier was used. This was a steam heated oven connected with a centrifugal pump to exhaust the air. This pump running under normal conditions was capable of maintaining a twenty five and one half inch vacuum.

Most of the equipment used in this work was standard laboratory equipment, such as sand bath, drying oven, hydrometers, funnels, beakers and test tubes.
METHODS

To reduce the ortho-nitro-benzoic acid, it was evident that the process was one which required the removal of the oxygen and the addition of the hydrogen. Reduction with hydrogen can be accomplished only when the hydrogen is in the nascent state. Molecular hydrogen will not afford reduction. We found that nascent hydrogen can also be generated in acid, alkaline, or neutral solutions; so our first problem was to determine the solubility of the ortho-nitro-benzoic acid in acids, alkali, water and alcohol.

The acids used were those which will liberate nascent hydrogen on the addition of some metal, namely: hydrochloric, sulphuric, acetic, and other organic acids. We found that the ortho-nitro-benzoic acid is almost insoluble in any of the acids named. Five grams of the ortho-nitro-benzoic acid were added to 100 c.c. of N/10 HCl. The solution was agitated for a period of one hour. The acid was then diluted and evaporated almost to dryness. The residue taken up with hot water and the ortho-nitro benzoic acid recrystallized. 4.78 grams of the acid were recovered or 95.30%. The results with the other acids were
somewhat unsatisfactory particularly the organic acids. We found later that addition compounds of the acids were formed.

The alkali used in the testing of the solubility was potassium hydroxide. (Potassium hydroxide was used in place of sodium hydroxide, because of the inability of the storeroom to supply the latter). The ortho-nitro-benzoic acid was readily soluble in the alkali which did not necessitate the determination of the degree of solubility.

Water was also tested but close observation was sufficient to report that the acid was not soluble in the water.

Conclusions from the tests on solubility and the results which have already been obtained and recorded in handbooks, we decided that the reduction reaction which we wished to make would have to be made in alkaline solution.

Since the potassium hydroxide proved to be the best solvent for the ortho-nitro-benzoic acid, and also because it was possible to produce nascent hydrogen in such a solution, we next proceeded to
determine whether alkali of different concentration varied the solubility. The result was obvious; the stronger the alkali the more soluble the acid. However, we found later that the concentration of the alkali varied the yield of the addition compounds formed. The results of this experimenting proved that 50 Baume potassium hydroxide gave the best yields of addition compounds of anthranilic acid.

The next problem was the selection of a metal which would produce nascent hydrogen. Zinc and aluminum were the metals selected to afford the liberation of hydrogen for the reduction. It was evident at the outset that each of these metals would produce the required results, but complications which arose later limited the selection. The aluminum proved unsatisfactory because of two reasons: one that the aluminum became coated with a film of oxide which prevented the further liberation of hydrogen; and second we found it impossible to secure any suitable means of removing the aluminum from the solution after the reduction had been completed.
The metal zinc was then used in the granular state because of its ability to liberate the hydrogen and also because an easy and efficient method for its removal from solution was known. Quantitative runs proved that very little of the zinc entered the solution. Samples of 5 grams of the ortho-nitro-benzoic acid was dissolved in 125 c.c. of the 5° Baume potassium hydroxide and 2 grams of the granular zinc added. Also 2 grams of the zinc was added to 125 c.c. of 5° Baume Potassium hydroxide with the absence of the ortho-nitro-benzoic acid. The two solutions were agitated for two hours after which reduction was complete in the one case and in the second all the potassium zincate was formed that the reaction called for. The solutions were then heated to about 85° C. and allowed to absorb H₂S under a pressure of two inches of water for one hour. The precipitate of zinc sulphide was filtered off, dried and weighed as zinc sulphide. The results showed that almost equal amounts of zinc entered the two solutions. This part of the work was only carried on in order to make a rough estimate of the quantity
of zinc which it would be necessary to remove if the method proved one of commercial importance. No effort was made on the part of the experimentors to prevent the zinc from entering the solution because of the ease with which it could be removed in the experimental work. It may have been necessary to obtain such a procedure, had the results of the thesis been positive.

The numerical results were as follows:
In the solution of ortho-nitro-benzoic 66.23% of the original zinc was precipitated in the form of zinc sulphide from the zincate solution.

\[
\begin{align*}
\text{Zn} & \quad 2\text{KOH} \quad K_2\text{ZnO}_2 \quad 2\text{H} \quad K_2\text{ZnO}_2 \quad \text{H}_2\text{S} \quad \text{ZnS} \quad 2\text{KOH}.
\end{align*}
\]

62.50% of the zinc was recovered from the second sample which did not contain the ortho-nitro-benzoic. Whether the ortho-nitro-benzoic acid favored the solubility of the zinc, or whether it was an error on the part of the experimentors, was not determined because the item carried little weight.

The next problem which confronted us was to make the solution from which the zinc had been extracted, one in which it would be possible to
crystallize the acid which we were looking for. This proved to be the most difficult problem in that anthranilic acid has a great affinity for nearly all metal salts. The proof of this conclusion rested wholly in the salt formed with nickel sulphate. Upon the addition of nickel sulphate to the solution of anthranilic acid, we found that it was impossible to obtain a precipitate of nickel sulphide, because of the inability of the nickel to ionize in such a solution.

We also found that it was possible to obtain solutions with other acids which would render the anthranilic acid less insoluble. Great care was exercised in the evaporation of the resulting solutions because of the tendency of the organic acids to form addition and substitution compounds, and tar. For this reason we found that it was necessary to evaporate the solutions under reduced pressure and at a low temperature so that the product would not go to tar or be burnt. The vacuum oven described in the paragraph on apparatus, was used for this purpose.
Among the acids which were used to precipitate the anthranilic acid were citric, acetic, oxalic, tartaric, and hydrochloric. With the addition of the citric acid no precipitate was formed. We drew a conclusion from this that the citric acid formed an addition compound with the anthranilic acid which was soluble. The addition of oxalic, tartaric, and hydrochloric acids gave similar results. When acetic acid was added to the solution, a precipitate was obtained. This precipitate was washed from the filter paper and dissolved in warm water, and allowed to evaporate in the vacuum oven. The resulting material was of a spongy amorphous nature, yellow in color and having a melting point of 198.5° Centigrade. An analysis was not necessary to prove its composition, however to obtain the satisfaction that the product was an addition compound of acetic and anthranilic acids or acet-anthranilate, the following method was employed: A small portion of the material was mixed with an equal proportion of crystals of phosphoric acid. It was then diluted with water and distilled in a distilling flask,
condensing the vapor in a water cooled condenser. The theory of this operation was that the phosphoric acid being a stronger acid than the acetic would replace the acetic, changing the acet-anthranilate to phosphoric-anthranilate. This would liberate the acetic acid and allow it to be distilled over into the receiving flask. This distillate can be tested for the presence of acetic acid by some of the standard methods. The one which was employed by the experimentors was a physical property, namely the odor.

We found that acetic acid was present in the distillate proving the aforesaid statement, that the addition of the acetic acid to the solution of anthranilic acid forms an addition compound. No suitable means was at hand to separate the addition compound formed so the method was discarded. The addition of the other acids would have presented the same difficulty had we tried to isolate the soluble addition compounds formed.

After consulting the literature again we found that the real problem in the thesis was the separation of anthranilic acid from the salts used
to precipitate it. Because of the small amount of material in the literature, this subject was not touched upon so the experimentors decided to find a metal salt which would not form an addition compound and also allow the anthranilic acid to crystallize from the solution.

Anthranilic acid was prepared by the phthalimide method, as described in the introduction. The product was tested for its purity and determined to be 98.3% pure. The melting point of the product was 145° C. The melting point of the acid given in the handbooks is 144° C.

(Note). All of the melting points determined in this work and mentioned in this experiment were determined as follows:— A small portion of the material was ground to a fine powder and inserted in a capillary tube. The tube was then fastened to a thermometer so that the bulb of the thermometer and the bottom of the capillary tube were at the same level. This was then immersed in two beakers of sulphuric acid, one beaker set inside of the other to assure an equal temperature of the acid. Heat
was then applied to the beakers, and the acid kept thoroughly agitated until the material in the capillary tube melted. This point can readily be seen by the observer and the temperature also noted.

The anthranilic was first tested to determine from which solvent it would crystallize best. Alcohol, ether, and water were used as solvents. We found that the acid crystallized readily from ether and alcohol, but not so readily from water. Later, difficulties arose which prohibited the use of alcohol and ether, so the experimentors were forced to use water, however we found it very easy to recrystallize the anthranilic acid.

A small quantity of the acid was then dissolved in water and the following salts were added to each of 12 small portions of the anthranilic acid. The solutions were then heated and allowed to absorb \( \text{H}_2\text{S} \) under a pressure of two inches of water for a period of one hour.

PORTION 1.

Copper nitrate was added giving a precipitate of copper-anthranilate of blue color. \( \text{H}_2\text{S} \) was then passed and the precipitate blackened in color,
supposedly that of CuS. The precipitate was filtered off and the filtrate evaporated to dryness in the vacuum oven. The residue was a yellow crystalline mass undoubtedly an addition compound of copper anthranilate. The melting point was found to be 219° C.

PORTION 2.

Silver nitrate was added giving a black precipitate of silver anthranilate. H₂S was then allowed to pass through the solution for one hour at a pressure of two inches of water. There was no visible change in the nature of the precipitate but it was supposed and afterwards proven that the silver precipitate was Ag₂S. The filtrate was allowed to evaporate in the vacuum oven which left a dirty yellow mass, amorphous in structure and having a melting point of 223° C.

PORTION 3.

Lead nitrate was next employed, giving a white precipitate. Upon the addition of H₂S the white color turned black. The solution was filtered and the filtrate evaporated as before. The residue this time was brown having a crystalline form and
melting at 220° C.

PORTION 4.

Mercuric nitrate also gave a precipitate white in color, which upon the addition of the \( \text{H}_2\text{S} \) darkened considerably. This was likewise filtered and the filtrate evaporated as before. This time a white crystalline mass resulted which when tested for its melting point gave 232° C.

PORTION 5.

Barium was the last of the nitrates to be tested for its ability to form addition compounds with the anthranilic acid. For some unknown reason no precipitate was formed on the addition of the barium salt and on the addition of the \( \text{H}_2\text{S} \) only sulphur was precipitated. Results discarded.

CONCLUSIONS FROM FIRST FIVE PORTIONS.

The salts used in portions 1 to 4 inclusive gave only addition compounds, while 5 seemed to have no affect whatsoever on the acid solution.

SAMPLE 6.

Barium chloride was next added to the anthranilic acid solution. This salt behaved as did the barium nitrate but when the \( \text{H}_2\text{S} \) was passed
a precipitate was formed unlike the one formed in the case of sample 5. The precipitate was filtered off and the filtrate evaporated. The result of this salt was a positive one in that the residue left in the evaporating dish resembled the anthranilic acid which we had started with, and which also had a melting point of 146° C. Believing that for some unknown reason this salt of barium might behave different under different conditions, experimenting was not stopped at this point.

SAMPLE 7.

Because of the inspiring results obtained when the chloride was used, and also from the amount of information which we had found in the literature concerning the salt of copper we decided to use copper chloride. Copper anthranilate precipitated very nicely, and changed color upon the addition of the HgS, but to no avail. When the precipitate was filtered and the filtrate allowed to evaporate in the vacuum oven only a resinous tarry mass was left.
SAMPLE 8.

Another chloride was used namely the mercuric chloride. This was likewise added to the solution of anthranilic acid. A white precipitate was formed which turned black upon the addition of the H₂S. This was filtered and the filtrate evaporated to dryness in the vacuum oven. The crystalline mass which remained proved to be anthranilic acid having a melting point of 147.50°C.

SAMPLE 9.

This sample was tested by the addition of aluminum sulphate, but was rapidly discarded because of the condition of the aluminum precipitate, which rendered it almost unfilterable.

SAMPLE 10.

When nickel sulphate was used we found results which were very much out of the ordinary. Nickel anthranilate precipitated, but upon the addition of H₂S no further change took place. This was readily observable because the color of the nickel anthranilate was green, and upon the addition of H₂S it did not turn black, which
is the color of the NiS₂. This proved that the nickel anthranilate does not ionize as a nickel salt and could not be precipitated by the use of H₂S.

SAMPLE 11.

Zinc sulphate was the salt added to this sample but no precipitate was formed either on the addition of the ZnSO₄ or on the addition of the H₂S. Evaporation of the solution resulted in a tarry mass.

SAMPLE 12.

Lead subacetate was lastly used in the attempt to recrystallize the acid from solutions of salts. The result in this case was an amorphous yellow mass which melted at approximately 287° C.

CONCLUSIONS FROM SAMPLES 6 to 12.

Samples 6 and 8 were the only ones which anthranilic acid could be recovered from.

Samples 7, 9, 10, 11, 12 were discarded for the various reasons named.

The results from the anthranilic recrystallization only lend additional problems in this work.
Conditions may have altered the results materially, but owing to the number of addition compounds formed we deemed it unnecessary to try such a thing as a quantitative run. The size of the addition compounds or rather the bulk of them was sufficient evidence for us that addition compounds were the only things we had thus far obtained.

From the results on the experimenting just described, we proceeded from the original basis namely the reduced solution of ortho-nitrobenzoic acid, using all of the data obtained from the experimenting on the anthranilic.

PROCEDURE NUMBER 1.

A 5 gram sample of ortho-nitro-benzoic acid was dissolved in 125 c.c. of 5° Baume potassium hydroxide.

Case A. The solution was boiled before agitating.
Case B. The solution was agitated with no boiling.

2 grams of granular zinc was also added to each solution.

PROCEDURE NUMBER 2.

The solution was decanted, boiled and allowed to absorb H₂S for a period of one hour
under a pressure of two inches of water. The solutions were heated again if the temperature fell below 80° C. The precipitate which was formed was filtered off, which when tested gave positive results for zinc sulphide.

PROCEDURE NUMBER 3.

This is where the process branches, because of the addition of different salts to favor the crystallization of the ortho-amino-benzoic acid.

SAMPLE 1.

The 5 gram sample of the ortho-nitro-benzoic acid was treated as in procedure 1, case B, and procedure 2. In procedure 3, acetic acid was employed. Dilute acetic acid was added to the solution until it showed an acid reaction with phenophthalein. When this point was reached a yellow precipitate was formed. The precipitate was washed from the filter paper and dissolved in a small quantity of hot water, evaporated in the vacuum oven and recrystallized from water. The resulting residue was an amorphous spongy yellow mass similar to that obtained when acetic acid was added to the solution of anthranilic acid. The melting point of this body was 201° C.
SAMPLES II and III.

These were also 5 gram samples of the ortho-nitro-benzoic acid, treated as in procedure 1, case A and B, and procedure 2. Both samples, the one which had been boiled and the one which was allowed to react without the aid of heat, were treated as follows:— Copper acetate was added, giving the precipitate of copper anthranilate, as it did in the case of the solution of anthranilic acid. H₂S was then passed into both of the solutions and the precipitate of copper sulphide filtered off. The filtrate was evaporated in the vacuum oven under a reduced pressure of 23.5 inches of mercury and at a temperature of 68° C. Both of the samples gave a yellow amorphous mass which was dried and treated with carbon bisulphide to remove the sulphur. This caused the mass to change color from the original yellow to a dirty white. The melting point of both of these products was about 187° C.
SAMPLES IV, V, VI, VII, Vlll.

These samples were treated as in procedure 1-B and 2, and the following salts were added:

IV Sodium acetate.
V Lead acetate.
VI Zinc acetate
VII Lead subacetate.
Vlll Ammonium acetate.

Sample IV was discarded because of the tarry residue which was left upon evaporation.

Sample V was recrystallized from water and the product tested for its melting point. 210° C.

Sample VI was discarded because there was no precipitate upon the addition of the zinc acetate.

Sample VII was carried through by the regular procedure but the product showed a melting point of 200° C.

Sample Vlll was discarded because of the failure to precipitate upon the addition of the ammonium acetate.

The following salts which were employed were
either used because positive results had been obtained from the anthranilic acid experiments or because of the property of the salt to form addition compounds with the anthranilic acid. We thought it necessary to use such salts as those which had formed addition compounds, to prove that the ortho-nitro benzoic acid had been reduced by the process to which it had been subjected.

SAMPLE IX.

Copper nitrate was used to precipitate the anthranilic acid. After the removal of the copper by the addition of the H₂S the filtrate was evaporated and the residue tested for anthranilic acid. The melting point of the product was 215° C. which was only 4° from the melting point of the product obtained when the copper nitrate was added to the solution of anthranilic acid. It was extremely hard to get this compound. Five such samples were run, four of which resulted in only a tarry resinous mass.

SAMPLE X.

Lead nitrate was next used in an effort to obtain the pure anthranilic acid. When the nitrate
was used in experimenting with the anthranilic acid, an addition compound was formed which melted at 223° C. Five such samples were used in this effort but each of the five times only a tarry mass remained in the evaporating dish after evaporation. Temperature as low as 60° C. were employed to try and prevent the organic compounds from turning to tar, but with no result.

SAMPLE XI.

Barium chloride was one of the salts which had permitted the anthranilic acid to recrystallize when added to a solution of the acid. Extreme care was taken in the evaporation of the filtrate so as to prevent, if possible, the formation of tar. In this case the solution was evaporated and left a crystalline mass of yellow material. This was redissolved in a small amount of hot water and recrystallized. The product looked as though we had found the suitable salt, but the melting point of the product, instead of being 144–5° C. as is that of anthranilic, was 210° C.
SAMPLE XII.

Copper sulphate was added to this sample. The solution was carried through the same processes as were the others. The residue was a brown crystalline mass melting at 219° C.

SAMPLE XIII.

Zinc sulphate gave approximately the same results as did the copper sulphate.

SAMPLE XIV.

Mercuric chloride, one of the salts which had also allowed the anthranilic acid to recrystallize was used. The sample was carried through the same procedures as were those in the above cases. The residue was recrystallized from water solution but to no avail. The melting point was found to be 197° C. The melting point when the mercuric chloride was added to the solution of anthranilic acid was 146° which is somewhat near the melting point of anthranilic acid.

Since all of the above methods failed in some way or other, the experimentors decided to try some of the other methods used in organic chemistry for
the separation of the metal from the salt. These methods did not offer a very wide field due to various reasons. With the use of acid to precipitate calcium or barium, only addition compounds would be formed and with the second possibility that the organic material would be reduced to tar. Salts of barium and calcium were used, however, and an effort made to precipitate them from the solution by the passage of carbon dioxide under a pressure of 2 inches of water. Conditions of temperature were varied and also the time of absorption, but the precipitate formed could not be readily filtered. It was evident at the outset from our knowledge of quantitative chemistry that either of these precipitates would be hard to handle.

CONCLUSIONS.

From the results of all of the experimenting, it follows that the ortho-nitro-benzoic acid was reduced in alkaline solution by nascent hydrogen produced by the action of granular zinc on potassium hydroxide. We can draw this conclusion from the facts that copper nitrate when added to a
solution of anthranilic acid gave an addition compound which resembled and melted four degrees from the addition compound formed when the copper salt was added to the reduced solution of ortho-nitro-benzoic acid. We also found that no heat was necessary for this reduction, however, heat was generated to a small extent in the reaction.

Even though the reduction can be accomplished we are forced to draw the conclusion that anthranilic acid cannot be made by this process because no suitable means was found that will successfully separate the acid from its salt. It is also evident that anthranilic acid has a strong affinity for most acids and metals, thereby rendering it difficult to obtain it in the free state.

It may be possible however to make indigo blue without first obtaining the free anthranilic acid by forming the chloracetic addition compound which is really the intermediate product between anthranilic acid and indigo blue.

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