PREPARATION OF AMINO CONTAINING DERIVATIVE OF CELLULOSE

By

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FOREWARD

I wish to express my appreciation to Dr. Philip C. Scherer, Jr., for his many invaluable suggestions in the development of this thesis.

I also wish to extend thanks to Dr. J. W. Watson, Head of the Department of Chemistry, for his willing cooperation in obtaining materials necessary for this investigation.

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INTRODUCTION

On January 6, 1928, Philip C. Scherer, Jr., discovered that KNH_2 would react with a solution of cellulose nitrate to form a brownish-yellow product which was soluble in water. The filtrate gave a positive test for nitrate. From this he assumed a reaction between KNH_2 and cellulose nitrate had taken place to give cellulose amine and KNO_3.

In 1938-39 Vernon R. Mattox(10) investigated this reaction further, in an attempt to determine whether the product was cellulose amine, whether it contained any cellulose nitrate, what its properties were and what derivatives could be made from it. He was able to isolate a derivative, cellulose acetyl amine on which he made a study of properties and reactions.

Since a derivative(10) was employed, with the use of KNH_2 to isolate a product, Dr. Scherer suggested in 1939, that the above reactions be investigated using $Na\ NH_2$ in an attempt to isolate the pure cellulose amine.

The work discussed in this thesis followed directly in line with the work done by Mattox. Following the general procedure developed by Mattox and using any new procedure which might be developed, it was the purpose of this investigation, to prepare, purify and analyze a cellulose amine and determine its properties.

From this arose two objectives. First it was hoped to determine some method of isolating cellulose amine without the aid of a second conversion. The necessity of such an indirect method came from the fact that the products burned spontaneously when exposed to the air unless the excess Na NH_2 was reacted on and when this was done, the resulting product was highly impure.

Secondly it is hoped that the further accumulation of evidence as presented in this paper may help to establish the structure and mechanism of the reaction in the preparation of the cellulose amine.

HISTORICAL

As a compound ammonia has been known to chemists for a long period of years, but only at the close of the 19th century was the study of ammonia in the liquid state begun. The first investigators were primarily interested in the physical properties, and only comparatively recently have the possibilities of liquid ammonia as a solvent been brought forward and studied. At the present time there is a great amount of data (concerning the solvent action), accumulated which is very clearly summed up by E. C. Franklin in his book "The Nitrogen System of Compounds."

The physical properties of liquid ammonia were pretty well determined by 1910. The boiling point of liquid ammonia was determined by Franklin(4) and was found to be -33.46°C. This value was checked later by Gibbs(7) and it is now assumed to be correct to .1°C. Since this investigation was carried out in liquid ammonia at atmospheric pressure the temperature was -33.46°C.

The heat of volatilization of liquid ammonia at its boiling point at atmospheric pressure was found by Franklin and Krause(6) in 1898 to be between 336 and 340 calories.

Other physical properties such as molecular boiling point elevation and freezing point depression, etc., have been determined and are given by Franklin in Chapter I of his book.

Although Seely(12) started the investigation on liquid ammonia as a solvent it was not until 1898 that publications of any importance appeared. This work was done by Cady(1) and Franklin and Krause(6). In general they found that the alkali elements and the alkaline earths dissolve readily without reaction with the solvent. Metallic magnesium dissolves slightly. Iron, sulfur and phosphrous dissolve readily but immediately react with the solvent. Of the salts, most of the halides, nitrates, nitrites, cyanides, cyanates and thiocyanates are soluble but in varying degrees. The generally insoluble salts are the sulphates, sulphites, carbonates and phosphates. Most of the organic compounds, with the exception of paraffine hydrocarbons and most of their higher derivatives, were found to be soluble, or miscible, in varying degrees.

Due to the great amount of information on liquid ammonia there is practically nothing of the properties of liquid ammonia which are not known today.

A complete review of the properties of liquid ammonia as a solvent has been made by Fernelius and Johnson(3) and after summing up all the known facts they arrived at the following conclusions:

(1). A system of compounds exist which is related to ammonia in the same manner in which our familiar compounds are related to water.

(2). Franklin's suggestion that oxygen acids, bases and salts, be called aquo acids, aquo bases and aquo salts, and ammonia compounds corresponding to these, called ammonia acids, ammono bases, and ammono salts be accepted.

(3). Ammonia is an excellent ionizing solvent, like water, but it is not as powerful as an ammonalizing agent as water is a hydrolyzing agent. The dissociation constant of anhydrous liquid ammonia was found to be 5 x 10^{-11} Kohlraush units which is about one thousandth that of water.

The general conclusion, to be drawn from the above work, is that liquid ammonia can be substituted for water as a medium for carrying out many reactions, therefore it was decided to attempt to prepare cellulose amine by using liquid ammonia as a solvent.

Trying to introduce amino nitrogen into cellulose goes back as far as 1861. It was then that Thenard and Schutzenberger(9) treated cellulose with ammonia in an autoclave. By this treatment it appeared that a small amount of amino nitrogen was introduced.

Some years after Thenard's and Schutzenberger's work, Vigon(9) claimed that he produced an amidated cellulose by treatment with ammonia at a temperature between 100° and 200°C. This method appeared to have introduced as much as 3% amino nitrogen into cellulose which then possessed an affinity for acid dyes.

The inability of reproducing this work led to the belief that the above described products were merely cellulose in which the air spaces were filled with ammonia.

It was not until Karrer(9) produced amino cellulose by an indirect method that it seemed possible to introduce an amino group in the cellulose molecule. He made use of the fact that where as the esters of carboxylic acids are decomposed by ammonia and amines into acid amides and alcohols, the esters of the mono and di-sulphonic acids react with ammonia to produce amines and the ammonium salt of the particular sulphonic acid.

Karrer's reaction introduced one amino group to every 9 to 11 $C_6H_{10}O_5$

residues that entered into reaction. The resulting product had characteristics dyeing properties.

In 1939 Mattox(10) prepared a compound he called cellulose acetyl amine. He prepared cellulose amine by the reaction of KNH_2 on cellulose nitrate in liquid ammonia. He allowed acetyl chloride to react with the cellulose amine to give his final product cellulose acetyl amine. He was able to introduce one amino nitrogen group into the cellulose molecule. This product also underwent most of the reaction of primary amines.

THEORETICAL

The work done on the preparation of cellulose amine in this investigation makes use of the following facts(11):

(1). Cellulose nitrate is soluble in liquid ammonia.

(2). When metallic sodium is added to a solution of cellulose nitrate in liquid ammonia a reaction takes place.

In addition to the above, the following assumptions are submitted:

(1). The following reaction will take place

$$(Cell) - O\text{-}NO_2 + 2Na \xrightarrow{NH_3} (Cell) - O\text{-}NO + Na_2O$$

(2). This Na_2O, if formed during the reaction, is known to be a catalyst for the preparation of $NaNH_2$ in liquid ammonia. This therefore gives the basis for the following reaction:

$$Na + NH_3 \xrightarrow{Na_2O} NaNH_2 + \tfrac{1}{2}H_2$$

(3). The NO_3 or (the probable NO_2 group left) in cellulose nitrate will be replaced by an amino group obtained from the $NaNH_2$ formed during the reaction. This leads to the following reaction as being possible:

$$(Cell) - O\text{-}NO_2 + NaNH_2 \xrightarrow{NH_3} (Cell) - NH_2 + NaNO_3$$

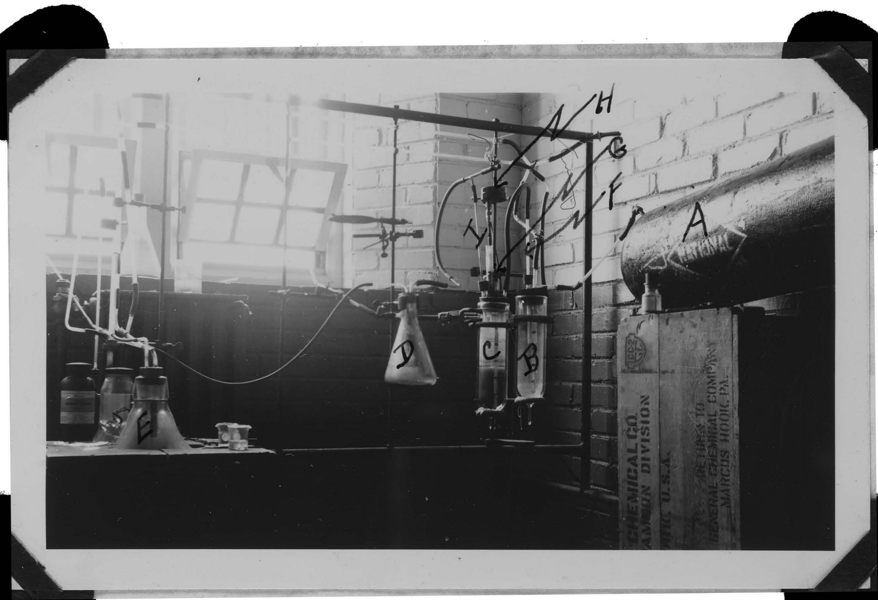
and if a NO_2 be present, when Na_2O is formed, $NaNO_2$ will be formed.

(4). That the desired product cellulose amine will be insoluble in liquid ammonia thus offering a method of separation and purification.

(5). The cellulose amine formed will be a primary amine and will react as such.

(6). Cellulose amine might be expected to have some of the chemical and perhaps physical properties of the proteins and of silk.(14)

DESCRIPTION OF APPARATUS AND EXPERIMENTAL TECHNIQUE



Apparatus used to prepare cellulose amine

Ordinary commercial anhydrous liquid ammonia was used in this investigation.

Cellulose nitrate containing 11.7% nitrogen and giving analysis for a di-nitrate was used.

The analytical procedure employed in the determination of nitrogen was that of Kjeldahl as described by F. H. Fish(2).

The following general method is the one used in nearly all experiments.

Liquid ammonia was allowed to run into the Dewar flask (B). This was used more or less as an intermediate storage tank. The liquid ammonia when needed was forced by pressure over into flask (C) through a movable tube F. Flask (C) was used as the reaction chamber. The material used in the investigation was introduced into the reaction flask through (G), (a short piece of glass tube). (H) a mechanical stirrer, fitted with a mercury trap to prevent escape of ammonia fumes, was used to agitate the reaction mixture. (I) and adjustable tube was used to syphon off any excess ammonia into flask (D). (D) was used as a storage tank to allow the evaporation of excess ammonia. (E) a container filled with water was used to trap the ammonia fumes.

EXPERIMENTAL

I.

Five grams of cellulose nitrate were dissolved in 150 c.c. of liquid ammonia and to this 7 grams of metallic sodium were added, small pieces at a time.

A blue color resulted, due to the excess of sodium. After about half an hour the blue color vanished slowly and a yellow precipitate remained.

The reaction was allowed to stand four hours. During this four hours there was excessive bubbling of the ammonia and most of the ammonia evaporated. This was believed to be due to the heat given off by the reaction and to evolution of hydrogen gas.

Five c.c. of water were added just before the complete evaporation of ammonia. A dark brown viscous liquid resulted on the complete evaporation of ammonia under vacuum.

This viscous liquid was used in an attempt to reproduce the work of Mattox. His procedure(10) was followed but with such little success that it lead to the proposal to repeat the above experiment and attempt to separate the pure cellulose amine from the viscous brown liquid.

II.

Twenty grams of cellulose nitrate were dissolved in 600 c.c. of liquid ammonia. To this 21.5 grams of sodium were added, small pieces at a time. The reaction proceeded as before and this time 15 c.c. of water were added to react with the excess sodium and $NaNH_2$ present.

The resulting brown viscous liquid was tested and found to be soluble in water, alkalis and acids. It was insoluble in ether and slightly soluble in alcohol.

Since no method, making use of ordinary solvents, was found which could made a complete separation, the work turned to finding a means of obtaining the precipitate from the Dewar flask without the use of water. It was believed that working with a solid, a method of purification might be perfected. This within itself presented a new problem as it was known that when the ammonia was allowed to evaporate, a spontaneous combustion resulted on exposing the product to the air. The first method suggested as a means of obtaining a precipitate which could be handled was washing the precipitate formed in the Dewar flask with liquid ammonia for it was believed all impurities would be soluble in liquid ammonia whereas the product might not.

This required a new type of apparatus. The apparatus for the following work is shown in picture on page 11. This apparatus also offered a second advantage. Materials could be added to the reaction flask without allowing ammonia fumes to escape into the room, which up to this time were found to be very annoying.

III.

In the new apparatus 5 grams of cellulose nitrate were dissolved in 200 c.c. of ammonia. An excess of sodium was added and the reaction mixture was stirred for eight hours. The excess ammonia was allowed to evaporate over night. The precipitate was washed with 100 c.c. portions of liquid ammonia until the wash liquor was clear. The resulting product was dried under vacuum.

A portion of this product, yellow in color, was burned. An alkali inorganic residue indicated incomplete purification, so it was necessary to further treat this product before an analysis could be made.

Distilled methyl alcohol left impurities and dissolved some of the product.

Acetone when hot would make a separation on basis of specific gravity. Each portion was tested but an alkali inorganic residue resulted on burning.

Carbon disulphide, ethyl acetate and many other solvents were used on the original precipitate but nothing was found which would remove the inorganic impurities.

IV.

Several attempts were made to continue work on the separation of inorganic impurities, but each time the ammonia evaporated and the product was exposed to air, a spontaneous combustion of product resulted. This led to the belief that, since $NaNH_2$ was only slightly soluble in liquid ammonia, the ammonia failed to remove all the $NaNH_2$ present, and the absorption of moisture from the air by the $NaNH_2$ liberated enough heat to initiate combustion. The work therefore turned to the addition of a soluble ammonium salt such as NH_4I to react with the excess $NaNH_2$. This should also leave soluble inorganic salts which could be easily removed by liquid ammonia.

V.

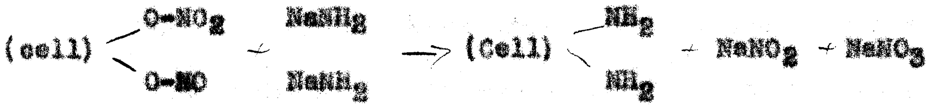
Following the above suggestions, 15 grams of cellulose nitrate were allowed to react with an excess of sodium. At the end of the reaction time NH_4I was added to react with the excess $NaNH_2$. The product was washed with liquid ammonia. This method gave a substance which could be handled, but, as before, no method was found which would remove the inorganic impurities. The difficulty found here was that all solvents tried as an agent to remove the inorganic impurities also dissolved the product and no method of re-precipitation was found.

The quantity of NH_4 salt used turned the work to the use of calculated amounts of cellulose nitrate and sodium.

The following reactions were assumed as one possible mechanism:

$$\text{(Cell)} - O{-}NO_2 + Na \xrightarrow{NH_3} \text{(Cell)} - O{-}NO + Na_2O$$

$$Na + NH_3 \xrightarrow{Na_2O} NaNH_2 + \tfrac{1}{2}H_2$$



$$\text{(cell)}\begin{matrix} O{-}NO_2 \\ O{-}NO \end{matrix} + \begin{matrix} NaNH_2 \\ NaNH_2 \end{matrix} \longrightarrow \text{(Cell)}\begin{matrix} NH_2 \\ NH_2 \end{matrix} + NaNO_2 + NaNO_3$$

VI.

On the basis of the above reaction, 4 atoms of sodium are required to give a complete reation. Therefore 92 grams of sodium should react with 252.8 grams of (molecular weight) of cellulose nitrate.

On this basis several experiments were run in which 4 atoms of sodium were allowed to react with cellulose nitrate in liquid ammonia, over a time range from 6 to 24 hours. As before a spontaneous combustion resulted in the evaporation of the ammonia unless some soluble ammonium salt was used, indicating incomplete reaction of $NaNH_2$, or sodium. If either were present it would indicate the reaction had not taken place as shown above. This seemed to be entirely possible due to the several ways the reaction could take place. A series of experiments using 2, 4, 6, and 8 atoms of sodium over a time range from 6 to 24 hours was next tried.

In these experiments the same previous difficulties were met. On the evaporation of the ammonia, a spontaneous combustion resulted. By the use of a soluble ammonium salt a product was obtained which could be handled. No method was found which would remove the inorganic impurities. When the reaction time was less than four hours the product showed presence of the nitrate radical as well as inorganic impurities.

Since none of the previous experiments during the investigation had given a product which could be purified, to the extent that analysis could be carried out, it was decided to investigate the reaction between the cellulose nitrate and $NaNH_2$, prepared by the action of sodium on ammonia in the presence of a catalyst. This had not been tried previously due to the very slight solubility of the $NaNH_2$ in liquid ammonia. It had been hoped, as shown on page 16, that Na_2O would be formed by the action of sodium on the nitrate group which would act as a catalyst in the forming of the desired $NaNH_2$. As this would be formed during the reaction it was believed that the soluble cellulose nitrate would react with the $NaNH_2$ as fast as it was formed, but the results of the investigation to this point indicated that the assumed reactions on page 16 did not show the proper mechanism for the reaction.

VII.

Working on the assumption that enough $NaNH_2$ would be soluble in ammonia to react with the soluble cellulose nitrate it was decided to prepare $NaNH_2$ first and then react cellulose nitrate with it, assuming the following reaction as plausible:

$$(\text{Cell}) - O\text{-}NO_2 + NaNH_2 \xrightarrow{NH_3} (\text{Cell}) - NH_2 + NaNO_3$$

The $NaNH_2$ was prepared in the following way(14): 600 c.c. of liquid ammonia was collected in flask (B) then it was syphoned into the reaction flask (C). To this a very small amount of powdered ferric nitrate was added, as a catalyst, then small pieces of sodium. The reaction taking place was:

$$Na + NH_3 \xrightarrow{Fe(NO_3)_3} NaNH_2 + \frac{1}{2}H_2$$

Since the cellulose nitrate used contained 11.7% nitrogen it took .3 grams of $NaNH_2$ to react with one gram of cellulose nitrate. It took .18 grams of sodium to produce .3 grams of $NaNH_2$. In the following experiment .2 grams of sodium were used to every gram of cellulose nitrate used to insure sufficient $NaNH_2$ for a complete reaction.

To the solution of $NaNH_2$ in liquid ammonia 5 grams of cellulose nitrate were added. This mixture was stirred for nine hours. A dark yellow precipitate resulted from the reaction which took place.

This precipitate was washed with 100 c.c. portions of liquid ammonia until no color remained in the wash liquor.

The precipitate, very fine in texture, darkened to some extent on the evaporation of the ammonia. Methyl alcohol was used to remove any cellulose nitrate and ammonia which may not have reacted. The final product was soluble in water and was neutral to phenolphthalein. On burning a portion of the precipitate no inorganic residue resulted. The brown ring test for nitrates was negative when made on the final product. This product was taken as pure and analyzed by Kjeldahl method(2) for amino nitrogen and total nitrogen.

Results:

Amino nitrogen	Total nitrogen
8.50%	7.59%

VIII.

The above prodedure was repeated using 10 grams of cellulose nitrate and two grams of metallic sodium.

It was believed that improper digestion was the reason for the low total nitrogen analysis. This time 10 grams K_2SO_4 was added in addition to .3 grams of $CuSO_4$ to raise the temperature of the H_2SO_4. This insured complete digestion.

Results of analysis:

Amino nitrogen	Total nitrogen
7.92%	8.15%

IX.

The above procedure was repeated once again as it was believed that the same nitrogen was being measured in both samples of above experiment.

Results:

Amino nitrogen	Total nitrogen
7.98%	8.27%

Yield: 74.4% of theoretical. The formula used for this computation will be discussed in "Discussion of Results."

X.

Repeating the experiment once more analysis gave:

Amino nitrogen	Total nitrogen	Yield
8.24%	8.50%	73.60%

Average of results:

Amino nitrogen	Total nitrogen
8.05%	8.30%

The final product was soluble in water, and was neutral to phenolphthalein, methyl orange, and methyl red. It was soluble in alkalis, concentrated H_2SO_4 and dilute HCl. It was insoluble in methyl alcohol, ethyl alcohol, ether and acetone.

Heating the product with NaOH failed to evolve NH_3 gas.

The Schotten-Bauman(13) test for amines was positive.

$$R-C{\lt^{O}_{Cl}} + RNH_2 + NaOH \longrightarrow RC{\lt^{O}} -NHR + NaCl + H_2O$$

Diazotization and coupling with beta naphthol in solution gave a green dye.

Diazotization and coupling with resorcinal in solution gave a dark solution which had a red color with transmitted light and a yellowish green color in thin layers.

When the product was treated with nitrous acid a white sediment formed which probably was cellulose as it was soluble in cuprammonium solution.

The amine gave no precipitate with $AgNO_3$ solution.

Two grams of the amine were placed in a small pyrex test tube with 3 c.c. of concentrated HCl. A rubber stopper was wired in with copper wire crossing at right angles.

The test tube was then suspended in boiling water for 30 minutes. It was diluted with 6 c.c. of water cooled and filtered. The filtrate was evaporated to dryness on water bath and redissolved in 10 c.c. of water.

To this was added .25 grams of crystallized sodium acetate and one drop of benzoyl chloride. This mixture was shaken violently for one minute. Four drops of 10% aqueous ferric chloride solution was added and four drops of concentrated HCl.

A red violet or purple color would indicate that a hydroxylamine had been present in the original compound. The color would be due to the formation of benzoxlhydroxamine acid.

$$C_6H_5COCl + NH_2O\ R \longrightarrow C_6H_5 \cdot NHOR + HCl$$

This test was negative. The reason for this test will be discussed later.

An apparatus was assembled by which the volume of nitrogen given off during diazotization and subsequent decomposition could be measured. 91% of the theoretical nitrogen volume was collected in this form.

The above two experiments were carried out for the purpose of establishing whether the final product was an amine or a hydroxylamine. This will be discussed more fully later.

DISCUSSION OF RESULTS

There were two possible formulas based on Haworth's(9) (modified Irvine) formula for cellulose, that would give a good agreement with the actual amount of nitrogen found by analysis in the final product.

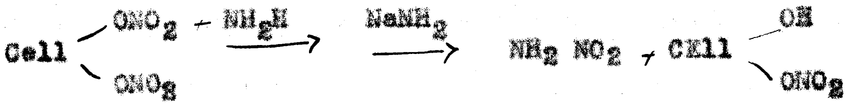
$C_6H_9O_5NH_2$ a hydroxylamine containing 7.91% nitrogen was one possibility while $C_6H_9O_4NH_2$ a true amine containing 8.69% nitrogen the other. Although all expectations would indicate the formation of the true amine, the possibility of a hydroxylamine being formed was investigated since there was such a close agreement between theoretical and actual yields of nitrogen.

In general hydroxylamines are basic in water solutions; soluble in alcohol and ether. They will give a white precipitate with silver solutions which on heating will give metalic silver. They will liberate ammonia when heated with NaOH. They would not be expected to undergo diazotization and should give a red violet to purple color when subjected to the benzoyl chloride--ferric chloride test.

All of the above tests for hydroxylamine were negative while the final product gave such positive tests for amine as diazotization, coupling and Schotten-Baumann reactions.

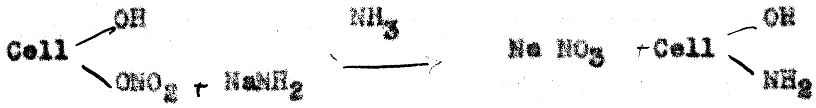
Representing by (Cell) a single C_6 unit of the Haworth formula for cellulose, the following reactions may offer an explanation for the mechanism by which a C_6 unit containing two nitrate groups was converted to a C_6 unit containing only one amine group as indicated by the analysis given in the experimental part.

The reaction is given in two steps but it would seem logical that they would take place simultaneously. The reactions are numbered for later discussion.

(1) 

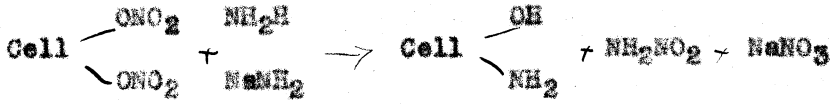
$$\text{Cell}\begin{array}{l} ONO_2 \\ ONO_2 \end{array} + NH_2H \longrightarrow \xrightarrow{NaNH_2} NH_2\,NO_2 + \text{CEll}\begin{array}{l} OH \\ ONO_2 \end{array}$$

then

(2) 

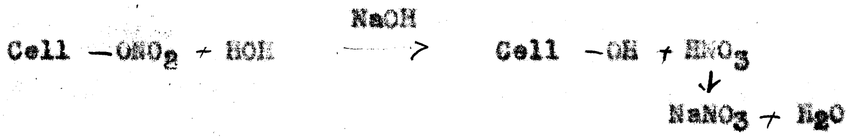
$$\text{Cell}\begin{array}{l} OH \\ ONO_2 \end{array} + NaNH_2 \xrightarrow{NH_3} Na\,NO_3 + \text{Cell}\begin{array}{l} OH \\ NH_2 \end{array}$$

and the combined reaction would be

(3) 

$$\text{Cell}\begin{array}{l} ONO_2 \\ ONO_2 \end{array} + \begin{array}{c} NH_2H \\ NaNH_2 \end{array} \longrightarrow \text{Cell}\begin{array}{l} OH \\ NH_2 \end{array} + NH_2NO_2 + NaNO_3$$

The reaction number (2) was based on the following analogous reaction in the denitrification of cellulose nitrate:



$$\text{Cell}-ONO_2 + HOH \xrightarrow{NaOH} \text{Cell}-OH + \begin{array}{c} HNO_3 \\ \downarrow \\ NaNO_3 + H_2O \end{array}$$

As mentioned previously, it seemed logical that the reactions, involved in the formation of the cellulose mono-amine, would take place simultaneously.

If the rate of reaction in case of number (1) was much greater than number (2) then it would seem logical that the final product would contain less than one amino nitrogen per C_6 unit.

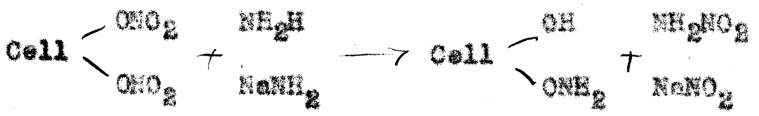
If the rate of the reaction of number (2) was much greater than number (1) then it would seem logical that the final product would contain more than one amino nitrogen per C_6 unit.

If however the rate of reaction of numbers (1) and (2) were equal then there should be one amino nitrogen per C_6 unit in the final product. It is believed that while the results from the analysis as given in the experimental part are not in perfect agreement with the theoretical, they are, however, within experimental error, thus indicating the rate of reactions of numbers (1) and (2) were approximately equal.

The NH_2NO_2(nitramide) which might be formed should be very acid in nature and would probably go over to more complex nitrite compounds of ammonia.

The basis of the above reaction was the fact, that, while it is not known just where the NO_3 groups are in cellulose nitrate they are in different positions, thus it would seem logical that they would have different tendencies to reaction. The reactivity of the different positions of cellulose is sustained by the action of sodium on cellulose. One sodium is introduced into the molecule much easier than a second, and a second much more easily than a third.

In considering the possibility of the formation of a hydroxylamine the reaction could have taken place in the following way:



$$\text{Cell}\left\langle\begin{array}{l}ONO_2\\ONO_2\end{array}\right. + \begin{array}{l}NH_2H\\NaNH_2\end{array} \longrightarrow \text{Cell}\left\langle\begin{array}{l}OH\\ONH_2\end{array}\right. + \begin{array}{l}NH_2NO_2\\NaNO_2\end{array}$$

Even though the above reaction is entirely possible, the following is offered as evidence that it did not occur:

1. The final product was insoluble in solvents in which alpha hydroxylamines in general, are soluble.

2. The final product was neutral to phenolpthalein in water solutions whereas alpha hydroxylamines should be strongly basic.

3. NaOH failed to evolve free ammonia which would be evolved from alpha hydroxylamines under the conditions employed.

4. The benzoyl chloride--ferric chloride test, a special test for hydroxylamines, was negative.

5. The volumeteric nitrogen determination by diazotization and decomposition with water also indicated that no hydroxylamine was present since hydroxylamine would not be expected to diazotize.

CONCLUSION

1. Cellulose mono amine has been prepared by the action of $NaNH_2$ on cellulose nitrate.

2. Cellulose mono amine containing 8.1% (average) nitrogen as amino nitrogen has been prepared by the action of $NaNH_2$ on cellulose nitrate with a 74% yield (average).

3. The cellulose mono-amine was found to have the following properties:

   (a). Soluble in water resulting in a neutral solution to phenolphthalein, methyl orange and methyl red. (It was impossible to get a precipitate from this solution).

   (b). Insoluble in methyl alcohol, ethyl alcohol, ether and acetone.

   (c). Soluble in alkalis, concentrated H_2SO_4 and in dilute HCl.

   (d). Would not give off free ammonia when heated with NaOH.

   (e). Would give positive test for primary amines.

   (f). The regenerated cellulose obtained by action of nitrous acid on the amine was soluble in cuprammonium solution.

SUGGESTIONS FOR FURTHER INVESTIGATION

The following are offered as an aid in the continuation of this investigation:

1. One possibility is the investigation of improving the yield. This may be done by changing the time of reaction in order to get a better conversion of the cellulose nitrate to the amine, and by recovering the amine which may be soluble in the alcohol that is used to wash out the free cellulose nitrate and ammonia which may not have reacted. No attempt was made along these lines in this investigation. The recovery of the amine from the alcohol washing was suggested as the first filtrates were colored when there was an apparent free ammonia present. On successive washings the filtrate color decreased until there was no color at all.

2. Another possibility is to determine the position of the amino group in the final product.

3. The possibility of the preparation of the di-amine is also suggested. It should be interesting to use the cellulose trinitrate and see if only one amino group is still introduced.

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