A STUDY OF THE REACTION BETWEEN CELLULOSE NITRATE AND SODIUM ACETYLIDE IN LIQUID AMMONIA MEDIA

by

George Archer Saul

A Thesis Submitted to the Graduate Committee in Partial Fulfillment of the Requirements For the Degree of

MASTER OF SCIENCE

in

CHEMISTRY

Approved:

In Charge of Investigation

Head of Department

Chairman, Graduate Committee

Virginia Polytechnic Institute

Blacksburg, Va.

1947

ACKNOWLEDGEMENTS

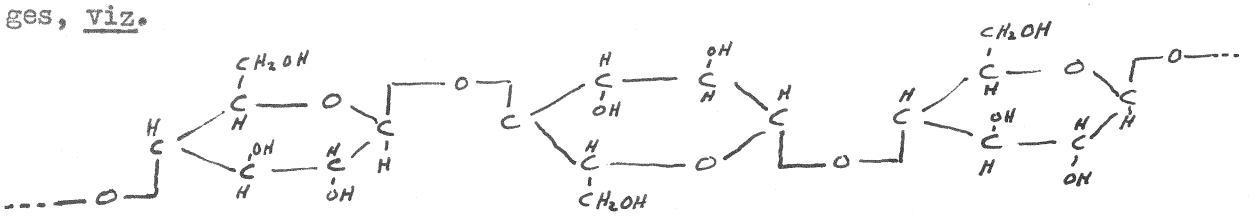
The author wishes to express his gratitude to Dr. Phillip C. Scherer, Jr., for the many suggestions which made possible the results shown in this thesis.

Thanks are also given to Dr. J. W. Watson for his cooperation in obtaining the materials necessary for the investigation and to the other members of the faculty who were ever willing to be of assistance when called upon.

TABLE OF CONTENTS

I. INTRODUCTION

The cellulose molecule has been assigned (10) a structure consisting of many cellobiose units connected by means of oxygen bridges, viz.



The long chains resulting from this linkage tend to allign themselves in parallel bundles which aggregate into the cellulose fiber. The fiberlike properties of cotton and other cellulosic materials is due to the strong attraction set up between the long parallel chains, largely by the secondary valences between the three hydroxyl groups of each anhydro-glucose unit. If the hydroxyl groups could be reduced, the secondary valence forces between chains would be largely destroyed, and the resulting product might be expected to show interesting changes in its properties.

Degradation of the cellulose might be expected to result during direct reduction, so it appeared necessary to attempt an indirect reduction in order to avoid this degradation. The plan of approach to this problem was to react an ester, cellulose nitrate, with an alkali alkyl in liquid ammonia in order to remove the nitrate groups from the cellulose nitrate and to replace them metathetically by a hydrocarbon group. Sodium acetylide was chosen as the alkali alkyl to be used, due

to its property of being highly ionized in liquid ammonia solution and its ease of preparation.

Specifically, this problem was the determination of the nature of this reaction, the products formed, and the properties of the products.

II. THE REVIEW OF LITERATURE

Liquid Ammonia as a Solvent.

A very comprehensive review of the use of liquid ammonia as a solvent is given by E. C. Franklin [7] in his book "The Nitrogen System of Compounds". The boiling point of liquid ammonia at standard atmospheric pressure was determined by Franklin and was found to be $-33.46^{\circ}C$.

In 1898 Cady [1] investigated liquid ammonia as a solvent. In the same year Franklin and Kraus [8] carried on research along the same lines. Among other things these investigators found that the alkali metals dissolve easily and are recovered unchanged on evaporation of the solvent. Sodium chloride was found to be moderately soluble, and, in general, nitrites and nitrates were soluble. Many organic compounds were found to be soluble or miscible.

According to Fernelius and Johnson [5], ammonia is a good solvent but is not a powerful ammonolyzing agent due to its low dissociation constant. For this reason cellulose nitrate can be dispersed in liquid ammonia and can then be recovered chemically unchanged on evaporation of the ammonia. Despite ammonia's low dissociation constant, Fernelius and Bowman [4] state that ammonium salts exhibit a catalytic effect upon many ammonolytic reactions. Feild [3] assumed that solvent NH_3 was catalyzed by $NaNH_2$ so that it entered into a reaction with cellulose dinitrate.

Sodium Acetylide.

The recent monograph by Nieuwland and Vogt (13) is the result of many years research in the field of acetylene chemistry. It states that the hydrogen atoms present in the acetylene molecule are more labile than those of other hydrocarbons. Conductivity measurements of acetylene in water, and in liquid ammonia have shown that it is only very slightly ionized in solution. When one hydrogen of acetylene has been replaced by a substituent group, the lability of the remaining hydrogen atom is influenced. Nothing more is said in the monograph about the comparative lability of the atoms in mono-substituted acetylenes as this field has received little study.

A method for preparation of sodium acetylide in liquid ammonia is given by Fieser and Fieser (6). It is pointed out that the hydrogens of acetylene are labile and are replacable by metals. By passing a stream of acetylene through a solution of sodium in liquid ammonia at or below its boiling temperature, it is converted smoothly into a monosodio derivative. Under more drastic conditions of temperature and pressure the disodio derivative can be formed (13). The original acetylene can be obtained from the sodium derivatives on treatment with water.

Cottrell (2) showed that mixtures of ammonia and acetylene do not show electrical conductivity comparable with solutions of alkali carbides or acetylides, and so inferred the non-existence of ammonium carbide, or acetylide.

Moissan[11] found that nascent hydrogen when produced by sodium in liquid ammonia solution hydrogenated a portion of the acetylene which was passed through. Hydrogenation of the mono-substituted acetylenes has also been reported[12]. This hydrogenation is usually so slight that it is neglected.

In 1913 Lebeau and Picon[9] produced 1-alkynes in good yield by the action of certain alkyl iodides on sodium acetylide in liquid ammonia. Picon[14] later showed that this was a general reaction for all alkyl iodides up to the one with sixteen carbon atoms.

Later Vaughn, et. al.[16], investigated this reaction further, and several metal acetylides were found to be unstable in air. The degree of stability varied with each compound. Sodium and potassium acetylides being the most stable, remained in white crystalline form for approximately ten hours when exposed to dry air. Other acetylides began turning color in air almost instantly.

They mentioned the possibility that sodium acetylide in liquid ammonia might react slightly in a reversible reaction

$$NaC{\equiv}CH + NH_3 \rightleftharpoons NaNH_2 + HC{\equiv}CH$$

and so cause traces of sodamide to be present.

A number of side reactions in the alkyne synthesis were investigated by the same group. The first was the formation of alkenes.

$$R\text{-}CH_2\text{-}CH_2X + NaC{\equiv}CH \longrightarrow RCH{=}CH_2 + NaX + C_2H_2$$

Cyclohexyl bromide gave no alkyne and moderate yields of cyclohexene. Another side reaction resulted in the formation

of dialkylethynes. Moissan[11], as well as Vaughn[16], seemed to agree that sodium acetylide prepared in liquid ammonia was substantially free from sodium carbide. The following series of reactions was then concluded to be largely responsible for the production of the dialkylethynes.

(1) $RX + MC{\equiv}CH \longrightarrow RC{\equiv}CH + MX$

(2) $RC{\equiv}CH + MC{\equiv}CH \rightleftharpoons RC{\equiv}CM + C_2H_2$

(3) $RC{\equiv}CM + R'X \longrightarrow RC{\equiv}CR + MX$

The mechanism of these reactions was confirmed experimentally by Vaughn[16] and fellow workers.

III. THE INVESTIGATION

A. Object of Investigation.

The object of the investigation of the reaction between cellulose nitrate and sodium acetylide is the determination of the nature of the reaction, the products formed, and properties of those products. In other words, it is a problem of fundamental research.

The original investigation also included a study of the reaction products of other alkali-alkyls such as sodium methyl, sodium ethyl, and sodium triphenyl methide, time permitting. Due to the interesting things that developed in the study of the derivative of sodium acetylide, however, the investigation was never extended to include these other reactions.

The first part of the investigation was primarily concerned with the determination of conditions under which the reactions are to be carried out. Tests were then made which indicated the completeness of reaction and the properties of the product which results. After the process was adjusted so as to favor the most complete reaction, emphasis was then placed upon purification and analysis of the resulting product. For those groups which defy ordinary analytical means in their detection, derivatives will be attempted by which the groups present could be determined.

B. Apparatus and Materials.

The ammonia used in this work was ordinary anhydrous liquid ammonia purchased from E. I. du Pont de Nemours. It was not further purified.

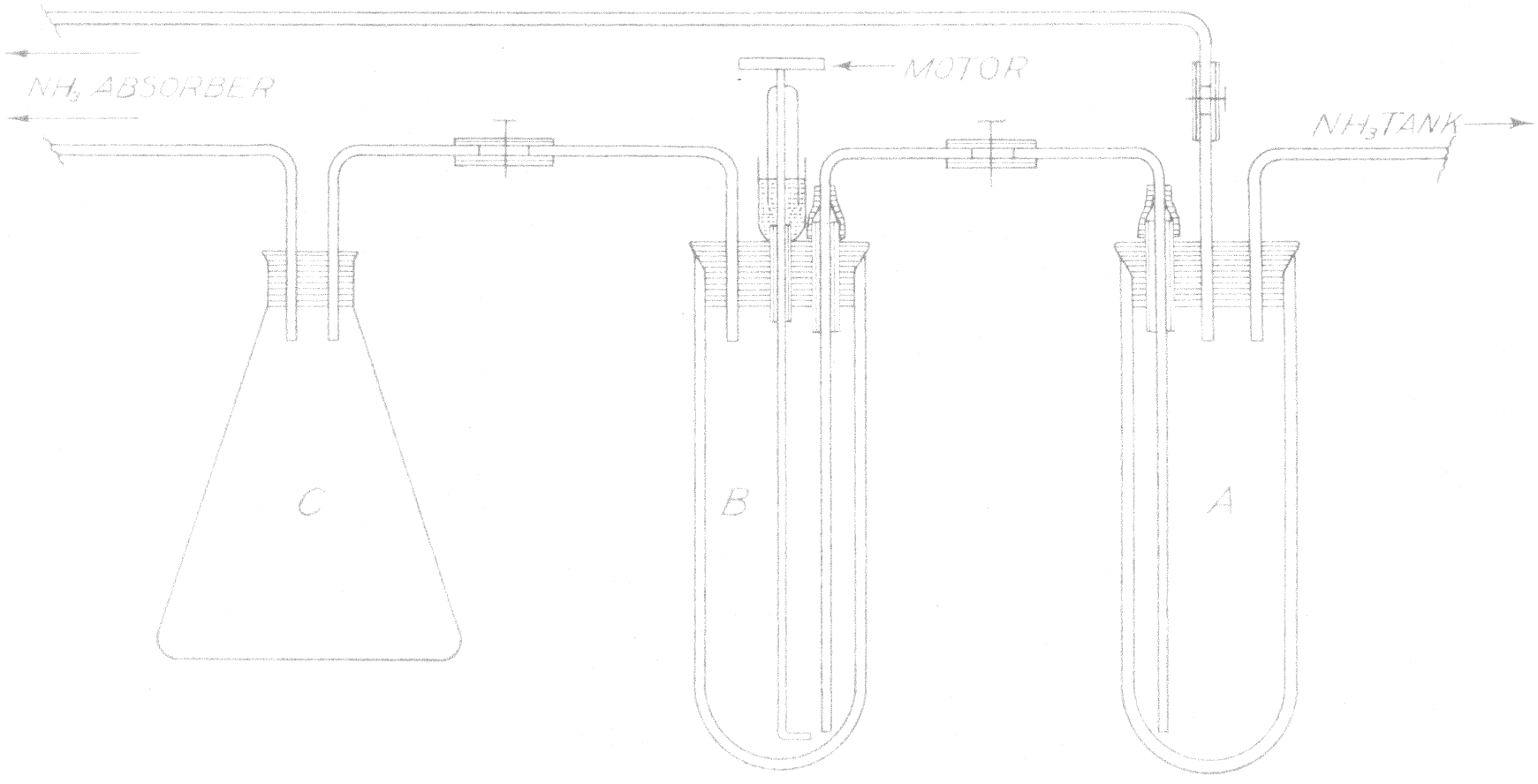
The cellulose nitrate which was used, was obtained from the Hercules Powder Company. It contained 11.9% nitrate nitrogen as determined by the du Pont nitrometer and so corresponded approximately to a di-nitrate.

The acetylene was obtained from the Linde Air Products Company. It was further purified for use in this work by means of the apparatus shown in Drawing Number 2. Acetylene from the cylinder was bubbled through about six inches of concentrated sulfuric acid in the tower (E) in order to remove acetone vapors. The gas left the top of the acid tower and went through a length of silicone tubing into the bottom of a soda lime tower where sulfuric acid and sulfur dioxide vapors were removed. After this purification the acetylene was considered satisfactory for this work.

The sodium used came from the stock room of the Chemistry Department and was not marked with the manufacturer's name.

All other chemicals used in the course of the investigation came from the stock room and were generally of CP grade.

The apparatus which was used in the preparation of the product can be seen in Drawings 1 and 2. The acid tower (E) and the soda lime tower (D) have already been mentioned and require no further



LEGEND

A - COLLECTION FLASK

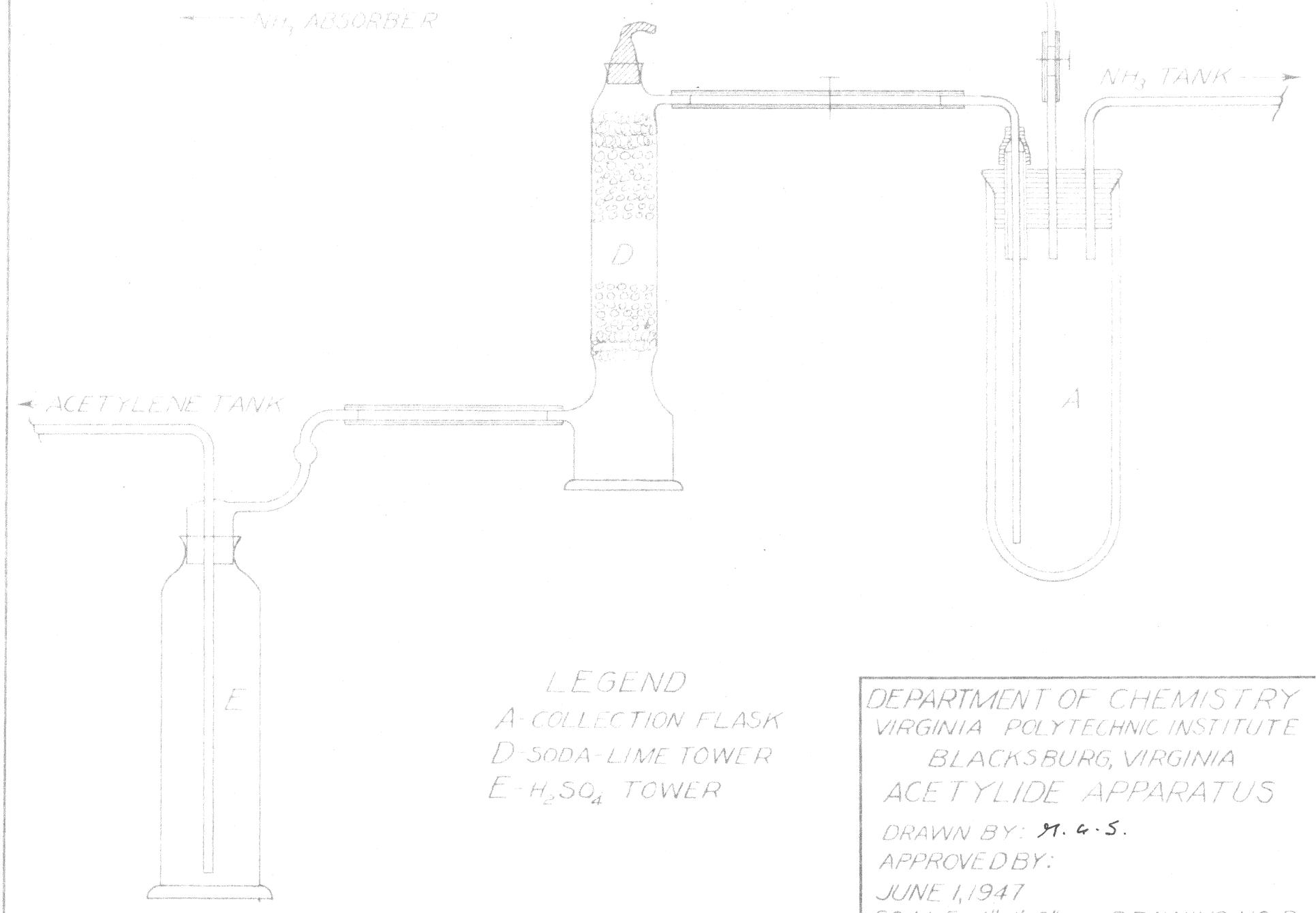
B - REACTOR

C - SAFETY TRAP

DEPARTMENT OF CHEMISTRY
VIRGINIA POLYTECHNIC INSTITUTE
BLACKSBURG, VIRGINIA

REACTION APPARATUS

DRAWN BY: M. A. S.
APPROVED BY:
JUNE 1, 1947
SCALE: 4" = 1'-0"
DRAWING NO. 1



LEGEND

A - COLLECTION FLASK

D - SODA-LIME TOWER

E - H_2SO_4 TOWER

DEPARTMENT OF CHEMISTRY
VIRGINIA POLYTECHNIC INSTITUTE
BLACKSBURG, VIRGINIA

ACETYLIDE APPARATUS

DRAWN BY: M. G. S.

APPROVED BY:

JUNE 1, 1947

SCALE: 4" = 1'-0" DRAWING NO. 2

explanation. It will be noticed that the Dewar vacuum flask(A), which is called the collection flask, is shown in both drawings. It can be used both with the acetylide system and the reaction system by merely connecting a rubber tube to the system desired. The Dewar flask (B) shown in Drawing No. 1 is the same as the other Dewar flask but is equipped with a mechanically operated stirrer which operates through a mercury seal. The long glass tubes in both flasks (A) and (B) can be raised and lowered at will. The Erlemeyer flask (C) was used merely as a safeguard to protect against any sucking back of water from the carboy which was used to catch ammonia fumes from the system.

Because of the system of clamps, shown in Drawing No. 1, and the two-way exhaust system, it was possible to remove either (A) or (B) from the system for washing while the other was in use.

C. Experimental Data.

Inasmuch as several methods of attack were attempted in order to obtain a successful reaction, it was found expedient to segregate these experiments so as to give the reasons for certain experimental steps and consequently to be able to present a clearer picture of the work as a whole.

Experiment No. 1

The purpose of this experiment was to determine whether acetylene would itself react with cellulose nitrate.

A ten gram sample of cellulose nitrate was weighed out on the rough balances and placed in the reactor flask (B). About 350 ml. of liquid ammonia was then run from the tank into the collection flask (A) and from there siphoned over to (B) under pressure. After an hour of stirring in the liquid ammonia the cellulose nitrate was dispersed. The movable tube in (B) was then connected to the acetylene cylinder and the gas flow commenced. The tube was then lowered below the surface of the liquid and acetylene bubbled through for six hours. The ammonia was allowed to evaporate off overnight. A hard pale yellow residue remained. The solid was soluble in acetone and insoluble in water so reprecipitation from solution was done two times as a means of purification. The precipitate was dried. It was insoluble in alcohol also in ether. However, it was soluble in a mixture of alcohol and ether. On treating with boiling water, a

filtrate was obtained which gave a positive diphenylamine test for nitrates. The product was fast-burning, disappearing in a flash when a flame was applied to it.

From all of these tests it was concluded that the attempted reaction between acetylene and cellulose nitrate had been unsuccessful, and that the material which had been tested was unreacted cellulose nitrate.

Experiment No. 2

This experiment describes the proportions of chemicals used, the techniques involved, and the times of reaction for a series of runs which were made to develop the most satisfactory procedure for carrying out the reaction between cellulose nitrate and sodium acetylide in liquid ammonia.

Run #1. About two grams of metallic sodium were cut into small pieces about one cubic centimeter on edge, and dropped into the reactor flask which contained 400 milliliters of liquid ammonia. The sodium went into solution coloring the solution deep blue. Carefully dried acetylene was then led into the solution and after a short time the solution became colorless and flecked with white flakes which was an indication that all the free sodium present had been used up. Ten grams of cellulose nitrate were then weighed out, dried and added to the sodium acetylide solution and a mechanical stirrer started. As the cellulose nitrate was broken up by the action of the stirrer, the whole solution took on a rust-brown color. After four hours, dispersion appeared to be fairly complete and the brown color had intensified. Five grams of ammonium chloride were then added with the idea of removing any excess sodium acetylide through the formation of gaseous acetylene and soluble sodium chloride. The solution lost its rusty color and its opaque appearance and became transparent but very dark brown in color. The ammonia was then allowed to evaporate off overnight.

Run #2. Ten grams of cellulose nitrate were placed in the reactor flask. About 400 milliliters of ammonia were run into the collection flask from the tank and from there into the reactor flask with the nitrate. The mechanical stirrer was then started so that the nitrate would be dispersing while the sodium acetylide was being made. This method was adopted as standard procedure in all succeeding runs. The sodium acetylide was made in the collection flask by the method previously described. After the nitrate had been dispersed for about an hour, the sodium acetylide solution was forced over into the reactor flask. A light-brown to yellow precipitate appeared immediately and seemed to form an almost solid mass throughout the solution. This was broken up by the action of the mechanical stirrer into very small particles. After two hours the stirrer was shut off and the reaction mixture allowed to evaporate to dryness overnight.

Run #3. The reaction in this case was carried out exactly as in Run #2, described above. Observations made during this run concerning the color changes during reaction confirmed those previously described. After the reaction had proceeded for four hours, 400 milliliters of ethyl alcohol were added in order to see if it were possible to precipitate the product directly from the liquid ammonia solution without waiting for evaporation. Alcohol did not seem to precipitate out any of the product, so was discarded as a possible precipitant for future work.

Run #4. Another reaction was carried out in the manner previously described but using only five grams of cellulose nitrate and one gram of sodium in the preparation of the acetylide. Again no ammonium chloride was used in this procedure. At the end of four hours reaction time, ether was added until the composition of the solution was roughly seventy per cent ether by volume. A heavy precipitate was thrown down. The product was collected by filtration and was washed several times with an ammonia-ether solution of approximately the same composition as that from which it was precipitated. The product was allowed to sit in the open air for about four hours while the ammonia and ether vapors were evaporating off. It was then placed in a dessicator to evaporate further overnight. The next morning the precipitate had changed from the form of rust-colored crumbs to a shrunken, coherent, and hard mass which was very dark brown, almost black, in color. A small amount of the product which was allowed to react only forty five minutes before washing with the ammonia-ether solution was allowed to dry overnight and did not undergo the same shrinkage and change of color as did the first sample.

Run #5. The procedure of the previous run was duplicated up through the point where the product was washed with an ammonia-ether mixture. The filter paper holding the washed product was put into a beaker which was placed in an oven at 50°C. This was done in order to evaporate off the ammonia and ether from the product in an atmosphere which was essentially free from moisture, and in so doing determine the possible causes behind the observed change in color and

appearance of the product reported in the last Run. When the sample in the oven was checked the next morning, it was discovered that the product had ignited during the night due to some unknown cause and had burned to ashes.

Run #6. A sample similar to that made in Run #5 was made with only one variation. It was allowed to react only two hours before it was removed and be washed with the ammonia-ether mixture. After washing, this product was placed in a beaker and then put in a cold oven. The product shrank and darkened as was observed in Run #4 but did not ignite. It was therefore assumed that the escaping ether vapors from the product in Run #5 were ignited by a spark in the electrical circuit of the oven, and that spontaneous combustion of the compound did not take place.

Run #7. Five grams of cellulose nitrate were reacted with the acetylide produced from two grams of sodium. The added amount of sodium was used so as to force the reaction more nearly to completion. The reaction proceeded normally for six hours, the solution changing gradually from a light yellow color to a rust-brown color. Six grams of ammonium chloride were then added slowly. As the ammonium chloride was added, it was seen that the finely broken up brown solid which was held in suspension was dissolving and forming a transparent dark-brown solution similar to that one observed in Run #1. An attempt was then made to throw the product out of solution by the addition of ether, but this did not work as the ether formed an immiscible layer on the

top of the transparent brown ammonia solution. This was evidently due to the presence of the inorganic salts in the solution. The flask was left for two days so that complete evaporation of the ammonia and ether could take place.

Run #8. Ten grams of cellulose nitrate were reacted with the sodium acetylide produced from four grams of sodium. The reaction mixture was stirred for five hours at which time eight grams of ammonium chloride were added. The usual dissolution and change of color took place. The solution was then allowed to evaporate to dryness over a period of 36 hours.

Run #9. Two grams of cellulose nitrate were reacted with the sodium acetylide produced from one gram of sodium. After stirring for five hours, excess ammonium chloride was added followed by four grams of mercuric iodide to the clear, dark solution. No visible reaction occured with the addition of the mercuric iodide. The solution was allowed to evaporate almost to dryness and then a small amount of ether was added to keep the product from being exposed to the air when all the ammonia had evaporated.

Run #10. One half gram of cellulose nitrate was reacted with the sodium acetylide produced from one tenth gram of sodium. After the reaction mixture had been stirred for six and one half hours, the motor was stopped and the product, a brown powder, settled to the bottom of the flask. The supernatant ammonia was decanted off in order to rid the product of inorganic salts. Fresh ammonia was added to the flask,

and the washing of the product was repeated two more times. More ammonia was then added to the flask and then one gram of triphenyl tin iodide was added to the solution. A whitish flocculent-looking precipitate settled leaving the supernatant liquid clear and with a slightly greenish tint. The ammonia was then allowed to evaporate off.

Experiment No. 3

Variations in the method of preparation of samples were described in the last experiment. It is the purpose of this experiment to show how various methods were attempted to rid the dried product of inorganic salts which might be present and which would interfere with the analytical work necessary in its identification. Run numbers in this experiment correspond to the products obtained from the Runs discussed in Experiment No. 2.

Run #1. The Dewar flask containing the dried product was half filled with water and the product dislodged from the bottom and sides by mechanical means. The precipitate was partially water soluble because the water was observed to turn dark brown in a week's time. The solid material was then extracted with hot water in a Soxlett extractor for eight hours. It was observed that this water was also colored on passing through the thimble containing the product.

Run #2. The dried precipitate was placed in the collection flask and a porous glass filter was fitted onto the end of the long glass tube which extended to the bottom of the flask. Ammonia was then added to the flask in an attempt to dissolve out the inorganic salts. The ammonia above the product took on a dark brown color. The filter was then inserted below the surface of the liquid and the liquid forced over into the reactor flask. This was repeated several times, and it was seen that the brown color of the wash liquor was due to a slight solubility of the material. Most of the

product was carried over into the reactor flask in the ammonia filtrate and for this particular sample, at least, washing with ammonia appeared to be impractical.

Run #3. About 400 milliliters of alcohol were added to the reaction mixture in liquid ammonia. No precipitation occurred. However, after the ammonia had evaporated off it was seen that at least part of the product had precipitated out in particles almost colloidal in size. An attempt was then made to increase the size of these particles by placing a beaker containing the alcoholic solution on the steam bath for fifteen minutes. The product precipitated out in a coherent dark mass on the bottom of the beaker. After the precipitated material was allowed to stand in the open air for four days, it became a dark brown or black color. It was completely soluble in warm water but could be reprecipitated by adding alcohol then heating to increase the particle size. Due to the color change which occurred in the material obtained in this way, and to the difficulty involved in getting a reprecipitated particle without forming a fused mass, it was decided to discard this avenue of investigation for a means of purification.

Run #4. An attempt was first made to wash the precipitate from this Run with pure ammonia, but the product itself appeared to be too soluble in the ammonia to permit this to be done. The precipitate on a filter paper in a funnel was then washed with a mixture of about twenty per cent ammonia and eighty per cent ether. The product did

not seem to be soluble in this mixture.

Run #5. This material was washed with the ammonia-ether mixture described in Run #4.

Run #6. The same washing procedure was repeated.

Run #7. Twenty four hours after the last of the ammonia had evaporated from the product in the Dewar flask, about 300 milliliters of water were added. After two days the water had only turned color slightly indicating that this product was not extensively water-soluble. The caked product was removed from the flask with mechanical agitation, was ground to a fine state of subdivision in a mortar, and was then transferred to a filter funnel where it was washed with cold distilled water. When the wash water no longer contained enough Cl^- to give a test with $AgNO_3$ solution, it was assumed that all chlorides and nitrogen-containing inorganic salts had been removed. The product was then set aside for drying.

Other Runs. All succeeding runs were washed by the procedure described for Run #7.

Experiment No. 4

It would appear that due to the variations in conditions under which the runs were carried out, none of the products exhibited exactly the same physical characteristics. This experiment attempts to describe these different products and the tests which were made on them.

Run #1. The product in this experiment was an amorphous solid and was dark brown in color. It could not be dislodged from the bottom of the flask so water was added. The water quickly acquired a brown color. After two days the water had become a deep brown, almost black, color. The water was tested with diphenylamine and found to contain nitrates. A positive test for nitrates was also obtained from the water solution using a brown ring test for nitrates. The solid product was dislodged from the Dewar flask and was extracted in a Soxlett extractor with water for eight hours. The water became very brown in color and gave a positive diphenylamine test for nitrates when tested. A sodium fusion test was run on the solid product and appeared to be positive.

Run #2. Solubility tests were run on the solid product which had been prepared six weeks previously. All were carried out at room temperature. Reagents used included water, ethyl alcohol, methyl alcohol, acetone, toluene, benzene, n-butyl alcohol, ethyl acetate, 1,4 dioxane, ethylene glycol, chloroform, pyridine, nitroethane, glacial acetic acid, 20% NaOH, concentrated NH_4OH. Of these, only water, 20% NaOH and concentrated NH_4OH dissolved the product. The glacial acetic acid appeared to react with the solid, breaking it up into smaller pieces and turning it lighter

in color. The product was reprecipitated from water solution by addition of alcohol.

Run #3. A beaker containing alcohol and water and some of the reprecipitated product was placed on the steam bath for about fifteen minutes. The product changed from a light to a dark brown color and formed a coherent mass on the bottom of the beaker. The supernatant liquid was decanted off and solubility tests run on the solid. Again, organic solvents had no effect. 20% NaOH dissolved it readily. 5% NaOH dissolved it, but at a slower rate. Water exerted only a partial dissolving effect in contrast to the results found in the previous run. Some of the solid product was exposed to air for four days and became almost black in color. Complete solution of this material occurred in hot water. On addition of alcohol to this water solution, the product was reprecipitated as had been previously observed.

Run #4. The color of the precipitate as first obtained from the ammonia solution was that of iron rust. After sitting overnight it changed to a dark brown color as previously described under Experiment No. 2. Some of this product was burned. The burning solid gave rise to an ash which resembled Pharaoh's Serpents in its formation.

Run #5. The product of this run burned while in the oven so no tests were possible.

Run #6. Some of the dry ash from this run was burned and gave rise to a Pharaoh's Serpent just as did that in Run #4. Some more of the product was then extracted ten times with acetone in order to remove any

unreacted cellulose nitrate that might be present. After this washed material had dried, it was ignited and still produced a Pharaoh's Serpent. Some of the acetone-treated product was placed in a test tube and taken into solution by the addition of water. Addition of methyl alcohol to the water solution did not result in reprecipitation. Ethyl alcohol, on the other hand, effected reprecipitation satisfactorily. The reprecipitated product was filtered and allowed to dry. Only a very small amount was available. This did not burn as did the original product. Complete dissolution of the original product on a large scale did not work when water was attempted as a solvent. After repeated extractions with water, a light brown solid was obtained on filtration. When dried this solid burned rapidly but not with the formation of the Pharaoh's Serpent as it had done originally. This washed product was soluble in 20% NaOH. It was washed several times with acetone to remove any unreacted cellulose nitrate and was dried. Diphenyl amine tests were then carried out on the unwashed product, on the washed product, and on the water-soluble material, and all were positive. These tests indicated that all nitrate groups had not been removed in the original reaction.

Run #7. Some of the dried and washed product was dissolved in concentrated sulfuric acid and the diphenylamine test for nitrates run. In previous tests the solution of the product had produced an intense blue coloring as soon as the acid solution of diphenylamine was added. In this case, however, no coloration appeared for several minutes. A blue

color gradually appeared in the solution and was intense after two hour's time. It was assumed that no nitrates or very few nitrates were present in the product, and that the gradual development of the blue color was due to oxidation of some of the amine groups present on exposure to the air. This product was not inflammable. Solubility tests were made with the following reagents at room temperature: water, alcohol, ether, toluene, benzene, n-butyl alcohol, ethyl acetate, 1,4 dioxane, ethylene glycol, nitroethane, and pyridine. The product was insoluble an all of these. Ten per cent NaOH swelled the product and dispersed it completely on allowing it to stand overnight. Reprecipitation was effected by adding alcohol to the NaOH solution. The reprecipitated product was water-soluble after it had been dried. Overnight solution was also obtained by the use of benzyltrimethyl ammonium hydroxide (30% solution). The product was also dissolved at elevated temperature with a 5% solution of hydrochloric acid. This indicated that the product might contain amine groups. The Hinsberg test was positive for primary amines. A brown ring test for nitrates was then run and was found to be negative. An attempt at diazotization and coupling with B-napthol was then made. The product was dissolved in warm HCl (3:5) and cooled to zero. One gram of $NaNO_2$ dissolved in five milliliters of water was then added. Colorless nitrogen gas bubbled from the reaction mixture indicating that diazotation had taken place. This liquid was added immediately to a cold solution of B-napthol in sodium hydroxide solution. A dark substance came out of the solution. This

substance was brown by reflected light. It was water insoluble but was benzene and alcohol soluble. If, in the above procedure, the diazotization mixture were allowed to sit at zero degrees for fifteen minutes, a large amount of orange-red precipitate came out of solution and rose to the top of the test tube. This might indicate that the diazonium chloride was unstable.

Experiment No. 5

The work up to this point has qualitatively established the presence of an amine group in the reaction product. The possibility of the presence of an acetylide group must also be investigated. In ordinary monomolecular organic compounds the qualitative detection of such an unsaturated linkage could be accomplished by the use of bromine water, permanganate or some other such means. These means fail in the case of the product under investigation here, however, due to the dark coloring which it has in solution, also to the other groups present which might complicate the tests.

The problem was met by an attempt to prepare metallic salts of the compound. This was done by adding to the reaction mixture immediately after the NH_4Cl step a calculated amount of a salt of the metal.

In the first case ammonium chloride was added to the reaction mixture after five and one half hours. Silver nitrate was then added to the mixture in the flask and the flask left to evaporate for two days. By the time the ammonia had all evaporated off both the product and the walls of the flask and turned a jet black in color indicating that AgCl had been formed and had been reduced to metallic silver by the action of light. This made it impossible to determine the amount of metallic derivative because the metallic silver could not be removed.

The preparation of a copper derivative was then attempted. A small sample of the thesis product was dissolved in warm dilute

hydrochloric acid. A solution of cuprous chloride was added and some material precipitated out. The material was collected on a filter paper and shed with water, then with dilute ammonium hydroxide. It was then dried, ashed, and placed in a muffle furnace at 800°C. The residue was then dissolved in hydrochloric acid. On neutralization with ammonium hydroxide the solution became blue in color. On acidifying again and passing in hydrogen sulfide, a black substance precipitated out which was assumed to be cupric sulfide.

A mercury derivative was then attempted. After the cellulose nitrate-sodium acetylide reaction mixture had been allowed to react for five hours, ammonium chloride was added. Then mercuric iodide was added to the solution. The red mercuric iodide became colorless on entering the ammonia solution. After the ammonia had evaporated the red color of the iodide crystals was again apparent. The product was removed from the Dewar flask, and an attempt was made to wash out all of the unreacted iodide by washing with ether. Washing was not complete when the ether supply gave out and no more was available. Washing was continued using a very dilute solution of sodium thiosulfate. The material was dried and then digested in a mixture of sulfuric and nitric acids to get rid of all organic matter. A white crystalline substance remained in the bottom of the test tube. This substance was soluble in dilute nitric acid. Hydrogen sulfide was passed into the solution and a yellow-brown solid precipitated out. The solid was soluble in sodium sulfide solution but precipitated out again on addition of water or

ammonium chloride. Aqua regia was added to a portion of the sulfide precipitate. The solid went into solution, and yellow sulfur separated out. When a piece of copper wire was placed in this solution, shiny mercury plated out on it. This is fairly definite evidence that the compound contained the acetylide grouping originally.

Since the product obtained in the reaction between cellulose nitrate and sodium acetylide exhibited certain solubility phenomena with ammonium chloride in liquid ammonia, it was suspected that the acetylide grouping, if present, had a sodium atom connected instead of a hydrogen atom. It was then decided to attempt a confirmation of this theory by an attempted reaction with an organo-metallic tracer. Triphenyl tin iodide was chosen. Starting with one half gram of cellulose nitrate, the reaction was carried out for six and one half hours. The product was heavier than the ammonia solution so settled to the bottom of the flask. The supernatant liquid was decanted off to remove inorganic salts. This was repeated three times. More ammonia was added to the product, and then one gram of triphenyl tin iodide was added to the solution. A flocculent looking white precipitate came down at this point. The product obtained was washed with water, dried, and then extracted with ether to remove any unreacted triphenyl tin iodide. It was then digested in a hot sulfuric acid-nitric acid mixture to get rid of all organic matter. The material which was obtained was dissolved in dilute hydrochloric acid. Hydrogen sulfide was bubbled through one portion of the solution. A yellow-brown colloidal suspension

appeared which settled out on heating on a water bath. This precipitate was soluble in concentrated hydrochloric acid. To a second portion of the original solution was added just enough sodium hydroxide solution to make it alkaline. On standing for a few minutes, a white gelatinous precipitate appeared. This precipitate was soluble in an excess of base. Sodium carbonate and ammonium hydroxide also precipitated out this white compound. From all this evidence, it was evident that the organic compound which had been decomposed had contained tin.

Experiment No. 6

In order to determine the effect of time of reaction on amine formation a series of Kjeldahl determinations was run. The procedure used was a standard one in which the sample was digested in a Kjeldahl flask with concentrated sulfuric acid, ten grams of potassium sulfate and one half gram of cupric sulfate added, and digestion carried out on a hot plate. After digestion was complete one hundred and fifty milliliters of water were added to the cooled solution and the solution recooled. Eighty-five milliliters of concentrated sodium hydroxide were then added to the flask carefully so as to form two separate layers, a pinch of zinc metal added, and the flask connected to the condenser. The flask was then shaken, heat applied, and the ammonium hydroxide which was formed, was collected in one hundred milliliters of four per cent boric acid solution. The sample was titrated with tenth normal hydrochloric acid using methyl red as an indicator. The titration was carried out until the color of the unknown matched the color of a blank containing the same amount of boric acid and indicator.

Several total nitrogen determinations were made in the same fashion by a slight modification of the procedure. In dissolving the product, a sulfuric acid solution containing one gram of salicylic acid was used. This mixture was added to the product and allowed to stand for one half hour. Then approximately two grams of powdered zinc were added and the mixture shaken around for ten minutes or so. Potassium

sulfate and cupric sulfate were then added and the process continued exactly as described for amino nitrogen.

The results of the nitrogen determinations are given below in tabular form.

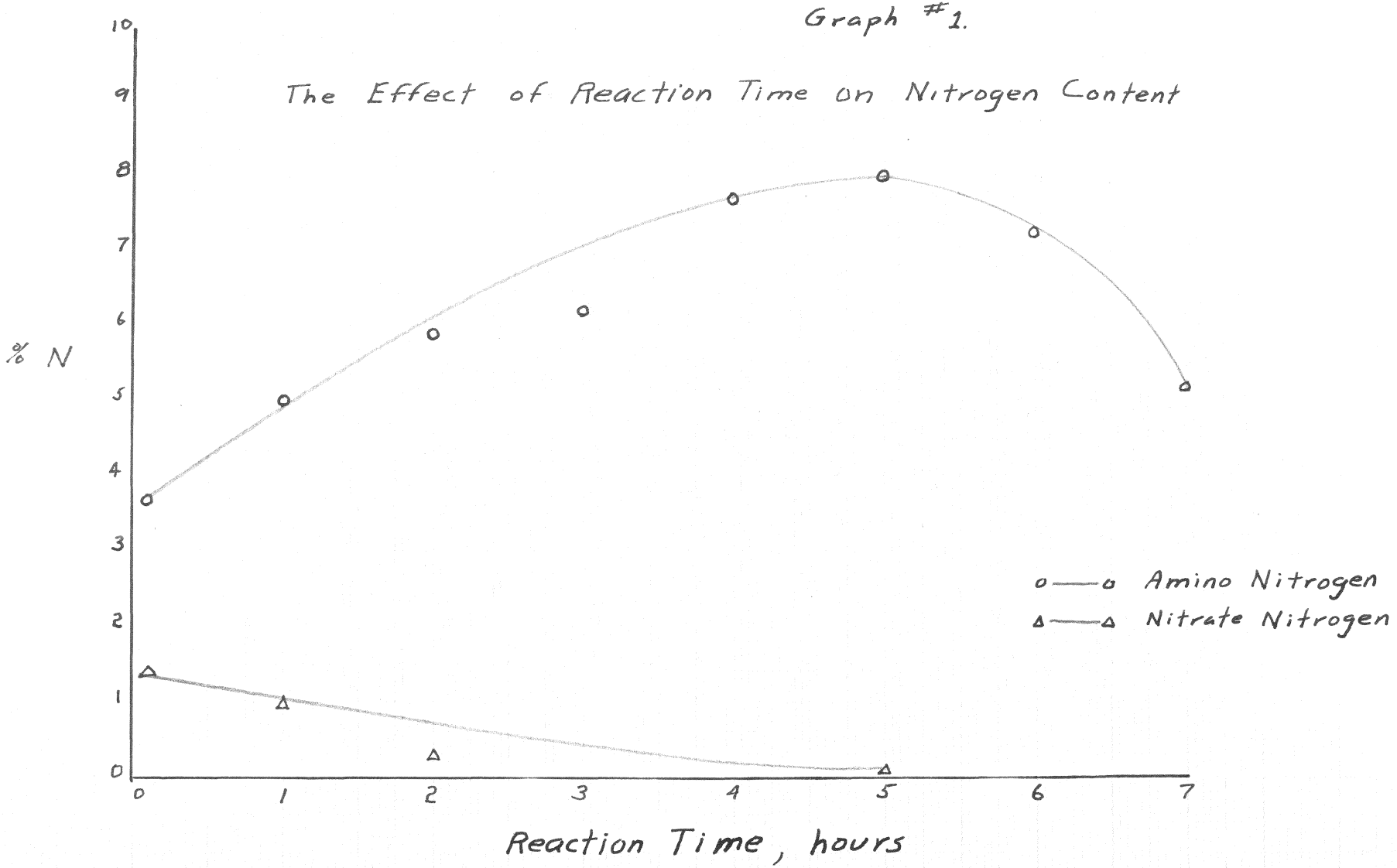
TABLE NO. 1

The Effect of Reaction Time on Nitrogen Content

Reaction time	%Amino nitrogen	%Total nitrogen
six minutes	3.7	5.11
one hour	5.0	6.06
two hours	5.9	6.25
three hours	6.2	____
four hours	7.7	____
five hours	8.0	7.9
six hours	7.25	____
seven hours	5.18	____

It will be observed that the maximum amino content was reached after around five hours reaction time. Beyond five hours the amino content began to drop rather sharply.

Graph #1.


The Effect of Reaction Time on Nitrogen Content
% N
10
9
8
7
6
5
4
3
2
1
0
0
1
2
3
4
5
6
7
Reaction Time, hours
Amino Nitrogen
Nitrate Nitrogen

Determination of the Acetylide Group.

The product produced from two grams of cellulose nitrate was then reacted with four grams of triphenyl tin iodide. In order to carry out this reaction in a satisfactory manner, it was first necessary to remove most of the inorganic sodium salts which were present and which would have reacted with the iodide themselves. It was observed that the product did not settle out in this case in the same manner as it did when washing by decantation was carried out in the qualitative experiment. This was attributed to the higher specific gravity of the ammonia solution in this case due to its higher salt concentration. More ammonia was added, and the product then settled to the bottom of the flask thus permitting decantation to be effected. The product was washed three times in this way, more ammonia was added, and then the triphenyl tin iodide was added to this solution. The solution was stirred for one half hour and was then poured into a pyrex beaker where it was allowed to evaporate to dryness in the open air. The sample was scraped from the beaker and extracted with ether for twelve hours in order to remove all of the unreacted triphenyl tin iodide. It was then washed with alcohol several times in order to remove any sodium iodide that was present. The material was dried in an oven at fifty degrees for three hours while in an open weighing bottle. A weighed portion was then placed in a porcelain evaporating dish, covered by a watch glass, and about ten milliliters of concentrated sulfuric acid added. Heat was applied

until the acid began to boil, and then two or three drops of concentrated nitric acid was added cautiously to aid in the decomposition of the organic matter and to oxidize the tin. This was continued until the solution of acid in the dish was clear. The dish was then taken to dryness. It was then transferred to a furnace at six hundred degrees Centigrade for about a half hour to complete the removal of the remaining acid and to insure the tin's being in the form of stannic oxide. The dish was removed from the furnace, cooled, and weighed.

This identical procedure was carried out on four samples with but one variation each time. The triphenyl tin iodide was added to the first sample after a total of forty five minutes reaction time, to the second after three hours reaction time, to the third after five and a quarter hours reaction time, and to the fourth after seven hours reaction time. The results obtained on analysis are listed below:

TABLE No. 2

Effect of Reaction Time on Tin Content of Product

Sample number	Reaction time	%Tin in sample
1	45 minutes	24.0
2	3 hours	23.9
3	5¼ hours	24.4
4	7 hours	22.6

It was observed that the tin content of this product remained constant throught, which indicated a fast replacement of nitrate groups by acetylide groups in the original reaction.

IV. DISCUSSION

It is significant that in the preparation of the reaction product that the addition of ammonium chloride is essential to a stable product upon evaporation of ammonia. Originally added to remove excess sodium acetylide, it was soon observed that the product itself seemed to dissolve when the ammonium salt entered the solution. This was explained by assuming the existance on each glucose unit of an acetylide grouping which contained a sodium atom. This compound was assumed to be ammonia insoluble whereas, when ammonium chloride was added, an ammonia soluble derivative was formed.

$$\text{Cell-C}\equiv\text{C-Na} + \text{NH}_4\text{Cl} \longrightarrow \text{Cell-C}\equiv\text{CH} + \text{NaCl}$$

This idea was substantiated by the observation that if ammonium chloride was not added the product was very hygroscopic, going into solution after several hours contact with the open air, whereas this property was not present if ammonium chloride was added. A possible explanation of the presence of this sodium derivative is as follows:

(1) $\text{Cell-ONO}_2 + \text{NaC}\equiv\text{CH} \rightarrow \text{Cell-C}\equiv\text{CH} + \text{NaNO}_3$

(2) $\text{Cell-C}\equiv\text{CH} + \text{NaC}\equiv\text{CH} \rightarrow \text{Cell-C}\equiv\text{CNa} + \text{C}_2\text{H}_2$

During the purification of the product obtained after reaction with ammonium chloride by washing with water, there was a slight solubility of material as evidenced by the brown color of the wash water. The color apparently was due to particles which were colloidal in size as shown by observation of the Tyndall effect.

This colloidal material could not be precipitated from solution by the use of alcohol. This seems to indicate the presence of a homologous series of compounds of varying solubilities.

In order to account for the presence of the amine group found in the product, formation of a small amount of sodium amide is hypothesized.

$$NaC{\equiv}CH + NH_3 \rightleftharpoons NaNH_2 + HC{\equiv}CH$$

This might react with the cellulose nitrate as follows,

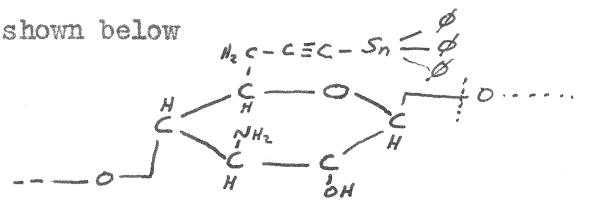
$$Cell\text{-}ONO_2 + NaNH_2 \longrightarrow Cell\text{-}NH_2 + NaNO_3$$

and once the amide is used up the reaction will proceed so as to form more, as is indicated in the first equation. In a reaction such as this, one would expect time to be a factor. This is shown to be the case in Graph #1. The decrease in amino nitrogen after five hours cannot be explained at this time.

The tin content of the derivative obtained from the reaction with triphenyl tin iodide is seemingly independent of time within the range investigated. It indicates that there is one acetylide grouping per glucose unit.

$$Cell\text{-}C{\equiv}CNa + I\text{-}Sn(\phi)_3 \longrightarrow Cell\text{-}C{\equiv}C\text{-}Sn(\phi)_3 + NaI$$

This is shown by calculations of the theoretical percentage of tin in the compound shown below



which has a molecular weight of 517 and contains 23% Sn by calculation.

Previous work by Dr. Philip C. Scherer[15] had shown that triphenyl tin iodide would not react with a trisodium cellulosate. This would indicate that the sodium atoms of this compound did not posess sufficient lability to permit reaction. The lability of the sodium atom in the -C≡CNa group is evidently sufficient to permit a metathetical reaction.

Future attempts to reduce cellulose might profitably follow the preparative procedure of this investigation including the addition of ammonium chloride after five hours of reaction. The product thus formed might be dissolved in dilute hydrochloric acid, diazotized, and then the diazo-group replaced by hydrogen as can be done in the production of aniline from its diazo derivative.

$$C_6H_5.N_2.OH + CH_3.CH_2.OH \rightarrow C_6H_6 + CH_3.CHO + H_2O + N_2$$

If this were possible, the remaining hydroxyl group in the cellulose molecule might be nitrated, aminated, diazotized and replaced by hydrogen in exactly the same way as the first one. In this way all three of the hydroxyl groups of the cellulose unit would have been replaced, two by hydrogen atoms and one by an acetylide grouping which would probably be converted to an ethyl group by the hydrogenation step illustrated above.

V. CONCLUSIONS

1. Both of the nitrate groups from a cellulose dinitrate have been replaced under optimum conditions. One nitrate group was replaced almost instantaneously by a metathetical reaction with sodium acetylide. Due to the equilibrium formation of $NaNH_2$, the second nitrate group is replaced more slowly by an amine group, maximum amino nitrogen being attained at five hours reaction time.

2. A sodium atom, presumed to be present on the acetylide grouping after it is attached to the cellulose molecule, must be removed by reaction with ammonium chloride in order to obtain a compound which is not hydrolyzed on exposure to the air.

3. The product is insoluble in most organic solvents, but is soluble in dilute and concentrated HCl, NaOH solutions, and 30% benzyltrimethyl ammonium hydroxide solution.

4. A possible method for the completion of the reduction of the cellulose molecule has been opened up in which two of the hydroxyl groups might be replaced by hydrogen atoms and the third by an acetylide grouping.

5. The mechanism of the reaction between cellulose nitrate and sodium acetylide up to the five hour reaction time has been satisfactorily accounted for. The mechanism beyond this point, however, is obscure.

VI. SUMMARY

A method for carrying out the reaction between cellulose nitrate was used in which the cellulose nitrate was dispersed in liquid ammonia in one flask, while in an adjacent flask sodium acetylide was being prepared by bubbling acetylene through a solution of sodium in liquid ammonia. The solution of sodium acetylide was forced over into the flask containing the cellulose nitrate and the stirrer started. After the reaction had proceded for a desired time, enough crystalline ammonium chloride was added to cause dissolution of all of the solid product in the flask. The ammonia solution was then poured into a beaker and allowed to evaporate to dryness.

Washing was accomplished by grinding the dried product to a powder and washing it in a filter funnel with distilled water. A product which had been reacted five hours and so washed was brown in color. It was soluble in dilute hydrochloric acid and in dilute sodium hydroxide solutions. It was insoluble in all organic solvents investigated with the exception of benzyltrimethyl ammonium hydroxide. It burned when a flame was applied to it, but it did so slowly.

Nitrogen determinations were made using the Kjeldahl procedure. This was modified in the total nitrogen determination by the use of salicylic acid in the original digestion of the product and subsequent reduction by 30 mesh zinc metal. The product after five hours reaction was found to contain approximately one amino group per

glucose unit. This was a maximum amino content which decreased sharply on further reaction time.

The presence of an amino group provided a ready explanation for the solubility of the product in dilute hydrochloric acid. A diazotization of the product and a coupling with B-napthol was then attempted which gave rise to an alcohol-soluble brown dye.

Presence of a -C≡CNa group was determined qualitatively by reaction with mercury and copper salts with triphenyl tin iodide. Quantitative reactions with the last compound indicated the presence of one acetylide group per glucose unit.

VII. BIBLIOGRAPHY

(1) Cady, H.P., J. Phys. Chem., 1, 707 (1897).

(2) Cottrell, F.G., J. Phys. Chem., 18, page 85-100, (1914).

(3) Feild, J.M., Master's Thesis, Virginia Polytechnic Institute, 1940.

(4) Fernelius, W.C. and Bowman, G.B., Chem. Reviews, Vol. 26, page 14, (1940).

(5) Fernelius, W.C. and Johnson, W.C., J. Chem. Education, 5, 828-35, (1928).

(6) Fieser, L.F. and Fieser, M., "Organic Chemistry", Heath Publishing Company, Boston, 1944, page 76.

(7) Franklin, E.C., "The Nitrogen System of Compounds", Reinhold Publishing Corporation, New York, 1935.

(8) Franklin, C.C. and Kraus, C.A., Am. Chem. J., 20, 820 (1898).

(9) Lebeau, P. and Picon, M., Compt. rend., 156, 1077 (1913).

(10) Meyer, K.H., and Mark, H., Ber., 61, 593 (1928).

(11) Moissan, H., Compt. rend., 126, 302-6 (1898).

(12) Moissan, H. ibid, 127, 911 (1898).

(13) Nieuwland, J.A., and Vogt, R.R., "The Chemistry of Acetylene", Reinhold Publishing Corporation, New York, 1945, ibid, page 44.

(14) Picon, M., Compt. rend., 169, 32 (1919).

(15) Scherer, P.C., private communication.

(16) Vaughn, T.H., Hennion, G.F., Vogt, R.R., and Nieuwland, J.A., The Journal of Organic Chemistry, Vol.2, No. 1., page 1; ibid., page 17; ibid., page 17, (1937).