

**A STUDY OF THE REACTION OF CELLULOSE NITRATE
WITH VARIOUS REDUCING AGENTS**

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**Thesis Submitted to the Faculty of the
Virginia Polytechnic Institute
in Candidacy for the Degree of**

DOCTOR OF PHILOSOPHY

in

CHEMISTRY

APPROVED:

Chairman/Advisory Committee

June, 1953

Blacksburg, Virginia

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III. INTRODUCTION

Cellulose, and products which depend upon their cellulosic content for the properties which make them useful, have been utilized by man since the beginning of civilization. However, for thousands of years very little scientific progress was made in the field of cellulose. Being the main constituent of the cell wall of higher plants, cellulose came from natural sources, and the only progress made was in the development and cultivation of such sources. Furthermore, the uses of cellulose utilized the physical properties of wood and fibers, and were not dependent on any knowledge of the fundamental chemistry and physics of cellulose.

The beginning of scientific research in cellulose chemistry is credited to Jean Baptiste Payen (140, 144) whose investigations, in the years 1837-1842, led him to the conclusion that the fibrous constituent of all plant cells was a carbohydrate composed of glucose anhydride units. He named this carbohydrate cellulose.

Cellulose isolated from different sources have the same percentage composition, and are therefore one and the same substance. The word "cellulose", however, does not always have the same connotation when used by different people. Viewed by the pulp and paper chemist,

cellulose denotes the residue obtained by subjecting wood to the action of certain chemicals. To the organic chemist, cellulose is a natural high polymer built up of glucose anhydride units. To the cellulose chemist, cellulose specifically applied to alpha-cellulose which is... "a polysaccharide of sufficient chain length to be insoluble in water or dilute acids and alkalies, consisting of glucose anhydride units linked through the 1 and 4 carbon atoms with a beta-glucosidal linkage and giving a typical X-ray diagram" (195). (See Figure 1.) But even to the cellulose chemist the name cellulose does not stand for a well defined homogeneous chemical compound. It serves rather to define a family of products which have certain features in common, but which differ primarily with respect to the size of the molecule. Therefore, only in a limited sense is it proper to speak of a product as "cellulose".

The unusual property that makes alpha-cellulose so useful is attributed to the linearity of the cellulose chain. The beta-linkage minimizes curling and spiraling, and permits the long chains to line up parallel to each other with a high degree of orientation. This results in a fibrous structure held together largely by secondary valence forces between the three hydroxyl

groups of the glucose unit. If the hydroxyl groups of cellulose could be reduced (replaced by hydrogen), the secondary valence forces between the chains would be almost entirely destroyed, and the resulting desoxy cellulose would be expected to show properties quite different from those of the original cellulose. The direct hydrogenation of cellulose has been attempted, but at present no method is known by which the process may be carried out without complete destruction of the starting material.

Another method of altering the secondary valence forces between the chains would be to replace the hydroxyl groups by alkyl radicals, so that the substituent group is attached directly to the carbon atoms of the glucose residue, and not to the oxygen atom as is the case with cellulose ethers and esters. To the author's knowledge no such derivatives have ever been prepared.

In view of the interesting changes that would result by the preparation of a reduced derivative of cellulose, and the theoretical aspects thereof, it was decided to study the problem. The direct reduction of cellulose is not feasible, so the investigation has been directed to the reduction of a cellulose derivative. Previous investigations in this laboratory have shown

the possibility of reducing, and in some cases removing, the nitrate group from cellulose nitrate. This factor together with the solubility characteristics of cellulose nitrate made this ester a logical choice.

Specifically, the aim of this investigation is:

(a). To attempt the preparation of an undegraded desoxy cellulose from cellulose nitrate.

(b). To attempt the preparation of an undegraded alkyl derivative of cellulose from cellulose nitrate.

(c). To study the properties of cellulose derivatives which, under suitable conditions, may be used to prepare the above mentioned compounds.

IV. HISTORICAL AND THEORETICAL DISCUSSION

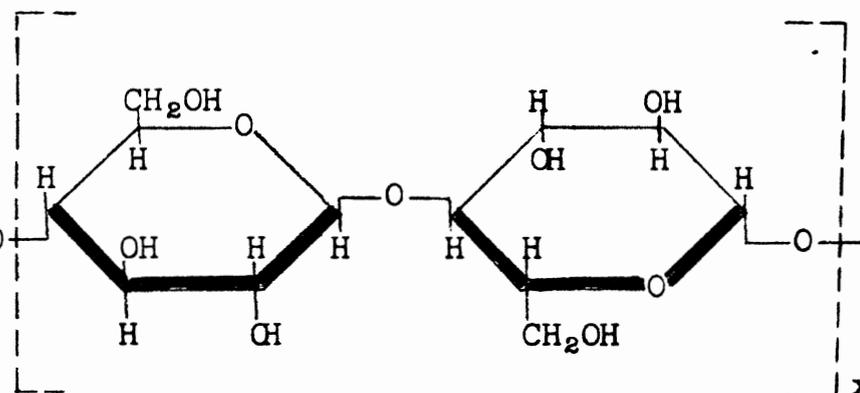
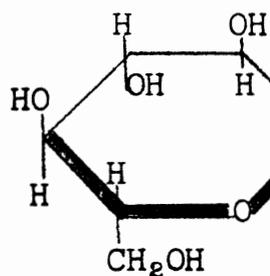
A. CELLULOSE

1. Chain Structure

Although cellulose ($C_6H_{10}O_5$) has been known as a chemical entity for over one hundred years, it is only within the last thirty years that investigators have been able to arrive at a structural formula which is in agreement with both its chemical and physical properties. According to present concepts (78) ... "cellulose is a polysaccharide composed of linear macromolecules (or, possibly, of long polymeric chains, occasionally cross-linked), each consisting of glucose anhydride units bonded together, through the 1 and 4 carbon atoms, with a beta-glucosidal linkage". The configuration of a portion of the cellulose macromolecule most widely accepted today is shown in Figure 1 (57).

Cellulose has a very high molecular weight. Since all evidence indicates that cellulose is predominantly linear, the molecular weight corresponds to the number of glucose anhydride units in the chain molecule multiplied by 162 - the formula weight of one glucose anhydride unit ($C_6H_{10}O_5$). The number of glucose anhydride units in the chain is termed the degree of polymerization. This, however, does not mean that cellulose

Nonreducing
End Group



Reducing
End Group

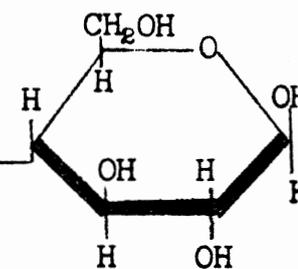


Figure 1.

Theoretical Configuration of the Cellulose
Molecule

$$D.P. = 2x + 2$$

From "The Chemistry of Large Molecules", edited by
R. E. Burk and O. Grummit. Interscience Publishers.
New York (1943). p. 250.

consists of identical molecules as do compounds of low molecular weight. The number of glucose anhydride units per chain molecule may vary over a wide range, and a given sample of cellulose (or one of its derivatives) may contain many chain molecules of different length. Therefore, the degree of polymerization merely represents the average number of glucose anhydride units in the chain molecule.

The configuration of the cellulose macromolecule has been established both by chemical and physical methods. The presence of a six carbon (glucopyranose) unit in the cellulose molecule has been confirmed by acid hydrolysis, which gives an almost quantitative yield of glucose (80). Esterification, etherification, and other chemical reactions confirm the presence of three alcoholic hydroxyl groups per C₆ unit (156). Exhaustive methylation of cellulose followed by acid hydrolysis yields 2,3,6-trimethylglucose, thus establishing the position of the three hydroxyl groups (81). If carbon-5 is involved in the ring structure, as is the case with glucose, then the glucopyranose units in the chain must be joined through carbons 1 and 4 (58). Optical rotation (106) of cellulose, X-ray data (116, 117), and studies on the kinetics of hydrolysis

and acetolysis (43) show the presence of the beta-glucosidic linkage but not the alpha.

The terminal glucose residues are distinguished from those in the body of the chain; one by the presence of a potential aldehyde (hemiacetal) group in the 1-position; the other by the presence of a fourth hydroxyl group in the 4-position. The presence of the fourth hydroxyl at the non-reducing end has been proven by the isolation of a small but definite quantity of 2,3,4,6-tetramethylglucose (59). The presence of the reducing type of group has never been conclusively demonstrated. Its presence depends to a large extent upon the prior treatment to which cellulose has been subjected. Measurement of the copper number, or the iodine number, of cellulose obtained by acid degradation of a product of higher molecular weight indicates a certain reducing action by the molecule (8). If the degradation is produced by hydrolytic cleavage of the glucosidic linkage, then the system will remain unchanged from the standpoint of the types of end groups. Thus, at each point of cleavage, one reducing and one non-reducing type of terminal units are formed. However, cleavage of the chain by other degradation processes may result in the formation of very different types of terminal groups.

Due to the difference in the nature of the terminal groups, the analysis of a cellulose sample will agree with the empirical formula within the accuracy of measurement, only if "x" in Figure 1 is large enough. The value of "x" is indefinite, but for a sample of

commercially useful cellulose it will have a value ranging from about 25 to about 2500 (178) or even higher (95).

2. Fiber Structure

Cellulose possesses a complex physical structure. X-ray analysis has conclusively shown that cellulose has a definite crystalline pattern, which is the same regardless of the source of the cellulose (65), and an amorphous pattern. The cellulose fiber, however, is not to be regarded as a single crystal; it is an aggregate consisting of small crystal areas (crystallites or micelles) separated by amorphous areas. In the micelles the individual long chain macromolecules exist in a highly ordered arrangement, strictly parallel to each other (116), and stabilized laterally by hydrogen bonds between opposing hydroxyl groups of individual chains (38).

Originally it was assumed that the length of the micelle was identical with the length of the chain molecule - approximately 600 Å (64). However, physicochemical measurements (177) indicate that cellulose contains chains which are considerably longer (10^4 Å and longer). With this concept firmly established, the micelles lost most of their individuality.

At present the long cellulose macromolecules are believed to grade continuously from the crystalline portion to the amorphous portion, with a mesomorphous

portion as the region of transition. The amorphous component represents the most disordered part of the fiber structure; the crystalline component the most ordered arrangement. In the process of formation of cellulose, the long chains crystallized in such a manner that the crystalline regularity is interrupted by warped or irregular regions which behave as amorphous material toward X-rays. If the chains are long enough they extend through the whole system; i.e., they pass through crystalline, mesomorphous, and amorphous regions (105).

Recent studies have estimated that the crystalline component is present to the extent of about 94%, the other 6% being equally divided between the amorphous and mesomorphous components (128).

3. Reactions of Cellulose

The chemistry of cellulose is adequately covered in a number of excellent reference books (70, 107, 134) and need not be repeated here. However, a few salient points on the reactivity of cellulose will be considered.

The chemical reactions which cellulose can undergo may be divided into two general classes: those involving the degradation of the cellulose chain, and those involving the hydroxyl group. Under the action of

acids, and certain oxidizing agents, the 1,4-glucosidic linkages of the chain molecule are hydrolyzed, and shorter chain molecules result. As a rule, these low molecular weight derivatives have very little - if any - industrial importance. The reactions involving the hydroxyl groups lead to the introduction of new groups into the cellulose chain, and to the formation of commercially useful derivatives. It is these reactions which are discussed in this section.

The cellulose macromolecule is, and reacts as, a polytrihydric alcohol. The hydroxyl groups react to form addition compounds with alkalies and certain complex salts, and with sodium metal to form cellulosates. Other typical reactions lead to the formation of organic and inorganic esters, and ethers.

(a). Substitution Possibilities

The three hydroxyl groups present in each glucose unit are not equivalent; the one in the 6-position being primary and those in the 2- and 3-positions being secondary. It is possible to substitute any one glucose unit in the cellulose chain in seven different ways: any one of the three hydroxyl groups (2-, 3-, and 6-positions); any one of a combination of the two hydroxyl groups at one time (2,3-, 2,6-, or 3,6-positions); all

three at one time. Therefore, it is theoretically possible under ideal conditions to prepare seven different derivatives of cellulose from the same reagent. Outside of the trisubstituted derivatives, and a few cases of monosubstituted derivatives (30, 75, 180), such ideal conditions are never realized.

It is very difficult, and from the technical viewpoint undesirable, to replace all three hydroxyls by a single substituent. In order to obtain a derivative with fewer than three substituents per glucose unit, having a simple integral ratio of substituents (one or two) there must be a predominating tendency for formation of a particular structure for each glucose unit. This condition is seldom fulfilled, and then only in the case where a specific reagent for a particular hydroxyl group has been found. The degree of substitution may have any value between zero and three, including fractional values. However, with any product in which the degree of substitution is less than three we must deal with averages. Specifically, the substituents in any cellulose derivative are distributed along the cellulose chains in a manner determined by the relative reactivities of the hydroxyl groups, the effect of reactivity due to substituents in neighboring positions, and the laws of chance (174). The number of possible

derivatives is astronomical; according to Spurlin (173)... "A chain of 100 glucose units having an average substitution of 1.5 glucose units could be arranged in some 10^{89} different manners".

(b). Reactivity and Availability of Hydroxyl Groups

In the preparation of any cellulose derivative uniform distribution of the substituent groups over all chain molecules would be expected if the reaction could be made to proceed in a homogeneous manner; that is, if the reaction were carried out in solution. Under such ideal conditions all the hydroxyl groups on every single chain molecule would be equally accessible to the reagent, and the predominating factor would then be the reactivity of the individual hydroxyl groups. It has recently been demonstrated (46) that in such a homogeneous media, the primary hydroxyl groups are more reactive than the two secondary groups together. According to Timmell (186) the rate constants are in the order $k_6 > k_2 > k_3$ for all homogeneous cellulose reactions.

There are very few solvents known for cellulose and most of its reactions take place in the solid state, usually in the natural fiber form. Under these heterogeneous conditions the most important factor appears to be the availability of the various hydroxyl groups and not their relative reactivity.

At the start of any given heterogeneous reaction any one of a number of hydroxyl groups has a good chance of reacting. On the assumption (173) that about half of the hydroxyl groups are exposed on the surface of the micelles, it is conceivable that these will react first. The reaction then comes to a standstill unless the reagent can penetrate the intramicellar spaces. The penetration of the reagent is dependent on its ability to diffuse into the micelle. If the rate of diffusion is slow, the reaction advances slowly from layer to layer of the micellar system, and is said to proceed topochemically. If the rate of diffusion is fast, the reaction proceeds almost simultaneously throughout all layers of the system. The latter are known as permutoid reactions (173).

With reference to the degree of substitution, the uniformity of the reaction product is dependent upon the mode of reaction. In permutoid reactions it is probable that all chains, and all glucose units on any one chain, are - on the average - substituted to the same extent. In topochemical reactions it is possible to have the chains on the surface of the micelles more completely substituted than those in the interior of the micelle. Furthermore, since that portion of the

chain in the amorphous region would be expected to react faster than the portion in the crystalline region, the degree of substitution may vary from one part of the chain to another.

B. CELLULOSE NITRATE

1. Preparation

Cellulose nitrate the only inorganic ester of cellulose which has attained commercial importance was discovered by Braconnot (15) in 1832. Schonbein (162) in 1845 was the first to prepare the ester on a commercial scale, and thus he is generally credited with its discovery.

The ester may be prepared by subjecting cellulose to the action of nitric acid in the presence of a dehydrating agent such as sulfuric acid. For each hydroxyl group which is esterified one mole of water is liberated. The reaction (assuming complete nitration) may be expressed by the following equation:



Recent investigations (90) have shown that the oxygen of the hydroxyl group is not eliminated in the reaction.

Theoretically, three "cellulose nitrates" may be obtained: the trinitrate (14.14% N), the dinitrate (11.11% N) and the mononitrate (6.76% N). With the exception of the trinitrate, however, the above products do not represent stoichiometric compounds, since no homogeneous reaction product composed of a single indivi-

dual cellulose mono- or dinitrate has knowingly been obtained. The nitrate groups are distributed along the entire length of the cellulose chain according to the laws of chance and the reactivity of the hydroxyl groups. Depending on the conditions of esterification, a cellulose nitrate of any desired nitrogen content may be obtained. The name cellulose nitrate, therefore, does not refer to a single stoichiometric compound, but it is a generic term denoting a family of compounds.

Commercially, the production of cellulose trinitrate is both unattainable and undesirable; the upper nitrogen limit being approximately 13.5-13.8%. Above this nitrogen content the ester becomes insoluble in commercially available solvents. A lower limit exists at about 10.5% nitrogen, since products below this nitrogen content are difficultly soluble and do not possess the desirable physical properties of higher nitrogen types (63).

Within the last thirty years two theories have been advanced to explain the manner in which the nitration reaction proceeds. According to the first of these theories, the reaction proceeds in a topochemical fashion, whereby the nitrating reagent diffuses progressively from the outside to the interior of the

fiber, so that the chains on the surface are nitrated first. According to the second theory, the nitrating reagent penetrates uniformly in all parts of the cellulose fiber, and the reaction proceeds quickly throughout the whole micellar system in a permutoidal fashion.

Herzog (66), on the basis of X-ray studies of the structure of cellulose nitrate found evidence to support the topochemical theory of nitration, and claimed that all cellulose nitrates (below the trinitrate) were made up of cellulose trinitrate and unchanged cellulose. This theory has been supported by a number of other investigators (69, 152, 189). Recent developments, however, have shown that the use of X-ray diagrams as a means of elucidating the course of the reaction can be applied only to a limited extent. The X-ray pattern of cellulose nitrate changes at a nitrogen content of about 7.5 per cent from a crystalline to an amorphous pattern. Only when a nitrogen content of about 12.5 per cent is reached does the pattern become crystalline again and approach that of a trinitrate (171). The evidence from X-ray examination may be interpreted as indicating that the lower stages of nitration are mixtures of various degrees of nitration, and not of cellulose trinitrate and cellulose (110). Miles and Craik (119) on the basis of X-ray evidence theorize that in the preparation of

cellulose nitrate of less than 12.5 per cent nitrogen the reaction is topochemical, whereas above this nitrogen content the reaction is permutoidal.

A considerable number of investigations have been published to support the permutoid theory of cellulose nitration. According to Berl and Hefter (10) an equilibrium exists between the nitrating medium and the cellulose nitrate over a wide range of substitution, the equilibrium value being determined by the composition of the nitrating solution. Fiber structure has no effect on the product of reaction (120). The nitrating reagent penetrates uniformly in all parts of the fiber and the cellulose chains are nitrated at approximately the same time. Thus, the nitrate groups become rather uniformly distributed along the chains and there is little likelihood of any one chain being completely nitrated before the rest (118).

Opposition to the topochemical theory has also resulted from the failure to separate the substituted chains from the unsubstituted chains by extraction with solvents; nor has it been possible to separate an incompletely substituted nitrate into mono-, di-, and tri-nitrates by fractionation (71, 72).

An attempt has been made to determine the distribution of the nitrate groups in the individual glucose

units by replacing the primary nitrate groups with iodine through the medium of sodium iodide. The results obtained indicated that at least one half of the nitrate groups in the low substituted nitrates (2.5 - 9%N) were in the primary position (126). This method proved to be unsatisfactory for highly nitrated compounds because of oxidative side reactions.

Cellulose nitrate is often referred to as nitrocellulose. This term is not correct since cellulose nitrate is an ester of the type RONO_2 and not a true nitro compound of the type RNO_2 (25). The term nitrocellulose although widely used is not recommended by the Commission on Macromolecules of the International Union of Pure and Applied Chemistry (78).

2. Chemical Reactions

Cellulose nitrate undergoes very few chemical reactions, and the majority of these lead to the formation of products in which the cellulose chain is highly degraded. The chemistry of these reactions is complicated by the presence in cellulose nitrate of a number of reactive groups, namely: the nitrate group; the carboxyl and sulfate groups resulting from the esterification process; the unesterified hydroxyl group from the original cellulose. In any given reaction the re-

activity of all the above mentioned groups must be considered. At present in many reactions there is no evidence to show conclusively which of them have entered into the reaction. Furthermore, cellulose nitrate is an ester, and the inherent chemical properties of the ester linkage itself must be considered in elucidating the course of any reaction.

(a). Saponification

Since cellulose nitrate is an ester it may be readily saponified. However, saponification with alkali is unsuitable because the reaction is accompanied by extreme degradation of the cellulose chain (31). The saponification process is extremely complicated and involves a number of competitive side reactions. The nitrate group is reduced to the nitrite, and the oxygen from the nitrate group oxidizes the cellulose chain. Among the products of decomposition which have been reported are organic acids, aldehydes, ketones, and other organic compounds (6), nitrites, ammonia, elementary nitrogen, and complex nitrogenous compounds (88).

Hydrolysis may also be effected by the use of mineral acids, but the reaction is much slower than when alkalies are used (40). Strong sulfuric acid, for example, will convert the nitrate group into nitric acid,

but the chain is so completely degraded that it cannot be regenerated. Saponification of cellulose nitrate also occurs on treatment of the ester with a more dilute mixed acid than was used in preparing the cellulose nitrate (10).

(b). Denitration

Denitration is a special case of saponification and is limited to those reactions in which the process is carried out in such a fashion whereby the cellulose is regenerated with the least amount of degradation. The denitrated fibers, however, still contain from one to two per cent nitrogen. The process was formerly carried out commercially for denitrating cellulose rayon.

A varied number of denitrating agents have been used. Some of the earliest denitrating agents for cellulose nitrate rayon were acid solutions of metallic salts which are in the lowest state of oxidation and which are capable of passing into a higher state of oxidation. Suitable salts found were (200) cuprous chloride, cuprous oxychloride, ferrous, manganous, chromous, antimonous, stannous, mercurous, and cobaltous salts. Other denitrating agents which have been employed are ammonium nitrate, ferrous chloride, formaldehyde and thiocarbonates (200). However, best results

are obtained with mild reducing agents such as alkali sulfides and polysulfides, and thiocarbonates, but more particularly alcoholic solutions of alkali and ammonium hydrosulfides (145, 188).

The inorganic reactions involved in the process of denitration may be adequately expressed by the following equations:



Contrary to earlier theories it has been shown that denitration, even under the mildest conditions, is accompanied by a hydrolytic attack on the cellulose (32).

(c). Solvation

The solubility of cellulose nitrate in organic solvents is attributed to the formation of molecular addition compounds between the cellulose nitrate and the solvent. The polymer is converted into essentially a new derivative, and on dispersion, the solubility corresponds to the properties of the solvated chain and not to the cellulose nitrate (110, 133, 175). Berl and Koerber (11) have shown that samples of cellulose nitrate which are insoluble in certain solvents at room temperature, may become soluble - in these same sol-

vents - at lower temperatures. They explain this phenomenon by the formation of molecular addition compounds which dissociate at elevated temperatures, but which are stable at lower temperatures. The dispersion of cellulose nitrate in mixed solvents has also been attributed to the formation of molecular compounds (11). Trogus and co-workers (192) state that for mixed solvents one component may form the addition compound which then dissolves in the other component.

Numerous investigations have been published to support the theory that the absorption of solvent by cellulose nitrate leads to the formation of a molecular addition compound (28, 68, 87, 189, 191, 192). However, there is little agreement as to the number of solvent molecules fixed by the cellulose nitrate chain (111, 141, 189), and on this basis there are several investigators who believe that there is no evidence to support the formation of a definite stoichiometric compound (36, 87, 111). Campbell and Johnson (22) have recently reviewed the literature of compound formation between cellulose nitrate and acetone and they are of the opinion that..."although solvent-polymer interaction is by no means negligible, it cannot be considered permanent". They conclude as follows:

"It seems likely that some of the difficulties arise from a certain looseness

in using the term 'compound' to describe the product of interaction between cellulose nitrate and acetone. In the strict sense of the term, a compound must not only contain its constituents in stoichiometric proportions, but must also possess considerable stability. This involves the existence of an energy of activation for the dissociation which is greater than the thermal energy involved in intermolecular collision. In the absence of information of this type, it is scarcely justifiable to speak of compounds of cellulose nitrate and acetone."

Little attention has been paid to the method by which the solvent is absorbed by the cellulose nitrate; the few theories which have been developed, are for the most part, contradictory. Blaker and Badger (12) attribute the absorption to the polar nature of the cellulose nitrate molecule, but they fail to distinguish between the effect of the hydroxyl and the nitrate groups. Calvet (20) states that acetone absorbed by cellulose nitrate is not fixed by the nitrate groups. Sihtola and Svedberg (170) believe that the hydroxyl groups do not take part in the solvation, while Soler (172) attributes solvation to the action of the unesterified hydroxyl groups. Chedin and Vandoni (26) attribute the solution of cellulose nitrate in ketonic solvents to the reaction between the basic oxygen of the ketone and the acid component of the cellulose nitrate. This acidity is not due to the nitrate group, but to the

presence of at least one hydrogen atom attached to the carbon atom bearing the nitrate radical, a hydrogen that is rendered acidic to some extent.

(d). Coagulation

Solutions of cellulose nitrate in organic solvents may be coagulated by the addition of suitable inorganic compounds. Aparé (3) observed that the addition of finely divided lead oxide, calcium oxide or calcium hydroxide to a dilute solution of cellulose nitrate caused first an increase in viscosity and then gelation. However, oxides or hydroxides of copper, mercury, bismuth, aluminum, iron, zinc, cesium and barium merely caused an increase in viscosity. Similar results have been reported by Morozov (123). Other oxides which have been found to act as coagulants are cuprous oxide (136), antimony oxide and titanium oxide (193).

Zinc sulfate, magnesium chloride and aluminum chloride are among the few salts which have been reported as being coagulants for cellulose nitrate (138). Barsha (5) states that calcium carbonate brings about gelation, but this has not been verified by Campbell and Johnson (21) who found that it caused only an increase in viscosity. These investigators (21) also reported sodium acetate, sodium chloride, potassium chloride and calcium stearate to be without coagulating

effect. Copper powder and copper salts appear to be highly effective gelling agents and have been investigated by a number of people (21, 123, 136). Similar results have been reported for borax (21) and boric acid (123).

Although several investigations have been published to show that gelation of cellulose nitrate involves only a physical change (136, 137), a considerable amount of evidence has been presented to support a chemical change (5, 21, 83, 123, 193). According to present concepts, gelation is attributed to the formation of some type of cross linking between originally quite separate cellulose nitrate chains and the gelling agent, leading to the formation of a molecular complex which may be represented as follows:

Cell-nitrate - coagulant - Cell-nitrate

The long chain molecules become joined at points along the entire length of the chain giving rise to a more or less continuous but irregular network throughout the body of the solution which thereupon take the characteristic properties of a gel. The formation of the complex, does not involve primary valences; it is due apparently to secondary valence forces or coordinating linkages.

There is little agreement, however, as to which of the active groups on cellulose nitrate are responsible for the formation of the complex. In studying the effect

of titanium chloride on the gelation of cellulose nitrate solutions, Jullander and Blom-Sollin (83) concluded that gelation is brought about by cross linking between un-esterified hydroxyl groups of adjacent cellulose chains. Since the rate of gelation has been found to increase with an increase in nitrogen content (5) this concept seems untenable.

Gloor and Spurlin (123) found that when small amounts of both bronzing powder and copper salts (cuprous or cupric) are added to cellulose nitrate solutions in acetone, a clear solid gel of deep emerald green color is obtained. They attribute this gelation to a reaction between the copper ion in some form and the nitrate group.

Campbell and Johnson (21) and de Waele (193) attribute gelation as being caused not by the hydroxyl or nitrate groups, but by the carboxyl groups introduced during the nitration, or possibly, to the sulfate groups arising from the sulfuric acid in the nitrating mixture. On this basis the cross linking action of a divalent metallic salt is believed to form a bridge of the type:



involving either ionic or covalent bonds.

The above theory is not applicable to monovalent ions, and the authors (21) speculate on the possibility

of some type of electrostatic binding arising from the association of monovalent cations and two neighboring dissociated carboxyl groups, leading to a bridge of the type:



The gelation of cellulose nitrate is a complicated process which at present is not completely understood, and perhaps, under the experimental conditions involved, one or more of the above theories may be applicable (142). Furthermore, no attempts have been made to correlate gelation with the solvating action of the solvent, and thus the possibility remains that the solvent may play a more important role than has hitherto been suspected.

(e). Miscellaneous Reactions

The reactions of cellulose nitrate leading to the formation of amino derivatives and halogenated derivatives are discussed in the next section.

C. REDUCED DERIVATIVES OF CELLULOSE

The principle reactions of cellulose involving the hydroxyl group lead to the formation of derivatives, such as esters and ethers, in which the substituent group is attached to the glucose residue through an oxygen linkage. A number of specific reactions, however, lead to the formation of products in which the substituent group is attached directly to one of the carbon atoms of the glucose residue. Henceforth, such derivatives, irrespective of the substituent group, will be called "reduced derivatives of cellulose".

1. Cellulose Amine

The introduction of basic nitrogen into the cellulose molecule has been the aim of cellulose chemists for a number of years. It was believed that such products would have some of the dyeing properties of natural silk, and thus have considerable commercial value. The importance of this field is emphasized by the fact that to-date over one thousand patents have been issued describing the preparation of nitrogenous derivatives of cellulose. For further information on this subject, the reader is referred to the reviews of Marsh and Wood (108) and Gardner (45).

When dealing with amino derivatives of cellulose it is necessary to distinguish two types of compounds. The first type contains the amino nitrogen attached to an ester or ether linkage and may be represented by the general formula Cell-O-R-NH_2 , where R is either aliphatic or aromatic; the second type contains the amino nitrogen attached directly to the glucose residue and may be represented by the general formula Cell-NH_2 , or Cell-NR_2 . It is this second group of compounds which will be discussed in this section.

Cellulose amine should not be confused with ammonia-cellulose, a labile addition compound formed by the action of liquid ammonia on cellulose (4). Ammonia-cellulose has a different X-ray pattern than normal cellulose, and exhibits greater reactivity. When heated to 105°C for several hours it loses all its ammonia, and the X-ray pattern of the fiber gradually reverts to that of normal cellulose.

(a). Use of p-Toluenesulfonyl Chloride

Karrer and Wehrli (85, 86) in 1926 were apparently the first to prepare a compound which might be called a cellulose amine. They esterified fibrous cellulose with p-toluenesulfonyl chloride (tosyl chloride) in the presence of sodium hydroxide or pyridine at room

temperature to obtain a tosyl cellulose of low tosyl content. The ester was then treated with a concentrated aqueous solution of ammonia, and a reaction ensued by which the tosyl groups on carbon-6 were metathetically replaced by an amino group. The resulting product had approximately 0.8 per cent amino nitrogen, corresponding to about one amino group to every nine to eleven glucose residues. Somewhat similar results were obtained by Sakurada (151) who heated the tosyl ester with saturated ethyl alcoholic ammonia in a sealed tube at 150°C and obtained a degraded product whose nitrogen content indicated the presence of one amino group per two glucose units. The reactions may be represented by the following equations:



The cellulose amines prepared by the above method never contain more than 2 per cent nitrogen, and investigators have questioned whether the amine content of the final product is actually due to an exchange of tosyl groups with ammonia. Indeed, Hess and Ljubitsch (67) believe that the action of ammonia consists chiefly of partial saponification of the tosyl groups, and that the

small amount of ammonia left in the fiber is due to a combination of the ammonia with the chlorine, rather than to a substitution of the tosyl group.

Wolf from and associates (198) treated mesylated cellulose (Cell-O-SO₂CH₃) with concentrated aqueous ammonia and obtained a product containing up to four per cent amino nitrogen. They attribute the amino nitrogen to the presence of ammonia combined with the mesyl group, and not to a metathetic replacement of the mesyl group by ammonia.

(b). Use of Liquid Ammonia

As shown in Table I, the solubility of cellulose nitrate in liquid ammonia appears to be dependent upon the nitrogen content and viscosity of the ester, and the temperature of the ammonia (181, 183). To some extent, the degree of polymerization of the ester is important (153), but this factor has not been investigated. It appears (183) that a chemical reaction occurs between cellulose nitrate and liquid ammonia, but so far as the author knows, no evidence has been presented to substantiate this fact, and no reaction products have been isolated.

Sodium Amide. Recently a cellulose amine has been prepared by the action of sodium amide on cellulose dinitrate dispersed in liquid ammonia (41, 49, 94).

TABLE I

DISPERSION OF CELLULOSE NITRATE
IN LIQUID AMMONIA

<u>Percentage Nitrogen</u>	<u>Viscosity in sec.</u>	<u>Behavior at bp NH₃</u>	<u>Behavior at Room Temp.</u>
12.84	---	Considerable	Complete Dispersion
12	17	Considerable	Complete Dispersion
12	3-20	Considerable	Complete Dispersion
11.44	3-20	Complete	Complete Dispersion
11.64	43	Considerable	Complete Dispersion
11.10	58	Considerable	Complete Dispersion
Unknown	18	Considerable	Complete Dispersion
Unknown	70	Considerable	Complete Dispersion
Unknown	4-20	Considerable	Complete Dispersion

Adapted from: Taft, R.: J. Phys. Chem., 34, 2792-2800 (1930)

The amination was carried out by reacting a suspension of sodium amide in liquid ammonia with cellulose nitrate for a period of from six to nine hours. The cellulose amine, being insoluble in liquid ammonia settled to the bottom; the supernatant liquid was removed and the product washed several times with liquid ammonia. Attempts to purify the amine proved unsuccessful, as it was found impossible to remove all the inorganic impurities by extraction with solvents without simultaneously decreasing the amino nitrogen content of the product.

The cellulose amine prepared by the above method was reddish-brown in color. It was so soluble in water that once dissolved it could not be precipitated by the addition of non-solvent. The amine was also soluble in alkalies and dilute and concentrated mineral acids, but insoluble in ether, acetone, simple alcohols and other common organic solvents. The product gave a negative test for nitrites, nitrates, and the hydroxylamine group, but a positive Schotten-Bauman test for amines (149).

Analysis of the reaction products showed an amino nitrogen content ranging from 8.1 to 8.4 per cent, indicating the presence of only one amino group per glucose residue (theoretical for a monoamine is 8.6%). Since the original nitrate was a dinitrate, this indicated that only one-half of the nitrate originally present re-

acted to form the amino group. The other half of the nitrate was metathetically replaced by the hydroxyl group.

The exact reactions involved in the formation of cellulose amine are not known, but the following mechanism has been suggested (154). It is possible that two reactions take place, one reaction being a metathetic removal of the nitrate group from the cellulose nitrate by sodium amide; the other being ammonolysis of the remaining nitrate group by the solvent. If both reactions occur to nearly equal extent the resulting product should be a monoamine of cellulose. The reactions involved might be formulated thus:



The upper reaction appears to be favored by an excess of cellulose nitrate, while the lower reaction appears to be favored by an excess of sodium amide (49).

Assuming that all the nitrate groups of cellulose amine are equally available for reaction, it may be argued - on the basis of the reactivity of the hydroxyl groups in cellulose (186) - that the nitrate group on carbon-6 is more reactive, and therefore, it is the one which is ammonolyzed. The other nitrate groups on

position-2 and -3 are more stable to ammonolysis and are metathetically replaced by the amino group. The resulting cellulose amine would then have the amino group attached on a carbon atom of the pyranose ring.

Cellulose amine possesses the remarkable property of being diazotized and coupled in a manner analogous to the aromatic amines (155). The dyes thus formed are stable to reduction. Such stable diazo derivatives would not be expected if the amino group were on carbon-6 because this would have a purely aliphatic nature. However, on carbon-2 and -3, the amino group would be attached to the pyranose ring which apparently can confer stability to the diazonium salt.

Other Amides. Cellulose amine may also be prepared by treating cellulose nitrate with potassium amide. The reaction is very fast and the product, containing about 7.5 per cent amino nitrogen, is extremely difficult to separate. An acetyl derivative of the amine has been prepared by treating an aqueous solution of cellulose amine (prepared from KNH_2) with acetyl chloride (113).

In a patent issued in 1950, Wagner and Axe (194) claim that lithium, cesium and rubidium amides react with cellulose nitrate in liquid ammonia to form a cellulose amine. To the author's knowledge this information has not been supported by other publications.

Metallic Sodium. A monoamino derivative of cellulose may conveniently be prepared by the action of metallic sodium on cellulose nitrate dispersed in liquid ammonia (41, 94). Under favorable conditions the properties of the product so obtained correspond to those of cellulose amine prepared by the use of sodium amide. The reaction is obscure, and at present no satisfactory mechanism can be offered.

Cellulose Trinitrate. An attempt has been made (94) to react cellulose trinitrate (13.44% N, 2.73 nitrate groups) with sodium or potassium amide in liquid ammonia. The products obtained were extremely unstable, and on exposure to air spontaneously ignited.

(c). Use of Gaseous Ammonia

For some time it has been known that ammonia - either in the gaseous state or in solution - has a marked effect on the physical properties of cellulose nitrate solutions. The most noticeable effect is a change in viscosity of the solution, and while the idea has been advanced that a compound is formed by the reaction between cellulose nitrate and ammonia, it is only within recent years that any serious attempt has been made to isolate and identify the compound.

Ammoniacal Solutions. The study of the effect of ammonia on cellulose nitrate was apparently initiated by

Barsukov (7) who in 1933 investigated the addition of ammoniacal alcohol to acetone solutions of cellulose nitrate. He found that the viscosity of the solution increased at the beginning and then decreased to a certain minimum, depending on the amount of ammonia and the temperature. Similar results in the change in viscosity have been obtained using ammoniacal ether-alcohol as the solvent (50). Gol'dman (48) found that even though the viscosity of an ammoniacal alcohol-acetone solution of cellulose nitrate decreased on ageing, the mechanical properties of films prepared from such solutions were not impaired. In fact, he even noticed an increase in the elasticity of the films.

Aqueous ammonia appears to have a similar effect on the viscosity of cellulose nitrate solutions. Pascal and Grevy (139) added a two per cent solution of ammonia to a solution of cellulose nitrate in 65-35 ether-alcohol and reported a large viscosity increase followed by a decrease.

Kargin (84) has explained the change in viscosity as follows: "Nitric acid is strongly adsorbed by cellulose nitrate, and the conductivity of cellulose nitrate solutions is due to the presence of nitric acid and other inorganic electrolytes. On adding ammonia to the solu-

tion, the viscosity passes through a maximum to a point corresponding to the exact neutralization of the acids present".

Previous treatment of fibrous cellulose nitrate with aqueous ammonia decreases the viscosity of its acetone solutions (7, 122, 124, 125). The concentration of ammonia does not appear to be critical since reduction of viscosity has been obtained with solutions containing as little as 0.002 per cent ammonia, although the usual experimental range has been between 0.2 and 2 per cent ammonia.

Recently Reeves and Giddens (139, 147) have shown that unstable cellulose nitrate may be stabilized by boiling with dilute solutions of aqueous ammonia. Their investigations show that it is the undissociated NH_4OH and not the NH_4^+ ion which brings about stabilization. Stability is achieved by neutralization of the residual sulfuric acid present in the fiber. The concentration of ammonia is not critical, for approximately equal stability was given by 0.02, 0.05, and 1.0 per cent solutions.

Gaseous Ammonia. The action of gaseous ammonia on dry cellulose nitrate has not been investigated to any great extent. Reeves and Giddens (146) placed unstable cellulose nitrate (12.6% N) in a stoppered flask in an atmosphere of dry ammonia gas and examined the product at

various intervals. At the end of four hours the sample showed a slight yellowing, and at the end of forty eight hours the sample was dark, and according to the authors, "obviously degraded".

Scott (163) passed gaseous ammonia over dry cellulose nitrate (11.9% N) at room temperature and observed no visible change after ten minutes of gas flow. When the reaction vessel was heated with steam, the cellulose nitrate began to turn yellow immediately after the introduction of the ammonia, and a few minutes later the reaction vessel was blown to pieces by a violent explosion. He attributed the explosion to a reaction between the cellulose nitrate and the ammonia with the subsequent formation of unstable ammonium salts. It is unlikely that cellulose nitrate itself would explode after such a short exposure to a relatively low temperature.

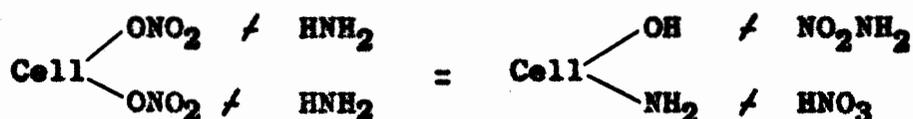
Compound Formation. Charnitskaya and co-workers (27) were probably the first to suggest that a reaction occurred between cellulose nitrate and ammonia yielding colored products. They postulated that the reaction occurred at the nitrate groups of the cellulose nitrate, with a subsequent destruction of the ester. They found that the reaction would proceed in the absence of water or oxygen, but that it required a temperature of about 60-65°C. Earlier Gol'dman (48) had noted that alcohol-

acetone solutions of cellulose nitrate turned slightly yellow on addition of ammonia. He attributed this color change to the presence of "resinous admixtures" in the acetone, and claimed that the presence of ammonia intensified the process of resinification.

Experiments carried out in this Laboratory (121, 127, 163) have shown that a reaction occurs between gaseous ammonia and cellulose nitrate dispersed in an organic solvent. The reaction product has been shown to contain up to one amino group per glucose residue, which is presumably attached to a carbon atom of the glucose residue.

The reaction is easily carried out, but the experimental conditions have not been standardized. In general, the procedure consists in passing gaseous ammonia through a dispersion of cellulose nitrate, and allowing the solution to stand for a certain length of time. The cellulose amine is then precipitated by the addition of an appropriate non-solvent.

No data has been presented to show the course of the reaction, but the following generalized scheme may be used:



The above equations are purely speculative, as no evidence has been presented to show that the nitrate and nitramide

groups are present in the reaction mixture. That an amino group is present in the reaction product has been shown by chemical analysis for amino nitrogen. Furthermore, the product gives a positive Hinsberg test for primary amines and under suitable conditions will form a diazonium salt. Unfortunately, however, the Hinsberg test when carried out on such a complex substance as cellulose amine could be questioned, and one observer (163) has failed to obtain a diazonium salt with the cellulose amine which he prepared. The absence of the hydroxylamine group has been proven experimentally.

The cellulose amine prepared by the use of gaseous ammonia differs from the product prepared by the use of liquid ammonia in two important aspects, namely:

(1). The amine prepared by the use of gaseous ammonia always contains some nitrate (or nitrite) nitrogen. This can probably be attributed to incomplete reaction.

(2). The amine prepared by the use of gaseous ammonia is insoluble in water. This can probably be attributed to the presence of non-amino nitrogen, or, more probably, to a smaller degree of degradation.

The accompanying table (Table II) summarizes in tabular form the work which has been done. An inspection

TABLE II

PREPARATION OF CELLULOSE AMINE IN VARIOUS SOLVENTS

No. ³	Solvent	Concentration	Time NH ₃ ¹ Treatment	Total Time Before Ppt.	Precipitant	%N in Product ²		No. of Groups in Product		
						NH ₂	ONO ₂	NH ₂	ONO ₂	OH
1	ethyl acetate	5g./100 ml.	1 hour	-----	water	6.08	3.82	0.80	0.50	1.70
2	ethyl acetate	2.5g./100 ml.	saturate	4 days	chloroform	9.37	3.25	1.20	0.42	1.38
2a	Gum from No. 2 dried at 110°C.						11.7	----		
2b	Gum from No. 2 dissolved in acetone and precipitated with H ₂ O; then dissolved in HC ₂ H ₃ O ₂ and ppt. with H ₂ O.						6.04	----		
3	ethyl acetate	-----	1 hour	1 hour	water	5.94	4.36	0.80	0.58	1.62
4	ethyl acetate	-----	1 hour	1 hour	chloroform	7.64	3.00	0.97	0.39	1.64
5	ethyl acetate	8g./500 ml.	saturate	5 days	chloroform	9.11	0.82	1.08	0.10	1.82
6	Chloroform product from No. 5.				dissolve in acetone, ppt. with heptane	9.02	1.26	1.08	0.15	1.76
6a	Gum from No. 6 dissolved in glacial acetic acid, precipitated with water.						5.93	----		
6b	Gum from No. 6 dissolved in glacial acetic acid, and solvent evaporated.						4.17	----		
7	Chloroform product from No. 5.				dissolve in acetone, ppt. with water	6.83	1.31	0.82	0.16	2.02
8	ethyl acetate	10g./600 ml.	saturate	4 days	chloroform	7.94	----			
8a	Part of solution from No. 8.				n-heptane	8.74	----			
9	ethyl acetate	10g./600 ml.	saturate	12 days	n-heptane	9.41	----			
9a	Gum from No. 9 dissolved in acetic acid, precipitated with water.						7.06	----		
9b	Gum from No. 9 treated with 95% alcohol and water.						7.95	----		
10	acetamide	-----	15 min.	-----	water	4.3	5.8	0.61	0.82	1.51
10a	Part of solution from No. 10				chloroform	6.23	4.50	0.84	0.61	1.55
11	n-butyl acetate	5g./200 ml.	2 hours	2 hours	add acetone, ppt. with H ₂ O	6.41	3.19	0.82	0.41	1.77
12	n-butyl acetate	5g./200	6 hours	6 hours	add acetone, ppt. with H ₂ O	6.46	3.04	0.83	0.39	1.78
13	n-butyl acetate	5g./200 ml.	2 hours	2 hours	add acetone, ppt. with H ₂ O	8.09	1.02	0.96	0.12	1.92
14	n-butyl acetate	5g./200 ml.	4 hours	4 hours	add acetone, ppt. with H ₂ O	6.92	1.82	0.85	0.22	1.93
15	n-butyl acetate	5g./200 ml.	1½ hours	1½ hours	add acetone, ppt. with H ₂ O	6.70	2.26	0.83	0.28	1.89
16	4:1 acetone toluene	4g./200 ml.	20 min.	8 hours	heptane, dis. in acetone, ppt with H ₂ O	12.1	6.63	1.76	0.96	0.28
17	3:2 acetone toluene	4g./200 ml.	20 min.	8 hours	heptane, dis. in acetone, ppt. with H ₂ O	8.30	7.56	1.26	1.15	0.59
18	2:3 acetone toluene	4g./200 ml.	20 min.	8 hours	heptane, dis. in acetone, ppt. with H ₂ O	4.97	9.72	0.83	1.63	0.54
19	acetone	4g./200 ml.	20 min.	8 hours	heptane, dis. in acetone ppt. with H ₂ O	5.40	9.53	0.90	1.58	0.52
20	acetone	4g./200 ml.	15 min.	12 hours	water	5.39	2.36	0.67	0.29	2.04
21	acetone	5g./200 ml.	saturate	24 hours	n-heptane	9.89	0.55	1.16	0.06	1.78
21a	Gum from No. 21 treated with water						8.19	----		

1. Composition of cellulose nitrate: (a). Experiments 1, 11, 15: 11.90% N, 2.23 ONO₂ groups.
 (b). Experiments 2, 10, 21: 12.10% N, 2.29 ONO₂ groups.
 (c). Experiments 16, 19: 13.38% N, 2.72 ONO₂ groups.
 (d). Experiment 20: unknown.

2. Temperature of Reaction: All reactions carried out at room temperature except:
 (a). No. 10; 81°C.
 (b). No. 13, 14; 75°C.
 (c). No. 15; 95°C.

3. Reference: (a). No. 1, 11-15; Ref No. 163.
 (b). No. 2-9, 21; Ref No. 121.
 (c). No. 16-19; Ref 19.
 (d). No. 20; 127.

of the table showed that there is no correlation in the work of different investigators, even when using the same solvent. The reason for these discrepancies is in all probability due to a number of factors, namely: the nature of the starting material; the time of the reaction; the temperature; the nature of the precipitating agent; the method of analysis; the experience of the investigator; and many others. To discuss the importance of one factor while holding the others constant would be of no value since in the majority of cases there is insufficient data from which to draw valid conclusions. A few salient points however, may be considered.

Role of the Solvent. The importance of the solvent has not been evaluated. The solvents which have been used contain the C=O group, which is known to form addition compounds with ammonia. Therefore, there is the possibility of the addition compound and not the ammonia being the actual agent involved in the substitution.

Brown (19) attempted to prepare a cellulose amine by passing gaseous ammonia into a dispersion of cellulose nitrate in toluene but was unsuccessful. He then investigated the use of a mixture of acetone-toluene as a solvent and found that as the toluene concentration decreased, the degree of substitution of the amino group increased.

Time of Reaction. It has been shown that the amino nitrogen content of the cellulose amine seems to reach a maximum after a certain length of time and then decrease. However, it is seldom explicitly explained as to what is meant by "time of reaction", and we have two factors to consider. The first is the actual time during which the gaseous ammonia is passed through the cellulose nitrate dispersion. The second is the time during which the ammoniacal reaction mixture is allowed to stand before precipitation of the reaction product. There is little - if any - correlation between the two factors.

Temperature of Reaction. With few exceptions the experiments listed in Table II were all carried out at room temperature. Scott (163) using n-butyl acetate as the solvent, and continuous treatment with ammonia, carried out the reaction at 75°C, and found that an increase in temperature increased the rate of reaction. Again, after a length of time at this temperature there appears to be a decrease in the degree of substitution of the amino group.

Precipitant. A number of precipitating agents have been investigated, but only n-heptane, chloroform and water have been successfully used. Miller (121) investigated the precipitating action of these non-solvents

using the same reaction mixture and found that the amino nitrogen content depended on the solvent used; heptane giving the highest amine content and water the lowest. He attributed the decrease in amino nitrogen content to a hydrolytic attack on the amino group by the non-solvent.

His data, however, does not completely support his conclusions. If the decrease in amino content is due to a hydrolytic attack on the amino group, there should be no change in the number of nitrate groups. But, as his data shows, the number of nitrate groups in the product vary over a wide range.

The variance in amino nitrogen content with respect to the non-solvent should be interpreted in the light of the following considerations:

(1). The non-solvent might fractionally precipitate the amine so that the very small chains, which are probably more uniformly substituted remain in solution.

(2). There is no criteria for a pure "cellulose amine", and thus it is possible that a decrease in the amino nitrogen is not due to hydrolysis, but to a purification process in such a fashion as to approach the true amine content of the product.

(d). Miscellaneous Methods

As explained elsewhere cellulose nitrate and cellulose p-toluene sulfonate on treatment with sodium iodide replace the ester grouping in the 6-position with iodine. These halogenated compounds may be treated with ammonia or amines to give derivatives with nitrogen directly substituted on the glucose unit. Again degradation of the chain cannot be avoided, and the resulting amines have not been properly identified (135).

Gardner (45) attempted to prepare cellulose amine by treating tosylcellulose acetate and 6-iodocellulose with ammonia. The tosyl ester was partly de-esterified, and the iodine was removed from the iodocellulose. In no case, however, was any appreciable amount of nitrogen introduced into the glucose residue. He also investigated the action of sodium amide on 6-iodotosyl cellulose in liquid ammonia and obtained a highly degraded product containing only a small amount of nitrogen.

British patent 393,242 (18) deals with the treatment of cellulose with acetic acid, acetic anhydride and mineral acids, and an amino compound such as urea or aniline. The resulting product contains nitrogen partly as nitrate and partly as amino bound directly to the carbon atom of the cellulose, the proportions being at least 1 per cent NH_2 and less of NO_2 .

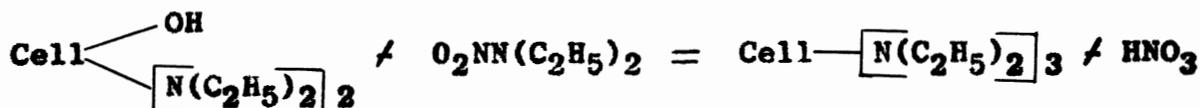
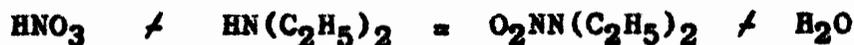
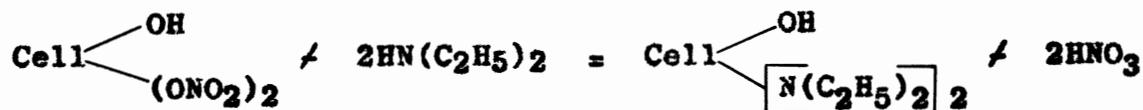
2. Alkyl Cellulose Amine

Two alkyl substituted amines have been prepared by allowing the respective alkyl amines to react directly with cellulose nitrate. Scherer and Rogers (157) prepared a triaminodiethylcellulose by adding a solution of diethylamine in ether to cellulose dinitrate. The brown amorphous powder which they obtained showed the presence of 12.84 per cent amino nitrogen, corresponding favorably to the theoretical value of 12.82 per cent for a triaminodiethylcellulose. The amine was very soluble in water, very slightly soluble in chloroform and acetone and insoluble in benzene, ether, and carbon tetrachloride.

Rouse (150) and Hunnewell (77) prepared a tri-di-n-butyl amino cellulose by reaction of di-n-butyl amine in ether solution with cellulose dinitrate. A light brown powder was obtained which contained 8.16 per cent amino nitrogen (theoretical 8.48%). The amine was soluble in glacial acetic acid and pyridine, but insoluble in water and common organic solvents.

The formation of a tri-substituted cellulose alkyl amine from cellulose dinitrate cannot be entirely explained by assuming a metathetic replacement of the nitrate groups since this would only lead to the formation of a di-substituted amine. The following mechanism,

first proposed by Rouse (150), is plausible, but it is not supported by any experimental evidence. The reaction is assumed to take place in two distinct steps. The first step involves the metathetical replacement of the nitrate groups forming the di-alkyl cellulose amine and nitric acid. In the second step the nitric acid reacts with excess dialkylamine to form a dialkylnitramine, which in turn reacts with the remaining hydroxyl group to form the triamino derivative. The reactions may be formulated thus:



Alkyl substituted cellulose amines may also be prepared by treating cellulose p-toluene sulfonate with the respective alkyl or aryl amine (86, 151). The products of the reaction have not been fully characterized and it is believed (67) that there is no replacement of the tosyl group, but merely an addition of the amine to the tosyl group.

Evidence has been presented (5) that diphenylamine, p-dinitrodiphenylamine and urea react with nitrocellulose, but the reaction products have not been identified.

3. Hydrogenation of Cellulose

The direct hydrogenation of cellulose by treating cellulosic material with molecular hydrogen in the presence (or absence) of a catalyst has not been successful (13, 14, 44, 62). At low temperatures at which the cellulose remains unaffected no reaction seems to take place; at high temperatures at which thermal decomposition of cellulose begins, hydrogen is consumed. All evidence seems to indicate that the hydrogen reacts with the thermal decomposition products rather than with the cellulose itself. In general, the cellulosic material is converted entirely into complex liquids and gases, and occasionally, depending on the experimental conditions, into coal-like residues.

Investigations have also been carried out using substances other than molecular hydrogen. Willstatter and Kalb (197) subjected cotton to the action of hydriodic acid and red phosphorus at 250°C and obtained products consisting of nine per cent ether insoluble residue, eight per cent liquid hydrocarbons, and twelve per cent solid hydrocarbons. The remainder which was not

characterized is assumed to be gaseous. For other examples the reader is referred to the reviews of Henze (62) and Heuser (73).

Very little work appears to have been carried out on the hydrogenation of cellulose derivatives. A German patent (98) issued in 1927 claims the conversion of dimethylcellulose and diethylcellulose to dimethoxytrihydroxyhexane and diethoxytrihydroxyhexane respectively, by the action of molecular hydrogen at 250-260°C and 70-110 atmospheres in the presence of a nickel catalyst. A British patent (37) issued in 1940 deals with the reduction of cellulose ethers by molecular hydrogen in the presence of a nickel catalyst and a non-reducible solvent. By this treatment the cellulose ethers are stabilized against changes in viscosity, reduction, oxidation, and embrittlement.

4. Halogenated Derivatives of Cellulose

The introduction of chlorine and iodine in place of the hydroxyl groups in cellulose has never been accomplished by direct means. Cellulose p-toluene sulfonate on treatment with sodium iodide replaces the ester grouping in the 6-position by iodine; pyridine hydrochloride replaces the tosyl group in the 6-position by chlorine. The iodination is carried out by treating the tosyl ester with sodium iodide in acetone at 100°C

in an autoclave, or at 115-120°C using acetylacetone as solvent. The chlorinated derivatives are prepared by treating the tosyl ester in pyridine solution with pyridine hydrochloride at 85°C. No bromo derivatives of cellulose have been reported in the literature.

The halogenated products vary from white to yellow or light tan color. They retain their fibrous structure, but are somewhat degraded. In general, they are soluble in acetone and insoluble in water, chloroform, glacial acetic acid, ethyl ether, simple alcohols and many ketones.

The following is a list of the iodo and chloro derivatives of cellulose which have been reported in the literature.

<u>Product</u>	<u>Reference</u>
6-iodotosyl cellulose	74, 176
6-iodocellulose	176
6-iodo cellulose nitrate	126
6-iodo cellulose acetate	30
6-iodotosylcellulose acetate	30, 45, 46, 102
6-iodo ethylcellulose	100, 101
6-iodo methylcellulose	101, 185
6-iodotosyl hydroxyethylcellulose	184
6-iodocellulose dicarbonylate	61
6-chlorotosyl cellulose acetate	30, 102
6-chlorotosyl hydroxyethylcellulose	184

Originally it was believed that the halogen atom was substituted specifically on carbon-6. Recent analyses of some halogenated products imply the introduction of slightly more than one halogen atom per glucose unit into tosylated cellulose (74, 102).

Sodium iodide in ketone solvents at 115-120°C removes a portion of the nitrate group from cellulose nitrate and replaces it with iodine (126). The iodo cellulose nitrates are white, changing to brown with increasing iodine content. They are soluble in acetone, but insoluble in water. This method of iodination is applicable only to cellulose nitrates of low nitrogen content.

5. Desoxy Cellulose Derivatives

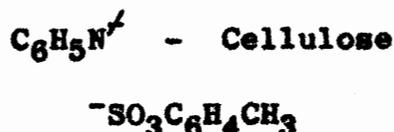
The term "desoxy sugars" is applied to those sugars in which one or more CHOH groups have been converted into CH₂ groups. The same designation would be applicable to a cellulose derivative in which the OH groups were replaced by hydrogen; i.e., reduced.

A 6-desoxycellulose has been prepared (176) by allowing 6-tosyl cellulose to stand in contact with dry piperidine or sodium piperidine for three days. The resulting reduced derivative was a water insoluble amorphous colorless product containing 0.35-0.55 reduced primary hydroxyl groups, and 0.5-0.8 double bonds per glucose residue. Reduction was also accomplished using zinc-acetic acid and palladium in acetic acid. The reduced derivative obtained in this manner was extremely degraded.

Purves and co-workers (30) prepared a degraded 6-desoxycellulose acetate by reduction of 6-iodocellulose acetate with a Zn-Cu couple in glacial acetic acid. They also attempted (126) the same reduction with 6-iodocellulose nitrate, but were unsuccessful in isolating a product.

6. Miscellaneous Derivatives

Acetyldesoxyquaternary Salts. Hayes and Lin (60) prepared acetyldesoxycellulose quaternary salts by treating tosyl cellulose acetate with piperidine, 3-picoline or isoquinoline. Similar reactions of p-toluenesulfonate esters with tertiary amines are well known (89) and by analogy the cellulose derivative would be expected to have the following formula:



Aminocellulose Acetylide. An aminocellulose acetylide has been prepared (153) by treating cellulose dinitrate with sodium acetylide in liquid ammonia. One of the nitrate groups of cellulose nitrate reacts very rapidly with sodium acetylide while the other group is slowly converted to an amino group. This amino group results from the sodium amide which is present through a secondary reaction of the sodium acetylide and ammonia.

During isolation of the amino cellulose acetylide polymerization occurs, presumably through the acetylide group, and the resulting polymer is soluble only in strong alkalies. A triphenyltin derivative has been prepared by reacting triphenyltiniodide with the amino-cellulose acetylide in liquid ammonia.

V. THE INVESTIGATION

A. MATERIALS, METHODS, AND APPARATUS

1. Materials

During the course of the investigation a varied number of reagents, both organic and inorganic, were used. No attempt will be made to describe them all. The inorganic reagents were the best available from the Chemistry Supply Room. Whenever possible they were C.P. or Reagent grade and taken from freshly opened bottles. The organic reagents were all Eastman products, White Label or Yellow Label as available, and were obtained from the Organic Chemistry Supply Room. The various acids and bases, and solvents were obtained from the Chemistry Supply Room as available.

The following reagents because of their nature, or treatment, require special mention.

Cellulose Nitrate. Three samples of cellulose nitrate were used. The major portion of the investigation was carried out using RS type, 60-80 seconds viscosity, Lot 5519, 12.12% N, and Lot 4755, 12.10% N. In a few experiments Hygrade, Lot 5422, 13.35% N was used. All the cellulose nitrate was obtained from the Hercules Powder Company, Parlin, New Jersey.

Methyl Cellulose. Pharmaceutical grade, viscosity 15 cps., Lot No.1396. Obtained through the courtesy of

the Dow Chemical Company, Midland, Michigan.

Sodium Carboxymethyl Cellulose. Purified CMC, Lot No. C-12143-E. Obtained through the courtesy of the Wyandotte Chemicals Corporation, Wyandotte, Michigan.

Sodium Cellulose Sulfate. Low viscosity grade. Obtained through the courtesy of Tennessee Eastman Corporation, Kingsport, Tennessee.

Sodium Borohydride. Obtained from Metal Hydrides, Inc., Beverly, Massachusetts. Analysis of the hydride by measurement of the hydrogen gas evolved upon acidification of an aqueous solution showed 90 per cent sodium borohydride. The nature of the impurities was unknown, but on the basis of published information were assumed to be sodium borate (33). The hydride was ground with a mortar and pestle and stored in a screw-cap bottle which was kept in a desiccator over calcium chloride. The bottle was opened intermittently with no special precautions to prevent access of atmospheric moisture. Under these conditions the rate of dissociation is stated (23) to be less than two per cent per year. Solutions in sodium hydroxide were prepared immediately before using.

Liquid Ammonia. The ammonia used was the ordinary anhydrous liquid ammonia of commerce. In the major portion of the investigation it was used without further

purification. In a few experiments it was distilled over sodium, but no difference in the results was evident. During the course of the investigation ammonia from four different tanks was used. Two of these were obtained from E. I. du Pont de Nemours, Polychemicals Division, Philadelphia, Pennsylvania. The others were a du Pont product, origin unknown.

Acetone. Most of the research was carried out using C.P. grade product obtained from the Commercial Solvents Corporation, Peoria, Illinois. In a number of experiments Baker and Adamson reagent grade product was used.

Absolute Ether. Absolute ether was prepared by distilling reagent grade product over phosphorous pentoxide and storing over sodium wire.

Ethyl Bromide. Ethyl bromide was prepared and purified by a method described by Norris (132).

n-Butyl Bromide. The product was a student preparation obtained from the Organic Chemistry Supply Room. It was purified by a method described by Adams and Johnson (2).

Tin Foil. The tin foil was obtained from the Chemistry Supply Room; origin unknown. The tin foil was cut into small squares about $\frac{1}{2}$ -cm. on edge, and just before using was washed with carbon tetrachloride

alcohol, and ether, and dried in a warm current of air.

Sodium Metal. The sodium was obtained from the Chemistry Supply Room; origin unknown. It was freshly cut under petroleum ether, weighed in mineral oil, washed carefully in petroleum ether and then introduced into the reaction flask.

Potassium Metal. The potassium was supplied by the Fisher Scientific Co. It was treated in a manner similar to sodium.

Zinc Chloride. The zinc chloride was C.P. grade obtained from J. T. Baker Chemical Co. The reagent was fused just before using.

Sodium Hydroxide. Baker and Adamson product, 76% flake, suitable for Kjeldahl nitrogen determination was used. A 10 N solution of the reagent was prepared as needed using freshly boiled water. The solution was stored in a paraffin lined bottle.

Diacetoneamine. Diacetoneamine was prepared by a modification of the methods of Everest (39), Haeseler (52), and Cohen (29). Acetone (232 grams) and anhydrous calcium chloride (40 grams) were introduced into a vessel fitted with a reflux condenser and an inlet for ammonia. Gaseous ammonia was then passed into the mixture. Much heat was developed during the addition of the ammonia, but with an effective condenser there was no loss of

solvent. When 40 grams of ammonia had been added the vessel was tightly stoppered and allowed to remain at room temperature for a period of ten days. Once a day the flask was thoroughly shaken.

At the end of the allotted time, the whole was poured into a separatory funnel and allowed to stand for several hours to insure complete separation of the layers, and to allow the calcium chloride to settle. The lower layer, and the solid calcium chloride, were removed and discarded. The upper layer was placed in a flask and air rapidly drawn through it for several hours, thereby removing most of the excess ammonia. A sample of the solution was then titrated with 0.5N oxalic acid, litmus being used as an outside indicator. The amount of oxalic acid necessary to form the acid salt was dissolved in ethanol (95%), three times the volume of the reaction mixture being used, and the amine was then poured slowly into the alcoholic solution, the whole being kept well agitated.

When all the amine had been added the resulting mixture was heated on a steam bath with vigorous stirring until the temperature of the mixture reached 75°C. The mixture was then filtered while hot through a previously heated Buchner funnel. The filtrate, on cooling, deposited diacetoneamine hydrogen oxalate (m.p. 125-127°C)

in crystalline condition. It was filtered, washed with ethanol, and dried.

To a portion of the crystalline product an excess of 2N sodium hydroxide solution was added and the mixture extracted with ether. On distilling the ether, diacetoneamine remained behind as a liquid.

Cuprous Chloride. Cuprous chloride was prepared by a method proposed by Desha and Farinholt (35). In a 250 ml. Erlenmeyer flask, 30 grams of hydrated copper sulfate were dissolved in 100 ml. of water by heating, and 8.8 grams of sodium chloride were added to the hot solution. In another flask 8.1 grams of anhydrous sodium sulfite and 2.0 grams of sodium hydroxide were dissolved in 50 ml. of cold water. During the course of five minutes the latter solution was poured with stirring into the hot solution, and the mixture was immediately cooled to room temperature. The white precipitate of cuprous chloride was allowed to settle and the supernatant liquid decanted. After being washed once with cold water, the precipitate was immediately dissolved in a solution of 34 ml. of concentrated hydrochloric acid and 10 ml. of water. The flask was stoppered and placed in an ice bath until needed.

Cuprous Bromide. Cuprous bromide was prepared by a method proposed by Robertson (148). A solution con-

taining 25 grams of hydrated copper sulfate was divided into two equal portions. To one portion 3.2 grams of zinc dust was added and the flask thoroughly shaken, then just enough additional zinc was added to discharge the blue color of the solution. The precipitated copper was allowed to settle and the supernatant liquid decanted. The precipitate was washed with 6N sulfuric acid, to destroy any unreacted zinc, then with water, the wash liquids being decanted each time. To the copper powder was then added the second portion of the copper sulfate, 11.7 grams of sodium bromide and 3 ml. of concentrated sulfuric acid. The solution was thoroughly shaken, the flask stoppered and stored in an ice bath until needed.

2. Apparatus

The apparatus used to carry out reactions in liquid ammonia is shown in Figure 2. Ammonia from the tank was allowed to condense in an unsilvered Dewar flask (A). As needed, the liquid ammonia was forced into the reaction vessel (B) through a sliding tube (a), by closing valve (b) and opening valve (c). Usually, the pressure exerted by the ammonia vapor was sufficient to effect the transfer. However, when necessary a slight pressure was exerted on flask (A) by opening the valve on the ammonia tank. Ammonia vapors from flasks (A) and (B) passed into the ammonia absorber. This was a fifteen

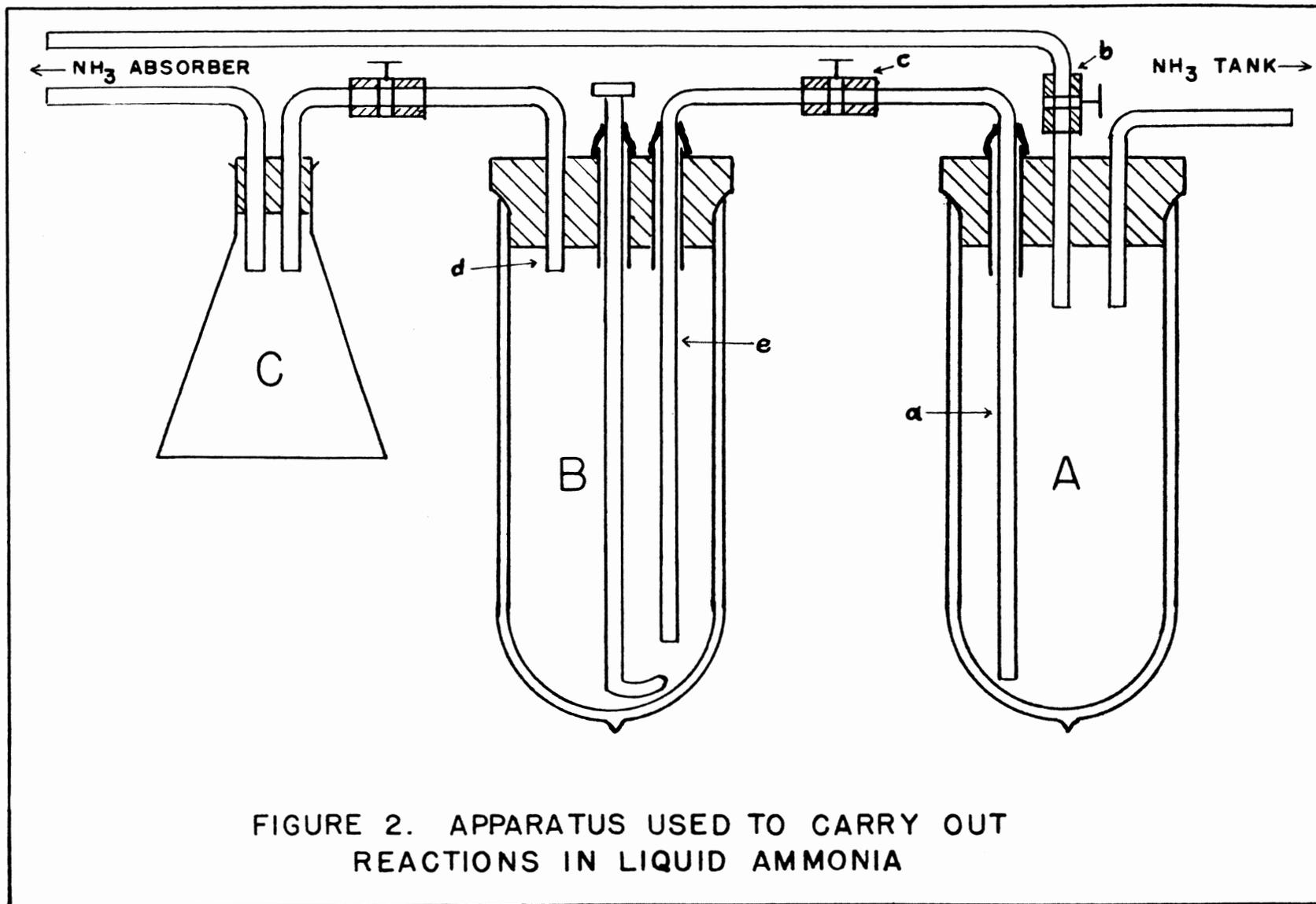


FIGURE 2. APPARATUS USED TO CARRY OUT REACTIONS IN LIQUID AMMONIA

gallon carboy filled with water which was changed periodically. Flask (C) was used as a trap.

In a few experiments tube (d) was replaced by a sliding tube which could be lowered into flask (B) to syphon off liquid ammonia which was then allowed to evaporate from flask (C). Tubes (a), (e), and the stirrer were inserted through a rubber sleeve, lubricated with glycerol. This made a gas tight seal, and enabled the stirrer to rotate. The rubber stoppers in the flasks were held in tightly by an iron bar clamped across them.

The stopper flask (B) was equipped with four holes, only three of which are shown in Figure 2. The fourth hole, approximately 1.5 cm. in diameter, was located in front of the stirrer. It could be equipped with a dropping funnel or an adapter, and was used to introduce reagents into the reaction flask. When not in use it was closed with a No. 1 rubber stopper.

3. Nitrogen Determination

The quantitative determination of amino and total nitrogen was carried out by the Kjeldahl method used by previous investigators in this laboratory (94). Briefly, the method consists in the oxidation of the sample by digestion with hot concentrated sulfuric acid in the presence of copper sulfate which acts as a catalyst.

Potassium sulfate is added to raise the boiling point of the sulfuric acid which materially aids in the oxidation process. The amino nitrogen in the sample is converted into ammonium sulfate. When oxidation of the material is complete, the solution is made alkaline with sodium hydroxide and the liberated ammonia is distilled into a saturated solution of boric acid. The amount of ammonia is determined by titration with standard hydrochloric acid using methyl red indicator.

In order that the Kjeldahl method may be applied to nitrates, the sample must first be reduced so as to convert the nitrate nitrogen to amino nitrogen. This is accomplished by treating the sample with a salicylic acid-sulfuric acid mixture which prevents the escape of nitric acid by the formation of nitrated derivatives of salicylic acid. Subsequently, the nitrogen is reduced by the addition of zinc powder, and the digestion and distillation carried out as described above.

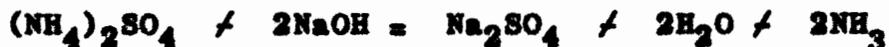
With substances which contain both amino and nitrate nitrogen two samples must be analyzed. One sample is analyzed for total nitrogen, the other sample for amino nitrogen; nitrate nitrogen is obtained by difference.

The chemistry and techniques of the Kjeldahl determination are adequately described in a number of refer-

ence books (164, 196) and need not be considered here. However, a few aspects based on the writer's experience will be discussed, in the hope that they will simplify the work of future investigators in this field.

Digestion of Sample. Unlike cellulose nitrate, cellulose amine is only soluble in cold concentrated sulfuric acid on standing. If the amine-acid mixture is heated before complete dissolution occurs, the sample decomposes violently with the evolution of nitrogenous fumes. The sample must be allowed to dissolve completely before heating.

Neutralization with Sodium Hydroxide. The addition of sodium hydroxide to the digested sample serves two purposes: it neutralizes the excess sulfuric acid; it liberates ammonia from ammonium sulfate according to the following equation:



In the literature, the concentration of sodium hydroxide to be used is given as 10N, 12N, 50% (19N), and occasionally the term "very concentrated" is used.

The procedure used by previous investigators in this Laboratory stipulates the use of twenty five ml. of concentrated sulfuric acid for the digestion, and one hundred ml. of "very concentrated" sodium hydroxide

solution for the neutralization. Concentrated sulfuric acid (sp. gr. 1.84; 95% H_2SO_4) has a normality of 35.6, therefore:

$$35.6 \times 25 = 890 \text{ meq of } H_2SO_4$$

Assuming a concentration of 10N for the sodium hydroxide solution:

$$10 \times 100 = 1000 \text{ meq of NaOH}$$

Under these conditions the sodium hydroxide will be sufficient to neutralize the sulfuric acid and liberate the ammonia. Precautions, however, should be taken to measure out accurate volumes of the reagents.

Standard Hydrochloric Acid. Almost all of the laboratory procedures for the Kjeldahl determination specify the use of 0.2N hydrochloric acid. The writer suggests that the acid used be no stronger than 0.1N. The following calculation will make this point clear.

The per cent nitrogen is calculated from the following formula:

$$\%N = \frac{V \times C \times Q \times 100}{W}$$

where: V = volume of HCl
C = normality of HCl
Q = meq weight of nitrogen (0.014)
W = weight of sample in grams

Laboratory directions specify the use of approximately 0.3 g. of sample. Substituting this value in the above formula, and assuming 0.2N hydrochloric acid is used, we have the following relationship:

$$\%N = \frac{V \times 0.2 \times 0.014 \times 100}{0.3}$$

$$\%N \approx 0.9V$$

The per cent nitrogen encountered in this work ranges from 5% to 10%, corresponding to a volume of ten ml. or less of acid. This low value may introduce an appreciable error in the analysis.

Choice of Indicator. The determination of ammonia is carried out by titration of ammonium borate - which titrates exactly as if it were free ammonia - to a methyl red end point. The color changes of the indicator - yellow to red - is rather difficult for the beginner to recognize, even by comparison to a standard reference solution. Kolthoff and Sandell (91) advocate the use of bromocresol green as indicator. The color change of this indicator - blue to yellow - is more pronounced, and it is suggested that it's use be investigated by future workers.

Distillation of Ammonia. The greatest source of error in the Kjeldahl determination lies in the distil-

lation of the ammonia; furthermore, this step is time consuming. Recently, Marcali and Reiman (103, 104) have proposed a procedure which eliminates the ammonia distillation, but which employs a standard Kjeldahl digestion. The application of this procedure to pure organic compounds gave results in satisfactory agreement with the theoretical nitrogen present. It is suggested that the procedure be investigated for application to cellulose amine and other nitrogenous cellulose derivatives.

Treatment of Sample. In all determinations a representative sample was taken for the nitrogen analysis. Difficulty was experienced in weighing out the desired quantity due to the tendency of the powdered cellulose derivative to adhere to the sides of the glass container and to the spatula. The following procedure proved to be satisfactory, and was used in all determinations. A sample of the amine, weighing approximately 0.3 g. was introduced into a weighing bottle which was then placed in an oven and dried at 55-60°C for a period of six hours. After cooling to room temperature, the weighing bottle and its contents were accurately weighed and the amine carefully poured on a sheet of cigarette paper. The weighing bottle was reweighed, and the difference in weight taken as the weight of the amine. The cigarette

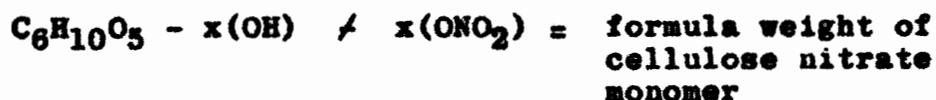
paper was carefully folded and introduced into the Kjeldahl flask. Addition of concentrated sulfuric acid disintegrated the paper. Samples of the cigarette paper taken at random were found to be nitrogen free.

4. Calculation of Degree of Substitution

(a). One Substituent

The calculation of the degree of substitution of cellulose derivatives containing only one species of substituent group would be a relatively simple matter if such derivatives were formed having a single integral ratio of substituents (one, two, or three). For example, the per cent nitrogen in cellulose dinitrate is 11.11; therefore, any nitrated cellulose analyzing 11.11% N is a dinitrate, irrespective of the location of the nitrate groups on the glucose residues. Such conditions, however, are seldom fulfilled, since cellulose derivatives of any desired degree of substitution may be prepared. In such cases, the degree of substitution can be calculated as shown below.

Cellulose Nitrate. Let 'x' be the number of nitrate groups (-ONO₂) in the product. For every nitrate group introduced into the glucose residue one hydroxyl group (-OH) must have been replaced. Then:



Each $-\text{ONO}_2$ group contains one atom of nitrogen; therefore, ' xN ' must be the weight of nitrogen in $x(\text{ONO}_2)$ groups.

The per cent nitrogen may then be calculated by the following relationship:

$$\frac{xN}{\text{C}_6\text{H}_{10}\text{O}_5 - x(\text{OH}) - x(\text{ONO}_2)} \cdot 100 = \%N$$

Substituting the atomic weight of nitrogen and the formula weight of the radicals and cellulose there is obtained:

$$\frac{14.0x}{162.1 - 17.0x - 62.0x} \cdot 100 = \%N$$

Let $A = \%N$, and solving the above equation for ' x '

$$x = \frac{162.1A}{1400.0 - 45.0A}$$

where: x = number of nitrate groups per glucose residue; it may have any value between (and including) 0 and 3.0

A = per cent nitrogen found on analysis

Cellulose Amine. The per cent amino nitrogen in cellulose amine may be calculated from the following expression:

$$\frac{xN}{\text{C}_6\text{H}_{10}\text{O}_5 - x(\text{OH}) - x(\text{NH}_2)} \cdot 100 = \%N$$

Let B = %N; substituting atomic and formula weights and solving for 'x':

$$x = \frac{162.1B}{1400.0 - B}$$

where: x = number of amino groups

B = per cent amino nitrogen found on analysis

Cellulose Butyl Amine. Using the arguments presented above the following formulas may be derived for cellulose butyl amine.

$$\frac{xN}{C_6H_{10}O_5 - x(OH) - x(N(C_4H_9)_2)} \cdot 100 = \%N$$

and

$$x = \frac{162.1C}{1400.0 - 111.2C}$$

where: x = number of di-n-butyl amine groups

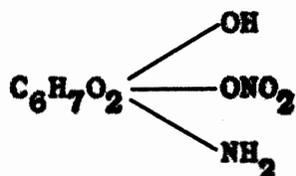
C = per cent amino nitrogen

(b). Two Substituents

The calculation of the degree of substitution in cellulose derivatives containing two species of substituents is more complicated.

Consider a cellulose derivative containing one amino (-NH₂) and one nitrate (-ONO₂) groups per glucose unit.

The formula of the monomer may be written:



The formula weight of the monomer is given by the relation:



Let:

x = number of -OH groups per glucose unit

y = number of -NH₂ groups per glucose unit

z = number of -ONO₂ groups per glucose unit

The formula weight may now be represented by the following relation:



Let:

A = per cent amino nitrogen

B = per cent nitrate nitrogen

then it follows that:

$$\frac{yN}{\text{C}_6\text{H}_7\text{O}_2 \neq x(\text{OH}) \neq y(\text{NH}_2) \neq z(\text{ONO}_2)} \cdot 100 = A$$

$$\frac{zN}{\text{C}_6\text{H}_7\text{O}_2 \neq x(\text{OH}) \neq y(\text{NH}_2) \neq z(\text{ONO}_2)} \cdot 100 = B$$

Substituting atomic and formula weights and clearing fractions there is obtained:

$$17.0Ax \neq (16.0A - 1400.0)y \neq 62.0aZ = -111.1A \quad (1)$$

$$17.0Bx \neq 16.0By \neq (62.0B - 1400.0)z = -111.1B \quad (2)$$

Each glucose monomer has only three replaceable -OH groups, and it must therefore follow that:

$$x \neq y \neq z = 3$$

$$x = 3 - y - z \quad (3)$$

Substituting Equation 3 in Equations 1 and 2 and simplifying, the following expressions are obtained:

$$(1400.0 \neq A)y - 45.0Az = 162.1A$$

$$By \neq (1400.0 - 45.0B)z = 162.1B$$

Since A and B may be quantitatively determined there are two simultaneous equations from which the two unknowns -y' and 'z' may be readily calculated.

Cellulose Butyl Amine. If a cellulose derivative contains both nitrate and di-n-butyl amine groups the degree of substitution may be calculated from the following equations:

$$(55.1A - 1400.0)y \neq 45.0Az = -162.1A$$

$$55.1By \neq (45.0B - 1400.0)z = -162.1B$$

where:

A = per cent amino nitrogen

B = per cent nitrate nitrogen

x = number of -OH groups

y = number of -N(C₄H₉)₂ groups

z = number of -ONO₂ groups

5. Stoichiometry of Cellulose Nitrate

Since the true molecular weight of cellulose nitrate is unknown use is made of the formula weight of the monomer, which is based upon the degree of substitution of the monomer.

Consider a cellulose nitrate containing 12.12% nitrogen. The degree of substitution is obtained from the relationship:

$$x = \frac{162.1A}{1400.0 - 45.0A}$$

$$x = \frac{162.1(12.12)}{1400.0 - 45.0(12.12)}$$

$$x = 2.3$$

The formula weight is then obtained from the relationship

$$FW = C_6H_{10}O_5 - 2.3(OH) + 2.3(ONO_2)$$

$$FW = 265.6$$

Consider the reaction:

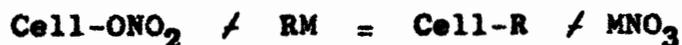


Using ten grams of ethyl tin, the required weight of cellulose nitrate would be:

$$\frac{10 \times 266}{177} = 15 \text{ grams}$$

B. REACTION WITH ORGANOMETALLIC COMPOUNDS

This series of experiments was carried out in an attempt to effect a metathetic replacement of the nitrate groups ($-\text{ONO}_2$) of cellulose nitrate by an alkyl or aryl radical. If the reaction could be made to proceed in the following manner:



where R is an alkyl or aryl radical, the resulting cellulose derivative would have the substituent attached directly to the carbon atom of the glucose residue.

1. Organozinc Compounds

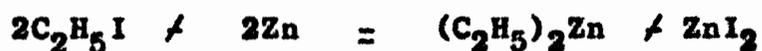
(a). Introduction

Organozinc compounds, discovered by Frankland (168) in 1849, played an important role in the development of synthetic organic chemistry, but at present they have been replaced by the more easily handled Grignard reagents.

The zinc dialkyls are colorless volatile liquids. The lower members catch fire very easily and decompose violently in the presence of water, forming zinc hydroxide and the corresponding hydrocarbon. The danger of spontaneous inflammability has been overcome by Noller (129) who found that... "by dissolving the pure zinc alkyls

in an equal weight of solvents of the desired boiling point, for example toluene, xylene, or tetralin, the solutions could be readily handled in the open air and poured from one flask to another without danger of ignition".

Various methods have been used for the preparation of zinc dialkyls. The earlier methods were a modification of Frankland's method (168). He used metallic zinc to remove the iodide from iodine alkyls according to the following equation:

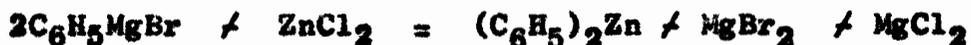


At present the above reaction is carried out using an equimolecular mixture of alkyl iodide and bromide in the presence of a zinc-copper couple (130). The zinc dialkyls can also be prepared by the action of metallic zinc on the mercury dialkyls or, better, by treating the corresponding Grignard reagent with anhydrous zinc chloride (129,130).

The zinc diaryls can be made from metallic zinc and mercury diaryls, or by treating the corresponding Grignard reagent with anhydrous zinc chloride (168). They are not spontaneously inflammable, but are readily decomposed in the presence of water.

(b). Experimental

Preparation of Diphenylzinc. Diphenylzinc was prepared from the corresponding Grignard reagent (24). To 3.2 grams of magnesium turnings in a 3-necked 500 ml. round-bottom flask provided with a dropping funnel and a reflux condenser fitted with a calcium chloride tube, were added 78 ml. of absolute ether and 20.7 grams of bromobenzene. The mixture was gently heated on a water bath. Within a few minutes the reaction started and was allowed to proceed at room temperature. When most of the magnesium was used up the solution was heated for fifteen minutes on a water bath and then allowed to cool to room temperature. There was then added dropwise a suspension of 9.0 grams of anhydrous zinc chloride in 50 ml. of absolute ether. Reaction took place immediately. Fifty ml. of toluene were added, the flask thoroughly shaken, and the ether removed by distillation on a water bath. The diphenylzinc was used without further purification. The reactions took place according to the following equations:



Treatment with Cellulose Nitrate. To the reaction vessel there was then added cellulose nitrate (10 grams)

and the mixture refluxed on a water bath for a period of several hours. The flask and its contents were allowed to cool to room temperature, and the whole filtered rapidly through a Buchner funnel. The residue was washed several times with toluene, the washings being discarded. The residue was then cautiously treated with water to decompose any adhering diphenylzinc, washed with water and then alcohol, and finally dried in air.

The filtrate was cautiously treated with water to decompose the diphenylzinc, filtered, and the filtrate analyzed for nitrites and nitrates by the brown ring test. Negative results were obtained in all runs.

A small portion of the air dried residue was treated with water and filtered. The halide ions were precipitated by the addition of silver sulfate and the filtrate analyzed for nitrites and nitrates. Negative results were obtained in all runs.

The remainder of the residue was steeped in acetone for several hours and then rapidly filtered through a sintered glass filter. The mixture remaining on the filter was washed with several small portions of acetone, the washings being combined with the filtrate. The acetone solution was concentrated under vacuum and then poured into a large volume of water. A white precipitate formed which was filtered on a Buchner funnel, washed

with water and alcohol, and dried in air. Nitrogen analysis of the product showed it to be the original cellulose nitrate. By this procedure approximately ninety to ninety five per cent of the original cellulose nitrate could be recovered. The loss may be attributed to the following sources: incomplete solution in the acetone; incomplete precipitation from water; incomplete removal of the residue from the reaction flask.

A number of runs were made in which the time of reflux was varied from two to twenty four hours. The results obtained were similar to those described above.

Reaction with Diethylzinc. Diethylzinc was prepared in a manner similar to diphenylzinc and then treated with cellulose nitrate. The resulting mixture was treated as previously described. No evidence of any reaction was obtained.

2. Diethyl Tin

The study of a possible reaction between cellulose nitrate and diethyl tin was undertaken because diethyl tin could be conveniently prepared in liquid ammonia, a suitable solvent for the cellulose nitrate.

(a) Introduction

Diethyl tin was first prepared in 1852 from ethyl

iodide and tin-sodium alloy, and by the action of metallic tin on diethyltin dichloride (169). In 1911 Pfeiffer (143) prepared the compound both by the action of anhydrous stannous chloride on ethyl magnesium bromide, and by the action of sodium amalgam on diethyltin dichloride. On the basis of these investigations, the compound has been variously described as a colorless, yellow, or red oil, insoluble in water but soluble in organic solvents.

Harada has recently prepared the compound by the reduction of diethyltin dibromide with metallic sodium dissolved in liquid ammonia (54), and by the action of sodium hemistannide (Na_2Sn) on ethyl bromide dissolved in liquid ammonia (56). The diethyl tin thus prepared was entirely different in appearance and physical properties from that prepared by previous investigators. Harada (54) described it as... "an orange-yellow solid ...insoluble in water, but very slightly soluble in alcohol and acetone, and moderately soluble in ether, benzene, etc. It decomposes above 150°C in a capillary tube. It ignites slowly in air". Diethyl tin is insoluble in liquid ammonia.

The chemical properties of the compound prepared by Harada are those of the diethyl tin described in the literature. The difference in color and physical proper-

ties may possibly be attributed to the difference in electronic constitution (electroisomerism) or to the method of preparation. It is known (55) that other tin compounds (for example $(C_2H_5)_3Sn$) prepared by two different reactions do not have the same properties, although similar in appearance. In the case of diethyl tin there is just the reverse phenomena. Furthermore, the possibility remains that the various investigators have never prepared the compound with the same degree of purity.

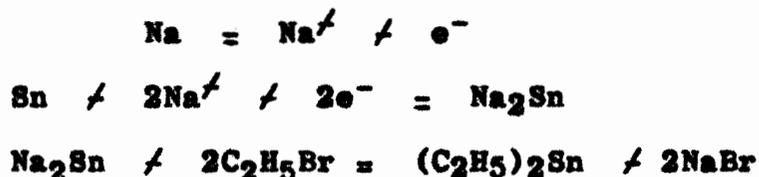
Very little is known about the chemistry of diethyl tin, and some of the published information, even by the same author, is conflicting. It reduces silver nitrate to metallic silver and reacts strongly with concentrated nitric acid. When dried it ignites spontaneously, but in the moist state oxidation is relatively slow. In solution it readily oxidizes to diethyltin oxide.

(b). Experimental

Preparation of Diethyl Tin. Diethyl tin was prepared by a modification of the procedure described by Harada (56). Eight grams of tin foil cut into small pieces were treated with 1.0 grams of sodium in about 200 ml. of liquid ammonia for a period of two hours, the solution being continuously stirred with a mechanical stirrer. At the end of this time another 1.0 gram

of sodium was added and the solution stirred for an additional period of two hours. At this point the solution was an opaque dark blue color; reddish streaks were visible on the side of the Dewar flask. Ten grams of ethyl bromide were added dropwise from a dropping funnel. A light brown colored precipitate was formed and the ammonia solution turned brown. The rate of addition of the ethyl bromide was found to be very critical. If the addition was too rapid the reaction became very vigorous and could not be kept under control.

The reactions involved in the preparation of diethyl tin are in accordance with the following equations:



Treatment with Cellulose Nitrate. Cellulose nitrate (8 grams) was added to the Dewar flask immediately after the addition of the ethyl bromide. The reaction mixture was stirred for a period of from one to six hours, and the ammonia then allowed to evaporate. The residue was extremely heterogeneous in color and appearance, ranging from yellow to gray, and from a powder to lumps. Its physical composition appeared to be independent of the time the reaction mixture was stirred.

A plan of attack was formulated to attempt to find a solvent, or group of solvents, which would remove the impurities or, better, selectively dissolve the possible reaction product. A number of solvents were investigated. The following experimental procedure was the one most commonly used.

To the Dewar flask were added 100 ml. of ethanol, the solid mixture broken up with the aid of a long stirring rod, and the mixture allowed to stand for about thirty minutes with occasional stirring. The whole was filtered, and the residue again treated with 100 ml. of ethanol, stirred and filtered. The extraction was continued using 50 ml. portions of ethanol, until about 500 ml. of filtrate were collected. In a similar manner the residue was extracted with ether and then with acetone, in each case about 500 ml. of filtrate being collected. The residue remaining after the final extraction was dried in air. An attempt was made to carry out the extraction in a Soxhlet extractor, with very poor results being obtained.

A portion of each filtrate was evaporated to dryness on a hot plate, the temperature being kept at about 50°C; the last traces of solvent were removed in a current of air. The residue and filtrate were then treated as described below. The results reported are based on an average of a number of experiments.

Alcohol Extract. The alcoholic solution, light yellow in color, became turbid on standing. It readily reduced silver nitrate and gave a positive sodium flame test. No non-solvent was found which would precipitate the dissolved matter.

The residue left after evaporation of the alcohol was heterogeneous in color, ranging from white to orange brown. A portion of the residue was heated in a crucible and the carbonaceous ash digested with sulfuric acid-nitric acid solution. The residue was taken up in dilute hydrochloric acid and treated with hydrogen sulfide. A yellowish-brown precipitate of stannous (or stannic) sulfide was formed. Sodium fusion of the residue showed a faint trace of nitrogen.

The residue was slightly soluble in water. The solution so formed was neutral to litmus, and precipitated silver bromide on addition of silver nitrate. Silver sulfate was added to precipitate the bromide ion and the filtrate was then analyzed for nitrites and nitrates. Results were not conclusive. The aqueous solution had neither reducing nor oxidizing properties.

Ether Extract. The ether extract, dark yellow to orange in color, became turbid on standing, and gradually deposited a white to very faint yellow powder. Both the extract and white powder readily reduced silver

nitrate but on standing the reducing strength decreased.

The residue obtained on evaporation and the white deposit from the ether extract were shown to be diethyltin oxide. Treatment of the residue with various solvents failed to indicate the presence of other organic compounds. It was concluded that the ether extract consisted of diethyl tin which on standing gradually oxidized to diethyltin oxide.

In one experiment the ether extract was rapidly concentrated and poured into a dispersion of cellulose nitrate in liquid ammonia. The mixture was stirred for about two hours during which time it attained the consistency of meringue. Evaporation of the ammonia deposited an orange residue, insoluble in water, alcohol, and ether, but slightly soluble (on standing) in acetone and ethyl acetate. The addition of water to the acetone solution deposited a white flocculent precipitate which had the characteristics of cellulose nitrate. The orange residue was stable in air, homogeneous in color, and very flammable. Analysis showed the presence of nitrate nitrogen and tin.

Acetone Extract. The acetone extract, yellow to light amber in color, became turbid on standing. It readily reduces silver nitrate and gave a faint but positive test for sodium. The addition of water re-

sulted in the formation of a very finely divided substance which could not be separated by filtration, and which did not settle on standing.

The slightly hygroscopic residue left on evaporation was very heterogeneous in color, ranging from white to light brown. On ignition it burned readily depositing a carbonaceous ash containing tin, bromine and sodium. The brown-ring test for nitrates was negative. Kjeldahl determinations showed the presence of up to five per cent amino nitrogen, but the values varied markedly from sample to sample, and check results could not be obtained. The organic matter appeared to be a mixture of cellulose amine and undefined organic compounds.

Residue Left After Extraction. The residue left after extraction with the various solvents consisted of unreacted tin, bromide and sodium ions, nitrogen containing organic matter, and organotin compounds. The residue was slightly soluble in water, but no substance could be precipitated from the solution.

Variation in Order of Extraction. A number of experiments were carried out in which the order of extraction was changed from that given above. On the whole similar results were obtained.

Use of Water as Solvent. The addition of water to the Dewar flask after the evaporation of ammonia removed

the inorganic salts, but also dissolved some organic matter. The aqueous solution contained sodium, bromide ion, and traces of tin. Extraction of the residue with various solvents did not lead to the isolation of a single homogeneous product.

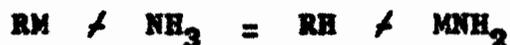
In one experiment the addition of water resulted in a violent explosion which shattered the Dewar flask. This explosion can only be attributed to the presence of unreacted sodium on the sides of the flask, the reaction of which with water generated sufficient heat to ignite the cellulose derivative.

Use of Other Solvents. A number of other solvents, namely: aniline, pyridine, carbon tetrachloride, benzene, ethyl acetate, glacial acetic acid, were used. No fraction was ever obtained from which it was possible to extract an organic compound free from nitrogen or tin.

Identification of Diethyl Tin. The presence of diethyl tin was shown by converting it to diethyltin dichloride. The ether solution of diethyl tin was evaporated to dryness whereby a white amorphous powder, diethyltin oxide, was deposited. The powder was suspended in acetic anhydride, treated with dilute hydrochloric acid and extracted with ether. Upon evaporating the ether solution a colorless crystalline compound melting at 76-78°C was left behind, indicating diethyltin dichloride (53).

3. Sodium and Potassium Triphenylmethide

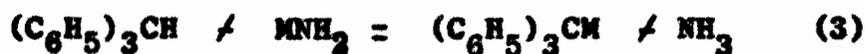
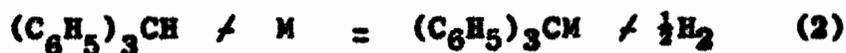
Attempts were made to cause a reaction between alkali metal derivatives and cellulose nitrate in a suitable solvent. The reactive alkali metal alkyls are immediately ammonolyzed in liquid ammonia according to the following reaction (42, 199):



Solvents in which they are relatively stable are non-solvents for cellulose nitrate. The alkali metal triphenylmethides, on the other hand, are soluble and stable in liquid ammonia. For this reason, and because of their reactivity, the sodium and potassium derivatives were studied.

(a). Introduction

The sodium and potassium triphenylmethides may be prepared in liquid ammonia from triphenylmethylchloride or triphenylmethane according to the following reactions (96, 97, 99).



Reactions 1 and 2 take place somewhat slowly, but Reaction 3 takes place immediately. The end of the re-

action is indicated by an intense red coloration of the solution.

The sodium and potassium triphenylmethides are conductors in liquid ammonia, thus indicating that they are true salts and that they undergo normal ionization. Sodium triphenylmethide may be considered to be the salt of a weak acid, triphenylmethane, and a weak base, sodium amide. It ammonolyzes to a slight extent in liquid ammonia. The potassium salt is more stable, since potassium amide is a stronger base than sodium amide.

(b). Experimental

Reaction with Sodium Triphenylmethide. To a solution of 1.0 gram of sodium in liquid ammonia was added 10.6 grams of triphenylmethane and the solution stirred with a mechanical stirrer. At the end of several hours the characteristic color of the sodium disappeared and the solution turned a deep red color. In other experiments the sodium was first converted to sodium amide, using a piece of rusty iron as catalyst, and then an equivalent amount of triphenylmethane added to the sodium amide. A slight excess of triphenylmethane was always added to insure complete conversion of the sodium or the amide.

Immediately after the completion of the reaction, cellulose nitrate (10 grams) was added, the solution

stirred for a period of several hours and the ammonia then allowed to evaporate. The residue was extremely heterogeneous in color, varying from white to deep brown, and occasionally streaked with red bands. The residue was extracted with 200 ml. of ethanol, in 50 ml. portions, and then with an equal volume of acetone.

Alcohol Extract. The alcohol extract, slightly yellow in color, was distinctly alkaline to litmus. It showed a positive sodium flame test and a faint test for nitrates. Addition of water precipitated a fine white powder which could be filtered after allowing to stand for about one hour. It dried to a faint yellow colored powder melting at 90-93°C. The powder was dissolved in hot alcohol and precipitated from the cold solution by the addition of water. By this method a white (sometimes very faintly yellow) crystalline solid was obtained having a melting point of 91-93°C. Triphenylmethane melts at 92.5°C (131).

Acetone Extract. The acetone extract, faintly yellow in color, was neutral to litmus. It gave a faint sodium flame test but a negative nitrate test. Addition of water precipitated a white powder which was dissolved in ethanol and precipitated by the addition of water. The product melted at 91.5-93°C.

Residue Left After Extraction. The physical characteristics of the residue were dependent on the method of preparation. The product obtained from sodium was of a dark brown color, hygroscopic, and very soluble in water; the product obtained from sodium amide was of light brown color, non-hygroscopic, but somewhat soluble in water. In both cases the aqueous solution was alkaline to phenolphthalein, and gave a negative nitrate test. Dissolution of the product in concentrated sulfuric acid gave a solution showing a positive test for nitrate nitrogen. The presence of an amino group was shown by diazotization and coupling with alpha-naphthol to form a blue-black dye (49). Kjeldahl analysis of the product indicated the presence of up to six per cent amino nitrogen and up to four per cent nitrate nitrogen.

4. Alkali Metal Alkyls

(a). Introduction

When aryl or alkyl halides are treated with sodium or potassium metal in liquid ammonia, a number of reactions occur in accordance with the following simplified series of equations (9, 34, 181):



Shreve and co-workers (165, 166) have shown that the above equations do not necessarily account for the mechanism of the reaction because the final product consists of a mixture of hydrocarbons, and primary, secondary and tertiary amines. However, it is generally agreed that a metallic alkyl is formed as an intermediate product.

If the reaction between an alkyl monohalide and an alkali metal be carried out in liquid ammonia in the presence of cellulose nitrate several other reactions are theoretically possible. For example, the cellulose nitrate might react with the amine to form a cellulose alkyl amine



or, it might react with the sodium alkyl to form an alkyl cellulose:



The formation of the alkyl cellulose, however, would be dependent upon the rate of reaction of the various competitive reactions, and would be possible only if the rate of Reaction 5 were faster than the rate of Reactions 2 and 4.

(b). Experimental

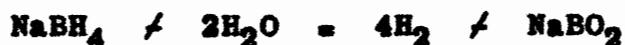
To a dispersion of cellulose nitrate (11.5 g.) in liquid ammonia were added ethyl bromide (4.7 g.) and sodium metal (2.0 g.) in that order. The blue color indicative of sodium dissolved in liquid ammonia was discharged as fast as the metal went into solution, and vigorous boiling of the liquid ammonia indicated that a reaction ensued. The resulting mixture was dark yellow in color, but after stirring for several hours it turned light red, and all suspended matter went into solution, whereupon the liquid ammonia was allowed to evaporate. The product obtained was dark tan in color and was shown to contain both amino and nitrate nitrogen.

Additional experiments were carried out using n-butyl bromide with sodium metal, and the two bromides with potassium metal. In all cases the product obtained was shown to contain both amino and nitrate nitrogen.

C. ACTION OF SODIUM BOROHYDRIDE ON CELLULOSE NITRATE

The synthesis of sodium borohydride (NaBH_4) by Schlesinger and co-workers (159) in 1946 introduced a powerful reducing agent to the chemical field. Within the last few years a number of investigations have been published describing its use for: the reduction of inorganic ions in analytical analysis (109, 114); the selective reduction of aldehydes, ketones, and acid chlorides (23); the reduction of simple sugars (1); the generation of hydrogen (161).

Sodium borohydride is a white crystalline salt-like compound, stable in air up to 300°C . It is very soluble in liquid ammonia (104g./100 g. solvent), the lower aliphatic amines, and water. In cold aqueous solutions it is fairly stable, but reacts rapidly at higher temperatures and in the presence of acids in accordance with the following equations (33, 114, 160):



The mechanism of the reduction of organic compounds has not been definitely established, but the course of

the reduction of ketones has been formulated as follows
(23, 160):



1. Introduction

The study of a possible reaction between sodium borohydride and cellulose nitrate was initiated because of the publications referring to the reducing action of the hydride, and to its solubility in liquid ammonia. In the preliminary investigations the reaction was carried out by dispersing the cellulose nitrate in liquid ammonia, adding sodium borohydride, and after stirring for several hours allowing the ammonia to evaporate. A white residue remained. Acetone was then added to dissolve any unreacted cellulose nitrate, and to react with any unreacted sodium borohydride. The white residue was insoluble in acetone, and on standing, both the residue and the acetone turned yellow. The color change and the solubility phenomena were taken as evidence that some sort of a reaction had occurred between the cellulose nitrate and sodium borohydride in liquid ammonia. Subsequent work, however, showed that the reaction would proceed in acetone solution without previous treatment in liquid

ammonia, and the investigation was turned in that direction. It was concluded that no reaction had occurred in liquid ammonia.

Towards the end of the research the effect of liquid ammonia on cellulose nitrate was investigated. It was found that when cellulose nitrate was dispersed in liquid ammonia and the ammonia allowed to evaporate, a brown residue was obtained. This was in marked contrast to the white residue obtained in the presence of sodium borohydride. Therefore it became evident that some sort of reaction had occurred between cellulose nitrate and sodium borohydride in liquid ammonia, and that the reaction product was affected by the addition of acetone. This idea will be discussed in a later section.

The reaction between cellulose nitrate and sodium borohydride in acetone solution appears to be exceedingly complicated, and quantitative determinations of the stoichiometric relationship have not been worked out. The cellulose nitrate-sodium borohydride complex which is formed is insoluble in acetone, and its solubility in other solvents depends upon the initial concentration of sodium borohydride. By keeping constant the weight of cellulose nitrate (1.0 g.) and the volume of acetone (100 ml.) and varying the weight of sodium

borohydride, two types of complex are formed. Up to and including 1.5 g. of sodium borohydride, the complex is only very slightly soluble in water and 10 per cent sodium hydroxide solution. From 2.0 to 3.5 grams the complex is readily soluble in the above solvents. In all cases, however, the complex is very soluble in glacial acetic acid. No experiments have been carried out using more than 3.5 grams of the hydride. However, judging from the general trend, there is no reason to believe that there would be any difference in the solubility characteristics of the complex so obtained.

The division on the basis of water solubility is not very sharp. As the amount of sodium borohydride is increased the solubility of the complex increases until it is completely water soluble. The critical range appears to lie between 1.5 and 2.0 grams, but in no experiment has a completely water soluble product been obtained using less than 2.0 grams of sodium borohydride.

2. Water Soluble Complex

(a). Preparation of the Complex

To a solution of 1.0 gram of cellulose nitrate in 100 ml. of acetone contained in a 250 ml. Erlenmeyer flask were added 2.0 grams of powdered sodium borohydride

and the flask was gently swirled. The hydride did not dissolve. A few seconds after the addition of the hydride gelation began, and within a few minutes the entire solution had gelled. On further shaking a liquid phase was formed, and the gel was broken up into small lumps which settled to the bottom of the flask. The reaction was exothermic, and to prevent loss of the solvent the flask was fitted with a reflux condenser. During the course of the reaction both the gel and the supernatant liquid turned light amber in color. The color began to appear within a few minutes after the formation of the liquid phase, and about the same time that the temperature increase became noticeable.

The reaction was apparently complete after about thirty minutes, and the temperature gradually dropped to room temperature. To facilitate filtration, the reaction mixture was allowed to stand at room temperature for at least twelve hours. The gel was filtered, extracted with acetone, and dried in air.

The dried residue was amber in color, and slightly hygroscopic. It was insoluble (or only very slightly soluble) in all common solvents with the exception of 5-10% aqueous sodium hydroxide, water, and glacial acetic acid. Qualitative analysis showed the presence of sodium, boron, and nitrite nitrogen. The qualita-

tive procedures used throughout these experiments are discussed in another section.

On standing at room temperature for several days the filtrate deposited a light amber residue. The formation of this sediment was not due to evaporation of the solvent, as it formed even when the filtrate was kept in a sealed flask. The sediment appeared to be similar in every respect to the original residue except that it was much more hygroscopic.

The filtrate, light amber in color, was alkaline to litmus. Analysis showed the presence of boron, sodium, and a faint trace of nitrite nitrogen. On evaporation to dryness it left an organic and inorganic ash, which contained sodium and boron, but no nitrogen. Most of the filtrate distilled over in the range from 53-57°C, this fraction being acetone; above this temperature no sharp fraction could be obtained. The last drop distilled over at about 140°C. A trace of isopropanol was detected in the distillate coming over at about 80°. The filtrate appeared to be a solution of acetone, organic decomposition products, and inorganic salt, and possible condensation products.

(b). Sodium Hydroxide Solution

The complex was readily soluble in aqueous 10% sodium hydroxide solution. On acidification with dilute

hydrochloric or acetic acid there was a change in color at the neutralization point, from dark amber to light yellow. Upon addition of an excess of acid, the solution became cloudy, and on standing, a brownish sediment formed. No distinct solid residue was obtained on filtration. The same results were obtained using alcoholic sodium hydroxide solution.

(c). Aqueous Solution

The solubility and the properties of the aqueous solution of the complex were found to be dependent on the volume of water used to effect solution.

Large Volume of Water. The complex was entirely soluble in a large volume of water (over 50 ml.), the solution being light yellow to light orange in color. On the addition of a large volume of ethanol (over 200 ml.), the solution became turbid, and after standing for several days a small amount of residue deposited. Most of the residue, however, remained in suspension and would not settle. It was so finely divided that it could not be easily separated by filtration or centrifugation.

Small Volume of Water. When a small volume of water (20-30 ml.) was used, the complex was apparently hydrolyzed. Part of the hydrolysis product went into

solution, and part remained undissolved. The residue was filtered, washed with alcohol, then ether, and dried in air. The dried product had a faint yellow color and was soluble in an excess of water. It appeared to be an inorganic compound of sodium and boron, with some organic (yellow) impurities. No nitrogen was present.

The filtrate after removal of the hydrolysis product gave positive tests for sodium, boron, and nitrite nitrogen. It was treated with about 100 ml. of ethanol. A flocculent light tan precipitate formed immediately and slowly settled to the bottom. At this point (but not before) it filtered readily, and frequently decantation was sufficient to assure complete separation. The color of this residue varied from light brown to dark amber in color, and was somewhat waxy in appearance.

The waxy residue was dissolved in a minimum amount of water, filtered to remove any undissolved material, treated with ethanol, and the precipitate which was formed allowed to settle. This process of dissolution and precipitation was repeated four or five times, and a light tan powder was obtained which was still insoluble in acetone. It gave positive tests for sodium and boron, but negative tests for nitrogen.

At each step the filtrate became lighter in color and finally became almost water white. The amount of dissolved material decreased and after the fourth or fifth precipitation was negligible. Sodium and nitrogen were detected in the first few steps.

Acetone could be used in the place of alcohol to effect precipitation. The precipitate was similar to the one obtained from alcohol. The volume of acetone required, however, was much larger than the volume of alcohol, and the precipitate took a much longer time to settle.

(d). Glacial Acetic Acid Solution

The cellulose nitrate-sodium borohydride complex dissolved in glacial acetic acid forming a dark amber colored solution. On standing for about two or three days, a white to pale yellow residue was deposited. The formation of the residue appeared to be independent of the amount of acetic acid used, although for subsequent treatment, better results were obtained when the volume was kept small. On the other hand, if the volume was too small, a thick viscous solution was obtained which could not be easily handled. The precipitate was filtered, washed with acetic acid, then ether, and dried in air. The final product was very pale yellow, and soluble in a large volume of water. It appeared to be an inorganic

compound of sodium and boron, together with some organic (yellow) impurities. No nitrogen was present.

The amber colored filtrate contained sodium, boron and nitrogen. The addition of ether deposited a curdy yellow precipitate which could be readily filtered. Further treatment of the filtrate with ether deposited a voluminous white crystalline precipitate. Both precipitates were somewhat unstable and required immediate treatment.

First Precipitate. The precipitate had a strong odor of acetic acid which could not be removed by repeated washing with ether. When placed in a beaker it slowly reverted to a dark amber colored very viscous liquid; when left in the filter paper the liquid was absorbed by the paper. The residue (or liquid) could be stabilized by treatment either with glacial acetic acid or with water.

i. Glacial Acetic Acid. Although precipitated from acetic acid solution the yellow residue was now only partially soluble in acetic acid. The insoluble portion was readily filtered and after being thoroughly washed with acetic acid and ether was stable in air. It dried to a light tan colored solid, insoluble in acetone, and which burned readily without leaving an ash. It appeared to contain no inorganic matter.

Treatment of the filtrate from above with ether precipitated a slight amount of curdy yellow residue which could be stabilized as described. The filtrate contained sodium, boron, and nitrogen.

ii. Water. The yellow residue (or liquid) was dissolved in a small volume of water, and a voluminous light brown precipitate obtained by the addition of alcohol. The precipitate was filtered, washed with alcohol and ether, and dried in air. The dried product was very slightly soluble in acetic acid and insoluble in acetone. It was a light tan amorphous powder which appeared to contain no inorganic matter. The filtrate contained traces of boron, sodium and nitrogen.

Second Precipitate. After removal of the yellow residue the filtrate was treated with an additional 50-100 ml. of ether. Within a few minutes a voluminous white crystalline residue was deposited. If allowed to stand in air, it absorbed water and dissolved. In this state it could not be recrystallized even by dissolution in acetic acid and treatment with ether.

It could be recrystallized by immediate dissolution in acetic acid, precipitation with ether, and thorough washing with ether. By this procedure it was possible to obtain a white powdery substance stable in air. It was identified as sodium acetate.

(e). Diagram of Experimental Procedure

Schematic diagrams of the experimental procedure for the treatment of the complex with water or glacial acetic acid are given in Figures III and IV.

3. Water Insoluble Complex

(a). Preparation of the Complex

In general the procedure for the preparation of the water soluble complex using 1.0 gram of sodium borohydride was similar to that for the preparation of the water soluble complex. The reaction was slightly exothermic, but reflux conditions were not necessary. The reaction was apparently complete within a few hours, but to facilitate filtration the reaction mixture was allowed to stand for at least twelve hours. The complex was light yellow in color, and gave positive tests for sodium, boron, and nitrogen.

The filtrate, light yellow in color, was treated in a similar manner to the filtrate obtained from the water soluble complex. The results were the same.

(b). Treatment with Sodium Hydroxide

The complex was very slightly soluble in cold aqueous 10% sodium hydroxide, and charred by hot sodium hydroxide. Similar results were obtained with alcoholic sodium hydroxide.

(c). Treatment with Water

Cold Water. The complex was only slightly soluble in cold water. When kept in contact with water for a period of time, the water layer became light yellow and the color of the insoluble residue decreased in intensity. The solubility of the complex increased with an increase in the initial concentration of sodium borohydride. Thus the complex obtained from 1.5 grams of sodium borohydride was completely soluble, but no samples were ever obtained which were completely water soluble.

Treatment of the aqueous extract with alcohol precipitated a light colored residue which settled only on long standing. The amount of precipitate formed was small, and increased with an increase in the solubility of the complex. The precipitate was difficult to separate and the results were not conclusive.

The water insoluble portion of the original complex was now light yellow in color. It burned readily without leaving an ash, and gave a positive diphenylamine test for nitrogen. It was insoluble in acetone and soluble in glacial acetic acid. No tests for sodium and boron could be obtained.

Hot Water. When the complex was refluxed with water for several hours the aqueous layer gradually became turbid and chocolate brown in color, and gave

positive tests for sodium and boron. The color of the insoluble residue gradually changed from yellow to light chocolate brown. On prolonged boiling it turned to a creamy white solid insoluble in acetone. It gave a positive diphenylamine test.

(d). Glacial Acetic Acid Solution

The complex dissolved readily in glacial acetic acid forming a light yellow to light orange solution. On standing for several days, a white to faint yellow residue deposited. The residue was filtered, washed with acetic acid and ether and dried in air. The residue was soluble in water, and appeared to be an inorganic compound of sodium and boron. It did not contain nitrogen. As in the case of the water soluble complex the volume of acetic acid did not appear to be critical.

The filtrate, light amber in color, contained sodium, boron, and nitrogen. It was treated with water or with ether.

Treatment with Water. The addition of water to the acetic acid solution precipitated a white residue which dried to a light tan colored solid, insoluble in alcohol and ether, but soluble in acetone. The product burned readily without leaving an ash. It gave a positive diphenylamine test, but negative tests for sodium and boron. The filtrate gave a faint test for sodium and boron.

Neutralization of the glacial acetic acid solution with sodium hydroxide precipitated a residue having properties similar to those outlined above.

Treatment with Ether. The light orange colored filtrate on treatment with about 100 ml. of ether deposited a curdy yellow residue which could be readily filtered. On further treatment of the filtrate with ether, a voluminous white precipitate identified as sodium acetate was obtained.

The yellow residue was similar to the one obtained from the water soluble complex in having a strong odor of acetic acid and the tendency to revert to a viscous light yellow oil. However, it differed in being insoluble in water, and could be stabilized by treatment with water, or with glacial acetic acid.

i. Glacial Acetic Acid. The residue was only partially soluble in acetic acid. The insoluble portion after being thoroughly washed with acetic acid and ether was stable in air. It dried to a light tan colored solid insoluble in acetone, and which burned readily without leaving an ash. It did not appear to contain any inorganic matter.

Treatment of the filtrate from above with ether precipitated a slight amount of curdy yellow residue which could be stabilized as described. The filtrate contained sodium, boron and nitrogen.

ii. Water. Treatment of the solid (or liquid) with water stabilized it and deposited a dark white residue insoluble in alcohol and ether, but soluble in acetic acid. The solubility in acetone appeared to increase with the initial amount of sodium borohydride. No product, however, was ever obtained which was completely soluble in acetone. It contained a trace of nitrogen, but no sodium or boron, and it burned readily without leaving an ash. The filtrate gave faint tests for sodium, boron and nitrogen.

(e). Diagram of Experimental Procedure

The schematic diagram of the experimental procedure for treatment of the complex with glacial acetic acid is given in Figure 5.

4. General Discussion

Table III gives a comparison of the important steps in the treatment of the water soluble and water insoluble addition compounds. It has been found impossible to develop a procedure applicable to all experiments, even when using the same concentrations of sodium borohydride. With the exception of the original volume of acetone, all volumes of solvents and precipitants are only approximate. The procedures and analytical results given in the various sections are based upon a

**Cellulose nitrate, NaBH₄
in acetone**

Residue	Filtrate
<p>Light amber colored residue. Extracted with acetone. Air dried to give amber colored slightly hygroscopic material. Contains Na, B, N. Soluble in 10% NaOH, water. Addition of small volume of water results in partial solution.</p>	<p>Light amber colored sol. Contains Na, B, N. Reject.</p>

Residue	Filtrate
<p>Washed with alcohol and ether. Dried product is light yellow colored solid. Appears to be inorganic compound of Na and B. No N.</p>	<p>Dark amber colored solution. Contains Na, B, N. Precipitate formed on addition of large volume of alcohol.</p>

Residue	Filtrate
<p>Dissolved in very small volume of water and reprecipitated with alcohol. Final product is light tan powder. Procedure repeated 4-5 times. Insoluble in acetone. Contains Na and B. No N.</p>	<p>Contains Na, N. Reject.</p>

FIGURE 3

**TREATMENT OF WATER SOLUBLE COMPLEX
WITH WATER**

Cellulose nitrate, NaBH ₄ in acetone					
Residue	Filtrate				
As previously described. Complex totally soluble in glacial acetic acid. On standing 2-3 days a white residue is deposited.	As previously described.				
Residue	Filtrate				
Washed with acetic acid and ether, dried in air. Product white to light yellow in color. Appears to be compound of Na and B. No N.	Light amber colored solution. Contains Na, B, N. Yellow curdy precipitate formed on addition of ether.				
	<table border="1"> <thead> <tr> <th style="text-align: center;">Residue</th> <th style="text-align: center;">Filtrate</th> </tr> </thead> <tbody> <tr> <td style="vertical-align: top;">Precipitate reverts to viscous oil on standing. Treated with acetic acid or water.</td> <td style="vertical-align: top;">On addition of ether sodium acetate deposited.</td> </tr> </tbody> </table>	Residue	Filtrate	Precipitate reverts to viscous oil on standing. Treated with acetic acid or water.	On addition of ether sodium acetate deposited.
Residue	Filtrate				
Precipitate reverts to viscous oil on standing. Treated with acetic acid or water.	On addition of ether sodium acetate deposited.				
Acetic Acid	Water				
Precipitate only partially soluble in HC ₂ H ₃ O ₂ . Stable product obtained by treatment with HC ₂ H ₃ O ₂ and washing with ether. Insoluble in acetone. No Na, B, N.	Precipitate soluble in water. Addition of ethanol forms light brown precipitate insoluble in acetone. No Na, B, N.				

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FIGURE 4

**TREATMENT OF WATER SOLUBLE COMPLEX
WITH GLACIAL ACETIC ACID**

Cellulose nitrate, NaBH_4 , in acetone

Residue	Filtrate
Light yellow residue. Extracted with acetone, dried in air. Contains Na, B, N. Insoluble in 10% NaOH, water; soluble in acetic acid.	Light yellow solution. Contains Na, B, N. Reject.
Residue	Filtrate
Washed with $\text{HC}_2\text{H}_3\text{O}_2$ and ether, dried in air. Product white to light yellow in color. Appears to be compound of Na, and B. No N.	Light amber colored solution. Contains Na, B, N. May be treated with water or ether. Water: Precipitates white residue soluble in acetone. Positive diphenylamine test for N. No Na, or B. Burns without leaving ash. Ether: Forms curdy yellow precipitate.
Residue	Filtrate
Acetic Acid	Water
Stable product obtained by washing with acetic acid and ether. Insoluble in acetone. No Na, B, N.	Reverts to viscous oil on standing. Treated with acetic acid or water. On addition of ether $\text{NaC}_2\text{H}_3\text{O}_2$ deposited. Dark white product formed. Slightly soluble in acetone. Traces of N. No Na or B. Burns readily.

FIGURE 5

TREATMENT OF WATER INSOLUBLE COMPLEX
WITH GLACIAL ACETIC ACID

TABLE III

COMPARISON OF WATER SOLUBLE AND WATER INSOLUBLE COMPLEX

	<u>Water Soluble Complex</u>	<u>Water Insoluble Complex</u>
1. Amount of NaBH ₄ .	Over 2.0 grams.	Under 2.0 grams.
2. Time of Reaction.	Less than one hour.	Several hours.
3. Temperature of Reaction.	Reaction vigorous; reflux conditions necessary.	Reaction slightly exothermic; no reflux necessary.
4. Characteristics of complex.	Light amber color which deepens with increase in concentration of NaBH ₄ . Slightly hygroscopic. Contains Na, B, N.	Light yellow color which deepens with increase in concentration of NaBH ₄ . Contains Na, B, N.
5. Effect of cold H ₂ O on complex.	Complex totally soluble in large volume of H ₂ O. Only partially soluble in small volume. Insoluble residue soluble in excess H ₂ O. It is inorganic with small amount of organic impurity. Appears to be compound of Na and B; No N.	Slightly soluble. Solubility increases with increase in concentration of NaBH ₄ .
6. Nature of residue from 5.	-----	Light yellow color. Burns without leaving ash. Insoluble in acetone. Diphenylamine test positive.
7. Addition of alcohol to aqueous sol. of complex.	Precipitate formed. Process of solution and precipitation may be continued. Final product organic in nature but contains Na, and B; no N. Insoluble in acetone.	-----
8. Effect of HC ₂ H ₃ O ₂ on complex.	Complex soluble. On standing white residue deposits. Appears to be compound of Na and B; no N.	Same as water soluble complex.
9. Addition of ether to filtrate from 8.	Curdy yellow precipitate deposits.	Same as water soluble complex.
10. Addition of ether to filtrate from 9.	Sodium acetate precipitated.	Same as water soluble complex.
11. Nature of yellow precipitate from 8.	Has strong odor of acetic acid which cannot be removed by washing with ether. On standing reverts to dark amber colored liquid.	Same as water soluble complex. Liquid yellow in color.
12. Addition of H ₂ O to filtrate from 8.	-----	Light tan solid deposits. Soluble in acetone. Positive diphenylamine test for N; No Na and B. Burns without leaving ash.
13. Effect of HC ₂ H ₃ O ₂ on yellow ppt. from 9.	Light tan colored solid. Insoluble in acetone. Nitrogen test negative. No Na, B.	Same as water soluble complex.
14. Effect of H ₂ O on yellow ppt. from 9.	Precipitate completely soluble.	Precipitate insoluble, stabilized to dark white solid, slightly soluble in acetone. Contains trace of N. No Na or B. Burns readily without leaving ash.
15. Addition of alcohol to aq. solution of 14.	Light brown precipitate, insoluble in acetone. Negative tests for Na, B, and N.	-----

large number of determinations and are not to be taken as being indicative of any one experiment. In general, the procedures described in the previous sections are applicable to all concentrations of sodium borohydride within the given solubility range.

The following points are of importance:

Stability of Gel and Complex. Once formed the cellulose nitrate-sodium borohydride gel was extremely stable. Two samples kept at room temperature for about six months gave the same results on treatment with acetic acid as gels which were treated after standing for one day. The gels were also stable to further reaction, that is, a water insoluble gel could not be converted to a water soluble gel by the addition of sodium borohydride.

The air dried complex was stable at room temperature. Samples kept for a period of two years did not change in appearance and on treatment with acetic acid gave the same results as previously described.

All the investigations were carried out using the air dried complex. In one experiment the filtered gel was washed with acetone, and the excess acetone removed by suction. The acetone-wet complex on being dissolved in the appropriate solvent gave the same results as the air dried complex.

Effect of Temperature. A decrease in the temperature of the reaction mixture decreased the rate of reaction. Thus when sodium borohydride was added to acetone solutions of cellulose nitrate at 0°C gelation occurred, but no pronounced color change was observed until the mixture was allowed to warm up to room temperature. On the other hand, an increase in temperature did not appear to have any noticeable effect. In one experiment the reaction mixtures were refluxed on a water bath for about thirty minutes. The mixtures were exceedingly difficult to filter, but the residues gave the same results. Furthermore, it was not possible to convert a water insoluble gel to a water soluble gel by heating the reaction mixture.

Effect of Solvent. Acetone is reduced to isopropanol by the action of sodium borohydride. The reaction takes place in aqueous solution and then only on hydrolysis of an intermediate addition compound by sodium hydroxide. The reaction is described as being almost instantaneous.

No results have been reported in the literature on the action of solid sodium borohydride on acetone. In this investigation it was found that when powdered sodium borohydride was added to acetone, the hydride settled to the bottom of the flask and remained as a

free flowing powder for several hours. There was no change in the color of the solution. Under these conditions the addition of cellulose nitrate resulted in the formation of a yellow product. The cellulose nitrate was not in solution and the reaction product was heterogeneous in color. Unreacted cellulose nitrate was always present in the product. However, on standing, the cellulose nitrate went into solution and the reaction product became homogeneous.

When dry cellulose nitrate and powdered sodium borohydride were kept in contact with each other for several days, no reaction was evident.

Nitration of Final Product. The products which were obtained free from any inorganic material were treated with nitrating mixtures of $\text{HNO}_3\text{-H}_3\text{PO}_4\text{-P}_2\text{O}_5$ and $\text{HNO}_3\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ of varying concentrations. In each case the substance was decomposed and no reaction product could be obtained.

Yields. The yields of the products obtained from the acetic acid and water treatment were very low. In a few experiments as much as 0.3 gram of the product was obtained. This, however, was the exception and not the rule. The losses may be attributed to a number of causes: loss from incomplete precipitation of the gel during its formation; loss from incomplete precipitation of the products; manipulative losses.

5. Analytical Procedures

The analytical procedures used for the qualitative analysis of sodium, boron and nitrogen were based on the standard procedures given in the text-book by Treadwell and Hall (190) and need not be repeated here.

Various methods were used in preparing the sample for analysis. Solids were burned in a crucible, the organic ash ignited, and the residue extracted with water. The analysis was then carried out on the aqueous extract. Those solids which burned without leaving an ash were decomposed with concentrated sulfuric acid, evaporated to dryness, ignited, and extracted with water. The filtrates were troublesome because of their color, and, frequently, because of their alkalinity. They were evaporated to dryness, the residue ignited and extracted with water.

Sodium. Sodium was detected by the familiar yellow flame test and by the use of magnesium uranyl acetate.

Boron. A number of reagents were used for the determination of boron. Wherever possible the silver nitrate and mercuric chloride tests were used. Silver nitrate produces from cold borax solutions a white precipitate of silver metaborate. On warming a brown

precipitate of silver oxide is formed. Mercuric chloride produces a red precipitate of basic mercuric salt. In alkaline solutions the above tests could not be used. In such cases the solution was treated with barium chloride which produced a white precipitate of barium metaborate soluble in an excess of barium chloride. Whenever possible the characteristic green color flame of burning methyl borate was used as a check.

Nitrogen. The analysis of nitrogen presented the greatest difficulty because of the possibility of both nitrites and nitrates being present. The reaction with ferrous salts in the presence of acetic acid gives a positive test for nitrites in the presence of nitrates. However, there is absolutely no reliable qualitative test for the detection of nitrates in the presence of nitrites. When nitrites were found the solution was also found to have both reducing and oxidizing properties, indicative - but not conclusively - of nitrites.

When possible the solid product was decomposed by sodium fusion. The ensuing reaction was vigorous enough to melt soft glass, and the fusions had to be carried out in pyrex test tubes.

The diphenylamine-sulfuric acid test was occasionally used. The test is positive for both nitrites and

nitrates, but, unfortunately, it is so sensitive that a trace of impurity is sufficient to give positive results.

6. Reactions of Cellulose Nitrate With Sodium Borohydride in Solvents Other Than Acetone

In view of the possible reactivity of acetone with sodium borohydride a number of experiments were carried out in solvents unaffected by the hydride.

Cellulose nitrate (1.0 gram) was dispersed in ethyl acetate (100 ml.) and approximately one gram of sodium borohydride was added. The hydride did not go into solution, and no gelation occurred. On standing at room temperature a white residue slowly formed and gradually increased in quantity. The rate of formation of the residue was independent of the amount of sodium borohydride present. After standing for about one week the reaction mixture was filtered.

The filtrate reduced silver nitrate, and this was taken as an indication of the presence of unreacted sodium borohydride.

The residue was stable in air when dry. On ignition it burned readily leaving an ash which contained sodium and boron. It was soluble in water and all common cellulose nitrate solvents. In contact with acetone it

gradually turned light yellow, but never became water soluble. However, when the residue was kept in hot water for a period of time it became acetone soluble. The same results could be obtained by repeated washing with cold water. In this case the wash water had a reducing action on silver nitrate which gradually disappeared with continued washing. With the decrease in the reducing action of the wash water, the acetone solubility of the product increased.

From the results obtained it may be concluded that some type of addition compound was formed between sodium borohydride and cellulose nitrate and that the addition compound was readily hydrolyzed by water. Subsequent experiments were carried out in an attempt to establish a stoichiometric ratio between the reactants. No such ratio could be established. In all experiments, unreacted sodium borohydride was found in the filtrate. The filtrate, after the removal of the addition product was found to contain some organic matter which appeared to be unreacted cellulose nitrate.

Essentially similar results were obtained using 1-1 ether-alcohol solutions of cellulose nitrate. No indication of complex formation was evident using methanol or nitromethane as solvents. Sodium borohydride is decomposed in methanol (114) and this might explain

the negative results. In the case of nitromethane, however, no satisfactory explanation can be given at present.

After this phase of the investigation was concluded it was discovered that liquid ammonia converted cellulose nitrate to cellulose amine which is brown in color. In the preliminary experiments with sodium borohydride, the reaction was carried out in liquid ammonia, and a white residue was obtained on evaporation of the solvent ammonia. These experiments were repeated and it was found that the white residue contained only traces of amino nitrogen, but contained sodium and boron. The residue was readily hydrolyzed by water as described above, and it was assumed to be an addition compound of the ester and the hydride.

7. Reaction of Cellulose Nitrate (13.35% N)

With Sodium Borohydride

If the formation of the cellulose nitrate-sodium borohydride complex takes place through the nitrate groups, it is reasonable to expect that there should be a difference in the properties of the complex if the nitrate content of the ester is varied, and all other conditions held constant. To verify this assumption, cellulose nitrate containing 13.35 per cent nitrogen was treated with sodium borohydride.

The reactions were carried out using one gram of air dried cellulose nitrate dissolved in 100 ml. of acetone. Three sets of determinations were made using 1.0, 1.5 and 2.0 grams of sodium borohydride respectively. In general, the reactions were somewhat more vigorous than when the lower nitrate (12.12% N) was used, so that reflux conditions were necessary for the 1.5 g. sample, and in all cases the time required for the reaction to reach completion was decreased. For each concentration of sodium borohydride the color of the complex was somewhat deeper than that obtained by use of the lower nitrate. The water solubility increased, so that the complex prepared from 1.5 g. sodium borohydride was almost completely water soluble.

The reaction product was filtered, extracted with acetone and dried in air. The complex was dissolved in water and/or acetic acid and precipitated by the addition of appropriate non-solvents. The precipitates were treated according to the standard procedure. In all cases the results were similar in nature to those obtained with cellulose nitrate of lower nitrogen content.

8. Reaction of Cellulose and Cellulose Derivatives

With Sodium Borohydride

On the basis of the increased reactivity between cellulose nitrate and sodium borohydride as the nitrate

content of the ester increased, it was assumed that the complex was being formed through the nitrate groups. To verify this assumption, a number of experiments were carried out in which cellulose derivatives other than the nitrate were treated with sodium borohydride. To eliminate any effect due to the presence of a reactive solvent, water soluble cellulose derivatives were used.

One per cent solutions of methylcellulose, sodium carboxymethylcellulose and sodium cellulose sulfate were prepared, and one gram of sodium borohydride was added to each solution. The reaction mixtures were allowed to stand at room temperature for one day. There was no evidence of any reaction. Titration of the solutions with standard hydrochloric acid showed that the sodium borohydride had not reacted.

In other experiments cotton was steeped in 20% sodium hydroxide for a period of one hour. It was then pressed to remove excess caustic and added to a 2% solution of sodium borohydride in dilute sodium hydroxide. No evidence of any reaction was obtained.

9. Treatment of Acetone Solutions of Cellulose

Nitrate With Boron Compounds

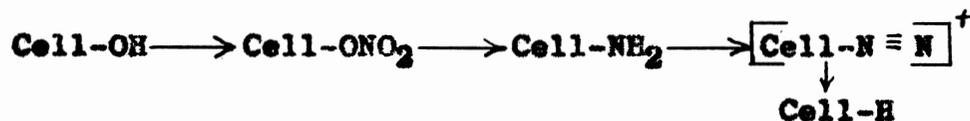
It has been known for some time (52), (82) that the physical properties of various polysaccharides are altered in a striking manner by the addition of borates.

Boric acid is said to increase the viscosity of cellulose derivatives, but borax is said to be without effect (79). The cellulose derivatives are not specified. With reference to cellulose nitrate it has been reported that both borax (21) and boric acid (123) cause gelation.

To test the gelling effect of boron compounds on cellulose nitrate the following experiments were carried out. Solutions of cellulose nitrate were made up containing 1.0 gram of the nitrate ester in 100 ml. of solvent, and 1.0 gram of the boron compound under investigation was added. The following compounds were used: ammonium perborate ($\text{NH}_4\text{BO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$), sodium perborate ($\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$), lead metaborate ($\text{Pb}(\text{BO}_2)_2 \cdot \text{H}_2\text{O}$), sodium borate ($\text{Na}_2\text{B}_4\text{O}_7$), borax, and boric acid. None of the above compounds were soluble in the acetone solution. The mixtures were allowed to stand at room temperature for several days and examined periodically. Although a slight increase in viscosity was evident, in no case was there any sign of coagulation. The cellulose nitrate could be recovered, apparently unchanged, by precipitation with water. No coagulation was observed after a period of three months.

D. PREPARATION OF CELLULOSE AMINE

Previous investigators (41, 49) in this Laboratory have shown that cellulose monoamine could be diazotized and coupled in a manner similar to aromatic amines. If it were possible to deaminate the cellulose diazonium salt it would then be possible to prepare a desoxy cellulose starting from cellulose. The steps in the following reaction are outlined in the following scheme:



This section deals with the experimental procedure for the preparation of cellulose amine. The diazotization and deamination of cellulose amine are discussed in the next section.

Due to the degradation of the cellulose chain occurring in the various steps of the scheme outlined above it was deemed advisable to start with a cellulose amine which was not too degraded. It was shown in a previous section (Part IV, Section C) of this thesis that the cellulose amine prepared by the reaction of cellulose nitrate and gaseous ammonia in acetone solution was insoluble in water, and, therefore, probably was not as degraded as the product obtained by the use

of sodium amide in liquid ammonia. This factor, together with the simplicity of the experimental technique involved made this method a logical choice for the preparation of cellulose amine.

Unfortunately, the present knowledge concerning the preparation of cellulose amine by the reaction of cellulose nitrate and gaseous ammonia is rather limited. Previous investigators (121, 127, 163) have shown that the method is feasible, but they were unable to obtain a stable product. It was originally proposed to study the problem in an effort to obtain a stable product, and to elucidate, if possible, the course of the reaction. During the course of the research it became apparent that a cellulose amine was the end product whenever cellulose nitrate was placed in contact with ammonia, either in the gaseous or liquid state. Furthermore it also became apparent that the mechanism of the reaction as previously proposed (41) was not entirely correct. For these reasons cellulose amine was prepared by several different methods, and the reaction was studied in far greater detail than had been anticipated.

1. Reaction of Cellulose Nitrate With Gaseous
Ammonia in Acetone Solution

In these experiments the reaction was carried out in an Erlenmeyer flask fitted with a two-hole rubber stopper.

One hole was fitted with a glass delivery tube reaching to the bottom of the flask and leading from the ammonia tank; the other hole was fitted with a piece of glass tubing leading to the ammonia absorber. All connections were made by rubber tubing. Using this apparatus the contents of the Erlenmeyer flask could be saturated with gaseous ammonia and the rubber connections then clamped so as to obtain a gas tight seal, and thus maintain an atmosphere of ammonia in the reaction vessel.

Into a solution containing ten grams of cellulose nitrate dispersed in 250 ml. of acetone contained in a 500 ml. Erlenmeyer flask was passed a stream of gaseous ammonia for approximately thirty minutes. The flask was then sealed and allowed to remain at room temperature. During the passage of the ammonia there was a slight change in the color of the solution (water white to pale yellow) and a very slight but noticeable increase in temperature.

On standing, the color of the solution gradually deepened to light yellow, dark yellow, and finally to a dark cherry red color. The color change took place within the first ten hours, and there was no further change for the next three or four days. The solution then became very dark and turbid, but no deposit was formed.

There was no increase in the temperature of the solution on standing. There was, however, an increase in pressure as evidenced by the fact that the stopper of the reaction flask was occasionally blown out. After several hours standing a vacuum developed in the flask and from then on there was no further change. When the stopper was blown out the solution was again saturated with ammonia and sealed.

The cellulose amine was precipitated from the reaction mixture by the addition of an appropriate non-solvent. Two non-solvents were used in these experiments: n-heptane and water.

n-Heptane. To the reaction mixture was added an equal volume of n-heptane. The cellulose amine separated out as a dark-red viscous layer which readily settled to the bottom of the flask; the supernatant liquid turned to a dark straw yellow color. The volume of n-heptane added was more than was necessary. However, below a certain volume of n-heptane there was an incomplete separation of the two phases, and since it was rather difficult to determine the exact volume required, an excess was always used.

Previous investigators (121, 127) separated the red layer and either dried it to obtain the product in the form of a dark brown gum, or, they dissolved it in

acetone and precipitated the reaction product by the addition of water. In the latter case, however, the product was unstable, and on standing reverted back to a gum. In this research it was found that excellent results were obtained by placing the whole in a separatory funnel, letting it stand for a sufficient length of time to insure complete separation of the two phases, and draining the lower (viscous) layer into a large volume of water with vigorous stirring. The cellulose amine precipitated out in the form of large tan flakes which were collected on a Buchner funnel and washed with a large volume of water. Under these conditions the final air dried product was stable on standing. Several samples kept for a period of fourteen months showed no tendency to revert to a gum.

When the supernatant liquid was treated with water two phases were formed, and a solid residue was observed at the interface of the two phases. The quantity was small in comparison to the total yield and no attempt was made to separate it.

Water. The cellulose amine obtained by the use of water as the non-solvent was similar in appearance and properties to that obtained by the use of n-heptane. Difficulty was encountered, however, due to the tendency of the product to precipitate out in the form of a very

fine suspension. Under this condition, filtration was carried out with difficulty, and a large part of the precipitate passed into the filtrate from which it was almost impossible to separate. It was found advantageous to concentrate the acetone solution under vacuum and then to pour the whole into a large volume of water with vigorous stirring. In this manner the cellulose amine precipitated in the form of large tan flakes which could be readily filtered on a Buchner funnel. The cellulose amine was thoroughly washed with water and dried in air.

The colloidal suspension was not observed in every experiment. In general those solutions which were precipitated before five days standing and those which were precipitated after thirty days standing showed the greatest tendency to revert to a colloidal state.

Purification. The products obtained by the above procedures were dissolved in a small volume of acetone and the syrupy solution was then poured into a large volume of water with vigorous stirring. The cellulose amine precipitated in the form of large flakes which could be readily filtered. The product was thoroughly washed with water, dried in air, ground with a mortar and pestle and stored in screw-cap bottles. The final product was light tan in color and somewhat lighter in shade than the original unpurified product.

The volume of acetone used to dissolve the amine was very critical. If the resulting solution was too concentrated the amine precipitated as a semi-solid gummy mass when poured into water; if too dilute the amine passed into a colloidal state.

n-Heptane could not be used as a precipitant in these purification steps. A gum was formed which was not destroyed when poured into water. The stability of the gum was independent of the amount of acetone used.

With one sample the process of purification was repeated four times but there was no change in the color or the nitrogen content after the second step. At each step, however, a small quantity of the product was lost through incomplete precipitation.

Time of Reaction. When discussing the "time of reaction" previous investigators made no distinction between the length of time that the gaseous ammonia was passed through the solution, and the length of time that the reaction mixture was allowed to stand before precipitation of the amine. In these experiments it was found that of the two, the time of standing before precipitation was the more important factor. The minimum time before precipitation appeared to be about twelve hours, although evidence of amine formation was observed at the end of one hour. With respect to time of treatment

with ammonia, the important factor was to saturate the solution. In these experiments treatment with gaseous ammonia was arbitrarily standardized at thirty minutes, but no difference in results was evident when ammonia was passed through the solution continuously for a period of two hours, or intermittently for several days.

In order to study the effect of time of reaction (and incidently, the effect of the non-solvent), the following experiments were carried out. Twelve solutions were made up containing ten grams of cellulose nitrate dissolved in 250 ml. of acetone. Each solution was saturated with gaseous ammonia for a period of thirty minutes, the flasks then stoppered and allowed to stand at room temperature. At the end of a predetermined time interval each solution was divided into two parts; one part was precipitated by the addition of n-heptane, the other part by the addition of water was previously described. In this manner four samples were precipitated at the end of twelve, eighteen, twenty four, and forty eight hours respectively; six samples at five day intervals; one sample at the end of two months; and one sample at the end of three months.

The color of the products obtained in the above series of experiments varied from light tan (twelve hours)

to light brown (three months). As shown in Table IV the nitrogen content varied but little. The most pronounced difference was in the water solubility. The product obtained after thirty days reaction time was somewhat soluble in water but could be precipitated by the addition of water to the acetone solution. The products obtained from two or three months reaction time were so water soluble that they could not be precipitated from water solution, and only a small amount of product was obtained by the use of n-heptane. The other amines were insoluble in water. The solubility in other solvents was essentially the same. The aqueous solutions of cellulose amine were neutral to phenolphthalein.

Concentration of Acetone Solution. No study was made on the effect of concentration of the nature of the final product. The concentration was arbitrarily chosen in the ratio of two grams of cellulose nitrate to 100 ml. of acetone.

Temperature of Reaction. All reactions were carried out at room temperature. It has been shown (163) that an increase in temperature markedly increases the rate of formation of the amine, but leads to decomposition of the product. In this research it was shown that a decrease in temperature decreases the rate of reaction.

TABLE IV

NITROGEN CONTENT OF CELLULOSE AMINE PREPARED
IN ACETONE SOLUTION

No.	Time	Precipitant	Per Cent Nitrogen In Product		No. of Groups In Product		
			<u>NH₂</u>	<u>ONO₂</u>	<u>NH₂</u>	<u>ONO₂</u>	<u>OH</u>
1	12 hours	water	7.64	----			
2	12 hours	n-heptane	7.80	1.07	0.93	0.13	1.94
3	18 hours	water	8.20	----			
4	18 hours	n-heptane	7.72	0.85	0.92	0.19	1.98
5	24 hours	water	7.64	0.87	0.91	0.10	1.99
6	24 hours	n-heptane	8.01	1.04	0.95	0.12	1.93
7	5 days	water	7.53	----			
8	5 days	n-heptane	7.93	----			
9	10 days	water	7.70	----			
10	10 days	n-heptane	8.24	0.97	0.98	0.12	1.90
11	15 days	water	7.65	----			
12	15 days	n-heptane	7.99	----			
13	20 days	water	7.54	----			
14	20 days	n-heptane	8.05	0.72	0.95	0.09	1.96
15	25 days	water	7.69	----			
16	25 days	n-heptane	7.85	----			
17	30 days	water	8.06	----			
18	30 days	n-heptane	7.94	0.75	0.94	0.09	1.97
19	2 months	n-heptane	7.83	0.57	0.92	0.07	2.01
20	3 months	n-heptane	7.61	0.92	0.90	0.11	1.99

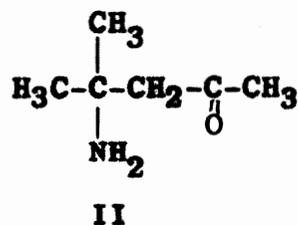
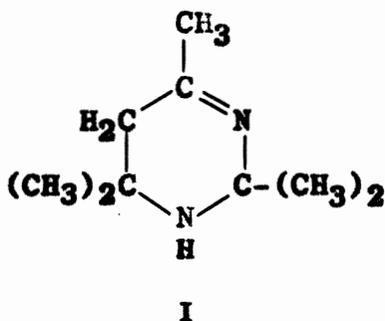
In several experiments the reaction mixture after saturation with ammonia was kept in a cold room at a temperature of 15°C. No color change to dark cherry red was observed within four or five days. When these solutions were allowed to come to room temperature, the reaction proceeded in the normal fashion.

Characteristics of the Amine. The product obtained in these various experiments contained up to one amino group per glucose anhydride unit, and some nitrate nitrogen as indicated by a positive brown ring test. The amine content decreased somewhat when the product was dissolved in acetone and precipitated with a non-solvent, but whether this was due to a hydrolytic attack on the amino group or to a removal of impurities could not be determined. To a lesser extent the same phenomena was true in the case of nitrate nitrogen. The amines were flammable, but unlike cellulose nitrate they left a carbonaceous ash. They gave a positive Hinsberg amine test (167), and a negative hydroxylamine test (41).

The solubility in various solvents was determined by placing about twenty milligrams of the amine in a test tube, adding a few milliliters of solvent, and letting stand at room temperature. The samples were examined at the end of one, twelve, and twenty four

hours, and classified as shown in Table V. The solutions in acetone, glacial acetic acid, and acetic anhydride were dark cherry red in color. The solutions in other solvents were light brown in color. The solubility in liquid ammonia was determined by adding the amine to liquid ammonia contained in a Dewar flask. The solution had a light cherry red color.

Effect of Solvent. In view of the reactivity of ammonia with the carbonyl group of various organic compounds it is not surprising to find a reaction occurring between acetone and ammonia. The main reaction product (16, 112) is 2,2,4,4,6-pentamethyl-2,3,4,5-tetrahydropyrimidine (I), commonly known as acetone, which on hydrolysis yields diacetoneamine (II).



Cellulose amine may be prepared by adding cellulose nitrate to a saturated ammoniacal acetone solution. The reactivity of cellulose nitrate with various amines is well known, and therefore it is possible that either

TABLE V

SOLUBILITY OF CELLULOSE AMINE

<u>Readily Soluble in</u>	<u>Slightly Soluble in</u>	<u>Soluble With Decomposition in</u>	<u>Insoluble in</u>
acetone	ethanol	10% NaOH	chloroform
glacial acetic acid	aniline	85% H ₃ PO ₄	carbon disulfide
acetic anhydride	ethyl acetate	Conc. H ₂ SO ₄	carbon tetrachloride
pyridine	n-butyl acetate	Conc. HCl	ether
methanol		Conc. HNO ₃	n-butyl bromide
1-1 ether-alcohol			ethyl bromide
liquid ammonia			isopropanol
			10% NaHCO ₃
			10% Na ₂ CO ₃
			6N Mineral acids
			6N acetic acid

diacetoneamine or acetoneamine, and not the ammonia, is the actual reactant with cellulose nitrate. Furthermore, as shown in Table VI, the nitrogen content of a hypothetical "cellulose diacetoneamine", or "cellulose acetoneamine" fall within the range of the nitrogen content of cellulose amine, and therefore the nature of the reaction product cannot be determined by nitrogen analysis alone.

No definite proof can be advanced to show that diacetoneamine, or acetoneamine, are not the actual reactants, but the following evidence is offered to show that it is highly improbable:

(1). Due to the low solubility of ammonia in acetone, the process of preparing acetoneamine by passing gaseous ammonia into acetone is a long one which requires numerous resaturations at intervals of five to seven days. The reaction of cellulose nitrate in ammoniacal acetone solution takes place within twelve hours. An ammoniacal solution of acetone was kept at room temperature for a period of three months. The solution turned yellow within several days, but then there was no further color change. No diacetoneamine could be isolated from the solution.

(2). It has been shown (16, 182) that the formation of diacetoneamine is catalyzed by am-

TABLE VI

THEORETICAL NITROGEN CONTENT OF CELLULOSE AMINE
AND SUBSTITUTED CELLULOSE AMINES

Amine	Generic Formula Degree of Substitution = 1	Per Cent Nitrogen		
		DS = 1	DS = 2	DS = 3
Cellulose Amine	$C_6H_7O_2 \begin{matrix} (OH)_2 \\ \\ NH_2 \end{matrix}$	8.69	17.49	26.40
Cellulose hydroxylamine	$C_6H_7O_2 \begin{matrix} (OH)_2 \\ \\ ONH_2 \end{matrix}$	7.91	14.58	20.28
Cellulose di-n-butyl amine	$C_6H_7O_2 \begin{matrix} (OH)_2 \\ \\ N(C_4H_9)_2 \end{matrix}$	5.13	7.68	8.48
Cellulose diacetoneamine	$C_6H_7O_2 \begin{matrix} (OH)_2 \\ \\ NHC_6H_{11}O \end{matrix}$	5.40	7.85	9.24
Cellulose acetoneine	$C_6H_7O_2 \begin{matrix} (OH)_2 \\ \\ N_2C_9H_{17} \end{matrix}$	9.39	12.89	14.72

monium salts, especially the nitrite and the nitrate. In view of the possibility of the formation of ammonium nitrite or nitrate as a by-product of the reaction between cellulose nitrate and ammonia, the amination was carried out in the presence of the above salts. The rate of reaction was not increased, nor was the nitrogen content of the final product. The results are tabulated in Table IV.

(3). Diacetoneamine hydrogen oxalate was prepared and added to cellulose nitrate dispersed in acetone. No reaction was observed within twenty four hours. Attempts to cause a reaction between cellulose nitrate and diacetoneamine were unsuccessful. Since diacetoneamine decomposes rapidly this should not be taken as an indication that no reaction is possible.

(4). The product of the reaction between cellulose nitrate and ammonia in acetone solution has the singular property of being diazotized and coupled with alpha- and beta-naphthol. This phenomena would not be expected with a product such as cellulose diacetoneamine or cellulose acetone.
Filtrate. The filtrate obtained on the precipitation of cellulose amine with water was dark red in color.

It was basic to litmus and gave a positive brown ring test for nitrites. On evaporation to dryness it deposited a carbonaceous ash, the aqueous extract of which gave a negative nitrite test.

2. Reaction of Cellulose Nitrate With Gaseous Ammonia

The effect of gaseous ammonia on dry cellulose nitrate at room temperature has not been investigated to any extent, although it has been reported (146) that gaseous ammonia has a degrading effect on the ester. In this research it was shown that under the effect of gaseous ammonia cellulose nitrate is converted to a cellulose amine.

A sample of cellulose nitrate was kept in an atmosphere of gaseous ammonia for a period of five days at room temperature. There was no change in the appearance of the nitrate within the first twenty four hours. Within the first two days, however, it became very light brown in color. The color gradually deepened, but after the third day there was no further visible change. The final product still retained its fibrous structure, but it had the chemical and physical properties attributed to cellulose amine. It contained both amino and nitrate nitrogen. The results of the nitrogen analysis are given in Table VII.

TABLE VII

NITROGEN CONTENT OF CELLULOSE AMINE PREPARED BY USE
OF GASEOUS OR LIQUID AMMONIA

<u>No.</u>	<u>Condition</u>	<u>Time</u>	<u>Per Cent Nitrogen In Product</u>	
			<u>NH₂</u>	<u>ONO₂</u>
1	Gaseous ammonia	3 days	5.92	6.34
2	Gaseous ammonia	3 days	6.04	5.76
3	Gaseous ammonia	5 days	7.21	4.67
4	Gaseous ammonia	5 days	7.03	4.52
5	Liquid ammonia	1 day	6.38	4.68
6	Liquid ammonia	1 day	6.01	5.31
7	Liquid ammonia	3 days	7.83	2.04
8	Liquid ammonia	3 days	7.92	1.84
9	Liquid ammonia and NaNH ₂	10 hours	7.82	0.52
10	Liquid ammonia and NaNH ₂	10 hours	7.63	----

The product was steeped in water and filtered. The filtrate, light yellow in color, gave a positive nitrite test and exhibited both oxidizing and reducing properties. On evaporation to dryness it deposited a slight amount of organic residue whose aqueous extract gave a negative nitrite test and had neither oxidizing nor reducing properties. The nitrogen content of the amine was decreased on washing.

3. Reaction of Cellulose Nitrate With Liquid Ammonia

The solubility of cellulose nitrate in liquid ammonia was investigated by Taft (183) who reported that the ester was degraded, but he made no mention of the possibility of a reaction occurring. Other investigators (181) have reported that cellulose nitrate may be recovered unchanged from liquid ammonia solution.

In this research a sample of cellulose nitrate was added to liquid ammonia contained in a Dewar flask, the mixture stirred for several hours, and the ammonia then allowed to evaporate. The light brown residue containing both amino and nitrate nitrogen had all the physical and chemical characteristics of a cellulose amine. The fibrous structure was lost as the amine was deposited in the form of a horny mass which could be easily ground with a mortar and pestle.

No color change was observed in the liquid ammonia within the first twelve hours, but then the solution turned light yellow, and the color gradually deepened to a light cherry red. When the reaction was stopped by the addition of water the product contained unreacted cellulose nitrate; when the ammonia was allowed to evaporate the product appeared homogeneous. The results of the nitrogen analysis are given in Table VII.

The product was steeped in water and filtered. The results obtained were similar to those described above.

4. Reaction of Cellulose Nitrate With Sodium Amide in Liquid Ammonia

The procedure used in these experiments was essentially that developed by Feild (41) and Green (49). The apparatus used is shown in Figure 2. The sodium amide was prepared by reacting sodium metal with liquid ammonia in the presence of a piece of rusty iron as a catalyst. When the formation of the sodium amide was completed cellulose nitrate was added and the mixture stirred for a period of about nine hours. The insoluble cellulose amine was allowed to settle and the supernatant ammonia was syphoned out of the flask. The amine was washed with several portions of liquid ammonia until the washings were white. The product obtained had all the physical and chemical properties of cellulose amine as described by Feild and Green.

The washings showed the presence of nitrite nitrogen. Previous investigators have reported the presence of nitrate nitrogen, but not nitrite nitrogen. The cellulose amine was dissolved in concentrated sulfuric acid, diluted with water, and treated with a saturated solution of ferrous sulfate. Due to the dark color of the solution no conclusive results were obtained, but it appeared that the nitrate test was positive. The diphenylamine test on the solid cellulose amine was positive.

E. PREPARATION AND PROPERTIES OF CELLULOSE DIAZONIUM SALTS

1. Diazotization

Diazotization, the reaction whereby a primary aromatic amine is converted into the diazonium salt, is usually carried out by dissolving the amine in dilute aqueous acid and adding a solution of sodium nitrite. It is necessary to keep the temperature low, as otherwise both the nitrous acid and the diazonium salt may decompose. Diazotization is a very well known reaction, and numerous experimental procedures have been published. These procedures, however, are in general specific for one species of amine, and not necessarily applicable, insofar as temperature, concentration, acid, etc., are concerned, to other amines.

In this research it was not possible to carry out the diazotization by the above procedure because of the insolubility of the cellulose amine in dilute mineral acids. Diazotization was effected by dissolving the amine in glacial acetic acid and adding a concentrated solution of sodium nitrite at a temperature between 15 and 20°C. This temperature was somewhat higher than that generally used for diazotizations, but it was necessary due to the high freezing point of

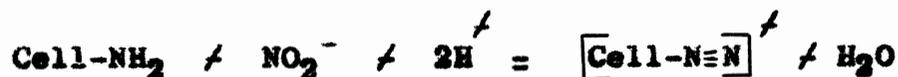
acetic acid, 16.6°C. However, numerous diazotizations have been successfully carried out at this temperature (92). A very small volume of water was used in preparing the sodium nitrite solution, so as to prevent precipitation of the cellulose amine. One mole of sodium nitrite is necessary for the diazotization of one mole of the amine, but a slight excess of the nitrite is frequently used to insure complete diazotization. In these experiments, due to the uncertainty of the formula weight of cellulose amine, it was found advantageous to use a large excess of the nitrite, and when necessary, to destroy the unreacted nitrite by adding urea to the solution.

The experimental procedure was as follows: Two grams of cellulose amine were dissolved in 100 ml. of glacial acetic acid and the solution was placed in an ice bath. When the temperature of the solution was down to 15-16°C, two grams of sodium nitrite (97% NaNO_2) dissolved in a few ml. of water were added with vigorous stirring. The reaction mixture was kept in an ice bath below 20°C until needed.

Diazotization was also carried out by passing gaseous nitrous acid (76) through a solution of the amine dissolved in acetic acid. Treatment was continued until the color of the amine solution turned from dark red to a light brown color.

In a number of experiments a water soluble cellulose amine was used. Diazotization was then carried out in dilute (3N) hydrochloric acid solution. Essentially the same experimental procedure was used.

Diazotization of cellulose amine is presumed to occur in accordance with the following equation:



2. Coupling

The coupling of diazonium salts takes place when an aromatic intermediate is treated with a diazonium salt solution.

In these experiments coupling was carried out by treating (at a temperature below 20°C), the diazonium salt prepared from two grams of cellulose amine with three grams of beta-naphthol dissolved in twenty ml. of ten per cent sodium hydroxide solution. The solution turned black immediately, and on addition of water a dark green precipitate settled out. It was collected on a Buchner funnel, washed with several small portions of water, and dried in air. The product was very slightly soluble in water, and completely soluble in acetone, ether, and ethanol, giving a dark yellow to light red solution. It was soluble in ten per cent sodium hydroxide solution giving a green solution.

Using essentially the same procedure coupling was also carried out with alpha-naphthol.

In these experiments an excess of the naphthol was used. This, however, had no influence on the results as shown by the following experiment. Acetic acid was treated with nitrous acid and then beta-naphthol added. The solution turned black. The beta-naphthol, however, was precipitated on the addition of water. It is noteworthy that a much larger volume of water was necessary to precipitate the beta-naphthol than to precipitate the coupled product.

In other experiments it was shown that there is no reaction between beta-naphthol and cellulose amine in acetic acid solution without previous treatment with nitrous acid.

The dyes thus formed were stable to reduction with such reducing agents as stannous chloride or zinc-hydrochloric acid. Nitrogen analyses on the product made from beta-naphthol showed 5.3 per cent nitrogen. This value is much lower than would be expected if a mono-azo compound were formed (theoretical 8.83% N).

The results obtained in these experiments are in agreement with those obtained by Green (49) who studied the coupling of cellulose diazonium salts to some extent.

3. Deamination

Methods of reduction are available for the replacement of the diazonium group by hydrogen; the reaction is described as deamination. Diazonium compounds have been treated with a great variety of deaminating agents, however, the more important of these processes involved reduction by alcohols or hypophosphorous acid (92).

(a). Use of Ethyl Alcohol

Some diazonium salts are converted to the corresponding hydrocarbon by heating them with ethyl alcohol. This method, is not very general since ethers are frequently formed as the principle product of reaction (93). However, in many cases, depending upon the nature of the amine, and the experimental conditions, excellent results are obtained (92).

Deamination was carried out by adding 20 ml. of ethanol (95%) to the cellulose diazonium salt prepared from two grams of cellulose amine. The solution was allowed to stand at room temperature for twenty four hours, and the reaction product then precipitated by the addition of water. The precipitate was collected on a Buchner funnel, washed with water, and dried in air. The reaction product was similar in appearance to the original amine, but there was a loss in the amino nitrogen content.

In other experiments the solution after the addition of alcohol was heated under reflux to the boiling point of alcohol. The solution was then either treated with water immediately, or allowed to stand at room temperature for twenty four hours and then treated with water. The precipitate was separated as described above. The increase in temperature appeared to have no effect on the course of the reaction as evidenced by nitrogen analysis. Time appeared to be the more important factor. No appreciable decrease in nitrogen content was observed unless the reaction mixture was allowed to stand at least twelve hours, but no increase in deamination was observed after twenty four hours.

In other experiments finely divided copper, and zinc, were added with the alcohol, without beneficial results being obtained.

(b). Use of Hypophosphorous Acid

A more general procedure for the deamination of diazonium salts is treatment with hypophosphorous acid. The procedure is simple in its operation and is more widely applicable than the one using alcohol.

To a solution of cellulose diazonium salt prepared from two grams of cellulose amine were added 25 ml. of ice cold 50 per cent aqueous hypophosphorous acid (15 grams H_3PO_2) and the reaction allowed to proceed at

a temperature below 20°C for several hours, and then allowed to stand at room temperature for an additional twenty four hours. The deaminated product was precipitated by the addition of water, filtered, washed with water, and dried in air. The dried product was light tan in color, and was much lighter than the original amine. It exhibited essentially the same solubility characteristics as cellulose amine.

Several deaminations were attempted at the boiling point of the reaction mixture but on heating to about 70°C the reaction became vigorous and could not be kept under control. A colorless, inert gas, presumably nitrogen, was evolved.

(c). Results

In Table VIII there is listed the results of eighteen typical deamination experiments using three different samples of cellulose amine. The cellulose amine in sample A was a water soluble product prepared by reaction in liquid ammonia in the presence of sodium amide; samples B and C were prepared by reaction with gaseous ammonia in acetone solution.

All deaminations with alcohol or hypophosphorous acid were carried out by allowing the reaction mixture to stand for twenty four hours at room temperature. No

TABLE VIII

NITROGEN CONTENT OF DEAMINATED AMINES

<u>Sample</u>	<u>Per Cent Nitrogen in Original Amine</u>		<u>Per Cent Nitrogen in Deaminated Product Using</u>	
	<u>NH₂</u>	<u>ONO₂</u>	<u>C₂H₅OH</u>	<u>H₃PO₂</u>
A	7.82	0.52	5.62	1.78
			4.30	1.47
			4.06	1.52
B	8.01	1.04	5.79	1.63
			4.86	0.52
			5.04	1.37
C	7.64	0.87	6.31	1.27
			4.75	1.84
			4.93	2.02

results are given for deamination with alcohol carried out under reflux, but if such reactions were allowed to stand for twenty four hours the results were in accord with those listed, otherwise, there was very little if any deamination.

Each sample was analyzed for both amino and nitrate nitrogen; the nitrate content remained essentially constant, the greatest difference 0.3 per cent. On this basis it may be presumed that the nitrate groups present in the cellulose amine were not effected.

4. Sandmeyer Reaction

The replacement of the diazonium group by halogens is known as the Sandmeyer reaction. The reaction is carried out by treating the diazonium salt with one equivalent of the cuprous salt of the chloride or bromide. The introduction of the iodine atom, however, does not require the use of a cuprous salt; hydrogen iodide or one of its salts may be used.

The reactions were carried out by treating the diazonium salt with freshly prepared cuprous chloride or bromide. When the reaction mixture was allowed to stand for any appreciable length of time, or warmed on a steam bath, no reaction product could be isolated. This was in all probability, due to the degrading effect

of the acid cuprous halide solution. If the reaction product was treated with water shortly after the addition of the halide solution a reaction product was obtained which contained very little - if any - halogen.

Iodination was carried out by adding one equivalent of finely ground potassium iodide and allowing the reaction mixture to stand for twenty four hours. The addition of water precipitated a dark purple product which contained between 12 and 20 per cent iodide, as estimated by titration with sodium thiosulfate solution. The product on standing in contact with carbon tetrachloride for a period of time gradually lost its iodine, and the residue was very similar in appearance to the original amine. Nitrogen analysis showed a decrease in amino nitrogen of about two per cent, based on the original amino nitrogen content; and a decrease in nitrate nitrogen of about the same magnitude.

In other experiments the reaction mixture after the addition of potassium iodide was heated on a steam bath. Iodine vapors were liberated, and no iodinated reaction product could be isolated.

In all the halogenation experiments excess nitrous acid was decomposed by the addition of urea.

F. PREPARATION AND DEALKYLATION OF CELLULOSE BUTYL AMINE

The stepwise reduction of the three hydroxyl groups in cellulose involves a series of chemical reactions all of which have a degrading effect on the cellulose chain molecule. If such a derivative were to be prepared by the methods described in the previous sections it would probably be so degraded so as to lose all of its polymeric character. An indirect reduction involving relatively few steps appeared plausible using cellulose butyl amine. It has been reported (77, 150) that when cellulose nitrate is treated with di-n-butyl amine the ester is converted to the tri-di-n-butyl amine derivative. If it were possible to dealkylate cellulose tri-di-n-butyl amine to cellulose triamine, and then deaminate the triamine, a 2,3,6-trideoxy cellulose would be the final product.

1. Preparation

To twenty grams of cellulose nitrate contained in a 500 ml. round bottom flask fitted with a reflux condenser, were added 150 ml. of ethyl ether, and 40 ml. of di-n-butyl amine. (The order of addition is very critical, and under no circumstances should the amine be added to the cellulose nitrate without the presence of ether. In the absence of an inert solvent the re-

action between cellulose nitrate and di-n-butyl amine is very vigorous, with spontaneous and violent decomposition of the cellulose nitrate.) The reaction mixture was then refluxed on a water bath for a period of six hours. A short time after the addition of the butyl amine the cellulose nitrate turned yellow, then dark brown, and finally formed a very dark viscous layer which settled to the bottom of the flask. The supernatant liquid was decanted and the viscous layer washed with small portions of ether until the washings were no longer colored. The excess ether was then removed with a stream of dry air.

The viscous residue was dissolved in glacial acetic acid and the solution poured into a large volume of water with vigorous stirring. A brown gum was deposited which was collected, dissolved in acetic acid and again precipitated in water. By repetition of this process of dissolution and precipitation, the amine was finally obtained in the form of brown flakes which were collected on a Buchner funnel, washed thoroughly with water, and dried in air. The cellulose butyl amine could also be purified by repeated dissolution in acetone and precipitation in water. The final product was similar in appearance to that obtained by the use of glacial acetic acid.

Cellulose butyl amine could also be prepared by allowing the reaction mixture to stand at room temperature for a period of from three to five days. The product so obtained was purified as described above.

The air dried product was light tan in color and stable in air. It burned readily, but not with the vigor of cellulose nitrate. The amine was readily soluble in pyridine, aniline, methanol, and liquid ammonia, and slightly soluble in ethanol. It was insoluble in non-polar solvents. Dissolution in concentrated mineral acids and ten per cent sodium hydroxide solution was accompanied by degradation. It was insoluble in dilute mineral acids.

The amino nitrogen content indicated a product having a degree of substitution of about two. This was in marked contrast to previous investigators who claimed a degree of substitution of three. There was a decrease in nitrogen content on purification. The amine contained some nitrate nitrogen. The results of the nitrogen analyses and the degree of substitution are given in Table IX.

The supernatant liquid decanted from the reaction product gave a positive nitrite test and had both reducing and oxidizing properties.

TABLE IX

NITROGEN CONTENT OF CELLULOSE BUTYL AMINE

No.	Treatment	Per Cent Nitrogen In Product		No. of Groups in Product		
		$N(C_4H_9)_2$	ONO_2	$N(C_4H_9)_2$	ONO_2	OH
1	Reflux 6 hours	7.62	0.87	1.32	0.15	1.53
2	Reflux 6 hours	7.19	----			
3	1 day at R. T.*	4.91	5.31	0.89	0.89	1.22
4	1 day at R. T.	4.63	----			
5	3 days at R. T.	6.72	2.36	1.17	0.41	1.42
6	3 days at R. T.	5.18	----			
7	5 days at R. T.	7.31	0.69	1.23	0.11	1.66
8	5 days at R. T.	7.64	----			

*Room Temperature

2. Dealkylation

A perusal of the literature showed that very few procedures for the dealkylation of tertiary amines have been reported. For the most part these few known methods involve vigorous treatment of the amine and thus do not lend themselves readily to use with a cellulose derivative. The dealkylation studies which were made are discussed below.

An acetone solution of cellulose butyl amine was boiled under reflux with flowers of sulfur in accordance with the procedure of Rosser and Ritter (148). No reaction ensued, and the cellulose butyl amine could be recovered unchanged by precipitation with water.

The method of Braun and Weissbach (17) for the dealkylation of tertiary amines was not found to be applicable. The method consists in heating the amine with an organic acid in a sealed tube. Such a procedure leads to complete degradation of the amine. No reaction was observed when the amine was heated under reflux with acetic or propionic acid. Prolonged heating degraded the amine.

Stoelzel (179) has reported the cleavage of tertiary amines by heating in the presence of potassium metal and absolute ether in a seal tube. This procedure leads

to the removal of one alkyl group and to the formation of the potassium salt of the diamine. It was not investigated.

Finally, cellulose butyl amine was treated with sodium metal in liquid ammonia. The sodium liberated hydrogen from the amine and the sodium salt was formed, but no dealkylation ensued.

VI. DISCUSSION OF RESULTS

During the course of the investigation a varied number of experimental procedures were used. Each experiment was designed to accomplish a certain purpose, and was not necessarily related to the rest of the research. In view of the difference in the experimental techniques involved and the theory thereof, it is necessary to discuss each experiment separately.

1. Reaction With Organometallic Compounds

On the basis of the results obtained it is apparent that under the experimental conditions used, no reaction occurred between cellulose nitrate and the organometallic compounds under investigation. Any reaction of the cellulose nitrate should be attributed to the action of the solvent alone.

Organozinc Compounds. Due to the nature of the experimental conditions used in this investigation it cannot be conclusively stated that no reaction is possible between cellulose nitrate and organozinc compounds. Because of the reactivity of the zinc alkyls the process had to be carried out in the non-polar solvent, toluene. Such a solvent does not penetrate the intramicellar spaces of the cellulose nitrate fiber, so that any possible reaction would be limited to the surface of the fiber, and therefore, exceedingly limited in extent.

Diethyl Tin. In this investigation the course of the reaction in the preparation of diethyl tin was somewhat different from that described by Harada (56). The end results, however, were the same. This discrepancy may plausibly be attributed to two factors, namely:

(1). Concentration of the Solution. The work described herein was carried out with a solution about one-fifth as concentrated as that of Harada. This was due to the fact that the equipment on hand did not lend itself to working with small volumes of liquid ammonia.

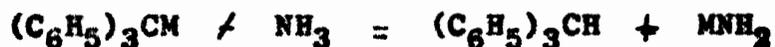
(2). Purity of the Tin. Nothing is known about the purity of the tin used by this investigator or by Harada. It is known (153) that in the preparation of organotin compounds small amounts of impurities (such as zinc) frequently effect the course of the reaction.

The treatment of cellulose nitrate with diethyl tin in liquid ammonia is complicated by the presence of ammonia which undergoes a reaction with the cellulose nitrate. The formation of the cellulose amine found as a reaction product is believed to be due to the ammonolytic effect of the solvent, and not to the effect of the diethyl tin. Furthermore, diethyl tin which is insoluble in

liquid ammonia is believed to polymerize on standing, and such a product would not be expected to react with cellulose nitrate.

Organosodium and -potassium Compounds. The very fact that the reactive sodium and potassium triphenylmethides did not react with cellulose nitrate is the basis for the belief that no reaction is possible with organozinc or organotin compounds.

The excellent yields of cellulose amine obtained in the reaction between the triphenylmethides and cellulose nitrate may be attributed to two factors: the first is the effect of the solvent ammonia, the second is the catalytic effect of the alkali metal amide which is formed by ammonolysis of the triphenylmethides.



This concept of amine formation will be discussed in greater detail in a subsequent section.

With respect to the alkali metal alkyls it appears evident that the ammonolysis of the metal alkyl is faster than any possible reaction between the metallic alkyl and cellulose nitrate. The resulting mixture of amines would then be expected to react with cellulose nitrate. The final product would then be a mixture of various cellulose alkyl amines and, probably, cellulose amine.

2. Reaction With Sodium Borohydride

From the results obtained in these experiments it is logical to assume that some sort of a reaction occurs between cellulose nitrate and sodium borohydride. The reaction appears to be exceedingly complicated, and the nature of the final product, or the mechanism of the reaction, are at present unknown.

The reaction is presumed to take place by an initial formation of an addition complex between some functional group of the cellulose nitrate and sodium borohydride. The functional groups in cellulose nitrate are the $-\text{ONO}_2$, $-\text{OH}$, $-\text{O}-$, $-\text{CHO}$, $-\text{COOH}$ and $-\text{CH}$ groups arising from the ester itself, and possibly $-\text{SO}_3\text{H}$ groups arising from the action of the nitrating medium. Of these, the only one which is definitely known to be reduced by sodium borohydride is the $-\text{CHO}$ group. Glucose is reduced by sodium borohydride to the corresponding alcohol. Complex sugars are also reduced, but no reaction product has ever been isolated from the reaction mixture (1). Sodium borohydride does not reduce the $-\text{NO}_2$ group, but nothing is known about its effect on the $-\text{ONO}_2$ group.

When cellulose nitrate of 13.35 per cent nitrogen (2.7 nitrate groups) was reacted with sodium borohydride

the reaction was faster than when cellulose nitrate of 12.12 per cent nitrogen (2.3 nitrate groups) was used. As the number of nitrate groups increases there is a corresponding decrease in the number of hydroxyl groups, so the increased reactivity of cellulose nitrate of 13.35 per cent nitrogen cannot be attributed to a decrease in the number of reactive hydroxyl groups. There was no apparent reaction between sodium borohydride and cellulose, or water soluble cellulose derivatives which have a preponderance of hydroxyl groups.

The potential aldehyde (-CHO) group is found on the terminal glucose unit of the cellulose chain so that there is one such group per chain molecule. Unless there is a great difference in the number of chains of the two cellulose nitrate samples, there should not be too great a difference in the number of aldehyde groups. As a matter of fact, the ester of lower nitrate content had a lower viscosity than the ester of higher nitrate content, thus indicating a greater number of short chains, and consequently a greater number of aldehyde groups. Therefore, the increased reactivity should not be attributed to the aldehyde groups. Furthermore, water soluble cellulose derivatives contain a very large number of short chain molecules, and these derivatives

did not react with sodium borohydride. On the basis of the above argument it is logical to assume that the cellulose nitrate-sodium borohydride complex is formed primarily by reaction between the nitrate groups of cellulose nitrate and the sodium borohydride, although reaction with the aldehyde group cannot be entirely excluded.

A second important consideration is the role of the solvent. In the light of present knowledge the effect of the solvent on the course of the reaction cannot be properly evaluated. A cellulose nitrate-borohydride complex was formed in the presence of three different solvents, namely: acetone, ethyl acetate, and 1-1 ether-alcohol. The complex formed in the last two solvents was easily hydrolyzed by water to the original reactants; the complex formed in the presence of acetone was hydrolyzed to unknown substances.

The third important aspect is the formation and nature of the gel. Acetone may be reduced to isopropanol. Consider a mixture containing 100 ml. of acetone (1.3 moles), one gram of cellulose nitrate, and four grams of sodium borohydride (0.1 mole). Assuming complete reduction 0.4 moles of isopropanol would be formed (23), thus leaving 0.9 moles of acetone. The reaction mixture will then contain approximately 52 grams of

acetone and 24 grams of isopropanol. Such a mixture is still an excellent solvent for cellulose nitrate. However, isopropanol is not formed until the intermediate acetone-borohydride complex is hydrolyzed by sodium hydroxide. In these experiments gelation was almost instantaneous. Therefore, on the basis of the above argument the gelation of cellulose nitrate cannot be attributed to the presence of isopropanol.

Nor can gelation be attributed to the presence of boron salts in the reaction mixture. First of all it was shown that boron salts do not gel acetone solutions of cellulose nitrate. Secondly it must again be remembered that no boron salts are formed until the intermediate acetone-borohydride complex is hydrolyzed.

On the basis of the above arguments the only reasonable conclusion is that gelation is brought about by reaction of some type between the nitrate groups of cellulose nitrate and the sodium borohydride molecule. Cross linkages are formed between quite separate cellulose nitrate chains and the hydride leading to the formation of a molecular complex which may be represented as follows:

Cell-nitrate - sodium borohydride - Cell-nitrate
The solvent which was formerly the medium in which the cellulose nitrate was dispersed is now converted to a

dispersed phase held between the interlinked lattice of the gel complex, and therefore is incapable of exerting its solvent power.

In the presence of ethyl acetate or ethyl alcohol the reaction apparently terminates with the formation of the gel, which as has been shown, readily undergoes hydrolysis. In the presence of acetone the solvent exerts some effect on the gel as evidenced by the fact that nitrite nitrogen was present in the acetone phase, while no nitrogen was ever found in the liquid phase of the other solvents. What effect the acetone has on the nature of the gel cannot be answered in the light of present knowledge.

There is at present no logical explanation to account for the reaction ensuing when the gel is treated with water or glacial acetic acid. Any conclusions which may be reached are merely based on suppositions which cannot be experimentally substantiated, and which cannot be explained by analogy to other reactions. Presumably the complex is hydrolyzed to a sodium borate and a nitrogen and boron free highly degraded cellulose derivative, the nature of which is at present unknown.

No doubt the alkaline nature of the sodium borohydride is responsible for some of the degradation of the cellulose chain. This probably accounts for the

increased water solubility of the complex with an increase in the initial concentration of sodium borohydride.

Further proof for the formation of the complex between the nitrate groups of cellulose nitrate and sodium borohydride is obtained when the reaction is carried out in liquid ammonia. As will be explained in the next section cellulose nitrate in liquid ammonia is converted to a tan colored cellulose amine. In the presence of sodium borohydride no cellulose amine is formed. This can only be interpreted by assuming the nitrate groups to be tied up in complex formation.

3. Preparation of Cellulose Amine

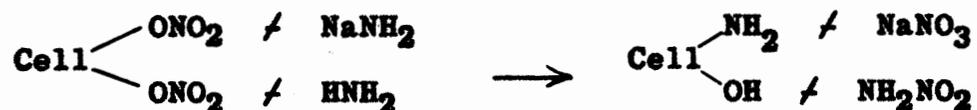
This investigation has shown that cellulose dinitrate is converted to a cellulose monoamine by the action of ammonia. The reaction may be carried out by dispersing cellulose nitrate in liquid ammonia in the presence, or absence, of an ammono base, or, by treating cellulose nitrate either in the fibrous state or in acetone solution with gaseous ammonia.

The product obtained from the above reactions contains amino nitrogen and nitrate nitrogen. Under optimum conditions approximately one amino group is introduced into the glucose unit and the nitrate content

is relatively low (See Tables IV and VII). When the amino content is low, the nitrate content is high (Table VII). Therefore the presence of appreciable amounts of nitrate nitrogen may be taken as an indication of incomplete reaction.

When the nitrogen content is relatively low it may be due to residual nitrate groups or to nitrogenous impurities, some of which might have come from the cellulose nitrate itself, or which might have been introduced during the course of the amination. However, no matter what degree of substitution is obtained, all products prepared by the above methods are believed to be chemically similar as they show the same fundamental property of being converted to stable diazonium salts.

No conclusive evidence can be presented to account for the mechanism of the amination reaction, or to explain why only one amino group is introduced. Feild (41) who first studied the reaction in the presence of sodium amide advanced the argument that the formation of cellulose amine was dependent upon two simultaneous reactions: the first was the metathetic replacement of one nitrate group by sodium amide; the second was ammonolysis of the remaining nitrate group.



This mechanism did not account for the formation of cellulose amine in liquid ammonia in the presence of sodium metal, nor does it now account for the mechanism of the reaction when carried out with gaseous or liquid ammonia.

Cellulose amine prepared in the presence of sodium amide or sodium metal is water soluble, cellulose amine prepared by other methods is water insoluble. This discrepancy, it may be argued, is due to a difference in the chemical nature of the product, but this argument does not appear valid in view of the fact that both types of amines can be diazotized and coupled with the same intermediates to form what are apparently the same diazo derivatives.

In cellulose nitrate the nitrate groups are believed to be distributed at random among the various reactive positions of the glucose anhydride units (2-, 3-, or 6-position). Theoretically, therefore, the mono-amine group may become substituted on any one of the three positions. On this basis it may be concluded that the difference in solubility is due to the difference in the location of the substituent so that the two amines are isomeric. This conclusion is not tenable. If the amine were substituted on carbon-6 it would be purely aliphatic and would not be

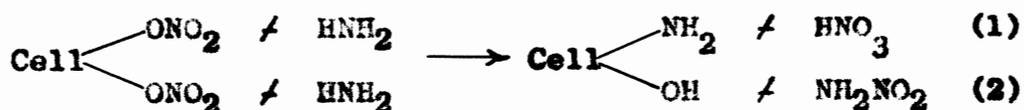
expected to form stable diazo derivatives. Therefore it may be inferred that aminations occur on carbon-2 or -3, which by the nature of their location in the stable pyranose ring would confer stability to the diazo derivative. Since the 2-position is believed to be the more reactive of the two, substitution would predominate on this position. However, there is no reason to believe that one type of amine is more preferentially substituted in this position than the other.

Furthermore, if the difference in solubility is due to an isomeric difference in the amines, the same mechanism which satisfies the reaction in the case of sodium amide should satisfy the reaction in the case of metallic sodium. At present, no valid mechanism similar to that for sodium amide can account for the formation of cellulose amine in the presence of sodium. It has been shown (74) that no sodium amide is formed as a by product in the reaction between cellulose nitrate and sodium in liquid ammonia.

Water solubility can also be attained by prolonged treatment of cellulose nitrate in acetone solution; this factor being attributed to degradation of the chain. Under such conditions the amino nitrogen content is relatively constant.

This investigator is of the opinion that sodium amide and sodium metal function primarily as catalysts, and that the reaction between cellulose nitrate and ammonia is due primarily to the ammonolytic effect of the solvent. The water solubility of some of the amines is due to a marked degradation of the cellulose chain in the presence of an ammono base in much the same way that cellulose nitrate is degraded in the presence of an aquo base. Chemically, the cellulose amines are one and the same substance, even though their physical properties may differ.

Although the formation of cellulose amine can be attributed to ammonolysis no conclusive evidence can be given, nor can any mechanism be formulated. The reaction would have to occur in such a fashion whereby one molecule of ammonia metathetically replaces the $-ONO_2$ group while another replaces the $-NO_2$ group in accordance with the following scheme:



In view of the slow rate of reaction in the formation of cellulose amine, Reaction 2 probably takes place to a greater extent on the very reactive carbon-6, and

the slow amination takes place on the carbons of the pyranose ring. Therefore, as the amine content increases, the nitrate content of the product decreases. The above equation is to be considered as a generalized equation.

The nature of the inorganic nitrogenous constituents in the filtrate from the reaction medium is unknown, although positive nitrite (and therefore nitrate) tests are obtained in all procedures for preparing cellulose amine. Very little is known of the chemistry of nitramide (NH_2NO_2) or its derivatives. Therefore, in view of our lack of knowledge of the products obtained, the above reaction is to be regarded as a speculative one which indicates the trend of the reaction, although not necessarily the true reaction.

The aminated product gives a negative test for the hydroxylamine group ($\text{Cell-O}\overset{\cdot}{\text{N}}\text{H}_2$), but it might be possible that the method of analysis is not sensitive enough to detect a small amount of such a product.

4. Diazotization and Deamination of Cellulose Amine

In this investigation it has been shown that cellulose amine prepared by any one of several different procedures can be diazotized and coupled with aromatic intermediates to form azo compounds. The ease with which

diazotization occurs appears to be dependent on the amount of nitrate nitrogen present. Those amines with the greatest amount of nitrate nitrogen were found to be the most difficult to diazotize. The ease of coupling, however, appeared to be independent of the amount of nitrate nitrogen present in the amine.

On treatment with hypophosphorous acid the diazonium salts were deaminated, probably to a desoxy derivative. The loss in amino nitrogen was about 80-90 per cent of the original nitrate nitrogen (See Table VIII). Although complete deamination was never achieved the amino nitrogen content of the deaminated product was fairly constant.

The reason for incomplete deamination may be due to any one, or a combination, of the following reasons:

- (1). The possibility of incomplete deamination must be considered in the light of the reactivity of the amino groups with respect to their position in the glucose unit. This factor cannot be proven directly, but it is possible that one amino group (say in position-2) is more reactive and would undergo preferential diazotization. In cellulose chemistry such differences in reactivity are known.

(2). The possibility of incomplete deamination must be considered in the light of the stability of the diazonium salt. Thus the diazonium salt in one position may be more stable than in the other position, and therefore would offer greater resistance to reduction.

(3). The effect of the residual nitrate groups may be pronounced. Such groups are known to increase the stability of diazonium salts, and thus they might prevent complete deamination from being achieved. Incidentally, this might also explain the low nitrogen values obtained with coupled derivatives.

(4). Part of the amino nitrogen might be present in the form of an hydroxylamine group.

The reaction of the cellulose diazonium salt with hypophosphorous acid might follow a course leading to formation of an hydroxyl group and not to a desoxy group. No conclusive experimental evidence can be offered to show that deamination is the true reaction. On the other hand, no evidence can be presented to show that it is not the true reaction. With aromatic diazonium salts excellent yields of deaminated products are obtained; at the same time the yields of phenols are very poor. By analogy, the course of the reaction with

cellulose diazonium salts may be presumed to be the same. Therefore, in the absence of any direct evidence to the contrary, the final product is believed to be a desoxy cellulose.

The reaction of cellulose diazonium salts with ethanol leads to the removal of only part of the amino group. Theoretically, the same arguments can be advanced for incomplete deamination by alcohol as were advanced for hypophosphorous acid. However, in this case the nature of the deaminating agent must be taken into consideration.

In deamination reactions ethanol is not to be considered as a substitute for hypophosphorous acid; it has many limitations and its use is not as general as hypophosphorous acid. The main product of the reaction is frequently an ether, and not a hydrocarbon (92). Therefore, it is possible that in the reaction of cellulose diazonium salts with ethanol, very little deamination occurs, the main reaction product being the formation of the ethyl ether. At present no unequivocal proof of this concept can be advanced.

5. Preparation and Dealkylation of Cellulose Butyl Amine

By the reaction of di-n-butyl amine and cellulose nitrate a cellulose di-n-butyl amine with degree of

substitution between one and two was formed. This is in marked contrast to the results of previous investigators who claimed a degree of substitution of three. Their high results were probably due to incomplete removal of impurities from the product.

The course of the reaction may be presumed to occur in a manner similar to that between cellulose nitrate and ammonia. Thus, part of the amine reacts metathetically with the $-ONO_2$ group on carbon-6, while the rest of the amine slowly reacts with the $-NO_2$ groups on the 2- and 3-positions. The degree of substitution of two may be due to the greater strength of butyl amine which would lead to a greater degree of reaction. The presence of nitrate nitrogen in the final product can be attributed to incomplete reaction or to the presence of unknown impurities. The positive test for nitrites in the filtrate from the reaction mixture is not inconsistent with results on the ammonolysis of cellulose nitrate.

The dealkylation of cellulose butyl amine has not been realized. The few dealkylation procedures which are known involve for the most part vigorous treatment of the product, such treatment being destructive to the cellulose chain. In general the dealkylation of

tertiary amines proceeds by the elimination of the most complex group, which in this case would be the cellulose chain.

No evidence can be presented to dispute the fact that the butyl amine group is linked to the cellulose chain through an ether linkage. By analogy to cellulose amine this theory is not tenable.

VIII. SUMMARY

An attempt was made to cause a reaction between cellulose nitrate and organometallic compounds so as to effect a metathetic replacement of the nitrate group of cellulose amine by an alkyl or aryl radical. No reaction ensued when diphenyl zinc in toluene or diethyl tin in liquid ammonia were used as reactants. Sodium and potassium triphenylmethides in liquid ammonia did not react with cellulose nitrate.

The reaction between sodium borohydride and cellulose nitrate in acetone was studied. A cellulose nitrate sodium borohydride complex was formed which on hydrolysis yielded a nitrogen free cellulose derivative which could not be properly identified.

The preparation of cellulose amine by the action of ammonia on cellulose nitrate was studied by several different methods. From the results it was concluded that the mechanism of the process was the same in all reactions and independent of the experimental conditions. Sodium amide and sodium metal acted only as catalysts and did not take part in the reaction. A plausible mechanism for the reaction was advanced.

It was shown that cellulose amine prepared by any one of several different methods could be diazotized and coupled with aromatic intermediates to form stable

diazo derivatives. The final product was the same and its properties were independent of the physical characteristics of the amine.

Cellulose amine was deaminated by the action of hypophosphorous acid on the cellulose diazonium salt to a desoxy cellulose containing between one and two per cent nitrogen. Several theories were advanced to account for the fact that complete deamination was not realized.

The reaction between cellulose nitrate and di-n-butyl amine yielded a cellulose butyl amine having a degree of substitution between one and two. The mechanism of the reaction was presumed to be the same as that for the reaction between cellulose nitrate and ammonia. The attempted dealkylation of cellulose butyl amine was unsuccessful.

VII. CONCLUSIONS

On the basis of the experimental evidence obtained from this investigation the following conclusions were reached:

(1). Cellulose nitrate does not react with diphenyl zinc or diethyl tin under the experimental conditions used.

(2). Cellulose nitrate does not react with sodium or potassium triphenylmethides in liquid ammonia.

(3). Cellulose nitrate in acetone solution forms an addition complex with sodium borohydride. The complex is hydrolyzed by the action of water or glacial acetic acid to a nitrogen free cellulose derivative the nature of which is unknown.

(4). Cellulose nitrate is converted to cellulose amine by the action of liquid or gaseous ammonia. In the presence of ammonio bases such as sodium amide the rate of reaction is increased, but the final product is degraded.

(5). The mechanism of the reaction between cellulose nitrate and ammonia is independent of the solvent or the state of the ammonia.

(6). All cellulose amines may be diazotized and coupled with aromatic intermediates to form the

same mono azo compound. The chemical properties of the amine are independent of the physical properties.

(7). Cellulose amine may be deaminated by the action of hypophosphorous acid on the diazonium salt. The desoxy derivative contains some amino nitrogen.

(8). A disubstituted cellulose butyl amine may be prepared by the action of di-n-butyl amine on cellulose nitrate. The mechanism of the reaction is the same as that proposed for the formation of cellulose amine.

(9). Cellulose butyl amine cannot be dealkylated under the conditions used in these experiments.

The objective of this research was to prepare an undegraded desoxy cellulose or an alkyl derivative of cellulose, and to study the properties of cellulose derivatives which could be used to prepare reduced derivatives of cellulose. No alkyl derivatives of cellulose have been prepared, but a derivative has been prepared which appears to be a desoxy cellulose. The preparation and properties of some cellulose intermediates have been studied, and theories have been proposed to account for various reactions of cellulose

nitrate. It is hoped that the work presented herein will offer the fundamental theory and a starting point for future research in this field.

IX. ACKNOWLEDGEMENTS

The author takes this opportunity to acknowledge his indebtedness to Dr. Philip C. Scherer to whose patience and understanding this thesis owes its existence, and without whose help this thesis could not have ended. He is particularly appreciative of the continued encouragement and cooperation, and of the many hours of discussion which suggested new and fruitful lines of investigation.

It is the author's pleasure to express his gratitude to Professors F. H. Fish, R. C. Krug, J. B. Lucas, J. W. Murray, F. A. Vingiello, and J. W. Watson, and the other members of the Chemistry Staff, all of whom at one time or another gave advice and encouragement in the preparation of this thesis.

To Miss Helen G. Gillam, Reference Librarian, for her aid in locating obscure periodicals, and to Professor P. H. Watkins for his aid in preparing the drawings, the author owes a great debt of gratitude which cannot be adequately acknowledged.

Finally the author wishes to record his thanks to Mr. Joe W. Guthridge, and the other members of the University Club, for their friendship which made life in Blacksburg worth living.

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XI. VITA

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A STUDY OF THE REACTION OF CELLULOSE NITRATE
WITH VARIOUS REDUCING AGENTS

an

Abstract of a Thesis Presented by

Frank John Masuelli, B.S., M.S.

to the

Faculty

of the

Virginia Polytechnic Institute

in

Candidacy for the Degree of

DOCTOR OF PHILOSOPHY

in

CHEMISTRY

June, 1953

Cellulose nitrate does not react with diphenyl or diethyl zinc dissolved in toluene, nor does it react with diethyl tin in liquid ammonia solution. In the latter case the cellulose nitrate is converted to cellulose amine by the ammonolytic effect of the ammonia.

Powdered sodium borohydride added to a dilute solution of cellulose nitrate in acetone causes immediate gelation of the ester. The gel is presumed to be formed by the reaction of the hydride with the nitrate groups of cellulose nitrate. Hydrolysis of the complex with water or glacial acetic acid yields a boron and nitrogen free derivative the nature of which is unknown.

Cellulose nitrate reacts with ammonia either in the gaseous or liquid state to form cellulose mono-amine. The mechanism of the process is the same in all reactions and is independent of the experimental conditions. When the reaction is carried out in the presence of ammono bases such as sodium amide the cellulose amine is considerably degraded and is soluble in water; in all other cases the amine is water insoluble.

Cellulose amine in glacial acetic acid solution may be diazotized and coupled with aromatic intermediates to form stable mono-azo derivatives whose properties are independent of the physical properties of the amine. Cellulose amine is deaminated by the action of hypophosphorous acid on the cellulose diazonium salt to a desoxy cellulose containing between one and two per cent amino nitrogen. Several theories are advanced to account for the fact that complete deamination is not realized.

The reaction between cellulose nitrate and di-n-butyl amine yields a cellulose di-n-butyl amine of degree of substitution between one and two. The mechanism of the reaction is presumed to be the same as that for the formation of cellulose amine. The cellulose di-n-butyl amine could not be dealkylated.