# THE SELECTIVE DENITRATION
# OF CELLULOSE NITRATES

A Thesis

by

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Ph.D. Chemistry

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# THE SELECTIVE DENITRATION
# OF CELLULOSE NITRATES

Cellulose nitrate was subjected to decomposition in various basic reagents in order to discover conditions that would differentiate between the three kinds of nitrate groups in the substance. Two new selective reactions which remove one third of these groups without affecting the remainder are described, and the products of denitration characterized. The product in the first reaction was a cellulose dinitrate and those in the second reaction were the O-methyl oxime and the oxime of a monocarbonyl oxycellulose dinitrate. Possible mechanisms for the denitration reactions are presented, and derivatives of the products described. This research formed part of the confidential N.R.C. war project XR-74.

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# SELECTIVE DENITRATION OF CELLULOSE NITRATES

- SEGALL

# GENERAL INTRODUCTION

Although the reaction between cellulose nitrates and alkali has been frequently studied, the conditions used invariably brought about severe degradation and produced low molecular products. Nevertheless, the nitrate groups in the second, third and sixth positions of the glucose residues constituting cellulose almost certainly differ in reactivity. Proper experimental conditions should therefore make it possible to remove one nitrate group selectively without substantially affecting the rest. The discovery of such conditions was the initial object of the present research, which forms part of the confidential N.R.C. war project XR-74 on the thermal and alkaline stability of nitrated celluloses.

Nitrate esters were known to decompose in alkali in two general ways, one yielding the alcohol and nitrate salt as in a normal saponification and the other, nitrite and an oxidation product of the alcohol. Since previous work indicated that in the case of cellulose nitrates much of the decomposition occurred by the latter route, it was probable that the extensive degradation was caused by secondary decomposition of the oxidized glucose residues in the alkaline reagent. Therefore the research was aimed at providing reaction conditions in which any oxidized carbohydrate produced on denitration would be protected against further decomposition. Since the initial oxidized group was almost certainly a carbonyl group, the denitration was carried out in the presence of such reagents as hydroxylamine, cyanide and bisulfite solutions, which might react with and thus protect, any carbonyl groups as they were formed.

Cellulose trinitrate was used for most of the research since any selectivity in the reactions studied would be immediately obvious. With lower nitrates in which the distribution of nitrate groups between the three available positions in the anhydroglucose unit is uncertain, the results of a partial denitration would be more difficult to interpret.

The denitrations attempted with buffered solutions of sodium cyanide and sodium sulfite were unpromising and have not been described in detail. An excess of hydroxylamine or methoxyamine in dry pyridine however, removed an average of one nitrate group per glucose unit from cellulose trinitrate with little degradation. The cellulose dinitrate formed was practically stable in excess of the reagent. Indecisive evidence suggested that the group removed had occupied either the second or the third position of the glucose residues. Monomethyl and monoacetyl derivatives of the dinitrate are described.

Another new and successful denitration was effected by pyridine solutions either of methoxyamine hydrochloride or hydroxylamine hydrochloride. In this case the methyloxime or the oxime of an oxycellulose dinitrate was obtained in high yield.

Possible reaction mechanisms for these new and sharply distinct decompositions of cellulose trinitrate are suggested.

# HISTORICAL INTRODUCTION

It was early recognized that the action of alkaline reagents on nitrate esters was complex. In most cases hydrolysis was accompanied by the formation of nitrite and an oxidation product of the alcohol, in contrast with acyl esters which produced alcohol and the salt of the acid exclusively, on saponification.

In 1899, Nef (1) pointed out that the correct analogy was between alkyl nitrates and halides or sulfates, in that nitrates behaved similarly in many well known reactions. The oxidation-reduction reaction was a consequence of the special nature of the nitrate group in being at a high state of oxidation. A similar reaction could occur in the hydrolysis of an alkyl halide if carried out in the presence of an oxidizing agent. Thus sodium ethylate, freshly precipitated mercuric oxide and alkyl halides produced carbonyl derivatives. Conversely, benzyl nitrate reacted in the same manner as benzyl chloride with acetoacetic ester in sodium ethylate, forming benzyl and dibenzyl acetoacetic esters and sodium nitrate without a trace of nitrite. In the similar reaction with sodiomalonic ester, benzyl nitrate yielded benzyl malonic ester and sodium nitrate with a small amount of nitrite. The familiar condensation of alkyl halides with amines to form quaternary ammonium salts was paralleled by the reaction of benzyl nitrate with dimethyl aniline, at 100° to give benzyldimethylphenylammonium nitrate.

While benzyl nitrate was wholly analagous to benzyl chloride in its reaction with alcoholic potassium acetate at 150°, giving benzyl alcohol and benzyl acetate; with alcoholic potassium hydroxide or with sodium ethylate, not a trace of ethyl benzyl ether was produced as was the case when benzyl chloride was used. Instead, a nearly quantitative yield of inorganic nitrite and benzaldehyde or its decomposition products in alkali resulted. When treated with excess sodium methylate, benzyl nitrate gave 83% of the theoretical amount of nitrite possible and a mixture of benzyl alcohol and ethyl benzoate, the latter two being the usual products from benzaldehyde in alcoholic sodium methylate.

Nef listed three types of reactions undergone by alkyl nitrates in alcoholic potassium hydroxide:

1. Ether formation
2. Aldehyde formation
3. Normal hydrolysis to alcohol and nitrate.

Methyl nitrate with two moles of alcoholic potassium hydroxide at 30° gave dimethyl ether without a trace of nitrite. Ethyl nitrate with same reagent, in five days at room temperature produced ethyl ether, an aldehyde resin and a mixture of salts of which 24% was potassium nitrite. With one and one quarter moles of alkali at 50-70° for two hours, similar products resulted except that the salt mixture contained only 11% potassium nitrite.

Normal propyl nitrate with excess alcoholic potassium hydroxide gave propylethyl ether, n-propyl ether and mixed nitrate-nitrite salts. Similar results were obtained with isopropyl, isobutyl and isoamyl nitrates.

From glycol dinitrate in alcoholic potassium hydroxide Nef obtained glycolic acid, presumably by an intramolecular Cannizzaro reaction of the glyoxal initially formed, and potassium nitrite. Nitroglycerine with alcoholic potassium hydroxide yielded the salts of nitrous, formic and acetic acids, presumably through an intermediate keto-dialdehyde.

Nef's results indicate clearly that alkyl nitrates are analogous to the halides in many reactions, and that the mode of reaction in alkali is dependent on the conditions and the particular nitrate concerned.

In 1900, Berthelot (2) treated ethyl nitrate with solid potassium hydroxide at 100° and obtained an acetaldehyde polymer together with potassium nitrite. After investigating the alkaline hydrolysis of nitroglycerine he concluded that alcohol and carbonyl groups could be formed in the same molecule, the former corresponding to the recovery of nitrate and the latter to nitrite salt. This conclusion was in opposition to Nef's (1) view that the nitrates of polyhydroxy alcohols underwent the redox cleavage exclusively. The point was soon settled by Berl and Delpy (3) who isolated $\alpha,\alpha'$-glycerol dinitrate as well as oxalic and mesoxalic acid from the reaction products of glycerol trinitrate and alcoholic potassium hydroxide at 25°. The ratio of nitrate to nitrite salts produced was 1: 2.37.

Vignon and Bay (4) in 1902, investigated nitrite and nitrate formation as well as the ammonia produced in the alkaline decomposition of several nitrates. To 5g. of ester was added 7.7g. of sodium hydroxide dissolved in 300 cc. of water and the mixture was boiled for various periods.

### TABLE I

### Decomposition of Nitrates in Boiling 2.8% aqueous Caustic Soda[(a)]

| Nitrate | Nitrous Acid (grams) | | | Ammonia (gms) |
|---|---|---|---|---|
| | 1 hr. | 4 hr. | 8 hr. | |
| Methyl | 0 | 0.050 | 0.025 | 0 |
| Ethyl | 0 | 0 | 0.030 | 0 |
| Glyceryl | 0.205 | 0.205 | 0.205 | 0.250 |
| Erythritol | 0.206 | 0.481 | 0.205 | 0.200 |
| Pentaerythritol | 0 | 0.132 | 0.059 | 0 |
| Mannitol | 0.413 | 0.413 | 0.206 | 0.250 |
| Dulcitol | 0.412 | 0.205 | 0.205 | 0.200 |
| Cellulose | 0.206 | 0.206 | -- | 0.300 |

(a) Vignon and Bay. Ref.4

It is apparent that the results (Table I) varied widely and in some cases the amount of nitrite produced passes through a maximum. Perhaps the ammonia was produced by reduction of nitrite by the carbonyl derivatives formed.

Carlson (5) measured the amounts of nitrite formed in the hydrolysis of several nitrates in 95% ethyl alcohol solution, made 0.5N with respect to nitrate at 70°. The concentration of potassium hydroxide also present in the alcohol was not stated.

### TABLE II

### Decomposition of Nitrates in Alcoholic Potassium Hydroxide at 70°[a]

| Nitrate | % Nitrite Formed | Nitrate | % Nitrite Formed |
|---|---|---|---|
| Methyl | trace | Isoamyl | 20 |
| Ethyl | 7 | Glycerol | 67 |
| Propyl | 17 | Glycol | 87 |
| Isobutyl | 35 | Cellulose (12.5%N) | 82 |

(a) Carlson. Ref.5

In the presence of hydrogen peroxide or mercaptans the original was regenerated. It was found that benzyl nitrate condensed with the potassium salt of phenyl mercaptan to give the thio ether, rather than undergoing a redox reaction.

$$C_6H_5CH_2NO_3 + KSC_6H_5 \rightarrow C_6H_5CH_2SC_6H_5 + KNO_3$$

The condensation, which was quantitative with no nitrite formation, completed the analogy with benzyl chloride which had eluded Ref (1).

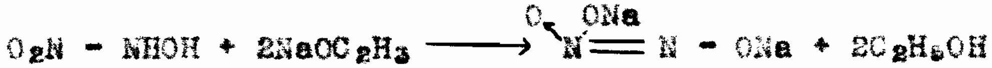
Some anomalous results are in the literature.

Mixter (6) in 1891 claimed that ethyl nitrate with alcoholic potassium hydroxide yielded ethanol and nitrate salt. However, with glycol dinitrate in the same reagent, he obtained carbon dioxide and nitrite. With barium hydroxide he was able to isolate the sparingly soluble barium oxalate and barium nitrite. From nitroglycerine, oxalic acid, nitrite and ammonia were detected after reaction with concentrated aqueous potassium hydroxide.

The hydrolysis of butyl nitrate was studied under various conditions by Ryan and Coyle (7). They found that cold aqueous potassium hydroxide gave only 15% hydrolysis in seventeen days while at 100° concentrated aqueous potassium hydroxide hydrolysed 20% of the butyl nitrate in twelve hours. At higher temperatures in an oil bath the butyl nitrate was converted into butanol, a resin, potassium nitrite and nitrate. Alcoholic potassium hydroxide produced 20% hydrolysis in one hundred and seven hours at room temperature while at 60° for eighteen and one half hours, 90% of the ester was decomposed into butanol, butyl ethyl ether, a resin and potassium nitrate and nitrite. An ethanol solution of ammonia hydrolysed not more than 4% of the ester in eighty-four hours, but the presence of hydrogen sulfide increased the rate. This increase was probably caused by the reduction of the nitrate groups since spontaneous boiling took place and sulfur was deposited. Butanol and a substance described as a mercaptan were formed. Iron and acetic acid reduced the ester with the evolution of nitric oxide but only one third of the ester was obtained as butanol. Acetic anhydride and sodium acetate had no apparent action on butyl nitrate. It was of interest that a sharp increase in rate of hydrolysis occurred when alcoholic potassium hydroxide was used rather than aqueous solution. This seemed to be a general phenomenon.

An interesting non-oxidative denitration of ethyl nitrate was achieved by Angeli (8) in his synthesis of the sodium salt of nitrohydroxamic acid from ethyl nitrate, sodium ethylate and hydroxylamine;

$$C_2H_5ONO_2 + H_2NOH \longrightarrow NO_2 - NHOH + C_2H_5OH$$



$$O_2N - NHOH + 2NaOC_2H_3 \longrightarrow \overset{O\;\;ONa}{N} = N - ONa + 2C_2H_5OH$$

That no oxidation-reduction took place was shown by the fact that nitrohydroxamic acid could oxidize an aldehyde (9), being itself reduced to nitrite and a hydroxamic acid, the latter yielding hydroxylamine on hydrolysis. In a further investigation (10) the writers obtained 50% as the maximum yield and attributed the loss to reaction between ethyl nitrate and sodium ethylate.

The hydrolyses of the very unstable nitrotartaric and the more stable nitromalic acid were studied by A. Lachman (11). The hydrolysis of nitrotartaric acid was remarkable in that the redox cleavage occurred in dilute acid solution, giving quantitative yields of nitrite and excellent yields of dihydroxy tartaric acid. In either aqueous or alcoholic alkali solution, nitrite was again produced quantitatively, but the dihydroxy tartaric acid decomposed into tartronic and oxalic acid. Normal hydrolysis to tartaric and nitric acids occurred only in extremely concentrated nitric acid, containing the stoichiometric amount of water.

The properties of nitrotartaric acid made a controlled measurement of hydrolysis difficult although it had the very desirable property of being soluble in water and organic solvents and thereby making possible a study of the effect of solvent. The hydrolysis of the more stable nitromalic acid $COOH.CH_2CHONO_2COOH$, soluble in water and the common organic solvents, was studied in aqueous sodium hydroxide, aqueous sulfanilic acid, and in neutral aqueous solution. In the case of aqueous sodium hydroxide, the concentration of alkali, temperature and time of reaction had no effect on the final nitrite concentration. In all cases about 0.2 moles of nitrite were produced. In methanolic sodium hydroxide the yield of nitrite was again independent of temperature, concentration, or excess of alkali, but nearly twice as much was produced as when water was the solvent; from 0.32 to 0.39 moles.

The reaction of nitromalic acid at 100° with aqueous sulfanilic acid at its own pH gave 65% nitrite in two hours and 78% in five hours. These percentages were measured by the evolution of nitrogen, which was assumed to be produced by the reaction.

$$HNO_2 + C_6H_4(SO_3H)NH_2 \longrightarrow C_6H_4(SO_3H)OH + N_2 + H_2O$$

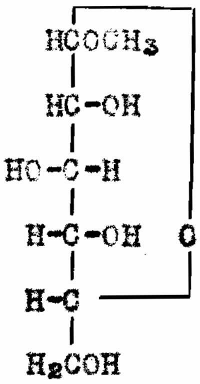
Lachman concluded that the reaction was monomolecular and did not involve a direct reaction between nitromalic acid and sulfanilic acid. A 20% yield of crude oxaloacetic acid $COOHCH_2CO.COOH$ was obtained. The hydrolysis of nitromalic acid in neutral solution was complete in two hours at 100° and yielded only 8% nitrous acid. The presence of large amounts of nitric acid was demonstrated and malic acid was identified as the main product of the reaction. Lachman interpreted the results as indicating that normal hydrolysis and redox cleavage proceeded at independent rates. In dilute acid solution the slow redox reaction was still faster than the normal hydrolysis. In neutral solution, the normal hydrolysis became relatively faster, while in alkaline solution, the normal hydrolysis was catalysed to a greater extent than the redox cleavage, the extent of the difference depending on the solvent.

Gladding and Purves (12) studied the reaction between some glucose mononitrate derivatives and alkali. They recognized that nitrates were in many respects similar to the corresponding alkyl halides and p-tolnenesulfonates, the latter having been shown to be removed in alkali with Walden inversion, perhaps through a carbonium ion intermediate, like the alkyl halides. The hydrolysis of a nitrate group by a like mechanism should involve the formation of an internal ether or anhydro ring, or a mixed ether, or an alcohol, with Walden inversion wherever possible. Thus tetraacetyl α- glucosyl nitrate yielded B-methylglucoside (I) when treated with sodium methylate for ten minutes at room temperature. The yield of B-methylglucoside was 28% but the properties of the crude product indicated the presence of the 1, 6 glucosan (II) in equal amount. Glucosan $\langle 1, 5\rangle\beta\langle 1, 6\rangle$ was isolated from a similar hydrolysis in an aqueous dioxane solution of sodium hydroxide as the trimethyl derivative. Nitrite was produced to the extent of 4.5% of the original nitrate groups. The solution darkened in contrast to the slight yellow of the previous experiment. The formation of glucosan completed the analogy between tetraacetyl -α- glucosyl nitrate and the corresponding bromide. It was therefore plausible to assume that alkali formed the same carbonium ion from the α- nitrate and the α- bromide and that Walden inversion occurred on combination either with solvent methanol or with the primary alcohol group of the glucose residue. This explanation was put forward with reserve as it failed to account for the formation of glucosan from beta, but not from alpha, phenylglucoside under similar conditions. It was noted that the hydrolysis of the nitrate group was as rapid as that of the four acetyl groups.

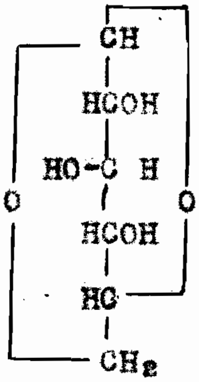
Triacetyl methyl -α- glucopyranoside -6- nitrate was hydrolysed with aqueous-ethanolic sodium hydroxide and with sodium methylate in anhydrous methanol yielding almost colorless solutions. In both cases a 77-80% yield of methyl 3, 6 anhydro -α- glucoside (III) was obtained with 2% of the nitrate groups reduced to nitrite. The reactions were much slower than the corresponding hydrolyses of the glucosyl nitrates, requiring seventy minutes at 75-80° in aqueous-ethanolic sodium hydroxide and forty-eight days in sodium methylate at room temperature.

Methyl 3,4,6 triacetyl-α-glucoside-2-nitrate heated with sodium hydroxide dissolved in aqueous dioxane for two hours at room temperature, gave an 84% yield of clear, colorless nitrate-free syrup. The reaction was more rapid than that of the isomeric 6-nitrate and gave 2.3% of the original nitrate groups as nitrite. The product was difficult to characterize, but the absence of appreciable amounts of free glycol groups as shown by the nearly negligible reaction with periodic acid, indicated the presence of a 2-3 anhydro ring. The analytical data were consistent with that of a slightly impure anhydromethylhexoside IV. This denitration was therefore similar to the deacylation of methyl 2-p-toluenesulfonyl-β-glucoside to a syrup consisting mainly of methyl 2,3-anhydro-β-mannoside. The difficulty in characterizing the product of denitration may have been caused by the partial rearrangement of the 2,3 anhydro derivative to the 3,6 isomer.

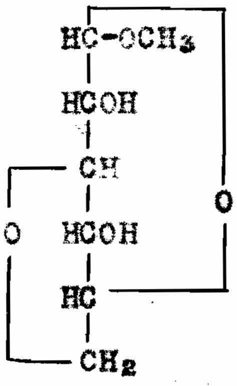
To observe the course of denitration when anhydro ring formation was blocked by other groups, methyl 2,3,4-trimethyl-β-glucoside-6-nitrate was heated at 60° for twenty four hours with sodium hydroxide dissolved in aqueous methanol. Complete denitration resulted in 20% of the original nitrate groups being reduced to nitrite while 25% of the methylated carbohydrate was decomposed to a discolored tar that slowly neutralized some of the excess alkali. Methyl 2,3,4-trimethyl-β-glucoside was obtained in 75% yield. The rather drastic conditions used in this experiment were necessary since the methylated 6-nitrate was stable to alkali in aqueous dioxane at 25° even after one hundred hours.



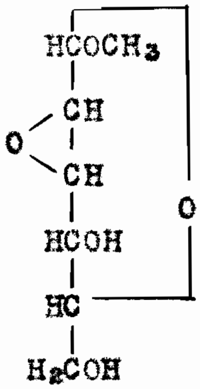
I



II



III



IV

The denitrations of the three acetate-nitrates tended to show that the preferred alkaline cleavage of carbohydrate nitrate groups took place in the sense $R_1R_2CH - ONO_2$ and led to the quick expulsion of the elements of nitric acid in a substantially unreduced condition. This method of elimination seemed to be dependent on the facile production of methyl glucoside or anhydro structures, as illustrated by the relatively great stability of methyl 2,3,4-trimethyl-β-glucoside-6-nitrate. More drastic conditions promoted a straightforward normal hydrolysis of the "blocked" nitrate group in the latter compound. The alkaline hydrolyses of the "blocked" tosyl radicals in such substances as methyl-2-tosyl-3,4,6-trimethyl-β-glucoside, methyl-2-methyl-3,4-isopropylidine-6-tosyl-α-galactoside and methyl-2,5-dimethyl-3-tosyl-β-xylofuranoside proceeded with difficulty but often in high yields along exactly the same lines. No Walden inversions were observed and the hydrolyses were therefore attributed to scission in the sense $R_1R_2CH-O \vdots SO_2C_2H$ . Therefore it seemed legitimate to assume the similar mechanism, $R_1CH_2-O \vdots NO_2$ for the scission of the blocked nitrate group.

The reaction between hydroxylamine and ethyl nitrate in anhydrous sodium ethylate (8);

$$C_2H_5-O \vdots NO_2 + NH_2OH \longrightarrow O_2N-NHOH + C_2H_5OH$$

would seem to require scission in the sense discussed above.

Earlier speculations about the mechanisms of nitrate hydrolysis are briefly reviewed by Lowry and coworkers (13) and by J. Barsha (14). Only a brief outline is included here.

Nef (1) stated that alkyl nitrates reacted with alcoholic caustic potash to produce a "methylene" radical, $R-CH\langle$ , which could add the elements of ethyl alcohol to form an ether or an oxygen atom from the nitrate group to form a carbonyl compound.

Berthelot (2) considered the hydrolysis of nitrate groups to consist of normal saponification proceeding with the simultaneous abnormal reaction which he wrote,

$$RCH_2\text{-}O\text{-}NO_2 + KOH \longrightarrow RCHO + KNO_2 + H_2O.$$

Berl and Delpy (3) thought that hydrolysis proceeded by a normal saponification. In some cases the nitrate released was supposed to oxidize the alcohol formed, this process occurring almost simultaneously with the first.

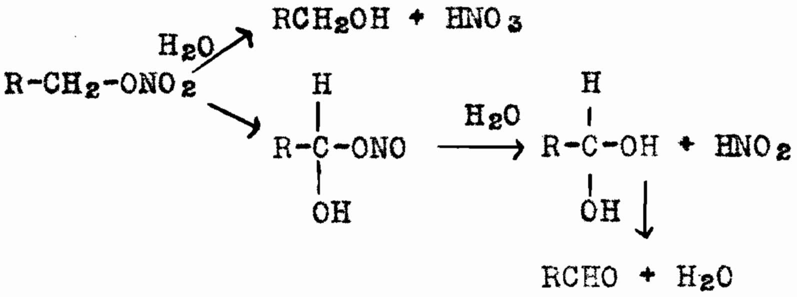
Klason and Carlson (15) formulated the abnormal redox cleavage using the peroxide structure for nitrates as proposed by Bruhl (16).

$$RCH_2\text{-}O\text{-}O\text{-}NO + KOH \longrightarrow RCH_2OOH + KNO_2$$

$$RCH_2OOH \longrightarrow RCHO + H_2O.$$

They accounted for the normal hydrolysis of nitrocellulose and other esters in the presence of mercaptans and other reducing agents, as a reduction of the intermediate peroxide.

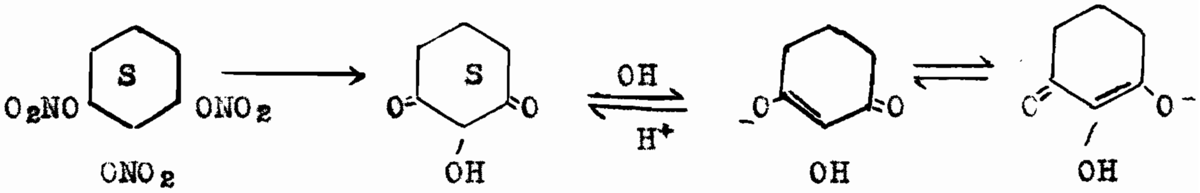
Lachman (11) revived a much earlier mechanism of Vignon and Maquenne (17) and attributed the abnormal cleavage to the hydrolysis of an intermediate, isomeric nitrite.



$$R\text{-}CH_2\text{-}ONO_2 \xrightarrow{H_2O} RCH_2OH + HNO_3$$

$$R\text{-}CH_2\text{-}ONO_2 \rightarrow R\text{-}\overset{H}{\underset{OH}{C}}\text{-}ONO \xrightarrow{H_2O} R\text{-}\overset{H}{\underset{OH}{C}}\text{-}OH + HNO_2 \rightarrow RCHO + H_2O$$

In a recent research, Christian (18) studied the hydrolyses of the three isomeric cyclohexane 1,2,3-trinitrates in 0.1N aqueous alcoholic sodium hydroxide at 20°. The rates of alkali consumption, nitrite and colour formation were measured. The cis-cis-cis isomer hydrolysed most rapidly, developed the most colour, but strangely, formed the least nitrite. As a tentative explanation for colour formation, it was assumed that intensity of colour was caused by a diketone whose resonating forms were analagous to those of many dyes.

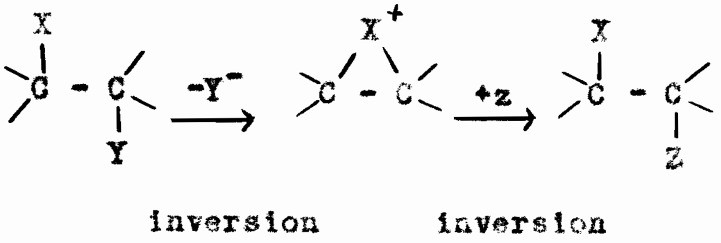


cis-cis-cis colourless coloured

It was argued that a small amount of the diketone could account for the colour and that it was more likely to arise from the cis-cis-cis derivative where the central nitrate group was sterically hindered and might be the last to undergo reaction. The abnormal cleavage is more likely to occur in the first groups to react as they are adjacent to negative groups, as in nitrotartaric acid and nitroglycerin. The least colour was developed in the hydrolysis of the cis-trans-cis isomer, where the central nitrate group might be expected to hydrolyse first.

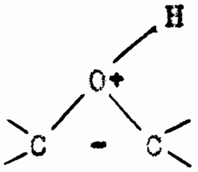
The cis and trans isomers of the more stable cyclohexane 1,2-dinitrates were hydrolysed in the same reagent at 100°, the cis compound again reacting more rapidly and producing less nitrite, (0.52 moles against 0.50 moles). Colour formation was the same in each case and less than in the trinitrate series. In the hydrolyses of the trinitrates, the cis-trans-cis derivative produced about 1 mole of nitrite and the other isomers about 0.6 moles.

Winstein and Buckles (19) developed a mechanism to explain replacement reactions of trans cyclohexane 1,2 derivatives which took place with retention of configuration.



This mechanism was assumed to account for the reactivity of trans-1-acetoxy-2 chlorohexane towards silver acetate under conditions where the cis compound was completely unreactive, since a trans "onium" ion cyclic intermediate could not form. Christian found that in general cis-ni -

trate groups reacted with alkali more rapidly than trans groups, which might indicate that in the compounds studied, a primary dissociation in the sense C - $ONO_2$ to produce a carbonium ion did not occur and that scission may have taken place in the sense C-O - $NO_2$ as discussed before for "blocked" sugar nitrate groups. Christian, however, mentioned a mechanism analagous to that of Winstein and Buckles as possibly having some importance. Winstein's mechanism provides for anhydro ring formation in the case of a nitrate trans to a hydroxyl where the intermediate



could stabilize itself by elimination of a proton.

Lucas and Hammett (20) recently investigated the kinetics of the reactions with water and hydroxyl ion of t-butyl nitrate and benzyl nitrate. Butyl nitrate underwent two solvolytic reactions, one (A), producing t-butyl alcohol and the other, (B), butene.

$$(A)\quad 2H_2O + C_4H_9ONO_2 \xrightarrow{k_1} C_4H_9OH + H_3O^+ + NO_3^-$$

$$(B)\quad H_2O + C_4H_9ONO_2 \xrightarrow{k_2} C_4H_8 + H_3O^+ + NO_3^-$$

Since the rate was unaffected by hydroxyl ion, or reduced when it lowered the activity of the water, the reactions were true solvolyses. Since activation energies and ratios of products were identical with those observed in parallel solvolyses of t-butyl chloride, it was likely that the same mechanism prevailed in both cases.

Benzyl nitrate underwent solvolytic reactions (C) and (D):

$$(C)\quad C_6H_5CH_2ONO_2 + 2H_2O \xrightarrow{k_3} C_6H_5CH_2OH + H_3O^+ + NO_3^-$$

$$(D)\quad C_6H_5CH_3ONO_2 + H_2O \xrightarrow{k_4} C_6H_5CHO + HNO_2$$

and hydroxyl ion catalysed reactions (E) and (F):

$$(E)\quad C_6H_5CH_2ONO_2 + OH^- \xrightarrow{k_5} C_6H_5CH_2OH + NO_3^-$$

$$(F)\quad C_6H_5CH_2ONO_2 + OH^- \xrightarrow{k_6} C_6H_5CH_2OH + NO_2^-$$

The hydroxyl ion reactions were much faster than the solvolyses, producing from 33 to 42.5% benzaldehyde at 50° and 58 to 68% at 25°. The solvolyses produced 6-9% benzaldehyde. Hydroquinone completely suppressed the redox reactions (B) and (F) as would be expected from the reactions of nitrates with alkaline sulfides and other reducing agents. The solvolytic reaction (A) of butyl nitrate was considered to proceed through an incipient solvation of the anion leading to a rupture of the carbon-oxygen bond with more or less transient formation of a carbonium ion. The solvolysis of benzyl nitrate to the alcohol (C), was largely through the same mechanism as for the t-butyl derivative. As far as the redox reaction was concerned, the authors concluded that; "at the present stage of our knowledge it would seem to be premature to offer any mechanism for the oxidation-reduction reaction".

The work reviewed to this point indicates that ester nitrate groups may cleave to give a variety of products, the nature of which may be influenced by the solvent, alkali concentration and the specific natures of the reactants. The reaction types fall into the five general groups:

1. $RNO_3 + KOH\ (aqu) \rightarrow ROH + KNO_3$
2. $RNO_3 + R'X \rightarrow RR' + XNO_3$

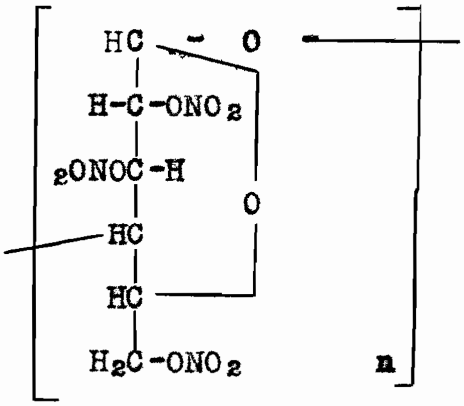
   cf. Benzyl nitrate and sodiomalonic ester
3. $RNO_3 + \text{alcoholic } KOH \rightarrow ROC_2H_5 + KNO_3$
4. $RCHR'NO_3 \longrightarrow RCR'O + HNO_2$

   This reaction may occur in acid, neutral or alkaline solution, depending on the nitrate ester involved.
5. $RNO_3 \xrightarrow{H_2O} \text{olefin} + HNO_3$

The reactions of the sugar mononitrates show a definite preference for a given reaction type i.e., 3., to form an alkyl glycoside or intramolecularly to form an anhydro sugar. When such a mechanism is blocked, the reaction proceeds with difficulty and possibly by scission of the nitrate groups in the sense $R{-}O \mid NO_2$ rather than $R \mid ONO_2$. Perhaps a reaction of the type Angeli (8) showed to occur between ethyl nitrate and hydroxylamine might facilitate the removal of such blocked nitrate groups.

The nitrates of polyhydroxy alcohols decompose in alkali with types 1 and 4 occurring in the same molecule. It may be significant that ether formation has not been observed in these cases, possibly because a carbonium ion intermediate is not formed. Support for this view is found in the alkaline hydrolyses of cis and trans cyclohexane-1,2 dinitrates, in which the cis derivative hydrolyses more rapidly than the trans compound, contrary to what would be expected if a carbonium ion intermediate were formed. The cleavage of all nitrate groups in polynitrates may thus occur in the sense $R-O \vdots NO_2$ giving rise to the observed products.

The alkaline hydrolysis of cellulose nitrates might be expected to partake of the properties of the sugar nitrates and the nitrates of polyhydroxy alcohols; particularly the latter when it is recalled that many of the nitrate groups in nitrocellulose are "blocked". Cellulose trinitrate is made up of chains of the repeating unit



in which there are no free hydroxyl groups with which anhydro ring formation can occur. Hence the nitrate groups perhaps react like the "blocked" nitrate group in methyl -2,3,4-trimethyl-β-glucoside-6-nitrate with the increased reactivity observed in nitrotartaric acid. The hydroxyl groups in cellulose are markedly different with respect to each other in their reactivities and hence their nitrates might be expected to hydrolyse at different rates and possibly by different mechanisms. However, no reaction selective for one of the three nitrate groups has been described with the exception of the replacement of the primary nitrate group by iodine (48).

Gladding and Purves (12) showed the analogy in the alkaline hydrolyses of sugar nitrate and tosyl groups in producing identical anhydro sugars or methyl glycosides. Gardner and Purves (21) had previously some evidence that in the deacylation of a tosyl cellulose acetate, a cleavage to produce intermolecular ether linkages between neighbouring glucose units occurred. However, the analagous reaction in the denitration of nitrocellulose has not been observed.

The literature on the alkaline decomposition of nitrocellulose is largely an account of the isolation or identification of the complex products of the advanced degradation of individual glucose units and inorganic nitrogen in various stages of oxidation. As such the literature has been recently reviewed by Kenyon and Le B. Gray (22) and Barsha (14). Substances ranging from carbon dioxide to oxidized derivatives of propionic and butyric acids are described as decomposition products of nitrocellulose in alkali. Berl and Smith (23) obtained a 7-8% yield of oxypropionic acid by treating nitrocellulose with alcoholic sodium hydroxide at temperatures below 25°. Lowry and coworkers (13) treated cordite, 12.2%N, with lime in an 6.5% aqueous solution of pyridine, which they claimed was the most effecient "catalyst" for the controlled decomposition of nitrocellulose. They obtained a sludge which on washing and drying contained 9.6%N. From the charred black cordite rods left in the reaction mixture they obtained a substance N 6.7%. They stated that decomposition proceeded to a "dinitrate" and then a "mononitrate" stage, after which the molecule decomposed completely. Farmer (24) held that the analyses of the two fractions were adventitious and did not represent any clean cut stage in the reaction.

Kenyon and Gray (22) made quantitative measurements of the carbon dioxide, nitrite and reducing substances formed by the action of aqueous sodium hydroxide in concentrations of from 1 to 30% on cellulose nitrate. About 60 to 70% of the nitrate groups present were reduced to nitrite. Danilov and Mirles (25) studied the viscosity changes of nitrocellulose in the presence of ammonia, pyridine, hydrazine, hydroxylamine, ammonium sulfide and sodium sulfite and found them greater than the corresponding reduction in viscosity produced by the strong bases, sodium hydroxide and tetramethyl ammonium hydroxide. Unfortunately, this paper was available only in abstract.

The decomposition of cellulose nitrate by pyridine was studied by Angeli (26). When moistened by pyridine, the nitrate yielded a semi-solid, transparent, rubbery mass whose viscosity gradually diminished towards that of pyridine itself during several days standing at room temperature. When freed from pyridine by extraction with alcohol and dilute sulfuric acid, and by reprecipitation, the product was obtained as a white amorphous powder in 80% yield. The original substitution of 2.3 had dropped to 1.5 to 1.7 nitrate groups per glucose unit. The product turned brown and then black on heating, reduced ammoniacal silver nitrate, reacted with phenylhydrazine, but had no action on Fehling's solution. These tests suggested that the substance was a nitrated highly degraded oxycellulose. Since the degree of denitration was not great and the substance was obviously highly oxidized it is likely that much of the denitration occurred by the abnormal redox route.

It is apparent that all denitrations of nitrocellulose in alkali, except in alkaline reducing agents, caused either complete degradation to monomeric debris or else great chain cleavage with relatively slight loss of nitrogen. No definite evidence was obtained for a possible variation in the reactivities of the three nitrate groups in each glucose unit or of the relative importance of the various mechanisms of nitrate cleavage, except that redox cleavage probably occurred to a great extent.

## THE THERMAL DECOMPOSITION OF ORGANIC NITRATES

While no one has demonstrated a parallel between the reactions of nitrate esters in alkali and their thermal decomposition, some similarities will be pointed out in this research. Therefore a brief summary of pertinent work on thermal decomposition is given. A more extensive review is available in a thesis by Grassie (27).

At temperatures of from 210° to 240° and 5 mm. to 15 mm. pressure, methyl nitrate (28) yielded nitrogen dioxide as one of the initial products of decomposition. Since formaldehyde and nitric oxide occurred in the final products it was postulated that the nitrogen dioxide took part in a secondary reaction. The initial reaction was written as

$$CH_3ONO_2 \longrightarrow {}^1/_2\ (HCHO) + {}^1/_2\ (CH_3OH) + NO_2$$

It has been suggested that the primary step (29) was the breaking of the $O-NO_2$ bond, giving nitrogen dioxide and the free radical $CH_3CH_2O$. in the case of ethyl nitrate. The free radical may be further oxidized to acetaldehyde and hence to carbon monoxide and carbon dioxide. The study of the explosive decomposition of a series of nitrates led Deniges (30) to the opinion that primary esters produce aldehydes and secondary esters produce ketones as the initial products of cleavage.

The earlier work on thermal decomposition of cellulose nitrates is not reviewed since little light is thrown on the stoichiometric changes involved. Sawn (31) recently suggested a mechanism for the thermal decomposition of cellulose nitrates based on the primary cleavage of nitrogen dioxide. The nitrogen dioxide then took part in secondary reactions with formaldehyde, and similar aldehydic products.

Wolfrom (32) extended the work of Frazer (32) in studying the burning of nitrocellulose at low pressures in unreactive gases at 2-10 mm. pressure. The products of reaction were divided into two fractions; a "white substance" (WS) which remained in the reaction chamber and a volatile "red substance" (RS) which was condensed in a dry ice-acetone trap. Yields of WS were in the range 40-55% and RS 30-45%. RS proved to be largely composed of formaldehyde, glyoxal, formic and acetic acids and water after oxides of nitrogen were permitted to boil away. The WS was purified by precipitation from methanol solution into water, when about 60% of the material remained in solution. The purified white substance (PWS), in which minimum degradation had occurred, was a carbohydrate derivative consisting of about six partially nitrated hexose units per molecule. Aldehydic and acid groups were present.

Using the data on the chemical nature of WS and RS Rice and Ginell (34) proposed a free radical mechanism for the thermal decomposition of cellulose nitrates based on the primary cleavage of nitrogen dioxide from the primary nitrate group. Subsequent stabilization of the carbohydrate free radical led to the observed products.

In a recent study of the decomposition of two specially synthesized cellulose nitrates, Grassie (27) obtained quantitative yields of reaction products. Since the nitrates used were synthesized by means which largely predetermined structure (39) it was possible to relate the products of reaction to the mode of decomposition. Grassie states;

"It was demonstrated that the thermal cleavage of one ester group in the mononitrate was accompanied by the formation of approximately one carbonyl group from the cellulose moiety. This carbonyl group largely remained with the non volatile residue but to some extent cleavage of the latter occurred with the liberation of volatile formaldehyde and glyoxal. The other primary product of thermal decomposition was nitrogen dioxide". The results quoted refer to a cellulose mononitrate substituted largely in the sixth position. With respect to a specially synthesized cellulose dinitrate it was stated - "results were not inconsistent with the above interpretation but were not so decisive." Certain differences in the behaviour of the two nitrates were noted. With regard to chain degradation;

"The cellulose chain was degraded to an extent roughly corresponding with one glycosidic cleavage for each mol of volatile carbonyl compound. Nonvolatile carbonyl units were apparently formed without involving degradation of the cellulose." These results strongly suggest that an elimination mechanism involving cleavage of the O-N bond was active in the thermal decomposition of the cellulose nitrates.

# EXPERIMENTAL PROCEDURES

## A. Analytical Methods

### 1. Nitrogen:-

Difficulty was experienced in analyzing the oxycellulose nitrate oximes by the Kjehldahl method because the samples deflagrated at the beginning of the estimation. Nitrate nitrogen was determined by Elving and McElroy's (35) semi-micro modification of the duPont nitrometer method. Total nitrogen was by the Dumas method as described by Gatterman and Wieland (36) or by the macro or micro-Kjehldahl methods. The latter, employing about 100 mg. or 10 mg. samples, respectively, were carried out as modified by Gunning (37). Some samples of high nitrogen content which ignited on contact with the strong sulfuric acid used in digestion, were successfully analayzed without ignition by drastic cooling of sample and acid before mixing.

### 2. Iodine:-

The determination of iodine was by boiling 30 to 40 mg. samples under reflux with 1 g. of potassium hydroxide and 25 cc. of water until solution was complete. Dilution to 100 cc., neutralization to phenolphthalein with 2 N sulfuric acid and the further addition of 2 cc. of acid followed. The iodide was oxidized to iodate by 10 to 12 drops of bromine, the excess bromine destroyed by excess formic acid, and the acidified solution was treated with potassium iodide. Titration of the iodine liberated by the iodate from the potassium iodide was with 0.02 N sodium thiosulfate.

### 3. Methoxyl:-

The Viebock and Schwappach estimation for methoxyl was used as described by Clark (38).

### 4. Acetyl:-

Acetyl was determined by a new method developed by R. U. Lemieux (39) in these laboratories. This method depended on the oxidation of the sample with chromic acid and distillation of the acetic acid so formed. The method determines acetyl groups and terminal methyl groups which oxidize to acetic acid.

### 5. Intrinsic Viscosity:-

The weight of sample was determined by the nature of the material. For undegraded nitrocellulose, samples of 1 to 5 mg. were weighed into glass stoppered tubes and a weighed amount of butyl acetate added. For degraded materials samples of from 25 to 100 mg. were used. After each determination of the relative viscosity,

$$\left( n\ \mathrm{rel} = \frac{n\ \mathrm{solution}}{n\ \mathrm{solvent}} \right)$$

, in an Ostwald viscometer at 25°± .02°, the samples were diluted with butyl acetate and the viscosity measured again. This process was repeated until $\frac{n_{sp}}{C}$ became constant; $n_{sp} = n\ \mathrm{rel} - 1$ and C was concentration per cent. The degree of polymerization, D.P., was calculated using Kraemer and Lansing's constant for nitrocellulose, D.P. $= 27\left(\frac{n_{sp}}{C}\right)_{C \to 0} = 270\,[n]$ where $[n]$ is the intrinsic viscosity (40).

## B. Materials

### 1. Cellulose Trinitrate:-

Dewaxed cotton linters, the gift of the Hercules Powder Company, were dried over phosphorous pentoxide and were nitrated according to Berl's directions (41). The linters 20. g. were kept immersed for two hours at 5° in 1700 g. of a mixture of phosphorous pentoxide (22%) and pure nitric acid (fuming nitric acid distilled from concentrated sulfuric acid) (78%). After recovery, the product was immersed in 50% aqueous ethanol at -14°, was stabilized in boiling ethanol and was dried under reduced pressure over phosphorous pentoxide all as Berl described. A yield of 35 g. with substitution 2.92 (N, 13.93%) corresponded to 96% of theory. Similar preparations varied in nitrogen content from 13.8 to 14.0%. Intrinsic viscosity $[n] = 20$, Apparent D.P. = 5400.

The trinitrate was kept in a dessicator over phosphorous pentoxide before use and all manipulations of this dangerous explosive were made with great care to avoid friction against glass or in ground glass stoppered receptacles.

### 2. Hydroxylamine from the Hydrochloride:-

The method of Hurd and Brownstein (42) was used on a ten-fold scale with slight changes which increased the yield from 50 to 65% of theory.

Metallic sodium 125 g., was added slowly to

1500 cc. of reagent butanol contained in a 5-litre 3-necked flask fitted with a mechanical stirrer and seal. The reflux condenser was equipped with a soda lime drying tube. The flask was cooled during addition of the sodium and was afterward cautiously heated under reflux for three hours or until all the sodium had dissolved.

In a 5-litre three necked flask fitted with a mechanical stirrer were placed 348 g. of dry powdered Eastman Kodak Company hydroxylamine hydrochloride, 1 g. of phenolphthalein and 300 cc. of butanol. The mixture was warmed gently with stirring for ten minutes and the hot sodium butoxide solution was then added as rapidly as was consistent with an avoidance of alkalinity as shown by the phenolphthalein indicator. The addition required three hours. The sodium chloride precipitated was removed by filtration and the mother liquor was kept at -14° in a brine bath overnight. The hydroxylamine which crystallized as beautiful white plates was recovered, shaken with three 80 cc. volumes and then with one 300 cc. volume of ether, dried <u>in vacuo</u> and stored at -10°. Yield 105 g. corresponding to 65% of theory.

## 3. Reagents:-

Eastman Kodak Company white label hydroxylamine hydrochloride, methoxyamine hydrochloride and methoxyamine were used throughout the research. Pyridine, dried over barium oxide and distilling in the range 115°-115.5°, was used throughout. Any use of specially prepared solvents is stated in the text.

## C. Effect of Pyridine Solutions of Hydroxylamine and its Derivatives on Cellulose Trinitrate

Comparable experiments were set up in which 1 g. samples of cellulose nitrate (N, 13.8%) were separately dissolved in 25 cc. of pyridine containing (a) no other reagent, (b) 6 g. of hydroxylamine hydrochloride, (c) 5 g. of methoxyamine and (d) 5 g. of methoxyamine hydrochloride. The solutions were kept at room temperature.

At daily intervals samples of each were poured into water; the resulting precipitates were washed with water, purified by solution in dioxane and reprecipitation into water and air-dried. Table III summarizes the yields, methoxyl and total nitrogen contents of the precipitates, together with approximate relative viscosities of the pyridine solutions just prior to precipitation. These viscosities were obtained by noting the times of discharge of the solutions from the same pipet.

The reaction (b) in presence of hydroxylamine hydrochloride was characterized by an initial evolution of colourless gas and by the development of very little colour, as compared to the bright yellow or orange observed in reaction (a). The products changed from short white fibres to powders after three days reaction time. Nitrogen analyses were difficult because the samples tended to deflagrate during the estimations. No nitrite was found in the filtrate from the samples.

When methoxyamine was present (solution (c) ) little colour was developed, no gas was evolved and a high viscosity was retained for two days. The products were isolated as long white fibres and the filtrates from the precipitations gave strong positive tests for nitrite. Solution (d), containing methoxyamine hydrochloride, also remained nearly colourless and yielded short cream-white friable fibres similar to those obtained in (b). The same characteristics were observed in a more detailed study of this reaction, the results of which are summarized in Table IV. The intrinsic viscosity of each sample was determined as well as nitrogen and methoxyl analyses. It was possible to obtain the product as white fibres up to and including the four day sample.

# TABLE III

## Properties of Products formed from Cellulose Trinitrate in various Pyridine Solutions

| | | Days at Room Temperature | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Solution (1) | Estimation | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| (a) Pyridine alone | n rel (2) | 1.1 | 1 | .. | .. | .. | .. | .. |
| (b) $HONH_2.HCl$ | | 2.43 | 1.92 | 1.68 | 1.66 | 1.64 | 1.52 | 1.44 |
| (c) $CH_3ONH_2$ | | .. | 10.6 | 2.74 | 2.00 | 1.67 | 1.47 | 1.40 |
| (d) $CH_3ONH_2.HCl$ | | 10.0 | 2.36 | 1.71 | 1.35 | .. | .. | .. |
| | | | | | | | | |
| (a) Pyridine alone | Yields %(3) | .. | .. | 40 | .. | 15 | .. | .. |
| (b) $HONH_2.HCl$ | | .. | .. | 75 | .. | 70 | .. | 50,73 (4) |
| (c) $CH_3ONH_2$ | | .. | .. | 80 | .. | 70 | .. | 70 |
| (d) $CH_3ONH_2.HCl$ | | .. | .. | .. | .. | 85 | .. | 95 (4) |
| | | | | | | | | |
| (a) Pyridine alone | %N (5) | 12.3 | 11.9 | 12.0 | .. | .. | .. | .. |
| (b) $HONH_2HCl$ | %N (5) | 13.8 | 14.4 | 13.8<br>14.4,14.8(7) | .. | 14.2,14.9(8) | .. | 14.4,14.9(8) |
| | %N (6) | 12.7 | 13.1 | 14.0,13.3(7) | .. | 13.9 | .. | 15.6 (8) |

## TABLE III (Cont'd)

### Properties of Products formed from Cellulose Trinitrate in various Pyridine Solutions

| | | Days at Room Temperature | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Solution (1) | Estimation | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| (c) $CH_3ONH_2$ | %N (5) | 12.0 | 11.3 | 10.9,10.8<br>(7) | .. | 10.7 | .. | 10.6 |
| | % $OCH_3$ | 0.85 | 1.05 | 1.75,1.83<br>(7) | .. | 2.14 | .. | 2.80 |
| (d) $CH_3O\ NH_2.HCl$ | %N (5) | .. | .. | .. | .. | 13.1 (9) | .. | 14.1(10)(11) |
| | % $OCH_3$ | .. | .. | .. | .. | 8.1 (9) | .. | 11.9 (10) |

Notes

(1) For details see text.
(2) Relative viscosity of solution prior to isolation of product.
(3) By weight on air-dry basis.
(4) Larger-scale runs.
(5) Kjehdahl method.
(6) Dumas method. All calues uncertain owing to instability of samples.
(7) Obtained on a duplicate, independent preparation.
(8) The mono oxime of a keto- (or aldo-) cellulose dinitrate has total N, 15.8%.
(9) Analyses correspond to substitution of 1.74 nitrate groups and 0.69 methyloxime groups.
(10) Analyses correspond to substitution of 1.62 nitrate groups and 1.02 methyloxime groups.
(11) Dumas nitrogen 14.2%

## TABLE IV

### Properties of the Reaction Product of Cellulose Trinitrate with a Pyridine Solution of Methoxyamine Hydrochloride.

| Time | %N. | % $OCH_3$ | (n) | D.P.[(a)] | D.S. Methyl Oxime Groups | Nitrate Groups |
|---|---|---|---|---|---|---|
| 24 hrs. | 13.2 | 1.84 | 1.94 | 520 | 0.17 | 2.45 |
| 60 hrs. | 13.2 | 4.7 | 0.59 | 160 | 0.41 | 2.14 |
| 4 day | 13.4 | 7.1 | 0.38 | 100 | 0.61 | 1.98 |
| 5 day | 13.1 | 8.1 | | | 0.68 | 1.72 |
| 7 day | 14.0 | 11.2 | | | 1.00 | 1.68 |
| | 14.1 | 11.7 | | | 0.97 | 1.70 |
| 12 day | 14.0 | 11.8 | 0.18 | 49 | 1.01 | 1.70 |

(a) D.P. = 270 (n)

## D. Cellulose Dinitrate

### 1. Preparation:-

Hydroxylamine, 100 g. was dissolved in 660 cc. of dry pyridine. The solution was added to 30 g. of dry cellulose nitrate, 13.9% N, contained in a 2-litre flask. A white opaque gel formed and large volumes of colourless gas were evolved. The reaction mixture was cooled during the exothermic reaction until the gas evolution slackened, after which the very viscous pale yellow solution, still containing many gas bubbles, was kept at 20° in the dark. The viscosity of the solution slowly decreased. After seventy-six hours the yellow solution, still viscous, was slowly poured into 3-litres of mechanically stirred distilled water, thus precipitating the nitrocellulose as strong white fibres. The fibres were washed with large volumes of distilled water and spread out to air dry. After twelve hours they still smelled strongly of pyridine. They were redissolved in 1-litre of 1:1 dioxane-acetone and reprecipitated into 6-litres of distilled water. The long white fibres were recovered, washed well with distilled water and spread out to dry in the air.Complete drying was first over anhydrous calcium chloride and then over phosphorous pentoxide under reduced pressure. Yield 24 g. or 98% based on the nitrogen content $[\eta] = 1.17$ on a product renitrated to 13.1% N by Berl's method (41).

Anal. Calcd. for cellulose with 1.68 nitrate and 0.08

oxime groups per glucose unit: N 10.43; nitrate N, 9.95. Found N, 10.47, 10.40, (macro-kjehldahl); 9.95, 9.94 nitrometer %. Oxime nitrogen by difference 0.48%.

Apparently identical products were obtained after reaction times of eleven and twenty four hours. The product described under C, using methoxyamine instead of hydroxylamine appeared to be identical except for a small amount of methyl oxime instead of unsubstituted oxime. The procedure failed when cellosolve was substituted for pyridine, the product retaining 13.5% nitrate nitrogen when carried out at room temperature. Heating at steam bath temperature for one half hour after keeping for two days at room temperature also yielded substantially unchanged trinitrate. Found, nitrate N, 12.6%. The "dinitrate" dissolved readily in acetone-dioxane (1:1), pyridine, ethanol-ether, (1:1), butyl acetate, and with progressively less ease in dioxane, acetone and glacial acetic acid.

### 2. Stability of the "Dinitrate" in Pyridine:-

One-half gram was dissolved in 10 cc. of dry purified pyridine and the mixture was shaken mechanically for eighteen hours. The slightly yellow solution was poured into water and the white fibres obtained were reprecipitated from dioxane solution into water. The yield of white fibres was quantitative. Anal. Found, (macro-kjehldahl) 9.98, 10.01%. Nitrogen content of the original dinitrate (10.43%), had therefore been little affected by the pyridine treatment.

In a Pyridine solution of Hydroxylamine:-

Cellulose dinitrate (Nitrate N, 10.0%) 1 g., was dissolved in 50 cc. of pyridine containing 2 g. of hydroxylamine. After three days at room temperature, the solution was poured into water and the product recovered as long white fibres which were purified by reprecipitation from dioxane-acetone (1:1) solution into water. Anal. Found N, 10.1% (nitrometer). The substance therefore retained the original nitrate content of 9.95% in the reaction medium in which it was formed.

In Sulfuric Acid:-

Two grams were dissolved in 90 cc. of 1:1:1 dioxane-ethanol-acetone. Ten cc. of a 10% aqueous solution of sulfuric acid in 10 cc. of acetone were added and the mixture was allowed to stand for thirty six hours. The nitrocellulose was recovered as white fibres when purified as before. Anal. Found N, 10% (macro-kjeldahl).

In Acidic Pyruvic Acid:-

Three grams were dissolved in 100 cc. of glacial acetic acid; 5 cc. of pyruvic acid and 5 cc. of concentrated hydrochloric acid dissolved in 10 cc. of dioxane were added to the acetic acid solution. After remaining at room temperature for six days, the mixture was precipitated into water. The fibrous product was reprecipitated from ethanol-dioxane as cream-white fibres, the colour probably being derived from the pyruvic acid. Anal. Found N, 9.56, 9.50 (macro-kjehldahl), 9.18, 9.23% (nitrometer). Since the analyses corresponded to substitutions of 1.50 for nitrate and 0.05 for oxime groups, the latter were equally stable to nitrate groups under conditions which might have hydrolysed oximes preferentially.

### In a Pyridine Solution of Methoxyamine Hydrochloride:-

The experiment described under C (d) was carried out on the "dinitrate". After nine days standing at room temperature, the nitrocellulose was recovered as long white fibres, apparently unchanged. Anal. Found $OCH_3$, 1.01, 0.99%. Therefore the dinitrate was stable under conditions which remove one nitrate group and introduce one methyloxime group in the trinitrate.

### Under other Oximating Conditions:-

One gram of cellulose "dinitrate" was dissolved in a mixture of 25 cc. of ethanol and 50 cc. of dioxane. A solution of 2.3 g. of methoxyamine hydrochloride in 13 cc. of water buffered to pH 5.3 with potassium hydroxide was diluted with 25 cc. of ethanol and added to the nitrocellulose solution. The mixture was allowed to stand two and one-half days at room temperature and was then poured into water. The white fibres so obtained were reprecipitated from ethanol-dioxane solution into water and recovered in a fluffy white state and in quantitative yield. Anal. Found N, 10.25, 10.24% (macro-Kjehldahl). No oxime group had been introduced.

The experiment was repeated at pH 3.5 for three and one-half days with apparently the same results as before. Anal. Found N, 9.5%.

Cellulose "dinitrate" 0.5 g. was dissolved in 25 cc. of ethanol and 25 cc. of ether containing 1.5 g. of methoxyamine hydrochloride. The ether was distilled off until the boiling point of the solution was 60°. The solution was then boiled under reflux for four hours. More ether was allowed to distill and the boiling continued under reflux for an additional hour at 75°. The nitrocellulose was recovered and purified as white fibres. Anal. Calc. for cellulose "dinitrate" mono-methyloxime, $OCH_3$ 11.8%, Found, $OCH_3$ 0.94%.

The failure to react appreciably under any of the above conditions indicated the absence of aldehydic or ketonic carbonyl groups.

### 3. Iodination of the "Dinitrate"

The cellulose dinitrate, 1.0 g. was dissolved in 35 cc. of acetone. Dioxane, 10 cc. with 7 g. of sodium iodide and 3 cc. of allyl alcohol (to remove the free iodine that was formed), was added to the mixture and the resulting solution was heated in a steel bomb at 100° for eighteen hours. The clear dark solution which resulted was poured into water and the gelatinous precipitate was washed free of iodide. The product was obtained as a hard brittle gray brown powder insoluble in acetone and dioxane. Yield 1.0 g. or 89% based on the analyses. Anal. Calcd. for cellulose with substitutions of 0.8 for iodine and 0.5 for nitrate: I , 35.5, N 2.42, Found, 35.8, 35.2; N, (Microkjehldahl) 2.43, 2.41%.

### 4. Denitration of the "Dinitrate":Reductive Acetylation:-

Cellulose dinitrate, N 11.0% prepared by the alternative synthesis (C. (c)), 0.5 g., was dissolved in 4 cc. of acetic anhydride and 0.5 cc. of trimethylamine. One gram of powdered zinc was added. Heating on the steam bath and the addition of more zinc were required to reduce the nitrate groups completely as indicated by the diphenylamine test for nitrate. The solution was filtered and the residue of zinc salt extracted with acetone. The combined solution and extract when poured into water yielded a brown precipitate. The product was reprecipitated from acetone into water. Yield 0.3 g. Anal. Found, Acetyl, 40.8% corresponding to an acetyl substitution of 2.52. Degradation was severe.

### Ammonium Polysulfide Denitration:-

Ice cold 5 N ammonium hydroxide was saturated with washed hydrogen sulfide gas. The resulting solution, 3.25 M with respect to sulfide was stored in a well stoppered brown bottle at 5°.

Cellulose "Dinitrate", 8 g., was shaken with 280 cc. of the ammonium polysulfide solution and 40 cc. of ethanol for two days at room temperature. The product was recovered washed with water, ethanol, carbon bisulfide, acetone and air dried. The pale yellow fibres weighed 5.3 g., corresponding to 98% of theory. Anal. Calcd. for cellulose with a substitution of 0.07 for sulfur: S, 1.36. Found, S 1.36, N 0.66%.

5. Nitration:-

Cellulose "Dinitrate", 1 g., was renitrated by Berl's method (41) for one and one half hours at 5°. The product was recovered, washed with large volumes of ice-cold 1:1 ethanol-water, dissolved in acetone and precipitated into water. The fibres were redissolved in acetone and again precipitated into water. The product was isolated as very white, fluffy, highly charged fibres which were insoluble in dioxane and very soluble in acetone. Anal. Calcd. for cellulose with a substitution of 2.62 nitrate groups, N, 13.1, Found, N, 13.1, 13.0%.

The experiment was repeated on the product described under D 2 from acid pyruvic acid, with similar results. Anal. Found, N, 13.15, 13.10% $[\eta] = 1.17$ apparent degree of polymerization 320.

The product of ammonium polysulfide denitration (D 4), 0.3 g. was nitrated and stabilized as described above. Anal. Calcd. for cellulose with a substitution of 2.8, N, 13.8, Found N, (nitrometer) 13.8%.

6. Acetylation of Cellulose "Dinitrate"

Cellulose "dinitrate", 1 g. was dissolved in 5 cc.

of dry pyridine and 25 cc. of acetic anhydride. After twenty four hours the solution was poured onto ice, and the product recovered. It was reprecipitated twice from acetone as long white fibres. These fibres were insoluble in butyl acetate and dioxane and very soluble in acetone. In contrast, the dinitrate was soluble in all three solvents although only slightly so in acetone. Anal. Calcd. for cellulose with substitutions of 1.68 for nitrate, 0.08 for oxime and 1.0 for acetate, N 8.8%. Found, N, (microkjehldahl) 8.89, 8.85%.

### 7. Methylation of Cellulose "Dinitrate". Attempted Methylation with Diazomethane:-

Cellulose dinitrate, 1 g., was dissolved in 60 cc. of pure dioxane and 25 cc. of an ether solution of diazomethane (4 g. in 150 cc.) was added. The mixture was kept at 0-5° for one week. Some pressure developed in the flask. Then an additional 20 cc. of the diazomethane solution and 2 cc. of water catalyst in 5 cc. of dioxane were added and the mixture allowed to stand an additional two days. The reaction was stopped by the careful addition of acetic acid and the solution poured into water. The product was purified by reprecipitation from dioxane into water, and obtained as long white fibres. Yield 1 g. Anal. Found, $OCH_3$, 0.5%. This possibly corresponds to methylation of the small amount of oxime groups.

### Methylation with Methyl Sulfate:-

A solution of 0.8 g. of cellulose "dinitrate" in 30 cc. of pure dioxane was shaken with 5 cc. of dimethyl sulfate and 5 cc. of 30% sodium hydroxide for twenty four hours. No colour developed. The mixture was poured into water and the methylated nitrocellulose was recovered as a white flocculent precipitate. When precipitated from 5% solution in acetone, the product was obtained as brittle white fibres. Yield 0.7 g. Anal. Calcd. for cellulose with substitutions of 1.72 for nitrate (all N calcd. as nitrate) and 1.00 methoxyl groups per glucose unit N, 9.5, $OCH_3$, 12.2 Found, N, (Microkjehldahl) 9.54, 9.46; $OCH_3$, 12.29, 12.29%.

The preparation was carried out on a large scale with similar results; 5.75 g. of cellulose "dinitrate" yielded 4.8 g. of methylated product. Anal. Calcd. for cellulose with substitutions of 1.83 for nitrate (all nitrogen calcd. as nitrate) and 0.97 for methoxyl, N, 9.9, $OCH_3$, 11.7, Found, N, 9.91, 9.97, $OCH_3$, 11.7%.

### 8. Denitration of the Methyl Cellulose Dinitrate:-

### (a) Ammonium Sulfide Denitration:-

Methyl cellulose "dinitrate" (N, 9.9%, $OCH_3$, 11.7%), 4 g., was denitrated by the procedure previously described ([illegible]4). The product was highly swollen and almost gelatinous. It was recovered, washed with water and alcohol, dried through methanol-benzene and heated under reflux for twelve hours with carbon bisulfide to remove any sulfur. Yield, 1.25 g. of dry cream coloured powder or 35% of the theoretical amount. Anal. Calcd. for cellulose with substitutions of 1.0 for methoxyl and 0.7 for nitrate, $OCH_3$, 14.7; N, 5.1, Found, $OCH_3$, 14.2, 14.7, 14.1, 14.7, N, 4.95, 5.32%. The analyses were difficult and good checks were not obtained. It was inferred that the substance was a mixture of fully denitrated material and the original substance.

### (b) Attempted Hydrogenolysis:-

An attempt was made to apply a recently described procedure for the hydrogenolysis of sugar nitrates (49) to the methyl cellulose dinitrate.

A solution of 0.5 g. of palladium chloride in 1-litre of solution was acidified with 5 cc. of concentrated hydrochloric acid, heated to 60° and neutralized to pH 7 with sodium barbonate solution. After adding 20 g. of freshly precipitated calcium carbonate, the palladium was reduced to the metallic state by boiling the stirred suspension for five minutes with 40 cc. of formalin. The black precipitate was collected on a filter, washed with distilled water until free of chloride ion and dried over calcium chloride *in vacuo*.

Methylated cellulose "dinitrate", 0.5 g., dissolved in 70 cc. of dioxane and 30 cc. of butyl acetate, was hydrogenated over 2.5 g. of the palladium-calcium carbonate catalyst in a Parr high pressure hydrogenation apparatus. The conditions used were 1000 p.s.i. hydrogen pressure at room temperature for one and one half hours.

The product was recovered unchanged. Reduction of sugar nitrates was complete in ten minutes according to the reference cited.

### 9. Periodate Oxidation of Partially Denitrated Methyl Cellulose Nitrate (0.8)

Separate 25 mg. samples were swollen by standing overnight with 5 cc. of 4% sodium hydroxide. The mixtures were then neutralized with N hydrochloric acid and 5 cc. of 0.1 normal periodic acid solution, buffered to pH 4.0, was added to each. Reagent blanks, identical except for the absence of the sample,were prepared. At intervals, one of the mixtures was analyzed for remaining periodic acid by neutralization with solid sodium bicarbonate followed by the addition of exactly 20 cc. of 0.05 N arsenite solution and 0.2 g. of potassium iodide. After standing fifteen minutes, the solutions were titrated with 0.0255 N iodine solution, using a starch indicator. The difference in titre between the reaction mixture and the blank was equivalent to the periodic acid consumed. Normal iodine solution was equivalent one half molar periodic acid solution. This estimation was originated by Malaprade (58)

## TABLE V

### Oxidation of Partially Denitrated Methylated Cellulose Dinitrate with Periodate(a)

| Time | cc. 0.0225N$I_2$ | Sample Wt. | Moles $HIO_4$ mole of glucose units |
|---|---|---|---|
| 2.5 hrs. | 0.60 | 0.02186 | 0.05 |
| 5.0 hrs. | 0.70 | 0.02461 | 0.05 |
| 24 hrs. | 0.91 | 0.02593 | 0.06 |
| 50 hrs. | 1.24 | 0.02273 | 0.09 |

(a) About 0.03 N and at pH 4.

The results (Table V) suggested that not more than 0.09 and probably not more than 0.06 mole of completely unsubstituted 2,3-glucose units remained in the methylated cellulose nitrate sample.

### 10. Estimation and Identification of Gas Evolved from Cellulose Trinitrate in Pyridine-Hydroxylamine:-

(a) A solution containing 5 g. of hydroxylamine in 50 cc. of dry pyridine was run from a dropping funnel into a flask containing 2.0 g. of cellulose nitrate, N, 13.9%. While the amine solution was being introduced, the three way stopcock connecting the flask to the gas buret was open to the atmosphere. The stopcock was then turned to connect the buret, which was filled with mercury and equipped with a leveling bulb. The rate of evolution of the colourless gas is given in Table VI and Fig. 1. The results are precise to 2%.

After eleven hours the reaction mixture was poured into water and the white fibres were washed free of pyridine, dried and purified by reprecipitation from dioxane-acetone as described before. Anal. Calcd. for cellulose with distributions of 1.70 for nitrate and 0.08 for oxime groups, N, (total, macro-Kjehldahl) 10.55, N, (nitrate, nitrometer) 10.09, Found, Total N, 10.60, 10.52, Nitrate N, 10.09, 10.08%.

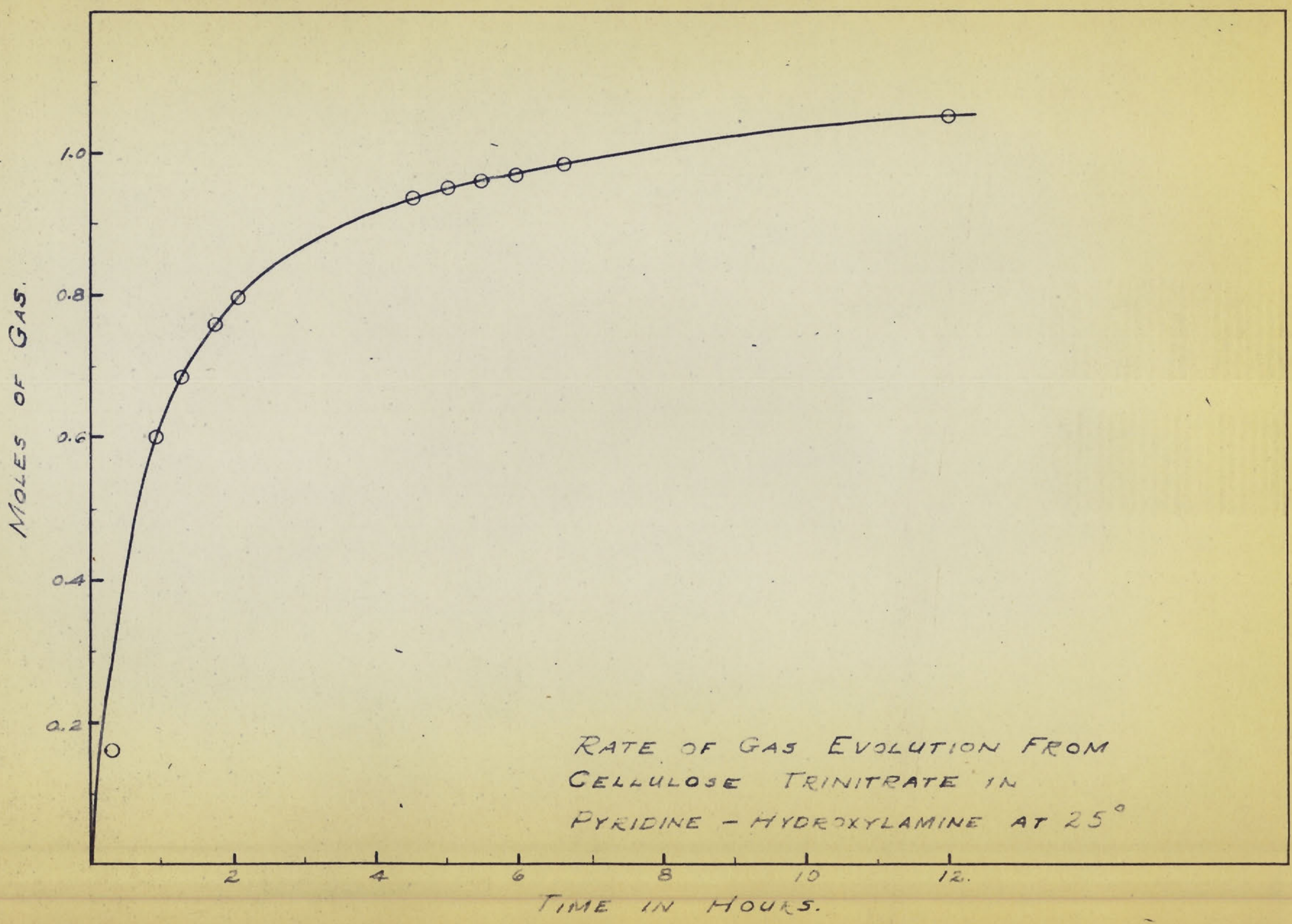
## TABLE VI

## Rate of Gas Evolution from Trinitrate in Pyridine-Hydroxylamine at 25°

| Time | cc. gas evolved (1) | Moles gas / mole of glucose units (2) |
|---|---|---|
| 20' | 28 | 0.16 |
| 55' | 105 | 0.60 |
| 1:15 | 119 | 0.68 |
| 1:45 | 133 | 0.76 |
| 2:00 | 138 | 0.79 |
| 4:30 | 163 | 0.94 |
| 5:00 | 166 | 0.95 |
| 5:30 | 168 | 0.96 |
| 6:00 | 169 | 0.97 |
| 6:40 | 172 | 0.99 |
| 11:00 | 183 | 1.05 |

(1) at 25° and 750 mm.

(2) Corr. for vapor pressure of 20 mm. of pyridine at 25°.



RATE OF GAS EVOLUTION FROM
CELLULOSE TRINITRATE IN
PYRIDINE - HYDROXYLAMINE AT 25°

FIG. 1

### (b) Analysis of the Gas Evolved from Cellulose Trinitrate and Pyridine-Hydroxylamine.

The analysis of the gas was performed using a standard Orsat apparatus (43) equipped with pipets containing 33% potassium hydroxide, 20% pyrogallol, 40% potassium hydroxide and 60% water; and ammoniacal cuprous chloride for the absorption of carbon dioxide, oxygen and carbon monoxide respectively. The gas was evolved in an apparatus as shown in Figs. 2 and 3. The cellulose trinitrate, 3 g., was placed in the reaction bulb (A) through the bottom opening which was then connected to the leveling bulb containing mercury. The bulb was then filled with mercury with the aid of a vacuum pump to remove any air trapped in the fibres, after which the stopcock was closed. A solution of 6 g. of hydroxylamine in 75 cc. of pyridine was run into the bulb from the cup. Two hundred and forty cc. of gas, or 1.00 moles per glucose unit were evolved in thirteen hours. The bulb was then connected to the Orsat apparatus and a sample of gas taken and analyzed. Found, $CO_2$, 0.0, 0.0; $O_2$, 0.1, 0.2; CO, 0.7, 0.6; Residual gas, 99.2, 99.2%. The gas was therefore nitrogen or a similar inert compound.

### (c) Density of the Gas

The apparatus used is shown in Fig. 3. The gas was generated as above. The rest of the system was evacuated. The gas from the reaction bulb (A) was then admitted slowly to the evacuated system. After all pyridine vapor had condensed in the dry ice acetone cooled trap (B), the stopcocks to and on the density bulb (C) were closed and the density bulb removed and weighed. The weight of gas, 0.1260 g., in the known volume, (159 cc.), of the density bulb, the pressure from the constant volume manometer (524 mm.) and the temperature (25°C) were observed. Substitution in the formula $PV = \frac{w}{M} RT$ then gave the molecular weight of the gas as

$$M = \frac{0.126 \times 0.0821 \times 298 \times 760}{524 \times .159} = 28.2$$

A duplicate experiment gave a value M = 28.6. Since the gas was not carbon monoxide (M,28) and was not condensable in liquid air trap (D), it was considered to be nitrogen.

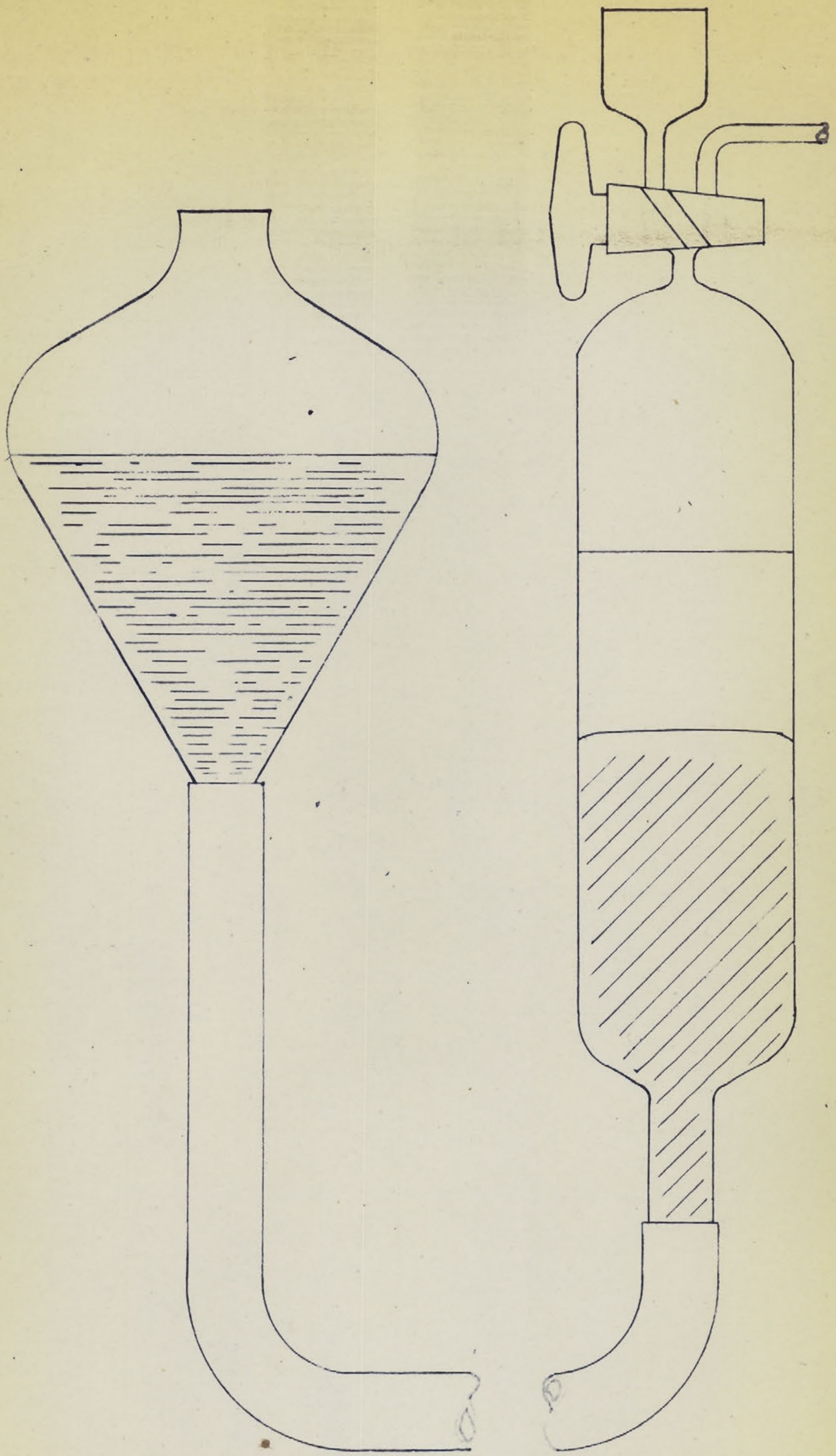


FIG. 2

GAS GENERATION APPARATU

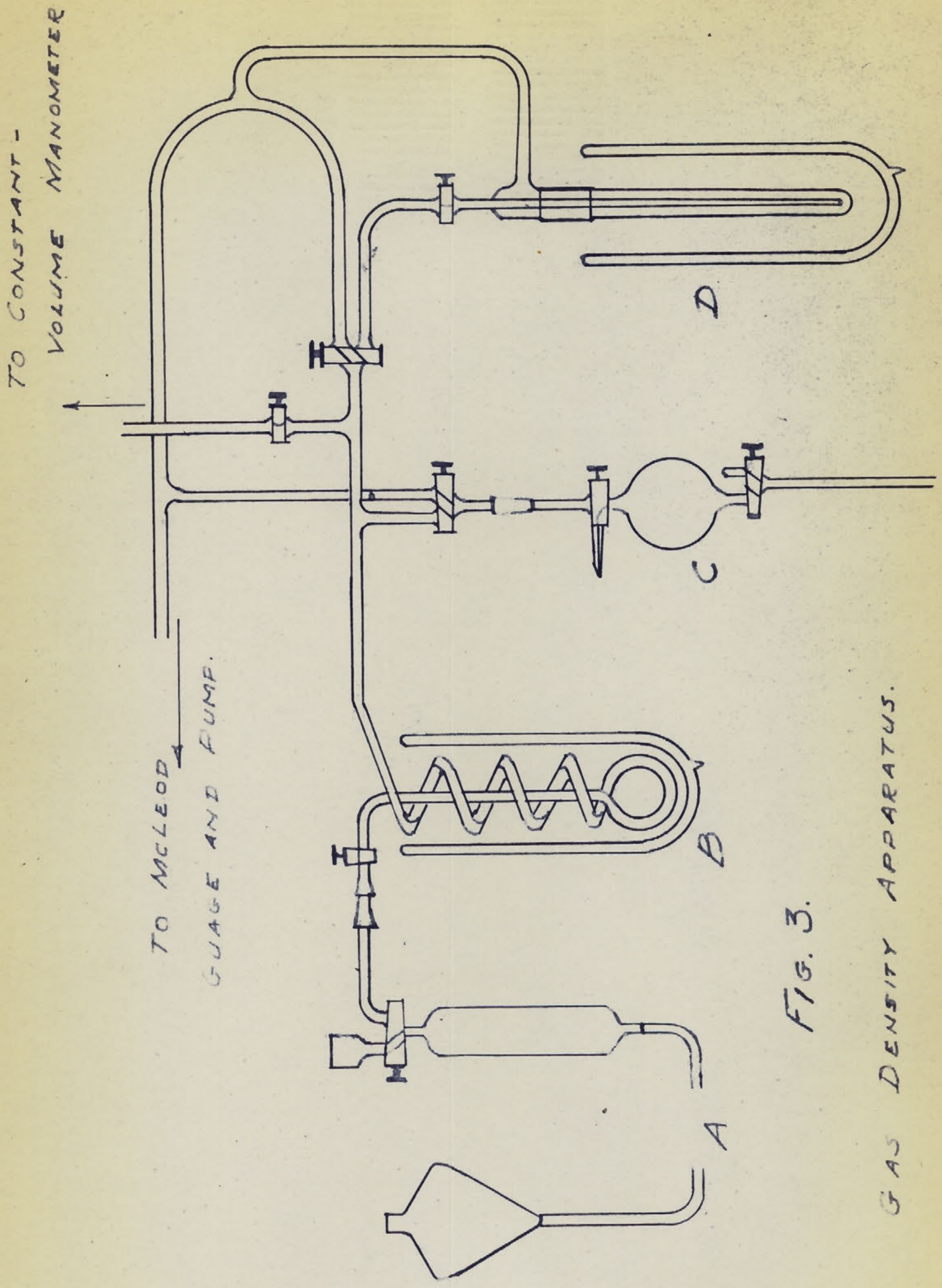


FIG. 3.

GAS DENSITY APPARATUS.

## E. Cellulose Dinitrate Oxime

### 1. Preparation:-

A solution of 60 g. of hydroxylamine hydrochloride in 250 cc. of dry pyridine was added to 10 g. of cellulose nitrate (N, 13.9%) in a glass stoppered flask. The solution was kept at 25° and the stopper was loosened frequently during the first day of reaction in order to relieve the pressure that developed. After four days the solution was poured into water and the nitrocellulose derivative separated as a yellow gum. The gum was dissolved in dioxane and reprecipitated into water as short cream coloured fibres. Upon drying, the fibres were easily powdered. Yield 7.35 g. or 85% based on the analysis. The substance could not be analyzed by the Kjehldahl method because it deflagrated on contact even with strongly cooled sulfuric acid. Anal. Calcd. for cellulose with substitutions of 1.7 for nitrate and 1.0 for oxime groups, N, 15.0; Found, N (Dumas) 15.0, 15.0%. The substance was soluble in dioxane, acetone, ethanol, acetic acid, butyl acetate and acetic anhydride.

### 2. Denitrations:-

Reductive Acetylation:-

The cellulose nitrate oxime, 1 g., was reductively acetylated as described before (D.4). Yield 0.85 g. or 71% of theory, of brown powder, nitrate free by the diphenylamine test. Anal. Calcd. for cellulose with substitutions of 2.0 for acetyl and 1.0 for acetyl oxime, N, 4.54%; Found, N, 4.63, 4.63%.

### Attempted Denitration with Ammonium Polysulfide:-

The cellulose nitrate oxime, 2 g., was denitrated with ammonium polysulfide solution as described before (D.4). Within two minutes the substance dissolved to give a clear orange solution which darkened on standing. It was therefore not considered worthwhile to investigate the reaction further.

## 3. Characterization of the Gas Evolved from Cellulose Trinitrate and Pyridine-Hydroxylamine Hydrochloride:-

### (a) Qualitative Tests:-

The gas was generated by the reaction between 2 g. of cellulose nitrate, (13.8% N) and a solution of 10 g. of hydroxylamine hydrochloride in 50 cc. of pyridine. The apparatus used was described under D.10(b) and in Fig. 2. Production of the gas was much slower than in the corresponding reaction with hydroxylamine and the volume evolved was observed to be dependent on the volume of pyridine used. A sample of the gas was found to support the combustion of a glowing splint which burst into flame. This test indicated the probable presence of oxygen or nitrous oxide. Another sample was taken in an evacuated bulb to which a similar volume of nitric oxide was admitted. The gas became only slightly yellow, the depth of the colour being very little compared to that produced by air and nitric oxide. It was inferred that the gas was mostly or entirely nitrous oxide.

### (b) Orsat Gas analysis:-

A suitable volume of gas was generated for analysis in the Orsat apparatus as described under D.10(b). The gas was somewhat soluble in all Orsat reagents indicating nitrous oxide. A pipet containing alcohol was installed in the apparatus and the gas was 78% soluble under the conditions used. A similar volume of commercial nitrous oxide was 92% soluble in alcohol. It was concluded that the gas was a mixture of about 85% nitrous oxide and 15% nitrogen.

### (c) Molecular Weight of the Gas:-

The determinations of molecular weight were performed as described under D.10(c). The density bulb, volume 159 cc., contained 0.2058 g. of the gas at 25° and 582 mm. pressure. As before, the relationship $M = \frac{wRT}{PV}$ gave 41.4 as the molecular weight of the gas. Calculated for 85% nitrous oxide (M = 44) and 15% nitrogen (M = 28), 41.6.

The gas was about 85% condensable in the liquid air trap (D Fig. 3) to a white solid. The density of the condensed gas was determined, on evaporation into an evacuated density bulb. The value obtained, M, 43.7 was close to that of nitrous oxide.

## F. Cellulose "Dinitrate" O-methyloxime

### 1. Preparation:-

Cellulose nitrate (N, 13.9%), 9.5 g. was allowed to react for seven days at 25° with 250 cc. of pyridine containing 60 g. of methoxyamine hydrochloride. The yellow solution was poured into water, from which the nitrocellulose derivative separated as a cream coloured flocculent precipitate. The precipitate was recovered, washed well with distilled water and purified by reprecipitation from dioxane. Yield, 8.5 g. or 93% of the theoretical amount based on the analysis. Anal. Calcd. for cellulose with substitutions of 1.68 for nitrate and 1.00 for methyl oxime groups, N 14.1; $OCH_3$, 11.7; Found, N, (macrokjehldahl) 14.1, 14.1; (Dumas) 14.2; $OCH_3$, 11.66, 11.75%.

A similar preparation yielded a product containing 1.70 nitrate groups and 0.97 methyl oxime groups per glucose unit. The substance was soluble in acetone, ethanol, dioxane and butyl acetate.

### 2. Attempted Selective Hydrolysis of the Methyloxime "Dinitrate":-

A 1 g. sample was shaken with 25 cc. of N phosphoric acid for two days at room temperature. The sample was recovered, washed with water and purified by solution in dioxane and precipitation into water. Found, $OCH_3$, 12.0, 12.0%, showing no removal of methyloxime units from the starting substance which had $OCH_3$, 11.7%.

A 1 g. sample was dissolved in 20 cc. of dioxane containing 0.6 cc. of concentrated hydrochloric acid. After one hour at room temperature the mixture was poured into water and the precipitate purified by reprecipitation from dioxane into water. Found, $OCH_3$, 10.5, 10.5%. In this case a slight amount of de-methyloximation occurred.

One gram of the methoxime "dinitrate" was dissolved in 15 cc. of dioxane and 2 cc. of 85% phosphoric acid in 4 cc. of water was added. After eighteen hours the substance was precipitated and purified as before. Found, $OCH_3$ nearly unchanged at 11.5%. These experiments make it clear that the methyloxime group was difficult to hydrolyse.

### 3. Iodination (48):-

The oxycellulose "dinitrate" methyloxime, 0.8 g., was dissolved in 10 cc. of acetone and the solution was heated with 5 g. of sodium iodide in a steel bomb at 100° for two hours. The solid residue was redissolved in 100 cc. of acetone with 10 g. of sodium iodide and 10 cc. of allyl alcohol which was included to remove the free iodine that was formed. After being heated in the bomb for sixteen hours at 100°, the clear dark solution was evaporated to 10 cc. and poured into water. The brown, powdery precipitate was washed with benzene to remove any allyl al-

## G. Resume of Experiments on Decomposition of Cellulose Nitrates with Sodium Sulfite and Potassium Cyanide solutions.

### Cellulose Trinitrate and Aqueous Sodium Sulfite:-

Four grams of cellulose nitrate, N, 13.9% was dissolved in 500 cc. of "Methyl Cellosolve". A solution of 2.5 g. of sodium sulfite and 2.5 g. of sodium bisulfite in 100 cc. of water was poured slowly into the mechanically stirred nitrate solution which was meantime heated on the steam bath. The heterogeneous mixture was heated for one hour, after which 100 cc. of water was added and the now homogeneous solution became pale yellow. After a further two hours heating the solution was poured into two litres of distilled water in which the cellulose nitrate precipitated as a fine white flocculent material. The precipitate was filtered, dried and reprecipitated from acetone solution into water. A qualitative test for sulfur was negative. Yield, 2.5 g. or about 60% of theory. Found, N, 12.7% or 2.48 nitrate groups per glucose unit.

In a similar experiment 8.5 g. of cellulose nitrate (N, 13.9%) was dissolved in 1 litre of "Methyl Cellosolve" and a solution of 8 g. of sodium sulfite and 4 g. of sodium bisulfite in 850 cc. of 1:1 "Cellosolve"-water was poured into the stirred and heated nitrate solution. The system became slightly heterogeneous at first but at the end of three hours stirring on the steam bath, became clear. The product was isolated as before. Yield, 3 g. of short white fibres. Found, N, 12.6%. One gram of this substance was renitrated with a 25% phosphorous pentoxide - 75% nitric acid nitration mixture. The product was stabilized in aqueous ethanol and reprecipitated from acetone into water. The nitrogen content was 13.3% although the nitration conditions used produced nitrates of N, 13.9 to 14.0% from cotton. The cause of this discrepancy was not determined.

### Cellulose Nitrate and Solutions of Potassium Cyanide:-

### Pyro powder (12.58%N) in ethanol-ether-water:-

A large excess of potassium cyanide, 1 g., dissolved in aqueous ethanol-ether buffered to pH 10.5 or 11.5-11.6 with potassium acetate, was added to 1% solutions of pyropowder in ethanol-ether (70:30). The mixtures were chosen to keep the system homogeneous. At various intervals of time, aliquots were removed and analyzed for cyanide by dropping into 30% sulfuric acid through which steam was passed. The distillate was collected in ammonium hydroxide solution and was titrated with silver nitrate using potassium iodide as a precipitation indicator. This analytical method recovered more than 99% of the cyanide in a reagent blank. The difference in titre between the reagent blank and the aliquot was taken as the measure of cyanide consumed by reaction with carbonyl groups produced in the cellulose nitrate. The results are graphically illustrated in Fig. 4. The reaction mixtures became yellow on standing but a large part of the cellulose derivative precipitated on acidification. Degradation was probably not too extensive but the extensive degradation observed in the more important reaction with cellulose trinitrate caused the discontinuance of further investigation.

Cellulose Trinitrate in "Methyl Cellosolve" Solution:-

To a solution of 0.8 g. of cellulose nitrate (N, 14.0%) in 200 cc. of methyl cellosolve was added 0.5 g. of potassium cyanide in 50 cc. of 20% aqueous cellosolve. The high viscosity of the nitrate solution decreased immediately on the addition of the cyanide solution and the mixture became intensely yellow orange. Very little material precipitated from the acidified solution after two days reaction. The product of cyanohydrin synthesis on oxycellulose is precipitated in aqueous acid (60).

The distillation method of analysis was inapplicable to "cellosolve" solutions, probably because it depended on rapid boiling so that hydrolysis of the cyanide would be slight, as in the ethanol-ether solutions. Therefore aliquots were titrated directly, with some uncertainty in the end point. The maximum consumption of cyanide was about 0.65 moles of cyanide per glucose unit in twenty four hours of reaction at room temperature. Further lengthening of the reaction period led to little increase in the cyanide utilized.

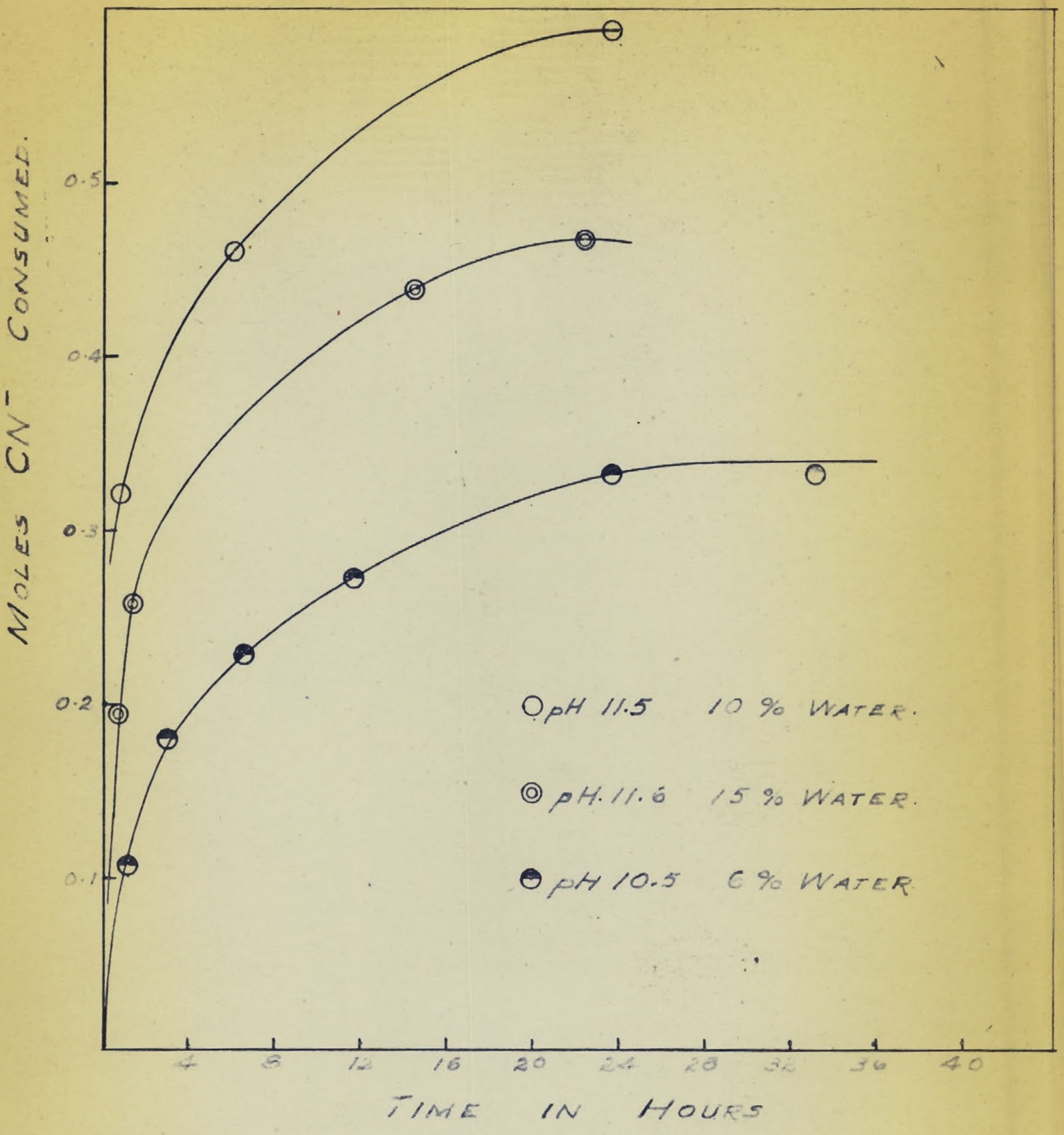


FIG. 4.

DECOMPOSITION OF NITROCELLULOSE
IN ETHANOL - ETHER - KCN.

## DISCUSSION OF RESULTS

Technical cellulose nitrates contain an average of 2.0 to 2.6 nitrates groups, distributed among the second, third and sixth positions of the glucose units in an undetermined way. This circumstance made such nitrates unsuited for experiments on selective denitration because the exact decrease in substitution corresponding to complete and selective denitration at one or other of the three positions could not be predicted. In order to avoid this uncertainty, the almost completely substituted derivative was preferred for the present research. It is obvious that with cellulose trinitrate a satisfactory selective denitration would result in a dinitrate.

As implied in the Introduction, acid hydrolysis of cellulose nitrate regenerates cellulose in a degraded condition but otherwise little changed. Alkaline hydrolysis produces deep-seated alterations whose course although obscure, appears to commence with oxycelluloses unstable in the presence of alkali. This view suggested that useful results might be obtained if the alkali contained reagents capable of combining promptly with carbonyl groups formed, and of protecting the latter from further action. Aqueous solutions of sodium bisulfite-sodium sulfite and of potassium cyanide were the protective agents tried.

The reactions in sodium sulfite-bisulfite solutions were not considered satisfactory for the purposes of the investigation. While degradation of the cellulose was slight when compared to similar reactions with sodium bicarbonate solution, the yields of water insoluble products were low and variable. Neither was the extent of denitration great, since only 0.45 nitrate groups per glucose unit were removed from the cellulose trinitrate.

Denitration in aqueous potassium cyanide solution led to very extensive degradation and the amount of cyanide consumed varied from 0.2 to 0.6 moles. When this reaction was applied to the trinitrate homogeneously dissolved in cellosolve, degradation was also rapid and extensive.

Apparently, neither the addition of hydrogen cyanide nor of sodium bisulfite to carbonyl groups protect the latter from alkali. An alternative explanation for the failure of the experiments was that the mode of decomposition assumed for the trinitrate was in error.

Qualitative experiments then indicated that the presence of hydroxylamine hydrochloride greatly moderated the degrading action of pyridine on cellulose trinitrate. The third attempt accordingly presumed that oxime formation might be effective in preventing the secondary decomposition of carbonyl groups.

Solutions of cellulose trinitrate in pyridine alone and in pyridine containing large amounts either of hydroxylamine, or hydroxylamine hydrochloride were then prepared together with similar solutions containing methoxyamine ($H_2NOCH_3$) and its hydrochloride. The use of the latter reagents for carbonyl permitted an independent estimation of any methyl oxime formed by analysis for the methoxyl group. The results (Table I) made it clear that pyridine reduced the nitrogen content from 13.8 to 12% with degradation so extensive that the viscosity of the solution was lowered to that of pyridine. Solutions containing the hydroxylamine derivatives on the other hand, retained much of their original viscosity and gave good yields of fibrous or semi-fibrous, more extensively denitrated products.

The reaction between cellulose trinitrate and a pyridine solution of hydroxylamine at room temperature was rapid and exothermic. Careful measurement showed that 1 mole of a gas was evolved per glucose residue. Chemical analyses, together with density measurements proved this gas to be pure nitrogen. The product isolated from the solution as strong white fibres in 98% yield, contained 1.7 nitrate and 0.08 oxime groups and could be recovered unchanged when kept redissolved for long periods in pyridine or pyridine-hydroxylamine. This "dinitrate" is therefore the first cellulose nitrate to be reported as having relatively high stability in pyridine and the observation suggests that instability of cellulose trinitrate in the same conditions is caused by a specific nitrate group in a definite position in the glucose residues.

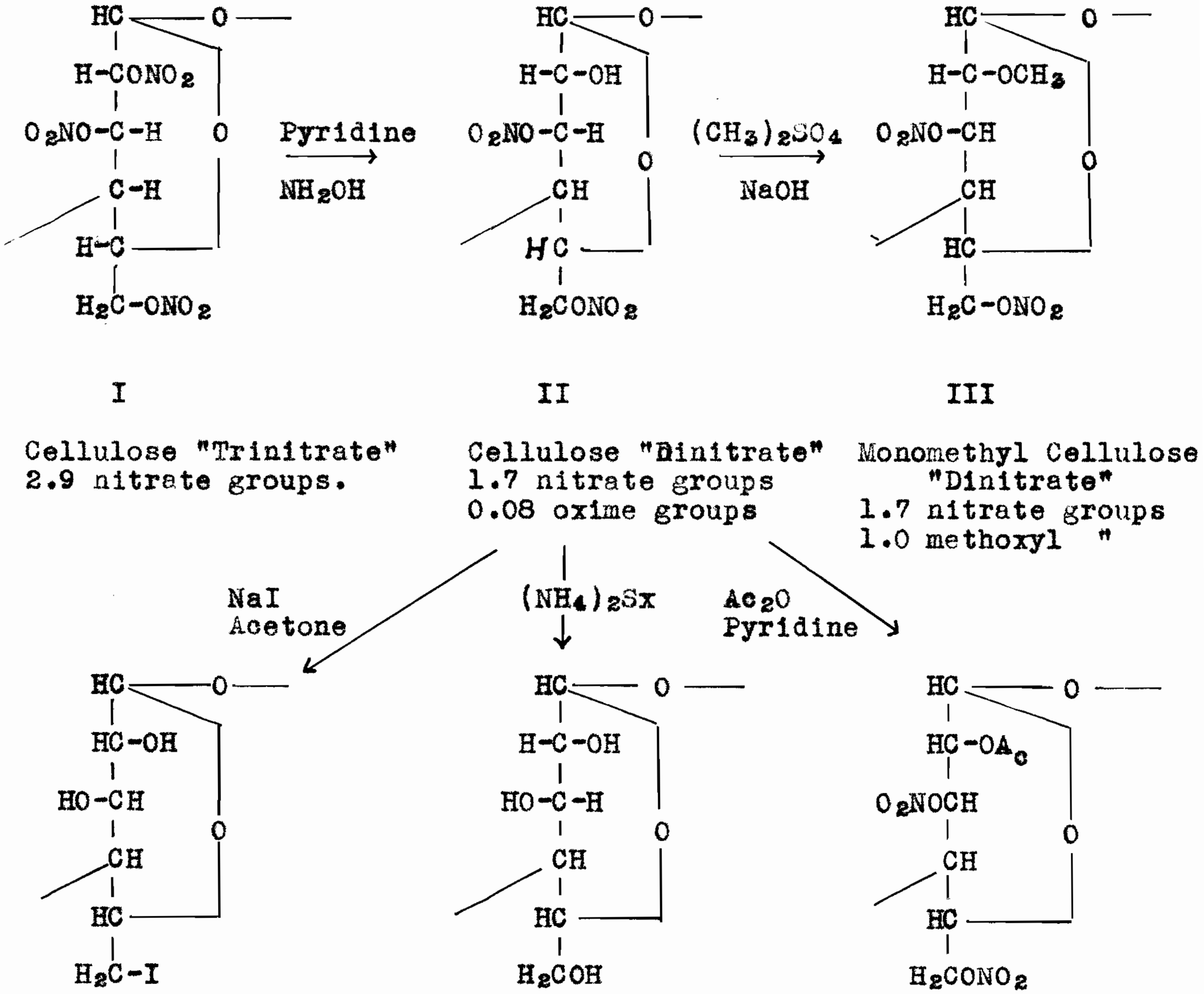
The characterization of the dinitrate (Table VII, Structure II) was carried out with a view to determining the nature and position of the group produced by the removal of the labile nitrate group. The failure to form an oxime under any of the conditions tried was confirmed by parallel experiments with methoxyamine hydrochloride. It followed that if any carbonyl group was present, it was of a ketonic, highly hindered type. Moreover, since cellulose trinitrate lost one nitrate group when dissolved in a pyridine solution of methoxyamine hydrochloride ( see below) and the present dinitrate was recovered unchanged from the same reagent, the dinitrate lacked the particular nitrate group removed from the trinitrate. Pyridine solutions of hydroxylamine or methoxyamine, and of the corresponding hydrochlorides therefore affected the same nitrate group in cellulose trinitrate.

The "dinitrate" could be renitrated nearly to the trinitrate stage. Exactly one methoxyl group was introduced with methyl sulfate, Structure (III) and apparently the dinitrate also formed a monoacetate, Structure (IV) although the estimation of acetyl in presence of nitrate is uncertain. These reactions made it plain that the removal of one nitrate group must have left a hydroxyl, and not a carbonyl group as was at first supposed.

The iodination product of the "dinitrate" with sodium iodide in acetone was Structure (IV) based on the experiments of Murray and Purves (48). Since the results indicated that least 0.8 nitrate groups were in the primary position, it was concluded that in the original reaction of the cellulose trinitrate, one nitrate group was removed selectively from either position 2 or 3 in the glucose residues. As a final confirmation of this inference it was proposed to denitrate the monomethyl "dinitrate" and to submit the resulting monomethyl cellulose to oxidation with periodic acid, which would be expected to cleave glycol units only when they were completely unsubstituted. A methoxyl group in position 2 or 3 would therefore prevent oxidation by periodate. Unfortunately the product of the ammonium polysulfide denitration was water soluble and a yield of only 35% of a substance containing 1.0 methoxyl groups and about 0.7 nitrate groups was obtained. The substance consumed only 0.05 to 0.09 moles of periodate. If this product was a gel of completely denitrated material surrounding particles of unchanged methyl dinitrate, as it might well have been, then on the basis of the analysis, it was composed of about one half monomethyl cellulose and one half monomethyl cellulose dinitrate. On this assumption, if the methyl group was distributed between primary and secondary positions, about 0.25 moles of periodate would be used; if the methyl group was secondary, little or no consumption of periodate would occur. The latter was found to be the case. Since the conclusion involves assumptions not tested by experiment, little weight can be given to it. The final proof of structure will depend on isolation of methyl glucose and its identification. This work had to be left incomplete because, with the limited supplies of methylated dinitrate available, a satisfactory method of carrying out the denitration was not discovered. Nevertheless, the cellulose "dinitrate" should eventually provide a route to new cellulose derivatives selectively substituted in either the second or the third position of the glucose residues. For example, a successful denitration of the methylated dinitrate would lead to a methyl cellulose probably with no primary substitution which would be valuable for further study.

The results show clearly that cellulose trinitrate contains one nitrate group of relatively great lability which is rapidly removed by hydroxylamine or methoxyamine in pyridine. The product, a cellulose dinitrate with good solubilities might well find special commercial or military uses, since it is remarkably stable. It also appears possible that the amount of nitrogen gas evolved from technical nitrocelluloses dissolved in the pyridine-hydroxylamine reagent would constitute a useful test for quality control and for research.

## TABLE VII



I

Cellulose "Trinitrate"
2.9 nitrate groups.

II

Cellulose "Dinitrate"
1.7 nitrate groups
0.08 oxime groups

III

Monomethyl Cellulose
"Dinitrate"
1.7 nitrate groups
1.0 methoxyl "

IV

6-iodo Cellulose
0.8 iodine atoms
0.5 nitrate groups

V

Cellulose
N,0.66%
S,1.36%

VI

Cellulose Monoacetate
"Dinitrate"

The reaction of cellulose trinitrate with a pyridine solution of hydroxylamine gave a good yield of a white partly fibrous product containing about 15% of nitrogen (Table IX, Structure VII). Nitrate nitrogen could not be reliably determined because the substance deflagrated in contact with strong acid. Like the "dinitrate" this substance was recovered unchanged after prolonged solution in pyridine. Careful chemical analyses and density determinations showed that in this case the gas evolved was a mixture of 85% nitrous oxide and 15% nitrogen. A quantitative estimation of the amount of nitrous oxide was not obtained, since pyridine is an excellent solvent for nitrous oxide. Hence the observed ratio of nitrous oxide to nitrogen is low compared to the true value which is probably about 95% to 5%.

Reductive acetylation yielded a nitrate-free product with the correct nitrogen analysis for an oxycellulose mono-oxime triacetate (Structure VIII). Denitration with ammonium polysulfide changed the molecule to a water-soluble state and gave no useful results.

Since the analysis of the oxycellulose "dinitrate" monoxime was difficult, methoxyamine hydrochloride in pyridine was used to produce a methyloxime dinitrate (IX) from cellulose trinitrate. Again a smooth selective reaction was observed, the fibrous product from which could be analysed by independent methods for methoxyl and nitrate content. The reaction was somewhat slower than the similar reaction using hydroxylamine hydrochloride. It was possible to study the reaction of cellulose trinitrate with pyridine solutions of the free base.

## TABLE VIII

### Comparison of Methoxyamine and Methoxyamine Hydrochloride reactions in Pyridine

### Substitution of Products

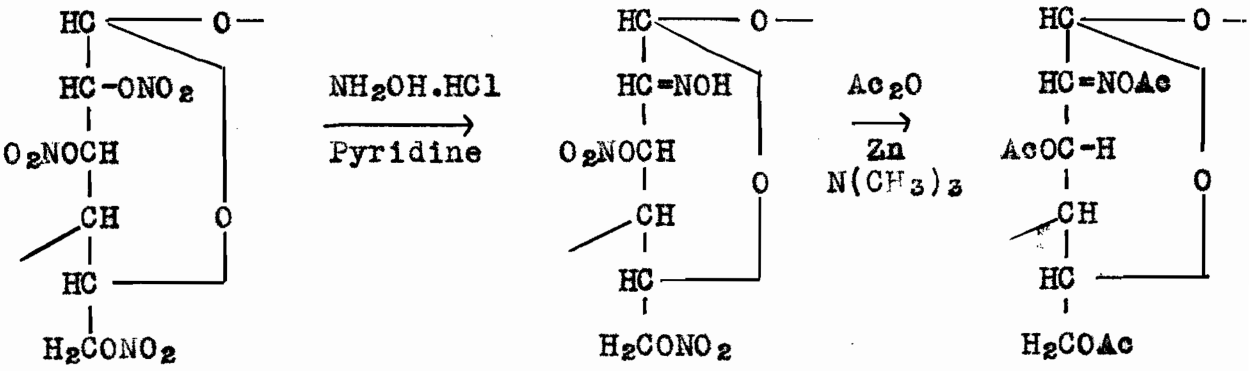
| Days | Methoxyamine | | The Hydrochloride | |
|---|---|---|---|---|
| | Nitrate | Methyloxime | Nitrate | Methyloxime |
| 0 | 2.92 | 0 | 2.92 | 0 |
| 1 | 2.17 | 0.07 | 2.45 | 0.17 |
| 2 | 1.95 | 0.09 | 2.14(a) | 0.41(a) |
| 3 | 1.74 | 0.14 | | |
| 4 | | | 1.98 | 0.61 |
| 5 | 1.69 | 0.17 | 1.72 | 0.68 |
| 7 | 1.60 | 0.22 | 1.68 | 1.00 |
| 12 | | | 1.70 | 1.01 |

(a) 60 hours.

The rates of denitration are different from the rates of oximation, as given by the methoxyl content. In the case of the free base, the latter is almost completely suppressed, amounting to only 0.22 mole after seven days. Use of the hydrochloride yielded the monoxime in the same time and the product underwent no further change in composition from the seventh to the twelfth day. These results, together with the evolution of nitrogen and nitrous oxide in the parallel work with hydroxylamine confirm the fact that the cellulose trinitrate was denitrated by two distinct mechanisms.

The methyloxime was very stable to hydrolysis and was therefore probably a ketoxime. This inference is in accord with the observation that the denitration of cellulose probably occurred at a secondary position, giving a product unreactive under conditions that yield the oxime from the trinitrate. Iodination of the oxycellulose dinitrate monomethyloxime, IX, with sodium iodide in acetone, resulted in extensive oxidation and a low yield of a degraded substance containing 0.4 iodine atoms, 0.78 methyloxime groups and 0.95 nitrate groups per glucose unit. Since replacement of nitrate groups was not complete, but a considerable amount of iodination occurred, this experiment was taken as evidence that at least some of nitrate groups were in the primary positions of the glucose residues. The methyloxime group would then be in the second or third position, or be a ketoxime.

## TABLE IX

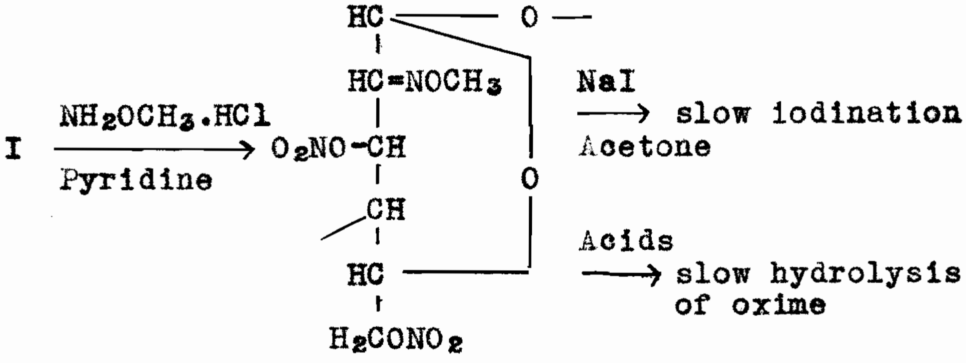


I VII VIII

Cellulose "Trinitrate"
2.92 nitrate groups

Oxycellulose
"Dinitrate Oxime
1.7 nitrate groups
1.0 oxime "
N,15.0

Oxycellulose Oxime
Triacetate
N, 4.63%



IX

Oxycellulose Dinitrate
Methyloxime
1.7 nitrate groups
1.0 methyloxime groups

Some comments may now be made concerning the details of reactions already discussed. Methylation of the cellulose "dinitrate" took place readily with dimethyl sulfate and sodium hydroxide, with no loss of nitrogen and with the introduction of exactly one methoxyl group. It is noteworthy that the "dinitrate" (1.7 nitrate) reacted as though it had exactly 1.0 free hydroxyl groups rather than 1.2 to 1.3, as calculated from the nitrate substitution. The unreactive 0.2-0.3 hydroxyls apparently were not oxidized, since the reaction with hydroxylamine introduced not more than 0.1 oxime groups. Similarly cellulose trinitrate (2.9 nitrate) with hydroxylamine or methoxylamine hydrochlorides in pyridine yielded monocarbonyl derivatives, the total substitution again being about 2.7 per glucose unit. Difficulty in preparing completely substituted cellulose derivatives is of frequent occurrence and several other examples are to be found in the Thesis prepared in this laboratory by R. U. Lemieux (62). It is possible that substituents already present determine the reactivity of the remaining hydroxyl groups. Thus renitration of the cellulose "dinitrate" by Berl's (31) method resulted in a nitrate of substitution 2.62, but, after the "dinitrate" was completely denitrated with ammonium polysulfide, the same renitration gave the expected "trinitrate" with substitution 2.9. Brown (45) on the contrary found that the product of a technical nitration, N, 12.2%, with a presumably random distribution of nitrate groups was readily nitrated by Berl's method nearly to the trinitrate stage.

The decrease in the degree of polymerization (D.P.) of the cellulose caused by the various reactions in pyridine was assessed by the viscosity method. Kraemer and Lansings' (40) relationship was used to convert intrinsic viscosity (n) to apparent degree of polymerization according to the equation D.P. = 270 (n) . The constant was determined for a nitrocellulose containing 12.1%N. Brown (45) found the intrinsic viscosity of a sample of the cotton linters nitrated to 12.2%N (Substitution 2.32) with a technical nitrating mixture to be (n) = 9.25. Upon renitration of this nitrocellulose by Berl's method (41) nearly to a trinitrate (N, 13.9%, substitution 2.9) the intrinsic viscosity was found to have increased to 14.9. Therefore denitration to the dinitrate stage even without any decrease in average chain length would be expected to decrease the observed intrinsic viscosity by at least 40 per cent. Since the intrinsic viscosity of our original trinitrate was (n) = 20, the D.P. was probably about 20 x 270 x 0.6 = 3240. The D.P. of the various products as calculated from the intrinsic viscosities, are shown in Table X. These products were all very soluble in butyl acetate and effects caused by poor solvents on intrinsic viscosity were probably minor.

## TABLE X

## Apparent Degrees of Polymerization

| Substance | D.P. | Cleavage (a) Required |
|---|---|---|
| 1.7 nitrate (Product of 3 days reaction nitrated to 13.1% N, Berl's Method.) | 320 | 0.0062 |
| 2.14 nitrate, 0.41 methyloxime (2.5 days reaction) | 160 | 0.0124 |
| 1.98 nitrate, 0.61 methyloxime (4 days reaction) | 100 | 0.0198 |
| 1.70 nitrate, 1.01 methyloxime (12 days reaction) | 50 | 0.0392 |

(a) Fraction of glycosidic links.

Kuhn's (47) relationship for the degradation of a polymer of infinite length is,

$$\alpha = \frac{2}{n + 1}$$

where $\alpha$ is the degree of cleavage for the production of the maximum number of n membered fragments. The right hand column of Table X shows the fraction of glycosidic bonds which would have to be broken in order to reduce the average D.P. of a cellulose molecule infinitely long to the values observed. It is seen that for the various reactions discussed, from 0.6 to 3.9% of the original glycosidic links were cleaved while one nitrate group was removed from each glucose unit. These are maximum values, as the original chain was not of infinite but of about n = 3240. Also, when cellulose trinitrate was dissolved with hydroxylamine in pyridine, there was evidence from the decrease in nitrogen evolution that the reaction was almost complete in four hours. The values for $\alpha$, determined for three days in the reaction mixture, is likely to be considerably greater than the actual chain cleavage occurring during the reaction proper. It was concluded that degradation of the trinitrate in the reactions discussed was insignificant in comparison to the extent of chemical change.

The survey of the literature made it clear that in many reactions the alkyl nitrates are analogous to the alkyl halides rather than to the carboxylic esters of organic acids. The substitution of the nitrate group by alkoxyl, alkyl and by substituted amines are cases in point. Such replacements must involve cleavage of the nitrate ester in the sense $R \,\vdots\, ONO_2$ with the transient existence of a carbonium ion. The occurrence of the oxidation-reduction reaction in the hydrolysis of nitrate esters has complicated mechanistic theories, but an interesting suggestion postulated the cleavage of the O-N bond (12).

$$RR'CHO \;\vdots\; NO_2 \longrightarrow RR'CO + HNO_2$$

It seems likely that hydrolysis in concentrated acid occurs by oxygen-nitrogen cleavage. The weight of opinion is that direct nitration of an alcohol occurs by the mechanism

$$RO\boxed{H \quad HO}NO_2 \longrightarrow RONO_2 + H_2O$$

with the oxygen atom in the water coming from the nitric acid. If the reverse were true, nitration of a sugar should involve stereochemical inversion which has not been observed. Since nitration, like other esterifications, is an equilibrium reaction, the acid hydrolysis must occur in the same sense as the nitration, otherwise epimerization of a sugar would occur on nitration. In other words, nitration and acid hydrolysis of nitrates occur by mechanisms analogous to the esterification and acid hydrolysis of organic acids. (53)

It is thus apparent that cleavage of nitrate esters may occur between carbon and oxygen, $C \mid O - NO_2$, and oxygen and nitrogen, $C - O \mid NO_2$. Cleavage between carbon and oxygen must involve the transient existence of a carbonium ion, $R^{+}{-}{-}{-}{-}{-}O{-}NO_2$, the relative ease of such cleavage being determined by the negativity of the group R. The more electronegative R becomes, the more difficult it should be to remove an electron to form the carbonium ion $R^{+}$. For example, methyl chloride is easily hydrolysed to methanol and water

$$CH_3 - - - - - \boxed{Cl\ H}\,OH \longrightarrow CH_3OH + HCl$$

but methylene chloride is very stable since it is difficult to form the carbonium ion CH Cl under the influence of the electron attracting the ahalogen atom remaining in the group.

Methylene bromide on this view is much more stable because it cannot undergo substitution readily and no easy mechanism is available for elimination. Gem-dihalides of higher alkanes, however, react very readily to eliminate HX. When a carbon atom is bound to a nitrate group and another very negative group by a carbon-carbon linkage, it is readily seen that the only elimination not involving carbonium ion formation or carbon-carbon cleavage is the elimination of nitrous acid.

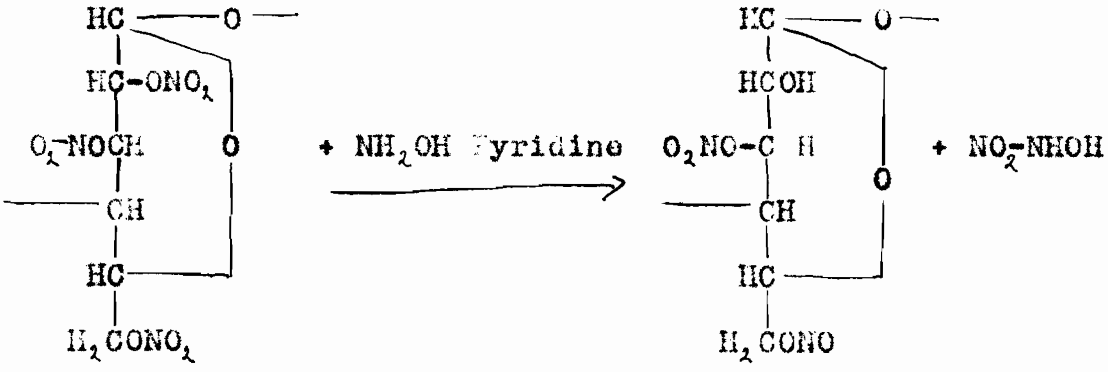
The work of the Ingold school on the mechanisms of elimination reactions has been summarized and discussed by Remick (55). It seems likely that the elimination reaction of importance in the case of cellulose trinitrates is second order, catalysed by the basic solvent, but the cleavage of the nitrate group presents an additional complexity not found among the more extensively studied alkyl halides. It is generally the case that elimination occurs to a lesser extent than substitution, where both mechanisms are possible, probably because the activation of two bonds requires more energy than one.

The mechanistic possibilities so far discussed give an adequate explanation for the observed reactions of cellulose trinitrate in pyridine solutions of hydroxylamine and its hydrochloride. The negativity of the molecule excludes carbonium ion formation as an important possibility. Since cleavage is restricted to the oxygen-nitrogen bond, substitution will take place where hydrogen ions or atoms are readily available and elimination where hydrogen is not available. Angeli's reaction (8) shows both processes going on together:

$$RCH_2ONO_2 + H_2NOH \xrightarrow{NaOEt} RCH_2OH + NO_2NHOH$$

where this, the substitution reaction occurs to the extent of 50%. The labile hydrogen in the hydroxylamine allows this reaction to compete with the elimination reaction and the carbonium ion substitution.

The reaction between cellulose trinitrate and hydroxylamine in pyridine is probably analagous to the above reaction except that the milder conditions used in the present work avoided the extensive elimination reaction. Since a twenty to thirty-fold excess of hydroxylamine was used, the intermediate nitrohydroxamic acid was probably quickly reduced, yielding the observed mole of nitrogen gas.

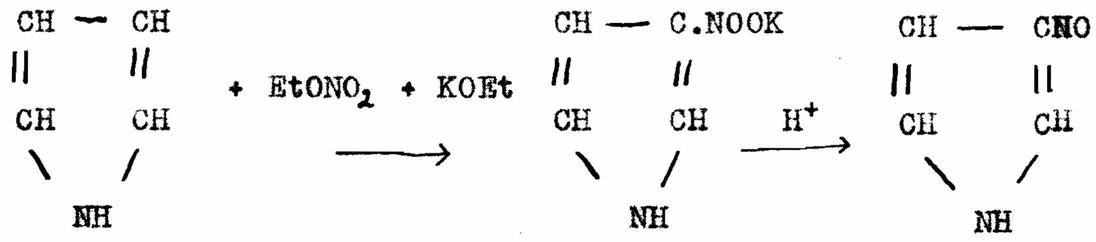


$$NO_2NHOH + NH_2OH \longrightarrow N_2\uparrow + HNO_2 + 2H_2O$$

This reaction was almost over in four hours, during which time the elimination reaction progresses only to a very slight extent.

The lack of gas formation in the corresponding reaction with methoxyamine is probably owing to the fact that methoxyamine is a much weaker reducing agent than hydroxylamine and the intermediate $NO_2NHOCH_3$ is relatively stable. Analogous reactions to give nitro compounds from ethyl nitrate and substances containing reactive hydrogen are known (56) e.g.

$$EtONO_2 + KOEt + \varphi CH_2.CO_2Et \rightarrow 2EtOH + \varphi.CH(NOOK)CO_2Et$$



The reaction between cellulose trinitrate and hydroxylamine hydrochloride is thought to have occurred almost exclusively by elimination

$$\rangle CHONO_2 \xrightarrow[NH\ OH.HCl]{Pyridine} \rangle C = O + HNO_2$$

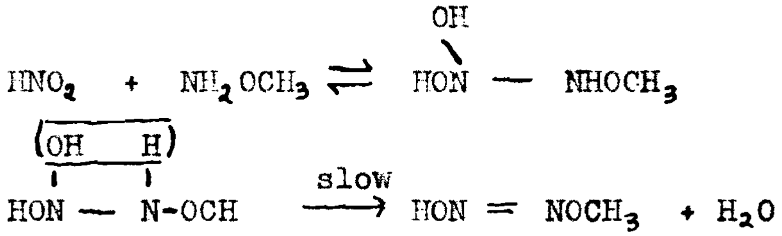
$$HNO_2 + NH_2OH.HCl \longrightarrow N_2O + 2H_2O + HCl \ (61)$$

Hydroxylamine is stabilized by salt formation and hence does not behave then as an active hydrogen compound. Trial showed that hydroxylamine hydrochloride in pyridine did not react rapidly with a pyridine solution of pyridinium nitrite. Hence, in the reaction, nitrous acid must have been eliminated as such and must have reacted immediately with the hydroxylamine hydrochloride to produce nitrous oxide. The latter was not evolved at a noticeable rate in the reaction using methoxyamine hydrochloride, although in aqueous solution methoxyamine reacts with sodium nitrite (52) according to the equation:

$$\mathrm{NaNO_2 + NH_2OCH_3.HCl \rightarrow HON = N{-}OCH_3 + NaCl + H_2O}$$

$$\mathrm{HON = N{-}OCH_3 \rightarrow N_2O + CH_3OH}$$

It is possible that the monomethyl ester of hyponitrous acid HON=N-OCH is relatively stable at room temperature in pyridine and also that the early intermediate steps (51) are slow.



$$\mathrm{HNO_2 + NH_2OCH_3 \rightleftharpoons \overset{OH}{HON} - NHOCH_3}$$

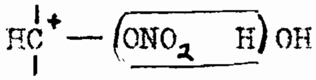
$$\mathrm{\overset{(OH}{HON} - \overset{H)}{N}{-}OCH \xrightarrow{slow} HON = NOCH_3 + H_2O}$$

That this may be the case is indicated by the fact that these solutions gave a test for nitrite while the ones with hydroxylamine hydrochloride did not.

The elimination reaction producing an oxycellulose dinitrate is very similar to the thermal decompositions carried out by Grassie (27), who found that his results were best explained by O-N cleavage, producing one mole of carbonyl derivative for each mole of nitrate removed. It is plain that the considerations involved in elimination in solution apply to an even greater extent to the thermal decomposition. Mechanisms involving carbonium ion formation which are possible in unblocked sugar nitrates in solution, where the energy requirements are lowered by solvation, are hardly probable in thermal decompositions, where the energy required for carbonium ion formation would be very high. Thus, as in the present experiments, involving hydroxylamine or methoxylamine hydrochloride, Grassie's cellulose mononitrate eliminated the elements of nitrous acid, although free hydroxyl groups were available for anhydro ring formation, if carbonium ion formation were possible.

Lachman's (11) results obtained in the hydrolyses of nitrotartaric and nitromalic acids may be re-interpreted using the postulates outlined above. Nitrotartaric acid includes two negative nitrate groups and two negative carboxyl groups, so that carbonium ion formation is probably excluded. In very concentrated acid the molecule slowly hydrolyses to tartaric acid and nitric acid. As the concentration of acid is reduced, the molecule is activated by solvation and the elimination reaction, catalysed by hydroxyl ions, becomes more important, while the acid hydrolysis must necessarily by slowed. In alkali, the only possible reaction is elimination as is found to be the case.

The nitrate group in nitromalic acid is linked to a less electronegative group than those in tartaric acid dinitrate and hence is more stable. In this case, too carbonium ion formation should be possible when the molecule is solvated and attacked by a negative ion. In dilute acid, carbonium ion formation is suppressed because the concentration of hydroxyl ion is low. Since the acid hydrolysis in dilute acid is also slow, the slow elimination reaction tends to predominate, which is what was found. In neutral solution a more rapid reaction through the carbonium ion begins as hydroxyl ion concentration increases



$$\mathrm{HC^{+}{-}(ONO_2 \quad H)OH}$$

and only 8% occurs via elimination. In alkaline solution both the carbonium ion reaction and the second order elimination reaction are catalysed (57), and a rapid reaction by both mechanisms occurs. Since the carbonium ion reaction depends on solvation by a polar solvent to lower the required activation energy, it should be more important in aqueous than in alcoholic alkali as was found to be the case.

## SUMMARY

A large excess of hydroxylamine, dissolved in pyridine was found to remove one mole of nitrate per glucose unit from cellulose trinitrate, the nitrogen being quantitatively recovered in the gaseous phase. The white fibrous cellulose dinitrate so produced was degraded only slightly and differed from the original trinitrate in being practically stable when dissolved in pyridine. The replacement of the hydroxylamine by methoxyamine gave the same product.

The cellulose "dinitrate" failed to yield an oxime or methoxime but readily yielded a monomethyl, and probably a monoacetyl derivative and could be re-nitrated. These observations showed that the removal of the nitrate group left an hydroxyl and not more than 0.1 mole of carbonyl group, in the cellulose portion. This hydroxyl group was probably of secondary alcohol type, since experiments showed that the primary alcohol positions of the glucose units were still occupied by nitrate groups.

Cellulose trinitrate with a pyridine solution of hydroxylamine hydrochloride, eliminated one nitrate group probably as nitrous acid and yielded the oxime of a monocarbonyl oxycellulose dinitrate. Nitrous oxide, probably formed from the nitrous acid produced and the excess hydroxylamine hydrochloride, was evolved. In

similar fashion, cellulose trinitrate with a pyridine solution of methoxyamine hydrochloride gave the methyloxime of a monocarbonyl oxycellulose dinitrate. The oxime group in this compound was not removed by acid hydrolysis but the nitrate groups could be eliminated by reductive acetylation. This product had the composition of diacetyl oxycellulose mono-oxime acetate. All these nitrates were stable in presence of pyridine at room temperature.

The production of the cellulose dinitrate and of the oxycellulose dinitrate mono-oxime or monomethoxime involved the removal of the same nitrate group from cellulose trinitrate. Mechanisms considered most probable for the two types of selective denitration are summarized by the equations:-

(a) $RHONO_2 + H_2NOH \longrightarrow RHOH + NO_2NHOH$

$NO_2NHOH + H_2NOH \longrightarrow N_2\uparrow + HNO_2 + 2H_2O$

(b) $RHONO_2 + (H_2NOH.HCl) \longrightarrow R{=}O + HNO_2$

$HNO_2 + H_2NOH.HCl \longrightarrow N_2O\uparrow + 2H_2O + HCl$

where R represents the cellulose residue.

Attempts to obtain selective partial denitrations of cellulose trinitrate by the action of solutions containing sodium sulfite or potassium cyanide failed owing to incomplete reaction or excessive degradation.

# CLAIMS TO ORIGINAL RESEARCH

(1) The discovery that although cellulose trinitrate is known to be completely decomposed by pyridine itself, the addition of hydroxylamine to the pyridine results in a nearly quantitative denitration of the trinitrate to the dinitrate with very little degradation. Pyridine containing methoxyamine gave similar results.

(2) The discovery that hydroxylamine hydrochloride dissolved in pyridine also promoted a nearly quantitative denitration of cellulose trinitrate to the dinitrate stage. In this case, however, the gas evolved was at least 85% nitrous oxide and the product formed was the dinitrate of an oxycellulose mono-oxime. Replacement of the hydroxylamine hydrochloride by methoxyamine hydrochloride yielded the corresponding monomethyloxime of the oxycellulose dinitrate.

(3) The discovery of the first cellulose nitrate (1) that is stable in pyridine. Monomethyl and probably monoacetyl derivatives of this cellulose dinitrate were prepared.

(4) The discovery of the first derivative of a monocarbonyl oxycellulose (2).

(5) The discovery that the labile nitrate group in cellulose nitrate is probably in a secondary position in the glucose residue.

(6) Mechanisms are advanced for the new denitration reactions (1) and (2).

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