THE LOCATION OF SUBSTITUENT GROUPS IN PARTIALLY NITRATED AND IN PARTIALLY XANTHATED CELLULOSES

A Thesis

by

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GENERAL INTRODUCTION

During a study of the degradative action of pyridine on cellulose trinitrate, G.H. Segall discovered that a solution of hydroxylamine in pyridine removed one nitrate group per anhydroglucose unit from the trinitrate. The selectivity of this reaction was demonstrated, and a possible specificity for one of the two secondary nitrate groups in the anhydroglucose units was suggested. The unusual stability of Segall's "dinitrate" to alkalies permitted methylation to a "mono-O-methyl dinitrate" with dimethyl sulphate and sodium hydroxide. In theory, the structure of the "dinitrate" could then be found by reduction of the mono-O-methyl-cellulose dinitrate to O-methylcellulose, which when hydrolysed would yield identifiable O-methylglucoses. However, Segall, and later Grassie, were unable to achieve this reduction in a satisfactory way, and failed to locate the nitrate groups in the dinitrate.

After many months of experiment, the denitration of the mono-O-methylcellulose dinitrate has now been accomplished with the aid of ammonium hydrosulphide in aqueous dioxane. The resulting O-methylcellulose, containing 1.12 methoxyl groups per anhydroglucose unit, has been hydrolyzed in 89% yield to a syrup containing partially methylated glucoses. Chromatography of this syrup yielded 84% of crystalline 2-O-methyl-β-D-glucose together with small amounts of 2,3-di-O-methyl- and probably 2,6-di-O-methyl-D-glucose. These results therefore identified Segall's cellulose dinitrate as essentially cellulose 3,6-dinitrate. This work is described in Part I of the Thesis.

The successful completion of the above research left the author

free to attempt the solution of a second problem, which concerned the location of the xanthate groups in cellulose sodium xanthate. This derivative is the most important intermediate in the manufacture of viscose rayon. The Ph.D. Theses of D.L. Vincent and of A.K. Sanyal described the preparation of completely substituted cellulose S-methyl-xanthate acetates which accurately reflected the xanthate substitutions of the original cellulose sodium xanthates. If the dexanthation of such products could be achieved without the occurrence of any acetyl migration or deacetylation, the location of the acetyl groups in the resulting partly acetylated cellulose could be determined by such classical techniques as tritylation, and tosylation-iodination. The location of the original xanthate groups could then be inferred. However, Sanyal's dexanthations were accompanied by a loss of acetyl groups large enough to destroy the value of the proposed method.

The present research continues the attempts at dexanthation without deacetylation, and to this end, the reactions of S-methylxanthate groups with chlorine dioxide and sodium chlorite have been studied for the first time. Rapid, exothermic dexanthations occurred with these reagents, but in all the experiments a few of the acetyl groups were also removed. This work, described in Part II of the Thesis, confirmed the results of the earlier workers, but failed to remove entirely the technical difficulty that prevents the complete success of the project.

During the course of the work, the literature surveyed in the previous Theses was collated, amplified, and brought-up-to date (1955). The surveys given in the present Thesis, although voluminous, are thought to be complete except for the patent literature.

PART I

THE ASSIGNMENT OF STRUCTURE TO CELLULOSE 3,6-DINITRATE

HISTORICAL INTRODUCTION

A. Denitration of Organic Nitrates by Saponification with Strong Alkali

The saponification of organic nitrate esters with alkali has long been a subject of investigation because of the complicated nature of the reaction. Most of the early work was concerned with explosives, such as glycerol trinitrate and glycol dinitrate, whose polyfunctional character made the kinetics of their decomposition complex and very unsuitable for a study of mechanism. However, even at this early stage, it was apparent that the alkaline hydrolysis of nitrate esters involved a much more complex decomposition than simple fission into alcohol and metallic nitrate, the presence of nitrite, carbonyl derivatives, olefins, and organic acids having been detected in the products. These results were summarized and discussed by Silberrad and Farmer (1), Lowry and coworkers (2), and Farmer (3). A recent review by Boschan, Merrow and Van Dolah (4) on "The Chemistry of Nitrate Esters" summarized some of the later work.

Segall (5) reviewed the alkaline decomposition of simple and polynitrate esters, and summarized five general reaction paths for these denitrations:

Normal saponification

$$RONO_2 + KOH \longrightarrow ROH + HNO_3 \qquad (1)$$

Olefin formation

$$RCH_2CH_2ONO_2 \longrightarrow RCH = CH_2 + HNO_3 \qquad (2)$$

Redox reaction

$$RCH_2ONO_2 \longrightarrow RCHO + HNO_2 \qquad (3)$$

Ether formation

$$RONO_2 + KOH + EtOH \longrightarrow ROEt + KNO_3 + H_2O \qquad (4)$$

Carbon-carbon bond formation

$$RONO_2 + R'\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}OR'' \xrightarrow{NaOEt} R'\overset{O}{\overset{\|}{C}}CHR\overset{O}{\overset{\|}{C}}OR'' + HNO_3 \qquad (5)$$

The complicated nature of these alkaline denitrations was a consequence of two or more of these competitive reactions being in operation at the same time.

Nef (6) in 1899 listed three types of reactions undergone by alkyl nitrates in alcoholic potassium hydroxide; viz., normal saponification, redox reaction to form carbonyl compounds and nitrites, and ether formation. He pointed out that carbonyl derivatives could also be formed from alkyl halides if the saponification were carried out in the presence of an oxidizing agent such as mercuric oxide. Benzyl nitrate and dimethyl aniline at 100° gave benzyl-dimethylphenylammonium nitrate, a substance which was analogous to the quaternary ammonium halides. Nef concluded that the differences in hydrolysis between alkyl nitrates and halides were related to the oxidative power of the nitrate group. Normal saponification to alcohols could be attained by the inclusion of reducing agents in the reaction mixture.

Klason and Carlson (7, 8) studied the decomposition of various nitrates in alcoholic potassium hydroxide at 70°. The proportion of nitrite formed was found to increase with increasing complexity of the alkyl substituent. Thus methyl nitrate gave only a trace of nitrite, isobutyl nitrate gave 35%, glycol nitrate, 87%, and a cellulose nitrate (12.5% N) gave 82% nitrite. The direct formation of nitrite was envisaged as a primary reaction with the simultaneous formation of an alkyl hydroperoxide:

$$RCH_2ONO_2 + KOH \longrightarrow RCH_2O.OH + KNO_2 \quad (6)$$

followed by decomposition of the peroxide into an aldehyde and water:

$$RCH_2OOH \longrightarrow RCHO + H_2O \quad (7)$$

In the presence of a thiol, the peroxide was reduced to the alcohol, and the thiol was oxidized to a disulphide:

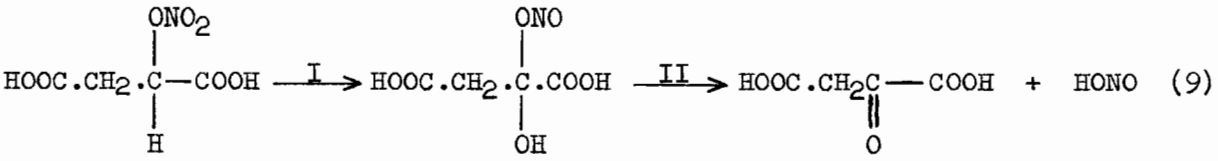
$$RCH_2OOH + 2R'SH \longrightarrow RCH_2OH + R'_2S_2 + H_2O \quad (8)$$

The incorporation of hydrogen peroxide in the alkaline medium also effected a regeneration of the original alcohol. Oxygen was evolved in the latter case, but not when the hydrogen peroxide was added after hydrolysis to aldehyde and nitrite had occurred. This view of an alkyl hydroperoxide intermediate was also supported by Lowry and his coworkers (2) who were able to explain the anomalous formation of many hydrolysis products by assuming that the carbonyl derivative resulting from the decomposition of the peroxide could further suffer hydrolysis, reduction and oxidation. The idea has now been discarded but was recently revived by Matsuhima (9) who reported the isolation of diethyl peroxide from the saponification of butyl nitrate in the presence of diethyl sulphate. The reduction of organic hydroperoxides to alcohols by sodium hydrosulphide has been investigated (10, 11).

The saponification of butyl nitrate under various conditions was studied by Ryan and Coyle (12) who found that the type of products, as well as the rate of hydrolysis, depended on such factors as the particular nitrate ester, the solvent, and the alkali employed. The rate of hydrolysis increased with temperature and also when alcoholic instead of aqueous potassium hydroxide was used. An ethanolic solution of ammonium hydrosulphide proved to be the most efficient hydrolytic agent, the denitration occurring with deposition of sulphur and the evolution of heat.

Iron and acetic acid reduced one-third of the nitrate ester to butanol, but acetic anhydride and sodium acetate had no apparent action.

Lachman (13) discovered that the very unstable nitrotartaric acid, $HOOC(CHONO_2)_2COOH$, reacted as the nitrous ester of dihydroxytartaric acid in aqueous acid, as well as in neutral, or alkaline solutions. The more stable nitromalic acid, $HOOC.CH_2.CHONO_2.COOH$, (14) could be studied in greater detail, and Lachman concluded that while the amount of nitrite formed was independent of temperature, concentration, or excess of alkali, the solvent medium was of extreme importance. Hydrolysis in alcoholic solution produced nearly twice as much nitrite as was formed in aqueous solution. Klason and Carlson (7) had found that the normal saponification of a nitrate took a measurable time, while the hydrolysis of a nitrite was practically instantaneous. Lachman was able to show that the reaction governing the rate of formation of nitrous acid obeyed first order kinetics, from which he assumed the occurrence of isomerization to a nitrous ester and subsequent hydrolysis according to the following scheme:



Reaction I was the slow process which governed the over-all kinetics. Concomitant with the above reaction scheme, the normal saponification to alcohol and nitric acid occurred, the real constant being the ratio of the rates of the two reactions and not the formation of nitrite. The true action of alcohol, which appeared to increase the amount of nitrite, was to slow down the normal hydrolysis to nitrate. The function of alkali was preferentially to catalyze the normal hydrolysis reaction.

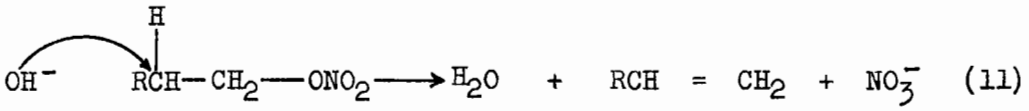
Kinetic studies by Lucas and Hammett (15) led to a renewal of Nef's analogy between nitrate esters and the corresponding chlorides. They concluded that the cleavages of t-butyl nitrate and of t-butyl chloride to form t-butanol and isobutene in acid, neutral, and alkaline dioxane - water mixtures were so similar that the same mechanisms of solvolysis and elimination could be postulated. This view was also accepted by Baker and Easty (16) although they also showed that the hydrolysis of primary and secondary alkyl nitrates occurred at approximately one-fortieth of the rate of that of the corresponding alkyl bromides. These workers interpreted the oxidation processes in the light of the modern electronic theories of nucleophilic substitution and elimination developed by Hughes, Ingold, and their collaborators (17, 18). Baker and Easty confirmed the formation of carbonyl derivatives and nitrite, but were skeptical of the older mechanistic suggestions involving oxidation of the alcohol to carbonyl compounds, because aqueous ethanol was not oxidized by potassium nitrate. The idea that the nitrate ion was the oxidizing agent was thus eliminated. Furthermore, the exceedingly slow solvolytic reactions in aqueous ethanol rendered oxidation by the nitrate ester very improbable. The difference in products was due to the particular mechanism of substitution or elimination, as well as to whether alkyl-oxy-($R-\dot{|}-ONO_2$) or nitryl-oxy-fission ($R-O-\dot{|}-NO_2$) occurred.

Baker and Easty considered three distinct types of reaction, viz:

Nucleophilic substitution (S_N)

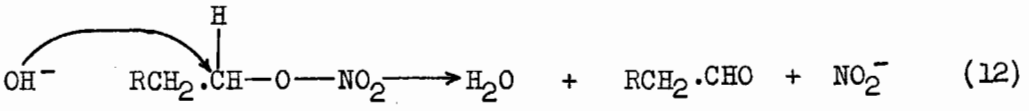
$$OH^- \curvearrowright CH_2R \\ | \\ CH_2\text{-}O.NO_2 \longrightarrow RCH_2CH_2OH + NO_3^- \qquad (10)$$

β-Hydrogen elimination (E)



(11)

α-Hydrogen elimination (E_{co})



(12)

In cases of solvolysis, the solvent molecule might act as the nucleophilic reagent instead of the hydroxyl ion. All three reactions might occur by uni- or bimolecular mechanisms depending on the degree of cooperation of the nucleophilic reagent in the rate determining stage of the reaction. In 90% alcohol, alkaline hydrolysis of methyl nitrate resulted only in second-order substitution (S_N2), but the elimination reactions increased with ethyl and isopropyl nitrates, and became considerable with t-butyl nitrate where the hydrolysis followed first-order kinetics. For methyl, ethyl, and isopropyl nitrates, the rates of hydrolysis were approximately in the ratios 70:7:1. Hydrolysis of t-butyl nitrate was very much faster and was not markedly accelerated by hydroxyl ions.

In neutral solvolysis neither olefin- nor carbonyl-elimination reactions could be detected with methyl, ethyl, or isopropyl nitrates, the reaction rates being in the order Me>Et>iso-Pr, but considerable first-order olefin elimination occurred with t-butyl nitrate, though to a lesser extent than in the case of alkaline hydrolysis. The use of 60% instead of 90% alcohol as the solvent served to lessen the percentage of olefin formed from t-butyl nitrate. The 60% alcohol decreased the

rates of alkaline hydrolysis of methyl and ethyl nitrates, but that of isopropyl nitrate was greater, and of t-butyl nitrate very much greater, in the more highly ionizing solvent. Neutral solvolyses were all faster in 60% than in 90% alcohol, especially for t-butyl nitrate, the order Me > Et < iso-Pr ≪ t-Bu being maintained in both solvents.

The conclusions of Baker and Easty paralleled those reached by Hughes, Ingold, and others (17, 18) in the study of the hydrolysis of alkyl halides. If the hydrolysis reaction was bimolecular, the effect of increasing the inductive electron-release (+I) of the group R in $R—CH_2ONO_2$ would be to induce a larger negative charge on the β-carbon atom, which would hinder the approach of the attacking nucleophilic reagent and decrease the rate of hydrolysis. In the less ionizing solvent, 90% alcohol, this was found to be the case. A more highly ionizing solvent would be expected to shift the position of change-over from a bimolecular to a unimolecular mechanism in the direction of smaller electron-release by the alkyl group; hence the explanation for the velocity sequence Me > Et < iso-Pr in 60% alcohol was that considerable incursion of the unimolecular mechanism had taken place with isopropyl nitrate. The presence of hydroxyl ions could therefore cause no significant increase in the velocity of hydrolysis of t-butyl nitrate, which proceeded predominantly by the unimolecular mechanism:

$$\text{t-BuONO}_2 \underset{}{\overset{\text{slow}}{\rightleftharpoons}} \text{t-Bu}^+ + NO_3^- \qquad (13)$$

$$\text{t-Bu}^+ + ROH \xrightarrow{\text{fast}} \text{t-BuOR} + H^+ \quad (R = H \text{ or Et}) \qquad (14)$$

S_N1

The general picture in the series of alkyl nitrates was

therefore very similar to that for the alkyl halides, the position of change-over from bimolecular to unimolecular mechanism in aqueous alcoholic solvents being located in the region of the isopropyl compound (19, 20). More highly ionizing solvents would be expected to effect a slight decrease in the rate of alkaline hydrolysis of nitrates participating in a bimolecular mechanism, since the reaction

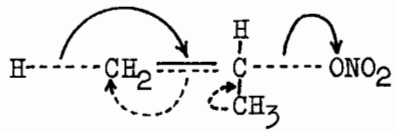
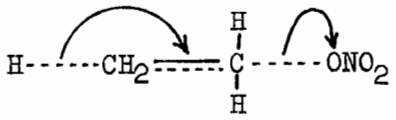
$$HO^- + RONO_2 \longrightarrow \overset{\delta-}{HO}\cdots\cdots R\cdots\cdots\overset{\delta-}{ONO_2} \longrightarrow HOR + NO_3^- \qquad (15)$$

would involve only a dispersal of the charge in the transition stage. In contrast, the rates of hydrolysis of nitrates participating in the unimolecular mechanism would be considerably greater in a more highly ionizing solvent, because the transition state $\overset{\delta+}{R}\cdots\cdots\overset{\delta-}{ONO_2}$ would involve an increase in the magnitude of the charge. The reagent in neutral solvolysis was the solvent molecule which brought about an increase in the magnitude of the charge in the transition state of the bimolecular mechanism

$$ROH + R'ONO_2 \longrightarrow \underset{H}{\overset{\delta+}{RO}}\cdots\cdots R'\cdots\cdots\overset{\delta-}{ONO_2} \longrightarrow \underset{H}{\overset{+}{ROR'}} + NO_3^- \longrightarrow ROR' + HNO_3 \qquad (16)$$

and a higher velocity was observed for methyl and ethyl nitrates in the more highly ionizing solvent. Elimination leading to olefins was found to obey a modified version of the Saytzeff rule (21) which states that in secondary and tertiary halides, the hydrogen atom lost is eliminated preferentially from the carbon atom most deficient in hydrogen. In halides (22), this phenomenon was controlled by the electromeric effect which would also apply in the present case. Thus increase of α-methyl substituents produced a greater proportion of olefin because of hyper-

conjugation with the forming double bond in the transition stage and consequent increased stabilization.

c.f.  and 

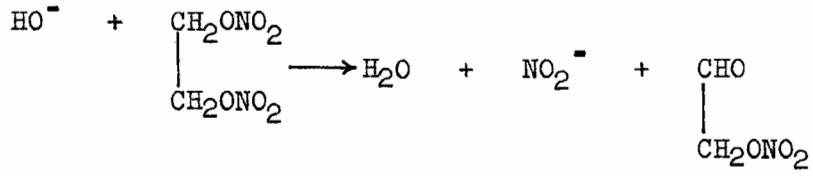
Elimination leading to carbonyl groups is specific to alkyl esters of a few oxy-acids including nitric acid.

$$H\text{-}\overset{|}{\underset{|}{C}}\text{-}O\text{-}NO_2 \longrightarrow H^+ + >C=O + NO_2^- \qquad (17)$$

Here predominant control by either the inductive or the electromeric effect would be determined in the general case, essentially by the electronic nature of the ester radical. In organic nitrates, the electron-attracting (-I) effect of the nitro group, normally a stimulant to the operation of the +I effect of the alkyl substituents, would be damped by the intervening oxygen atom. Bimolecular elimination from organic nitrates leading to carbonyl groups would be controlled predominantly by the electromeric effect, as in the case of alkyl halides. The inductive (+I) effects of the α-alkyl substituents, directly attached to the carbon atom from which proton elimination occurred, would exert a strong, first-order, retarding influence on such ionization, while the hyperconjugation effect with the forming double bond would serve to increase the proportion of reaction.

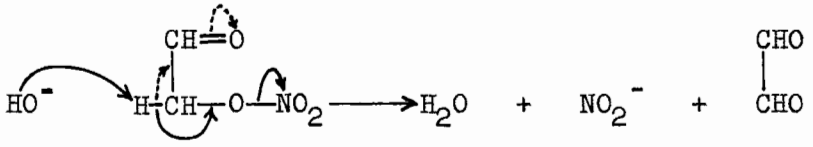
The simultaneous occurrence of the three reactions S_N2, E2, and $E_{co}2$ indicated the lines along which data in the early literature regarding the alkaline hydrolysis of polynitrates such as glycol dinitrate or glycerol trinitrate might be explained. The observed

formation of a variety of products such as glycollic acid, aldehyde resins, etc., could follow from the oxidation of products initially formed in an $E_{co}2$ reaction in accordance with schemes of the type:



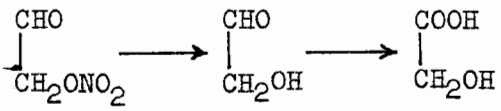
(18)

The electron-attracting aldehyde group thus formed would then greatly facilitate the ionization of the prototropically related hydrogen to favour a further E_{co} reaction.



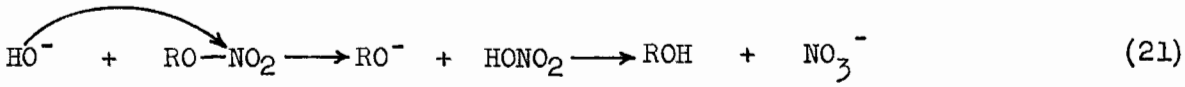
(19)

Such reactions would, of course, be superimposed on the ordinary substitution reaction giving nitrate ion and alcohol. Other products would be formed by modifications such as



(20)

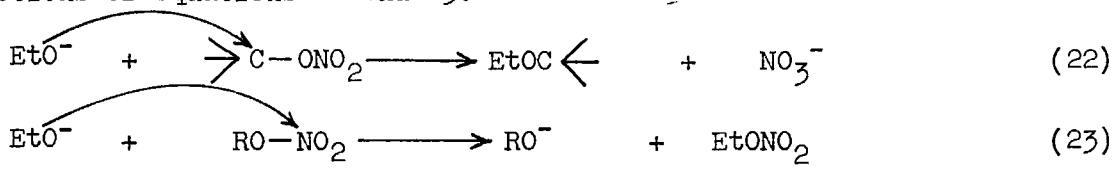
Cristol, Franzus, and Shadan (23) regarded the equations of Baker and Easty as incomplete, and recommended the inclusion of a fourth alternative mechanism, equation 21, involving nitryl-oxy cleavage analogous to that usually utilized by carboxylate esters (24).



(21)

This reaction would be superimposed on that of nucleophilic substitution (equation 10) but the results would be obscured by the related solvolytic

reactions of equations 22 and 23.



$$EtO^- + \rangle C-ONO_2 \longrightarrow EtOC \langle + NO_3^- \qquad (22)$$

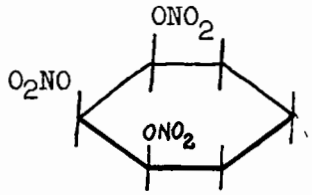
$$EtO^- + RO-NO_2 \longrightarrow RO^- + EtONO_2 \qquad (23)$$

Equations 10 and 22 would cause inversion, while equations 21 and 23 would result in an alcohol whose configuration was retained.

In support of these arguments, the alkaline hydrolysis of optically active 2-octyl nitrate in aqueous ethanol yielded 45.6% of the alcohol, 39.8% of ketone, and 14.6% of the ethyl ether, a total of 67% retaining configuration because of displacement on the nitrogen atom, and the remainder being inverted owing to displacement on carbon. In aqueous dioxane, where ether formation was impossible, the product contained 82% of octyl alcohol and was the result of configurational retention, 71% and inversion, 29%. Thus, in both aqueous ethanol and aqueous dioxane, about twice as much product was formed by the mechanistic route exemplified in equations 21 and 23 than was formed by equations 10 and 22. On the other hand, neutral solvolysis in aqueous acetone resulted in 87% alcohol and 13% ketone, of which 85% had suffered inversion; such behaviour being typical of alkyl halides and sulphonates. These results indicated that nitrate esters were borderline compounds with reasonably comparable abilities to undergo alkyl-oxygen cleavage, like sulphonate esters, and nitrogen-oxygen cleavage analogous to carboxylic esters. A similar conclusion was arrived at by Honeyman and coworkers (25, 26, 27) in their studies of the neutral and alkaline denitrations of glucoside nitrates (see pp. 15, 31).

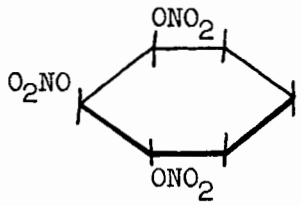
Christian and Purves (28) studied the effect of geometrical

isomerism on the alkaline hydrolyses in aqueous alcohol of the three isomeric cyclohexane 1,2,3-trinitrates:



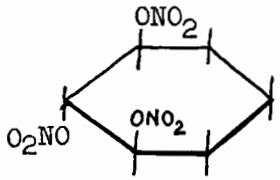
cis-cis-cis

I a



cis-cis-trans

I b



cis-trans-cis

I c

The rates of hydrolysis decreased in the order cis-cis-cis > cis-trans-cis > cis-cis-trans, while production of nitrite decreased from 0.9 mole for the cis-trans-cis isomer to 0.5 mole in the cases of the cis-cis-cis and cis-cis-trans isomers. Parallel saponifications of cis and trans isomers of the more stable 1,2-dinitrates of cyclohexane were carried out at 100° instead of 20° to increase the rates to values which would be comparable to those of the trinitrates. Here again the cis isomer reacted more rapidly and produced less nitrite (0.32 mole for cis and 0.50 mole for trans). Since the plot of moles nitrite formed against moles of sodium hydroxide consumed for the trans dinitrate at 100° was superimposable on that for the cis-trans-cis trinitrate at 20° the mechanism of nitrite formation was probably identical for both of these trans compounds. The principal conclusion to be drawn here is that the mechanism of hydrolysis of a nitrate group is also dependent on its stereochemical relation to other substituent groups. The effect of these substituent groups is not yet understood, but could in general involve steric hindrance, and electromeric effect, or both influences.

The inference that a mechanistic change occurred during the hydrolysis of the cyclohexane 1,2,3-trinitrates is supported by the occurrence of a sharp decrease in the rate of consumption of alkali after 2 moles per mole, the third mole being consumed at a much slower rate. The effect of neighbouring groups on reaction mechanisms has been discussed in a general manner by Winstein and his collaborators (29).

Gladding and Purves (30) studied the reaction between some mononitrated glucose derivatives and alkali, and found that anhydro derivatives (intramolecular ethers) were formed when suitably situated free, or potentially free, hydroxyl groups were present in the carbohydrate molecule. Normal hydrolysis resulted only with difficulty when such hydroxyl groups were blocked by methoxyl groups. Thus, methyl 2,3,4-tri-O-acetyl-α-D-glucoside 6-nitrate was hydrolyzed in 77-88% yield to methyl 3,6-anhydro-α-D-glucoside by heating with aqueous ethanolic sodium hydroxide at 75-80° for 70 minutes, 2% of the nitrate groups being reduced to nitrite. This observation was substantiated by Honeyman and his collaborators (27). Denitration of methyl 2,3,4-tri-O-methyl-β-D-glucoside-6-nitrate required 24 hours in aqueous methanolic sodium hydroxide at 60°. A 75% yield of methyl 2,3,4-tri-O-methyl-β-D-glucoside was obtained, with 20% of the original nitrate groups being reduced to nitrite and 25% of the methylated glucoside being decomposed to a discolored tar. Alkaline hydrolysis of methyl 3,4,6-tri-O-acetyl-β-D-glucoside 2-nitrate caused formation of an 84% yield of what appeared to be anhydro methylhexosides and only 2.3% of nitrite, although the 2-nitrate group was removed somewhat more rapidly than the nitrate group in the isomeric 6-nitrate. These workers concluded that the

alkaline cleavage of carbohydrate nitrate groups occurred preferentially by alkyl-oxy fission, provided that methylglucoside or anhydro structures were easily formed. The mechanism probably involved the momentary existence of a carbonium ion, as well as Walden inversion, when the nitrate group was attached to an asymmetric carbon atom. When methoxyl groups blocked anhydro ring formation, normal hydrolysis to hydroxyl groups was the main reaction, though the rate of hydrolysis was slow enough to render the still slower side reaction, $RCH_2ONO_2 \longrightarrow RCHO + HNO_2$, of considerable importance. The last reaction was postulated to involve a nitryl-oxy fission followed by loss of a methylene proton from the scission fragment RCH_2-O- and rearrangement to $RCH=O$. Analogies were also drawn with the behaviour of the corresponding p-toluenesulphonyl, sulphonyl, and halide derivatives (31, 32, 33). The similarity of these mechanisms to those previously discussed is obvious.

Honeyman and coworkers (25, 26, 27) determined the quantities of glucoside and 2,3-anhydro-D-alloside isolated from nitrated and tosylated derivatives of methyl 4,6-O-propylidene-α- and β-D- glucosides, methyl 4,6-O-ethylidene-β-D-glucoside, and methyl 4,6-O-benzylidene - α - D-glucoside. The following results (Table I) were obtained by the action of boiling methanolic sodium methoxide on derivatives of methyl 4,6-O-propylidene-α-D-glucoside:

TABLE I

Alkaline Hydrolysis of Esters of Methyl 4,6-O-Propylidene- α -D-Glucoside

	Approximate Yields, %	
Ester	Glucoside	2,3-Anhydro-Alloside
2,3-Ditoluene-p-sulphonate	undet'd	92
3-Nitrate	52	19
2,3-Dinitrate	32	13
2-Toluene-p-sulphonate 3-nitrate	18	trace

The corresponding ethylidene compounds produced less alloside than the propylidene derivatives, and the nitrated β-glucosides were much more stable to alkalies than were the corresponding isomers of the α-series. The labile nature of the C2 when compared with the C3 nitrate group in an alkaline medium was also exemplified by the observation that methyl 4,6-ethylidene-β-D-glucoside 2,3-dinitrate yielded 40% of the 3-nitrate and 40% of unchanged material after boiling in a 0.35% methanolic solution of sodium methoxide for one day. A cold methanolic-chloroform solution of sodium methoxide and methyl 4,6-O-benzylidene- α -D-glucoside 2,3-dimethanesulphonate yielded 40% of the 3-substituted derivative with some anhydro-alloside and unchanged material. This observation led Honeyman and Morgan (27) to argue that the almost quantitative yield of 2,3-anhydro-alloside obtained by the alkaline hydrolysis of the 2,3-ditoluene-p-sulphonate occurred by means of the removal of the sulphonate group on C2 by oxy-sulphonyl fission, followed

by that on C3 by carbon-oxy fission. Denitration of secondary nitrate groups was presumed to occur by a similar mechanism. A more extensive series of alkaline (sodium methoxide in methanol) hydrolyses of the esters of methyl 4,6-O-benzylidene- α -D-glucoside are reported in Table II. The behaviour of the nitrate groups was often typical in a lower degree of that of other common ester groups such as sulphonate or acetate. Migration of the nitrate group from C3 to C2 in the 3-nitrate derivatives were the first reported cases of nitrate group migration. The 3-toluene-p-sulphonate derivatives produced 2,3-anhydro- α -D-alloside even at low temperatures, whereas the 3-nitrates yielded this product only at elevated temperatures. The results in Table II confirmed that nitrate esters could be cleaved by alkali both by nitryl-oxy and alkyl-oxy fission but emphasized that yields were often low. In contrast to the purely sulphonated derivatives, extensive browning occurred with the nitrated derivatives and considerable amounts of nitrite were obtained. The low overall yields were blamed on the alkali lability of the α- diketones and α -hydroxy-ketones formed together with nitrite by α -hydrogen elimination. This view was verified by the formation of the quinoxaline derivative (Structure III) of the expected diketone, methyl 4,6-O-benzylidene-2,3-dideoxy-2,3-dioxo- α -D-glucoside (Structure II), when the reaction of the 2,3-dinitrate was carried out in the presence of O-phenylenediamine. Thus, the nitrate groups in nitrated glucosides could be removed to give:

(a) glucoside, i.e. like a carboxylic ester group;

(b) anhydro-alloside, i.e. with inversion on C3 as in sulphonates; and

(c) ketonic products (equation 12).

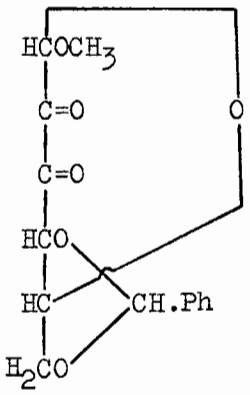
TABLE II

Alkaline Hydrolysis of Esters of Methyl 4,6-O-Benzylidene- α-D-Glucoside (27)

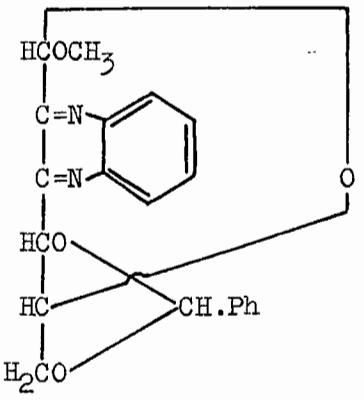
Group on C2:	ONO_2		OH		$OSO_2C_7H_7$		ONO_2	
Group on C3:	ONO_2		ONO_2		ONO_2		$OSO_2C_7H_7$	
Products (yields, %)	A	B	A	B	A	B	A	B
Unchanged	16	-	-	-	11	-	13	-
Glucoside	-	2	-	35	-	10	-	-
Anhydro-D-alloside	-	3.5	-	21	-	8	32	21
2-Nitrate	6	-	5	-	1	-	-	-
3-Nitrate	21	2	44	11	36	3	-	-
3-Toluene-p-sulphonate	-	-	-	-	-	-	9	-
Total:	43	7.5	49	67	48	21	54	21

A = hydrolysis at room temperature or 0°

B = hydrolysis in boiling solvent



II



III

The alkaline decomposition of nitrocellulose was reviewed by Kenyon and Gray (34) and by Barsha (35). Decomposition products were numerous and ranged from carbon dioxide and ammonia to oxidized derivatives such as trihydroxyglutaric acid and oxycelluloses. Kenyon and Gray made quantitative measurements of the carbon dioxide, nitrite, and reducing substances formed from nitrocellulose by the action of aqueous sodium hydroxide at various concentrations, and found that about 60-70% of the nitrate groups originally present were reduced to nitrite.

B. Denitration of Organic Nitrates with Weak Bases and Neutral Reagents

Many examples of the reactions of weak bases and neutral reagents with simple organic nitrates have appeared in the literature. Nitramination of the primary amino group occurred in the denitration of ethyl nitrate, with aniline in the presence of either sodium in ether (36), or potassium ethoxide (37); with ethylurea and ethylurethane in sulphuric acid (38); presumably, with hydroxylamine in the presence of sodium ethoxide (39, 40, 41) (see p. 35); and with hydrazine (42). Kuhn (43) reported that simple nitrate and nitrite

esters reacted with hydrazine in the presence of a palladium or platinum catalyst to give a high yield of alcohol together with nitrogen, nitrous oxide, and water as by-products. With methylhydrazine, methane and ethane were also formed. Earlier literature included the reaction of phenylhydrazine with ethyl nitrate at elevated temperatures to give nitrogen, aniline, and ammonium nitrate (44), and at ordinary temperatures in the presence of sodium methoxide to produce a complex variety of products including nitrogen, nitrite ion, nitrobenzene, aniline, azobenzene, phenyl azide, benzene, and biphenyl (45). Merrow and Van Dolah (42) investigated the reaction of nitrate esters with hydrazine, and obtained products such as nitrogen, hydrazoic acid, ammonia, nitrous oxide, nitrite and nitrate ions, alkylated hydrazines, alcohol, and traces of aldehyde. Primary aliphatic nitrates yielded all the above products; t-butyl nitrate suffered β-hydrogen elimination (equation 11) almost exclusively, forming isobutene and nitrate ion; while benzyl nitrate reacted primarily by the substitution process with some reduction to alcohol and some α-hydrogen elimination to benzaldehyde and nitrous acid. The mechanism of alcohol formation was postulated as

$$RONO_2 + N_2H_4 \longrightarrow RO^- + H_2N\overset{+}{-}NH_2NO_2$$

$$\rightleftharpoons ROH + H_2N.NH.NO_2 \qquad (24)$$

The denitration of nitrates with secondary amines often results in nitrosation of the amine. The overall reaction with trichloroethyl nitrate at 0° (46) was supposed to occur according to equation 25, and nitroso-diphenylamine was

$$CCl_3\,CH_2ONO_2 + 2R_2NH \longrightarrow CHCl_3 + R_2N.NO + R_2N.CHO + H_2O \qquad (25)$$

produced in the reaction of diphenylamine with ethyl nitrate (47). In other cases, alkylation of the denitrating agent occurred. Thus methyl, ethyl (48), and n-propyl (49) amines were prepared from the corresponding nitrates and ammonia in sealed tubes at 100°, and piperidine and diethylamine reacted with primary, secondary, and tertiary alkyl nitrates to give the amine nitrate and the N-alkylated amine (50). Primary aromatic amines reacted similarly with alkyl nitrates, but secondary and tertiary aromatic amines gave redox and condensation products (47). Benzylmalonic and benzylacetoacetic esters were prepared by the reaction of benzyl nitrate with the sodio-derivatives of malonic and acetoacetic esters (51), and N-substituted diphenylmethyl and triphenylmethylacetamides were produced together with nitric acid by heating the nitrates with acetamide (52), or in the latter case, even with acetonitrile (53). The preparation of diphenylmethanol was carried out by causing the nitrate to react with acetonitrile and aqueous sodium bicarbonate. Methyl, ethyl, and amyl nitrates with metallic sodium yielded the corresponding alkoxide and sodium nitrite (54). Evidence (53) has been presented for the limited participation during denitration of a mechanism involving alkoxy free radicals.

The reactions of hindered acyl nitrates such as benzoyl (55, 56), mesitoyl, pilvalyl, and diethylacetyl nitrates (57) with amines led to both nitration and acylation of the amines in relative proportions dependent on the particular compounds involved and their steric requirements. Similarly, alcohols formed carboxylic and nitrate esters

in reactions to which the same conditions applied.

Kaufman, Cook, and Davis (58) accomplished the reduction of ethyl, hexyl and cyclohexyl nitrates at a mercury cathode. The reduction was controlled by diffusion phenomena and was independent of pH between pH 3 and 13. The suggested mechanism was:

$$RONO_2 + 2e \longrightarrow RO^- + NO_2^- \qquad (26)$$

$$RO^- + H_2O \longrightarrow ROH + OH^- \qquad (27)$$

C. Denitration of the Nitrates of Cellulose and Other Carbohydrates

The reactions of the hexitol hexanitrates with pyridine are of considerable consequence to the present work. Wigner (59) prepared the pentanitrates of mannitol and dulcitol in good yield from the corresponding hexanitrates. The same mannitol pentanitrate was reported by Wigner to be the product of controlled nitration, and to have been obtained by Tichanowitsch (60) who passed dry ammonia gas into an ethereal solution of the hexanitrate. Urbanski and Kwiatkowska (61) recently carried out a similar denitration of sorbitol hexanitrate with alcoholic pyridine. Hayward and coworkers (62, 63, 64) showed that the pyridine reaction resulted in a selective removal of the nitrate groups in the fourth (or equivalent third) position of mannitol and dulcitol hexanitrates. The pyridine-mannitol hexanitrate reaction was also repeated by Elrick and his collaborators (65), who obtained similar success by using ammonium carbonate as the denitrating agent. The decomposition products in the reaction with pyridine (64) were nitrogen, nitrous and nitric oxides, and pyridinium nitrate. Two moles of pyridine

suffered ring cleavage, possibly forming glutaconaldehyde, while 0.25 mole of hexanitrate was completely denitrated and 0.75 mole of pentanitrate remained.

Danilov and Mirlas (66) found that the weak bases such as hydrazine, ammonium sulphide, sodium sulphite, and particularly ammonia and pyridine, gave a greater reduction in the viscosity of nitrocellulose than that produced by equivalent quantities of the strong bases sodium hydroxide and tetramethylammonium hydroxide. Walter (67) noted that when strips of cellulose nitrate were immersed in solutions of aromatic amines, such as dimethylaniline, the colour of the strips changed from green through blue to violet. The odour of methylphenylnitrosamine could be detected in samples with a strong violet discolouration. Staudinger and Sorkin (68) observed that the D.P. of a cellulose nitrate (N = 12.7%) fell from 2650 to 126 after standing in pyridine for 18 hours. Angeli (69) and Giannini (70) studied this decomposition and found that the viscosities of the initial very viscous solutions, or highly swollen gels, gradually diminished to that of pure pyridine after standing for a few days at room temperature. Precipitation in water and subsequent purification produced a white amorphous powder in 80% yield. The original substitution of 2.3 dropped to 1.5 to 1.7 nitrate groups per glucose unit. The product turned brown, then black on heating, reduced ammoniacal silver nitrate, reacted with phenylhydrazine, but had no action on Fehling's solution. The material appeared to be a nitrated, highly degraded oxycellulose. Oxidized and nitrated derivatives of diphenylamine were obtained when the amine was allowed to react with cellulose trinitrate in the presence of traces of copper salts (71, 72), while a

nitrogen dioxide - pyridine complex was isolated from the vigorous interaction of nitrocellulose and pyridine at steam-bath temperatures (30). From these examples it would appear that α-hydrogen elimination was the chief mode of denitration of cellulose nitrate in weak as well as in strong bases.

Denitration of nitrocellulose in a reducing medium has received much industrial attention, and numerous patents related to this problem have been granted. In 1878, before the "artificial silk" industry had commenced, the disadvantage of the inflammability of the cellulose nitrates was appreciated, as shown by the appearance of a patent (73) by Magnier and Doerflinger on methods of denitration (74). In 1900, Vignon (75) studied the reduction of nitrocelluloses by the action of ferrous chloride in boiling aqueous solution. He found that there was liberation of nitric oxide and that the nitrate groups were eliminated with the formation of carbonyl groups, thereby giving an oxycellulose with a large copper number. Conversely, when ammonium sulphide was used as the denitrating agent, and at 35 - 40°, the products were without action on copper solutions. Thus the indirect oxidizing effect of the alkalies could be diminished by the presence of certain reducing agents, such as cuprous, ferrous, and stannous salts, and the cellulosic constituent was regenerated in fibrous form, although the yield was not quantitative (76). Beside the above salts, other denitrating agents included ammonium nitrate, formaldehyde, thiocarbonates, and Devarda's alloy (74, 77). However, none of these proved as satisfactory as the alkaline sulphides and hydrosulphides, although the latter varied greatly in their action depending on the metal in combination (77). The

hydrosulphides of ammonia, sodium, potassium, and calcium were usually employed, and this method of denitration has been a long established process. The method had its origin in 1847 with Kopp, (78) who reported that ethyl nitrate reacted with hydrogen sulphide to form ethanol, ammonia and sulphur, and with ammoniacal hydrogen sulphide to form ethyl mercaptan. Application to nitrocellulose was carried out by Hadow (79), de Chardonnet (80), and more recently by Reichel, Van Dolah, and their respective colleagues (81, 82, 83).

A systematic study of the effect of various denitrating agents upon the properties of the regenerated cellulose was made by Rassow and Dörr (77). They found that the hydrosulphides of potassium and of ammonia were more effective in alcoholic than in aqueous solutions, but that the nitrate groups could not be eliminated entirely, the sulphuric acid - diphenylamine test indicating in all cases the presence of greater or smaller residues of oxidized nitrogen. Karrer and Schubert (84) found that the denitrated fibres retained as much as 1 - 2% of nitrogen, while the regenerated cellulose of Staudinger and Mohr (85) contained 0.5 - 1.0%

The results of Frey-Wyssling (86) indicated that the denitration should be facilitated by an aqueous instead of an alcoholic medium, because in the former, greater swelling of the nitrocellulose was achieved than in the latter. Under the microscope, denitration in alcoholic ammonium hydrosulphide was observed to begin in spots on the surface of the fibre and to proceed into the inner layers, while in aqueous solution the reaction proceeded as a uniform band from the outside to the centre of the fibre. Davidson (87) found that the time of treatment was the

essential factor. More than 20 hours were necessary to reduce the nitrogen content to 0.5%, whereas 10 hours resulted in a nitrogen content of 1.43%.

Earlier claims that cellulose was regenerated from the denitration treatment without degradation were based merely upon the observation that it retained its fibrous structure (88). The results of latter studies, however, revealed that the cellulose was attacked during denitration even under the mildest conditions. Staudinger and Mohr (85) found the degree of polymerization of the regenerated cellulose to be as low as 120 - 300, figures which were in agreement with the degree of polymerization of 200 for nitrocellulose rayon (89). Rogovin and Schlachover (90) as well as Davidson (87), observed that nitrocelluloses of widely different intrinsic viscosities were converted into celluloses which possessed approximately the same low viscosity value, and assumed that profound degradation occurred during the process of denitration. This degradation was also reflected in the relatively low yield of 95% reported for the regenerated cellulose (91).

The reactions involved in the process of elimination with ammonium hydrosulphide were postulated by Nadai (92) to be:

$$\begin{array}{l} \mathrm{HC{-}ONO_2} \\ \mathrm{HC{-}} \end{array} + \mathrm{OH^-} \longrightarrow \begin{array}{l} \mathrm{HC{-}OH} \\ \mathrm{HC{-}} \end{array} + \mathrm{NO_3^-} \qquad (28)$$

$$\mathrm{NO_3} + \mathrm{SH^-} \longrightarrow \mathrm{NO_2^-} + \mathrm{S} + \mathrm{OH^-} \qquad (29)$$

$$2\mathrm{NH_4HS} + 2\mathrm{S} \longrightarrow (\mathrm{NH_4})_2\mathrm{S_3} + \mathrm{H_2S} \qquad (30)$$

Recent studies by Merrow, Cristol, and Van Dolah (93) with n-butyl nitrate and sodium and ammonium hydrosulphides rendered untenable

the above mechanism. Butyl nitrate and sodium hydroxide reacted very slowly in 60% ethanol, so that after 16 days less than 10% hydrolysis had occurred as measured by loss of alkalinity. On the other hand, the reaction was essentially complete in about 4 hours in a similar solution containing hydrosulphide and a little polysulphide. A solution containing potassium nitrate and hydrosulphide showed that very little if any reaction occurred between nitrate and hydrosulphide ions even after standing for days. Thus, the Nadai mechanism could be eliminated since both steps involved were slower than the denitration process.

Butyl nitrite could not be an intermediate, since a vigorous evolution of nitrogen occurred when the nitrite was treated with hydrosulphide solutions, and butanol was formed in excess of 90% yield. No evolution of gas was observed in the corresponding reaction of n-butyl nitrate. However, sodium nitrite and excess ammonium hydrosulphide gave a vigorous exothermic reaction which led to the formation of polysulphide, as was observed in the butyl nitrate reaction. Three gram-atoms of sulphur were produced per mole of sodium nitrite. There was no reaction between sodium nitrite and sodium hydrosulphide after four days, but reaction took place if the pH of the solution was lowered by the addition of weak acids or carbon dioxide. This result was also demonstrated with n-butyl nitrate. With ammonium hydrosulphide, all the nitrate nitrogen was reduced to ammonia, and four gram-atoms of sulphur were produced per mole of nitrate. When sodium hydrosulphide was buffered with orthoboric acid below pH 10, a similar reaction occurred, but above pH 13, either of the hydrosulphide reagents reduced the nitrate only to nitrite ion, with the production of one gram-atom of sulphur per

mole of n-butyl nitrate. The denitration was apparently second order kinetically, and was catalyzed by polysulphide ion, and by hydroxyl ion in the presence of polysulphide. Isolation of butanol in nearly quantitative yield, and the absence of nitrate ion and mercaptan, indicated that the reaction did not involve displacement by the hydrosulphide reagent at the carbon atom bearing the nitrate group. Elimination processes to give olefin or carbonyl compounds were also removed from consideration.

Merrow and his coworkers considered the most reasonable mechanism to be one in which the rate-determining step involved attack of the nitrate group by a sulphide or polysulphide ion, and they postulated two reaction paths:

1. $RONO_2 + S_x^{=} \longrightarrow RO^- + NO_2S_x^- \quad (x \geq 1)$ (31)

$NO_2S_x^- + HS^- \longrightarrow NO_2^- + HS_{x+1}^-$ (32)

2. $RONO_2 + S_x^{=} \longrightarrow ROS_x^- + NO_2^-$ (33)

$ROS_x^- + HS^- \longrightarrow RO^- + HS_x^- + 1$ (34)

These reactions were then followed by the equilibrium reactions:

$HS_{x+1}^- + HS^- \rightleftharpoons HS_x^- + HS_2^-$, etc. (35)

$RO^- + HS_x^- \rightleftharpoons ROH + S_x^{=}$ (36)

$HO^- + HS_x^- \rightleftharpoons H_2O + S_x^{=}$ (37)

The first reaction in each case was supposed to be the slow rate-determining step.

The denitrations of nitrocellulose were not all confined to reactions in alkaline media. Denitration of cellulose nitrates also took place on treatment with acids, but much more slowly than when alkalies were used (3). According to Worden (74), one of the earliest processes of denitration consisted of digestion of dried "pyroxylin" with sulphur dioxide under pressure in a solution of sodium bisulphite containing phosphoric acid, or in a sodium thiosulphate solution. Acid denitration was also exemplified in the treatment of nitrocellulose with dilute acids, in particular dilute nitric acid, containing more water than the acid used to produce the nitrocellulose. The esterification equilibrium then shifted in the direction of lower nitrogen content. Denitration by acid hydrolysis would therefore be quite incomplete, and furthermore, would usually result in extensive degradation of the cellulose. The presence of reducing agents in solution proved to be beneficial in this case also. This behaviour was realized by Richter (94), who in 1901 obtained patent protection for a denitration in which a filament of nitrocellulose was treated with an acid solution of a metallic salt which was capable of passing to a higher state of oxidation. Suitable salts included cuprous chloride, cuprous oxychloride, ferrous, manganous, or cobaltous salts, ferrocyanides, and nitroprussides. This method was used more recently by Thinius (95).

Many sugar nitrates have been denitrated by reductive methods. Oldham (96) employed iron dust in acetic acid while Dewar and Fort (97) preferred a mixture of zinc and iron dust in hot glacial acetic acid. Kuhn (98) reported a method of catalytic hydrogenolysis employing a supported palladium catalyst and hydrogen at 300 - 1500 p.s.i. No results

with cellulose nitrates were mentioned. Ansell and Honeyman (26) denitrated methyl 4,6-O-propylidene-α-D-glucoside-2,3-dinitrate and its corresponding ethylidene derivative with lithium aluminium hydride in boiling ether. This method has since been used by Soffer and his colleagues (99) to obtain highly degraded cellulose from cellulose nitrate. Hoffman, Bower and Wolfrom (100) simultaneously denitrated and acetylated many nitrate esters of polyhydric alcohols and sugar derivatives by using acetic anhydride and zinc in the presence of either anhydrous hydrogen chloride or a pyridine catalyst. Application of the method to cellulose nitrate yielded an extensively degraded product.

Sodium iodide in ketone solvents also proved of value for the removal of nitrate groups and is of particular interest because of its selectivity. In this method the nitrate group in the sixth or primary position of aldohexosides was replaced by an iodine atom. Thus Oldham and Rutherford (101) were able to prepare methyl 2,3,4-tri-O-methyl-6-desoxy-6-iodo-β-D-glucoside from the corresponding 6-nitrate derivative by heating with acetone and sodium iodide in a sealed tube. Under more drastic conditions, nitrate groups on secondary carbon atoms were also replaced. In this way Dewar and Fort (96) converted methyl 4,6-O-ethylidene-β-D-glucoside-2,3-dinitrate into the 3-nitrate, and methyl 2,3-di-O-methyl-β-D-glucoside-4,6-dinitrate into methyl 2,3-di-O-methyl-6-desoxy-6-iodo-β-D-glucoside. The method has now been found to be useful for converting methyl 4,6-O-propylidene- α -D-glucoside-2,3-dinitrate into the 3-nitrate in high yield (26). Sodium iodide in acetic anhydride reacted with methyl 4,6-O-ethylidene- α -D-

glucoside-2,3-dinitrate to give, after three hours at 100°, methyl 4,6-O-ethylidene- α -D-glucoside-2-acetate-3-nitrate, or, after three hours boiling, the 2,3-diacetate (26). Honeyman and Morgan (27) carried out a comparative study of the reactions of a number of esters of methyl 4,6-O-benzylidene- α -D-glucoside with sodium iodide in acetone at 100°.

TABLE III

The Action of Sodium Iodide in Acetone on Esters of Methyl 4,6-O-Benzylidene- α -D-Glucoside

Ester	Product	% Yield
2,3-diacetate	unchanged	95
2,3-ditoluene-p-sulphonate	"	90
2,3-dimethane sulphonate	"	85
2,3-dinitrate	3-nitrate	60
3-nitrate	unchanged	60
	glucoside	20
2-toluene-p-sulphonate-3-nitrate	2-toluene-p-sulphonate	65
2-methanesulphonate-3-nitrate	2-methanesulphonate	75
2-acetate-3-nitrate	unchanged	35
	2-acetate)	45
	)	
	3-acetate)	

The stability of the acetate and sulphonate groups was noteworthy and might be explained (102) by the strong deactivation produced on one group by the electron-attracting effect of the other.

The presence of either group in the second position of a 3-nitrate caused a reduction in the stability of the latter group, and in the case of the 2-sulphonates the 3-nitrate became as easily removable as the 2-nitrate group of the 2,3-dinitrate. These workers also accomplished the conversion of the 2,3-dinitrate to 3-nitrate with sodium iodide in methanol, aqueous ethanol, and pyridine, and with sodium nitrite in aqueous ethanol. Although the reaction of sodium iodide with primary nitrate seemed to occur in a metathetical manner, a similar mechanism for the removal of secondary nitrate groups appeared unlikely. On the basis of quantitative determinations of free iodine and nitrite ion formed in the latter reactions, Honeyman and Morgan (27) suggested the following reaction sequences:

In acetone solutions:

$$\begin{matrix} \text{HC-O-NO}_2 \\ | \end{matrix} + \text{NaI} \longrightarrow \begin{matrix} \text{HC-ONa} \\ | \end{matrix} + \text{NO}_2^+\text{I}^- \qquad (38)$$

$$\text{NO}_2^+\text{I}^- + \text{NaI} \longrightarrow \text{NaNO}_2 + \text{I}_2 \qquad (39)$$

$$\text{CH}_3\text{COCH}_3 + \text{I}_2 \longrightarrow \text{CH}_3\text{COCH}_2\text{I} + \text{HI} \qquad (40)$$

$$\begin{matrix} \text{HC-ONa} \\ | \end{matrix} + \text{HI} \longrightarrow \begin{matrix} \text{HC-OH} \\ | \end{matrix} + \text{NaI} \qquad (41)$$

In methanol solutions:

$$2\begin{matrix} \text{HC-O-NO}_2 \\ | \end{matrix} + 2\text{NaI} + \text{CH}_3\text{OH} \longrightarrow 2\begin{matrix} \text{HC-OH} \\ | \end{matrix} + 2\text{NaNO}_2 + \text{I}_2 + \text{HCHO} \qquad (42)$$

$$3\text{NaNO}_2 + \text{CH}_3\text{OH} + \text{I}_2 \longrightarrow \text{NaNO}_3 + 2\text{NaI} + 2\text{NO} + \text{HCHO} \qquad (43)$$

The replacement of the primary nitrate groups in cellulose was accomplished with the sodium iodide-acetone reagent by Murray and Purves (103). These workers therefore seemed to be the first to describe a reaction showing a high degree of selectivity for one of the three nitrate groups of the anhydroglucose units in cellulose nitrate.

Solutions of sodium or potassium amide in liquid ammonia were reported by Scherer and Field (104) to replace one of the nitrate groups in a technical cellulose "dinitrate" by an amino group and the other by a hydroxyl group. The first reaction was thought to be a result of the metathetical removal of a nitrate group by the sodium amide to form sodium nitrate, and the second reaction was supposedly an ammonolysis of the remaining nitrate group in the presence of sodium amide to give a hydroxyl group. Since diazotization was possible, the amino group was assumed to be attached to one of the two secondary carbon atoms in the glucose unit. Scherer and Saul (105) made the interesting claim that an acetylide radical could be introduced into one of the secondary positions in a commercial cellulose "dinitrate" (N, 11.9%) by a solution of monosodium acetylide in liquid ammonia. Moulds (106) attempted to carry out the reactions of Scherer and his colleagues on Segall's "dinitrate" (which the present research shows to be substituted only in the third and sixth positions) but was unable to obtain any positive results of the kind reported by these workers. Analyses for amino and acetylide groups in the products were all almost negative, and the absence of sodium nitrate as a reaction by-product was demonstrated. The latter would necessarily be

present if any metathetical reaction involving a nitrate group had occurred.

Another case of partial denitration was recently reported by Segall and Purves (107). In an attempt to repeat Angeli's reaction with cellulose nitrate and pyridine, an excess of pure hydroxylamine base was dissolved in the pyridine in order to condense with, and so to protect, any carbonyl groups formed from further change. Practically no colour developed, the viscosity decreased much more slowly although the reaction was still exothermic, and large volumes of a colourless gas were evolved. The reaction was carried out on cellulose trinitrate containing 2.92 nitrate groups per anhydroglucose unit. Qualitative and quantitative examinations of the gas evolved showed that 1 mole of nitrogen was produced from each glucose trinitrate unit. A fibrous cellulose substituted with 1.70 nitrate groups and about 0.08 oxime groups per anhydroglucose unit was isolated from the reaction mixture in 98% yield, and this dinitrate was quite stable to pyridine.

O-methylhydroxylamine (CH_3ONH_2), when dissolved in pyridine yielded a product which proved to be similar to that from pyridine-hydroxylamine. There was, however, no evolution of nitrogen in this case, and the product contained traces of methyloxime instead of oxime groups. More recently, Moulds (106) attempted to duplicate the partial denitration by using the more stable N-phenylhydroxylamine instead of hydroxylamine. No heating or evolution of gas occurred, but the reaction mixture slowly developed a brown colour. A brown gum was isolated in poor yield, and it was concluded that the main reaction was probably of the degradative type brought about by pyridine alone on cellulose trinitrate.

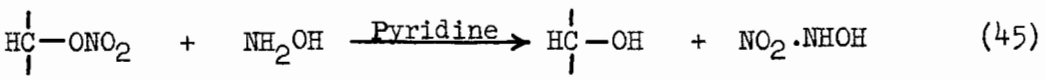
Segall also caused cellulose trinitrate to react with a pyridine solution of hydroxylamine hydrochloride, but in this case, the gas evolved proved to be 85% nitrous oxide and only 15% nitrogen. The cellulosic product, obtained in 85% yield, contained 1.7 nitrate groups and 1.0 oxime groups per glucose unit. The "oxycellulose mono-oxime dinitrate" was recovered unchanged after solution for several days in pyridine or pyridine containing free hydroxylamine. It followed from the latter observation that pyridine-hydroxylamine and pyridine-hydroxylamine hydrochloride both removed the same nitrate groups from cellulose trinitrate, although the mechanism was obviously different in the two cases.

The mechanism by which the hydroxylamine denitration occurred was not studied in detail, but the reaction seemed analogous to others in which a nitro group was transferred to a compound containing a reactive hydrogen atom. Ethyl nitrate and potassium ethoxide, for example, produced phenyl nitroacetic ester from ethyl phenyl acetate, and 3-nitrosopyrrole from pyrrole (108). Many examples of the lability of an α-hydrogen atom in hydroxylamine are known. One such example was demonstrated by Posner (109) who added a molecule of hydroxylamine across the double bond in β-nitrostyrene:

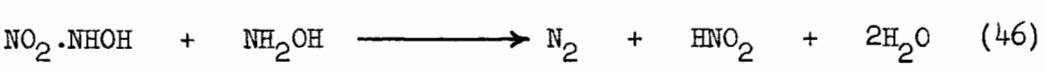
$$C_6H_5CH = CHNO_2 \quad + \quad NH_2OH \longrightarrow C_6H_5\underset{\displaystyle NHOH}{\underset{|}{CH}}-CH_2NO_2 \qquad (44)$$

The closest parallel to the denitration of cellulose trinitrate was found in the formation of nitrohydroxamic acid and ethanol from ethyl nitrate and hydroxylamine in the presence of sodium

ethoxide (39). The reaction did not occur as in equation 12, since it was shown that nitrohydroxamic acid could oxidize an aldehyde and was itself reduced to nitrite and hydroxamic acid (40). The latter on hydrolysis regenerated hydroxylamine. The low yield of 50% of nitrohydroxamic acid was attributed to losses caused by the direct reaction of sodium ethoxide with the ethyl nitrate (41). In the present case, the evolution of nitrogen was probably due to the reduction of the nitrohydroxamic acid by the excess hydroxylamine present.



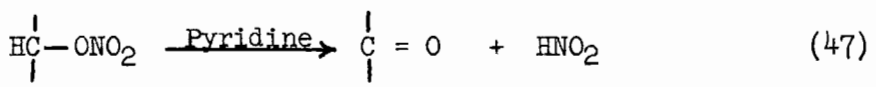
(45)



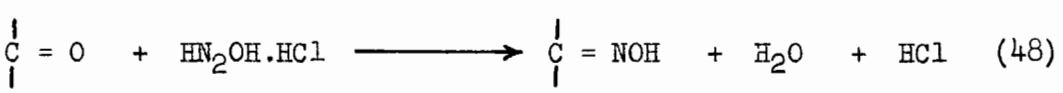
(46)

No evolution of nitrogen occurred when O-methylhydroxylamine was used because the O-methyl nitrohydroxamic acid was probably stable to the weaker reducing agent, O-methylhydroxylamine.

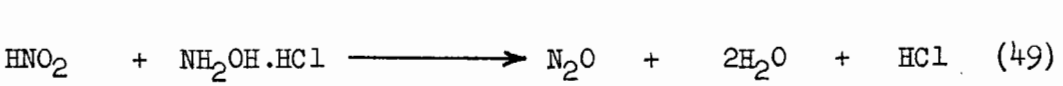
The dominant reaction between the trinitrate and pyridine-hydroxylamine hydrochloride was assumed to be that of the elimination type. In this case, the labile hydrogen atom present in the free base was assumed to have become more strongly bound in the hydrochloride. The carbonyl group was converted to oxime by the excess hydroxylamine hydrochloride, which also reacted with the nitrous acid to produce nitrous oxide.



(47)



(48)



(49)

Segall's "dinitrate" differed markedly in properties from randomly substituted nitrocelluloses of the same nitrogen content. It possessed a high stability toward alkaline reagents, being unaffected by the pyridine solution in which it was formed, and yielded a "monomethyl dinitrate" upon treatment with dimethyl sulphate and caustic alkali. Furthermore, the "dinitrate" could be renitrated to what was approximately a tri-substituted derivative, and cleavage of the single nitrate group had therefore regenerated a cellulose hydroxyl group.

Segall and Purves attempted to locate the position of the labile nitrate group in the following way: Iodination of the cellulose dinitrate yielded a desoxyiodocellulose nitrate containing 0.8 atom of iodine and 0.5 nitrate groups per anhydroglucose unit. According to Oldham and Rutherford (101), this result signified that the primary ester group was largely intact in the "dinitrate". The "dinitrate" was then methylated with dimethyl sulphate and the product was subjected to reduction with ammonium and with sodium sulphide in an effort to obtain nitrate-free methylcellulose. Products obtained in poor yields from such denitration reactions invariably contained nitrogen and sulphur, and were highly degraded and discoloured.

Another attempt at denitration of the monomethyl derivative was made by Grassie (110), who repeated the ammonium sulphide experiments of Segall, and attempted a reductive acetolysis of the "monomethyl dinitrate". While some denitration was obtained, the products were highly impure and extensively degraded. Iodination of the monomethyl cellulose dinitrate produced a methyl desoxyiodocellulose nitrate containing 1.06 methoxyl , 0.89 iodide, and 0.61 nitrate groups per glucose unit.

In an effort to throw more light on Segall's results with cellulose trinitrate, Hayward (111) employed methyl-β-D-glucoside-2,3,4,6-tetranitrate with the pyridine-hydroxylamine reagent. A similar denitration occurred with the evolution of 1.26 moles of pure nitrogen, but further work showed that about 70% of the nitrate groups were removed from the fourth position which was not available in cellulose trinitrate. Previous anomalous behaviour has been exhibited by the nitrate group in the second position of methyl-β-D-glucoside tetranitrate, where this normally labile group showed strong resistance to sodium iodide in acetone (112). The labile nature of this nitrate group in methyl-β-D-glucoside-2,3-dinitrate derivatives has already been mentioned (26, 27, 97). Results more consistent with those from cellulose trinitrate might be expected with methyl-4-O-methyl-β-D-glucoside-2,3,6-trinitrate.

Rooney (113) studied the interaction of hydroxylamine hydrochloride in pyridine on methyl-β-D-glucoside tetranitrate and found that at least two, and probably three, separate reactions proceeded simultaneously. The first produced a mixture of partly nitrated methylglucosides with the evolution of nitrogen; the second, a more complex mixture of what were probably polyoximes of polyketo-methyl-glucosides, nitrous oxide being evolved; and the third released minor amounts of nitric acid, presumably by hydrolysis of the tetranitrate. No selectivity was therefore apparent in this reaction of methylglucoside tetranitrate.

EXPERIMENTAL PROCEDURES

A. Analytical Methods

All nitrogen analyses were carried out by a semi-micro adaptation of the Kjeldahl-Gunning method (114).

The Vieböck and Schwappach estimation for methoxyl groups was used as described by Peniston and Hibbert (115) with the omission of the warm-water jacket for the condenser and trap. The joint between the air-condenser and the boiling flask was sealed with paraffin wax after the introduction of the sample. The upper ground-glass joint was lubricated with water and sealed with a drop of acetic anhydride.

Viscosities of cellulose nitrate samples were determined in a Cannon-Fenske (116) viscometer, size 50, using ethyl acetate solutions at 25°. A size 100 viscometer was used for the O-methylcellulose viscosities which were carried out in cupriethylenediamine (117). Kinetic energy corrections were applied in the manner described by Timell (118). Relative viscosities were determined at four different concentrations and graphical extrapolations of the linear reduced viscosity-concentration plots to zero concentration yielded the intrinsic viscosity ($[\eta]$) values reported. The K value for cellulose trinitrate in the relation : Degree of polymerization (D.P.) = K $[\eta]$ has been determined (119) as 80 when ethyl acetate is the solvent.

B. Materials

1. Cellulose Trinitrate

The nitrating mixture was prepared by dissolving 475 gm. of phosphorus pentoxide in 1677 gm. of 100% nitric acid at 0 to 5°. The solution was then immersed in a brine bath at −10° and stirred for two days. Twenty-five grams of bone-dry, dewaxed cotton linters was then added to the above nitrating mixture at −10°, and the reaction was allowed to proceed for 5 hours with stirring. The product was separated from the nitrating mixture on a sintered-glass funnel and pressed dry of the residual liquor. Careful immersion in well-stirred 50% aqueous ethanol (about 2500 ml) at −10°, and stabilization in three separate 750 ml. lots of boiling ethanol, followed. Drying was at room temperature in vacuo over phosphorus pentoxide. Yield, 44.9 gm., corresponding to 99.9% of theory on the basis of the nitrogen analyses. Calc. for cellulose with 2.88 nitrate groups per anhydroglucose unit, N = 13.8%. Found: N = 13.8, 13.8%. $[\eta]$ = 18.7.

2. Hydroxylamine

Preparation from the hydrochloride was carried out according to a published method (107).

Metallic sodium, 220 gm., was added slowly to 3 litres of n-butanol in a 5-litre three-necked flask fitted with a reflux condenser, and a mechanical stirrer with mercury seal. The flask was kept immersed in a water bath to prevent excessive heating in the primary stages of the reaction, and was then cautiously heated. The contents were allowed to boil until all the sodium had dissolved.

In a 5-litre three-necked flask fitted with a mechanical stirrer were placed 615 gm. of hydroxylamine hydrochloride, 1.5 gm. of phenolphthalein, and 550 ml. of butanol. The mixture was warmed to 50 to 60° and stirred for 10 minutes. The hot sodium butoxide solution was then added as rapidly as was consistent with the avoidance of alkalinity, as shown by the phenolphthalein indicator, the temperature of the mixture being maintained at 50 to 60° during the reaction. This addition required about 3 hours. The precipitated sodium chloride was removed and washed with a little butanol, and the filtrate was left overnight at -15° to allow crystallization of the hydroxylamine. The pearly-white plates of hydroxylamine were recovered in a refrigerated room on sintered glass, washed with a little butanol, and finally with freshly-distilled anhydrous ether. Drying was in vacuo and the crystals were stored at -15°. Yield, 210 gm, corresponding to 71.5% of theory.

3. Cellulose Dinitrate (c.f. 107)

Crystalline hydroxylamine, 170 gm., was dissolved in 1100 ml. of pure dry pyridine. The solution was added to 50 gm. of dry cellulose trinitrate in a 4-litre Erlenmeyer flask, and the reaction mixture was cooled in a water bath until the gas evolution slackened. The viscous, pale yellow solution was then allowed to stand in the dark at room temperature for 70 hours, the viscosity falling markedly during this time. Precipitation of the dinitrate as white fibres was carried out in 10 litres of well-stirred distilled water. Washing with large volumes of water followed, and the product was allowed to stand in distilled water for 4 hours. The dinitrate was air-dried, redissolved

in acetone-dioxane (1:1), reprecipitated in distilled water and thoroughly washed. After air-drying, final drying was carried out at room temperature in vacuo over phosphorus pentoxide. Yield, 40.2 gm., corresponding to 99% of theory on the basis of the nitrogen analyses. Calc. for cellulose with 1.72 nitrate groups per anhydroglucose unit, N = 10.0%. Found: N = 10.0, 10.1%. $[\eta]$ = 1.73. The intrinsic viscosity of a sample renitrated by the method of Alexander and Mitchell (120) to a nitrogen content of 13.51% was $[\eta]$, 1.22.

4. Mono-O-Methylcellulose Dinitrate (c.f. 107)

Dry cellulose dinitrate, 36 gm., was dissolved in 2100 ml. of peroxide-free dioxane in a 3-litre three-necked flask equipped with a mechanical stirrer and mercury seal. A light yellow viscous solution was obtained. The flask was flushed free of air with a brisk stream of nitrogen, and the nitrogen flow was then adjusted to a very slow rate. Dropping funnels were placed in the two side arms of the flaks and filled with 230 ml. of dimethyl sulphate and 173 ml. of 40% sodium hydroxide respectively. About 10 ml. of the sodium hydroxide was first added to the stirred solution of cellulose dinitrate, and the remainder was slowly added together with the dimethyl sulphate. The reaction was allowed to proceed in a nitrogen atmosphere at room temperature for 25 hours. Precipitation of the reaction mixture into water gave fine cream-coloured clots, which, after neutralization of the mixture with acetic acid, were recovered, washed, and air-dried. The resultant light yellow-brown powder was dissolved in acetone and reprecipitated into water. Short, light yellow-brown fibres were obtained. The fibres were recovered on sintered glass, washed with water,

pressed dry, and dried in vacuo over phosphorus pentoxide at room temperature. Yield, 36.4 gm., corresponding to 95% of theory on the basis of nitrogen and methoxyl analyses. Calc. for cellulose with 1.70 nitrate and 1.22 methoxyl groups per anhydroglucose unit, N = 9.31%; OCH_3 = 14.8%. Found: N = 9.30, 9.32%; OCH_3 = 14.8, 14.8%. [?] = 0.238. Another analogous preparation contained 1.67 nitrate and 1.13 methoxyl groups. [?] = 0.271.

5. Ammonium Hydrosulphide Solution

Hydrogen sulphide gas, after being washed with water, was bubbled into 400 gm. (450 ml.) of concentrated ammonium hydroxide (NH_3 = 28%) at 5 to 10° until the weight had increased by 142 gm. Approximate ammonium hydrosulphide (NH_4HS) concentration, 39%. Molar ratio, NH_3:H_2S = 1.58:1. The solution was stored at 5° in a bottle previously flushed with hydrogen sulphide gas.

C. Denitrations of Mono-O-Methylcellulose Dinitrate with Ammonium Hydrosulphide

The O-methylcellulose dinitrate used as the starting material in these experiments contained nitrate and methoxyl substitutions of 1.67 and 1.13 respectively except in the cases of experiments 2 and 8.

In Acetone-Water Media

Excessive contamination of the products with sulphur and sulphur compounds resulted when the denitrations were carried out in the presence of acetone. Degradative and manipulative losses were also considerable in many cases. Consequently, many attempts proved to be unproductive and were discarded. Those described below are

typical of the more successful experiments.

Experiment 1

O-Methylcellulose dinitrate, 2 gm., was dissolved in 50 ml. of acetone, and a solution of 170 ml. of 3.9% aqueous ammonium hydrosulphide was slowly added with vigorous stirring. A light yellow suspension formed. Hydrogen sulphide was bubbled for 8 hours through the reaction mixture at 5 to 10°, after which the stoppered flask was allowed to stand overnight at 5°. The impure product was recovered by centrifugation, washed thoroughly with water, alcohol-carbon disulphide, and petroleum ether, and finally dried *in vacuo* over phosphorus pentoxide. Weight of light yellow powder = 1.74 gm. Calc. for cellulose with 1.39 nitrate and 1.09 methoxyl groups per anhydroglucose unit, N = 8.11%; OCH_3 = 14.1%. Found: N = 8.04, 8.16%; OCH_3 = 14.0, 14.1%.

Experiment 2

The partly denitrated product from experiment 1 (substitutions: NO_3 = 1.39; OCH_3 = 1.09), 1.40 gm., was subjected to another similar denitration. A 0.74 gm. yield of a product containing 7.03% nitrogen was obtained.

Experiment 3

Mono-O-methylcellulose dinitrate, 2.0 gm., was dissolved in 90 ml. of acetone, and 60 ml. of 20% ammonium hydrosulphide was added as previously described. Two liquid layers were obtained. The vigorously stirred reaction mixture was maintained at 5 to 10° for 90 minutes and at room temperature for 3.5 hours. Water (about 30 ml.) was added to obtain homogeneity of the liquid phase and the reaction was continued for a total

of 24 hours. After this time water was added to ensure complete precipitation of water-insoluble material. Centrifuging, and purification were carried out as before with the inclusion of an acetone extraction of the solid residue. Weight of solid residue, 0.55 gm. Calc. for cellulose with 0.37 nitrate and 1.00 methoxyl groups per anhydroglucose unit, N = 2.69%; OCH_3 = 16.1%. Found: N = 2.67, 2.73%; OCH_3 = 15.8, 16.4%. The aqueous phase from the diluted reaction mixture was evaporated to a small volume and the dissolved cellulosic material was precipitated with acetone. Purification was effected by washing with organic liquids and drying was carried out as before. Weight of water-soluble material = 0.57 gm. Calc. for cellulose with 0.07 nitrate and 1.03 methoxyl groups per anhydroglucose unit, N = 0.55%; OCH_3 = 17.8%. Found: N = 0.56, 0.57%; OCH_3 = 17.5, 17.9%.

Experiment 4

Mono-O-methylcellulose dinitrate, 1.65 gm., was dissolved in 50 ml. of acetone and 50 ml. of ice-cold 20% ammonium hydrosulphide was added. The reaction mixture was vigorously stirred, causing emulsification of the separate layers, and the reaction was allowed to proceed for 10 hours at room temperature and 2 hours at 50°. After this time the flask was stoppered and stored for one day at room temperature. The solid residue was separated and washed thoroughly with water, acetone, carbon disulphide, and petroleum ether. Drying in vacuo yielded 3.12 gm. of a bright orange powder. The product was extracted with concentrated ammonium hydroxide solution (which dissolved some of the material), with water, acetone, and petroleum ether. Drying of the residue afforded

1.22 gm. of a yellow powder, still quite impure, and analysing for 3.40% nitrogen and 8.15% methoxyl contents.

The mother liquor from the reaction mixture, together with the aqueous washings, were evaporated under reduced pressure to about 20 ml. and were mixed with 200 ml. of acetone. The residue was washed thoroughly with acetone, alcohol, carbon disulphide, and again with acetone. Reprecipitation into acetone from water solution yielded fine, cream-coloured clots which were washed with acetone and petroleum ether, and then dried. Weight of light yellow-brown powder = 0.33 gm. Calc. for cellulose with 0.07 nitrate and 0.99 methoxyl groups per anhydroglucose unit, N = 0.55; OCH_3 = 17.1%. Found: N = 0.58, 0.58%; OCH_3 = 17.0, 17.2%.

In Dioxane-Water Media

Experiment 5

Mono-O-methylcellulose dinitrate, 2 gm., was dissolved in 50 ml. of peroxide-free dioxane; the flask was flushed free of air with a brisk stream of washed hydrogen sulphide gas, and a water bath at 35° was placed around the flask. Addition of 50 ml. of concentrated 39% ammonium hydrosulphide to the virogously-stirred solution produced a light orange emulsion. The temperature of the bath was maintained at 35° for 15 hours, then it was raised to 40°. After 38 hours, almost all the material had dissolved and the mixture was centrifuged to remove a small quantity of insoluble material.

The solution was evaporated almost to dryness at the vacuum of a water-pump; acetone was added, and the solids were separated by centrifuging. The crude O-methylcellulose was washed with acetone and

alcohol, then with a 4:3 mixture of carbon disulphide and acetone to remove sulphur. This solvent mixture possessed the peculiar property of swelling the methylcellulose to an almost transparent gel while neither component liquid possessed any comparable effect. The product was then washed with acetone to remove the carbon disulphide.

The mono-O-methylcellulose was stirred for several hours in 150 ml. of water, when some of the material dissolved. After separating the residue by means of the centrifuge, the procedure was repeated with another 150 ml. volume of water. The water washings were concentrated under reduced pressure and poured into acetone. The white, flocculent precipitate was washed with acetone and petroleum ether and then dried in vacuo over phosphorus pentoxide at room temperature. Yield of light-yellow powder, 0.30 gm., corresponding to 21% of theory on the basis of nitrogen and methoxyl analyses. Calc. for cellulose with 0.15 nitrate and 1.05 methoxyl groups per anhydroglucose unit, N = 1.15%; OCH_3 = 17.8%. Found: N = 1.17, 1.20%; OCH_3 = 18.1, 17.8%.

The water-insoluble material was washed with acetone and petroleum ether and dried in vacuo over phosphorus pentoxide at room temperature. Yield of light yellow powder, 0.75 gm., (53% of theory). Calc. for cellulose with 0.06 nitrate and 1.09 methoxyl groups per anhydroglucose unit, N = 0.47%; OCH_3 = 18.8%. Found: N = 0.45, 0.44%; OCH_3 = 19.1, 18.6%.

Experiment 6

Mono-O-methylcellulose dinitrate, 2 gm., was dissolved in 50 ml. of dry peroxide-free dioxane and was denitrated at room temperature for 19 hours with 50 ml. of concentrated ammonium hydrosulphide as already

described. Water, 50 ml., was then added, and the reaction was continued for another 2 hours. Centrifuging of the reaction mixture resulted in the deposition of a relatively large amount of material that proved to be soluble in acetone. The liquor was concentrated under reduced pressure and the dissolved cellulose was precipitated with alcohol as fine, white clots. Some of this material also dissolved in acetone. Denitration was therefore incomplete and the run was discarded.

Experiment 7

Dioxane, 25 ml. was added to 2 gm. of mono-O-methylcellulose dinitrate and the mixture was stirred until the dinitrate had almost completely dissolved, residual particles being in a highly swollen state. Concentrated ammonium hydrosulphide, 50 ml., was added to the stirred mixture at room temperature as previously described. A yellow, highly viscous gel formed. The mixture was left overnight with stirring, after which time little insoluble material remained. After 21 hours, 25 ml. of water was added and the reaction was continued for another 34 hours. Centrifuging produced a very small amount of undissolved material, and the clear, orange solution was concentrated under reduced pressure until the solid phase had begun to precipitate. Alcohol was then added, and the fine white clots which separated were washed with alcohol, acetone, and 4:3 carbon disulphide - acetone. The residual solution was concentrated, and the small amount of methylcellulose which precipitated was collected, washed with acetone and carbon disulphide - acetone, and added to the larger quantity. The product was finally washed with petroleum ether, air-dried, and dried *in vacuo* over phosphorus pentoxide at room temperature. Yield of light yellow powder, 1.24 gm.,

corresponding to 84.8% of theory on the basis of nitrogen and methoxyl analyses. Calc. for cellulose with 0.17 nitrate and 1.09 methoxyl groups per anhydroglucose unit, N = 1.30%; OCH_3 = 18.3%. Found: N = 1.28, 1.31%; OCH_3 = 18.5, 18.1%

Experiment 8 - Large Scale Denitration

Dry peroxide-free dioxane, 190 ml. was added to 15 gm. of mono-O-methylcellulose dinitrate (substitution: NO_3 = 1.70; OCH_3 = 1.22) in a one-litre three necked flask equipped with a mechanical stirrer and mercury seal, and the mixture was stirred for several hours until the dinitrate had almost completely dissolved. Concentrated ammonium hydrosulphide, 375 ml. was then slowly added to the well-stirred mixture at room temperature. A highly swollen gel resulted. After 24 hours, when almost all of the cellulosic material had dissolved to form an orange solution, 190 ml. of water was added, and the mixture was left stirring for another 29 hours. Centrifuging produced a small amount of light yellow-green, highly swollen material which was washed with water, alcohol, acetone, carbon disulphide - acetone (4:3), and petroleum ether. After drying in vacuo at room temperature over phosphorus pentoxide, 0.51 gm. of a light yellow green powder remained. Calc. for cellulose with 0.44 nitrate and 1.07 methoxyl groups per anhydroglucose unit, N = 3.13%; OCH_3 = 16.8%. Found: N = 3.11, 3.16%; OCH_3 = 16.7, 17.0%.

The transparent, orange solution was concentrated to the smallest convenient volume (about 100 ml.) under reduced pressure in a water bath at 45° with the addition of small amounts of butanol to prevent foaming. About 250 ml. of ethanol was added, and the precipitated

material, which was separated at the centrifuge, was washed with two 100 ml. volumes of ethanol. The washings were collected and evaporated under reduced pressure to about 50 ml. after which the remaining methylcellulose was precipitated with acetone, washed once with the same solvent, and added to the previously separated fraction. The impure O-methylcellulose was washed many times with acetone, and was then exhaustively extracted with carbon disulphide - acetone (4:3). The transparent, orange gel was finally washed with three 100 ml. volumes of light petroleum ether, air-dried, and dried in vacuo over phosphorus pentoxide at room temperature. Yield of light yellow powder, 9.37 gm., corresponding to a corrected yield of 90.8% of theory on the basis of nitrogen and methoxyl analyses. Calc. for cellulose with 0.14 nitrate and 1.12 methoxyl groups per anhydroglucose unit, N = 1.07%; OCH_3 = 18.9%. Found: N = 1.08, 1.06%; OCH_3 = 19.0, 18.8%. $[\eta]$ in cupriethylenediamine (117), 0.210.

D. Acid Hydrolysis of Mono-O-Methylcellulose

1. Mono-O-methylcellulose, 5 gm., when stirred into 20 ml. of ice-cold 20% hydrochloric acid, formed a somewhat translucent, light brown syrup. Water, 90 ml., was added and the solution was brought to boiling under a reflux condenser. A small amount of highly-swollen material separated from solution, but the mixture was allowed to reflux for 3 hours, after which time the insoluble material was separated by centrifuging. The clear, dark orange solution was decanted; 3 ml. of concentrated hydrochloric acid was mixed with the residue and the mixture was saturated at 0° with hydrogen chloride. After standing for 70 hours at 0°, the mixture was allowed to warm up to room temperature,

and the excess hydrogen chloride was removed at the vacuum of a water pump. Transfer to the flask containing the original acid solution was accomplished with the aid of 40 ml. of distilled water. The contents of the flask were heated under reflux for 4 hours, after which they were cooled and centrifuged. The light brown liquid was clarified with activated charcoal and filtered, the flask and residue being rinsed with 10 ml. of water. Heating under reflux for an additional 3 hours produced no change in the polarimetric reading, and the hydrolysis was adjudged complete.

The acidic components were removed on an "Amberlite" IR-4B anion-exchange resin column which was copiously washed with water, and evaporation of the eluate under diminished pressure yielded a light brown syrup. The syrup was partially dried by the concentration of solutions in absolute ethanol. Final drying was accomplished in vacuo over phosphorus pentoxide. Weight of brown syrup, 4.64 gm. This syrup partially crystallized on warming with a small amount of ethanol, but the crystals were redissolved in order to carry out purification procedures, and the brown syrup was dried again. A 3.43 gm. sample was dissolved in about 50 ml. of water, and the solution was heated below its boiling point. Small amounts of activated charcoal were then stirred in until a clear, supernatant liquid could be seen on standing. The charcoal was removed by a bed of "Hyflo" supercel, the filtrate and washings being concentrated and the syrup dried by the previous procedure. Weight of light yellow syrup, 3.30 gm., corresponding to an 83.8% yield on the basis of the methoxyl analyses. Calc. for glucose with 1.13 methoxyl groups, OCH_3 = 17.9%. Found: OCH_3 = 17.8, 18.0%.

2. Mono-O-methylcellulose, 5 gm., was stirred into 50 ml. of 72% sulphuric acid at 5° for 16 hours. The dark syrup was carefully diluted with 1150 ml. of cold distilled water to a IN acid concentration and boiled under reflux for 10 hours. Neutralization of the hydrolysate was effected partially with solid barium hydroxide and finally with barium carbonate. The filtrate was clarified with charcoal, concentrated, deionized with mixed IR-4B and IR-120 resins, and evaporated to a syrup which was dried as before. Weight of light yellow syrup, 4.75 gm., corresponding to 89.0% yield on the basis of the methoxyl analyses. Calc. for glucose with 1.16 methoxyl groups, OCH_3 = 18.3%. Found: OCH_3 = 18.3, 18.4%.

E. Chromatography of the Mono-O-Methylglucose Syrup

1. Qualitative Paper Chromatography

A small amount of the syrup was deposited from methanolic solution on the starting line of a paper chromatogram with adjacent reference spots of 3-O-methylglucose and glucose. The chromatogram was developed with the upper layer of a mixture of butanol, ethanol, water and ammonia in the ratio of 40:10:49:1 (121), and was sprayed with aniline acid phthalate solution (122).

Assuming an R_G value for 3-O-methylglucose of 0.27 (121), a bright brick-red spot corresponding to a monomethylglucose occurred at R_G 0.28, with other very faintly-visible spots occurring at R_G values of 0.16, 0.40 and 0.43, corresponding to glucose and two dimethylglucoses. No similarity to 3-O-methylglucose was shown by the monomethylglucose either in movement or in colour, the former sugar giving a brown spot with the aniline acid phthalate reagent.

Because development with the butanol - ethanol - water - ammonia solvent required as long as 24 hours, and because butanol was likely to prove a persistent contaminant of syrup fractions in column chromatography, a search was made for a more suitable developing solvent. After a few trials with mixtures of water-saturated methyl ethyl ketone and ethanol, a solvent mixture containing 4 parts of the former and 1 part of the latter was chosen. This solvent was approximately five times as fast as the previous developing solvent, but was extremely sensitive to temperature changes, and was less stable to ammonia, the presence of which was found to improve the paper chromatograms by producing more compact spots. The ammonia was added as 0.1% of concentrated ammonium hydroxide, but the solvent discoloured in a few days and had therefore to be changed more frequently than the butanol solvent. A better separation of the mono-O-methylglucoses was obtained however, as evidenced by R_F values of 0.11, 0.26, 0.46, and 0.60 for glucose, the monomethylglucose, and the two dimethylglucoses respectively. A sample of 2,3-di-O-methylglucose prepared by the hydrolysis of methyl 2,3-di-O-methyl-4,6-O-benzylidene-α-D-glucoside, showed identical chromatographic behaviour with that of the slower moving of the two dimethylglucoses.

2. Separation of the O-Methylglucoses on a Cellulose Powder Column

A tightly-packed cellulose powder column (70 x 4 cm.) was prepared and washed with water-saturated methyl ethyl ketone - ethanol (4:1). The syrup containing the O-methylglucoses, 3.00 gm., was thinned with a little methanol and pipetted carefully on to a tightly-packed

layer of dry cellulose powder placed on the top of the washed column. The flask was rinsed with a little methanol and with the developing solvent, and the washings were added to the top of the column. After a steady rate of flow of eluent had been established, a constant-levelling device was arranged at the top of the column in order to maintain a constant rate of flow. Samples were collected after 30 and 60-minute intervals, and analyzed by paper chromatography and by the visual intensity of the spot made by 0.1 ml. of the eluate which had been confined to a marked circle on filter paper, dried, and sprayed with aniline acid phthalate solution.

Dimethylglucose was detected in the eluate after 8 hours. An attempt to separate the di-O-methylglucoses completely failed because of mistimed changing of fractions. The fractions containing the dimethylglucoses were then recombined. After 19 hours, traces of monomethylglucose began to appear in the eluate, and the samples were collected until no more of the methylated sugar could be detected by the paper-spot technique described above. The dimethyl-glucose fractions were concentrated and the sugars were separated on a 94 x 2.2 cm. cellulose powder column using the methyl ethyl ketone - ethanol solvent.

The fractions containing the separate O-methyl-glucoses were concentrated to syrups, redissolved in small volumes of water and clarified with charcoal, and then reconcentrated to colourless syrups. Drying was carried out by the absolute ethanol evaporation technique followed by vacuum drying at 60°. Each of the syrups was shown by paper chromatography to have a single methylglucose component.

Yield of mono-O-methylglucose = 2.37 gm. or 84% of the original syrup. Crystallization from absolute ethanol yielded 2.17 gm. of white crystals. Calc. for $C_7H_{14}O_6$, OCH_3 = 16.0%. Found: OCH_3 = 16.0, 16.0%. Yield of di-O-methylglucose I (higher R_F value) = 0.05 gm. or 1.7% of the original syrup. Calc. for $C_8H_{16}O_6$, OCH_3 = 29.8%. Found: OCH_3 = 29.4%. Yield of di-O-methylglucose II (lower R_F value) = 0.34 gm. or 11.3% of the original syrup. Found: OCH_3 = 29.8, 29.9%.

F. Identification of the O-Methylglucoses

1. 2-O-Methyl-β-D-Glucose

The mono-O-methylglucose melted at 158-159°, the melting point of 2-O-methyl-β-D-glucose (123, 124). Crystals of the mono-O-methylglucose, 0.06230 gm., were weighed into a 2 ml. volumetric flask. Water at 25° was added to volume, and the flask was shaken until solution was complete. The solution was rapidly transferred to a polarimetric tube, and observations of the specific rotation (Table IV) were obtained in a 1 dcm. tube. These data coincided with the values of + 12° ⟶ + 66.0° given in the literature (123, 124) for the mutarotation of 2-O-methyl-β-D-glucose.

TABLE IV

Mutarotation of 2-O-Methyl-β-D-Glucose

Time	$[\alpha]_D^{25}$
5 mins.	+ 37.6°
7	40.1
10	43.0
15	45.9
30	51.0
60	56.8
120	62.0
210	64.8
16 hours (constant reading)	+ 65.2

Pure redistilled phenylhydrazine, 0.5 ml., was mixed with an equal volume of 50% acetic acid and 2 drops of 50% sodium bisulphite (125). A 0.2 ml. aliquot of this solution was added to a solution of 0.1 gm. of the monomethylglucose in 0.3 ml. of water. The tube containing the mixture was then stoppered and left overnight at room temperature. The clusters of pale yellow needles which had formed in good yield were recovered on a filter, washed with ethanol and twice recrystallized from the hot solvent. The colourless, flat needles of

2-O-methylglucose phenylhydrazone melted at 176-177° (123). Calc. for $C_{13}H_{20}N_2O_5$, OCH_3 = 10.9%. Found: OCH_3 = 10.9, 10.9%.

A 0.40 gm. sample of the mono-O-methylglucose was dissolved in 8 ml. of an aqueous solution containing 0.8 gm. of pure, white phenylhydrazine hydrochloride, 1.2 gm. of crystalline sodium acetate, and 7 drops of 50% sodium bisulphite solution (125). Ethanol, 1 ml. was then added and the solution was boiled gently under a reflux condenser. Yellow crystals began to separate after about 16 minutes, but heating under reflux was continued for 6 hours. A mass of yellow crystals separated on cooling, and microscopic examination revealed the characteristic shapes and clusters of glucosazone crystals (126). Recrystallization from 60% ethanol yielded 0.23 gm. of yellow crystals which decomposed at 204-205°. Calc. for $C_{18}H_{22}N_4O_4$, OCH_3 = 0.00%. Found: OCH_3 = 0.14, 0.12%

The glucosazone, 0.2 gm., was dissolved with heating in a solution consisting of 18 ml. of water, 0.3 ml. of 2N sulphuric acid, 0.6 gm. of crystalline copper sulphate, and 12 ml. of isopropanol (127). After heating under reflux for 1 hour, during which time the colour changed from orange-red to yellow-green, the solution was evaporated on a steam bath with a current of air to a volume of approximately 5 ml. The solution was left for a short while at 5° before the crop of crystals was recovered. The crystals were dissolved in 30 ml. of boiling water, the solution was clarified with charcoal, filtered, and left overnight in a refrigerated room at 5°. Recrystallization from 50% ethanol yielded 25 mgm. of white needles of phenyl-D-glucosatriazole melting correctly at 195-196°.

2. 2,3-Di-O-Methyl-D-Glucose

A paper chromatogram was spotted with di-O-methyl-glucose II (lower R_F value) as well as with an authentic sample of 2,3-di-O-methyl-D-glucose, and developed for 5 hours with water-saturated methyl ethyl ketone - ethanol (4:1). The dried chromatogram was sprayed with aniline acid phthalate solution and heated for 5 minutes at 105°. The movement and colour of the unknown dimethylglucose coincided exactly with those of the reference sample.

A sample of the unknown dimethylglucose syrup, 21.64 mgm., was weighed into a 2 ml. volumetric flask. The flask was filled to the mark with water, reweighed, and shaken vigorously to effect solution. After standing for a few hours, the rotation of the solution was determined. Reported for 2,3-di-O-methyl-D-glucose (128), $[\alpha]_D^{20}$ = + 64.4°. Found: $[\alpha]_D^{22}$ = + 63.3°.

A 0.104 gm. sample of the dimethylglucose was dissolved in 1 ml. of methanol and 0.3 ml. of aniline was added. The solution was heated under reflux for 3 hours, after which time the solvent was removed by evaporation on the steam bath first with a current of air and then under reduced pressure. A few drops of ethyl acetate were added to reduce the viscosity of the remaining syrup and the flask was left standing until crystallization occurred. A small yield of 2,3-di-O-methylglucose anilide was obtained. The crude material when recrystallized from ethyl acetate-petroleum ether, melted correctly at 133-134° (129).

No crystals could be obtained in a parallel attempt at anilide formation from a sample of 2,3-di-O-methylglucose syrup which

had been prepared by the acid hydrolysis of methyl 2,3-di-O-methyl-4,6-O-benzylidene-α-D-glucoside. Methoxyl analyses on the syrup obtained showed a methoxyl value of 33.1% instead of the expected value of 29.8%. Hydrolysis of the glucosidic linkage had therefore been only approximately 75% complete.

A minute sample of the crystals obtained from the anilide reaction on the unknown dimethylglucose was dissolved in 2 drops of methanol and used to spot a paper chromatogram. An adjacent spot contained a solution of the syrup from the reaction of the 2,3-di-O-methylglucose syrup with aniline. The chromatogram was developed with water-saturated methyl ethyl ketone - ethanol (4:1) for 5 hours, was dried and sprayed with alkaline 1% potassium permanganate solution. Two adjacent spots of R_F value 0.63 were obtained.

DISCUSSION OF RESULTS

The industrial denitration of nitrocellulose is generally effected with solutions of ammonium hydrosulphide in the presence of appropriate swelling agents for the starting material, but the sulphides of the alkali and alkaline-earth metals have also been used in this respect (77, 81, 82, 130). Rassow and Dörr (77) have pointed out that no definite conditions are possible, since various nitrocelluloses behave quite differently toward these reagents.

Reichel and his coworkers (81, 82) obtained the best results in the industrial field with 3.75% sodium hydrosulphide containing 1.75% of sodium polysulphide, buffered below a pH of 12 and kept at a temperature between 15 and 20°. Nevertheless, the use of ammonium hydrosulphide has always been preferred in laboratory procedures. Thus Atsuki (131) found that the optimum conditions for the denitration of nitrocelluloses involved the digestion of one part of the nitrate with 100 parts of 16% ammonium hydrosulphide solution at 25 - 30° for 6 - 10 hours, while Rassow and Dörr (77) improved the method by using a solution of the hydrosulphide in 60% ethanol and a reaction temperature of 18 - 20°. In the denitration of nitropectins, Bock, Simmerl and Josten (132) reported that relatively small variations in the strength of the ammonium hydrosulphide reagent, as well as in the temperature, could have profound influence on the degree of polymerization of the denitrated products. They recommended dilution of the aqueous ammonia to 3% before saturation with hydrogen sulphide and a temperature of 5 - 15° for the denitration. The mechanism for the denitrations of

nitrocellulose and nitropectin are assumed to be similar.

Recent work on the reaction of n-butyl nitrate with alkaline hydrosulphides by Merrow, Cristol and Van Dolah (93) clarified some of the general features of these denitrations, as was more fully discussed in the Historical Introduction (p. 26). The largest amount of polysulphide was formed when the reaction mixture was maintained below a pH of 10, the polysulphide ion had a strong catalytic effect, and alkali markedly increased the rate of denitration in the presence of polysulphide. The denitration was therefore autocatalytic in nature because of the formation of polysulphide as a reaction product. Thus the control of pH was a necessary measure in all these hydrosulphide denitrations, and the preference for ammonium hydrosulphide could be more readily appreciated, since the pH of the latter lay in the vicinity of 10. Merrow and coworkers were able to obtain results on n-butyl nitrate comparable to those with ammonium hydrosulphide by using sodium hydrosulphide containing enough boric acid to keep the pH of the reaction mixture below this critical value. Denitration occurred at higher pH values, but the reaction was slower and degradation probably greater.

Since the pH of the reaction mixture is to be considered as a major factor in these denitrations, the ionic character of the solvent would also be of considerable importance. In the denitration of cellulose nitrates, the accessibility factor also assumes great importance, and the solvent medium must necessarily be a swelling agent or solvent for both the cellulose nitrate and the cellulose produced. Reichel and Craver (81) listed acetone-water, dioxane-water, monoethanolamine-water, morpholine-water, methyl cellosolve-water, glacial acetic acid - water,

methanol-water, ethanol, and diethylene glycol as suitable swelling agents in the industrial field, where swelling must be accomplished without excessive deformation of the filaments. In the laboratory, solution is generally more desirable than swelling, and acetone and dioxane therefore appeared to be the most suitable media for the efficient denitration of the O-methylcellulose dinitrate. The best results would probably be obtained if a minimum amount of the solvent was used, so that addition of the aqueous hydrosulphide reagent would result in the precipitation of very highly swollen nitrate. Mono-O-methylcellulose, the reaction product, was soluble in aqueous but not in organic liquids. Consequently, if denitration were to be complete, the reaction medium would have to be changed during the course of the reaction from one containing predominantly acetone or dioxane to one of essentially aqueous content. This change was accomplished by the judicious addition of ammonium hydrosulphide and water.

The first denitrations of the mono-O-methylcellulose dinitrate were attempted by adding aqueous ammonium hydrosulphide to acetone solutions of the nitrate. A relatively low concentration (about 3%) of ammonium hydrosulphide at temperatures below 20° was employed in the first experiments as recommended by Bock, Reichel and their respective coworkers (81, 82, 132), but very little denitration was achieved. This behaviour was probably another manifestation of the unique stability of the present cellulose dinitrate to alkalies. An increase in the concentration of the hydrosulphide reagent led to increased decomposition of the sample. Large quantities of organic sulphur products such as

thioacetone and mercaptans were formed, and very little cellulosic material could be isolated. Such material sometimes contained large quantities of sulphur, which was apparently in a bonded form, and could not be removed by washing with water, acetone, alcohol, and carbon disulphide. In a few cases, exceedingly small yields of a mono-O-methylcellulose were isolated from the reaction mixture by precipitation from the concentrated aqueous solution with acetone and ethanol. In many other cases, the isolation of any of the required products was rendered too difficult by the presence of such large quantities of by-products. The use of acetone was therefore discontinued in favour of dioxane.

Immediate success was achieved with dioxane, and few by-products other than polysulphide could be detected. The most efficient denitrations of O-methylcellulose dinitrate were obtained when large excesses of ammonium hydrosulphide were employed in high concentrations. Dilution of the reaction mixture with water during the course of the reaction resulted in a nitrogen content of 1.30% in the products in comparison to a value of 0.65% when no water was added. Heuser (133) pointed out that the denitration was facilitated by a high liquid-nitrocellulose ratio. The rate of denitration was very slow for the methylcellulose dinitrate and required upward of 24 hours under the conditions used. One run, which lasted only 21 hours, led to the formation of acetone-soluble products, a result which was interpreted as incomplete denitration. It is probable that the presence of larger amounts of polysulphide and hydroxyl ions in the reaction mixture would have had a beneficial effect on the denitration, these ions having been shown by Merrow and his colleagues (93) to possess catalytic properties

in hydrosulphide denitrations.

After the denitration, the mono-O-methylcellulose was washed with acetone, and was swollen in a 4:3 mixture of carbon disulphide and acetone. This swelling presented a spectacular phenomenon, as the methylcellulose appeared to dissolve. However, a very highly swollen, almost transparent, orange gel separated easily after centrifuging the mixture, and this way of obtaining homogeneity in the product proved to be very satisfactory. Significant variation in the amounts of either carbon disulphide or acetone decreased swelling, and neither liquid alone exhibited any swelling power toward the methylcellulose. If this phenomenon was comparable with the solution of cellulose nitrate in ether-alcohol mixtures, the explanation would involve solvation of the O-methylcellulose by the acetone, together with modification of the energy relations in the liquid by the carbon disulphide, so that its resultant internal pressure would not be too different from that of the solvated methylcellulose (134, 135). The mixing of carbon disulphide and acetone is endothermic, and it is interesting to note that the maximum amount of heat (about 5 kilocalories per mole of mixture at 16°) is absorbed in the region of the concentration employed here (136). If the theory of solvation and internal pressure applies in the present case, it might be expected that a carbon disulphide - alcohol mixture would exhibit the same property, since the methylcellulose contains more hydroxyl than methoxyl groups, and the latter would be preferentially solvated by acetone. A test-tube experiment on the dried methylcellulose confirmed this suspicion, greater swelling being shown in carbon disulphide - ethanol (4:3) than in carbon disulphide - acetone. The mixture of carbon disulphide and ethanol exhibited only small

endothermic changes on mixing.

The mono-O-methylcellulose was obtained as a light yellow powder which was partially soluble in water but completely soluble in 4% sodium hydroxide. The product was obviously highly degraded. In the first denitration with dioxane, the methylcellulose was fractionated into 0.30 gm. of water-soluble and 0.75 gm. of water-insoluble material. The water-soluble fraction contained 1.18% of nitrogen and 18.0% of methoxyl groups, compared to 0.44 and 18.8% respectively for the nitrogen and methoxyl contents of the water-insoluble fraction. Since the product of higher nitrogen and lower methoxyl content dissolved in water, it would appear that this material was the more extensively degraded. The degradation during the process of denitration has been previously shown to be severe (see p. 26). On the present occasion, the intrinsic viscosity $[\eta]$, 18.7, for the original cellulose trinitrate (N = 13.8%) and $[\eta]$ 1.22, for the trinitrate (N = 13.5%) obtained by renitration of the dinitrate (N = 10.0%) are increased to values of 20.5 and 1.49 when corrected to a nitrogen content of 14.14% according to the method of Lindsley and Frank (137). Using a constant of 80 (119), corresponding D.P.'s of 1640 and 119 are derived. However, the latter value appears to be in error since the parent dinitrate, containing 10.0% nitrogen, possessed an intrinsic viscosity of 1.73. The studies of Lindsley and Frank (137) and of Harland (138) have both demonstrated that the intrinsic viscosities of cellulose nitrates are increased by any increase in their nitrogen contents. Renitration must therefore have been accompanied by degradation in the present case. No constants were available for the calculation of the D.P. values of the methylated celluloses, but inspection

of the intrinsic viscosity figures for the O-methylcellulose dinitrate and its denitrated product reveal little degradation in this step. Various authors have commented on the impossibility of obtaining completely nitrogen-free cellulose by denitration. The results here are in accordance with the findings of Karrer and Schubert (84) and Staudinger and Mohr (85), 0.4 - 1.3% of nitrogen being found in their denitrated products.

The hydrolysis of the methylcellulose was carried out with 3.5% hydrochloric acid after apparent solution in ice-cold 20% hydrochloric acid. After dilution and heating, however, some solid material precipitated and had to be redissolved in a little 43% hydrochloric acid. The low yield (83.8%) of the syrup recovered from the hydrolysis was possibly due to manipulative losses and to the presence of residual nitrate group in the methylcellulose. An improved yield of 89.0% was obtained when the hydrolysis was performed in sulphuric acid, a difference which was probably quite incidental. This syrup deposited crystals on stirring with a little absolute ethanol, and apparently contained one product in relatively great preponderance. This inference was confirmed by paper chromatographic techniques. Partition chromatography of the syrup on a cellulose powder column was then carried out with a 4:1 mixture of water-saturated methyl ethyl ketone and ethanol as the developing solvent. This mixture was preferred to butanol mixtures because the high boiling point of butanol made it difficult to remove from syrup fractions. The methyl ethyl ketone - ethanol mixture was very sensitive to slight temperature changes, and in consequence, different R_F values were obtained for the same sugar at different times. However, the same order and separation of the sugars were maintained at all times.

The addition of 0.1% of ammonium hydroxide to the solvent was beneficial in paper chromatography, and resulted in more compact spots and better separations. No ammonia was added when the solvent mixture was used in column chromatography since a slow reaction was found to take place, producing a "yellowing" of the solvent after a few days. Traube (139) reported that methyl ethyl ketone and ammonia reacted in the presence of ethanol after 2 - 3 weeks at room temperature to form a compound which was probably 2,3,6-trimethyl-2,6-diethyl-4-piperidone.

The syrup proved to contain one mono-O-methyl- and two di-O-methylglucoses. Good separations of the three methylated sugars were obtained, though a small amount of overlapping occurred in the case of the two di-O-methylglucoses. No tri-O-methylglucose could be detected in the hydrolyzates, with one possible exception when a very faint spot was noticed on a paper chromatogram in a position which would correspond to this sugar. This spot was not present on subsequent chromatograms. The mono-O-methylglucose crystallized, and was positively identified as 2-O-methyl-β-D-glucose by means of its melting point, mutarotation, the melting point of its phenylhydrazone, and the preparation from it of glucose phenylosazone and the corresponding osatriazole. One dimethylglucose, of lower R_F value, was identified as 2,3-di-O-methyl-D-glucose by means of its crystalline anilide. The other dimethylglucose was not positively identified owing to the small amount in which it occurred, though its methoxyl content confirmed its designation as a dimethylglucose. Since the hydrolyzate of the monomethylcellulose contained 84% of 2-O-methylglucose, the action of hydroxylamine-pyridine on cellulose trinitrate was to effect a quantitative or nearly quantitative removal

of the nitrate group in the second position of the glucose monomer with the consequent formation of cellulose 3,6-dinitrate. The di-O-methylglucoses probably originated from free hydroxyl groups in the cellulose trinitrate whose substitution was only 2.88. If it were assumed that all the nitrate groups in the second position of the anhydroglucose unit were eliminated, the unidentified di-O-methylglucose could only be the 2,6-isomer.

Little can be added to the mechanism presented by Segall and Purves (107). It is possible that the reducing action of hydroxylamine may be replaced by other more easily available reagents such as hydrazine, stannous chloride, or other pyridine-soluble reducing agents. Edwards and his coworkers (140, 141) reported a cuprous acetate-pyridine reagent which reduced nitrobenzene to aniline, benzaldehyde to benzyl alcohol, and certain aromatic halogen compounds to the parent hydrocarbons. Brown and Hayward (64) suggested that the development of colour in pyridine denitrations, was due to the presence of glutaconaldehyde derived from the pyridine, the colourless dioxime being formed in the presence of hydroxylamine or its hydrochloride. This would serve to explain the lack of colour in these reaction mixtures.

The superior reactivity of the second position in some carbohydrate reactions, particularly those involving glucose and its polymers, has long been recognized and has been attributed to the presence of an adjacent acetal grouping. The reactivity is enhanced in alkaline media, and Sugihara (142) ascribed this property to a permanent polarization of the second position. The weak acidity of certain sugars and their glycosides, as shown by conductometric and polarographic measurements

(143, 144, 145, 146), lead to dissociation constants which are much higher than those attributed to the monohydric and polyhydric alcohols. Fox, Cavalieri, and Chang have demonstrated that variations in the ultraviolet absorption spectra of pyrimidine nucleosides dissolved in aqueous alkali were due to the ionization of the 2-hydroxyl group of the sugar component with a very limited contribution from the other hydroxyl groups. All the free hydroxyl groups of cellulose are weakly ionizable, as evidenced by the exchange of hydroxyl hydrogen for deuterium atoms from deuterium oxide, a change which is virtually complete in 30 hours at 30° (148).

Timell (149) and Sugihara (142) have discussed the relative reactivities of the hydroxyl groups in cellulose and carbohydrates in general. The primary hydroxyl group was preferred in those reactions governed by the alcohol function, but in many other reactions the 2-hydroxyl group was as easily, and even preferentially substituted. Schorigin and Makarowa-Semljanskaja (150) caused trisodium cellulose in liquid ammonia to react with methyl iodide, and obtained an O-methylcellulose which yielded a mixture of O-methylglucoses with 2-O-methyl-D-glucose in the largest proportion. Compton (151) methylated a dispersion of cellulose in dibenzyldimethylammonium hydroxide with dimethyl sulphate, and isolated a crystalline derivative of 2-O-methyl-D-glucose after hydrolysis of the partly-methylated cellulose so obtained. Heddle and Percival (152) treated cellulose with alcoholic potassium hydroxide and subsequently with dimethyl sulphate. The only monomethylglucose to be detected in the hydrolysate was the 2-O-methyl ether. This sugar also predominated in the hydrolysates of cellulose samples methylated with dimethyl sulphate

and sodium hydroxide, with dimethyl sulphate and benzyltrimethylammonium hydroxide, and by the commercial method utilizing the reaction of methyl chloride with alkali cellulose (153). Other workers (154, 155) obtained similar results. Lemieux and Bauer (156) found that the mono-O-methyl-glucose fraction from the hydrolysate of a technical O-methylcellulose of substitution 1.58 consisted of the 2-, 3-, and 6-isomers in a ratio of approximately 10:1:5. Glucose and its derivatives behave in an analogous manner to alkaline methylations. Thus methylation of glucose thioacetals (157, 158, 159) occurred preferentially in the second position, while a mixture of tri-O-methyl ethers obtained from the reaction of methyl α-D-glucopyranoside with methyl iodide and thallous hydroxide was found to be substituted largely in the second and sixth positions (160).

An almost exclusive conversion of the 2-hydroxyl group was accomplished by Sugihara and Wolfrom (161) who obtained 2-sodio-cellulose by the action of a boiling butanolic solution of sodium hydroxide on cellulose. This derivative was condensed with other reagents to give a variety of 2-substituted cellulose products (161, 162). An analogous 2-sodio derivative of methyl α-D-glucopyranoside was prepared by the same method (162, 163). Similar selective substitutions were also accomplished by Gaver and his colleagues (164, 165, 166, 167) with starch and other carbohydrates. Some idea of the relative reactivities of the cellulose hydroxyl groups to metallation can be inferred from the data of Shimo, Ando, and Fuse (168) who found that the reaction of cotton linters with sodium in liquid ammonia required 43 minutes for the introduction of the first sodium atom, 5.5 hours for the second, and

28 hours for the third equivalent.

The second position also exhibits a high degree of selectivity in certain alkaline cleavages of ester groups. The work of Honeyman and coworkers (25, 26, 27) has already been discussed in the Historical Introduction (pp. 15, 31). Their mechanistic explanation involved removal of sulphonate and nitrate groups on C2 by oxy-sulphonyl or oxy-nitryl fission as compared to the slower carbon-oxy fission of the C3 ester grouping. This theory shows good compatibility with Sugihara's hypothesis concerning permanent polarization of the hydroxyl group in the second position of sugar molecules (142). Hodge and Rist (169) treated α- and β-D-glucose pentaacetates and 2,3,4,6-tetraacetates with piperidine and obtained N-(3,4,6-tri-O-acetyl-D-glucopyranosyl)-piperidine. This compound was used to prepare 2-substituted D-glucose derivatives. Haworth, Hirst, and Teece (170), Bourne, Stacey, Tatlow, and Tatlow (171), and Whistler and Kazeniac (172) found greater susceptibility to cleavage of the groups in the second positions of methyl 2,3,4-tri-O-acetyl- α -D-glucopyranoside, methyl 4,6-O-benzylidene-2,3 bis (O-trifluoroacetyl) α -D-glucopyranoside, and methyl 2,3-di-O-acetyl- α -D-glucopyranoside.

This preferential susceptibility to cleavage extends to the 2-nitrate group in many glucose and cellulose nitrates. Gladding and Purves (30) found that the nitrate group in methyl 3,4,6-tri-O-acetyl-β-D-glucoside 2-nitrate was removed more easily by alkaline hydrolysis than that in the isomeric 6-nitrate. Honeyman and his coworkers (25, 26, 27) isolated large amounts of the corresponding 3-nitrates following the action of strong alkalies on the 2,3-dinitrates of methyl glucosides. Sodium

iodide in acetone and other ketones afforded the 3-nitrate derivatives from the 2,3-dinitrates of various methyl glucosides (26, 27, 97, 173). Sodium iodide has also been used similarly in methanol, acetic anhydride, and in pyridine, and so has sodium nitrite in aqueous ethanol (26, 27). The magnitude of any participation of the steric factor in these selective ester cleavages has yet to be ascertained. The preferential removal of the 4-nitrate group of methyl β-D-glucoside tetranitrate by hydroxylamine in pyridine (111), when the same reagent removes the 2-nitrate group of cellulose trinitrate, probably finds its explanation in spatial arrangement and other structural variations. These apparent anomalies can only be clarified by studies of the denitrating action of this and similar reagents on other carbohydrate nitrates.

The conversion of cellulose to 2-O-methyl-D-glucose offers a new route for the laboratory preparation of this derivative, an overall yield of 63% of the pure sugar being realized. This yield is the highest yet achieved from any convenient starting material. In comparison, Weygand and Trauth (124) synthesized 2-O-methyl-D-glucose in 41% yield from monoacetoneglucose. Other methods of preparation of this sugar are given by Bourne and Peat (123) and by Lock and Richards (174) who used the borate form of a strongly basic ion-exchange resin to resolve a mixture of O-methylglucoses substituted in the 2- and 3- positions.

PART II

AN ATTEMPT TO LOCATE THE XANTHATE GROUPS IN PARTIALLY XANTHATED CELLULOSE

HISTORICAL INTRODUCTION

A. The General Chemistry of Organic Xanthates.

The word "xanthate" is derived from the Greek word "xanthos", (meaning yellow, in reference to the colour of the cuprous salt of O-ethyl-thionothiolcarbonic acid or ethyl xanthic acid (175). The salts and esters of this and other homologous O-alkyl acids comprise the chemical class known as xanthates or xanthogenates.

The alkyl xanthic acids are very unstable oils which decompose spontaneously, particularly in the presence of water, into alcohols and carbon disulphide. However, the alkali salts of the xanthic acids are fairly stable, crystallize well, and dissolve readily in water, but most other xanthate salts are insoluble. The alkali salts serve as intermediates in the preparation of other xanthates and are themselves prepared by causing carbon disulphide to react with alkoxides or with alcohols in the presence of alkalies. Sodium and potassium xanthates

$$ROH + CS_2 + NaOH \longrightarrow RO-\overset{\overset{S}{\|}}{C}-SNa \qquad (50)$$

are nearly colourless when pure, although they are often yellow owing to the presence of sodium trithiocarbonate.

The xanthate reaction (176) was reported to go readily with primary alcohols including 1,4-diols, more slowly with secondary alcohols, while tertiary alcohols did not react. Berl and Bitter (177) found that sodium glycollate condensed with carbon disulphide much more slowly than did sodium ethylate, and sodium glycerate only under pressure (177, 178). Monomethylglycol and dimethylglycerol reacted similarly

to primary alcohols. Side reactions such as the formation of sodium trithiocarbonate increased with the polyvalency of the alcohol.

Lieser and coworkers (179, 180) prepared the monoxanthates of glycol and glycerol by substituting barium hydroxide for sodium hydroxide, and by the same method converted methyl α-glucopyranoside and other monosaccharides (179 - 183) to products containing mainly the monoxanthates together with small amounts of the more highly substituted products. The xanthate group in glucose monoxanthate was regarded by Lieser (181), largely by analogy with his results on cellulose xanthate (p. 88) and with other glucose reactions, as being attached to the carbon atom in the second position of the molecule.

The alkali atom of alkali xanthates is strongly ionic in character and most reactions of xanthate salts are due to the high reactivity of this atom. Thus, these salts are easily hydrolysed (184), particularly in acid solution where decomposition of the unstable xanthic acid occurs. The decomposition has been reported (185) to occur through the undissociated acid but to be counteracted by its fairly strong ionization, the dissociation constant for O-methyl xanthic acid at 0° (186) being 0.034, and that for the O-ethyl acid, 0.030. Electrolysis of xanthate salts (187) leads to the anodic formation of the corresponding dixanthide (equation 51).

$$2ROCSSK \rightleftharpoons 2ROCSS^- + 2K^+ \qquad (51)$$
$$\downarrow -2e$$
$$(ROCSS)_2$$

Compounds containing an active halogen atom react with xanthate salts

to form stable xanthate esters of which the most important are the methyl esters, i.e. the O-alkyl S-methyl xanthates.

$$ROCSSNa + R'X \longrightarrow ROCSSR' + NaX \qquad (52)$$

A less common mode of preparation is represented by equation 53 (188).

$$Cl-\overset{\overset{S}{\|}}{C}-Cl \xrightarrow{R'SH} Cl-\overset{\overset{S}{\|}}{C}-SR' \xrightarrow{ROH} RO-\overset{\overset{S}{\|}}{C}-SR' \qquad (53)$$

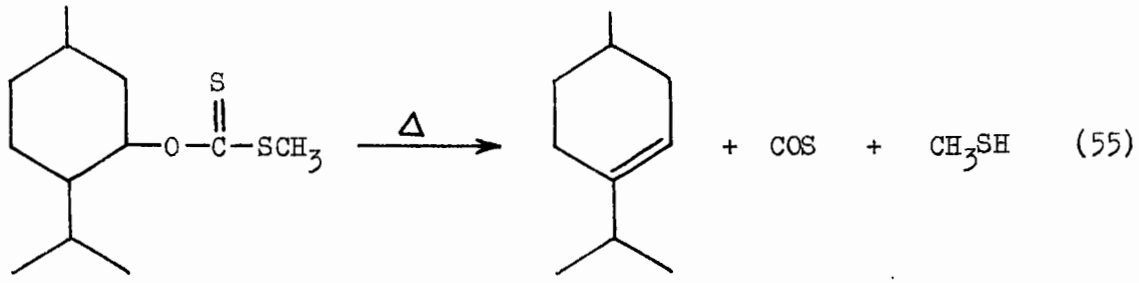
The xanthate esters are much more stable than the corresponding alkali salts, the lower members being high-boiling liquids, insoluble in water and possessing a garlic-like odour. Many of the higher members are crystalline. Another important and stable class of xanthate derivatives are the xanthamides, which are usually prepared by the action of ammonia or simple amines on xanthate salts (189), dixanthides (190, 191), or on xanthate esters (192) of which the xanthoacetic acids (193) are most commonly used.

$$ROCSSCH_2COOH + 2NH_3 \longrightarrow ROCSNH_2 + HSCH_2COONH_4 \qquad (54)$$

A number of cyclic derivatives may also be prepared from xanthate salts and certain amino derivatives. Ethyleneimine has been reported (194) to form thiazolidine derivatives in weakly acid solution and α-chlorobenzalphenylhydrazine to form a thiadiazole (195), while thiazoles apparently result with o-aminoarylthiocyanates (196, 197).

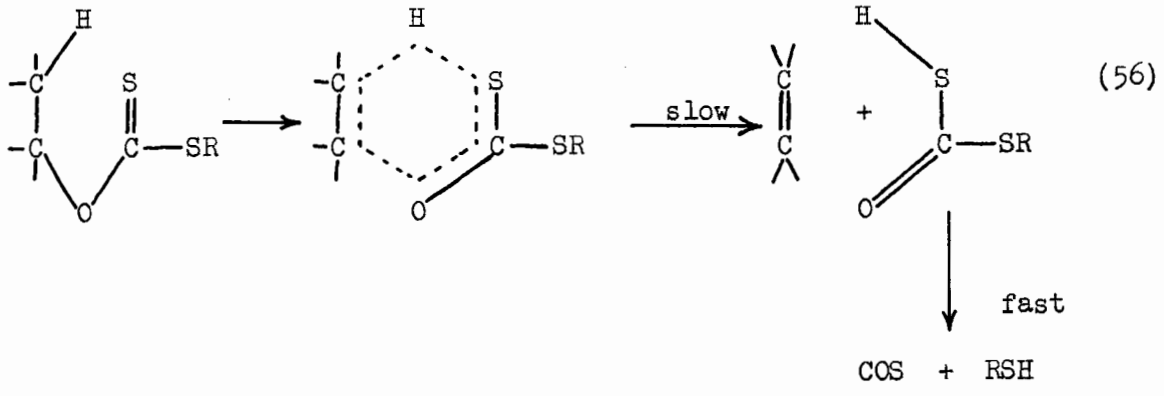
On heating, xanthate salts decompose readily to a mixture of products consisting principally of carbon disulphide, carbonyl sulphide, alcohol, mercaptan, alkyl sulphide and disulphide (198, 199). The

behaviour of xanthate esters on heating (200) depends largely on the nature of the particular ester. Those derived from primary alcohols are relatively stable to heat and can often be distilled <u>in vacuo</u>, while those from other alcohols decompose more easily to unsaturated hydrocarbons. This decomposition, known as the Chugaev reaction, (201, 202) has provided a useful method for the preparation of olefins from alcohols in cases where isomerization or other untoward reactions occur (202, 203). Extensive use of this method has been made, particularly in the terpene series, as in the preparation of methene from menthol.



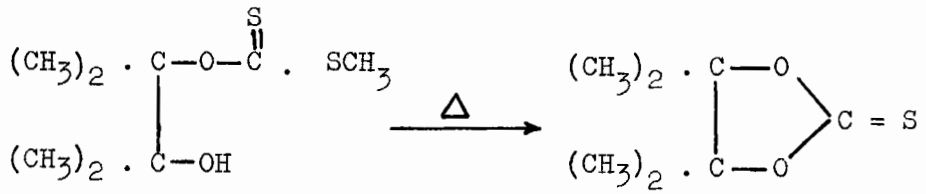
(55)

Some of the most interesting studies connected with this reaction are those of Whitmore and Simpson (200), McAlpine (204), Bulmer and Mann (205), Alexander and Mudrak (206), O'Connor and Nace (207), Cram (208), and Bourns and Baker (209). The reaction is considered (207 - 210) to involve a <u>cis</u>-elimination, in which, through a concerted process, the thion sulphur abstracts a hydrogen from the β-carbon atom at the same time that the α -carbon-oxygen bond is broken. Bourns and Baker (209) have suggested the two-step mechanism of equation 56.



(56)

Xanthate salts and esters when heated sometimes yield products other than those demanded by either the reaction of simple thermal decomposition or by the Chugaev reaction. The presence of an α -hydroxyl group caused the formation of cyclic thioketones (211, 212) according to equation 57, while O-benzyl xanthate esters yielded stilbene on heating (205, 212, 213) (equation 58).



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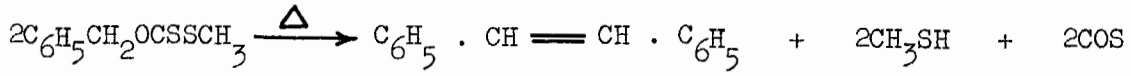


(58)

Transformation of xanthate esters to isomeric dithiocarbonates has also occurred (205, 214), although the reaction is sometimes complicated by the formation of other isomeric, thermally stable forms (204, 205, 214) whose nature is as yet undecided. Laakso (214) believed the "stable" form of the xanthate to be the isomeric dithiocarbonate, but Bulmer and Mann (205) showed this interpretation to be in error.

The hydrolysis of xanthate esters usually proceeds in high yields to the formation of alcohol, thiol, carbon dioxide, and hydrogen sulphide (215). The esters are fairly readily hydrolysed in alkaline solution, particularly in alcoholic alkali, but show considerable stability to acids (181, 216). Schmitt and Glutz (217) accomplished the hydrolysis of O-ethyl S-ethylxanthate by heating with water to 160° in a sealed tube. Alcoholic alkali and alkoxides give alcohol, thiol,

and salts of alkyl monothiocarbonic acids (215, 217, 218) according to equations 59, 60 and 61 (215), while Klamditz (219)

$$RO \cdot \overset{\overset{S}{\|}}{C} \cdot SR' + H_2O \longrightarrow ROH + COS + R'SH \qquad (59)$$

$$COS + H_2O \longrightarrow CO_2 + H_2S \qquad (60)$$

$$COS + KOR'' \longrightarrow R''O \cdot \overset{\overset{O}{\|}}{C} \cdot SK \qquad (61)$$

expressed the neutral hydrolysis at 24° of ethyl potassium xanthate in terms of equation 62, with equation 63 occurring in aqueous alkaline media.

$$6EtOCSSK + 3H_2O \longrightarrow 2K_2CS_3 + K_2CO_3 + 6EtOH + 3CS_2 \qquad (62)$$

$$EtOCSSK + 5KOH \longrightarrow 2K_2S + K_2CO_3 + EtOH + 2H_2O \qquad (63)$$

The formation of xanthamides by the action of alcoholic ammonia on xanthate esters was previously (p. 76) mentioned, but the reaction of aqueous ammonia with the esters in a sealed tube at 120 - 140° was reported by Salomon (220) to be given by equation 64.

$$RO \cdot \overset{\overset{S}{\|}}{C} \cdot SR' + 2NH_3 \longrightarrow NH_4SCN + ROH + R'SH \qquad (64)$$

Vincent (216) found that octadecyl methylxanthate was stable at room temperature to aqueous alcoholic ammonia, and to pyridine, but that extensive decomposition occurred on heating the ester in the latter reagent.

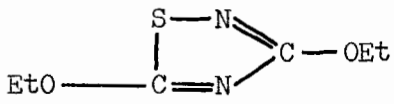
Few studies have been carried out on the oxidation of xanthates. Xanthate salts were oxidized under mild conditions to dixanthides (191, 221) and monoxanthides, $(ROCS)_2S$ (222). Strong oxidizing agents converted the xanthate sulphur atoms to sulphate ions and formed the basis of the bromine oxidation method (223) for the analysis of alkali xanthates. Alkaline potassium permanganate had a similar action (224), while certain aromatic nitro compounds oxidized the alkali xanthates to a mixture of stable xanthamide and alcohol according to equation 65 (225). The oxidation of xanthate esters

$$6ROCSSNa + 4R'NO_2 + 3H_2O \longrightarrow 4ROCSNHR' + 2ROH + 3Na_2S_2O_3 + CO_2 + CS_2 \qquad (65)$$

is greatly complicated by the stability of the thio-ether grouping (226) and little data are available on the course and mechanism of such reactions. However, the thionic sulphur is oxidized even in air at ordinary temperatures (227, 228, 229). Anhydrous chlorine in butane near the temperature of solid carbon dioxide reacted according to equation 66 (230) but cold aqueous chlorine resulted in the formation of alkyl chlorocarbonates and alkylsulphonyl chlorides (231).

$$ROCSSR' + 3Cl_2 \longrightarrow ROCCl_2SCl + R'SCl_3 \qquad (66)$$

Holmberg (232) as well as Dubsky (233) have given structure IV



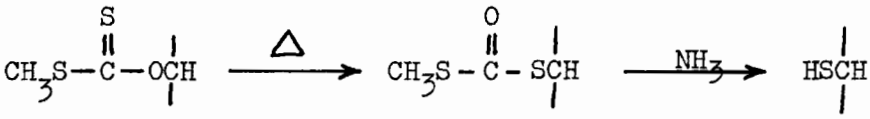
IV

to the product from the oxidation of ethyl xanthamide with hydrogen peroxide or iodine in neutral or acid alcoholic solution. Vincent (216) obtained derivatives containing three extra oxygen atoms by the action of hydrogen peroxide in glacial acetic acid on octadecyl and hexadecyl methylxanthates while a similar oxidation of benzyl methylxanthate yielded benzyl alcohol as the main product. The oxidized products of octadecyl and hexadecyl methylxanthates could be converted to the parent alcohols by hydrolysis in hot dilute alkali. Xanthates have also been desulphurized to the alcohol by solutions of salts of heavy metals, particularly those of silver and mercury (181, 216, 234), thallous ethoxide (216), as well as by the action of Raney nickel (216, 234).

B. Sugar and Cellulose Xanthates

Lieser and coworkers (179 - 182) prepared xanthates of glucose, methyl α- and β-D-glucopyranosides, phenyl β-D-glucopyranoside, 1,6-anhydro-D-glucopyranose, glucose phenylhydrazone, fructose, maltose, cellobiose, lactose, sucrose, raffinose, starch, glycogen, lichenin, mannan, inulin, and xylan. Various degress of xanthation were obtained with the monosaccharides, though the monoxanthate formed more easily, but the disaccharides and raffinose could only be substituted to the extent of one xanthate group per aldohexose unit. The β-linked fructofuranose units of sucrose and raffinose were presumed to be unreactive towards xanthation (180, 235). Some investigators have also experienced difficulty in the xanthation of xylan (236, 237).

Freudenberg and Wolf (238) prepared the methylxanthates of diacetoneglucose, diacetonemannose, and diacetonegalactose, and subjected them to pyrolysis in an attempt to prepare the appropriate glucoseen derivatives according to the method of Chugaev (201, 202). In no case were they able to effect the desired unsaturation. Instead, an isomerization occurred forming a dithiocarbonate which was then cleaved by ammonia to a thiol group.



(67)

Foster and Wolfrom (239) also attempted the Chugaev reaction with the 2-methylxanthate and the 2-tritylxanthate esters of methyl 3,4-O-isopropylidene-β-D-arabinopyranoside and the 2-methylxanthate of methyl 4,6-O-benzylidene-3-O-methyl-α-D-altropyranoside. The expected reaction did not occur, but derivatives were obtained which in the case of the first compound could be reductively desulphurized to methyl 3,4-O-isopropylidene-β-D-2-deoxy-riboside.

Starch xanthates have received some industrial attention, and patents have been issued for their use as adhesives for wood veneers (240) and in textile sizes (241). Another patent (242) covers their reaction with diazonium salts to give organic dithiocarbonates. The preparation and properties of the xanthates of starch have been investigated by Ost and his colleagues (243), and by Wolffenstein and Oeser (244). Both sets of workers have demonstrated the similarity in reactions between the xanthates of starch and cellulose.

The xanthation of cellulose was first accomplished by Cross, Bevan and Beadle (245, 246) in 1892. The reaction is of great industrial importance and has been given thorough treatments in the textbooks of Heuser (247), and of Ott, Spurlin and Grafflin (248). Only the general aspects, the more recent work, and other matters of particular interest to this study will be discussed here. The xanthation of cellulose may not be strictly analogous to that accepted for the formation of xanthates of simple alcohols, since alkali cellulose may not possess the simple alkoxide structure. Makolkin and coworkers (249) followed the isotope exchange of oxygen - 18 between water and alkali cellulose, and concluded that mercerization resulted in the formation of an addition product, $C_6H_{10}O_5$. NaOH, and not an alkoxide $C_6H_9O_4$. ONa. No particular advantage was obtained by using potassium and lithium hydroxides in the xanthate reaction (250), but trisubstituted derivatives were obtained by the use of certain tetraalkylammonium hydroxides (251, 252), and of metallic sodium in liquid ammonia (168, 253).

The usual preparation (247, 248, 254) of cellulose xanthate involves the mercerization of the cellulose to form alkali cellulose I, the pressing of the alkali cellulose to remove excess sodium hydroxide, shredding of the resulting cake, aging in the presence of air to degrade the cellulose and reduce its viscosity in solution, treatment of the aged alkali cellulose with carbon disulphide in revolving vessels, and solution of the orange-coloured xanthate crumbs in dilute sodium hydroxide to give the viscous solution known as viscose. Industrial preparations include the further step of aging or "ripening" of the viscose solution, thus improving its spinning and filterability

characteristics. Kline (248) has discussed these stages in detail.

The formation of the alkali cellulose is relatively rapid, but the rate of xanthation and the degree of substitution (D.S.) of the product is influenced by several factors such as the nature of the cellulose, the amounts of carbon disulphide, water, and alkali present, the temperature, and time of reaction. The amounts of alkali and water are controlled by the press-weight-ratio (P.W.R.) which usually varies from 2.5 to 4.0. Small P.W.R.'s have been reported to favour a rapid rate of formation of xanthate (255) while higher values promote higher degrees of substitution (256, 257). The xanthation reaction apparently best carried out at 25 to 35° (258), is very slow below 15° but doubles by a 10° rise in temperature. Scherer and Miller (259) have investigated the rate of xanthation of alkali cellulose with an excess of carbon disulphide at 25°, 29.5°, and 35°, and found that the D.S. of the xanthate increases rather steadily to values of 0.8 - 0.9 after 200 minutes, thereafter remaining practically constant for many hours. More detailed kinetic studies have been presented by Hess (260), Grotjahn (261), and Kargin and his coworkers (262). Although cellulose xanthation is generally believed to be monomolecular, Hess concluded that it was a bimolecular reaction. The reaction of equation 68 occurred first, but the adduct reacted rapidly with the cellulose and was present in amounts too small to be determined analytically. Grotjahn (261)

$$NaOH + CS_2 \longrightarrow NaS \cdot \overset{S}{\overset{\|}{C}} \cdot OH \qquad (68)$$

studied the reaction velocity at temperatures between 15.5° and 35°,

and proposed a detailed reaction scheme involving the formation of the complex NaOH . CS_2 and its subsequent reaction with cellulose hydroxyl groups to produce xanthate. A rate equation representing the absorption of carbon disulphide by cellulose was also presented. Kargin and his coworkers (262) determined the rate constants for the homogeneous xanthation of sucrose to be 0.123, 0.623, and 2.81 at 20°, 30° and 40° respectively, and of an alkali - soluble degraded cellulose (D.P. 82) from viscose rayon to be 0.042, 0.11, and 0.271 at 15°, 25° and 35° respectively. The heterogeneous xanthation of an alkali cellulose was carried out at 20°, 30°, and 40° with first order K values of 0.11, 0.245, and 0.643 respectively, and was regarded as a pseudomonomolecular reaction. The heat of xanthation of alkali cellulose has been reported (263) to be 7200 calories per mole of carbon disulphide.

A considerable amount of evidence has been developed in support of both the micellar, or topochemical, and the permutoid, or macromolecular, modes of xanthation of alkali cellulose, with the possibility of participation of both mechamisms. According to Timell (264), the reaction is initially macroheterogeneous or possibly micellar-heterogeneous, but the crystallites soon begin to react and the reaction then gradually becomes more and more permutoid. The various arguments have been admirably represented by Kline (248).

In addition to the conversion of hydroxyl groups to xanthate, a number of side reactions occur during xanthation (265). These include secondary reactions of the xanthate itself (for example, equations 62 and 63, p. 79), and direct reaction between carbon

disulphide and free alkali. Both types of reaction become more competitive with the main reaction of xanthation at higher temperatures and greater concentrations of alkali and water, and lead to the formation of carbonate, trithiocarbonate, sulphide and probably hydrosulphide. These secondary products are responsible for the yellow or orange colour of xanthate preparations.

The solution of cellulose xanthate to form viscose is usually carried out in dilute sodium hydroxide such that the alkali content of the viscose is between 4% and 9% and the cellulose content between 6% and 10%. From a colloidal standpoint, it has been regarded as essentially a peptization of a hydrophilic colloid which behaves in solution as a typical electrolyte, and exhibits such phenomena as high and anomalous viscosity, syneresis, and flow birefringence (266). The swelling and dispersion of cellulose xanthates has been reported (267, 268) to occur layer by layer rather than by single molecules.

Many complex chemical changes have been detected in the industrially important ripening process. Dexanthation was accompanied by depolymerization and redistribution of xanthate groups, thus forming a much more uniform structure (269). So effective was the trans-esterification that cellulose could be dispersed in viscose under conditions where it could not be dispersed in dilute sodium hydroxide alone (270). Hydrolysis, saponification, and other side reactions (271, 272) also occurred leading to the formation of many inorganic sulphur salts. Klauditz (219) expressed these changes in terms of reactions analogous to equations 62 and 63 (p. 79) with the

former predominating with cellulose xanthate in media up to an aqueous alkali concentration of about 20% sodium hydroxide. Ripening is usually omitted in laboratory preparations, where secondary chemical changes are preferably kept at a minimum. In many cases however, a pure cellulose xanthate has been required in solid form, and has been obtained by precipitation of the xanthate from solution using methanol, ethanol, or alkali and ammonium salts (256, 273 - 279). Methanol precipitations produce a better physical form of product (216, 256, 273, 278), but chemically, ethanol seems superior because of its lower reactivity (274, 276, 278, 279)., particularly when followed by washing with dilute acetic acid in alcohol (274, 276) solution to remove residual alkali and other inorganic impurities. The xanthate groups are apparently quite stable to this treatment, since cellulose xanthic acid with a reported dissociation constant of 2.1 to 5.5 x 10^{-5} (277) is a stronger acid than acetic acid and other monocarboxylic acids of the fatty series. Sodium trithiocarbonate is immediately decomposed even by such weak acids,but the treatments should be brief and should be carried out at low temperatures. The hydrolytic action of methanol on the xanthate groups was recognized by Staudinger and coworkers (278, 279) and by Lauer and Pauer (256) who noticed reductions in the xanthate contents of samples when the precipitating and washing agent was methanol. These reductions were absent or negligible with ethanol.

Under the usual conditions of laboratory and commercial xanthation, the average degree of xanthation is only of the order of one xanthate group per two anhydroglucose units. Higher degrees of

substitution have been obtained, but only after prolonged treatment under special conditions. The use of tetraalkylammonium hydroxides (251, 252) and of metallic sodium in liquid ammonia (168, 253) in the preparation of cellulose trixanthate has already been mentioned. Geiger and Weiss (265) reviewed the subject of perxanthation and were themselves able to obtain trisubstitution by reacting viscose with excess carbon disulphide. Cellulose xanthates of D.S. slightly higher than the initial values, were obtained by fractional precipitation from viscose (269), and as the N-diethylacetamide derivative (280, 281) from solutions of the latter. In their study, Chen, Montonna, and Grove (269) were able to demonstrate effectively the greater uniformity of distribution in ripened as compared to unripened cellulose xanthates. They also concluded that such uniformity was obtained at the expense of dexanthation, with little rexanthation of free hydroxyl groups.

The location of the xanthate groups on the anhydroglucose residues is of particular interest to the present study. Lieser (154, 282) attempted to decide this question by causing cellulose sodium xanthate to react with diazomethane, claiming that the O-methyl groups in the product originated through a quantitative reaction between the xanthate groups and the reagent. The diazomethane was supposed to leave the free hydroxyl groups unsubstituted, an unsatisfactory assumption in the light of findings by Reeves and Thompson (283), and by Sitch (284). Hydrolysis of the O-methylcellulose produced a very small yield (251) of 2-O-methyl-D-glucose on which Lieser based his earlier conclusion that the xanthate groups were preferentially

substituted in the 2 - position of the anhydroglucose unit. Partial methylation of cellulose has been shown (152, 153) to result in preferential substitution on the C2 carbon atom. Lieser later (183, 251, 285) amended his view and accepted a more random distribution of the xanthate groups. The cellulose xanthate - diazomethane reaction has been repeated with greater yields. Noguchi's (257) results indicated that the xanthate consisted of 2-xanthate and 2,6-dixanthate. Lauer (286) concluded that the heterogeneous xanthation of cellulose caused preferential substitution in the second position of the accessible glucose units, which amounted to about 50% of the total, and thereafter, preferentially in position three of the same units. Chen and his collaborators (269) obtained results suggestive of a random and uniform distribution. No sulphur analyses of the methylated products obtained in the above studies were reported.

Kuriyama and his colleagues (287, 288) investigated the conversion of purified cellulose xanthate to O-methylcellulose by nitrosomethylurea, nitrosomethylurethane, and diazomethane. Both the first and the last reagents were found to cause excessive methylation especially in the presence of alkali. Concentrated solutions of diazomethane also resulted in excessive methylation. Only nitrosomethylurethane resulted in a methoxyl substitution equivalent to the number of xanthate groups in the original cellulose xanthate. Once again, sulphur analyses of the products were not reported. Vincent (216) attempted to repeat the reaction with octadecyl sodium xanthate and benzyl potassium xanthate, but the only products were the xanthate methyl esters which formed almost quantitatively in the former case. No valid

conclusion about the distribution of xanthate groups in cellulose xanthate can therefore be made from the results of the diazomethane reaction.

The problem of the xanthate group distribution has been approached in other ways. Thus Lauer and his coworkers (289) in an earlier paper, assumed the xanthation of cellulose to be analogous to the condensation between cellulose and ethylene oxide. On this basis, the reactivity of the different kinds of hydroxyl groups in the glucose residues of cellulose was in the order C2 > C6 > C3. No experimental evidence was presented for this assumption. Matthes (290) suggested that the secondary hydroxyl groups probably reacted initially, but that the final equilibrium favoured the primary hydroxyl positions. Much earlier, Rassow and co-authors (291) opined that the 6 - position was preferred, but offered no experimental support.

Vincent (216) noted the stability of simple xanthate methyl esters to acid hydrolysis with hydrochloric acid of various strengths, and tried to hydrolyse cellulose methylxanthate to the corresponding glucose derivatives. However, severe dexanthation occurred with the cellulose ester. The methylxanthate was also unstable towards thallous ethoxide, thus invalidating the method of methylating unxanthated hydroxyl groups with the aid of this reagent; and the Raney nickel reduction of octadecyl methyl xanthate yielded the alcohol instead of the methyl ether which was obtained when the corresponding dithioesters were similarly reduced (292, 293). When paper chromatography was used, the R_f value of glucose 3-methylxanthate in n-butanol saturated with water was determined by Sanyal (234) to be 0.65. Another spot, believed

to be a characteristic hydrolytic decomposition product of glucose 6-methylxanthate, corresponded to R_f 0.70, and hydrolysis of a cellulose methylxanthate yielded products of R_f values 0.55 and 0.70. Evidence was also presented to show that any methylxanthate present in either of the secondary positions would have been totally destroyed under the conditions of the hydrolysis. Another approach by Sanyal involved the acetylation of cellulose methylxanthate with acetic anhydride and pyridine, but attempted dexanthations of the fully substituted xanthate acetate with inorganic salts and by reductive methods were accompanied by some deacetylation. The acetylation of methylxanthates of methyl α-D-glucopyranoside had already been accomplished by Lieser and Leckzyck (181) and by Wolfrom and El-Taraboulsi (163).

The majority of the xanthate groups in partially-substituted cellulose xanthates might be expected to be in the second position in accordance with the greater reactivity of this group in cellulose and other carbohydrates to reaction with alkali hydroxides and alkoxides, and to subsequent etherifications of such products (152, 153, 161 - 167). Aleksandru and Rogovin (294) determined the number of free primary hydroxyl groups in two cellulose methylxanthates of D.S. 0.50 and 1.00 respectively, by a tritylation procedure, and found that in both cases 80% of the xanthate groups were substituted in the two secondary positions. However, their method of esterifying the xanthate groups with dimethyl sulphate probably introduced some methyl ether groups which could have lowered the trityl substitution. Freudenberg and Dietrich (188) claimed that cellulose 6-methylxanthate was formed by

the condensation with cellulose of methylxanthyl chloride in pyridine.

$$\text{CH}_2\text{OH} + \text{Cl}-\overset{\overset{\text{S}}{\|}}{\text{C}}-\text{SCH}_3 \xrightarrow{\text{C}_5\text{H}_5\text{N}} \text{CH}_2\text{O} \cdot \overset{\overset{\text{S}}{\|}}{\text{C}} \cdot \text{SCH}_3 \qquad (69)$$

The reaction occurred with primary alcohols and phenols only. Specifically substituted xanthate derivatives such as the above could help greatly in solving the problem of locating the xanthate groups. Hydrolytic and other reactions could well reveal marked differences in the behaviour of differently located groups, and such differences could then be utilized in subsequent studies of the distribution.

The general chemistry of the cellulose xanthates is similar to that of the simple xanthates, and most of the chemical research has concerned the derivatives resulting from the reaction of the sodium salt with active halogen and amino compounds (295). Much of this research has been covered and sometimes obscured in the patent literature. The number of patents by Lilienfield (e.g. 295, 296) is noteworthy, but papers may be found on compounds such as cellulose dixanthides (191, 297), xanthoacetates and xanthamides (298), and the N-diethylacetamide derivatives (280, 281, 299).

Some interesting results were obtained by Aleksandru and Rogovin (300) who investigated the stability of cellulose sodium xanthate, methylxanthate, xanthoacetic acid, and xanthamide to dilute sulphuric acid, dilute sodium hydroxide, water, and heat. As expected, the three esters were much more stable to these reagents than was the xanthate salt. The xanthamide, which approximated cel-

lulose acetate in its stability, was the most stable compound, followed by the xanthoacetic acid and the methylxanthate. However, they were able to prepare only the last derivative in a quantitative manner from the sodium xanthate.

The present research proposes to investigate further possibilities of dexanthating without deacetylating the cellulose S-methylxanthate acetate prepared according to Sanyal (234).

EXPERIMENTAL PROCEDURES

A. Analytical Methods

All analyses, with one or two exceptions, were performed in duplicate.

The sulphur contents of the sodium xanthates were determined by oxidation with hypobromite to sulphate ion as described in Doree's textbook (223), with subsequent gravimetric estimation as barium sulphate. This method was inapplicable to the S-methylxanthates (c.f. 216) where apparently only the thion sulphur could be converted to sulphate. Accordingly, the Carius (301), and later, the Parr bomb (302) oxidation procedures were used in these analyses.

Acetyl determinations were carried out according to Clark (303) by saponification of the sample in 1N ethanolic potassium hydroxide, acidification of the solution, and titration of the steam distillate with 0.02N barium hydroxide.

Attempts were made to determine the methylthio, $-SCH_3$ group in cellulose methylxanthates using the Peniston and Hibbert modification (115) of the Vieböch and Schwappach method for methoxyl groups. These attempts were unsuccessful even when they employed the constant-boiling hydriodic acid for unusually long periods.

B. Materials

1. Alkali Cellulose (c.f. 216, 234)

Dewaxed, air-dried (3.02% water) cotton linters, 45 gm., were mercerized by steeping in 1 litre of 18% aqueous sodium hydroxide at room temperature, 21°, for 3 hours. The alkali cellulose

was recovered on a coarse sintered-glass filter and pressed between filter papers to a weight of 167.4 gm. Pressed weight ratio (P.W.R.), 3.72. After shredding, the material was "aged" in a glass-stoppered jar for 62 hours.

2. Cellulose Sodium Xanthate (c.f. 216, 234)

A weight of aged, shredded alkali cellulose corresponding to 15 gm. of cotton linters was placed in a glass-stoppered jar which was partially evacuated by a water pump and was connected by means of a three-way stopcock to a graduated tube containing carbon disulphide. By placing the test tube in warm water and cooling the jar, carbon disulphide, 15 ml., was allowed to distil into the jar of alkali cellulose. The jar was then warmed very slightly above room temperature and nitrogen was admitted to bring the system to atmospheric pressure. After stoppering, the jar was kept for 6 hours in a room at 26°, but was shaken frequently and vigorously. The dark orange granules of impure cellulose sodium xanthate were dissolved in 200 ml. of ice-cold 4% aqueous sodium hydroxide during approximately 2 hours. Three-fourths of the resulting viscose solution was diluted with an equal volume of ice-cold methanol and poured into 2.5 litres of vigorously stirred ice-cold methanol. After 30 minutes, there was a significant increase in the viscosity and small gelatinous particles could be observed in the liquid. After about one hour, the viscosity had apparently achieved a maximum value and stirring became difficult. During the next hour the viscosity of the solution fell slowly, and at the end of this time 500 ml. of acetone was added. The small gelatinous particles of

cellulose sodium xanthate were recovered with difficulty on two large, coarse sintered-glass filters. Washing was performed on the filters with cold methanol-acetone (1:1), and the product was then stirred for 10 minutes in 1 litre of cold 2% acetic acid in freshly distilled, anhydrous, diethyl ether. After recovery on filters, the xanthate was washed with cold methanol-acetone (1:1) until the washings were neutral to litmus, and solvent-exchanged with anhydrous peroxide-free diethyl ether. An analytical sample, 1.78 gm. when dried (corresponding to 1.43 gm. cellulose), was removed, and the remaining swollen, ether-soaked material was placed in a glass-stoppered jar for methylation. Calc. for cellulose sodium xanthate with 0.399 xanthate groups, S = 12.7%. Found: S = 12.7, 12.8%. Other cellulose xanthates prepared similarly had substitutions of 0.384 to 0.410. Slightly lower degrees of substitution were obtained when the xanthation reaction was conducted at 20°.

3. Cellulose S-Methylxanthate (c.f. 216, 234)

The above, swollen, ether-soaked cellulose sodium xanthate was stirred vigorously in about 300 ml. of ether in order to disperse the material as much as possible. Colourless, redistilled methyl iodide, 60 ml., was then added and the stoppered jar was allowed to stand in the dark at room temperature for 67 hours. The white material was solvent-exchanged by washing with, and stirring in, methanol and was then washed with aqueous 50% methanol until the filtrate produced no precipitate with silver nitrate solution when by-product sodium iodide was completely removed. After rinsing on the filter with ether, the cellulose methylxanthate was air-dried and

then dried *in vacuo* over phosphorus pentoxide at room temperature. A weight of 10.6 gm., corresponding to a yield of 90.9% based on 9.48 gm. of dry cellulose, was obtained. Calc. for cellulose S-methylxanthate with 0.414 methylxanthate groups, S = 13.3%. Found: S = 13.2, 13.4%.

4. Cellulose S-Methylxanthate Acetate (c.f. 234)

Cellulose S-methylxanthate (D.S., 0.413), 10 gm., was placed in a one litre three-necked flask equipped with a reflux condenser and a mechanical stirrer with mercury seal. Acetic anhydride, 150 ml., and pyridine, 240 ml., were added, and the flask was heated on the steam bath with stirring. Pronounced swelling of the methylxanthate occurred within 5 to 10 minutes when the temperature was about 80°, and this swelling increased until after about 20 minutes a highly viscous gel formed. Subsequent stirring was therefore difficult. During the next hour, a red-brown colour developed and the viscosity of the gel began to decrease. After 12 hours, when the viscosity had fallen markedly, 100 ml. of acetic anhydride and 160 ml. of pyridine were added. The reaction was continued on the steam bath with stirring for another 12 hours. An "extra-coarse" sintered-glass funnel was used to remove a few swollen lumps which remained undissolved. Acetone was used to rinse the filter and the product was precipitated by pouring the dark brown reaction mixture slowly into 3 litres of vigorously stirred ice-cold water. The short brown-grey fibres were washed with cold water and alcohol, and were dried for one hour in a vacuum oven at 50°. The material was then redissolved in acetone and reprecipitated into

ethanol. Drying in vacuo over phosphorus pentoxide afforded 14.6 gm. of O-acetylcellulose S-methylxanthate corresponding to a 94.3% yield on the basis of the sulphur and acetyl analyses. Calc. for cellulose S-methylxanthate acetate with 0.410 methylxanthate and 2.61 acetate groups per anhydroglucose unit, S = 8.51%; CH_3CO = 36.4%. Found: S = 8.50, 8.51%; CH_3CO = 36.3, 36.5%.

Attempts to conduct the acetylation at 67° instead of at 98° led to only a low degree of acetylation even after 9 hours, and the reaction was completed on the steam bath as above. Under such conditions, a cellulose methylxanthate with 0.335 methylxanthate groups was converted to an acetate whose analysis indicated the presence of 0.348 methylxanthate and 2.66 O-acetyl groups. When 10 gm. of a cellulose methylxanthate (D.S., 0.413) was reacted with 180 ml. of acetic anhydride and 280 ml. pyridine for 7 hours on the steam bath, a product analysing for 0.405 methylxanthate and 2.54 acetate groups was obtained. Another similar treatment yielded the fully substituted derivative.

5. Preparation of Chlorine Dioxide

The procedure of Heuser and coworkers (304, 305), as described by Doree (306), was used with little modification.

A mixture of 120 gm. of potassium chlorate and 100 gm. of crystalline oxalic acid dihydrate was placed in a one litre flask, and a cold solution of 60 ml. of sulphuric acid in 200 ml. of water was carefully added. The flask was then heated in a water bath whose temperature was rigidly controlled between 50° and 60° by means of a thermostatted electric heater. The gas evolved was washed with

strong aqueous sodium chlorite to replace any chlorine formed with chlorine dioxide (307), and was absorbed in 750 ml. of water contained in a flask immersed in an ice bath. The reaction was carried out in the dark and behind an explosion screen for 9 hours. A solution analysing iodometrically (308) for 3.2N (4.4%) chlorine dioxide was produced. The chlorine dioxide-acetic acid reagent used in some of the experiments was made by diluting this solution with an equal volume of glacial acetic acid. A saturated 1.3N solution of chlorine dioxide in 50% acetic acid was thus prepared (c.f. 309). Both solutions were stored in the dark at 5°, and gave negative silver nitrate tests for chloride ion even after long standing.

6. Sodium Chlorite

An analytical grade sodium chlorite of purity greater than 99%, manufactured by the Mathieson Alkali Works, was used. It was normally employed in the form of a 10% aqueous solution. This solution was quite stable and gave a negative test for chloride ion even after long standing at room temperature in a dark brown bottle.

C. Precipitation of Cellulose Sodium Xanthate from Viscose Solution into Methanol-Acetone-Isopropanol

The remaining one-quarter portion of the above viscose solution (see section B2) was quickly diluted with an equal volume of methanol and carefully poured in a slow thin stream into 1700 ml. of vigorously stirred methanol-acetone-isopropanol (1:1:1) precooled below 0°. The swollen, precipitated sodium xanthate was hardened

by standing in cold acetone, and was washed twice with cold methanol-acetone (1:1). After stirring vigorously for 10 minutes in 500 ml. of cold 2% acetic acid in anhydrous diethyl ether, the xanthate particles were washed with cold methanol-acetone until the washings were no longer acid to wet litmus paper. This treatment was followed by solvent exchange to anhydrous diethyl ether, recovery by filtration, and removal of a sample for analysis. Calc. for cellulose sodium xanthate with 0.247 xanthate groups, S = 8.50%. Found: S = 8.41, 8.60%.

Methylation of the sodium salt was performed as described above (section B3) using 20 ml. of methyl iodide. Calc. for cellulose S-methylxanthate with 0.279 methylxanthate groups, S = 9.56%. Found: S = 9.48, 9.64%.

D. Dexanthations of Cellulose S-Methylxanthates with Mercuric Acetate in Acetic Acid

1. Cellulose S-Methylxanthate

Cellulose S-methylxanthate (D.S., 0.335), 0.5 gm., was heated under reflux with a solution of 2 gm. of mercuric acetate in 50 ml. of glacial acetic acid. After some minutes, the fibrous cellulose ester blackened, but reverted to its white colour in a few hours. At the end of 12 hours the material was recovered on a filter and washed with water, but during this operation, the black colour returned to a large portion of the fibre mass. Though some sections still remained white, the experiment was terminated at this point.

2. Cellulose S-Methylxanthate Acetate

Cellulose S-methylxanthate acetate containing 0.410 methylxanthate and 2.61 O-acetyl groups, 0.5 gm., was dissolved in a solution of 0.5 gm. of mercuric acetate in 50 ml. of 97% acetic acid. A white precipitate formed when the solution was brought to a boil, but after heating under reflux for a few minutes, the colour of the precipitate changed to bright orange. Heating under reflux was continued for 30 minutes, and the mixture was then kept at 60° for 14 hours. The precipitate was separated at the centrifuge and washed with a small amount of acetic acid. Evaporation of the clear solution to about 20 ml. and precipitation in ice-cold water yielded short, cream-coloured fibres which were washed thoroughly with water and ethanol and finally rinsed with ether. Drying was performed *in vacuo* at 35° over phosphorus pentoxide, and yielded 0.45 gm. of product. Calc. for cellulose S-methylxanthate acetate with 0.179 methylxanthate and 2.30 O-acetyl groups, S = 4.18%; CH_3CO = 36.0%. Found: S = 4.18, 4.18%; CH_3CO = 36.0, 36.1%.

E. Dexanthation of Cellulose S-Methylxanthate with Aqueous Chlorine Dioxide

Thirty millilitres of a 1.3N solution of chlorine dioxide in 50% acetic acid, containing 0.5 gm. of crystalline sodium acetate, was added to 1.0 gm. of cellulose methylxanthate. A vigorous, exothermic reaction ensued, and the reaction mixture was kept stirred for 24 hours at room temperature. The fibres were separated on a filter and washed well with water and alcohol. Drying *in vacuo* at room temperature over phosphorus pentoxide yielded 0.85 gm. of a very

white fibrous product. Calc. for cellulose methylxanthate with 0.020 methylxanthate groups, S = 0.782%. Found: S = 0.735, 0.822%.

Six accurately weighed 0.2 gm. samples of cellulose S-methylxanthate (D.S. = 0.335; methylxanthate equivalent = 574.1 gm.) were placed in glass-stoppered flasks, and a 2 ml. aliquot of a buffer solution 1M with respect to both sodium acetate and acetic acid was added to each flask. The flasks were placed in a water bath at 20°, and a 25 ml. aliquot of 0.1N (0.02M) aqueous chlorine dioxide was added with shaking to each at intervals accurately noted on a stopwatch. After reaction times of 0.25, 0.50, 1.0, 3.0, and 5.0 hours, excess potassium iodide and acetic acid were added to five of the flasks and they were each titrated in turn against 0.05N sodium thiosulphate. A further 10 ml. aliquot of 0.1N chlorine dioxide was added to the remaining flask and the unreacted reagent in the flask at the end of 20 hours was determined iodometrically. The results are listed in Table V and represented graphically in Figure I.

TABLE V

The Reaction of Cellulose S-Methylxanthate with Aqueous Chlorine Dioxide

Sample Weight in Gms.	Time in Hours	Chlorine Dioxide Reacted: Equiv. Vol. 0.05146N Thiosulphate	Chlorine Dioxide Reacted: Moles per Methylxanthate Equiv. (a)
0.2227	0.25	39.0	1.03
0.2252	0.50	46.9	1.23
0.2132	1.0	42.2	1.17
0.2217	3.0	47.6	1.27
0.2273	5.0	54.3	1.41
0.1838	20.0	63.4	2.04

(a) One molecular weight of the group $-CSSCH_3$ was present in a sample weight of 574.1 gm. (D.S., 0.335)

F. Dexanthation of Cellulose S-Methylxanthate with Aqueous Sodium Chlorite

Cellulose methylxanthate (D.S., 0.335), 0.5 gm., was immersed in a solution of one gram of crystalline sodium acetate and 2 ml. of 3N acetic acid in 25 ml. of water. Stirring was begun and 5 ml. of 10% sodium chlorite solution was added. A vigorous exothermic reaction similar to that with chlorine dioxide occurred, the solution becoming deep yellow-green, with bubbles of a gas which was apparently chlorine dioxide being evolved. The reaction mixture was stirred for 10 hours at room temperature, and 0.42 gm. of a very white product was isolated as described in section E. Calc. for cellulose methylxanthate with

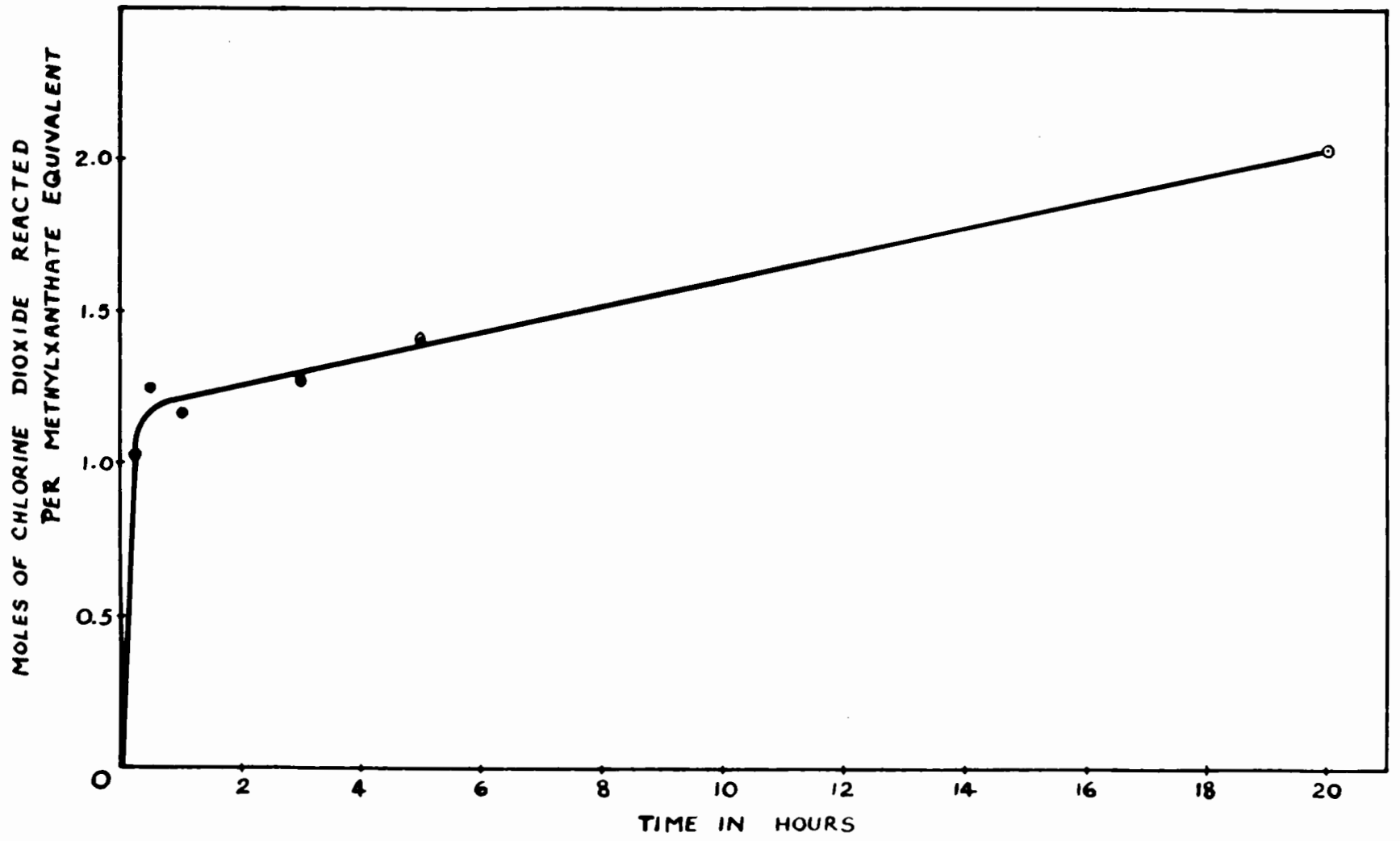


FIG. I. THE REACTION OF CELLULOSE S-METHYLXANTHATE WITH AQUEOUS CHLORINE DIOXIDE.

0.031 methylxanthate groups, S = 1.21%. Found: S = 1.15, 1.28%. When the 3N acetic acid was replaced with 5 ml. of the glacial acid, a product with 0.670% sulphur corresponding to 0.017 methylxanthate groups, was obtained. In this case, however, the filtrate from the reaction mixture was saved, and its sulphate content was determined by precipitation with barium chloride. Based on the weight of the starting material, which contained 11.2% sulphur, a sulphate sulphur content of 6.47% was found in the residual liquor.

G. The Action of Sodium Chlorite on Cellulose S-Methylxanthate Acetate

1. Experiments on Dexanthation

Cellulose methylxanthate acetate, containing 0.348 methylxanthate and 2.66 O-acetyl groups, 1.0 gm., was dissolved in 75 ml. of acetone. Fifteen millilitres of acetic acid were added, followed by the slow addition of 5 ml. of 10% sodium chlorite with vigorous stirring. A small amount of inorganic material was precipitated; the solution became cloudy and also yellow-green, while its temperature increased slightly. After 3 hours at room temperature, the solution was poured into an excess of water, and the precipitate was removed by centrifuging. Washing with water and alcohol followed. Drying in vacuo at 40° over phosphorus pentoxide yielded 0.89 gm. of short, very white fibres. Calc. for cellulose methylxanthate acetate with 0.106 methylxanthate and 2.46 acetate groups, S = 2.47%; CH_3CO = 38.5%. Found: S = 2.48, 2.48%; CH_3CO = 38.5, 38.5%. Precipitation of the above material into ethanol from acetone solution yielded very fluffy white fibres.

Calc. for cellulose methylxanthate acetate with 0.102 methylxanthate and 2.45 acetate groups, S = 2.38%; CH_3CO = 38.4%. Found: S = 2.39%; CH_3CO = 38.3, 38.5%.

A portion of the reprecipitated material was dissolved in acetone-acetic acid (5:1) and treated once more with aqueous sodium chlorite in the way described. Calc. for cellulose methylxanthate acetate with 0.095 methylxanthate and 2.48 O-acetyl groups, S = 2.22%; CH_3CO = 38.8%. Found: S = 2.20, 2.21%; CH_3CO = 38.5, 39.1%. Table VI contains the most significant results obtained in approximately 20 such dexanthations. The starting material contained 0.410 methylxanthate groups (S = 8.51%) and 2.61 O-acetyl groups (CH_3CO = 36.4%).

2. Effect of the Solvent on Cellulose S-Methylxanthate Acetate

Experiments were conducted to determine whether the solvent alone contributed to the deacetylation which occurred in the above dexanthations. Accordingly, the same procedure used in section G1 was applied with the omission of the sodium chlorite solution and its replacement with an equal volume of water. In two such experiments the starting material was recovered unchanged.

TABLE VI

Dexanthations of Cellulose

S-Methylxanthate Acetate with Sodium Chlorite

Experiment	% S	Methylxanthate D.S.	% CH_3CO	O-Acetyl D.S.
Starting Material	8.51	0.410	36.4	2.61
1 (a)	2.89	0.123	37.3	2.36
2 (b)	2.56	0.109	37.7	2.38
3 (c)	3.02	0.128	37.2	2.35
4 (d)	2.64	-	-	-
5 (e)	-	-	37.2	-
6 (f)	0.52	0.021	37.3	2.24
7 (g)	0.49	-	33.5 (h)	-

(a) A reaction time of 15 minutes was employed. Subsequent experiments were conducted for one hour.

(b) Sulphate sulphur content of the solution after reaction was 3.95% based on the weight of starting material.

(c) Acetic acid concentration lowered so that acetone-acetic acid ratio (v/v) = 40:1.

(d) Retreatment of the product of experiment 3.

(e) Acetic acid replaced by buffer solution 1M with respect to both acetic acid and sodium acetate.

(f) Acetic acid concentration increased so that acetone-acetic acid ratio (v/v) = 1:6.

(g) Reaction conducted in aqueous 90% acetic acid.

(h) This value believed to be lower than the time figure. Wide variation occurred in check determinations and the material showed signs of some inaccessibility to the saponifying reagents.

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3. Acetylation of the Dexanthated Product

The product of experiment 3 in Table VI, which contained 3.02% sulphur and 37.2% acetyl (substitutions: methylxanthate = 0.128; O-acetyl = 2.35), was reacetylated according to the procedure described in section B4. Calc. for cellulose methylxanthate acetate with 0.093 methylxanthate and 2.75 acetate groups, S = 2.08%; CH_3CO = 41.4%. Found: S = 2.03, 2.14%; CH_3CO = 41.3, 41.5%.

H. Dexanthations of n-Octadecyl and L-Menthyl S-Methylxanthates with Sodium Chlorite

n-Octadecyl (Stearyl) S-Methylxanthate, 0.3 gm., was dissolved in 50 ml. of acetone and 5 ml. of glacial acetic acid. Five millilitres of 10% aqueous sodium chlorite was added and the reaction mixture was stirred for 3 hours at room temperature. The solution was concentrated to small volume at 35° under reduced pressure, and the residue was extracted with ether. Evaporation of the ether yielded 0.25 gm. of a light cream-coloured wax. Theoretical yield of n-octadecanol, 0.225 gm. The product was partially purified by chilling its alcohol solutions, but subsequent

analysis revealed a sulphur content of 4.16%. Further purification was difficult and unsatisfactory. No crystalline derivative could be isolated when 0.05 gm. of the material, 0.1 gm. of 2,4-dinitrophenylhydrazine and 5 ml. of alcohol were heated in the presence of 0.1 ml. of concentrated hydrochloric acid, and allowed to cool to room temperature (310). Dilution of the reaction mixture with water and further heating also proved unsuccessful. This failure to obtain a hydrazone indicated the absence of carbonyl compounds in the product.

One-hundred milligram samples of n-octadecyl and L-menthyl S-Methylxanthates were weighed accurately and dissolved in mixtures of 25 ml. of acetone and 5 ml. of acetic acid contained in 100 ml. glass-stoppered flasks. From a 10 ml. burette, a 1% (w/v) (approximately 0.1N) solution of sodium chlorite was carefully added to the solution in the flask until a faint, permanent yellow colour was obtained. Ten millilitres of 2% potassium iodide was added to each solution and the liberated iodine was titrated with 0.05N sodium thiosulphate. It was customary to add a few ml. of 10% sulphuric acid to the solution near the end of the titration. Blank determinations were performed using 25 ml. of acetone, 5 ml. of acetic acid, and an exact 5 ml. aliquot of sodium chlorite. One mole of sodium chlorite (4 iodometric equivalents) was found to be completely reduced by 3.40 moles of n-octadecyl S-methylxanthate, and by 2.99 and 3.24 moles of L-menthyl S-methylxanthate.

DISCUSSION OF RESULTS

During the preparation of the cellulose sodium xanthate, difficulties were experienced in obtaining a "neutral" xanthate of substitution greater than 0.4, but were overcome by increasing the xanthation temperature from 20° to 26°. When the viscose solution was poured into methanol, the solution first formed deposited a quantitative or almost quantitative yield of cellulose sodium xanthate after standing for some time. However, when precipitation media containing large quantities of isopropanol or acetone were used, immediate precipitation of the xanthate salt occurred. In one such experiment, the sodium salt obtained by the former technique contained 0.399 xanthate groups while the product of the latter technique, prepared from the same viscose solution, contained 0.247 xanthate groups. Since little further xanthation would be expected to occur in the methanol solution, these results indicated greater hydrolysis of the xanthate groups in the latter case by the dilute acetic acid used in the purification procedure. The stability of the material precipitated from methanol solution could then be explained on the basis of transesterification of the xanthate groups to more stable positions. Further evidence for transesterification included the chance observation that samples of cellulose xanthate, suddenly precipitated into methanol-isopropanol (1:1), showed much less stability on standing than did similarly treated samples which had been allowed to precipitate from solution in methanol alone.

The happy conclusion of the problem of locating the xanthate groups in such products depended, firstly, on the corroboration of Sanyal's observation (234) that cellulose S-methylxanthate could be converted to an S-methylxanthate acetate which accurately reflected the original xanthate substitution; and secondly, on the ability to dexanthate the resulting acetate without incurring any loss or migration of acetate groups. The first condition was satisfactorily fulfilled by the results shown in Table VII. The differences in the sodium xanthate and methylxanthate substitutions were probably due to water soluble impurities present in the sodium salt which were removed when the S-methylester was washed with water to remove by-product sodium iodide. Deviations in the methylxanthate substitutions of the ester and its derived acetate from the calculated total of 3.0 seemed to be apparently within the analytical error.

TABLE VII

Number of Substituent Groups (a) in Cellulose Xanthate and its Derivatives

Sodium Salt	Methyl Ester	Acetylated Methyl Ester		
		Methylxanthate	O-Acetyl	Total
0.399	0.414	-	-	-
0.247	0.289	-	-	-
0.391	0.413	0.410	2.61	3.02
		0.408	2.61	3.02
0.336	0.335	0.348	2.66	3.01

(a) Per anhydroglucose unit

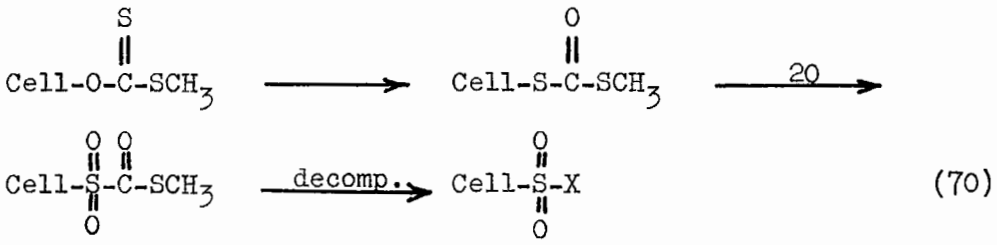
The second desideratum was not attained, and complete desulphurization was never achieved. Attempted dexanthations of cellulose S-methylxanthate and its acetate with mercuric acetate in acetic acid resulted in incomplete dexanthations with a residual sulphur content of 4.18% in the case of the acetate. If the sulphur remained as S-methylxanthate groups, then, on the basis of the analyses, deacetylation had also occurred. Since Sanyal (234) obtained similar results with other heavy metal salts, as well as when Raney nickel was used in the dexanthations, a search was initiated for new desulphurizing agents.

The literature contained some isolated references (311 - 317) to the reaction of sulphur, mercaptans, and other thio groups with chlorine dioxide and sodium chlorite. Furthermore, patent protection (318) was obtained for a process purporting to lower the residual sulphur content of cellulose regenerated from the xanthate from 0.4% to 0.006% by treatment with dilute chlorite solutions. It was therefore decided to investigate the reaction of the methylxanthate group with chlorine dioxide and with sodium chlorite in the anticipation that complete dexanthation might result under conditions known to be inert toward cellulose (319 - 322) and also toward O-acetyl (312, 323) groups. A rapid exothermic reaction occurred when cellulose methylxanthate was subjected to the action of either reagent. Both reagents apparently produced identical products, but in the case of sodium chlorite the initially clear reacting solution quickly developed a yellow-green colour with the simultaneous evolution of a gas which was probably chlorine dioxide. Approximately

one mole of chlorine dioxide was reduced by each methylxanthate group (see Figure I), and the dexanthated products exhibited residual sulphur contents of about 1%.

When cellulose S-methylxanthate acetate was dexanthated with sodium chlorite in aqueous solution, the residual sulphur amounted to 2 - 3% except when the reaction was conducted in strong aqueous acetic acid; the residual sulphur content was then about 0.5%. the oxidation potential of sodium chlorite is known to increase with decreasing pH (320, 321, 324) thus providing a possible explanation for this effect. When the medium was principally acetone, an apparent loss of about 0.3 O-acetyl groups occurred, thus invalidating any usefulness of the dexanthations for structural studies. The deacetylation reached greater proportions in a more strongly acid medium, and in some of these cases, a product only partially soluble in acetone was obtained. The acetyl analyses then varied greatly and little concordance could be obtained between duplicate determinations. This observation suggested that deacetylation was not owing to simple hydrolysis, a conclusion which was verified by the replacement of the sodium chlorite reagent by water in two of the experiments. The starting material was recovered unchanged. Furthermore, no added loss of acetyl groups occurred on further treatment with the reagent. The deacetylation mechanism was therefore closely related to that of dexanthation, suggesting the possibility of some interaction such as cyclization between suitably situated methylxanthate and acetyl groups.

The formation of a ring structure might also explain the sulphur residue in the dexanthated products. Four other possibilities were evident. The sulphur could have been present as methylxanthate groups which, because of inaccessibility or some similar phenomenon, exhibited a much lower reactivity than the other reacting groups. Unreactive contaminants such as dimethyl disulphide could have been present in the products. The dexanthation could have involved a rearrangement of certain xanthate groups to more stable units such as methylthio groups; and lastly, a few of the S-methylxanthate groups could have rearranged to dithiocarbonate followed by oxidation to sulphone groups.



(70)

where X = -H, $-CH_3$ or -Cl.

The second possibility, concerning the presence of stable xanthate groups, was unlikely, owing to the speed of the initial reaction, and also because the product was stable to any further action of the reagent. Sulphur-bearing contaminants would be expected to be soluble in either water or alcohol, but reprecipitations of the dexanthated material in either medium failed to lower the sulphur content in any way. The first, fourth and last possibilities seemed most probable. Methylthio groups could be formed if some

S-methylxanthate groups rearranged either spontaneously or during dexanthation to dithiocarbonate, Cell-$SCOSCH_3$ structures. The formation of hydroxyl groups in the dexanthation was demonstrated by the reacetylation of a product containing 37.2% acetyl and 3.02% sulphur to one containing 41.4% acetyl and 2.08% sulphur. These analyses represented an increase of 0.40 acetyl groups when the sulphur contents were treated as residual methylxanthate groups, and an increase of 0.41 if the sulphur occurred as methylthio groups. Table VIII contains the sulphur and acetyl contents of the products mentioned in the Experimental Section recalculated to methylthio and O-acetyl substitutions. This recalculation threw no light on any possible correlation between the losses of xanthate and ester groups. Oxidized sulphur atoms were, for the most part, converted to sulphate ions, although a complete sulphur balance was not attained. Other oxidized states of sulphur might have remained attached to the product, although these would be present only in minor amounts.

Sodium chlorite rapidly dexanthated both n-octadecyl and L-menthyl S-methylxanthates, about 3 moles of oxidant being reduced by each mole of xanthate. The product from n-octadecyl methylxanthate contained 4.16% of sulphur after being frozen out of alcohol solution in an attempt to remove fragmentary impurities such as dimethyl disulphide. This sulphur content corresponded to a mixture of 39% of thiomethyloctadecane and 61% of n-octadecanol. It was therefore apparent that there was very little difference in the reactions of primary and secondary xanthate ester groups with sodium

chlorite, and that complete desulphurization was difficult even with these simple esters.

TABLE VIII

Recalculation of Sulphur Contents to Methylthio Substitutions

% S	% CH_3CO	Methylxanthate D.S.	Acetyl D.S.	Methylthio D.S.	Acetyl D.S.
0.785	-	0.020	-	0.040	-
1.21	-	0.031	-	0.062	-
0.670	-	0.017	-	0.034	-
2.39	38.4	0.102	2.45	0.201	2.40
2.20	38.8	0.095	2.48	0.185	2.43
2.89	37.3	0.123	2.36	0.240	2.31
2.56	37.7	0.109	2.38	0.213	2.34
3.02	37.2	0.128	2.35	0.251	2.30
0.52	37.3	0.021	2.24	0.042	2.23
2.08	41.4	0.093	2.75	0.183	2.71

Although the reactions of sodium chlorite and chlorine dioxide with methylxanthate groups did not attain the success expected, it is possible that these reagents will yet find a place in synthetic organic chemistry through the proper application of their desulphurizing abilities.

Rapid and efficient methylation of mono- and oligosaccharides has been accomplished recently by the writer (325) using dimethyl

sulphate and solid pulverized sodium hydroxide in pure anhydrous tetrahydrofuran. The method has been extended to the polysaccharide field (326, 327). Since the methylation is carried out under anhydrous conditions, the possibility exists that the free hydroxyl groups of cellulose S-methylxanthate may be methylated without causing any loss of methylxanthate groups. If the solid alkali did react with the methylxanthate groups, it could be replaced with a sodium dispersion. Dexanthation might then be accomplished more easily and more drastic reagents could be employed in this stage without fear of causing demethylation. A study of the resulting partly methylated cellulose would reveal the positions from which xanthate groups had been removed. The method awaits experimental evaluation.

SUMMARY

Part I The Assignment of Structure to Cellulose 3,6-Dinitrate

Cellulose trinitrate, containing 2.88 nitrate groups per anhydroglucose unit and with a degree of polymerization (D.P.) of 1640, was partially denitrated with hydroxylamine in pyridine in the manner of Segall and Purves (107). The product was a 99% yield of a cellulose dinitrate with a degree of substitution (D.S.) of 1.72 and an apparent D.P. of 119. The latter result was shown to be in error, the true value being somewhat higher. Methylation of the cellulose dinitrate with dimethyl sulphate and alkali yielded 95% of Segall's mono-O-methylcellulose dinitrate with methoxyl and nitrate substitutions of 1.22 and 1.70 respectively, and an intrinsic viscosity in ethyl acetate of 0.238.

Although reductions of the methylated dinitrate with ammonium hydrosulphide in aqueous acetone were for the most part without success, the use of aqueous dioxane with a large excess of the reagent produced a 90.8% yield of a mono-O-methylcellulose containing 1.12 methoxyl groups per anhydroglucose unit. The intrinsic viscosity of this material in cupriethylenediamine was 0.210 and degradation during this, the first successful reduction of the methylated cellulose dinitrate on record appeared to be minor. Acid hydrolysis of this material afforded an 89% yield of partially methylated glucoses which were separated into a mono-O-methylglucose and two di-O-methylglucoses by partition chromatography on a cellulose column, using water-saturated methyl ethyl ketone-

ethanol (4:1) as the eluant. The mono-O-methylglucose, which occurred as 84% of the sugar syrup, crystallized and was positively identified as 2-O-methyl-β-D-glucose by means of its melting point, mutarotation, the melting point of its phenylhydrazone, and the preparation from it of glucose phenylosazone and the corresponding osatriazole. The di-O-methylglucose of lower R_f value, amounting to 11.3% of the original sugar syrup, was identified as 2,3-di-O-methyl-D-glucose by means of its crystalline anilide. The remaining di-O-methylglucose was not positively identified but was believed to be the 2,6-derivative. These results indicated that the action of hydroxylamine-pyridine on cellulose trinitrate was to effect a quantitative or nearly quantitative removal of the nitrate group in the second position of the anhydroglucose monomer with the consequent formation of cellulose 3,6-dinitrate.

Part II An Attempt to Locate the Xanthate Groups in Partially Xanthated Cellulose

Cellulose sodium xanthate, prepared from cotton linters in the usual manner, was converted to the methyl ester with methyl iodide in ether, and then acetylated according to Sanyal (234) with acetic anhydride and pyridine. A completely substituted cellulose S-methylxanthate acetate resulted, the xanthate substitutions remaining nearly constant throughout these manipulations. The purpose of this investigation was to remove the S-methylxanthate groups without disturbing the acetate groups, to locate the latter

in the anhydroglucose units and thereby to infer the location of the former. Attempted dexanthations of the S-methylxanthate and its acetate with mercuric acetate in acetic acid resulted in incomplete reactions. When cellulose methylxanthate was oxidized with chlorine dioxide or sodium chlorite in the presence of acetic acid, vigorous and rapid exothermic reactions occurred, but the dexanthated products contained about 1% of residual sulphur of unknown character. This sulphur could not be removed by further treatment with these reagents. Each methylxanthate group was found to reduce approximately one mole of chlorine dioxide and about 3 moles of sodium chlorite. When the dexanthations with sodium chlorite were extended to samples of cellulose S-methylxanthate acetate in aqueous acetone solution, a sulphur content of 2 - 3% remained, but these figures could be lowered to about 0.5% by conducting the reaction in strong acetic acid. An accompanying loss of about 0.3 O-acetyl groups per glucose unit was incurred and rendered the proposed method of investigation impractical. Reacetylation introduced about 0.4 O-acetyl groups into the partly acetylated dexanthated material, but a completely substituted product was not obtained. Dexanthations of n-octadecyl and L-menthyl S-methylxanthates with sodium chlorite failed to reveal any difference in behaviour between the primary and secondary esters, and were also incomplete.

CLAIMS TO ORIGINAL RESEARCH

1. "Segall's cellulose dinitrate" was characterized and shown to consist almost entirely of cellulose 3,6-dinitrate.

2. Denitration of Segall's mono-O-methylcellulose dinitrate was successfully accomplished with the aid of ammonium hydrosulphide in aqueous dioxane. The reaction was shown to be unsuccessful when conducted in aqueous acetone.

3. A mono-O-methylcellulose, substituted almost entirely in the second position of the anhydroglucose units, and the product of the above denitration, was indisputably prepared for the first time.

4. Acid hydrolysis of the mono-O-methylcellulose described in (3) resulted in a novel preparation of 2-O-methyl-D-glucose from cellulose in an overall yield of 63% of the theoretical amount. The previous best yield of this sugar was 41% from monoacetoneglucose.

5. A chromatographic solvent consisting of 4 volumes of methyl ethyl ketone saturated with water and one volume of ethanol was found to improve separations on paper chromatograms of the mono-O-methylglucoses* particularly when traces of bases such as

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* Another good solvent for this purpose has been reported (328) since the completion of the experimental portion of this thesis.

ammonia and pyridine were included in the mixture. Preliminary identification of these sugars was thus enhanced. This solvent also facilitated preparative column chromatography, since it contained no high boiling components such as butanol and pyridine, and provided a rapid chromatographic rate.

6. Dexanthations of cellulose S-methylxanthates with mercuric acetate in acetic acid at slightly elevated temperatures were shown to be incomplete.

7. The reactions of sodium chlorite and chlorine dioxide with S-methylxanthate groups were studied for the first time. The reactions were shown to be exceedingly rapid but to result in small residual sulphur contents in the dexanthated products. A loss of O-acetyl groups from cellulose S-methylxanthate acetate was incurred and could not be prevented.

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