A STUDY OF THE PERIODIC ACID OXIDATION OF CELLULOSE ACETATES OF LOW ACETYL CONTENT

By

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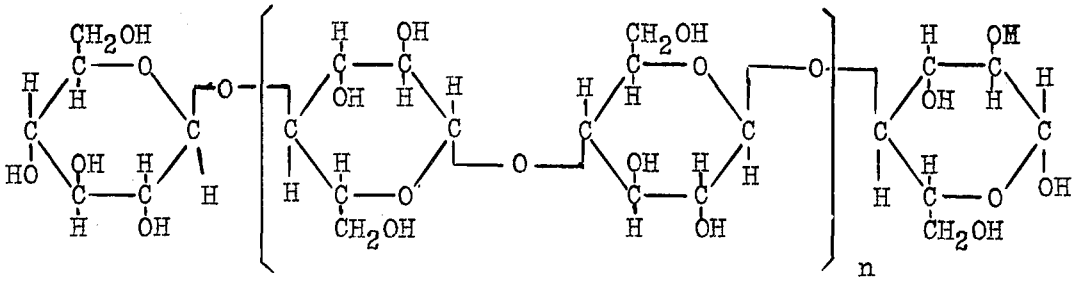
I INTRODUCTION

The Structure of Cellulose

During the past 50 years exhaustive investigations have been made in studying the structure of cellulose. These investigations have resulted in the following conclusion[27]: cellulose is a high-molecular-weight polymer composed of anhydroglucose units joined together by 1,4-glycosidic linkages. The simplest structural formula for cellulose may be shown as follows:



The chemical behavior of cellulose may be explained in terms of the reactions of the three hydroxyl groups in the anhydroglucose unit, and the sensitivity of the glycosidic linkage to cleavage by acids.

In the past 25 years physical chemists have investigated the manner in which the cellulose polymer is arranged in native cellulosic materials[27,61]. The theory of the micellar structure of cellulose may be briefly stated as follows: the cellulose polymer is arranged in parallel bundles of chains in the greater portion of a fiber, but these areas of high degree of orientation are disrupted at fairly well defined intervals with areas of relatively high disorder, i.e., random orientation of polymer chains. This theory is derived principally from X-ray studies of cellulosic fibers.

The Present Problem

There has been considerable argument among cellulose chemists regarding the course of the reactions by which various cellulose derivatives, such as esters and ethers, are prepared.

The purpose of this investigation was originally stated somewhat as follows:

"Prepare a series of cellulose acetates of low acetyl content and determine how the periodate oxidation of these preparations compares with that of the cellulose from which they were prepared. The comparison of the periodate consumption of a particular cellulose acetate with that of cellulose may lead to some conclusion regarding the average distribution of the acetyl substituents in this cellulose acetate. For example, if initial acetylation takes place at the primary hydroxyl group on carbon No. 6 of the anhydroglucose unit, then the periodate consumption of cellulose and a partially acetylated cellulose should be the same. However, if acetylation takes place at either of the secondary hydroxyl groups on carbons No. 2 or 3, the consumption of periodate by the cellulose acetate would be less than that of cellulose."

It was further suggested that conditions should be selected such that the rate of acetylation would be slow enough to permit the selective esterification (if any) of either primary or secondary hydroxyl groups.

During the course of this investigation a serious attempt was made to control all possible factors that might affect either the rate of acetylation of cellulose, or the subsequent periodate oxidation of cellulose and cellulose acetates of low acetyl content.

II GENERAL AND HISTORICAL

CELLULOSE ACETATE

The acetic acid ester of cellulose is today one of the most important of the plastic materials. The acetates have found use in filaments, films, molding powders, and lacquer resins. The turn of the twentieth century marked the beginning of the cellulose acetate industry, and since that time extensive research programs have been devoted to the study of these materials and to the improvement of acetate products.

The commonly used materials for the preparation of cellulose acetate are: a cellulosic raw material, an acetylating reagent, a starter or swelling agent, and some diluent or solvent. Cotton fibers or linters have been used most extensively as raw material, although purified wood celluloses are becoming more important in the modern industry.

The use of acetic anhydride as an acetylating agent is credited to Schützenberger[55], who in 1865 prepared a cellulose acetate by means of acetylation in a sealed tube at 140° C. for several hours. Present day knowledge indicates that this product must have been considerably degraded under these severe acetolytic conditions. Other acetylating agents have been used. Acetic acid is unsatisfactory and long refluxing produces only slight acetylation[41]. Acetyl chloride may be used if a base is present to react with the hydrogen chloride liberated, which otherwise might degrade the cellulose.

Whol[67] introduced the use of pyridine in conjunction with acetyl chloride. The gas ketene (CH_2CO) is mentioned as an acetylating agent in several patents[33,43,46].

Starters or swelling agents are used in the acetylating mixture to increase the rate of reaction. They are often called catalysts. The use of sulfuric acid was introduced by Franchimont[16] in 1879. He observed that the rate of acetylation was increased by the presence of this acid. Cross and Bevan[7] mention the use of such dehydrating salts as zinc chloride and sodium acetate. Hess[25] acetylated cotton with acetic anhydride in pyridine medium and in the absence of sulfuric acid. In this reaction pyridine functions as a swelling agent, and Hess noted that the rate of reaction under such conditions was considerably accelerated. Furthermore, in pyridine medium the extent of acid degradation is very much reduced. According to Krüger and coworkers,[36] perchloric acid ($HClO_4$) is far superior to any other catalyst, a very small concentration having a powerful effect. Even water may be regarded as a catalyst in this reaction. Elöd[10] found that very dry cellulose was acetylated with difficulty, but if the moisture content of the fibers were allowed to increase progressively, the reaction rate increased up to the point where water became a diluent, with added hydrolytic effect on acetic anhydride. The increased rate of acetylation, due to the presence of water in the cellulose structure, has been explained in terms of the swelling power of the water. The diffusion of the

acetylating mixture throughout the cellulose fibers is also facilitated by the presence of water.

Diluents or solvents that have been used in the preparation of cellulose acetates include glacial acetic acid, benzene, and pyridine. Acetic acid is a solvent for cellulose acetates, whereas benzene and pyridine are nonsolvents. When it is desired to preserve the fibrous structure of the original cellulose a nonsolvent medium is used. If glacial acetic acid medium is used, the end product is a clear viscous colloidal solution.

The properties of a cellulose acetate depend on the kind and quantity of reactants, the acetylation conditions, and the subsequent treatment of the product. In the usual acetylation in glacial acetic acid, a 2.5 to 4.0-fold excess of acetic anhydride, and about 2 to 5 percent of concentrated sulfuric acid are used. The amounts of acetic anhydride and sulfuric acid are based on the weight of cellulose. Reaction temperatures are controlled between 30 and 40° C., and complete acetylation is ordinarily achieved in about eight hours. Mechanical stirring facilitates the formation of a homogeneous reaction mixture. The acetate is recovered from the reaction mixture by first diluting with more acetic acid, and then pouring the liquid in a thin stream into a large amount of water. It is important that the aggregation of large lumps of acetate be prevented, as these will retain the acetylating reagents under surface films. The precipitate is worked mechanically and washed repeatedly with

water until free from acid and a final boiling with water helps to remove the last traces of sulfuric acid.

If benzene is used as a diluent, instead of acetic acid, the final product will be a fibrous mass similar in appearance to the starting cellulosic material. This reaction is more heterogeneous and generally requires a longer reaction time. Recovery of the acetate is made by filtration followed by thorough washing with water.

The stability of the final product is determined largely by the thoroughness of the washing operation. Sulfuric acid, in this case, reacts with cellulose to form mixed esters or sulfoacetates. Ost[47], who is responsible for much of the research dealing with the acetylation of cellulose, concludes that all acetate preparations retain some small percentage of combined sulfuric acid. To obtain a stable acetate this sulfate content must be removed or reduced to a minimum by boiling with water. A product which has not been stabilized tends to degrade slowly, becomes brittle, and develops an odor of acetic acid.

The degree of acetylation for any particular cellulose acetate may be determined by saponification with alcoholic alkali, and is expressed in terms of percent combined acetic acid or percent acetyl. These values may be used in a suitable equation (see page 28) to calculate the unit molecular weight of anhydroglucose acetate. A completely acetylated cellulose, the triacetate, would have a combined acetic acid content of 62.50%, or an acetyl content of 43.75%, and

a unit molecular weight of 288.25. Lower degrees of acetylation may be obtained by either reducing the amount of acetic anhydride available for reaction, or by allowing the reaction to proceed for a shorter length of time. A third alternative consists of adding acetic acid (approximately 50%) at the triacetate stage of a reaction mixture, and allowing this mixture to "ripen" for some time at a fixed temperature, usually not over 50° C. This process allows a limited amount of hydrolysis of the triacetate to take place, lowering the combined acetic acid content to between 50 and 57%. Miles[44], in patents obtained in 1903 and subsequent years, was the first to recognize the commercial possibilities of this technique. The partially hydrolyzed, so-called "secondary" acetate, was found to be soluble in acetone, a good, versatile and cheap solvent. The property of acetone solubility is associated with a certain limit in the amount of free hydroxyl groups present in the acetate. When the combined acetic acid content of an acetate falls below 50% or is above 57%, it is insoluble in acetone.

The strength and toughness, and in part the solubility of a cellulose acetate, is dependent upon its degree of polymerization (D.P.). The higher the D.P. of the original cellulose, the stronger and tougher the acetate product will be. Effort is always made to reduce the amount of degradation of the cellulose chain by means of improved reaction conditions and controls. Low reaction temperature, rapid acetylation, and stabilization of end products are important.

The average degree of polymerization and the molecular weight of cellulose acetates may be determined by viscosity methods. Viscosity and fluidity characteristics of cellulose acetates in solution are those of lyophilic colloids and are affected by such variables as concentration, temperature, solvent, instrument design, structure of polymer, and degree of association. The Ostwald type viscometer is commonly used, and the viscosity of a liquid is given by the equation: $\eta = Ktd$, where t is the time of flow of the liquid in the viscometer; d is the density of the liquid at some specific standard temperature, and K is a constant for the instrument. The Staudinger rule[58] states that the specific viscosity, ηsp, of a very dilute solution of polymer, is proportional to its molecular weight. The empirical relationship is written:

$$\frac{\eta r - 1}{C} = \frac{\eta sp}{C} = K_m M \ ,$$

where ηr is the ratio of the viscosity of the solution of linear polymer to that of the solvent; C is the molar concentration of the solution with respect to the structural unit of the polymer chain; M is the molecular weight; and K_m is a constant for the cellulose derivative in a specific solvent at specific temperature and pressure. The value of K_m must be calculated by substituting the value of the viscosity of a solution of cellulose acetate of known molecular weight in the equation. Osmotic pressure or ultracentrifuge methods are used as standards for the measurement of the molecular weight of high polymers.

Viscosities are measured for solutions having concentrations of the order of 0.002 to 0.005 molar. A common solvent used in cellulose acetate viscosity measurements is m-cresol[59]. Viscosity relationships are ideal only for very dilute solutions or at infinite dilution. For this reason it is customary to determine the viscosity of a series of dilute solutions of the same acetate. The value of $\eta sp/C$ is then plotted against the concentration, and the curve extrapolated to infinite dilution. The value of the specific viscosity at infinite dilution has been called the "intrinsic viscosity". The intrinsic viscosity is used in the Staudinger equation to calculate the molecular weight of a cellulose acetate. The degree of polymerization is obtained by dividing the molecular weight by the unit molecular weight (288) in the case of cellulose triacetate. Kraemer[35] has determined molecular weights as high as 250,000, and D.P. of 950 for cellulose acetates.

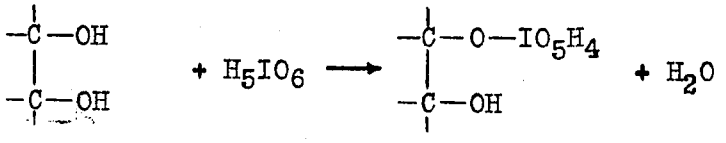
Cellulose acetates of high acetyl content are usually soluble in chloroform, halo-hydrocarbons, aromatic amines and phenols, aliphatic acids, and some esters, ketones, and alcohols. Ostwald and coworkers[48] have studied the solubility problem with respect to the molecular weight and degree of acetylation of cellulose acetate. They have classified solvents according to the dielectric function: μ^2/ϵ ; where μ is the dipole moment and ϵ is the dielectric constant. For liquids having solvent activity the function has a value between 0.251 and 0.528.

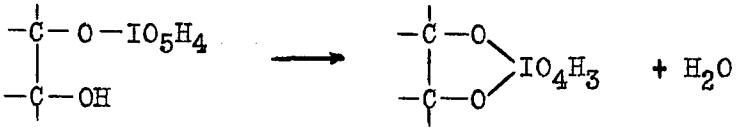
PERIODATE OXIDATION OF CELLULOSE

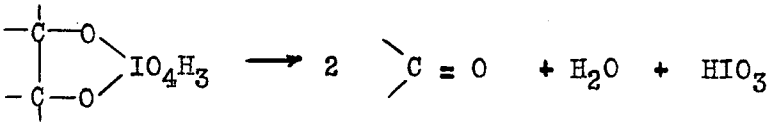
In recent years solutions of periodic acid and its alkali metal salts have been applied with considerable success to the analysis of 1,2-glycols in diverse fields of organic compounds[1]. The selective and quantitative aspects of the reaction have made it a valuable analytical and preparative tool, not only in applied but also in research chemistry.

The reaction was discovered in 1928 by Malaprade[39,40]. Fleury and coworkers[11-14] were responsible for investigating the scope of the periodate oxidation, and found that many 1,2-type oxygen and nitrogen functional groups were attacked. Thus 1,2-diol, α-hydroxy carbonyl, α-hydroxy amino, and diketo compounds are reactive. The present discussion will be confined to the periodate oxidation of the 1,2-diol or glycol groups in cellulose.

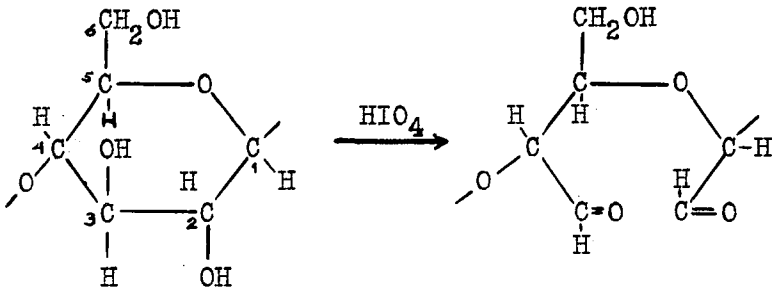
Criegee[6] has suggested the following mechanism for the oxidative cleavage of a 1,2-diol by periodic acid:

(a) 

(b) 

(c) 

Jackson and Hudson[30] applied the reaction to cellulose. The secondary hydroxyl groups in the 2 and 3 positions are oxidized to aldehyde groups, with cleavage of the carbon-carbon bond between them:



If cotton is oxidized with periodic acid, anhydroglucose rings will be opened at different points along the chain, and it will be seen that the polymer is no longer composed of successive anhydroglucose units, but at the points of oxidation, glyoxal and d-erythrose units will be present.

Since this type of oxidation produces new aldehyde groups, periodate oxycelluloses have a high reducing property. They are also sensitive to degradation by alkalies. These properties were demonstrated by Davidson[8] who made a thorough investigation of the action of periodic acid on cellulose. According to Davidson the oxidation causes a weakening of the glycosidic linkages, making a periodate oxycellulose very susceptible to alkaline degradation. Pacsu[50] has suggested that the glyoxal hemiacetal units may be enolized in basic medium, and that the degradation is due to an electrophilic attack by water on the hemiacetal bonds. Furthermore, a Cannizzarro type oxidation-reduction may occur between the aldehyde groups in basic medium.

Studies on the determination of aldehyde groups in periodate oxycellulose have been made by Harris and coworkers[53]. Mark and coworkers[19], Jayme[31], Head[22], and Timell[60] have also contributed to the knowledge of the periodic acid reaction on cellulose.

The experimental technique for oxidizing cellulose with periodic acid may be described briefly. A standard sample of cellulosic material is treated with an excess of a solution of periodic acid or its alkali metal salts. The concentration of the oxidizing solution is usually less than 0.1 molar. Buffer solutions may be added to maintain a standard pH, usually pH 4. Reaction temperatures of between 20 and 30° C. are convenient, and a standard temperature is maintained throughout the reaction by means of a thermostat. At the end of the reaction time, the cellulosic material is filtered off and washed, and the filtrate is analized for unreacted periodic acid. The amount of periodic acid consumed by a certain sample may be expressed in milliequivalents per gram, or perhaps more suitably in moles of periodic acid per unit molecular weight (anhydroglucose unit).

DISTRIBUTION OF HYDROXYL GROUPS IN CELLULOSE ACETATES

The art of preparing cellulose derivatives is still far ahead of the theory. Although research has been able to point the way in many cellulose problems, there remains much to be done to explain the specific mode of attack of esterifying and etherifying reagents on cellulose. Reaction kinetics fail in this field where reaction rates follow heterogeneous patterns and are usually associated with adsorption

and diffusion factors. The preparation of certain acetates with specific properties, for example that of acetone solubility, has added further interest to the investigation of the distribution of hydroxyl groups along the cellulose chain. Any reaction that has reproducible selectivity with respect to the hydroxyl groups of cellulose, and that does not destroy the substituents already present, might be of use in these studies.

Acetone soluble cellulose acetates have been investigated quite extensively. Sakurada and Kitabatake[54] condensed triphenylmethyl chloride with the acetate dissolved in pyridine. Assuming that this reagent reacts only with the free hydroxyl groups in the 6-position, they found that one-third of the total available hydroxyl groups were in this position. Purves and coworkers[4,5,17] have used p-toluenesulfonyl chloride (tosyl chloride). They observed that the hydroxyl group in the 6 position reacted with the reagent approximately twelve times as rapidly as those in the 2 and 3 positions. Furthermore, the tosylated acetate could be treated with sodium iodide in acetone to replace the tosyl group with an iodine atom. These experiments indicated that at least 35% and possibly 50% of the available free hydroxyl groups in these acetates were in the 6 position. In order to determine whether any glycol groups were present in acetone soluble acetates, a glycol oxidation with lead tetraacetate in glacial acetic acid was performed. This reagent acts in the same manner as periodic acid, cleaving the carbon-carbon bonds between adjacent hydroxyls and oxidizing them to aldehyde groups. Purves, using this method, could

account for only one glycol group for every 100 to 150 glucose residues.

Similar studies on the distribution of hydroxyl groups in cellulose ethers have been carried out[38]. Most recently periodic acid oxidation has been applied as a means of determining the glycol content of certain water soluble cellulose ethers[38,56,60].

III EXPERIMENTAL

PREPARATION OF CELLULOSE ACETATE

Materials

1. Cellulose: Kodak filter cotton, Eastman Kodak Co.
2. Acetic anhydride: C.P. grade.
3. Sulfuric acid: sp. gr. 1.84, 96.7%, C.P. grade.
4. Benzene: C.P. grade redistilled 79 to 81° C., dried and stored over sodium.
5. Washing solvents: benzene, technical grade, and 95% ethanol.
6. Water: laboratory distilled water.

All the chemicals used (above) conform with A. C. S. specifications.

Preparation of Standard Cellulose

Kodak filter cotton was found to be a high quality long fiber cotton of high purity and uniformity. The cotton was processed for experimental use as follows: 250 g. of cotton was placed in a 4-liter beaker and covered with 4 liters of water and allowed to stand in a hot room at 60° C. for 24 hours. The water was then squeezed out and the cotton covered with four liters of boiling water. When cool enough to work, the water was again squeezed out and the cotton was rinsed with another 4-liter portion of cold water. The thoroughly pressed cotton was then placed in a 2-liter beaker and covered with 2 liters of 95% ethanol and allowed to stand as

before at 60° C. for 24 hours. Rinsing with 4-liter portions of boiling and cold water was repeated. This treatment was considered sufficient to remove pectic materials and waxes from the cellulose fibers.

The purified cotton was pulled apart and dried for 24 hours at 60° C. Standard cellulose to be used for the preparation of cellulose acetate samples was dried in a vacuum oven at 60° for 24 hours and stored in a large desiccator over concentrated sulfuric acid. The moisture content of the vacuum dried cotton was determined by heating a 5 to 10-gram sample, contained in a 100-ml. weighing bottle, at 110° C. in a vacuum oven for 24 hours. Further heating did not reduce the weight. In all cases the moisture content of the vacuum dried cotton was found to be less than 1% by weight. For example, 5.9380 g. of this cotton lost 0.0469 g. by this treatment, and therefore contained about 0.8% moisture. Storage over concentrated sulfuric acid at room temperature was considered adequate to maintain, if not further reduce, the low moisture content of this standard cellulose.

Preparation of Cellulose Acetates of Low Acetyl Content

In this investigation it was desired to prepare a number of cellulose acetates of an acetyl content below 10%. This was accomplished by a method in which the acetylation reaction was interrupted. It was also desired that the acetylation reaction be slowed down somewhat, and that the fibrous nature of cellulose be retained.

Elöd[10] has shown that the rate of the reaction is decreased considerably when cotton of low moisture content is used. The proportions of the acetylating reagents and cellulose used in these preparations were established in a preliminary study[21].

The reaction mixture used for the preparation of all cellulose acetate samples was as follows: 10 ± 0.1 g. of vacuum-dried standard cellulose, moisture content <1%; 205 ml. of anhydrous benzene; 55 ml. of acetic anhydride; and 0.8 ml. of concentrated sulfuric acid. The following figures show the molar quantities of each component of the reaction mixture:

0.0617 mole of cellulose

2.305 mole of benzene

0.578 mole of acetic anhydride

0.0147 mole of sulfuric acid

The molar ratio in the same order would be: 1 : 37.33 : 9.37 : 0.238. The concentration of sulfuric acid would be 0.0563 M based on 260.8 ml. of acetylation medium.

Before starting the preparation of any cellulose acetate the proper quantities of benzene, acetic anhydride and sulfuric acid were mixed. Usually enough of this mixture was prepared to acetylate 5 samples of cellulose. This avoids small variations in the quantity of sulfuric acid used for each sample.

At zero reaction time 10 g. of vacuum-dried standard cellulose was rapidly weighed into a dry 400-ml. beaker and immediately covered

with 260.8 ml. of the acetylating mixture. Since small variations in the total amount of this mixture are not important, it was measured in a 500-ml. graduated cylinder. Air bubbles were removed from the cellulose mass by pressing with a glass rod. The beaker was covered with a watch glass and the reaction mixture was allowed to stand at room temperature for a length of time that varied with the degree of acetylation desired. It was found that during the first 5 minutes of the reaction, the temperature rose approximately 2° C. and then slowly came back to room temperature. The temperature of the reaction was recorded from time to time and did not vary after the first half hour of reaction time. Average temperatures ranged between 27 and 29° C.

At the end of the reaction time the cellulose acetate mass was transferred to a Buchner funnel-suction flask apparatus and pressed under suction with the bottom of a 250-ml. beaker. The mass was then returned to a 400-ml. beaker and washed with four 100-ml. portions of benzene and four 100-ml. portions of 95% ethanol, each washing being accompanied by agitation, and removal of the wash solvent by pressing under suction. At this point the acetate always tested acid to litmus. Water washings to remove all traces of acid were standardized as follows: two 4-liter washes with distilled water, the acetate mass being stirred in the second wash by means of an electric stirrer for 2 hours; one 2-liter rapid wash with dilute ammonia water (20 ml. of 14.7% NH_4OH in 2 liters of water); two 4-liter washes with water;

one 24 hour steep in one liter of water at 60° C.; and finally one wash with 4 liters of water. The acid-free cellulose acetate was air dried for 48 hours.

Conditioning and Cutting of Standard Cellulose and Cellulose Acetate.

The cellulose acetates and samples of standard cellulose were conditioned for several days in a desiccator containing 36% sulfuric acid in its well. The relative humidity of the atmosphere in this desiccator is approximately 65% at 25° C.[66]. The relative humidity in the laboratory also averaged about 65%. Conditioning at 65% relative humidity permitted handling and accurate weighing of acetate samples without too much danger of loss or gain in weight due to moisture transfer. The moisture content of conditioned samples was determined as described previously and was found to be about 5% for both cellulose and cellulose acetate samples. The weight of all samples of cellulose and cellulose acetate recorded in the data tables is the dry weight, i.e., the weight of the conditioned sample corrected for 5% moisture content.

In order to obtain a uniform sample suitable for oxidation studies, the long fibers were cut to 20-mesh linters. This was done in a Wiley mill, which cuts the fibers by means of rapidly spinning knives that pass by stationary cutting edges. A 20-mesh screen allows the desired size of linters to pass into a receiving jar. No heating effects were observed during the cutting procedure, and the cut ends of the linters were sharp and clean. The cut samples were stored in the conditioning desiccator at 65% relative humidity.

The Weighing of Linters

The method that was used to weigh cotton and cellulose acetate linters was kept standard throughout this investigation. Samples were weighed on an analytical balance to the nearest 0.1 milligram. The samples were weighed in a specially constructed weighing tube. This tube consisted of an outer jacket and a plunger. The outer jacket was made from a 1.5 x 9.5 cm. glass tube, which was fitted with a plunger which was a 1.2 x 9.5 cm. test tube. A pair of forceps was used to transfer the linters from a storage bottle to the cylinder tube which was held in a vertical position with one end against a piece of filter paper. The plunger was then used to compress the sample into a compact mass. The depth of this compressed sample was used to estimate the weight of linters present, and with a little practice, the desired weight could be judged quite easily. The sample could be ejected into the desired reaction flask by exerting pressure on the plunger. Adhering linters in the tube were dislodged by gently tapping the side of the flask with the tube and by manipulation of the plunger. Chamois finger protectors were used in handling the weighing tube. The weight of the sample was obtained by difference: the weight of the sample and tube minus the weight of the tube.

This method of weighing was found to be quite rapid. It prevented the very lightweight linters from escaping into the balance housing, and furthermore, protected the linters from excessive moisture transfer.

Analysis for Percentage of Combined Acetic Acid.

The alcoholic alkali saponification of Eberstadt[34] as modified by Howlet and Martin[29] was used to determine the combined acetic acid content of the cellulose acetate samples. The accuracy claimed for this method is ± 0.1% HOAc[18]. The concentrations of the reagents were modified slightly to add to the convenience of the analysis.

Standard potassium hydroxide solution, approximately 0.2 N (carbonate free) was prepared according to procedures used for the standardization of bases described by Willard and Furman[65]. Potassium acid phthalate was used as a primary standard, and phenolphthalein as an indicator of the equivalence point. Solutions of potassium hydroxide, approximately 0.5 N, and of sulfuric acid, approximately 0.6 N, were prepared and the concentrations checked by reference to the standard 0.2 N KOH, but it was not required that the concentration of these solutions be known, except for planning the proportions of solutions to be used in the analysis.

Three 0.5 to 1.0 g.-samples of the cellulose acetate to be analyzed were weighed in the weighing tube and transferred to 250-ml. glass stoppered conical flasks. At least three flasks containing approximate equivalent amounts of standard cellulose were also prepared for each group of analyses. These flasks were carried as blank determinations. Each sample of linters was wetted with 20 ml. of 95% ethanol, measured with a pipet, and allowed to stand for 15 minutes. Each sample was then treated with 20 ml. of approximately 0.5 N KOH,

measured with a standard pipet, and the sample and solution were mixed thoroughly and allowed to stand for 24 hours at room temperature. At the end of this time each sample was treated with 20 ml. of approximately 0.6 N H_2SO_4 measured with the same standard pipet. After mixing, the sample was allowed to stand 4 to 6 hours so that the excess alkali could be removed from the fibers. During the 24 hour saponification period the potassium hydroxide swelled the cellulose acetate and diffused into its capillary structure. Howlet and Martin[29] found that the addition of excess sulfuric acid to such a mixture did not neutralize the base on the inside of the cellulose fibers unless the mixture was allowed to stand for a 4 to 6 hour diffusion period, after which the excess acid could be titrated with standard base and reproducible results obtained. The excess acid present in each sample was titrated with standard 0.2 N KOH to the phenolphthalein end point. In this final step the contents of the flask was shaken repeatedly to insure complete neutralization of the acid.

The calculation of combined acetic acid was made from the equation:

$$\underset{\text{HOAc}}{\text{per cent}} = \frac{(T - t)\ (\text{N of KOH})\ (0.06005)\ (100)}{\text{sample weight}} ;$$

where T is the ml. of KOH to titrate the sample of cellulose acetate; t is the average of the blank determinations; and the figure 0.06005 is the milliequivalent weight of acetic acid.

Tabulation of Analyses of Cellulose Acetate Preparations.

The preparation of cellulose acetates of low acetyl content under the conditions used required some preliminary experimentation. Samples of cellulose acetate, No. 1 to 7, resulted from this investigation, and since they were not used in any oxidation studies, the data on these samples will be omitted. Cellulose acetate samples, No. 8 to 15, were prepared as a group and used in the study of the initial reaction (a 4 hour period) of periodic acid on cellulose acetate. Samples, No. 16 to 25, were also prepared as a group and were used in oxidations over a period of 60 hours.

Table I contains the data pertaining to the conditions of acetylation and the analysis of cellulose acetate samples. The symbol "CAc" is used to designate cellulose acetate. The value of the average titer for blank determinations is listed at the bottom of the titer column of each analysis. The sample weight listed as 0.0000 g. may be interpreted as an equivalent quantity of standard cellulose in the blank.

The progress of the acetylation reaction may be illustrated by plotting the percent combined acetic acid against the reaction time. Figure 1 shows the rate of acetylation for standard cotton cellulose (moisture content less than 1%) at 27 to 29° C. Although it was not intended that this study should reproduce the reaction curve of Elod[10], it can be seen that the rate of acetylation is the same even though the conditions of moisture content and temperature are slightly different.

TABLE I

ANALYSES OF CELLULOSE ACETATE PREPARATIONS

CAc No.	Reaction Time, hrs.	Temp. °C.	Analysis for percent combined acetic acid			
			sample wgt. g.	ml. of st. KOH	N of st. KOH	HOAc %
8	2.5	27	0.4782	29.25	0.2147	3.14
			0.4771	29.25		3.09
			0.4798	29.30		3.28
			0.0000	28.22		
					av.	3.17
9	5.0	27	0.4810	29.85	0.2148	6.57
			0.4864	30.00		6.89
			0.4860	30.05		7.03
			0.0000	27.40		
					av.	6.83
10	4.0	28.5	0.4841	29.65	0.2148	6.00
			0.4869	29.65		5.96
			0.4884	29.75		6.21
			0.0000	27.40		
					av.	6.06
11	7.5	28.5	0.4710	30.85	0.2148	9.45
			0.4895	31.10		9.75
			0.4796	30.90		9.41
			0.4768	30.92		9.53
			0.0000	27.40		
					av.	9.53
12	3.25	29	0.4760	28.60	0.2148	3.66
			0.4755	28.70		3.93
			0.4776	28.70		3.92
			0.0000	27.25		
					av.	3.84
13	6.0	29	0.4772	29.90	0.2148	7.17
			0.4761	29.80		6.92
			0.4758	29.90		7.20
			0.0000	27.25		
					av.	7.10

Cont'd next page

TABLE I - Continued

CAc No.	Reaction Time, hrs.	Temp. °C.	Analysis for percent combined acetic acid			
			sample wgt. g.	ml. of st. KOH	N of st. KOH	HOAc %
14	4.25	28	0.9532	10.48	0.1934	1.21
			0.9505	10.60		1.35
			0.9516	10.54		1.28
			0.0000	9.49		
						av. 1.28
15	7.0	28	0.5727	12.05	0.1934	5.19
			0.5744	12.10		5.27
			0.5728	12.08		5.25
			0.0000	9.49		
						av. 5.24
16	2.0	29	0.9537	10.00	0.1934	0.62
			0.9554	10.02		0.64
			0.9564	10.05		0.68
			0.0000	9.49		
						av. 0.65
17	4.0	29	0.4769	11.55	0.1934	5.04
			0.4800	11.65		5.24
			0.4776	11.58		5.10
			0.0000	9.48		
						av. 5.13
18	6.0	29	0.4769	12.88	0.1934	8.28
			0.4770	12.85		8.20
			0.4760	12.85		8.22
			0.0000	9.48		
						av. 8.23
19	8.0	29	0.4769	14.44	0.1934	11.94
			0.4804	14.50		12.12
			0.4781	14.50		12.20
			0.0000	9.48		
						av.12.09
20	10.0	29	0.4796	15.40	0.1934	14.34
			0.4764	15.25		14.07
			0.4796	15.25		14.01
			0.0000	9.48		
						av.14.14

Cont'd next page

TABLE I - Concluded

CAc No.	Reaction Time, hrs.	Temp. °C.	Analysis for percent combined acetic acid			
			sample wgt. g.	ml. of st. KOH	N of st. KOH	HOAc %
21	2.75	28	0.4821	10.95	0.1934	3.39
			0.4784	10.92		3.35
			0.4813	10.98		3.47
			0.0000	9.48		
						av. 3.40
22	3.5	28	0.4775	11.72	0.1934	5.30
			0.4796	11.70		5.23
			0.4807	11.78		5.40
			0.0000	9.48		
						av. 5.31
23	5.0	28	0.4804	12.30	0.1934	6.66
			0.4808	12.28		6.62
			0.4780	12.22		6.50
			0.0000	9.48		
						av. 6.60
24	7.25	28	0.4777	13.10	0.1934	8.65
			0.4815	13.12		8.63
			0.4768	13.10		8.66
			0.0000	9.48		
						av. 8.65
25	9.0	28	0.4792	13.65	0.1934	9.96
			0.4802	13.65		9.93
			0.4802	13.65		9.93
			0.0000	9.48		
						av. 9.94

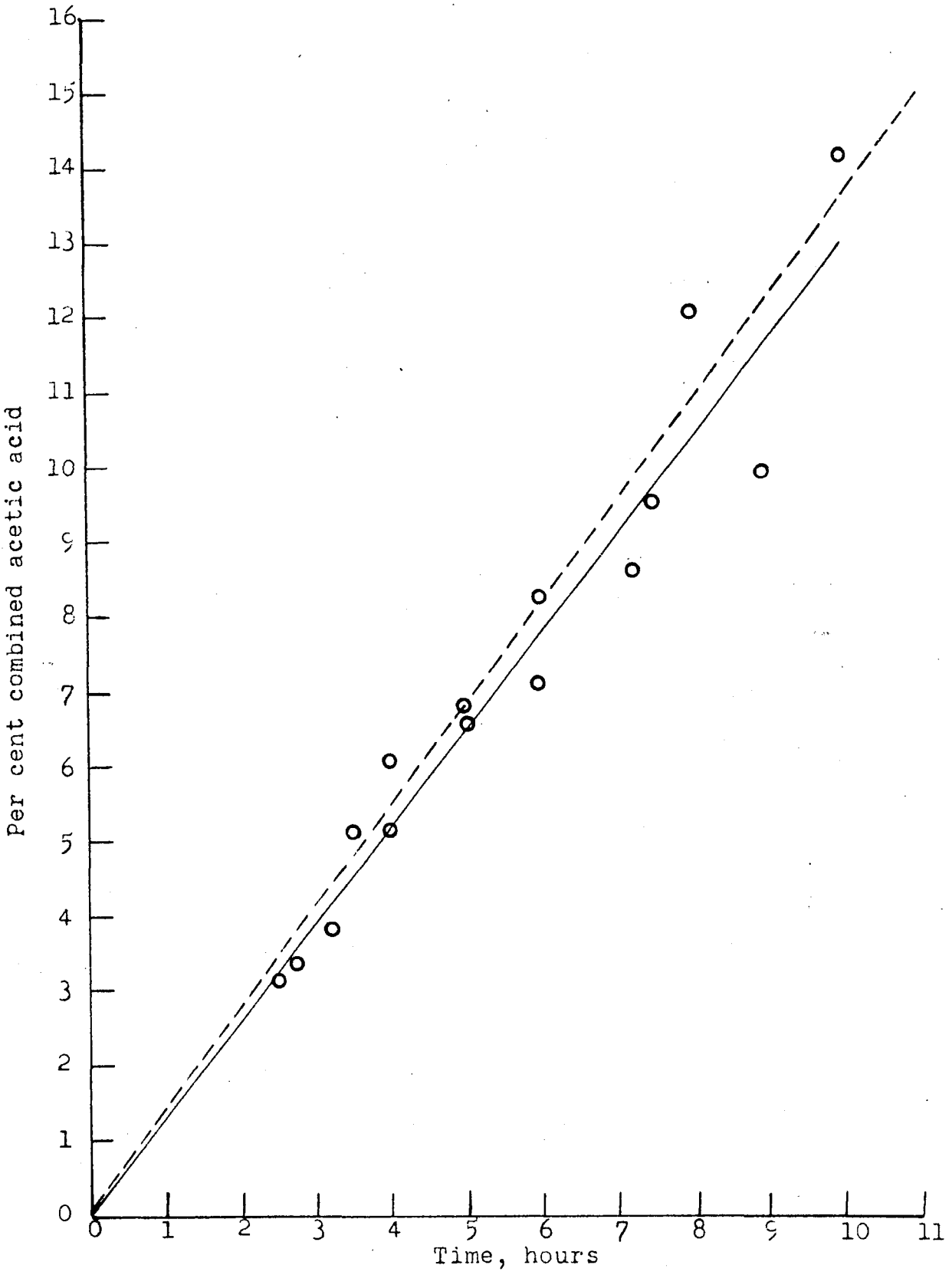


Figure 1

—— Acetylation of cotton, <1% moisture, at 27 to 29°C.

--- Acetylation of cotton, 0.1% moisture, at 45°C.,

Elöd and Schmidt-Bielenberg[10].

Calculation of the Degree of Substitution and the Unit Molecular Weight of Cellulose Acetates.

Combined acetic acid percentages may be converted to percent acetyl by multiplying by the ratio: molecular weight of an acetyl group to the molecular weight of acetic acid, i.e., 42/60. Percent combined acetic acid may be converted to degree of substitution by means of a mathematical expression[21] as shown below.

When cellulose acetate is saponified the elements of HOH are added to yield cellulose (unit molecular formula $C_6H_{10}O_5$) and acetic acid. In terms of acetic acid content, the unit molecular formula of any acetate may be written: $C_6H_{10-2D.S.}O_{5-D.S.}(HOAc)_{D.S.}$, where D.S. is the degree of substitution of acetic acid per anhydroglucose unit. The percent acetic acid in cellulose acetate may then be expressed by:

$$\frac{HOAc \cdot 100}{C_6H_{10-2D.S.}O_{5-D.S.}(HOAC)_{D.S.}} = HOAc\%$$

Substituting the proper atomic weights in this equation and solving for the degree of substitution:

$$D.S. = \frac{162\ (HOAC\%)}{6000 - 42(HOAc\%)}$$

The unit molecular weight of cellulose acetate will always be that of an anhydroglucose unit plus the weight of the acetyl content. Knowing the degree of substitution, the unit molecular weight of any acetate may be expressed:

$$\text{Unit molecular weight} = 162 + 42\ D.S.$$

The degree of substitution for a cellulose triacetate has the maximum value of 3. By the above equation its unit molecular weight is 288.

It was found convenient to calculate the unit molecular weight for cellulose acetates of 1 to 15% combined acetic acid, and to plot the HOAc% against unit molecular weight. A large piece of graph paper (2 feet square) was used for this graph, and the value of the unit molecular weight of any acetate in this range of percent combined acetic acid could be determined at a glance.

The values of the acetyl content, degree of substitution, and unit molecular weight for each acetate sample are recorded in table II.

TABLE II

DEGREE OF SUBSTITUTION AND UNIT MOLECULAR WEIGHT OF CELLULOSE ACETATE PREPARATIONS

CAc No.	Combined HOAc %	Acetyl content %	Degree of substitution (calc.)	Unit molecular weight (calc.)
8	3.17	2.22	0.0875	165.67
9	6.83	4.78	0.1936	170.13
10	6.06	4.24	0.1706	169.16
11	9.53	6.67	0.2758	173.57
12	3.84	2.69	0.1066	166.48
13	7.10	4.97	0.2018	170.47
14	1.28	0.896	0.0348	163.46
15	5.24	3.67	0.1466	168.12
16	0.65	0.455	0.0177	162.75
17	5.13	3.59	0.1436	168.03
18	8.23	5.76	0.2360	171.91
19	12.09	8.43	0.3560	176.95
20	14.14	9.90	0.4235	179.77
21	3.40	2.38	0.0940	165.94
22	5.31	3.715	0.1490	168.25
23	6.60	4.62	0.1868	169.84
24	8.65	6.05	0.2490	172.45
25	9.94	6.96	0.2880	174.10

PERIODATE OXIDATION OF CELLULOSE ACETATES

Materials

1. Standard cellulose (see page 15).
2. Cellulose acetates of low acetyl content (see page 16).
3. Paraperiodic acid: H_5IO_6, reagent grade, G. Frederick Smith Chemical Co.
4. Sodium bicarbonate: reagent grade.
5. Potassium iodide: C.P. grade.
6. Arsenious oxide: reagent grade.
7. Sodium hydroxide pellets: C.P. grade.
8. Potassium iodate: primary standard.
9. Hydrochloric acid: sp. gr. 1.19, 37-38.5%, C.P. grade.
10. Water: laboratory distilled water.

All of the above chemicals conform with A.C.S. specifications.

Determination of the Periodate Content of a Solution of Periodic Acid.

When periodic acid oxidizes cellulose it is reduced to iodic acid. The periodate content of a solution may be determined in the presence of the iodate ion. In neutral solution periodate is reduced by iodide to iodate. Thus, if a solution of periodic acid is neutralized with excess sodium bicarbonate, and then treated with excess potassium iodide solution, the reaction may be written:

$$NaIO_4 + 2KI + 2NaHCO_3 \longrightarrow NaIO_3 + I_2 + Na_2CO_3 + K2CO_3 + H_2O$$

The iodine in this solution may be determined by titration with standard arsenite solution, using a starch indicator[45]. Davidson[8] found that

this method yielded the same results as the more commonly used but less direct method of Fleury and Lange[14,15]. The latter method uses an excess of arsenite to react with the iodine, followed by a back-titration of the excess arsenite with standard iodine solution. The equation for the reduction of iodine by arsenite may be written:

$$I_2 + NaAsO_2 + 3NaHCO_3 \longrightarrow Na_2HAsO_4 + 2NaI + 3CO_2 + H_2O$$

Preparation and Standardization of Arsenite Solution.

Standard 0.015 N sodium arsenite solution was prepared according to directions described by Willard and Furman[65]. Arsenious oxide, As_2O_3 analytical reagent, was dried at 110° C. for 24 hours, and used as a primary standard. Seven liters of the solution were prepared at one time. Exactly 5.1928 g. of the dried arsenious oxide was weighed out on a tared watch glass, transferred quantitatively to a 250-ml. beaker, and treated with a solution of 10 g. of sodium hydroxide pellets in 50 ml. of water. The oxide dissolved readily when the solution was warmed slightly. The solution was transferred quantitatively to a 1-liter volumetric flask and diluted with water to 500 ml. An excess of concentrated sulfuric acid (10 ml.) was added to the alkaline arsenite solution. After thorough mixing the excess acid was destroyed by the addition of 10 g. of sodium bicarbonate added in small portions. Such a solution is saturated with carbon dioxide and contains excess sodium bicarbonate; therefore, it is a buffered solution. After thorough mixing and cooling to 20° C., the solution was made up to the mark. It was then poured into a 7.5-liter bottle and diluted with six liters

of water measured in the same volumetric flask. The storage bottle was fitted with a siphon apparatus and protected from the laboratory atmosphere with a calcium chloride-soda-lime tube at the air inlet.

The formation of sodium arsenite from arsenious oxide may be written: $As_2O_3 + 2NaOH \longrightarrow 2\ NaAsO_2 + H_2O$. The normality of the arsenite solution may be calculated from the equation:

$$N = \frac{\text{g. of } As_2O_3}{(0.049455)\ \ (\text{ml. of solution})}$$

From this equation, the normality of 7 liters of solution prepared from 5.1928 g. of arsenious oxide would be 0.015.

The normality of standard arsenite may be checked against a standard iodine solution or by an adaptation of the potassium iodate primary standard technique. The latter method was found to be more convenient. Three 0.25 to 0.30-g. samples of dried primary standard KIO_3 were weighed out. Each sample was dissolved in 50 ml. of water. This solution was transferred quantitatively to a 250-ml. volumetric flask, and diluted with water up to the mark. Twenty-ml. aliquots of these standard KIO_3 solutions were measured with a standard 20-ml. pipet into a 250-ml. glass stoppered conical flask. Each aliquot sample was diluted with 30 ml. of water and 5 ml. of 10% KI solution. The iodine in this solution was liberated with 5 ml. of dilute HCl (1 part of 38% HCl to 15 parts of water) according to the equation:

$$KIO_3 + 5KI\ (\text{excess}) + 6HCl \longrightarrow 6KCl + 3I_2 + 3H_2O$$

This solution is acidic and must be neutralized before the arsenite method of determining iodine can be applied. This requirement was fulfilled by adding 2 g. of solid $NaHCO_3$ in small portions, the flask

being tilted so that no loss of solution occured during the evolution of carbon dioxide. The solution was chilled in ice water and titrated at once with approximately 0.015 N arsenite solution delivered from a 50-ml. buret, using 1 ml. of 1% starch solution as indicator. Calculation of the normality of the arsenite solution was made as follows:

$$\text{N of arsenite} = \frac{(20)\ (\text{g. of } KIO_3)}{(250)\ (0.03567)\ (\text{ml. of arsenite})} \ .$$

When checking the normality of the arsenite solution, three aliquots of three different standard KIO_3 solutions were titrated. The normalities obtained for these nine trials were usually in agreement within 2 parts per thousand. The best average was used as the standard normality of the solution.

The normality of the arsenite solutions used throughout this investigation remained constant within 0.0001 N for several months. When the storage bottle was nearly empty, the concentration changed more rapidly, and therefore, when the solution was down to the 1 liter mark, a fresh solution was prepared.

Preparation and Standardization of Periodic Acid Solution.

Periodic acid solutions may be prepared by dissolving crystalline paraperiodic acid in the desired amount of water. The concentration of the periodic acid solution selected for the oxidation of cellulose and cellulose acetate was 0.03 N. The solution was made up in double strength (0.06 N) so that the linters of cellulose and cellulose acetate could be wetted and dispersed in a standard volume of water before addition of an equal volume of approximately 0.06 N HIO_4 solution.

To prepare a 6-liter volume of approximately 0.06 N solution, 42.5 ± 0.01 g. of H_5IO_6 was weighed and dissolved in 6 liters of distilled water. This solution was stored in a 7.5-liter bottle fitted with a siphon tube and protected from the laboratory atmosphere with a calcium chloride-soda-lime tube. Paraperiodic acid is very hygroscopic and contains some water in excess of the formula H_5IO_6. A trial solution was made up to establish the correct weight of the reagent to be used to prepare 0.06 N solutions. It was found that the reagent grade of H_5IO_6 contained about 3.5% water.

Three 10-ml. samples of the stock HIO_4 solution, measured with a standard 10-ml. pipet, were removed and transferred to 125-ml. Erlenmeyer flasks and neutralized with 10 ml. of saturated sodium bicarbonate solution. Each flask was chilled in an ice water bath for 2 minutes. Ten ml. of 10% potassium iodide solution was added and the liberated iodine titrated immediately with standard 0.015 N arsenite delivered from a 50-ml. buret. The arsenite was added as rapidly as possible at first, and then more slowly until the iodine color had almost disappeared or was a faint yellow. At this point 1 ml. of 1% starch solution was added as an indicator, and the titration was continued until the blue color of the starch-iodine complex just disappeared. The starch solution was prepared by adding 1 g. of soluble starch dispersed in 20 ml. of water to 80 ml. of boiling water, and allowing this mixture to boil for 10 seconds.

The periodic acid solutions were found to remain constant within 0.0002 N during any three day period. After a period of 5 or 6 weeks

the concentration of the stock solution decreased from .06 N to 0.055 N. As in the case of the standard arsenite solutions, when the volume of periodate was down to the 1 liter mark, a fresh solution was prepared. The normality of the periodic acid solution was calculated from the equation:

$$N \text{ of } HIO_4 = \frac{(N \text{ of arsenite})\ (\text{ml. of arsenite})}{(\text{ml. of } HIO_4)}$$

Preliminary Oxidations: The Selection of Oxidation Conditions.

A number of preliminary periodate oxidation experiments were performed on standard cellulose in order to select the proper oxidation conditions that would lead to reproducible results. It was found that many variables required either accurate or at least approximate control. These factors are described and discussed in this section.

The selection of the concentration of periodic acid solution to be used in the oxidation of cellulose and cellulose acetate was based on the work of Harris and coworkers[53]. This concentration varied between 0.0275 N and 0.03 N.

All reaction flask equipment was scoured thoroughly with a detergent scouring powder to remove oxidizable impurities or impurities that might catalyze the decomposition of periodic acid. After rinsing with water, the inside surface of each reaction flask was standardized by treatment with about 0.06 N HIO_4 solution for 24 hours before use. After the flasks had been used in oxidation experiments they were cleaned by rinsing with water and were dried in an inverted position.

The physical form of the material to be oxidized was standardized by using 20-mesh linters of standard cellulose and cellulose acetate fibers (see page 19). Weighing of these linters was performed as described on page 20.

Before addition of the oxidizing solution, the linters samples were prewetted with a standard volume of water and allowed to stand for 1 hour. An equal standard volume of stock periodic acid was added and the time of addition noted. The solution and linters were carefully mixed. The reaction flask was then thermostated at 30° C. in a constant temperature bath for the desired length of time.

The constant temperature bath consisted of a battery jar, 40 cm. in diameter and 30 cm. high, fitted with Precision Scientific Co. electronic thermostating apparatus, together with a stirring motor, and a 50° C. thermometer calibrated in units of 0.1° C. A wire rack was supported in the jar by three chains that could be adjusted to hold the rack at any desired depth. The jar was filled with enough water to cover the thermostat control and the rack was adjusted to a depth 5 cm. below the water level. The thermostat control was adjusted for a bath temperature of 30 ± 0.1° C. Small flasks thermostated in this bath were weighted with squares of heavy lead sheet with the corners turned up to clamp around the bottom of the flask.

No method of mixing was used in the case of these preliminary oxidations. A flask containing at least 100 ml. of the stock periodic acid solution was thermostated with the reaction flask and was used for blank determination of the concentration of periodic acid. Since

the concentration of a periodic acid solution decreases slowly, due to the decomposition of the periodate ion, the standardization procedure was repeated for each series of oxidations.

The pH of the reaction mixture was found to remain constant over a period of 72 hours. Since this pH was between 1.6 and 2.0 no buffer solutions were incorporated in the oxidation mixtures.

At the end of the reaction time the mixture was analyzed for unreacted periodic acid by the same procedure used for standardizing periodic acid solutions. In some cases the linters were filtered from the oxidizing medium with a specially constructed suction-filter apparatus. This was made from a 2.5-liter wide-mouth bottle, 8.5 cm. in diameter at the top. This bottle was large enough so that a 250-ml. conical flask could be placed inside it. The bottle was provided with a rubber stopper holding a 6-cm. long-stem funnel and an L-shaped glass tube. A Gooch crucible was supported in the funnel with a rubber adapter. The funnel extended halfway into the receiving flask inside the suction apparatus, so that during the filtering procedure, the filtrate coming from the Gooch crucible passed into the flask in a quantitative manner.

Three methods of sampling to determine the excess periodic acid in an oxidation mixture were studied: (1) the oxidation mixture was filtered and the sample removed from the filtrate; (2) the oxidation mixture was filtered and washed, the combined filtrate and washings were made up to a standard volume, and an aliquot of the standard volume removed as a sample; (3) the entire reaction mixture (without filtering) was used as the sample.

Method 1. A 1 to 1.5-G. sample of standard cellulose linters was weighed into a 250-ml. Erlenmeyer flask and suspended in 50 ml. of water measured with a standard pipet. Fifty ml. of approximately 0.06 N HIO_4 solution, measured with a standard pipet, was added and mixed with the suspended linters. The flask was stoppered with a cork and thermostated at 30° C. for 30 minutes. At the end of this time the flask was plunged into ice water at 0° C. for 2 minutes. The reaction mixture was filtered through a Gooch crucible into a clean 250-ml. Erlenmeyer flask. Three 20-ml. samples of the filtrate were analyzed for periodate content.

Method 2. Method 1 was followed exactly, except that after separation of the linters from the oxidizing solution, the linters were washed with 50 ml. of water added in about 5 ml. portions. The mixture of filtrate and wash water was transferred quantitatively to a 200-ml. volumetric flask and diluted to the mark with water. Three 50-ml. aliquots of this solution were analyzed for periodate content as usual.

Method 3. In this experiment the oxidation mixture was analyzed directly. A 0.2 to 0.25-g. sample of conditioned 20-mesh standard cellulose linters was weighed into a 125-ml. Erlenmeyer flask and suspended in 10 ml. of water measured with a standard pipet. Ten ml. of approximately 0.06 N periodic acid was measured with a standard pipet and mixed with the suspended linters. The flask was stoppered with a cork and thermostated at 30° C. for 30 minutes. At the end of this time the flask was plunged into ice water at 0° C. for 2 minutes, and the oxidation medium was immediately analyzed for periodate content.

At least four separate samples of cellulose were used to test each method of sampling described. The consumption of periodate by each sample was calculated. This figure is expressed as milliequivalents of HIO_4 consumed per gram of cellulose, and may be calculated from the equation:

$$HIO_4, \text{ meq./ g.} = \frac{(B - S)\ (N \text{ of arsenite})\ (F)}{(\text{g. of standard cellulose})}$$

where B is the average ml. of arsenite used to titrate the blanks; S is the ml. of arsenite used to titrate the solution or aliquot fraction; and F is a multiplication factor that depends on the fraction of the total solution analyzed. In method 1 this fraction was 1/5, therefore the multiplication factor would be 5. In method 2 the factor would be 4, and in method 3, since the whole solution was titrated, the factor is 1. In methods 1 and 2 the three titrations made on each sample did not vary more than $\pm$ 0.05 ml. and the average was recorded.

The data for the three methods of sampling are listed in Table III. The values of the blank titers are listed opposite the zero sample weights at the top of each group of analyses.

From the data in column 5 of table III it can be seen that the variations in the periodate consumption, as determined by the three methods of sampling, are so small that it may be concluded that any one of the three would be satisfactory.

It is difficult to decide the limits of reproducibility that should be considered as acceptable in the case of heterogeneous

TABLE III

RESULTS OF THE ANALYSES OBTAINED BY THREE METHODS OF SAMPLING

(Oxidations for 30 Minutes at 30° C.)

Method of Sampling	Sample Wgt., g.	Arsenite Titer, ml.	Normality of Arsenite	HIO_4 Consumed meq./ g.
1	0.0000	39.65	0.015	0.0000
	1.4395	38.30		0.0704
	0.9364	38.80		0.0689
	1.0241	38.60		0.0769
	0.9738	38.60		0.0808
2	0.0000	49.55	0.015	0.0000
	1.0272	48.42		0.0654
	1.0202	48.25		0.0765
	0.9664	48.28		0.0788
	0.9906	48.25		0.0788
3	0.0000	39.70	0.015	0.0000
	0.1910	38.80		0.0707
	0.1881	38.80		0.0718
	0.0000	39.50	0.0147	0.0000
	0.1929	38.52		0.0753
	0.0000	37.45	0.0152	0.0000
	0.2028	36.50		0.0720

reactions. It was thought that the maximum error in an arsenite-iodine titration (0.015 N arsenite) was one drop (0.05 ml.) of the arsenite solution. This error would correspond to 0.00375 milliequivalents of HIO_4 per gram of cellulose. Therefore, any method that gives periodate consumption figures which check within 0.004 meq./g. would be considered a satisfactory analytical method. Reproducibility within this limit was easily obtained in short time oxidations.

On the other hand, larger errors or variations in the periodate consumption by comparable samples may be encountered. Some of the factors to which these variations might be attributed are as follows:

(1) Variations in the volumes of solutions delivered from a standard pipet might result in a periodate consumption that would be too high or too low. An error of one drop (0.05 ml.) of 0.06 N periodic acid would correspond to 0.015 milliequivalents of HIO_4 per gram of cellulose.

(2) The presence of impurities might catalyze the decomposition of periodic acid and result in a periodate consumption that would always be too great. This effect would be more significant in long time oxidations.

(3) Differences in the swollen condition of the cellulosic material might permit more rapid or slower diffusion of the oxidant into the interior of the fiber and thus result in a periodate consumption that would vary according to the rate of diffusion. This effect would also be more apparent in long time oxidations.

Oxidation of Cellulose Acetates: The Four Hour Reaction.

Cellulose acetate samples No. 8 to 14 were oxidized in these experiments. Since it was found that the determination of the excess periodic acid in an oxidation mixture by direct titration yielded reproducible results, this simple technique was used in the following experiments.

At least two samples of each cellulose acetate and several samples of standard cellulose were oxidized for each of the following time periods: 0.5, 1.0, 1.5, 2, 2.5, 3, 3.5, and 4 hours. A few of the first oxidations were also recorded for time periods of 0.25 and 0.75 hours, but this practice was later abandoned. Time schedules that would allow the oxidation of 16 samples in one series were established. No two samples of the same cellulose acetate were oxidized for the same length of time in any one schedule. This rule was established so that the reproducibility of the results could be compared between experiments performed on different days and perhaps under slightly different conditions. The standard procedure used for all of these oxidation experiments is described below.

A sample of cellulose or cellulose acetate approximately 0.2 g. in weight was weighed into a 125-ml. Erlenmeyer flask and suspended in 10 ml. of water measured with a standard pipet at 20° C. The flask was weighted and thermostated at 30° C. for a 1 hour wetting and swelling period. A 250-ml. glass stoppered conical flask containing 200 ml. of stock periodic acid solution was also thermostated at 30° C. At zero time, 10 ml. of this periodic acid solution was measured with a

standard pipet (calibrated for 30° C.) into the reaction flask and mixed with the suspended linters. Care was taken to prevent the linters from clinging to the sides of the flask and thus avoid contact with the oxidizing medium. The linters were allowed to steep, without any mixing, in the reaction flask for the desired length of time. At the end of the reaction time the flask was plunged into ice water at 0° C. for 2 minutes and analyzed immediately for unreacted periodic acid. The standard arsenite solution was delivered from a 50-ml. buret. After analysis of the sample was completed, or during a 2 hour period following the time of analysis, at least three 10 ml. samples of periodic acid solution were removed from the conical flask that was previously thermostated at 30° C. These samples were also measured with a pipet calibrated at 30° C. and were used as blank determinations of the normality of the stock periodic acid solution.

The oxidation data for cellulose and cellulose acetates No. 8 to 14 are recorded in table IV. The symbols S.C. and CAc are used to designate standard cellulose and cellulose acetate respectively. The consumption of periodic acid expressed in milliequivalents per gram of cellulose or cellulose acetate is also recorded in table IV. This calculation was made for each sample from the equation:

$$HIO_4 \text{ meq./ g.} = \frac{(B-S)\ (N \text{ of arsenite})}{(\text{g. of S.C. or CAc})} \quad ;$$

where B is the average ml. of arsenite solution used to titrate the blanks, and S is the ml. of arsenite used to titrate the oxidation solution.

TABLE IV

OXIDATION OF CELLULOSE AND CELLULOSE ACETATES

(Oxidations up to 4 hours)

Sample Number	Reaction Time, hrs.	Temp. °C.	Sample Wgt., g.	Arsenite Titer, ml.	Normality of St. Arsenite	HIO_4 Consumed, meq./ g.
S.C.	0.0	29.95	0.0000	39.50	0.0147	0.0000
	0.5		0.1974	38.65		0.0637
	1.0		0.1965	37.90		0.1206
	1.5		0.2002	37.40		0.1550
	2.0		0.1944	36.82		0.2050
	2.5		0.1960	36.40		0.2340
	3.0		0.2010	35.90		0.2640
	3.5		0.1965	35.55		0.3003
	4.0		0.2005	34.90		0.3390
S.C.	0.0	30.00	0.0000	39.50	0.0147	0.0000
	0.5		0.1929	38.52		0.0753
	1.0		0.1976	38.87		0.1220
	1.5		0.1995	37.35		0.1590
	2.0		0.1966	36.90		0.1960
	2.5		0.2009	36.25		0.2400
	3.0		0.1972	35.90		0.2695
	3.5		0.1994	35.50		0.2970
	4.0		0.2003	35.00		0.3320
S.C.	0.0	29.90	0.0000	37.45	0.0152	0.0000
	0.5		0.2028	36.50		0.0720
	1.0		0.1975	35.90		0.1195
	1.5		0.1983	35.30		0.1650
	2.0		0.1995	34.75		0.2060
	2.5		0.1986	34.40		0.2340
	3.0		0.1985	33.90		0.2720
	3.5		0.2006	33.45		0.3030
	4.0		0.2013	33.10		0.3280
CAc No. 8	0.0	29.90	0.0000	38.25	0.0149	0.0000
	0.25		0.1903	37.75		0.0440
	0.5		0.1941	37.40		0.0651
	0.75		0.1912	37.05		0.0935
	1.0		0.1901	36.85		0.1096
	1.5		0.1922	36.27		0.1550
	2.0		0.1885	35.75		0.1980

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TABLE IV - Continued

Sample Number	Reaction Time, hrs.	Temp. °C.	Sample Wgt., g.	Arsenite Titer, ml.	Normality of St. Arsenite	HIO_4 Consumed, meq./ g.
CAc No. 8	0.0	29.90	0.0000	38.25	0.0149	0.0000
	0.25		0.1948	37.63		0.0474
	0.5		0.1925	37.35		0.0696
	0.75		0.1946	37.00		0.0956
	1.0		0.1922	36.75		0.1160
	1.5		0.1917	36.20		0.1480
	2.0		0.1943	35.70		0.1950
CAc No. 8	0.0	30.00	0.0000	39.50	0.0147	0.0000
	0.5		0.1983	38.63		0.0655
	1.0		0.1986	37.95		0.1154
	1.5		0.2019	37.35		0.1575
	2.0		0.2007	36.90		0.1920
	2.5		0.1987	36.45		0.2270
	3.0		0.1982	35.95		0.2650
	3.5		0.1998	35.60		0.2900
	4.0		0.1985	35.25		0.3170
CAc No. 9	0.0	29.90	0.0000	37.80	0.0147	0.0000
	0.25		0.2027	37.28		0.0378
	0.5		0.1940	37.00		0.0607
	0.75		0.1948	36.75		0.0790
	1.0		0.1995	36.60		0.0887
	1.5		0.2007	35.90		0.1390
	2.0		0.1998	35.55		0.1653
	2.5		0.1998	35.05		0.2020
	3.0		0.2016	34.60		0.2330
	3.5		0.1980	34.25		0.2640
	4.0		0.1942	34.05		0.2840
CAc No. 9	0.0	29.90	0.0000	39.50	0.0147	0.0000
	0.5		0.2016	38.65		0.0625
	1.0		0.2018	38.10		0.1025
	1.5		0.1971	37.65		0.1405
	2.0		0.1993	37.22		0.1690
	2.5		0.1969	36.80		0.2035
	3.0		0.1966	36.50		0.2260
	3.5		0.2023	35.90		0.2640
	4.0		0.1969	35.75		0.2830

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TABLE IV - Continued

Sample Number	Reaction Time, hrs.	Temp. °C.	Sample Wgt., g.	Arsenite Titer, ml.	Normality of St. Arsenite	HIO_4 Consumed, meq./ g.
CAc No. 10	0.0	29.80	0.0000	39.50	0.0147	0.0000
	0.5		0.1957	38.90		0.0456
	1.0		0.1944	38.30		0.0915
	1.5		0.1931	37.80		0.1300
	2.0		0.1983	37.30		0.1642
	2.5		0.1961	36.95		0.1920
	3.0		0.1988	38.45		0.2270
	3.5		0.1982	36.20		0.2460
	4.0		0.1950	35.90		0.2760
CAc No. 10	0.0	29.90	0.0000	39.50	0.0147	0.0000
	0.5		0.1933	-----		------
	1.0		0.1966	38.30		0.0905
	1.5		0.1967	37.85		0.1240
	2.0		0.2012	37.30		0.1620
	2.5		0.2017	36.90		0.1910
	3.0		0.2003	36.43		0.2270
	3.5		0.2001	36.20		0.2440
	4.0		0.1952	35.85		0.2770
CAc NO. 11	0.0	29.90	0.0000	39.50	0.0147	0.0000
	0.5		0.1957	38.55		0.0715
	1.0		0.2010	38.05		0.1064
	1.5		0.2010	37.65		0.1433
	2.0		0.1982	37.15		0.1760
	2.5		0.1970	36.75		0.2060
	3.0		0.2015	36.42		0.2260
	3.5		0.2024	36.05		0.2520
	4.0		0.1965	35.70		0.2860
CAc No. 11	0.0	29.90	0.0000	39.50	0.0147	0.0000
	0.5		0.1995	38.55		0.0702
	1.0		0.1976	38.05		0.1085
	1.5		0.2002	37.55		0.1440
	2.0		0.1961	37.10		0.1810
	2.5		0.1991	36.75		0.2040
	3.0		0.1952	36.50		0.2272
	3.5		0.1919	-----		------
	4.0		0.1978	-----		------

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TABLE IV - Continued

Sample Number	Reaction Time, hrs.	Temp. °C.	Sample Wgt., g.	Arsenite Titer, ml.	Normality of St. Arsenite	HIO_4 Consumed, meq./ g.
CAc	0.0	29.90	0.0000	37.45	0.0152	0.0000
No. 11	0.5		0.2013	36.50		0.0713
	1.0		0.1989	36.05		0.1065
	1.5		0.2009	35.60		0.1400
	2.0		0.1965	35.20		0.1740
	2.5		0.2019	34.80		0.2000
	3.0		0.2005	34.45		0.2275
	3.5		0.1985	34.20		0.2490
	4.0		0.1951	33.75		0.2880
CAc	0.0	29.90	0.0000	37.60	0.0152	0.0000
No. 12	0.5		0.1986	36.70		0.0690
	1.0		0.1985	36.20		0.1075
	1.5		0.1998	35.50		0.1600
	2.0		0.2001	35.15		0.1860
	2.5		0.2019	34.60		0.2260
	3.0		0.2007	34.15		0.2610
	3.5		0.2028	33.80		0.2860
	4.0		0.2018	33.30		0.3240
CAc	0.0	29.90	0.0000	37.60	0.0152	0.0000
No. 12	0.5		0.2025	36.65		0.0730
	1.0		0.2025	36.15		0.1090
	1.5		0.1986	-----		------
	2.0		0.1979	35.10		0.1920
	2.5		0.1983	34.60		0.2300
	3.0		0.1986	34.15		0.2640
	3.5		0.1988	33.80		0.2910
	4.0		0.1982	33.35		0.3260
CAc	0.0	29.90	0.0000	37.45	0.0152	0.0000
No. 13	0.5		0.2015	36.65		0.0605
	1.0		0.1982	36.05		0.1070
	1.5		0.1978	35.60		0.1420
	2.0		0.2018	35.20		0.1690
	2.5		0.2024	34.60		0.2120
	3.0		0.1995	34.40		0.2320
	3.5		0.1985	33.80		0.2800
	4.0		0.1995	33.60		0.2930

(Cont'd next page)

TABLE IV - Concluded

Sample Number	Reaction Time, hrs.	Temp. °C.	Sample Wgt., g.	Arsenite Titer, ml.	Normality of St. Arsenite	HIO_4 Consumed, meq./ g.
CAc No. 13	0.0	29.90	0.0000	37.45	0.0152	0.0000
	0.5		0.1988	36.65		0.0615
	1.0		0.1969	36.10		0.1040
	1.5		0.2028	35.55		0.1425
	2.0		0.2011	35.20		0.1695
	2.5		0.2020	34.80		0.1990
	3.0		0.2000	34.40		0.2310
	3.5		0.2011	33.90		0.2680
	4.0		0.1979	33.62		0.2940
CAc No. 14	0.0	29.90	0.0000	37.25	0.0152	0.0000
	0.5		0.1999	36.27		0.0745
	1.0		0.2019	35.65		0.1210
	1.5		0.2004	35.05		0.1660
	2.0		0.2008	34.60		0.2010
	2.5		0.2021	34.15		0.2340
	3.0		0.2012	33.75		0.2640
	3.5		0.2000	33.30		0.3000
	4.0		0.2009	32.85		0.3340
CAc No. 14	0.0	29.90	0.0000	37.25	0.0152	0.0000
	0.5		0.2005	36.35		0.0685
	1.0		0.2012	35.65		0.1210
	1.5		0.2007	35.15		0.1590
	2.0		0.2029	34.70		0.1920
	2.5		0.2018	34.10		0.2370
	3.0		0.2020	33.70		0.2680
	3.5		0.2010	33.30		0.2980
	4.0		0.1991	32.85		0.3360

In literature dealing with periodate oxidation the consumption of periodate is usually expressed in terms of moles of HIO_4 consumed per unit molecular weight. The conversion of milliequivalents per gram to moles per unit molecular weight can be made by multiplying by the unit molecular weight and dividing by 2000, as shown below:

$$\text{Consumption of } HIO_4 \text{ in moles per unit molecular weight} = \left[\text{meq./ g.}\right] \frac{\text{(unit molecular weight)}}{(2000)}$$

The average consumption of periodate expressed in meq./g. was converted to moles per unit molecular weight for all the oxidation time periods recorded for cellulose and cellulose acetates. These values are recorded in table V. Inspection of the figures for the consumption of periodate expressed in meq./g. shows that there is a consistent difference between the consumption of periodate by cellulose and that consumed by the cellulose acetates. In general, the consumption of periodate decreases slightly as the per cent combined acetic acid increases. However, the effect of an increasing degree of acetylation on the periodate oxidation of cellulose acetates cannot be seen when the consumption of periodate is expressed in meq./ g., since any cellulose acetate according to its acetyl content, contains less than 100% cellulose. On the other hand, the consumption of periodate expressed in moles per unit molecular weight shows this effect. In column 4 of table V it can be seen that the differences in the consumption of periodate between cellulose and cellulose acetates of low acetyl content are actually quite small for oxidation periods up to 4 hours.

The rate of oxidation may be illustrated by plotting the consumption of HIO_4 in moles per unit molecular weight against reaction time in hours. Such a graph shows the effect of increasing degree of acetylation on the periodate oxidation of cellulose acetates, i.e., the acetyl substituents on the glycol groups of cellulose prevent cleavage of these glycol groups by periodate oxidation, and therefore, the higher the degree of acetylation the lower the consumption of periodate per unit of time.

Figure 2 is a graph showing the rate of oxidation curves for standard cellulose and cellulose acetate No. 9 (6.83% HOAc). Curves for the other cellulose acetates are not shown because they are either the same as that for cellulose (CAc No. 14, 1.28% HOAc), or fall slightly below the curve for cellulose (CAc No. 8, 3.17% HOAc and CAc No. 12, 3.84% HOAc), or fall near the curve for cellulose acetate No. 9 (CAc No. 11, 9.53% HOAc, and CAc No. 13, 7.10% HOAc).

TABLE V

CONVERSION OF PERIODATE CONSUMPTION FROM MILLIEQUIVALENTS PER GRAM TO MOLES PER UNIT MOLECULAR WEIGHT

Sample No.	Reaction Time, hrs.	Periodate Consumption	
		Milliequivalents per Gram (av.)	Moles per Unit Molecular Wgt.
S.C.	0.5	0.0703	0.005695
	1.0	0.1204	0.009750
	1.5	0.1600	0.01295
	2.0	0.2020	0.01635
	2.5	0.2360	0.0191
	3.0	0.2690	0.0218
	3.5	0.3000	0.0243
	4.0	0.3330	0.0270
CAc No. 8 3.17% HOAc	0.5	0.0667	0.005525
	1.0	0.1137	0.00942
	1.5	0.1535	0.01272
	2.0	0.1950	0.01616
	2.5	0.2270	0.01881
	3.0	0.2650	0.02198
	3.5	0.2900	0.02403
	4.0	0.3170	0.02630
CAc No. 9 6.83% HOAc	0.5	0.0616	0.00524
	1.0	0.0956	0.00813
	1.5	0.1402	0.01192
	2.0	0.1671	0.01422
	2.5	0.2027	0.01722
	3.0	0.2300	0.01955
	3.5	0.2640	0.02245
	4.0	0.2835	0.02410
CAc No. 10 6.06% HOAc	0.5	0.0456	0.00386
	1.0	0.0910	0.00770
	1.5	0.1270	0.01075
	2.0	0.1631	0.01380
	2.5	0.1915	0.01620
	3.0	0.2270	0.01920
	3.5	0.2450	0.02072
	4.0	0.2765	0.02340

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TABLE V - Concluded

Sample No.	Reaction Time, hrs.	Periodate Consumption	
		Milliequivalents per Gram (av.)	Moles per Unit Molecular Wgt.
CAc No. 11 9.53% HOAc	0.5	0.0710	0.00616
	1.0	0.1071	0.00930
	1.5	0.1424	0.01235
	2.0	0.1770	0.01535
	2.5	0.2033	0.01765
	3.0	0.2270	0.01970
	3.5	0.2505	0.02174
	4.0	0.2870	0.02490
CAc No. 12 3.84% HOAc	0.5	0.0710	0.00590
	1.0	0.1082	0.00900
	1.5	0.1600	0.01333
	2.0	0.1890	0.01574
	2.5	0.2280	0.01900
	3.0	0.2625	0.02185
	3.5	0.2885	0.02400
	4.0	0.3250	0.02705
CAc No. 13 7.10% HOAc	0.5	0.0610	0.00520
	1.0	0.1055	0.00899
	1.5	0.1422	0.01212
	2.0	0.1692	0.01442
	2.5	0.2050	0.01747
	3.0	0.2315	0.01975
	3.5	0.2740	0.02338
	4.0	0.2935	0.02500
CAc No. 14 1.28% HOAc	0.5	0.0715	0.00584
	1.0	0.1210	0.00988
	1.5	0.1635	0.01335
	2.0	0.1965	0.01605
	2.5	0.2355	0.01923
	3.0	0.2660	0.02172
	3.5	0.2990	0.02430
	4.0	0.3350	0.02735

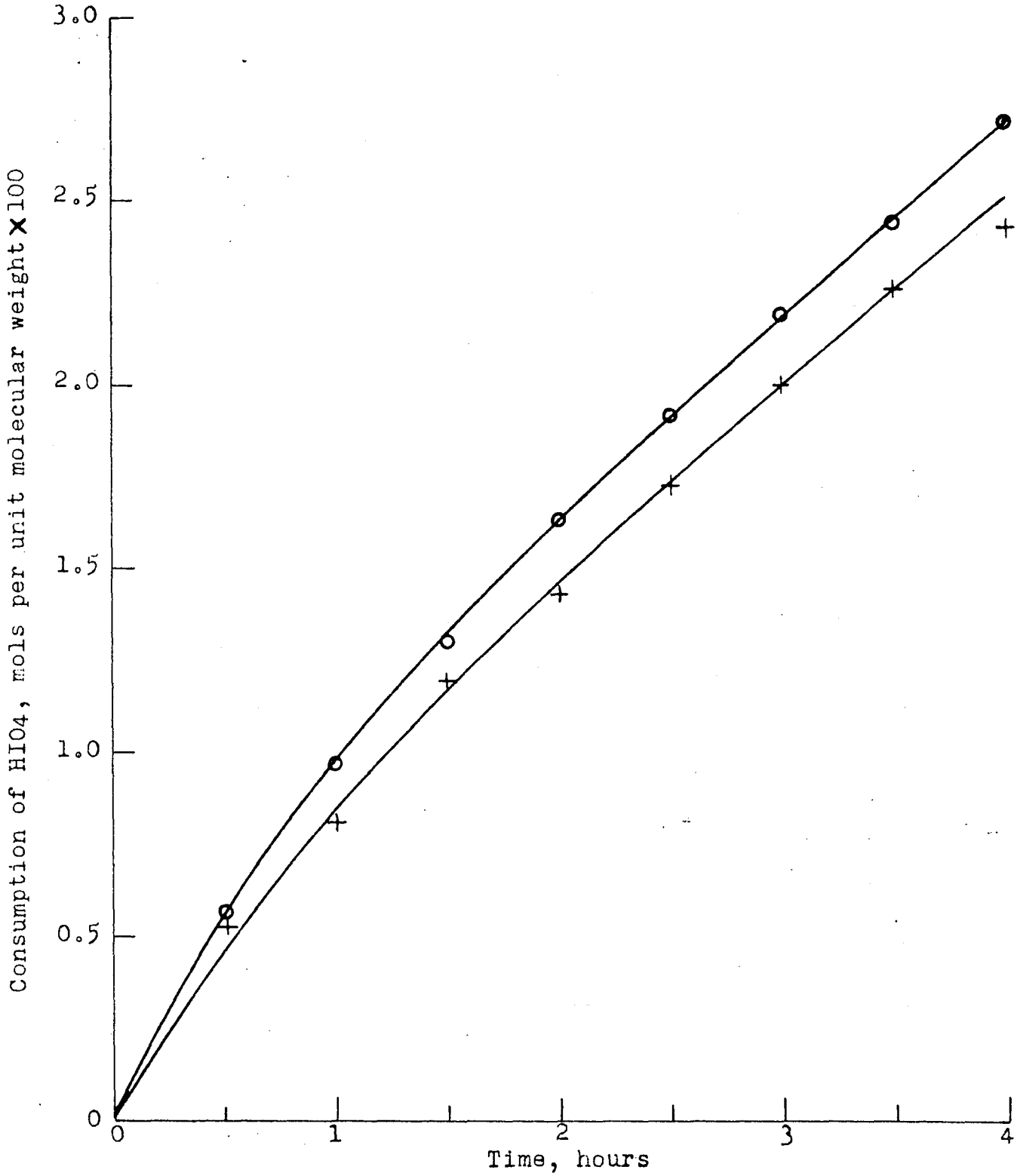

Figure 2

Periodate oxidation, initial reaction, 30°C.

O Cotton cellulose

\+ Cellulose acetate No. 9, 6.83% HOAc.

Long Time Oxidations and the Effect of Mixing.

In the preceding section cellulose and cellulose acetates were oxidized for time periods up to four hours. During this more or less initial phase of the reaction, with respect to the over-all theoretical oxidation, the rate of reaction is fairly rapid, due to the greater accessibility of the glycol groups present in the amorphous and semi-crystalline areas of cellulose. A study of the effect of partial acetylation on the periodate oxidation of cellulose would not be complete unless the oxidations were carried out over a fairly long period of time. This section deals with oxidation experiments that were performed for time periods of several days, and the reaction period that was selected for comparisons between cellulose and cellulose acetates was 60 hours.

The first experiment in long time oxidation was performed on standard cellulose for varying periods of time up to 120 hours. Except for the volume of oxidizing solution and the method of sampling for excess HIO_4, the oxidation procedure was the same as that used in the 4-hour oxidations. The total amount of available periodate in a 4-hour oxidation mixture was approximately 3 meq. per gram of cellulose or 0.243 moles of periodate per unit molecular weight. In 4 hours cellulose consumed 0.027 moles of HIO_4 per unit molecular weight, and therefore, the concentration of the oxidation medium changed a little over 10% during the course of the oxidation.

It was thought that the concentration of the oxidizing medium could be allowed to change as much as 50% without decreasing the rate

of reaction, since in this heterogeneous oxidation the rate of oxidation is dependent more on the rate of diffusion of periodate into the cellulose structure, than on the concentration of the oxidizing medium. However, in order to minimize any possible change in the rate of oxidation due to a decrease in the concentration of the oxidant, a considerable excess of periodic acid was used in these long time oxidations. The volume of oxidant selected for use in the following experiments was such that there were 7.5 milliequivalents of HIO_4 for each gram of cellulosic material.

A 0.2-g. sample of cellulose was weighed into a 125-ml. Erlenmeyer flask, wetted with 25 ml. of water, and 25 ml. of approximately 0.06 N HIO_4 solution was added. After oxidation and cooling the mixture was filtered through a Gooch crucible into a clean 125-ml. flask. Two 20-ml. samples of this filtrate were analyzed for excess periodate. Blank determinations were carried out at 24 hour intervals. The average titration volumes of arsenite solution were used for the calculation of periodate consumption. The equation used to calculate the consumption of periodate was as follows:

$$HIO_4 \text{ meq./g.} = \frac{(B-S)\ (N \text{ of arsenite})\ (2.5)}{(\text{g. of cellulose})}$$

where B is the ml. of arsenite used to titrate the blank; and S is the average titer for the 20-ml. fractions of the filtrate solution. The results of these oxidations are recorded in table VI.

TABLE VI

PERIODATE OXIDATION OF CELLULOSE UP TO 120 HOURS

Reaction Time, hrs.	Temp. °C.	Sample Wgt., g.	Arsenite Titer, ml.	Normality of St. Arsenite	HIO_4 Consumed meq./ g.	HIO_4 Consumed Moles per Unit Mol. Wgt.
0	29.85	0.0000	44.85	0.01462	0.0000	0.00000
3		0.1997	43.20		0.2923	0.02318
6		0.1993	42.10		0.5040	0.04082
12		0.2005	40.65		0.765	0.06195
18		0.2011	39.00		1.064	0.0862
24		0.2002	37.70		1.305	0.1057
36		0.2002	35.35		1.735	0.1405
48		0.1985	33.10		2.165	0.1754
60		0.1972	32.20		2.344	0.1900
77.5		0.2000	28.65		2.960	0.2398
96		0.2015	26.30		3.350	0.2713
120		0.1996	23.15		3.710	0.3004

In all of the previous experiments the oxidation mixture was not stirred or mixed in any way during the reaction period. Other investigators studying the periodate oxidation of cellulose have mentioned the use of "frequent shaking" or "occasional stirring" as having been applied during the course of the reaction. Any procedure of this sort would be very difficult to standardize for a great number of oxidation mixtures, and therefore, it was thought that the problem of applying c controlled stirring during the reaction period should be investigated.

Because of the limitations of space, equipment, and time, the application of stirring to a large number of small reaction flasks was considered to be unfeasible. A more efficient method of attack would

be to oxidize a fairly large amount of material with a proportionally larger volume of oxidizing solution, the mixture being stirred at a constant rate. Samples of the oxidation media could be removed at various time intervals, analyzed, and the decrease in concentration of the oxidizing solution used to calculate the periodate consumed by the cellulosic material. Sampling a reaction mixture that is a homogeneous solution in this way would only change the total volume of the mixture and would not change the concentration of the materials in solution. However, in any mixture of linters suspended in an oxidizing solution, it would be quite impractical if not impossible to obtain a homogeneous sample of the mixture. On the other hand, if a considerable excess of periodate is available at the beginning of an oxidation, small samples of the solution may be removed at intervals over a period of time without appreciably affecting the rate of the reaction. For example: in one particular oxidation reaction, the available periodate at the beginning of the oxidation was 7.18 meq./g., and at the end of 60 hours there was still 5.03 meq./ g. left in the reaction flask, even though four 10-ml. samples of the solution had been removed. This means that 70% of the initial periodate is still available, and therefore, the decrease in the amount of available periodate due to sampling would not have affected the reaction rate appreciably.

In the next experiments oxidations were carried out with mechanical stirring. The reaction mixtures were stirred with cone-drive electric stirring motors, and samples were removed from the reaction

mixture at various intervals of time. Several 1-liter 3-neck round bottom flasks were fitted with stirrers and filter sticks. The stirrer was a 6-mm. glass rod with a 45° bend 4 cm. from one end, and was held in place in the flask by a glass sleeve extending through a cork in the neck of the flask. The filter stick was made from a 7-mm. (inside diameter) x 25-cm. pyrex tube by shrinking the diameter of the tube in an oxygen flame to 1 mm. at a point 1 cm. from one end. A compact mass of fine glass wool was pressed into this small cup and trimmed even with the end of the tube. Three stirring motors were regulated to about 250 revolutions per minute. Three sets of the reaction flask-stirring apparatus could be placed in the constant temperature bath at one time.

Oxidations were performed as follows: a 2-g. sample of cellulose or cellulose acetate was weighed into the reaction flask and suspended in 250 ml. of water measured with a standard 50-ml. pipet at 20° C. This mixture was stirred for 1 hour at 30° C. At zero reaction time 250 ml. of approximately 0.06 N periodic acid was measured with the same standard 50-ml. pipet and added to the aqueous suspension of linters. The reaction temperature rose to 30° C. within five minutes. The available periodate in this oxidizing medium was 7.5 meq./g. or 0.607 moles of HIO_4 per unit molecular weight. At intervals of time, according to a previously arranged schedule, 10-ml. samples of the oxidizing solution were withdrawn through the filter stick with a standard 10-ml. pipet calibrated at 30° C. The inside diameter of the filter stick was such that the pipet could be inserted to the

point of constriction in the filter stick. The samples were analyzed for periodic acid content. Blank determinations were made at 24 hour intervals.

Several oxidations with stirring were performed on cellulose and cellulose acetate for periods up to 6 hours, with sampling at 0.5 hour intervals. This oxidation reaction was found to progress more rapidly than that previously observed during a 4 hour period without stirring. However, the results were not satisfactory from the standpoint of reproducibility. Apparently a variation in the rate of stirring affected the rate of the reaction. The data for one sample of cellulose is recorded in table VIII so that a comparison may be made between the rate of reaction between stirred and non-stirred reactions. All other data obtained in these experiments will be omitted.

The same oxidation procedure (above) was used to test the reproducibility of results that would be obtained during a reaction where the oxidation period was as long as 60 hours. The stirring motors were very carefully readjusted and synchronized for the same rate of stirring. The reaction medium was sampled at 12 hour intervals. The data obtained for cellulose and two samples of cellulose acetate are recorded in table VIII.

The calculation of the consumption of periodate by a known weight of cellulose is more complex in the case of a reaction mixture where samples of the oxidant are removed at intervals. The calculation may be simplified if, for each time of sampling the total periodate content of the solution is determined. For example, at zero time the normality

of the oxidizing medium (determined by a blank analysis) multiplied by the volume of the solution yields the total milliequivalents of periodate present at this time. Since the concentration of the solution is also determined at each sampling time, the total milliequivalents of periodate in the volume of solution present before sampling may also be determined for each sampling time. But each sample removed contains some periodate, and therefore, the sum of the milliequivalents of periodate removed in previous samples must be added to the milliequivalents present in the volume of solution at any sampling time. The difference between the periodate content of the reaction mixture at zero time, and periodate content present at any sampling time plus that present in the volumes of previously removed samples, represents the periodate consumption of the cellulosic material. This difference divided by the weight of cellulose or cellulose acetate is the consumption of periodate in meq./g. Table VII is the record of a typical oxidation reaction that was stirred and in which the progress of the reaction was followed by sampling the oxidizing medium at 12 hour intervals.

TABLE VII

RECORD OF DATA AND CALCULATIONS FOR A TYPICAL OXIDATION

Cellulose sample, 1.9667 g. Normality (N) of arsenite, 0.01506

		A	B	C	D	E	F	G		
Reaction Time, hrs.	Samp. No.	Total Vol. of HIO_4 Solution ml.	Arsenite titer for 10 ml., ml.	Normality of HIO_4 Solution $\frac{B \times N}{10}$	Meq. of HIO_4 removed in 10 ml. samp. B x N	Meq. of HIO_4 in Volume (A) $D \times \frac{A}{10}$	Meq. of HIO_4 in samples previously removed	Meq. of HIO_4 in Vol.(A) plus Meq. of HIO_4 in samp.removed(F)	Consumption of Periodate by the Cellulose Sample,Meq.	Consumption of HIO_4, meq./ g.
00	0	500	21.35	0.03215	0.000	16.08	0.000	16.08	0.000	0.000
12	1	500	19.05	0.0287	0.287	14.34	0.000	14.34	1.740	0.885
24	2	490	17.35	0.0261	0.261	12.81	0.287	13.097	2.983	1.518
36	3	480	16.05	0.0242	0.242	11.60	0.548	12.148	3.932	2.000
48	4	470	14.75	0.0222	0.222	10.45	0.790	11.240	4.840	2.461
60	5	460	13.70	0.0206	0.206	9.48	1.012	10.492	5.588	2.842

TABLE VIII

OXIDATION OF CELLULOSE AND CELLULOSE ACETATES WITH STIRRING

Samp. No.	React. Time, hrs.	Temp. °C.	Sample Wgt., g.	Arsenite Titer, ml.	N of St. Ars.	HIO_4 Consumed meq./ g.	HIO_4 Consumed moles per U.M.W.
S.C.	0.0	29.85	1.9079	22.42	0.01462	0.0000	0.0000
	0.5			21.95		0.1940	0.0157
	1.0			21.65		0.2880	0.0233
	1.5			21.50		0.3740	0.0303
	2.0			21.35		0.4190	0.0339
	2.5			21.25		0.4492	0.0364
	3.0			21.10		0.5110	0.0414
	3.5			21.00		0.5423	0.0439
	4.0			20.87		0.5940	0.0481
	5.0			20.65		0.6590	0.0534
	6.0			20.40		0.7320	0.0593
S.C.	00	29.85	1.9149	22.42	0.01462	0.0000	0.0000
	12			20.15		0.8780	0.0712
	24			18.60		1.479	0.1198
	36			17.40		1.910	0.1547
	48			16.30		2.300	0.1864
	60			15.15		2.706	0.2190
	72			13.90		3.132	0.2540
	96			11.65		3.900	0.3160
	120			9.65		4.560	0.3695
	168			5.30		5.950	0.4840
	250			0.00		7.600	0.6160
S.C.	00	29.85	1.9667	21.35	0.01506	0.0000	0.0000
	12			19.05		0.885	0.0717
	24			17.35		1.518	0.1230
	36			16.05		2.000	0.1620
	48			14.75		2.461	0.1995
	60			13.70		2.842	0.2302
CAc	00	29.85	2.0013	21.35	0.01506	0.000	0.0000
No. 18	12			19.65		0.639	0.0549
8.23%	24			18.25		1.106	0.095
HOAc	36			16.95		1.628	0.140
	48			15.90		2.000	0.172
	60			15.00		2.306	0.198
CAc	00	29.85	1.9987	21.35	0.01506	0.000	0.0000
No. 20	12			19.68		0.630	0.0566
14.14%	24			18.60		1.023	0.0918
HOAc	36			17.55		1.415	0.1272
	48			16.60		1.750	0.1575
	69			15.80		2.023	0.1820

Oxidation of Cellulose Acetates for 60 Hours with Standard Mixing.

The preceeding oxidation experiments, in which standard cellulose and cellulose acetates No. 8 and 14 were oxidized for 60 hours with stirring, and in which the oxidation mixtures were sampled at 12 hour intervals to determine the decrease in periodate concentration, indicated that there was an appreciable difference in the consumption of periodate between standard cellulose and cellulose acetates.over this period of time. The problem of synchronizing the electric stirring motors, so as to produce an equal rate of stirring, still remained to be solved. The only logical solution to this problem appeared to lie in the design and construction of a special standard mixing apparatus that would not only fulfill the limitations of space and the necessity of a constant temperature bath, but also permit the mixing of several reaction mixtures under exactly the same conditions.

The thermostating and standard mixing apparatus is illustrated in figure 3. The specifications and construction of the standard mixing apparatus are described below.

The main axis of rotation (2) was made from a 0.5-inch round steel rod, 46 cm. in length. A 1-cm. flat was machined along the top of this rod, except for 2 cm. at the points of support. The main axis was supported on the battery jar by two bearings that could be clamped firmly to the jar, and held in place by cotter pins at the bearings. Four motor arms, 20 cm. in length were made to fit on the axis, and could be fixed in any desired position by tightening a set screw on the flat of the axis. Three of the motor arms were fixed about 10.5 cm. apart on

the main axis. A 2-mm. hole was drilled in each end of these arms at a point 6 cm. from the axis. The fourth motor arm was fixed on the right end of the axis, and was connected to the source of power by means of a connecting rod attached 5 cm. off-center at the motor arm, and 1.5 cm. off-center on a wheel at the power source. The length of the connecting rod could be adjusted and was free to move around a bearing at the points of connection.

The source of power (4) was a one-third horse power, 1725 r.p.m. electric motor coupled with a reducing gear (reduction ratio, 21.5) by means of a 0.5-inch V belt operating on 1-inch pulleys. The angular speed of the power source was 80 r.p.m., so that the up and down motion observed in the reaction flasks also took place at a rate of 80 cycles per minute.

The reaction flask detail can be seen quite clearly in figure 4. Ten matched sets of this apparatus were assembled. The flask was a 250-ml. 3-neck round bottom pyrex flask, 10 cm. in diameter, and selected for uniformity of dimensions. The plunger was made of pyrex glass by fusing a 6-mm. x 12.5-cm. rod to a cup, 2.5 cm. in outside diameter and 3 cm. long. A No. 12 cork was fitted with a sleeve made from a 7-mm. (inside diameter) pyrex tube 5 cm. long, with a 1-cm. jacket of 6-mm. rubber tubing at one end. The glass rod portion of the plunger was put through this snugly fitting sleeve which acts as a bearing in the up and down motion cycle of the plunger. A 1-cm. length of 6-mm. brass rod, containing a 2-mm. transverse hole drilled 2 mm. from one end was fitted with a 1 x 1.4-cm. steel wire staple bent in

a ⊔ shape. The bottom half of the small brass rod was connected to the top of the plunger rod with a 1.5-cm. length of tough 4-mm. rubber tubing. This connection was wrapped with five turns of 1-mm. copper wire. The top part of the plunger rod was lubricated with a small amount of silicone grease to facilitate the operation of the plunger in the bearing sleeve.

The filter stick was made from a pyrex tube, 7 mm. in inside diameter, and 14 cm. in length. The diameter of the tube was carefully reduced in an oxygen flame to 1 mm. at a point 1 cm. from one end. The top of the filter stick was jacketed with a 1.5-cm. length of 6-mm. rubber tubing. The filter stick was held in position in one of the side necks of the reaction flask by a No. 8 cork. A cork of the same size was used to stopper the other side neck.

The flasks were held in a rigid position in the constant temperature bath by specially constructed clamps. These clamps were in turn held by universal clamps attached to a transverse rod as shown in figure 3. A flask clamp that would hold three 250-ml. flasks was made as follows: three holes 3 cm. in diameter were drilled with 10.5 cm. between centers along the width of a piece of wood 3 cm. thick, 5 cm. wide, and 27 cm. long. Eight-mm. holes were drilled transverse to the width and halfway between the centers of the large holes. The wood was then cut in half along the width, and each half was sanded down so as to fit comfortably between the necks of the flasks. One of the halves was bolted to a 20-cm. x 0.5-inch steel rod. The clamps when in position around the center necks of the three flasks were held together by two bolts with wing nuts.

To assemble the standard mixing apparatus for an oxidation experiment the main axis of rotation, with its motor arms, was mounted across the diameter of the constant temperature bath. Pieces of chamois leather were placed between the glass and metal and the supports were clamped firmly in place. This part of the apparatus could be left in place permanently if desired. The flasks containing samples to be oxidized were arranged in the flask clamps and were fixed temporarily in position in the bath. The motor arms were tilted up or down to permit passage of the flask assembly. A plunger with cork was placed in each flask and the wire staple at the top of the plunger rod was spread apart and pressed into the small hole at the end of the motor arm. A small pair of pliers was used in this operation. The cork was then seated firmly in the neck of the flask. The flask clamps were adjusted to permit smooth operation of the plungers. The mixing apparatus was then connected to the source of power which had been carefully aligned with the axis of rotation. The flask clamps were readjusted if operation seemed noisy or caused excessive vibration. Cross rods (not shown in figure 3) were clamped permanently between the vertical rods supporting the source of power. These rods maintained the alignment of the apparatus and reduced the over-all vibration considerably. When adjusted properly the apparatus could be left in operation for periods as long as a week without requiring any attention or servicing. While in operation the constant temperature bath was shielded from the electric motor by a thick asbestos sheet. This was found necessary because the motor operated at about 65° C. Bearings and plunger rods were occasionally lubricated with silicone grease.

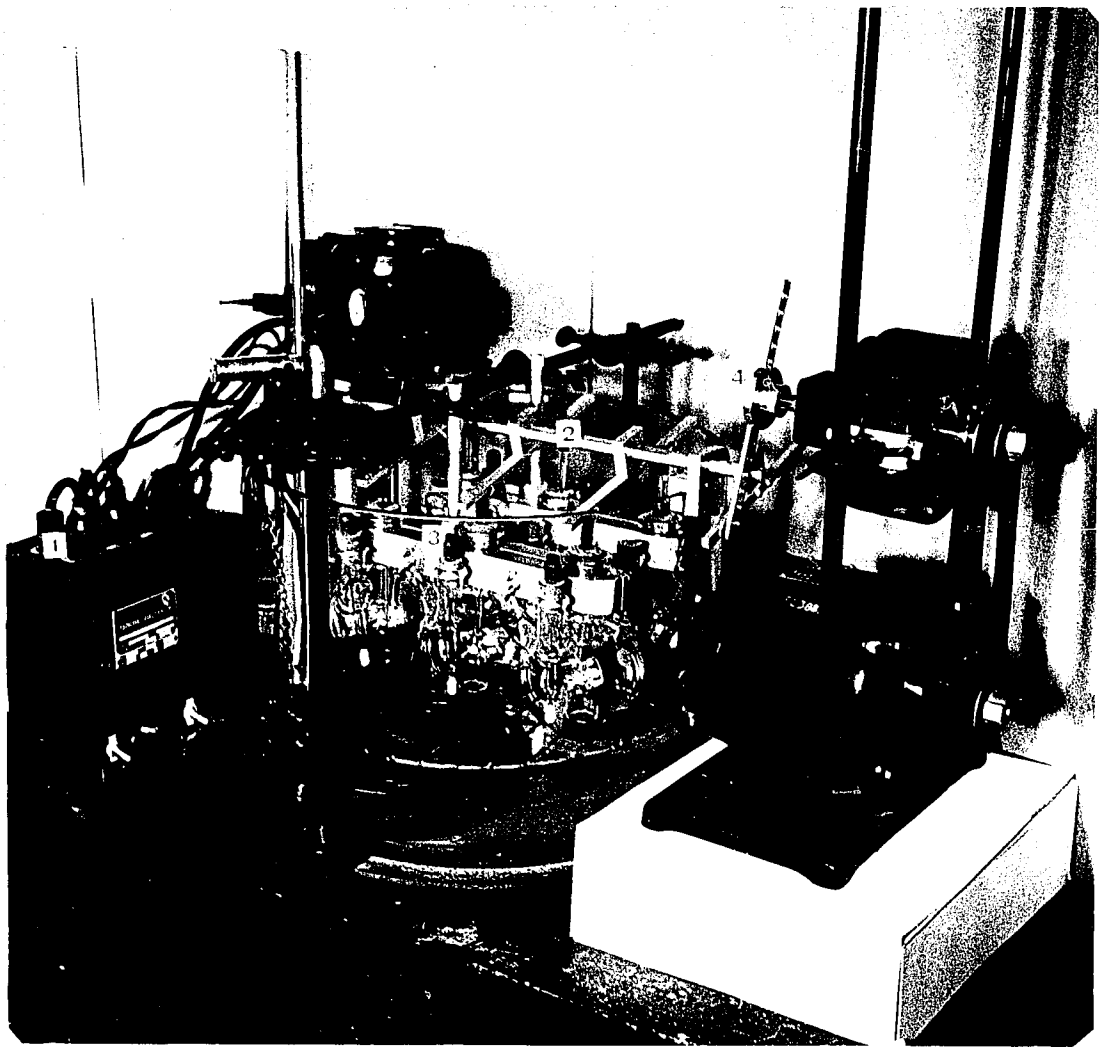

Figure 3

Thermostating and Standard Mixing Apparatus

(1) Thermostat.

(2) Axis of rotation with motor arms.

(3) Reaction flasks.

(4) Source of power.

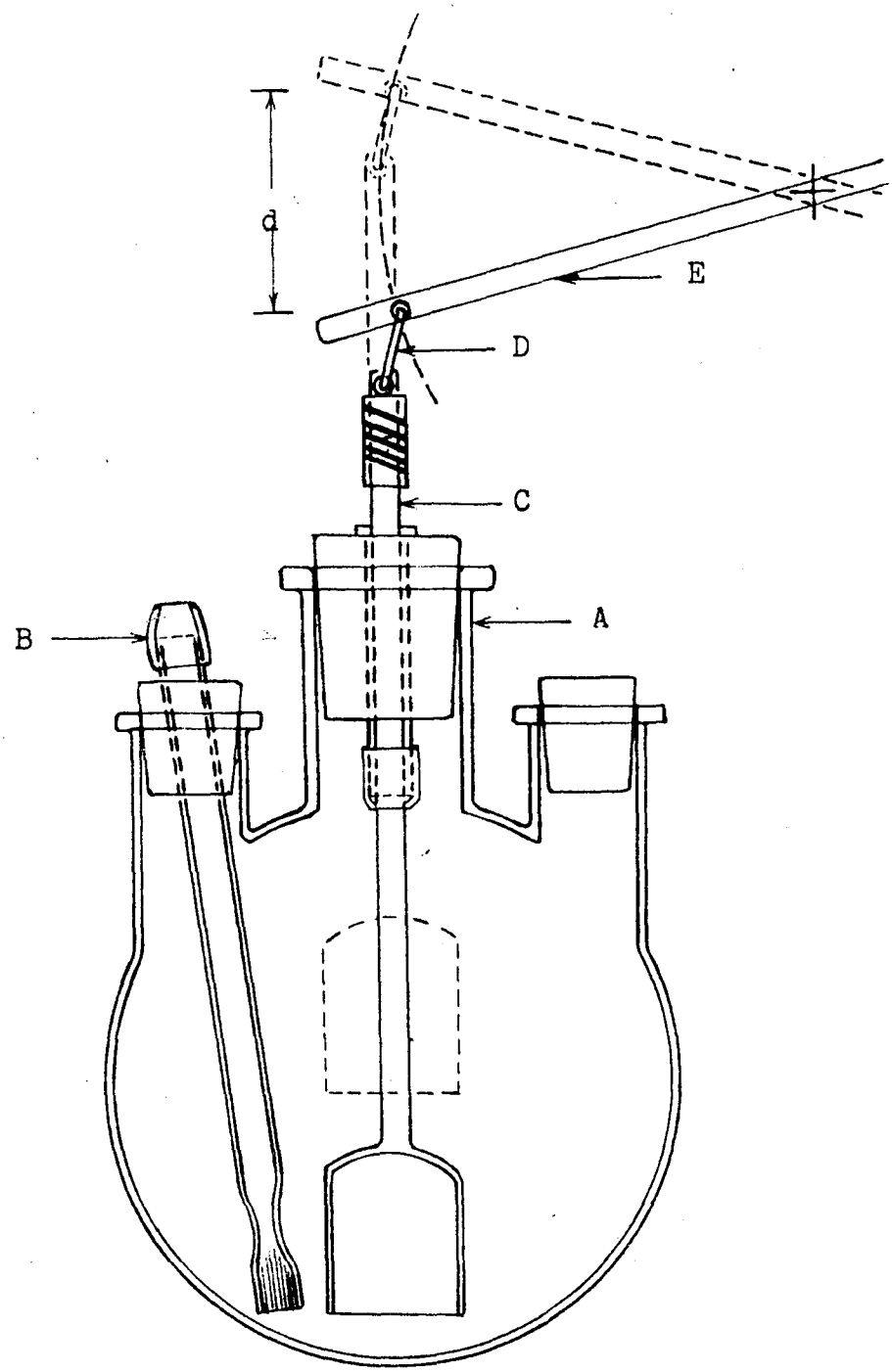

Figure 4

A Flask, 250 ml. 3-neck R.B.

B Filter stick

C Glass plunger moving through distance 'd'

D Flexible connection

E Motor arm, fixed on axis of rotation

Oxidation experiments on cellulose and cellulose acetates No. 16 to 25 were performed in the standard mixing apparatus. Six oxidations were performed at the same time. The procedure was as follows: one-g. samples of standard cellulose or cellulose acetate were weighed into the reaction flasks and suspended in 150 ml. of water measured with a standard 50-ml. pipet at 20° C. The flasks were then assembled in the constant temperature bath, and the plungers were placed in position and connected with the motor arms. The electric motor was started and the aqueous suspension of linters was mixed for 1 hour. Minor adjustments in the alignment of the flask apparatus was made during this time, so that the operation of the mixing apparatus was as smooth and quiet as possible. The filter sticks were also prepared during this period. A compact mass of pure glass wool was pressed into each filter stick cup and trimmed even with the end of the tube. The six reaction flasks were numbered from 1 to 6. At zero reaction time, 150-ml. volumes of approximately 0.06 N HIO_4 solution were measured with a standard 50-ml. pipet at 20° C. and added to the reaction mixtures in the order: 1, 2, 3, 4, 5, and 6. The additions were made at 5 minute intervals. A filter stick was placed in each reaction flask. At each sampling time, i.e., at oxidation periods of: 12, 24, 36, 48, and 60 hours; a 10-ml. sample of the oxidizing solution was removed from each flask through the filter stick with a 10-ml. pipet calibrated for 30° C., and analyzed for excess periodic acid. The 5 minute interval between sampling of different reaction flasks was sufficient to allow a short chilling period (30 seconds) and completion of the

arsenite titration for any sample before the next one was removed. The standard arsenite solution was delivered from a 25-ml. buret. Blanks were determined at 24 hour intervals.

At least two oxidations were performed for each cellulose acetate No. 16 to 25. No two oxidations of the same acetate were performed during any one 60 hour period or in the same reaction flask. This rule allows comparison of the reproducibility of results obtained on different days and perhaps under slightly different conditions. The data for oxidations of cellulose and cellulose acetates No. 16 to 25, for 60 hours with standard mixing, are recorded in table IX. Calculation of the periodate consumption was made in the same manner as described on page 60, and as illustrated in table VII. Table X shows the conversion of the average consumption of HIO_4 in milliequivalents per gram to moles per unit molecular weight. Figures 5 and 6 are graphs of the consumption of periodate in moles per unit molecular weight plotted against reaction time. It can be seen that over a reaction period of 60 hours, the rate of periodate oxidation of cellulose and cellulose acetates is approximately the same, but the acetates, in the order of increasing degree of acetylation, consume less periodate than is consumed by cellulose.

TABLE IX

OXIDATION OF CELLULOSE ACETATES FOR 60 HOURS WITH STANDARD MIXING.

Sample Number	Reaction Time hrs.	Temp. °C.	Sample Wgt., g.	Arsenite Titer, ml.	Normality of St. Arsenite	HIO_4 Consumed, meq./ g.
S.C.	00	29.85	1.0012	19.75	0.01506	0.0000
	12			17.95		0.8200
	24			16.80		1.3190
	36			15.70		1.7860
	48			14.70		2.2000
	60			13.80		2.5480
S.C.	00	29.85	1.0009	19.75	0.01506	0.0000
	12			18.00		0.7800
	24			16.75		1.3270
	36			15.70		1.7750
	48			14.70		2.1800
	60			13.70		2.5990
S.C.	00	29.85	1.0001	19.75	0.01506	0.0000
	12			17.95		0.8100
	24			16.90		1.2700
	36			15.90		1.6955
	48			14.80		2.1362
	60			13.90		2.5132
S.C.	00	29.85	0.9990	19.675	0.01506	0.0000
	12			17.87		0.8200
	24			16.65		1.3510
	36			15.68		1.7600
	48			14.70		2.1600
	60			13.80		2.5130
S.C.	00	29.85	1.0023	19.675	0.01506	0.0000
	12			17.90		0.8000
	24			16.60		1.3660
	36			15.55		1.8060
	48			14.55		2.2200
	60			13.65		2.5700

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TABLE IX - Continued

Sample Number	Reaction Time hrs.	Temp. °C.	Sample Wgt., g.	Arsenite Titer, ml.	Normality of St. Arsenite	HIO_4 Consumed, meq./ g.
S.C.	00	29.85	0.9973	21.72	0.01335	0.0000
	12			-----		------
	24			18.40		1.3400
	36			-----		------
	48			16.35		2.1320
	60			-----		------
CAc No. 16	00	29.85	1.0040	19.75	0.01506	0.0000
	12			18.20		0.6980
	24			17.00		1.2100
	36			15.95		1.6600
	48			15.00		2.0400
	60			14.10		2.3950
CAc No. 16	00	29.85	0.9995	19.55	0.01506	0.0000
	12			18.05		0.6800
	24			16.90		1.1780
	36			15.90		1.6040
	48			14.90		2.0100
	60			13.85		2.4200
CAc No. 17	00	29.85	1.0030	19.75	0.01506	0.0000
	12			18.35		0.6380
	24			17.25		1.1200
	36			16.40		1.4700
	48			15.50		1.8420
	60			14.60		2.1900
CAc No. 17	00	29.85	0.9998	19.75	0.01506	0.0000
	12			18.30		0.6600
	24			17.40		1.0445
	36			16.40		1.4725
	48			15.12		1.8965
	60			14.20		2.2490

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TABLE IX - Continued

Sample Number	Reaction Time hrs.	Temp. °C.	Sample Wgt., g.	Arsenite Titer, ml.	Normality of St. Arsenite	HIO_4 Consumed, meq./ g.
CAc No. 17	00	29.85	1.0008	19.75	0.01506	0.0000
	12			18.45		0.6000
	24			17.27		1.1020
	36			16.30		1.5120
	48			15.32		1.9147
	60			14.42		2.2657
CAc No. 18	00	29.85	1.0027	19.75	0.01506	0.0000
	12			18.50		0.5680
	24			17.48		1.0080
	36			16.60		1.3840
	48			15.80		1.7150
	60			15.00		2.0140
CAc No. 18	00	29.85	1.0000	19.75	0.01506	0.0000
	12			18.40		0.6100
	24			17.50		1.0030
	36			16.77		1.3145
	48			15.80		1.7070
	60			15.10		1.9945
CAc No. 19	00	29.85	1.0005	19.75	0.01506	0.0000
	12			18.65		0.5000
	24			17.70		0.9180
	36			17.00		1.2110
	48			16.30		1.5050
	60			15.60		1.7700
CAc No. 19	00	29.85	1.0017	19.75	0.01506	0.0000
	12			18.60		0.5190
	24			17.70		0.9080
	36			16.95		1.2310
	48			16.25		1.5150
	60			15.53		1.8000

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TABLE IX - Continued

Sample Number	Reaction Time hrs.	Temp. °C.	Sample Wgt., g.	Arsenite Titer, ml.	Normality of St. Arsenite	HIO_4 Consumed, meq./ g.
CAc No. 19	00	29.85	1.0018	19.75	0.01506	0.0000
	12			18.60		0.519
	24			17.62		0.938
	36			16.90		1.252
	48			16.10		1.578
	60			15.45		1.830
CAc No. 19	00	29.85	1.0005	19.55	0.01506	0.000
	12			18.35		0.540
	24			17.48		0.923
	36			16.75		1.230
	48			16.02		1.531
	60			15.30		1.810
CAc No. 20	00	29.85	0.9982	19.80	0.01506	0.000
	12			18.72		0.482
	24			17.92		0.840
	36			17.00		1.220
	48			16.25		1.535
	60			15.60		1.780
CAc No. 20	00	29.85	0.9980	19.75	0.01506	0.000
	12			18.85		0.401
	24			17.70		0.908
	36			16.90		1.252
	48			16.10		1.580
	60			15.40		1.850
CAc No. 20	00	29.85	1.0006	19.55	0.01506	0.000
	12			18.35		0.540
	24			17.60		0.873
	36			16.90		1.168
	48			16.10		1.494
	60			15.45		1.747

(Cont'd next page)

TABLE IX - Continued

Sample Number	Reaction Time hrs.	Temp. °C.	Sample Wgt., g.	Arsenite Titer, ml.	Normality of St. Arsenite	HIO_4 Consumed, meq./ g.
CAc No. 21	00	29.85	0.9986	19.80	0.01506	0.000
	12			18.20		0.721
	24			17.15		1.189
	36			16.15		1.600
	48			15.40		1.910
	60			14.45		2.275
CAc No. 21	00	29.85	1.0013	19.75	0.01506	0.000
	12			18.10		0.750
	24			17.15		1.175
	36			16.20		1.575
	48			15.30		1.931
	60			14.35		2.300
CAc No. 22	00	29.85	1.0028	19.80	0.01506	0.000
	12			18.30		0.669
	24			17.30		1.110
	36			16.45		1.460
	48			15.67		1.782
	60			14.90		2.085
CAc No. 22	00	29.85	1.0021	19.75	0.01506	0.000
	12			18.30		0.659
	24			17.25		1.112
	36			16.40		1.471
	48			15.55		1.904
	60			14.75		2.130
CAc No. 23	00	29.85	1.0015	19.75	0.01506	0.000
	12			18.45		0.640
	24			17.45		1.030
	36			16.50		1.427
	48			15.60		1.800
	60			14.80		2.103

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TABLE IX - Continued

Sample Number	Reaction Time hrs.	Temp. °C.	Sample Wgt., g.	Arsenite Titer, ml.	Normality of St. Arsenite	HIO_4 Consumed, meq./ g.
CAc No. 23	00	29.85	1.0022	19.75	0.01506	0.000
	12			18.40		0.578
	24			17.35		1.110
	36			16.45		1.438
	48			15.60		1.790
	60			14.85		2.085
CAc No. 23	00	29.85	1.0021	19.55	0.01506	0.000
	12			18.15		0.628
	24			17.10		1.095
	36			16.30		1.420
	48			15.40		1.790
	60			14.50		2.142
CAc No. 24	00	29.85	0.9989	19.75	0.01506	0.000
	12			18.58		0.522
	24			17.50		1.005
	36			16.65		1.357
	48			15.80		1.706
	60			15.05		2.000
CAc No. 24	00	29.85	1.0028	19.75	0.01506	0.000
	12			18.35		0.638
	24			17.50		1.000
	36			16.60		1.356
	48			15.85		1.685
	60			15.05		2.000
CAc No. 24	00	29.85	1.0003	19.55	0.01506	0.000
	12			18.20		0.610
	24			17.28		1.010
	36			16.50		1.335
	48			15.70		1.667
	60			14.80		2.021

(Cont'd next page)

TABLE IX - Concluded

Sample Number	Reaction Time hrs.	Temp. °C.	Sample Wgt., g.	Arsenite Titer, ml.	Normality of St. Arsenite	HIO_4 Consumed, meq./ g.
CAc No. 25	00	29.85	1.0006	19.80	0.01506	0.000
	12			18.50		0.580
	24			17.40		1.070
	36			16.72		1.360
	48			15.95		1.670
	60			15.20		1.956
CAc No. 25	00	29.85	0.9994	19.75	0.01506	0.000
	12			18.72		0.460
	24			17.60		0.960
	36			16.72		1.335
	48			15.85		1.683
	60			15.10		1.964

TABLE X

CONVERSION OF PERIODATE CONSUMPTION FROM MILLIEQUIVALENTS PER GRAM TO MOLES PER UNIT MOLECULAR WEIGHT

Sample No.	Reaction Time, hrs.	Periodate Consumption: Milliequivalents per Gram (av.)	Periodate Consumption: Moles per Unit Molecular Wgt.
S.C.	12	0.8080	0.0655
	24	1.3290	0.1077
	36	1.7645	0.1430
	48	2.1741	0.1760
	60	2.5460	0.2063
CAc No. 16 0.65% HOAc	12	0.689	0.0561
	24	1.194	0.0972
	36	1.632	0.1328
	48	2.025	0.1647
	60	2.407	0.1958
CAc No. 17 5.13% HOAc	12	0.633	0.0532
	24	1.090	0.0916
	36	1.484	0.1247
	48	1.881	0.1582
	60	2.235	0.1878
CAc No. 18 8.23% HOAc	12	0.590	0.0507
	24	1.005	0.0864
	36	1.349	0.1160
	48	1.711	0.1471
	60	2.004	0.1723
CAc No. 19 12.09% HOAc	12	0.5176	0.0458
	24	0.9216	0.0815
	36	1.231	0.1089
	48	1.532	0.1356
	60	1.800	0.1592
CAc No. 20 14.14% HOAc	12	0.474	0.0426
	24	0.874	0.0789
	36	1.213	0.1090
	48	1.536	0.1381
	60	1.792	0.1611

(Cont'd next page)

TABLE X - Concluded

Sample No.	Reaction Time, hrs.	Periodate Consumption: Milliequivalents per Gram (av.)	Periodate Consumption: Moles per Unit Molecular Wgt.
CAc No. 21 3.40% HOAc	12	0.735	0.0610
	24	1.182	0.0981
	36	1.587	0.1317
	48	1.920	0.1585
	60	2.287	0.1900
CAc No. 22 5.31% HOAc	12	0.6635	0.0558
	24	1.1110	0.0935
	36	1.465	0.1233
	48	1.843	0.1552
	60	2.107	0.1773
CAc No. 23 6.60% HOAc	12	0.615	0.0522
	24	1.080	0.0917
	36	1.435	0.1216
	48	1.793	0.1522
	60	2.110	0.1792
CAc No. 24 8.65% HOAc	12	0.590	0.0509
	24	1.005	0.0867
	36	1.350	0.1165
	48	1.686	0.1455
	60	2.007	0.1731
CAc No. 25 9.94% HOAc	12	0.520	0.0452
	24	1.015	0.0882
	36	1.347	0.1171
	48	1.676	0.1458
	60	1.960	0.1705

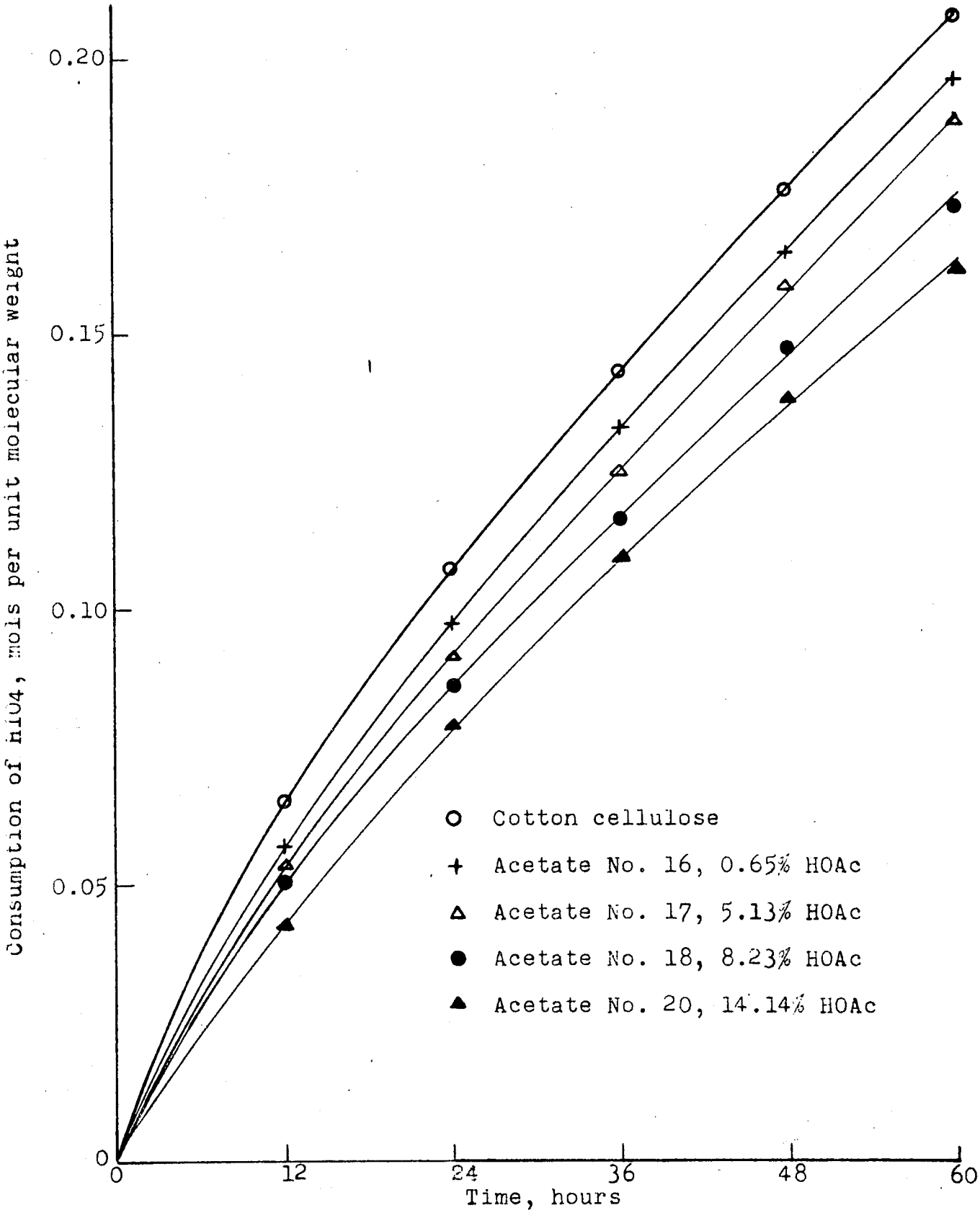


Figure 5

Periodate oxidation, 60 hours at 30° C., with standard mixing.

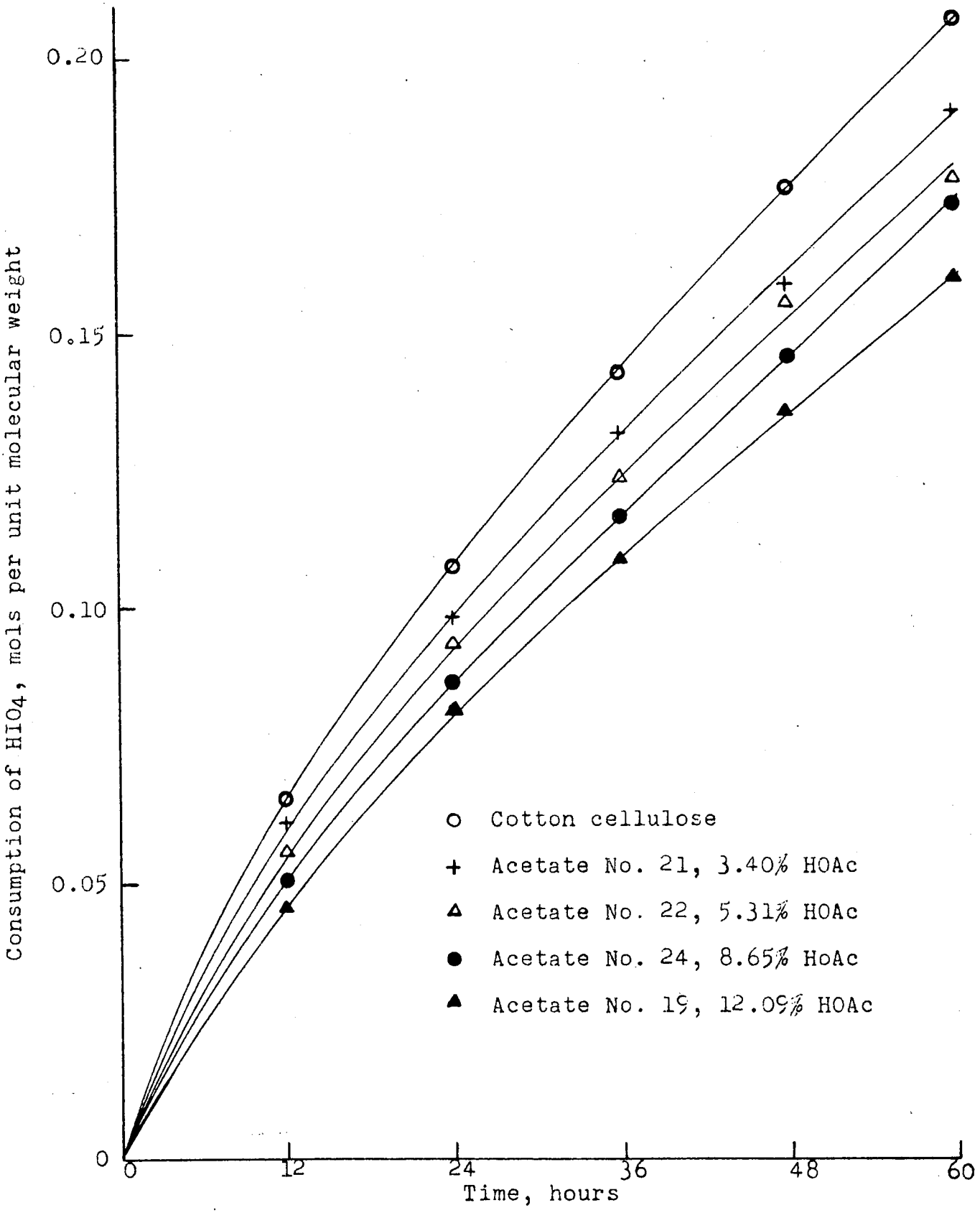


Figure 6

Periodate oxidations, 60 hours at 30°C., with standard mixing.

Periodate Oxidation of Sulfuric Acid Hydrocelluloses.

The cellulose acetates used in this investigation were acetylated in the presence of sulfuric acid. This acid may react with cellulose in two ways: (1) it may hydrolyze some of the glycosidic linkages of cellulose, and thereby decrease the degree of polymerization of the cellulose and increase the number of terminal groups (those that have three adjacent hydroxyl groups); (2) it may form sulfoesters with the hydroxyl groups of cellulose. In terms of the reaction of periodic acid with cellulose, an increase in the number of adjacent hydroxyl groups would increase the consumption of periodate, but, if some of the glycol hydroxyls are esterified with sulfuric acid, the consumption of periodate would be decreased.

In order to find out which of the reactions of sulfuric acid with cellulose had the greatest effect on the periodate oxidation of cellulose, the following experiment was undertaken. Four 5-g. samples of fibrous standard cellulose (numbered 1, 2, 3 and 4) were treated with 100-ml. portions of 0.5 M sulfuric acid and thermostated at 30° C. for 1, 2, 3 and 4 hours respectively. At the end of each reaction time, the sample was washed thoroughly until free from acid (ten 1-liter portions of water). It was then steeped in 600 ml. of water at 60° C. for 24 hours, after which it was washed with four 1-liter portions of water. The sample was pulled apart, dried in a vacuum oven at 55° C. for 4 hours, cut to 20-mesh linters, and conditioned at 65% relative humidity for several days.

Hydrocellulose samples 2, 3 and 4 were oxidized for 60 hours with standard mixing in exactly the same manner as used for the oxidation of cellulose acetates under these conditions. The data for these oxidations are recorded in table XI. The symbol H.C. is used to designate hydrocellulose.

At the top of table XI the average consumption of periodate is listed for standard cellulose. If the periodate consumption of the hydrocelluloses are compared with that of standard cellulose, it can be seen that the periodate consumption decreases slightly for hydrocelluloses according to increasing length of time that these hydrocelluloses were steeped in 0.5 M sulfuric acid. The sulfate content for the hydrocelluloses was not determined, as it was only desired to find out which of the two reactions of sulfuric acid with cellulose was predominant. The preparation of hydrocelluloses involved the use of a total of 0.0308 mole of cellulose units and 0.05 mole of sulfuric acid. The mole ratio would be 1 : 1.623, as compared with 1 : 0.238 used in the preparation of cellulose acetates. The concentration of sulfuric acid used in hydrocellulose preparations was 0.5 M as compared to 0.056 M used in the preparation of cellulose acetates. The reaction time was generally longer in the case of the cellulose acetates, but the sulfuric acid available for esterification was less, and the acid was more dilute. The data for the oxidation of the hydrocelluloses may show the effect of sulfuric acid on the consumption of periodate, but this data, due to the differences in conditions, cannot be accurately compared with that for the periodate consumption

TABLE XI

PERIODATE OXIDATION OF SULFURIC ACID HYDROCELLULOSE

Sample No.	Reaction Time, hrs.	Temp. °C.	Sample Wgt., g.	Arsenite Titer, ml.	N of Arsenite	HIO_4 Consumed meq./ g.	HIO_4 Consumed Moles per Unit Mol. Wgt.
S.C.*	00					0.0000	0.0000
	12					0.8080	0.0655
	24					1.3290	0.1077
	36					1.7645	0.1430
	48					2.1714	0.1760
	60					2.5460	0.2063
H.C. No. 2	00	29.85	0.9985	19.675	0.01506	0.0000	0.0000
	12			18.00		0.761	0.0616
	24			16.85		1.263	0.1022
	36			15.85		1.690	0.137
	48			14.85		2.098	0.170
	60			13.90		2.470	0.200
H.C. No. 2	00	29.85	0.7304	19.675	0.01506	0.000	0.0000
	12			18.55		0.700	0.0567
	24			17.60		1.260	0.1020
	36			16.90		1.680	0.1360
	48			16.80		2.070	0.1680
	60			15.48		2.450	0.1985
H.C. No. 3	00	29.85	1.0031	19.675	0.01506	0.000	0.0000
	12			17.95		0.778	0.0630
	24			16.75		1.300	0.1055
	36			15.68		1.752	0.1420
	48			14.70		2.150	0.1740
	60			13.85		2.483	0.2010
H.C. No. 4	00	29.85	1.0026	19.675	0.01506	0.000	0.0000
	12			18.15		0.688	0.0557
	24			16.88		1.239	0.1004
	36			15.85		1.679	0.1360
	48			14.95		2.043	0.1655
	60			14.10		2.372	0.1920

* Standard Cellulose values are taken from X.

of cellulose acetates. Further periodate oxidations of sulfuric acid hydrocelluloses was left as a subject for future research.

Oxidation of Acetone Soluble Cellulose Acetates.

The work of Purves and coworkers[5,17] on the lead tetra-acetate oxidation of acetone soluble cellulose acetates shows that a very small number of glycol groups may exist in these highly acetylated celluloses. It was thought that it would be interesting to determine whether or not the existence of such small amounts of glycol groups could be confirmed by the periodate oxidation method. Acetone soluble cellulose acetates of comparable specifications were oxidized in the following experiment.

Four Eastman Kodak commercial cellulose acetate samples were labeled as shown below.

No. 4644: Acetone soluble, low viscosity, high acetyl.

No. 4650: Acetone soluble, low-medium viscosity, high acetyl.

No. 4655: Acetone soluble, high-medium viscosity, low acetyl.

No. 2314: Cellulose triacetate.

The samples were in the form of a coarse powder. Each sample was inspected for uniformity and cut in the Wiley mill to a 20-mesh or finer powder and conditioned for several days at 65% relative humidity. Sample No. 4644 was found to contain 3.5% moisture. Each sample was analyzed for per cent combined acetic acid as described on page . The results are listed in table XII.

Powdered acetone soluble cellulose acetate was very difficult to wet with water and floated on top of the aqueous oxidizing medium.

TABLE XII

ANALYSIS OF COMMERCIAL CELLULOSE ACETATES

Cellulose Acetate No.	Analysis for per cent Combined Acetic Acid				Percent Acetyl	Degree of Substitution.	Unit Mol. Wgt.
	Sample wgt., g.	ml. of st. KOH	N of st. KOH	HOAc %			
EK4644	0.5856	36.65	0.1934	54.00			
	0.6253	38.40		54.10			
	0.5301	34.15		54.40			
	0.0000	9.40					
			av.	54.16	37.90	2.356	261.0
EK4650	0.5406	34.88	0.1934	54.90			
	0.5621	36.00		55.10			
	0.5779	36.80		55.30			
	0.0000	9.40					
			av.	55.10	38.55	2.421	263.8
EK4655	0.6004	37.20	0.1934	54.00			
	0.5086	33.05		54.20			
	0.5478	34.75		53.90			
	0.0000	9.40					
			av.	54.03	37.80	2.348	260.6
EK2314	0.5369	36.90	0.1934	59.65			
	0.5327	36.10		58.40			
	0.5311	37.10		60.80			
	0.0000	9.40					
			av.	59.62	41.72	2.767	278.2

The problem of wetting and dispersion was solved by the use of a very small concentration of detergent. A 0.01% aqueous solution of "Duponol Mn dry" was the smallest optimum concentration that would wet the powder in 10 minutes. A volume of this 0.01% solution of detergent, when mixed with an equal volume of approximately 0.06 N HIO_4, did not consume any periodic acid when the mixture was allowed to stand for 72 hours at room temperature.

The three acetone soluble cellulose acetates and the cellulose triacetate were oxidized in the standard mixing apparatus for 72 hours. A sample of standard cellulose and a blank made up with the detergent solution were oxidized at the same time. The method of oxidation was the same as used for the 60 hr. oxidation of cellulose and cellulose acetates with standard mixing, except that only three 10-ml. samples were removed from the oxidation reaction, and these at 24 hour intervals. Over the 72 hour period the concentration of periodate in the reaction flasks containing the four commercial cellulose acetates remained constant. This shows that no oxidation of the cellulose acetates occurred. The suspended solid particles appeared to be swollen and translucent at the end of the oxidation period, and there was no reason to believe that the oxidizing solution had not been able to penetrate throughout each particle.

The proportions of materials present during the lead tetra-acetate oxidation of cellulose acetate as performed by Purves[5,17] were: 0.01 mole of cellulose acetate (unit mol. wgt. 259.8) dissolved in 100 ml. of glacial acetic acid that was 0.025 N with respect to lead tetra-acetate.

The reaction temperature was 25° C. After a reaction time of about 80 hours, a break in the oxidation rate curve was interpreted to mean that true glycol oxidation had ended, and at this point the consumption of oxidant corresponded to 0.01 mole of glycol per unit molecular weight. This is the same thing as saying that there is 1 glycol group in 100 glucose residues, all of the other glycol groups having been blocked by acetyl groups.

The question remains whether this small amount (0.01 mole) of glycol could be detected over a 72 hour period of oxidation with 0.03 N periodic acid. The consumption of periodate by cellulose over a period of 72 hours under standard mixing conditions and at 30° C. was only .227 mole per unit molecular weight, and therefore only about 22.7% of the total glycol content had been oxidized. On the other hand, a commercial acetate is far more amorphous in structure than native cellulose and therefore should be penetrated and oxidized more rapidly. If the value of 0.01 mole of glycol per unit molecular weight is converted to a figure that would represent a difference between blank and sample titrations with 0.015 N arsenite (such as observed during the course of a periodate oxidation), this value would correspond to 0.17 ml. Although a titration difference of this order could be observed, it is doubtful that a smaller difference, say .05 ml. (that would correspond to only partial oxidation of a cellulose acetate), could be determined by the method of analysis used.

In conclusion, it was considered that the work of Purves had not been confirmed.

IV DISCUSSION

THE NATURE OF FIBROUS CELLULOSE ACETATES OF LOW ACETYL CONTENT

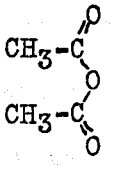
The Acetylation Reaction.

The reaction of cellulose with acetic anhydride to form cellulose triacetate may be expressed as:

$$C_6H_7O_2(OH)_3 + 3(CH_3CO)_2O \longrightarrow C_6H_7O_2(OCOCH_3)_3 + 3CH_3COOH$$

This equation shows that at least three moles of acetic anhydride are required to completely esterify the hydroxyl groups of cellulose.

The acetylation of cellulose proceeds very slowly unless a so-called catalyst is added to the reaction mixture. Sulfuric acid was used as the catalyst in the preparation of the cellulose acetates studied in this investigation. Some of the ideas that have been expressed concerning the specific role of sulfuric acid in the acetylation reaction should be reviewed briefly. Franchimont[16] considered that sulfuric acid reacted with acetic anhydride to form acetyl sulfuric acid. This acid is the acetylating reagent and reacts with cellulose to regenerate the sulfuric acid:



$$+ H_2SO_4 \longrightarrow CH_3COOH + CH_3COOSO_2OH$$

$$C_6H_9O_4OH + HOSO_2OCOCH_3 \longrightarrow C_6H_9O_4OCOCH_3 + H_2SO_4$$

Ost[47] studied the esterification of cellulose with sulfuric acid and the formation of cellulose sulfoacetates. His results indicate that the reaction of sulfuric acid with cellulose precedes the formation of acetyl cellulose, and that the sulfo group is replaced by the acetyl group.

Heuser[27] considers that: "the chief function of the sulfuric acid is to aid in the swelling of the cellulosic material and to degrade it". Degradation during the acetylation may reduce the degree of polymerization of the original material as much as 90%, depending on the severity and duration of the acid treatment.

The effect of the moisture content of the cellulosic material on the rate of acetylation was studied by Elöd and Schmidt-Bielenberg.[10] They measured the time of reaction necessary to obtain a product of a certain degree of substitution using celluloses that contained: 0.1%, 6.7%, and 24.4% water. The following figures are taken from the rate of acetylation curves of Elöd:

Combined Acetic acid in the product	10%	20%	30%	40%
Reaction time (hrs.) for cellulose:				
0.1% water	8	16.5	25.5	36
6.7% water	4	9.5	15.5	24
24.4% water	0⁻	0⁻	1.2	2.7

The experimental conditions used by Elöd were those for the preparation of fibrous cellulose acetates. Figure 1 on page 27, shows that there is no appreciable difference between the rate of acetylation at 45° C. of cellulose containing 0.1% water, and that for the acetylation of cellulose containing less than 1% water at 27 to 29° C., (the later contitions were used for the preparation of the cellulose acetate samples that were used in this study).

The Fibrous Structure of Cellulose and the Acetylation Reaction.

Cotton fibers are single plant cells that vary in length from 1 to 5 cm. and from 12 to 42 μ in thickness. Each cell is composed of a primary wall about 0.5 μ thick, a thicker secondary wall, and a main central core called the lumen. Raw cotton contains about 0.5 to 1.0% each of pectin and waxes that are considered to be a part of the primary cell wall, and may be removed by boiling with dilute alkali.

The proof of the chemical structure of cellulose and the arrangement of the long cellulose chains in crystalline and amorphous patterns in the so-called micellar structure, are the results of almost 100 years of study. X-ray studies have shown conclusively that there is a considerable degree of order in fine structure of cotton fibers. In recent years the study of the proportion of crystalline and amorphous regions in cellulose has received considerable attention[19,60]. The micelles that are made up of cellulose chains may have a certain periodicity of structure[49,50], in that some of the glycosidic linkages are apparently more vulnerable to attack by even the most mild acidic or oxidative treatment.

With the concept of the micellar and plant cell structures of cellulose well in mind, one can proceed to discuss the reactions of the hydroxyl groups of cellulose. Any reagent that will react with these hydroxyl groups must either proceed gradually inward from the surface of the fiber, or promote some rapid transformation in the micellar structure so that all of the hydroxyl groups can be reached. These are two extremes in reaction types, the first being called "topochemical",

and the second "permutiodal". The nitration of cellulose is a good example of a permutiodal reaction, wherein the nitration of cellulose is complete within a short time after the reaction begins. The acetylation reaction proceeds quite slowly and in a topochemical fashion[27].

Hess[26] has referred to the acetylation reaction as a "micellar-heterogeneous" reaction. The heterogeneous nature of the reaction may vary according to the procedure of acetylation. Herzog and Londberg[24] have shown that an outer layer of cellulose acetate may be dissolved away from a partially acetylated fiber with nitrobenzene, to leave a residue of unchanged cellulose. Kanamaru[32] has made photomicrographs of partially acetylated cellulose fibers (acetic anhydride and benzene). These photomicrographs show that the acetylation reaction starts at several fairly equally spaced points along the fiber, and bands of acetylated material start to form around these points of attack, and finally the bands expand gradually until all of the fiber is acetylated. Kanamaru concludes that the reaction at the surface of the fiber proceeds to the triacetate stage. The attack of the acetylating reagent at definite intervals along the fiber has been compared to that observed by certain wood destroying fungi[3], and both proceed along certain planes referred to as planes of hydrolysis.

The course of acetylation may be followed by X-ray techniques if the fibrous structure of cellulose is retained[24]. Hess and Trogus[26] found that the X-ray pattern of the original cellulosic material did not change upon acetylation until a degree of acetylation, corresponding to 43% combined acetic acid, had been reached. At this point the

pattern for triacetyl cellulose became noticeable and increased until at 53% combined acetic acid, the X-ray pattern of cellulose was no longer present. From this it might be surmised that the acetylation reaction may not proceed entirely to the triacetate stage until a fairly high degree of acetylation is attained.

The course of acetylation and deacetylation of cellulose fibers has been studied thoroughly by Vermaas and Hermans[63]. These investigators, being aware of the physical aspects of the cellulose structure, have attempted to prepare homogeneous partially acetylated cellulose filaments. According to the modern concept a swollen cellulose gel consists essentially of a molecular network structure. "In the course of a substitution reaction like acetylation, the degree of substitution at any given moment and at a given locus, will be a function of the degree of accessibility at that locus". Standard filaments of regenerated cellulose were pre-swollen in an ether-acetic anhydride acetylating mixture without catalyst. At the beginning of the reaction the catalyst (H_2SO_4) was in a very small concentration which was increased after the reaction was started. A series of partially acetylated cellulose fibers prepared in this manner was found to be microscopically homogeneous, but of increasing thickness and decreasing birefringence with increasing duration of the acetylation. Vermaas and Hermans concluded from these experiments that acetylation took place from the beginning of the reaction in both the intercrystalline (amorphous) regions as well as in the crystallites. The rate of conversion was considered to be greater in the amorphous regions of the gel. X-ray investigation showed

that a gradual increase in the spacing in the cellulose crystal lattice occurred due to the substitution of the large ester groups which force the glucose anhydride rings apart. Other dimensions in the lattice did not change.

The foregoing discussion may be best summarized with the statement of Lorand and Georgi[37]: "There is evidence to support the view that cellulose reactions do not follow a single pattern, and that the type varies, depending upon the reaction partner, its concentration, the reaction medium, temperature, etc. It is quite probable that all the reaction models, worked out for micro-heterogeneous systems, such as surface reactions, topochemical macro-heterogeneous reactions, permutoid or quasi-homogeneous reactions, as well as the previously mentioned micellar heterogeneous reactions, may apply to cellulose in one case or another, depending on circumstances."

In conclusion, some of the factors that must be kept in mind when discussing fibrous cellulose acetates of low acetyl content, such as those prepared in this investigation, may be listed as follows:

(1) The laboratory variables such as the moisture content of cellulose, the concentration of acetylating agent and catalyst, the time of reaction, and the temperature of reaction, must be controlled.

(2) Sulfuric acid present in the acetylating mixture reacts with cellulose to form sulfoacetates and to degrade the cellulosic chain.

(3) The acetylation of cellulose under these conditions is heterogeneous and will proceed faster in certain areas of the fiber.

(4) Different degrees of acetylation will be present at different points of attack, depending on the accessibility of the hydroxyl groups at these points.

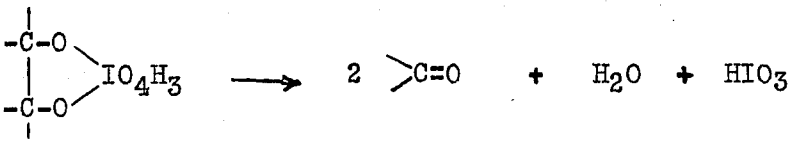
(5) A large proportion of the cellulose remains unchanged during the acetylation reaction, and there is a high probability that the proportion of such unchanged cellulose will be less in the amorphous regions of the cotton fiber.

(6) Any reaction to which cellulose may be exposed will yield results that are only average values and do not truly express the stoichiometric relationships resulting from the reaction.

PERIODATE OXIDATION OF CELLULOSE

The Mechanism of Periodate Oxidation

The work of Criegee[6] has been accepted by many authorities as a satisfactory explanation of the oxidative cleavage of 1,2-glycols by such reagents as lead tetraacetate and periodic acid. It is postulated that these reagents condense with the glycol group to form a cyclic intermediate that is unstable and decomposes by cleavage of the 2,3-carbon-carbon bond in the ring. In the case of periodic acid, the intermediate decomposes as follows:



Heidt and Purves[23] have listed the requirements that must be met by any reagent that might conceivably perform this type of oxydation.

(1) The central atom of the oxidant must have a diameter of about 2.5 to 3.0 Å which is large enough to bridge the space between the hydroxyl groups in a 1,2-glycol.

(2) The central atom must be able to coordinate with at least two hydroxyl groups in addition to the groups already attached to it.

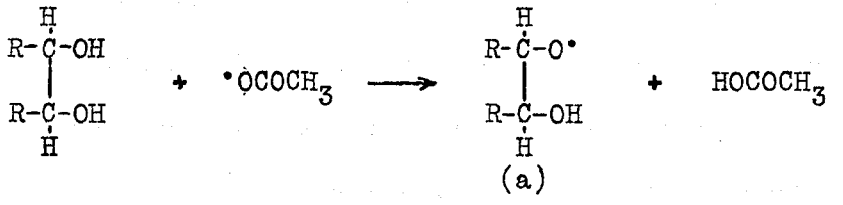
(3) The valence of the central atom must be 2 units (and not 1 or 3) higher than the valence of its next lower stable state.

(4) The oxidant should have a standard E_o oxidation potential in the neighborhood of about -1.7 v. with respect to the next lower stable state.

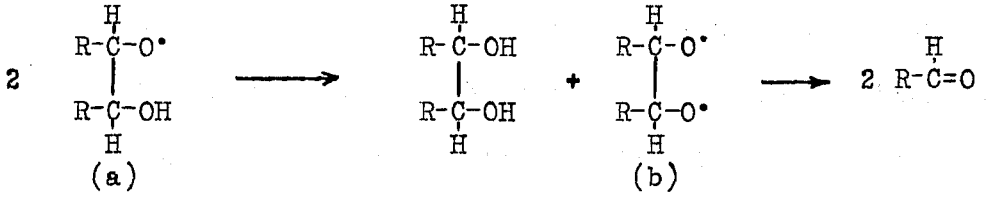
Reagents that fulfill the preceding requirements are: $Pb(OCOCH_3)_4$, HIO_4, $NaBiO_3$, and hydrated unstable Ag^{+++}. The last two have been tested and found active towards glycol cleavage. Commonly used oxidizing reagents such as NaOCl, $K_2Cr_2O_7$, $KMnO_4$, and HNO_3, lack one or two of the above requirements.

As opposed to the cyclic mechanism of Criegee, Waters[64] has presented a free radical mechanism that also explains the oxidative cleavage of 1,2-glycols. The mechanism of Waters involves an auto-oxidation reaction that is catalyzed by the oxidizing agent, and leads to a series of chain reactions that end with glycol cleavage. The following mechanism was proposed for the lead tetraacetate oxidation of glycols:

$$Pb(OCOCH_3)_4 \longrightarrow Pb(OCOCH_3)_2 + 2\ {}^{\bullet}OCOCH_3$$



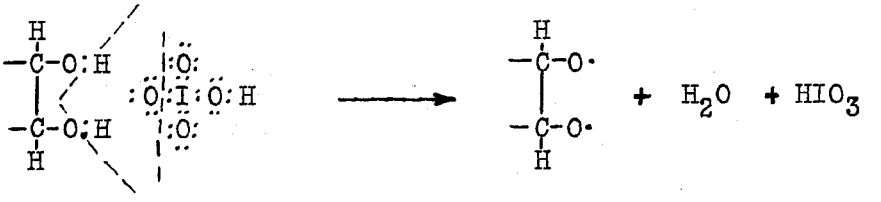
(a)



(a) (b)

The acetate free radicals react with the glycol group to form new free radicals (a), which may collide to form the biradical (b). The biradical (b) is stabilized more easily by the symmetrical fission of a C-C bond than by further action involving a-O-H bond. Waters postulates that in the case of periodic acid a corresponding free radical reaction

may be started by "atomic hydrogen abstraction by an I=O bond". The biradical is formed in one step:



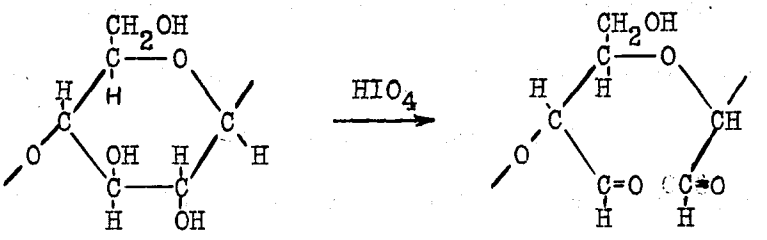
This mechanism would be in agreement with the requirements of space and configuration as outlined by Heidt and Purves[23], but does not involve actual condensation or chelation of the oxidizing agent in a cyclic structure such as proposed by Criegee.

Periodate Oxidation of Cellulose

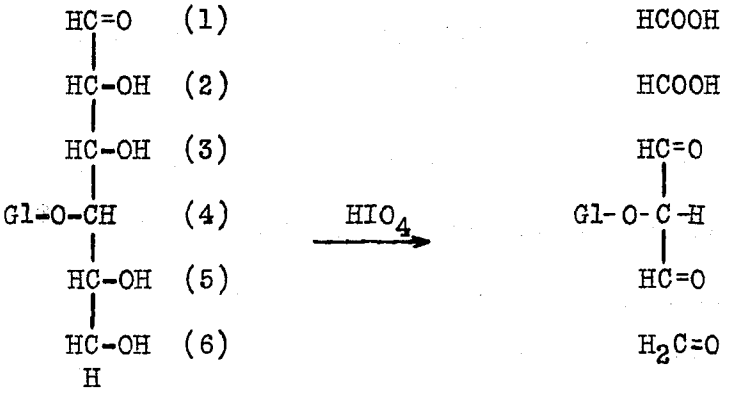
Jackson and Hudson[30] (1936) were the first investigators to apply the so-called Malaprade reaction to cellulose chemistry. The work of Hudson and Jackson has been extended considerably and at the present time the periodate oxidation of cellulose is finding application as an analytical method in certain phases of cellulose chemistry[56,60]. The literature cited for Jackson and Hudson, Jayme[31], and Pacsu[50], deals mainly with the theoretical reaction and with the identification of oxidation products, and does not furnish data that might be useful in a study of the rate of periodate oxidation of cellulose under different conditions.

Davidson[8] has made an extensive study of this oxidation reaction and the properties of periodate oxycelluloses. He found that the ideal reaction of periodic acid with cellulose did not stop at the point where

1 anhydroglucose unit had been oxidized by 1 mole of HIO_4, as shown in the reaction:



The actual oxidation, and especially during the later stages of the reaction, gave rise to measurable quantities of carbon dioxide, formic acid, and formaldehyde. Some of these products might be expected as a result of the normal oxidation of end groups along the cellulose chain. The periodate oxidation of an end groups may be written:



The symbol Gl is used to designate an anhydroglucose residue. The formation of formic acid results from the oxidation of carbons No. 1 and 2, and the formation of formaldehyde, from carbon No. 6. Further oxidation of formic acid may account for the carbon dioxide.

In a typical oxidation experiment, Davidson oxidized 1 g. of cellulose with 100 ml. of a solution of 0.2 N HIO_4. After about 350 hours,

the cellulose had consumed 1 mole of HIO_4 per unit molecular weight, and had produced CO_2, HCOOH, and $H_2C{=}O$, in the amount of: 0.096, 0.226, and 0.035 moles per unit molecular weight respectively. These figures correspond to a formation of these products to the extend of:

CO_2, 1 mole per 10 anhydroglucose units

HCOOH, 1 mole per 4 or 5 anhydroglucose units, and

$H_2C{=}O$, 1 mole per 33 anhydroglucose units.

It is obvious from these figures that these products did not arise solely from the end groups, but must have been formed as a result of side reactions. This particular experiment represents an extreme in side reactions. If periodate oxidations are carried out at pH values of between 2 and 5, and if the concentration of the oxidant is reduced to about .05 N, the production of CO_2, HCOOH, and $H_2C{=}O$ is decreased considerably.

Harris[53] and Purves[20] have studied periodate oxidation of cellulose and have determined the amounts of dialdehyde present in samples that were oxidized for various time periods. Purves found that a properly prepared oxycellulose contained at least 90% of the dialdehyde (as determined by the dinitrophenylhydrazone method) that would be expected from the periodate consumption. Purves further considers that the reaction (for starch) is only selective between the pH values of 2 and 5 and at temperatures below 20° C. "Oxidation of starch or cellulose with aqueous periodate takes place in a heterogeneous system and it is possible that some of the oxidant is dissipated in secondary reactions at

the surfaces while the interiors of the granules or fibers contain unchanged starch or cellulose.

The initial rate of periodate oxidation of cellulose is much faster than that observed for the over-all reaction. Mark[19] and Timell[60] have shown that this initial rapid oxidation corresponds to the attack of periodate on the amorphous portions of cellulose. If a curve is drawn to show the rate of oxidation of cellulose over a considerable period of time, (see figure 9), it can be seen that in the early stages of oxidation the observed rate of reaction is the net result of two reactions, one being the fast oxidation of the amorphous, and the other, the slower oxidation of the crystalline regions of cellulose, both of which take place at the same time.

Davidson[8] has studied the effect of periodate oxidation on the X-ray diagram of filter paper cellulose. As the degree of oxidation increased the X-ray pattern of the original cellulose became more and more diffuse. This indicates that no new crystalline structure is produced, and that the original crystalline order is gradually destroyed as oxidation proceeds. The conclusion would be that the crystalline areas are gradually opened up during the course of periodate oxidation.

Figure 7 shows the reaction rate curves for 8 periodate oxidations of cotton cellulose. Curves IV and VI were plotted from data obtained in this investigation; all other curves were plotted from data obtained from the references cited. An oxidation period of seven hours would cover mostly the rapid periodate oxidation of the amorphous regions of cellulose.

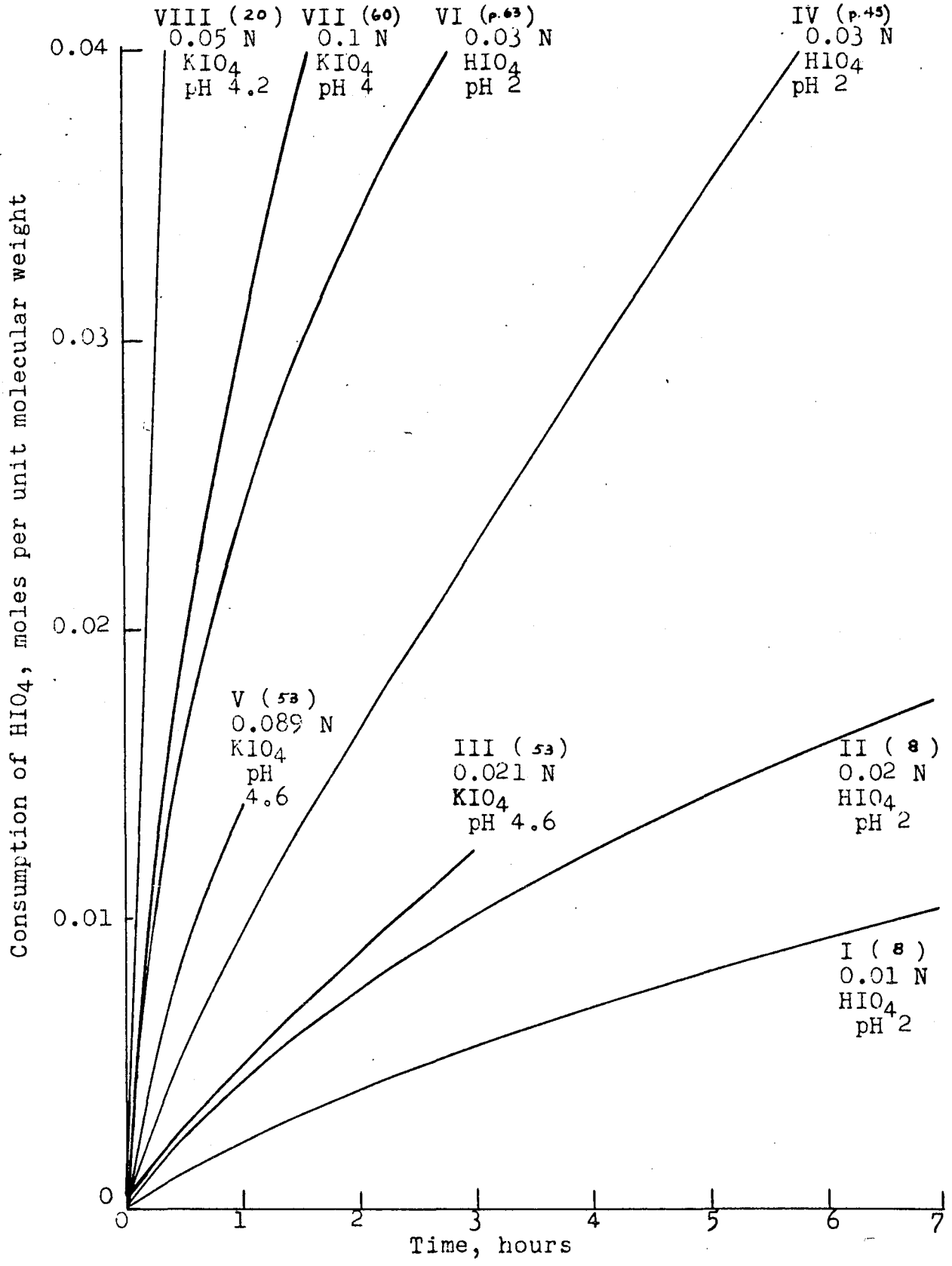


Figure 7

Periodate Oxidation of Cellulose Under Various Conditions.

A study of figure 7 would lead to the following observations:

(1) The rate of oxidation increases with an increase in the concentration of the oxidizing agent, as would be expected.

(2) The effect of swelling of the fiber on the rate of oxidation is indicated very clearly by the difference between curve VIII and all others. Curve VIII was obtained by Purves[20] from data resulting from the oxidation of cotton linters that had been pre-swollen, and Purves claimed that after such swelling the internal surfaces, directly available to any aqueous solution, contained from 10 to 20% of all the hydroxyl groups present in the fiber. Therefore, in any oxidation study, one must take into account the effects of pre-swelling treatments, and also the swelling effects resulting from the presence of certain reagents in the oxidizing mixture.

(3) The effect of vigorous stirring is shown by a comparison of curve VI with curve IV. All of the conditions were the same in both experiments, the only difference being that the reaction mixture was vigorously stirred in the case of curve VI. It is clearly seen that the oxidation rate is much faster when the reaction mixture is stirred vigorously, and this could be considered as evidence that the availability of the glycol groups is increased. Vigorous stirring might also increase the diffusion gradient of the oxidant in the fiber, which in turn would cause a greater probability of reaction between periodate and glycol.

(4) Apparently the rate of oxidation is not affected appreciably by differences in pH between 2 and 5.

Factors that Influence the Reproducibility of Results and the Rate of Oxidation of Cellulosic Materials.

If conclusions are to be drawn from any series of periodate oxidations of cellulosic materials, certain experimental conditions and factors must be kept in mind:

(1) The reaction flask apparatus should be free from oxidizable impurities or impurities that might catalyze the decomposition of periodic acid. After glassware has been cleaned it should be filled or treated with dilute HIO_4 solution and allowed to stand for at least 24 hours. After oxidation experiments the flasks should be rinsed with distilled water and dried in an inverted position.

(2) Oxidation experiments should be carried out on samples that have been standardized as to physical form.

(a) The state of division of the materials should be approximately uniform.

(b) The moisture content of the materials should be controlled so as to permit accurate weighing.

(c) Any swelling treatment prior to oxidation should be standardized.

(3) Extremes in reaction conditions should be avoided:

(a) The concentration of the oxidant should not be much more than 0.1 N and not less than 0.02 N.

(b) If a measure of the true rate of reaction is to be obtained, the volume of oxidant per gram of material should be selected so that the reaction period can be completed without decreasing the concentration of the periodic acid to an extent that would effect the reaction rate.

(c) The reaction media should have a pH between 2 and 5. A reaction mixture that is too acid yields an excessive amount of by-products caused by side reactions. A mixture that is alkaline causes degradative rearrangements of the periodate oxycellulose.

(d) All oxidation experiments should be performed at the same controlled temperature. Temperatures between 20 and 30° C. are suggested.

(e) The selection of a reaction time should be governed by the nature of the cellulosic material and the concentration of the oxidant to be used. Short reaction periods show almost stoichiometric selective oxidation according to the ideal reaction, whereas, prolonged oxidation periods may involve side reactions. The amorphous areas of cellulose will be attacked rapidly during the early stages of the reaction, and as the oxidation of these areas becomes complete, the reaction rate will be that corresponding to the oxidation of the crystalline areas of the cellulosic material.

(f) The contents of the reaction flask should be mixed at a moderate standard rate that permits the maintenance of a homogeneous suspension of the cellulosic material in the oxidizing solution.

(4) The method of analysis for excess periodate should be standardized, and blank determinations of the concentration of the periodic acid should be made at least once every 24 hours during the course of a oxidation reaction.

PERIODATE OXIDATION OF CELLULOSE ACETATES OF LOW ACETYL CONTENT

The Rate of Oxidation of Cellulose and Cellulose Acetates.

Figures 5 and 6 show the reaction rate curves for a series of cellulose acetate oxidations as plotted from data recorded in table X. All of the oxidation data resulted from experiments where the possible factors that might influence the rate of oxidation were kept standard. The consumption of periodate, in moles per unit molecular weight, listed in table X is the average consumption for six experiments in the case of standard cellulose, and the average of at least two experiments in which each cellulose acetate was oxidized.

The rate of the oxidation reaction has been shown by plotting periodate consumption against time. The progress of the reaction may also be shown by plotting the periodate consumption against the amount of free hydroxyl present in the cellulose acetates. The amount of oxidation of any cellulose derivative will be a function of the total number of free hydroxyl groups in that particular derivative. The percent of free hydroxyl in each cellulose acetate may be calculated from the equation:

$$\text{Percent of free hydroxyl} = \frac{(3 - \text{D.S.})\ 100}{3} ;$$

where D.S. is the degree of substitution (table II), and 3 is the maximum degree of substitution for an anhydroglucose unit. The conversion of D.S. to percent free hydroxyl for cellulose acetates No. 17 to 25 is recorded in table XIII.

TABLE XIII

CONVERSION OF DEGREE OF SUBSTITUTION TO PERCENT FREE HYDROXYL

CAc No.	Percent Combined HOAc	Degree of Substitution	Percent Free Hydroxyl
17	5.13	0.1436	95.21
18	8.23	0.2360	92.13
19	12.09	0.3560	88.18
20	14.14	0.4235	85.87
21	3.40	0.0940	96.87
22	5.31	0.1490	95.03
23	6.60	0.1868	93.77
24	8.65	0.2490	91.70
25	9.94	0.2880	90.40

Figure 8 is a graph of the consumption of periodate plotted against the percent free hydroxyl for various cellulose acetates of low acetyl content. The values for cellulose are recorded at 100% free hydroxyl.

The reaction rate curve for cellulose is shown in figure 9. This curve may be analyzed in terms of the oxidation of amorphous and crystalline regions of cellulose[19,60]. If the straight-line portion of the curve is extrapolated to zero time and displaced downward to the origin (line C) this straight line may be considered to represent the rate of oxidation of crystalline cellulose. If the differences between the actual observed curve and this line for any series of time values are plotted on this same coordinated system, the result will be curve A, which represents the oxidation of amorphous cellulose. Curve A shows that the oxidation of amorphous cellulose is for all practical purposes complete after a 24-hour oxidation period under the oxidation conditions used.

The basic problem that must be solved at this point may be suggested by the question: How many hours would be required to complete the periodate oxidation of cellulose (the oxidation of all glycol groups in cellulose, i.e., one glycol group per unit mol. wgt.)? A few assumptions must be made:

(1) That the ideal reaction holds true during the 60 hour period under these very mild conditions of oxidation.

(2) That the degree of periodate consumption at 24 hours (0.1077 moles per unit mol. wgt.) represents the end of the oxidation of amorphous cellulose.

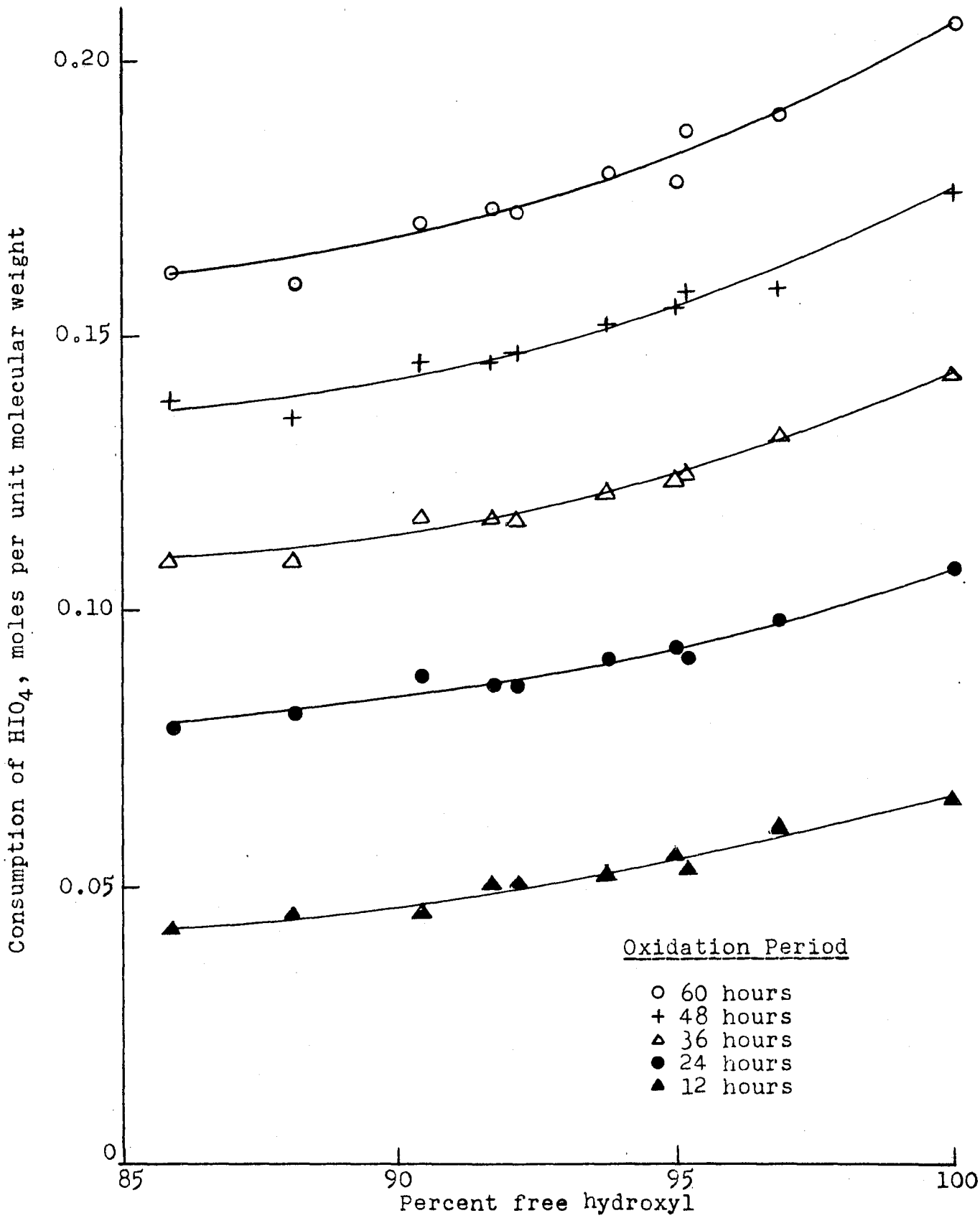


Figure 8

Periodate Oxidation of Cellulose and Cellulose Acetates at 30°C., with Standard Mixing.

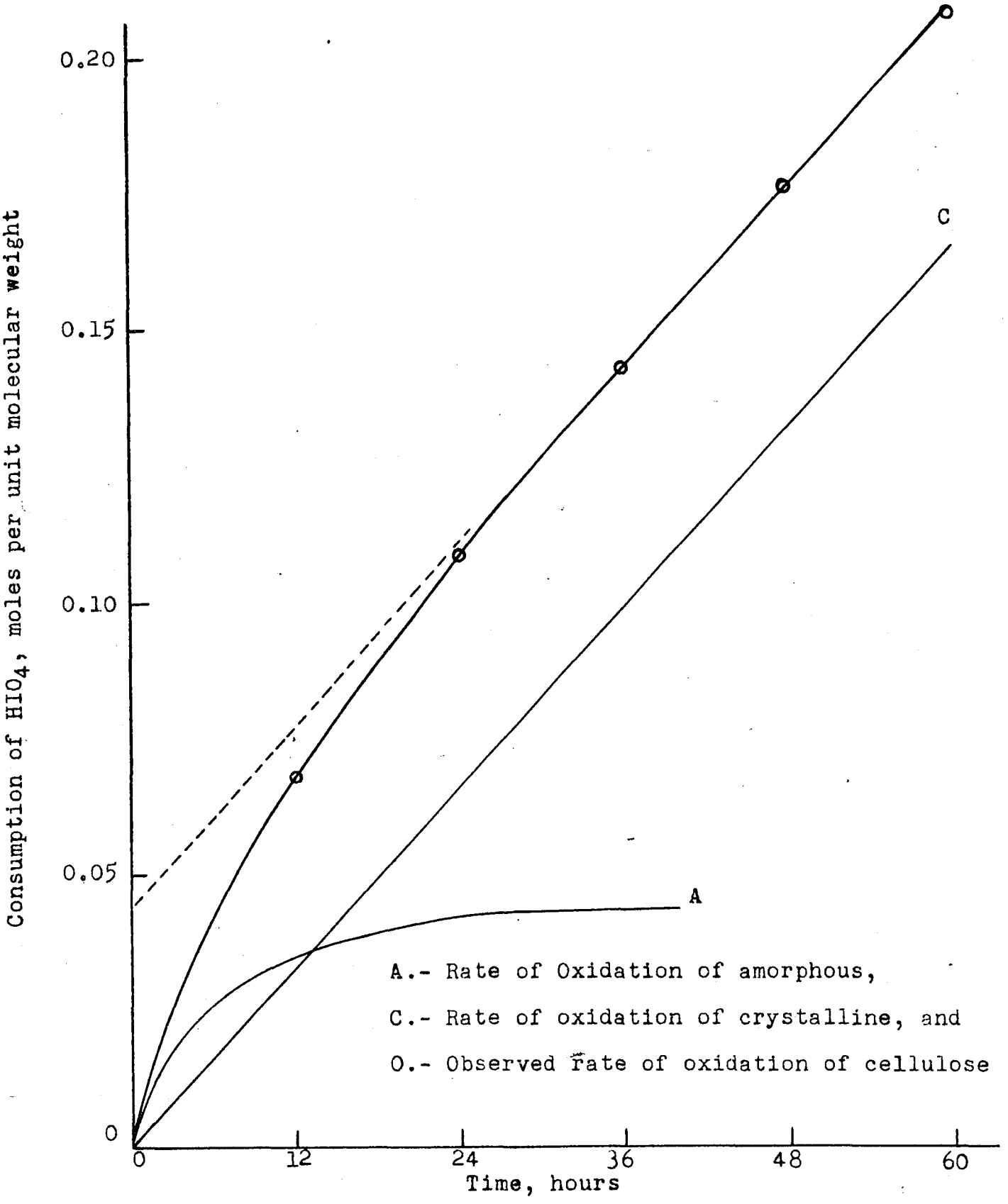


Figure 9

Oxidation of Amorphous and Crystalline Cellulose

(3) That the remainder of the reaction is governed by the rate of oxidation $\frac{dM}{dt}$ (0.0275 moles per unit mol. wgt. per hour) calculated from the slope of the line C in figure 9, where M represents the consumption of periodate in moles per unit molecular weight.

The consumption of periodate at the end of the theoretical reaction is 1 mole per unit mol. wgt. The consumption at 24 hours is 0.1077, so that the balance (or 0.8923) must be oxidized at the rate of 0.0275 mole per unit mol. wgt. per hour. This corresponds to a time period of 325 hours. The time period for the total reaction would then be 325 + 24 or roughly 350 hours.

The same procedure could be followed to determine the rate of oxidation of each cellulose acetate, but since the total number of glycol groups present in the acetates will be decreased by acetylation, it would be difficult to arrive at the correct time period during which the theoretical reaction is complete. The interest lies mainly in the difference (ΔM) between the periodate consumption of cellulose and that of any cellulose acetate. As oxidation proceeds this difference becomes greater and greater. Cellulose acetate samples No. 21, 23, 24, and 20 were chosen as representative of the series of cellulose acetates and the data for these samples will be used in the remainder of this discussion. The difference, ΔM, between the consumption of periodate by cellulose and cellulose acetate at the time intervals of 12, 24, 36, 48 and 60 hours are recorded in table XIV. A few of these figures were corrected slightly to correspond with figure 8. Figure 10 is a graph of

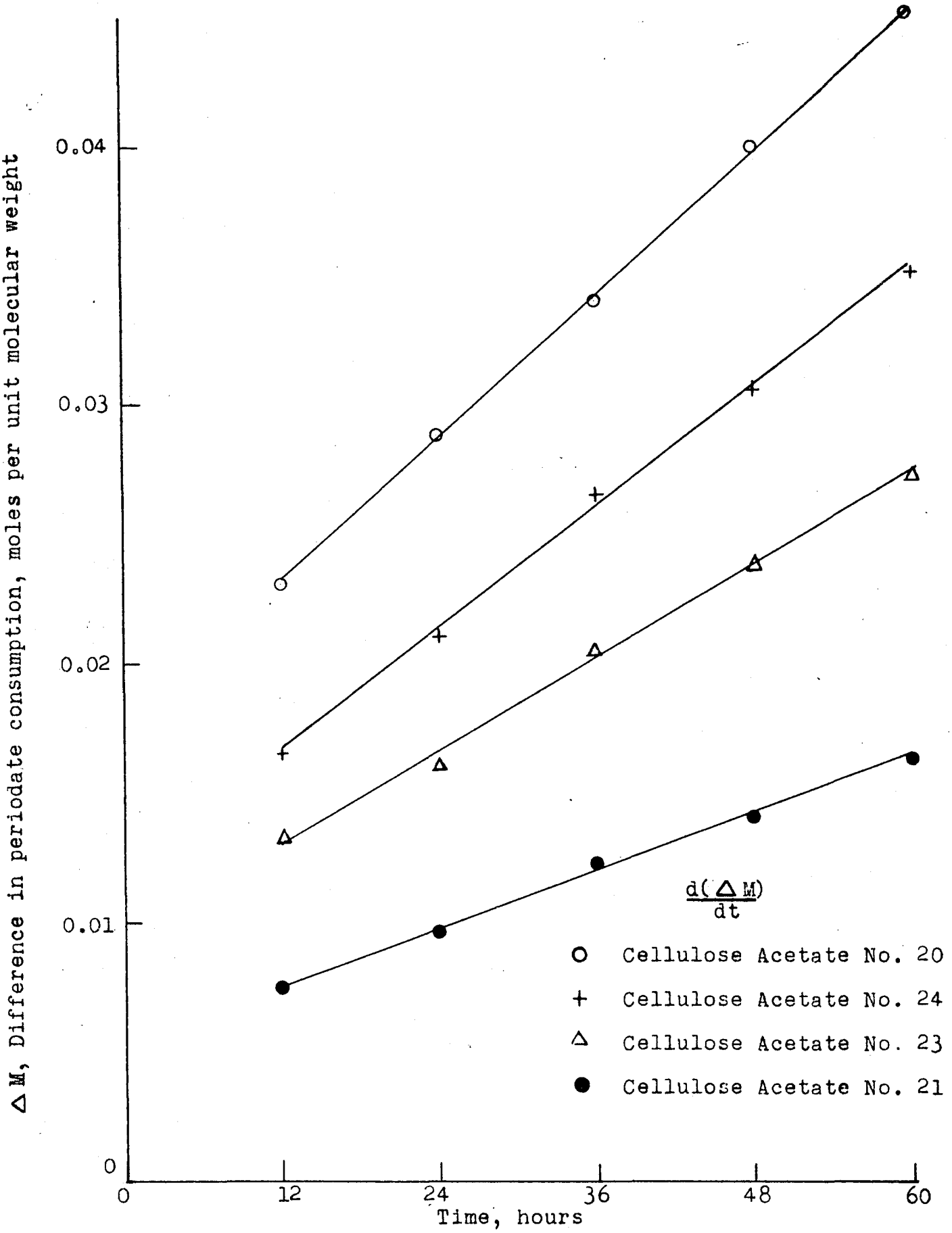


Figure 10

The Change of ΔM with Respect to Time

the difference, ΔM, in periodate consumption per unit mol. wgt. plotted against time. For every acetate sample the points plotted can be joined by a straight line, even down to 12 hours. This would indicate that the value ΔM changes at the same rate, $\frac{d(\Delta M)}{dt}$, and if it is assumed that this rate holds true during the theoretical reaction period (350 hours), the total difference between the periodate consumption of cellulose and any cellulose acetate may be calculated. The difference ΔM at 24 hours may be added to the difference ΔM over a period of 326 hours to obtain the total difference:

$$\text{Total difference, } \Delta M_{350} = \Delta M_{24} + (326)\frac{d(\Delta M)}{dt} .$$

These figures are recorded in table XIV.

Allowing a margin of error of $\pm$ 24 hours in the calculation of the period of time required to complete the theoretical reaction, this would correspond to a difference of $\pm$ 6% in the value ΔM_{350}.

The Course of the Acetylation Reaction.

In the preceding discussion certain fundamental assumptions were made that permitted the calculation of the difference between the periodate consumption of cellulose and any cellulose acetate at the end of the theoretical reaction. Partial justification for making these assumptions may be granted from the standpoint that all of the experiments were carried out under the same controlled conditions, and that oxidations of all cellulose acetates were compared at every reaction period with the corresponding oxidation of the standard cellulose from which they were prepared. It is considered that the increase in end groups (that have 3

TABLE XIV

CALCULATION OF ΔM_{350}

Sample Number	Reaction Time, hrs.	ΔM moles per unit mol. wgt.	$\frac{d(\Delta M)}{dt}$ (moles per unit mol. wgt. per hour)	ΔM_{350} moles per unit mol. wgt.
CAc No. 21	12	0.0073	0.000192	0.0722
3.4% HOAc	24	0.0096		
	36	0.0113		
	48	0.0140		
	60	0.0163		
CAc No. 23	12	0.0133	0.0003	0.1138
6.6% HOAc	24	0.0160		
	36	0.0205		
	48	0.0238		
	60	0.0271		
CAc No. 24	12	0.0165	0.000388	0.1475
8.65% HOAc	24	0.0210		
	36	0.0265		
	48	0.0305		
	60	0.0350		
CAc No. 20	12	0.0229	0.000458	0.1783
14.14% HOAc	24	0.0288		
	36	0.0340		
	48	0.0379		
	60	0.0452		

adjacent hydroxyl groups), caused by degradation during the acetylation reaction, is offset by a small amount of combined sulfuric acid that will block some of the hydroxyl groups which might otherwise be oxidized (see page 84).

The value ΔM_{350} is the difference between the consumption of periodate by cellulose and a cellulose acetate at the end of the theoretical reaction. This value corresponds to the amount of glycol groups that were esterified by acetic anhydride when the cellulose acetate was prepared. When cellulose is acetylated the reaction may take place with the hydroxyl groups on carbons No. 2, 3, and 6. If either the No. 2 or 3 hydroxyl group is acetylated, the glycol group will be blocked and would not be oxidized by periodic acid. However, if the No. 6 hydroxyl is acetylated the glycol group is free (not blocked) and can be oxidized by periodic acid. The values for ΔM_{350} as shown in table XV are the observed (experimental) values for the amount of glycol that must have been blocked by acetylation.

Table XV contains some of the calculated data for cellulose acetates No. 21, 23, 24 and 20 which were chosen as representative of the series of cellulose acetates prepared. Column B shows the average degree of substitution of the acetyl groups in each cellulose acetate, and this value may also be thought of as the moles of hydroxyl groups that are blocked by acetyl groups. Columns D, E, F and G represent hypothetical distributions of this total amount of blocked hydroxyl among the three hydroxyl groups of an anhydroglucose unit. Both columns D and E represent the distribution of acetyl groups between carbons 2 or 3.

TABLE XV

DISTRIBUTION OF SUBSTITUENTS IN CELLULOSE ACETATE*

CAc No.	Percent Combined HOAc	Total -OH Acetylated	Blocked Glycol Found	Distribution of Acetylated hydroxyl groups			
				-OH No. 2 or 3	-OH No. 2 or 3	-OH No. 6	If Product is a triacetate
	A	B	C	D	E	F	G
21	3.4	0.094	0.0722	0.0722	0.0218	0.000 min.	0.031
				0.0722	0.0000	0.0218 max.	
23	6.6	0.1868	0.1138	0.1138	0.0730	0.0000 min.	0.0623
				0.1138	0.0000	0.0730 max.	
24	8.65	0.249	0.1475	0.1475	0.1015	0.0000 min.	0.083
				0.1475	0.0000	0.1015 max.	
20	14.14	0.4235	0.1783	0.1783	0.1783	0.0669 min.	0.141
				0.1783	0.0000	0.2452 max.	

* The units of the figures in columns B through G are expressed in moles per unit molecular weight.

The purpose of this investigation was to determine if possible where the initial acetylation of cellulose takes place; whether it is at the primary hydroxyl group (carbon No. 6), or at one of the secondary hydroxyl groups (carbon No. 2 or 3). It is felt that the figures in table XV can be used to answer this question. For example, cellulose acetate No. 21 (3.4% HOAc) has an average degree of substitution of 0.094 moles per unit mol. wgt. This is the number of moles of hydroxyl per anhydroglucose unit that have been acetylated. Periodate oxidation of CAc No. 21 showed that 0.0722 moles of glycol were blocked. The hydroxyl groups (0.094 moles per unit mol. wgt.) that are acetylated in this particular cellulose acetate may be distributed according to the following two extremes:

(1) 0.0722 moles of acetylated hydroxyl on carbon 2,
0.0218 on carbon 3, and
0.0000 on carbon 6.

(2) 0.0722 moles of acetylated hydroxyl on carbon 2,
0.0000 on carbon 3, and
0.0218 on carbon 6.

The figures for these two extremes are shown in table XV. The first extreme would leave a minimum amount of acetyl on carbon 6, and the second extreme would leave the maximum.

From the data in table XV the following conclusions may be drawn regarding the course of the acetylation reaction:

(1) The observed amount of esterification on the 2 or 3 position of the glycol rules out the probability of the formation of anhydroglucose triacetate (as postulated by Kanamaru[32]) in any phase of the initial reaction. For example, if this were

the case, the distribution of acetyl groups would be 1/3 on each hydroxyl (column G table XV) and the amount of blocked glycol that should be observed would be approximately 40 to 75% of what was actually observed for samples containing from 3.4% to 14.14% combined acetic acid.

(2) It appears from results of this investigation that at the beginning of the acetylation reaction the secondary hydroxyls are more vulnerable to attack by acetic anhydride esterification than the primary. It is clearly evident from the figures shown in table XV that it might be possible to acetylate cotton to the extent of 3% combined acetic acid or even as much as 9% HOAc, and have no acetylation take place on hydroxyl No. 6. However, if cotton is acetylated to a greater extent (for example 14.14% HOAc) some of the No. 6 hydroxyls must be acetylated. The figures in table XV do not prove that no acetylation takes place at the No. 6 hydroxyl during the early stages of the reaction, but they do show that this is a possibility. If the other extreme (maximum acetylation of No. 6 hydroxyl) is considered, it is found that when cotton is acetylated to the extent of 3% HOAc, the maximum amount of acetylation that could take place at the No. 6 hydroxyl is about 0.02 moles per unit mol. wgt. This amounts to about 23% of the total moles of acetylated hydroxyl. If cotton is acetylated to the extent of 14% HOAc, the maximum amount of No. 6 hydroxyl that could be acetylated is about 0.25 moles per unit mol. wgt.

which is about 60% of the total. The increase in the maximum probability of acetylation at the No. 6 hydroxyl is to be expected. During the early stages of acetylation the secondary hydroxyl groups are attacked to a greater extent then the primary and as acetylation proceeds, the number of secondary hydroxyl groups decreases, and it would be expected that more acetylation would take place at the No. 6 hydroxyl.

Sönnerskog[56] (1948) has studied the etherification of cellulose by alkyl halides. His observations also lead to the conclusion that the secondary hydroxyl groups of cellulose are attacked first.

(3) As a corollary to the above conclusion (2), it can be said that in the early stages of acetylation the primary hydroxyl groups of cellulose are attacked to a lesser extent than the secondary. The reason for this may be that the primary hydroxyls are either less reactive or less available for reaction. The availability of the primary hydroxyl groups of cellulose may be small due to hydrogen bonding which is assumed to occur between polymer chains in the cellulose micelle[56]. This would be true in cellulose, but when cellulose is acetylated the introduction of acetyl groups forces the cellulose chains apart. This would break many hydrogen bonds and increase the availability of primary hydroxyl groups. X-ray measurements confirm this hypothesis[63].

It is well known that in general a primary alcohol is more reactive than a secondary. The apparent reversal of this rule in the acetylation of cellulose can be explained as resulting, not from a decrease in the reactivity of the primary hydroxyl, but from the fact that the primary hydroxyl is less available at the beginning of the reaction, due to hydrogen bonding. The hydrogen bonding is slowly eliminated as the polymer chains are spread apart.

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