The Institute of Paper Chemistry

Appleton, Wisconsin

(1)

Doctor's Dissertation

Study of the Mechanism of the Esterification of Cellulose and its Effect on the Solubility of the Product

John Edward Ward

June, 1951

STUDY OF THE MECHANISM OF THE ESTERIFICATION OF CELLULOSE AND ITS EFFECT ON THE SOLUBILITY OF THE PRODUCT

A thesis submitted by

John Edward Ward

B.S. 1944, Wabash College
M.S. 1948, Lawrence College

in partial fulfillment of the requirements
of The Institute of Paper Chemistry
for the degree of Doctor of Philosophy
from Lawrence College,
Appleton, Wisconsin

June, 1951

TABLE OF CONTENTS

INTRODUCTION

Cellulose acetate is used in the manufacture of plastics and rayon. In 1941 it ranked fifth among the various plastics, and it accounted for one third of all the rayon produced.

Commercial cellulose acetate is produced by treating cellulose suspended in acetic acid with acetic anhydride and a catalyst, usually sulfuric acid. The reaction is allowed to proceed until the cellulose is substantially completely esterified, at which point it dissolves completely in the acetic acid. This material is then partially hydrolyzed to remove some of the acetyl groups in order to obtain a product which is soluble in acetone.

This is an indirect process, but a cellulose acetate which is produced by the partial esterification of cellulose directly to the same acetyl content as commercial acetate has different physical properties. One of the most important differences is the insolubility of the esterified product in acetone or other common solvents.

HISTORICAL REVIEW

Cellulose consists of long chains of anhydroglucose units linked together by β-1,4 linkages. Three hydroxyl groups per glucose unit, those on the second, third, and sixth carbon atoms, are available for reaction. Of these, the hydroxyl on the sixth carbon is a primary hydroxyl, and the others are secondary.

The hydroxyl groups on adjacent chains are capable of forming hydrogen bonds. In portions of a cellulose fiber where the chains are arranged very regularly, large numbers of these bonds may be formed, and crystalline regions may occur. Other portions where the arrangement of the chains is less regular and where few hydrogen bonds are formed are known as amorphous regions.

Cellulose exhibits the typical reactions of primary and secondary hydroxyl groups. The course of these reactions, as well as the physical properties of cellulose fibers, is strongly influenced by the existence of crystalline and amorphous regions.

Spurlin (1), in discussing the solubility of high polymers, says, "The trisubstituted (cellulose) derivatives, as a class, are relatively insoluble. As substitution is decreased, the derivatives become much more generally soluble until a maximum is reached between 2 and 2.5. At lower substitutions, the solubility is controlled to an increasing extent by the interaction between hydroxyl groups, and solubility in all but hydroxylated solvents decreases. If the distribution of the hydroxyls along the chain approaches randomness, it may be expected that the chance

of two hydroxyls on adjacent chains being near each other will be proportional to the square of their concentration in the derivative. Hydrogen bonding will therefore be negligible if most of the hydroxyls have been substituted and will increase rapidly as the substitution is lowered."

In the case of cellulose acetates this has long been understood practically if not theoretically. Cellulose triacetate is soluble in a few solvents, notably chloroform. A patent was filed by Miles (2) in 1904 on the production of an acetone-soluble acetate by acetylating to produce a substantially completely esterified material (the "primary acetate" of commerce) and then hydrolyzing with water and acid in solution to the acetone-soluble product (commercial "secondary acetate"). Ost (3) analyzed these products accurately and found that the production of acetone-soluble derivatives was accompanied by deacetylation. Kita, et al. (4) showed that acetone solubility was not produced by degradation alone when they reacetylated a secondary acetate to a trisubstituted "tertiary" acetate which was soluble in chloroform but not in acetone.

Although acetone-soluble derivatives can be produced by completely acetylating cellulose and partially hydrolyzing the product to a degree of substitution of 2.6 to 2.1, the corresponding derivative produced by partial esterification directly to the same degree of substitution has very different properties. It is only slightly soluble in acetone. It is horny, rather than soft and fluffy. This material is not sufficiently acetylated to correspond to the commercial primary acetate, and it will be referred to as a partially esterified acetate. The commercial secondary acetates will be referred to as partially hydrolyzed acetates.

Partially hydrolyzed acetates have been extensively investigated, but little information has been published about the corresponding partially esterified ones. Sakurada and Kitabatake (5) prepared the triphenylmethyl (trityl) derivative of a partially hydrolyzed cellulose acetate and found that about one third of the hydroxyl groups reacted to form trityl ethers. Shortly afterward a number of investigators (6-9) succeeded in preparing trityl derivatives of sugars which had no primary hydroxyls available for reaction, and the tritylation method of distinguishing primary hydroxyls fell into disrepute.

Purves and his students (10-12) applied the method of Oldham and Rutherford (13) to commercial cellulose acetates. They prepared p-toluenesulfonyl (tosyl) esters of the unesterified hydroxyls and iodinated these derivatives to determine the proportion of primary hydroxyls. Gardner and Purves (12) determined that in a commercial acetate with a degree of substitution of 2.44, 35% of the free hydroxyls were primary, 40% were secondary attached to carbon three, and 25% were secondary attached to carbon two. Of these secondary hydroxyls, only 2.6% were present in the form of glycols. This is less than the amount predicted for random deacetylation and much less than that predicted for localized deacetylation.

Cramer and Purves (10) cited a patent issued to Clarke and Malm (14) for reacetylating partially hydrolyzed cellulose acetate (restoring substantially most of the acetyl groups) by boiling it for 200 hours with glacial acetic acid, producing an acetone-insoluble product. Cramer and Purves state:

"The acetone-soluble acetate loses this property when heated with glacial acetic acid which probably re-esterifies the primary hydroxyls preferentially. ... a directly acetylated product might have the same acetyl content and the same average molecular weight as an acetone-soluble acetate produced by the partial saponification of the triacetate. The distribution of acetyl and hydroxyl would nonetheless be sharply different, as primary hydroxyl would be present in the latter case and none in the former. Free primary hydroxyl may prove to be necessary for true solubility in acetone."

Since this work was done, the tosylation-iodination method has come in for its share of criticism. A tosylated primary hydroxyl may be rendered stable against iodination by the presence of an adjacent keto group (15) or acetalic group (16). When treated with iodine, a tosylated derivative with two neighboring tosyl groups or a tosyl group beside a secondary hydroxyl may form a double bond and liberate iodine (17-20).

The method was critically evaluated by Malm, et al. (21) who concluded:

"The method of tosylation and iodination did not give exact results in the determination of primary hydroxyl in cellulose and cellulose acetate; since as the reaction conditions in both the tosylation and iodination steps were extended, increasing amounts of primary hydroxyl were indicated.

In view of these difficulties, the reaction conditions must

be standardized in comparing the amounts of primary hydroxyl in different samples of cellulose acetate."

More recently Timell (22) studied the method and set the following conditions under which reliable results may be obtained.

"The sample should be soluble or at least capable of swelling in anhydrous pyridine. If the latter be the case, then the esterification must be carried out with continuous and vigorous stirring. Higher temperatures than 25° C. are to be avoided.

In the tosylated preparation the number of secondary tosyl groups must not substantially exceed half the number of primary ones.

At 120° C. the iodination should not be allowed to proceed for more than 2.0 hrs. Most samples dissolve or swell sufficiently for the solvents used (acetone or acetonylacetone), the sodium iodide also contributing to this.

It is advisable to carry out several tosylation-iodination experiments, slightly varying the degree of tosylation. Finally, the average value of the iodine may be used."

At the same time that doubt was being cast on the reliability of the results obtained by tosylation-iodination, the tritylation reaction was being re-examined. Hearon, et al. (23) found that under moderate reaction conditions tritylation may be carried out to cover approximately 90% of the available primary hydroxyls, and a small proportion of the secondary hydroxyls also react. Honeyman (24) later reached the same conclusions. Malm, et al. (25) applied the method to studying various cellulose acetates and to following the course of the

hydrolysis of cellulose under varying experimental conditions.

There are two methods available for the determination of the number of glycol groups in a cellulose derivative. Cramer, et al. (11) applied the lead tetraacetate method originated by Criegee (26) to a commercial cellulose acetate. Since their work, lead tetraacetate has been largely replaced by periodic acid which behaves similarly in many ways (27).

While no intensive studies appear to have been made of the partially esterified acetates formed, the course of the acetylation reaction is understood quite well. Heuser (28) and Malm and Fordyce (29) give good summaries of the extensive work on this subject. The reaction proceeds rapidly in the amorphous regions of the fiber and more slowly in the crystalline regions. The rate of the latter portion of the reaction may be increased by various pretreatments designed to swell the crystalline regions. However, the slow rate of penetration of these regions remains the chief obstacle to the acetylation reaction, which is of essentially topochemical character. A recent study by Signer, et al. (30), using streaming double refraction, ultracentrifuge sedimentation diagrams, and electron micrographs, showed the presence of fusiform particles which appear to be macromolecular aggregates and which persist in an acetylation for a long time after the cellulose acetate has gone into solution in the acetic acid. These particles could be concentrated with the more insoluble portions of the acetate by fractionation.

PRESENTATION OF PROBLEM

There are at least two explanations of the mechanism of esterification of cellulose acetate and the lack of acetone solubility of the partially esterified acetates. According to one explanation the more reactive, primary hydroxyl groups on carbon six in the glucose units of the cellulose are esterified first, and a portion of these hydroxyls must be free in order for the acetate to be acetone-soluble. The other explanation of the phenomenon is that the acetylating reagent attacks the more accessible portions of the cellulose fiber first. Although the primary hydroxyl on carbon six may be more reactive, the controlling factor is the accessibility of the chains. The reaction proceeds slowly into the highly ordered, crystalline regions, which persist for a long time during the course of the acetylation but eventually break up as the triacetate stage is reached.

According to the latter view, the acetone-soluble, partially hydrolyzed acetates are formed by random deacetylation of the nearly completely acetylated cellulose chain. Approximately equal proportions of all three of the differently located hydroxyls are free in the partially hydrolyzed acetate, and their distribution is random, so that a chain of uniform characteristics is produced along its full length. The partially esterified acetates with the same degree of substitution have the same number of free hydroxyls but they are clustered together in the portions of the chain which were protected from acetylation by their location deep in the crystalline regions. The cellulose acetate chain is not uniform along its length. This leads to different solubility

properties. In addition, there is the possibility of strong hydrogen bonding between unacetylated portions of adjacent chains. This would lead to the formation of polymolecular aggregates whose effective molecular weight would be too large for easy solubility.

The problem in this investigation is the preparation of partially esterified acetates and partially hydrolyzed acetates of corresponding degrees of substitution. These will be studied with every possible means in order to characterize both as completely as possible. The results should support one or the other of these explanations of the mechanism of the esterification of cellulose.

EXPERIMENTAL PROCEDURES

ACETYLATION

Acetylations were carried out in a laboratory-model, sigma-blade, Baker-Perkins mixer. The desired temperature was maintained by circulating water in the jacket of the mixer. The temperature of the acetylation mixture followed very closely (within one degree) that of the water in the jacket. The temperature of the latter was measured since a thermometer could be more easily suspended in it.

One hundred grams of cotton linters (109 grams airdry) were placed in the mixer with 816 grams of glacial acetic acid and mixed at 35° C. for 45 minutes. Then 324 grams of glacial acetic acid mixed with 2.76 grams of sulfuric acid were added, and mixing was continued at 35° C. for one hour. The mixture was then cooled to 18° C. This temperature was held for 15 minutes. Meanwhile the slow addition of 310 grams of acetic anhydride over a period of one hour was begun. After the first 15 minutes, the temperature of the mixture was slowly raised to 50-55° C. at the end of the hour. This temperature was maintained until a chloroform-soluble, fiber-free product was obtained (2.25 hours). Then 1080 grams of 50% acetic acid which contained 2.5% sulfuric acid were added slowly for the hydrolysis. This took place at 50-55° C. The time of hydrolysis was adjusted to give acetates of the desired degree of substitution. Partially esterified acetates of corresponding degrees of substitution were obtained by stopping the acetylation reaction before it had gone to completion.

The acetylation mixture was precipitated by pouring it through a small-orifice funnel into water near the vortex created by a rapidly rotating Lightnin' mixer. The precipitate was washed with boiling water until the wash water was free of acetic acid (basic toward bromothymol blue). Then the acetate was air dried for storage.

ACETYL ANALYSIS

The method of Whistler and Jeanes (31) was modified for use in the apparatus designed for Institute Tentative Method 19 (32). Anhydrous methanol was prepared by refluxing commercial absolute methanol for six hours with magnesium ribbon, after which the methanol was distilled. Freshly cut sodium was dissolved in the methanol to make a 0.2 N solution. The sodium hydroxide solution used was 0.1806 N, and the sulfuric acid used for back titration was 0.0893 N.

A 0.3-gram sample of acetate, previously dried *in vacuo* over phosphorus pentoxide, was introduced into a 250-ml. round-bottom flask, together with 20 ml. of anhydrous methanol and three glass beads to promote smooth boiling. The flask was attached to the condensers, which were arranged for refluxing, and placed in a hot-water bath. Its contents were allowed to reflux for half an hour in order to wet the sample thoroughly. Another 250-ml. flask containing 25 ml. of sodium hydroxide solution and three glass beads was attached to the other end of the condensers and placed in an ice-water bath. The condensers were arranged for distillation, and 10 ml. of sodium methylate solution were added to the cellulose acetate through the dropping funnel. The rate of distillation was adjusted to 35 drops per minute and maintained until less than 5 ml.

remained in the flask. Then a fresh 20-ml. portion of methanol was added to the flask. When it had been distilled, it was followed by two 10-ml. portions. After this, the heat was removed, and the apparatus was swirled to mix the contents of the receiving flask. The water bath beneath it was then heated so that the contents of the flask boiled for 15 minutes to complete saponification of the methyl acetate. Then the source of heat was removed. The contents of the flask were diluted with 75 ml. of boiled, distilled water and titrated with sulfuric acid solution and phenolphthalein indicator. From the amount of base consumed in the determination, the acetyl content of the sample could be calculated.

The calculation was made as follows:

$$CH_3CO\ (\%) = \frac{0.043(\text{ml. NaOH} \times \underline{N}\ \text{NaOH} - \text{ml. } H_2SO_4 \times \underline{N}\ H_2SO_4)}{\text{Wt. of ovendry sample, g.}} \times 100$$

TOSYLATION

The method of Cramer and Purves (10) was followed, with modifications. Anhydrous pyridine was prepared by distilling commercial pyridine from barium oxide. A technical grade of tosyl chloride was recrystallized from benzene to obtain a product with a melting point of 67-69° C.

The moisture content of the cellulose acetate was determined, and a weight of acetate corresponding to the ovendry weight of acetate containing the desired number of moles of free hydroxyls was dried *in vacuo* over phosphorus pentoxide overnight. This material was then dissolved in 115 ml. of anhydrous pyridine. At the same time, 125 grams

of tosyl chloride were dissolved in 240 ml. of pyridine. The two solutions were cooled to 20° C., mixed, and stored at 20 ± 1° C. Samples were taken periodically to be analyzed for sulfur content.

The reaction was stopped by mixing the sample with an equal volume of 10% aqueous acetone at 0° C. for five minutes. The cellulose acetate derivative was precipitated by pouring the mixture slowly into distilled water, with agitation. After standing 20 minutes, the precipitate was filtered and dried over phosphorus pentoxide in vacuo.

The amount of cellulose acetate which was required to provide the desired number of moles of free hydroxyls varied; the amount of solvent which was required to dissolve it had to be varied accordingly. The partially esterified acetates proved to be insoluble in pyridine. If they were dissolved in chloroform, however, a solution of tosyl chloride in pyridine could be added without precipitating them. The materials used in each tosylation are listed in Tables I and II.

The use of chloroform in the tosylation system necessitated modification of the procedure for isolating samples during the course of the reaction. Chloroform is not miscible with water, nor is it miscible with a water-pyridine-acetone mixture. When an aliquot of the reaction mixture containing chloroform was mixed with 10% aqueous acetone, the solution slowly turned milky white. When this mixture was poured into water, the chloroform remained in the cellulose acetate derivative and formed a second liquid phase. The chloroform was removed, and the derivative was precipitated by pouring the mixture into

TABLE I

COMPOSITION OF TOSYLATION MIXTURES

TOSYLATION-RATE STUDIES

Cellulose Acetate	Partially Esterified Acetates		Partially Hydrolyzed Acetates		
	A	B	C	D	E
Acetate, g.	30.54	56.12	37.06	50.25	15.00
Hydroxyl, moles	0.0535	0.0590	0.0679	0.1084	0.0323
Pyridine, ml.	—	—	305	305	115
Chloroform, ml.	205	455	—	—	—
Tosyl chloride, g.	125	125	125	125	125
Tosyl chloride, moles	0.656	0.656	0.656	0.656	0.656
Pyridine, ml.	250	150	150	150	240
Ratio, tosyl chloride: hydroxyl	12.5	11.1	9.7	6.1	20.3

TABLE II

COMPOSITION OF TOSYLATION MIXTURES

FIVE-GRAM BATCH TOSYLATIONS

Cellulose Acetate	Partially Esterified Acetates		Partially Hydrolyzed Acetates		
	A	B	C	D	E
Acetate, g.	5.00	5.00	5.00	5.02	5.00
Hydroxyl, moles	0.0088	0.0053	0.0092	0.0108	0.0108
Pyridine, ml.	—	—	41.2	30.5	38.3
Chloroform, ml.	34.0	40.6	—	—	—
Tosyl chloride, g.	20.8	11.3	16.9	12.5	41.7
Tosyl chloride, moles	0.109	0.059	0.089	0.066	0.219
Pyridine, ml.	41.5	13.4	20.2	15.0	80.0
Time, hr.	144	192	192	144	144
Ratio, tosyl chloride: hydroxyl	12.5	11.3	9.7	6.1	20.3

boiling water to drive off the chloroform. The mixture was then cooled by adding cold water. The precipitate formed in this way was not flocculent. It was ground in a Waring Blendor for one minute to reduce the material to a finely divided form. This material was allowed to stand in contact with water for 20 minutes, then filtered, washed, and dried. A second purification by redissolving and reprecipitating the sample was found to be necessary in the case of the acetates with higher degrees of substitution (i. e., 2.7), in order to remove entrapped p-toluenesulfonic acid.

SULFUR ANALYSIS

The Parr sulfur bomb (33) was used for sulfur determinations. The charge consisted of 0.2 gram of tosylated acetate, 0.2 gram of benzoic acid, 0.2 gram of sucrose, 1.0 gram of potassium nitrate, and 15 grams of sodium peroxide. These were mixed in the bomb by shaking for one minute. A few drops of water were placed on the cover of the bomb. The bomb was placed on a wire gauze and heated with a Bunsen burner until the water on the top boiled. It was then removed from the flame and, after 30 seconds, quenched in running water.

The melt was washed out of the bomb into a 400-ml. beaker with hot water. This solution was acidified and filtered to remove carbon. The filtrate was heated to boiling and treated with 20 ml. of 10% barium chloride solution. The barium sulfate precipitate was allowed to settle overnight before being filtered into a tared Gooch crucible, ignited, and weighed.

The sulfur content was calculated as follows:

$$\text{Sulfur content } (\%) = \frac{32(\text{Wt. of } BaSO_4, \text{ g.})}{233(\text{Wt. of ovendry sample, g.})} \times 100$$

IODINATION

Iodination was carried out by heating one gram of tosylated cellulose acetate derivative with two grams of sodium iodide in 75 ml. of redistilled acetonylacetone for two hours at 120° C. The iodinated product was isolated by cooling the mixture and pouring it with rapid agitation into two liters of ice water. The derivative was allowed to stand in contact with water for one hour, then centrifuged to concentrate the precipitate, filtered, washed with 0.1 N sodium thiosulfate to remove adsorbed iodine, washed with water, and dried. This washing with thiosulfate solution removes adsorbed iodine and yields derivatives which are free of the yellow color often reported by other experimenters.

IODINE ANALYSIS

The aliphatic iodine determination described by Clark (24) was used to analyze iodinated derivatives. The sodium thiosulfate solution used to titrate the iodine liberated was 0.0912 N. A 0.1-gram sample was weighed into a 250-ml. Erlenmeyer flask. Twenty milliliters of a 10% solution of sodium acetate in glacial acetic acid and a few drops of bromine were added to the flask. It was then heated on a steam bath for 30 minutes or until the material being analyzed had been completely dissolved. At that time the flask was removed from the heat, cooled, and diluted with 25 ml. of a 25% solution of sodium

acetate and 100 ml. of water. A few drops of 98-100% formic acid were added to destroy excess bromine. The mixture was allowed to stand for 10-15 minutes before the next step. Ten milliliters of 10% sulfuric acid and one gram of potassium iodide were added to the solution. The iodine liberated was titrated with sodium thiosulfate solution immediately.

The equations for the reactions involved are:

$$HI + Br_2 \rightarrow HBr + IBr$$

$$IBr + 2\ Br_2 + 3H_2O \rightarrow HIO_3 + 5\ HBr$$

$$HIO_3 + 5\ HI \rightarrow 3\ I_2 + 3\ H_2O$$

The calculation was made as follows:

$$\text{Iodine content (\%)} = \frac{0.167 \times 127\ (\text{ml. } Na_2S_2O_3 \times N\ Na_2S_2O_3)}{1000\ (\text{Wt. of ovendry sample, g.})} \times 100$$

TRITYLATION

Trityl derivatives were prepared by treating the acetates with an excess of trityl chloride (Eastman Kodak triphenylchloromethane, m.p. 109-111° C.) in pyridine, following the method of Malm, et al. (25). Ten-gram samples of acetate previously dried in vacuo over phosphorus pentoxide were dissolved in 50 ml. of anhydrous pyridine. The amount of trityl chloride added was calculated from the formula:

$$\frac{\text{Weight of trityl chloride, g./10 g. of cellulose acetate}}{} = 10 + 12\ (\text{OH per glucose unit} - 0.50)$$

The trityl chloride was added to the cellulose acetate dissolved in pyridine in a bottle with a ground-glass stopper. The bottle was

placed in an oven maintained at 70-75° C. During the first few minutes, it was inverted occasionally to dissolve the solid trityl chloride. After that, it was allowed to remain in the oven for 24 hours. The product was isolated by diluting the mixture with acetone and pouring it into methanol with rapid agitation. The precipitate was washed with methanol and dried.

The partially esterified acetates were dissolved in chloroform which had been diluted with pyridine before the addition of trityl chloride. In order to check on the effect of this modification, partially hydrolyzed acetate "D" was tritylated in a chloroform-pyridine mixture as well as in pyridine.

TRITYL ANALYSIS

The method of Hearon, et al. (23) was used to analyze for the trityl content of the derivatives. The samples consisted of one gram of tritylated cellulose acetate derivative which had been previously dried in vacuo over phosphorus pentoxide. This was placed in a 250-ml. Erlenmeyer flask, and 10 ml. of concentrated sulfuric acid were poured over it. This mixture was stirred until the derivative had completely dissolved. Then water was added slowly, in a fine stream, until the solution changed to a gray color, at which point 90 ml. of additional water were added. The precipitated triphenylcarbinol (Ph_3COH) was filtered through a tared, fritted-glass crucible of fine porosity, washed until free of sulfate, dried at 100° C. for one hour, cooled, and weighed. The percentage of trityl was calculated according to the formula:

$$\text{Trityl } (\%) = \frac{243(\text{Wt. of } Ph_3COH, \text{ g.})}{260(\text{Wt. of ovendry sample, g.})} \times 100$$

CALCULATION OF DEGREE OF SUBSTITUTION

Cellulose acetate derivatives were analyzed for acetyl content as well as for sulfur, iodine, or trityl, as the case might be. The only exceptions to this were the tosylated-iodinated derivatives. Iodine interferes with the acetyl determination, and the acetyl content of these derivatives could not be determined. The degree of substitution of acetyl in these derivatives was assumed to be the same as that found by analysis for the corresponding tosylated derivatives.

The degree of substitution was calculated using the formula:

M.W. = 111 59 $\underline{X}$ 171 $\underline{Y}$ 127 $\underline{Z}$ 17 (3 - $\underline{X}$ - $\underline{Y}$ - $\underline{Z}$).

Acetyl, (%) = 43 $\underline{X}$ x 100 / M.W.

Sulfur, (%) = 32 $\underline{Y}$ x 100 / M.W.

Iodine, (%) = 127 $\underline{Z}$ x 100 / M.W.

$\underline{X}$ = Degree of substitution, acetyl

$\underline{Y}$ = Degree of substitution, tosyl

$\underline{Z}$ = Degree of substitution, iodine.

For trityl derivatives, the formula used was:

M.W. = 111 59 $\underline{X}$ 259 $\underline{W}$ 17 (3 - $\underline{X}$ - $\underline{W}$).

Trityl, (%) = 243 $\underline{W}$ x 100 / M.W.

$\underline{W}$ = Degree of substitution, trityl.

LEAD TETRAACETATE OXIDATION

Each of the cellulose acetates studied was oxidized with lead

tetraacetate to obtain a measure of the number of unesterified vicinal hydroxyl pairs (glycols) on carbons two and three. The method of Cramer, et al. (11) was followed with slight modifications. Lead tetraacetate was prepared according to directions given by Bailar (35). In a 500-ml. three-neck, round-bottom flask fitted with a thermometer and mercury-sealed stirrer, 270 grams of glacial acetic acid were mixed with 90 grams of acetic anhydride. To this mixture, 150 grams of dry minium (Pb_3O_4) were added gradually in small amounts with cooling at first and later warming to keep the temperature at not above 65° C. When all the minium had dissolved, the mixture was cooled, and the lead tetraacetate was filtered through a large Buchner funnel. The lead tetraacetate was stored under glacial acetic acid until used.

For the determination, a weight corresponding to 0.01 mole of cellulose acetate was dissolved in 25 ml. of glacial acetic acid in a 100-ml. volumetric flask with ground-glass stopper. To this was added 25 ml. of a 0.1 N solution of lead tetraacetate in glacial acetic acid. The flask was then filled to the mark with glacial acetic acid and stored in a constant temperature bath at 25 ± 0.1° C. The contents of the flask were protected from exposure to light with heavy aluminum foil wrapper. A blank solution was also prepared.

Samples were withdrawn with a 10-ml. pipet at 12, 24, 36, 48, 80, 120, 200, and 360-hour intervals. The pipet was discharged into 20 ml. of a 25% solution of sodium acetate containing an excess of potassium iodide, and the pipet was well rinsed with 5 ml. of glacial acetic acid. The iodine liberated was titrated with 0.0912 N sodium

thiosulfate contained in a microburet, using starch as an indicator. The end point was difficult to judge because of the presence of golden yellow lead iodide in suspension.

The partially esterified acetates were not completely soluble in glacial acetic acid, and 50 ml. of chloroform were added in each determination to put them into solution. This had no effect on the consumption of lead tetraacetate, as shown by the constant results obtained with a blank prepared with chloroform.

The consumption of lead tetraacetate was calculated by subtracting the volume of thiosulfate used for each sample from the volume used for the blank. An average of the eight values for the blank was used to minimize errors. This showed an initial, rapid reaction, superimposed on a gradual, continuous one. The rapid reaction was taken to be the consumption of oxidant by glycols. The continuous reaction was extrapolated to zero hours, and this value was taken as a measure of the glycols present. One mole of oxidant consumed corresponds to one mole of glycol.

DEGREE OF POLYMERIZATION

Viscosity measurements were made on dilute solutions of the acetates to determine intrinsic viscosity and average degree of polymerization. Solutions were prepared by weighing 0.25-gram portions of the acetates into 100-ml. volumetric flasks, filling with solvent, and shaking until solution took place. These solutions were diluted to give solutions with specific viscosities between 0.1 and 0.3. Viscosities

were measured in modified Ostwald, constant-overflow viscometers in a constant-temperature bath at 25 ± 0.01° C. Intrinsic viscosity was calculated using Badgley and Mark's (36) formula:

$$[\eta] = \eta_{sp} / c\,(1 + k' \times \eta_{sp}).$$

Concentration c was expressed in grams per liter, and k' was taken as 0.3. The average degree of polymerization was calculated, using the values given by Heuser (37) of K_m is 5.3×10^{-4} for partially esterified cellulose acetates in chloroform and K_m is 6.3×10^{-4} for partially hydrolyzed cellulose acetates in acetone. The relationship between intrinsic viscosity and degree of polymerization is: $D.P. = [\eta] / K_m$.

FRACTIONATION OF ACETATES

The partially esterified acetates were not completely insoluble in acetone, but only a small portion of the acetate dissolved. Separation of the soluble and insoluble portions was carried out in an effort to determine qualitative differences.

A 10-gram sample of acetate was placed in a centrifuge jar with 100 ml. of redistilled acetone and was shaken for half an hour. Then it was centrifuged at 2000 r.p.m. for 15 minutes to settle the undissolved portion. The solution was decanted and concentrated under reduced pressure at room temperature. The procedure was repeated four times, and the acetone solutions were consolidated. Finally, the insoluble residue was dried at 60° C., first under atmospheric pressure, then under reduced pressure. The same procedure was followed after the acetone solutions had been concentrated as much as possible under

vacuum at room temperature. The fractions obtained were analyzed for acetyl content, and viscosity measurements were made to determine the degree of polymerization.

DISCUSSION OF RESULTS

ACETYLATION

The values for acetyl analyses of the five acetates studied are listed in Table III. Partially esterified acetate A, with a degree of substitution of 2.53 corresponds very closely to partially hydrolyzed acetate C with a degree of substitution of 2.51. Acetate B is obtained after the acetylation reaction has proceeded further toward completion and a degree of substitution of 2.71 has been achieved. Acetates D and E each have a degree of substitution of 2.43. Tritylation studies show that they have the same number of primary hydroxyl groups. Lead tetraacetate oxidation indicates that they have practically the same number of unesterified glycol groups. It may be assumed that these two acetates are very similar.

TABLE III

ACETYL ANALYSES

	Partially Esterified Acetates		Partially Hydrolyzed Acetates		
Cellulose Acetate	A	B	C	D	E
Acetyl, %	40.6	42.2	40.4	39.6	39.6
Acetyl, D. S.	2.53	2.71	2.51	2.43	2.43

TOSYLATION

Acetates A, B, and C were tosylated with an excess of tosyl chloride over unesterified hydroxyls of approximately 10:1. Acetates C and E were treated with a 6:1 and a 20:1 excess of tosyl chloride,

respectively. The exact figures are in Tables I and II. The tosylation-rate studies described in Table I and in Appendix I were sampled at 1, 2, 3, 4, 6, 8, 10, 12, 24, 48, 96, 144, 192, and 240 hours. The partially hydrolyzed acetates reacted very smoothly with tosyl chloride, and the sulfur content of the derivatives followed a course similar to that reported by Purves and his students (10-12, 38) and other workers. However, the sulfur content of derivatives of the partially esterified acetates varied erratically. For this reason it was impossible to use the rate of tosylation to calculate the proportion of the two secondary hydroxyls in acetates A and B. The calculations for acetates C, D, and E are described in Appendix I.

The only samples to approach complete tosylation were those of acetate E, which was tosylated with the greatest excess of reagent. Even so, of the 0.567 hydroxyl theoretically available for tosylation, only 0.450 reacted in 144 hours. It has been pointed out by Purves and his students (10-12, 38) that a slow substitution with chlorine takes place, although this can be held to a minimum by working with low temperatures (i.e., 20° C.). The 240-hour sample of the tosylation of acetate E was analyzed and found to contain 0.98% chlorine, corresponding to a degree of substitution of 0.092. That left 0.025 or more hydroxyl per glucose unit, or one per 13.3 glucose units, unaccounted for in the 144-hour sample. The presence of these unsubstituted hydroxyls was not satisfactorily explained. They may have been present because steric hindrances prevented complete tosylation, or because the theoretical number of hydroxyls were not available for substitution.

Infrared analysis of a film of the material (cast from an acetone solution) was carried out. A chloroform-soluble partially esterified acetate with a degree of substitution of 2.88, and a cellulose triacetate (44.44% acetyl) prepared by Minnesota Mining & Manufacturing Company were also analyzed. The transmittance curves are reproduced in Figure 1.

Interpretation of these curves is difficult. There is a small inflection in the second curve but none in either the first or third curves at 3360 cm.$^{-1}$. This is the region where hydrogen-bonded hydroxyls usually are found. From this one may conclude that the acetate which by analysis has 0.12 free hydroxyl per glucose unit actually has some free hydroxyls. The tosylated derivative may have no free hydroxyls because of the presence of some substituent for which no analysis was made.

A chart by Williams (39) shows unbonded hydroxyls appearing in the vicinity of 3500 cm.$^{-1}$. No compounds analyzed at the Institute have been found to have absorption bands in this region. All three acetates show bands at 3500 and at 3650 cm.$^{-1}$. The appearance of two bands gives rise to the speculation that they represent primary and secondary hydroxyl absorption bands. If these bands are caused by unbonded hydroxyls, one might conclude that the triacetate had some free hydroxyls, the tosylated derivative had more, and the partially esterified acetate had still more. This order is in agreement with the chemical analyses.

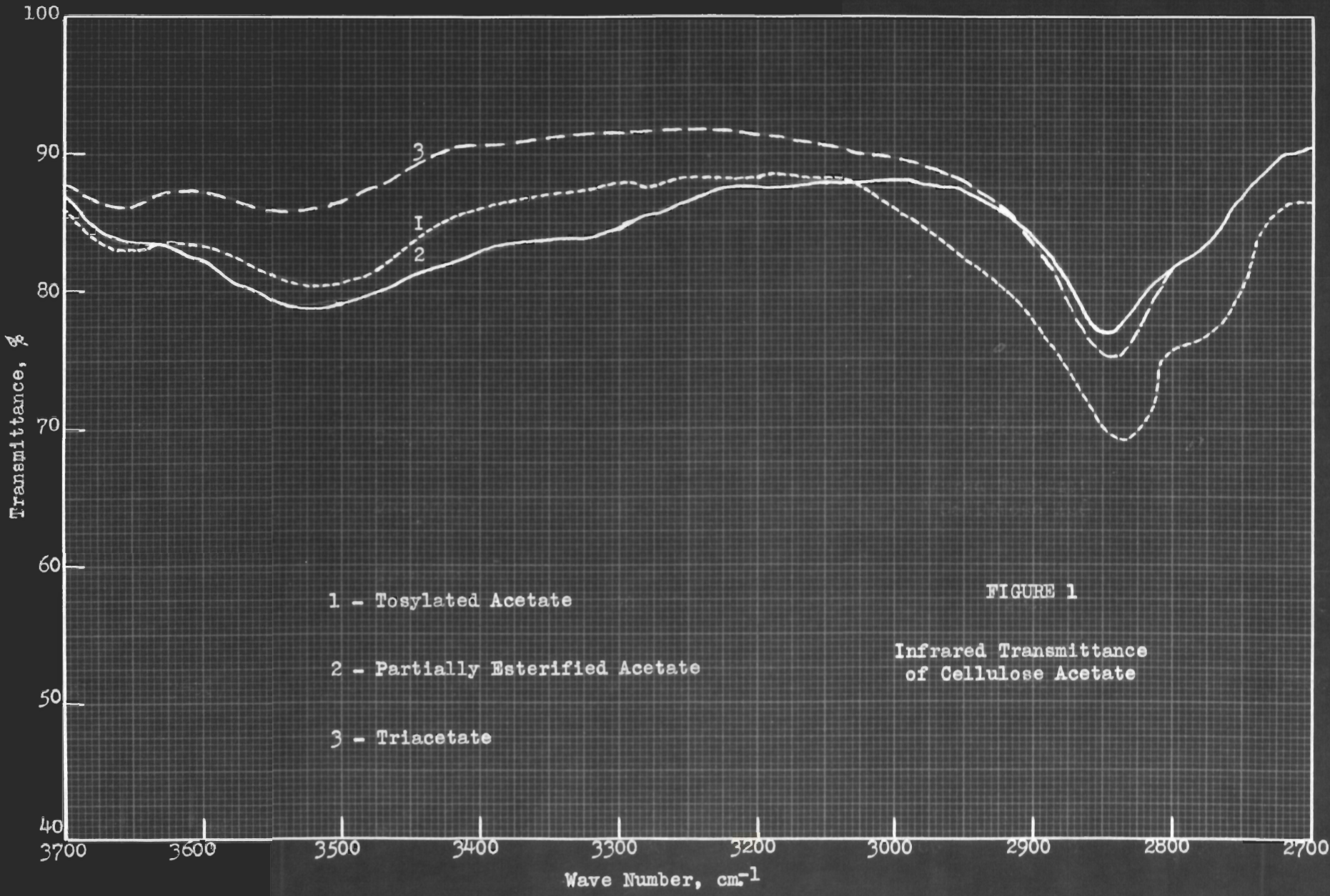


FIGURE 1

Infrared Transmittance
of Cellulose Acetate

Tosylation of acetate D with a 6:1 excess of tosyl chloride gave a maximum of 2.18% sulfur, corresponding to a degree of substitution of 0.201, as compared with 4.32% sulfur, or 0.450 tosyl per glucose unit obtained when acetate E was tosylated with a 20:1 excess of reagent. Thus the number of tosyl groups introduced appears to be dependent upon the excess of tosyl chloride used.

Five-gram batches of acetate were tosylated. The reaction conditions, listed in Table II, were the same as those used for the tosylation-rate experiments. The products of these tosylations were analyzed for sulfur and for acetyl content. These figures appear in Table IV, together with the figures for the sulfur content of the acetates in the tosylation-rate reactions. It is interesting to note that in every case except that of acetate D, which was allowed to react 48 hours longer in the batch tosylation, the sulfur contents obtained were lower for the batch tosylations than for the rate experiments. It would seem from this that the tosylation reaction is not accurately reproducible.

Analysis of acetates C and E showed that they lost acetyl groups during tosylation. This deacetylation makes more hydroxyl groups available for tosylation and iodination, which introduces a source of error into the results.

IODINATION

The iodinated samples were analyzed for sulfur and for iodine. Acetyl analyses could not be carried out because iodine interferes with

TABLE IV

FIVE-GRAM BATCH TOSYLATION
SULFUR AND ACETYL ANALYSES

Cellulose Acetate	Partially Esterified Acetates		Partially Hydrolyzed Acetates		
	A	B	C	D	E
Sulfur, %	2.00	1.12	2.81	2.47	4.21
Acetyl, %	37.0	40.0	34.4	35.3	30.4
Tosyl, D.S.	0.16	0.10	0.27	0.23	0.43
Acetyl, D.S.	2.51	2.71	2.44	2.48	2.29
Sulfur, max., %[a]	2.09	2.32	2.94	2.39	4.32

[a] Tosylation-rate study; see Appendix I

the determination. The degree of substitution of acetyl groups was assumed to be the same as it was in the tosylated derivatives. The analytical values and calculated degrees of substitution for each substituent are listed in Table V.

It will be noticed that the combined degree of substitution of tosyl and iodine groups does not equal the degree of substitution of tosyl groups in the tosylated samples. There is no clear trend in these discrepancies, and it is probable that they are due to experimental error rather than to the presence of large amounts of chlorine which would be replaced by iodine (10-12, 38).

TRITYLATION

Tritylated derivatives of each acetate were analyzed for trityl and for acetyl content. These figures and the calculated degrees

TABLE V

IODINATION OF
FIVE-GRAM BATCH TOSYLATION PRODUCTS
IODINE AND SULFUR ANALYSES

Cellulose Acetate	Partially Esterified Acetates		Partially Hydrolyzed Acetates		
	A	B	C	D	E
Iodine, %	4.26	1.92	6.64	5.84	9.49
Sulfur, %	0.86	0.56	1.28	1.08	1.72
Iodine, D.S.	0.10	0.04	0.16	0.14	0.23
Tosyl, D.S.	0.08	0.05	0.12	0.10	0.15
Acetyl, D.S.	2.51	2.71	2.44	2.48	2.29

of substitution of each group appear in Table VI. It is of interest to compare these values with those obtained by iodination, since both methods are supposed to measure primary hydroxyls. There is close correspondence between the values for each acetate, and in only one case are the values obtained by tosylation-iodination higher than those obtained by tritylation. This is acetate E, treated with a 20:1 excess of tosyl chloride. It would appear that if such large excesses of reagent are avoided in the tosylation step, Timell's (22) limitation on the number of secondary hydroxyls which may be tosylated was too strict. In each case more than half as many secondary hydroxyls have been tosylated as primary hydroxyls, and yet the iodination values do not exceed those obtained by tritylation when the proportion of tosyl chloride does not exceed 12.5:1.

Since it is known that neither method is absolutely accurate,

TABLE VI

ANALYSES OF TRITYLATED ACETATES

Cellulose Acetate	Partially Esterified Acetates			Partially Hydrolyzed Acetates		
	A	B	C	D	D[a]	E
Trityl, %	8.4	4.5	13.8	15.5	15.8	15.9
Acetyl, %	37.6	39.8	34.6	32.0	31.0	33.5
Trityl, D.S.	0.10	0.05	0.18	0.19	—	0.19
Acetyl, D.S.	2.58	2.47	2.48	2.26	—	2.40

[a]Sample tosylated in chloroform-pyridine mixture.

it would appear that tritylation is to be preferred as much the simpler method for obtaining an approximate measure of the number of primary hydroxyls in a cellulose derivative.

LEAD TETRAACETATE OXIDATION

The titration in the lead tetraacetate oxidation has an end point which is exceedingly difficult to determine. Even the least degraded starches used as indicators finally turned purple, then red, as the end point was approached. When this color change was superimposed on the golden yellow color of the precipitated lead iodide, the color change observed was from muddy brown to golden yellow. The titration data and the curves plotted from them are given in Appendix II. The variation in the values obtained for the blank titration gives an indication of the precision of the titration. The calculated values for the degree of substitution of glycols are given in Table VII. The calculated values for the occurrence of glycols with random distribution of the

TABLE VII

UNESTERIFIED GLYCOL GROUPS
LEAD TETRAACETATE OXIDATION

Cellulose Acetate	Partially Esterified Acetates		Partially Hydrolyzed Acetates		
	A	B	C	D	E
$Na_2S_2O_3$, ml.	0.243	0.071	0.333	0.578	0.518
Vol. x N	0.022	0.006	0.030	0.053	0.047
Hydroxyls in pairs	0.022	0.006	0.030	0.053	0.047
Glycol groups, D.S.	0.011	0.003	0.015	0.026	0.024
Glycols, calcd.[a]	—	—	0.018	0.017	0.028

[a] D.S. of C_3-OH x D.S. of C_2-OH. See Appendix I.

secondary hydroxyls calculated for acetates C, D, and E in Appendix I are also tabulated. In no case is the figure obtained by oxidation measurements significantly different from the value calculated for random distribution of the hydroxyls. This finding is in disagreement with the observation of Gardner and Purves (12) which has puzzled other observers (28).

The values obtained are open to the objection that acetyl groups on cellulose derivatives may rearrange in acetic acid solution (21). However, the close agreement between acetates A and C does not necessarily indicate that the distribution of substituents is random in both acetates.

DEGREE OF POLYMERIZATION

The degree of polymerization of the respective acetates as shown in Table VIII contributes nothing positive to the study of their solubility properties. All acetates fall within the range of values required for good

acetone solubility. A degree of polymerization of 200 is usually expected in a commercial acetate. A comparison of the values obtained by measuring the viscosity of acetate C in chloroform with those obtained in acetone shows that the constant used in converting intrinsic viscosity in chloroform is too low in relation to that used for acetone. The degree of polymerization should, of course, be the same in both solvents. This discrepancy would raise the values obtained in chloroform slightly in relation to the values measured in acetone, but the difference would not be enough to explain the lack of acetone solubility of partially esterified acetates.

TABLE VIII

INTRINSIC VISCOSITY AND AVERAGE DEGREE OF POLYMERIZATION
(x = chloroform, y = acetone)

	Partially Esterified Acetates			Partially Hydrolyzed Acetates		
Cellulose Acetate	A	B	C	C	D	E
G.g./l.	1.153	1.573	2.703	1.188	1.530	2.030
Solvent	x	x	x	y	y	y
Viscometer	E	E	E	D	D	D
Solvent, seconds	136.1	136.1	136.6	146.6	146.6	146.6
Solution, seconds	146.4	150.4	162.2	166.6	181.4	185.2
sp.	0.0757	0.1051	0.1874	0.1364	0.2365	0.2633
	0.0642	0.0648	0.0656	0.1095	0.1445	0.1202
D.P.	121	122	124	174	229	191

FRACTIONATION OF ACETATES

The information obtained by the attempted fractionation of

acetates A and B, presented in Table IX, is disappointing. From the decrease in both degree of substitution and degree of polymerization, of the isolated fractions, it would appear that degradation took place even under the mild conditions used. However it is interesting to note that, in both cases, the insoluble fractions showed higher degrees of substitution and higher degrees of polymerization than the soluble fractions. This may be due solely to the fact that the insoluble fractions were subjected to the fractionation conditions for shorter periods of time.

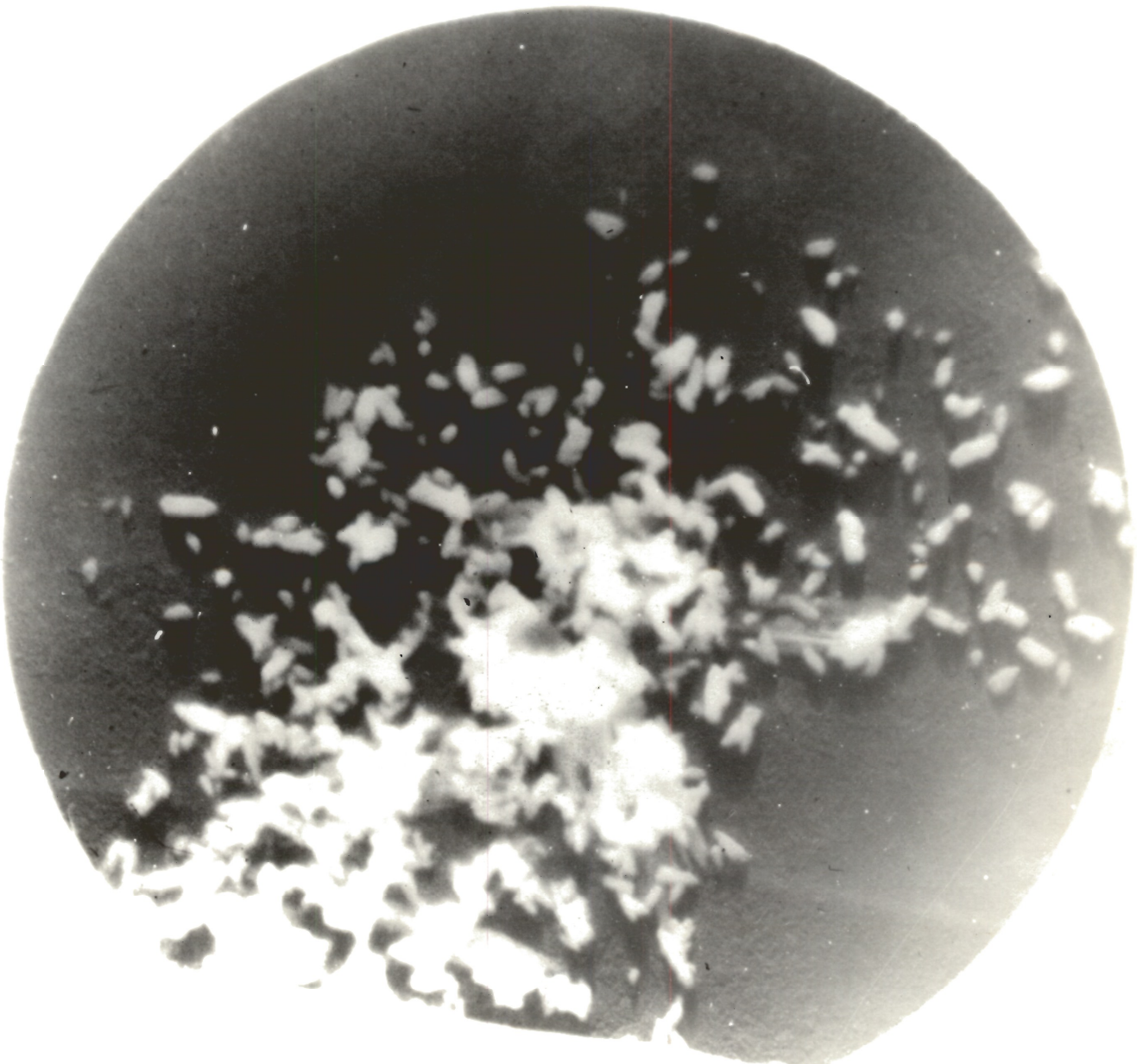
TABLE IX

PARTIAL ACETONE SOLUBILITY

Cellulose Acetate	A	B
D.S.	2.54	2.71
D.P.	121	122
Acetone soluble, %	35.9	30.0
D.S. soluble	2.37	2.36
D.P. soluble	61	84
D.S. insoluble	2.49	2.62
D.P. insoluble	130	143

ELECTRON MICROGRAPHS

Films were cast from 0.4% chloroform solutions of acetates A and C, shadow cast with 16.3 A. of gold at an angle of 1:5, and examined in the electron microscope. In films cast from partially esterified acetate A, small particles, similar to those observed by Signer, et al. (30) may be seen. No such particles were observed in the films of acetate C. Figure 2 shows a cluster of these particles. These particles



Signer presumed to be crystalline regions which had only been superficially esterified. The fact that they are not present in acetate C indicates that these particles are destroyed by the complete esterification to which C has been subjected.

SUMMARY AND CONCLUSIONS

The results of this work tended, in the main, to support the view that in the esterification of cellulose, the acetylating reagents attack the more accessible portions of the fiber first, and then penetrate slowly into the crystalline regions. Although the primary hydroxyl on carbon six may be more reactive, the controlling factor appeared to be accessibility of the chains.

There was a slight difference in the proportions of primary hydroxyls at various stages of the reaction, but primary hydroxyls were always present in considerable amounts. The fact that there were fewer primary hydroxyls unsubstituted in the partially esterified acetates could be attributed to their greater reactivity. The drop in the proportion of free primary hydroxyls in the partially esterified acetates as the acetylation reaction approached completion was interpreted as a sign that the acetylating reagents were penetrating the crystallites more deeply, and that the primary hydroxyls were reacting more rapidly with the reagents.

However, the clustering of unesterified hydroxyls in regions which formed crystalline portions of the cellulose fiber would produce a higher proportion of glycol groups than would occur in the case of random distribution of the secondary hydroxyl groups. This was not observed in the partially esterified acetates studied. There is the possibility that the reaction medium used in the lead tetraacetate oxidation for the estimation of glycols permitted the migration of acetyl

groups. This would tend to randomize the distribution of hydroxyls and bring the number of glycols down into the range of observed values.

There are three properties of polymers which tend to resist solution. They are stiffness of polymer structure, perfection of packing of adjacent molecules, and nature of substituent groups in the molecule. These must be counterbalanced by equivalent forces before solution can occur.

Applying these criteria to partially esterified cellulose acetates, it was noted that cellulose acetate is a very stiff chain (1). The completely substituted triacetate is particularly stiff. If partially esterified acetates consisted of chains which were almost completely acetylated for portions of their length, with very slightly acetylated portions between, the completely acetylated portions would be very stiff and would resist solution.

Electron micrographs and other measurements show the existence of fusiform bodies in solutions of partially esterified acetates. It appears likely that these are the slightly acetylated remnants of crystalline regions of the cellulose fiber. If this be the case, then the perfection of packing of adjacent molecules would be good. Acetates containing such bodies would resist solution.

The existence of insoluble fusiform bodies lends weight to the theory that the cellulose chain in partially esterified acetates is highly acetylated along portions of its length and very slightly

acetylated along other portions which were protected from the acetylating reagents by being buried deep in crystalline areas. If this is the case, then highly acetylated portions of the chain would tend to be soluble in solvents for cellulose triacetate. The slightly acetylated portions of the chain would more nearly resemble cellulose, which requires entirely different solvents. This extreme difference in the nature of the substituent groups at different points in the same molecule would also prevent solution in most solvents.

Thus, partially esterified cellulose acetate appeared to possess in a high degree all three of the properties of polymers which resist solution.

It appeared that acetone solubility is a complex property which is affected by the average degree of polymerization of the acetate, by the average degree of substitution of the acetate, and by the regularity of distribution of unesterified hydroxyls along the chain. Regular distribution and good acetone solubility may be obtained by complete acetylation to destroy hydrogen bonding between cellulose chains of the fiber, followed by random deacetylation in solution.

In addition to finding evidence which elucidated the mechanism of esterification and its effect on the solubility of the product, the investigation brought to light a number of points which had not previously been reported.

The excess of tosyl chloride which was used in tosylation governed the number of tosyl groups introduced. If complete

substitution is desired, a 20:1 excess or greater should be used. For customary tosylation-iodination methods of estimating primary hydroxyls, a 10:1 excess appeared to be ample.

The tosylation reaction was not completely reproducible.

Deacetylation of samples being tosylated did occur. This made available for tosylation more hydroxyl groups, introducing a factor of uncertainty into any analytical results calculated for samples which suffered deacetylation.

The stricture of Timell (22) concerning the proportion of secondary hydroxyls which may be tosylated without interfering with accurate iodination results may be disregarded, provided results comparable to those obtained by tritylation are sufficiently accurate.

Lead tetraacetate oxidation to determine glycols showed no deviation from the values which might be expected for random distribution of secondary hydroxyls. This finding conflicts with the observation of Gardner and Purves (12), who postulated that deacetylation of one secondary hydroxyl stabilized the glucose unit against further deacetylation.

A partially hydrolyzed acetate was found to contain 2.51 acetyl groups per glucose unit, 32% of the unesterified hydroxyls on carbon six, 50% on carbon three, and 18% on carbon two. Of the secondary hydroxyls, 6.2% occurred as glycols. A partially esterified acetate with 2.53 acetyl groups per glucose unit had 21% of its unesterified hydroxyls

in the primary position and 4.7% of the secondary hydroxyls present as glycols. Esterification to 2.71 acetyl groups per glucose unit decreased the proportion of primary hydroxyls to 16% and glycols to 2.0%.

Partially esterified acetates had not been studied previously with these methods. The establishment of unesterified primary hydroxyls in these acetates contradicted predictions which had been made concerning them. The number of glycols found in partially hydrolyzed acetates was also in contradiction to previous findings. The picture of the mechanism presented by these studies makes it appear unlikely that there can be any short cut in the present, indirect commercial process of manufacturing cellulose acetate. Complete esterification followed by random deacetylation appears to be the only method of obtaining the desired acetone-soluble product.

LITERATURE CITED

1. Spurlin, H. M., J. Polymer Sci. 3:714-734 (1948).

2. Miles, George W., U. S. patent 838,350 (Dec. 11, 1906); Official Gaz. U. S. Pat. Office 125:1932 (1906).

3. Ost, H., Z. angew. Chem. 32:76-79 (1919).

4. Kita, G., Sakurada, I., and Nakashima, T., Cellulosechemie 9:13-17, 27-29 (1928).

5. Sakurada, Ichiro, and Kitabatake, Tozo, J. Soc. Chem. Ind. Japan, 37: Suppl. binding 604-605 (1934); C. A. 29:1243 (1935).

6. Hockett, R. C., and Hudson, C. S., J. Am. Chem. Soc. 56:945-946 (1934).

7. Jackson, E. L., Hockett, R. C., and Hudson, C. S., J. Am. Chem. Soc. 56:947-949 (1934).

8. Verkade, P. E., van der Lee, J., and Meerburg, W., Rec. trav. chim. 56:613-622 (1937).

9. Hurd, Charles D., Mack, Clinton O., Filachione, E. M., and Sowden, John C., J. Am. Chem. Soc. 59:1952-1954 (1937).

10. Cramer, F. B., and Purves, C. B., J. Am. Chem. Soc. 61:3458-3462 (1939).

11. Cramer, F. B., Hockett, R. C., and Purves, C. B., J. Am. Chem. Soc. 61:3463-3464 (1939).

12. Gardner, Thomas S., and Purves, C. B., J. Am. Chem. Soc. 64:1539-1542 (1942).

13. Oldham, John Walter Hyde, and Rutherford, Jean Kerr, J. Am. Chem. Soc. 54:366-378 (1932).

14. Clarke, Hans T., and Malm, Carl J., U. S. patent 1,668,946 (May 8, 1928).

15. Levene, P. A., and Tipson, R. Stuart, J. Biol. Chem. 120:607-619 (1937); C. A. 32:503 (1938).

16. Müller, H., and Reichstein, T., Helv. Chim. Acta 21:263-272 (1938).

17. Tipson, Stuart R., and Cretcher, Leonard H., J. Org. Chem. 8:95-98 (1943).

18. Hann, Raymond M., Ness, A. T., and Hudson, C. S., J. Am. Chem. Soc. 66:73-76 (1944).

19. Tipson, Stuart R., Clapp, Mary A., and Cretcher, Leonard H., J. Org. Chem. 12:133-137 (1947).

20. Karrer, P., Schick, E., and Schwyzer, R., Helv. Chim. Acta 31:784-786 (1948).

21. Malm, Carl J., Tanghe, Leo J., and Laird, Barbara C., J. Am. Chem. Soc. 70:2740-2747 (1948).

22. Timell, Tore. Studies on cellulose reactions. Especially p. 105-116. Dissertation. Stockholm, Sweden, Kungl. Tekniska Högskolan, 1950. 275 p.

22a. Timell, Tore, Svensk Kem. Tid. 61:146-155 (1949).

23. Hearon, W. M., Hiatt, Gordon D., and Fordyce, Charles R., J. Am. Chem. Soc. 65:2449-2452 (1943).

24. Honeyman, John, J. Chem. Soc. 1947:168-173.

25. Malm, Carl J., Tanghe, Leo J., and Laird, Barbara C., J. Am. Chem. Soc., 72:2674-2678 (1950).

26. Criegee, Rudolf, Ber. 64:260-266 (1931).

27. Fleury, P., and Lange, J., Compt. rend. 195:1395-1397 (1932); C. A. 27:1617 (1933).

28. Heuser, Emil. The chemistry of cellulose. Especially p. 226-263. New York, Wiley, 1944. 660 p.

29. Malm, Carl J., and Fordyce, Charles R., Cellulose organic acid esters. In Ott, Cellulose and cellulose derivatives. p. 667-694. New York, Interscience Publishers, 1946.

30. Signer, R., Aeby, A., Opderbeck, F., and Studer, H., Monatsh. 81:232-238 (1950).

31. Whistler, Roy L., and Jeanes, Allene, Ind. Eng. Chem., Anal. Ed., 15:317-318 (1943).

32. Institute Tentative Method 19. 1940.

33. Parr Instrument Co. Directions for using the Parr sulfur bombs and the Parr turbidimeter. Booklet 113. Moline, Ill., The Company. 1934. 31 p.

34. Clark, E. P. Semimicro quantitative organic analysis. Especially p. 60-62. New York, Academic Press, 1943. 135 p.

35. Bailar, John C., Jr. Lead tetracetate. In Inorganic syntheses. Vol. 1. p. 47-49. New York, McGraw-Hill Book Co., 1939.

36. Badgley, W. J., and Mark, H., J. Phys. & Colloid Chem. 51:58-70 (1947).

37. Heuser, Emil. The chemistry of cellulose. Especially p. 592. New York, Wiley, 1944. 660 p.

38. Mahoney, John F., and Purves, C. B., J. Am. Chem. Soc. 64:9-15 (1942).

39. Williams, Van Zandt, Rev. Sci. Instruments 19:135-178 (1948).

APPENDIX I

TOSYLATION-RATE STUDY

Mahoney and Purves (38) used the rate of tosylation to distinguish between the secondary hydroxyls in a cellulose derivative. Iodination of the tosylated derivative gives the degree of substitution (D.S.) of unesterified primary hydroxyls. Subtraction of this value from the total D.S. of unesterified hydroxyls gives the D.S. of secondary hydroxyls, C_s. The D.S. of these secondary hydroxyls which have reacted to form tosyl derivatives, Z_s, can be determined by subtracting the D.S. of the iodinated derivative from the total D.S. of tosyl groups at any given time.

A plot of log $C_s/(C_s - Z_s)$ versus time shows a rapid initial reaction, a sharp break at about one day, and another, slower reaction. If C_b is the initial D.S. of the slower-reacting hydroxyl (assumed to be that on carbon three), and K_b is the reaction-rate constant of this hydroxyl, the equation for the slower reaction is:

$$\log C_s/(C_s - Z_s) - \log C_s/(C_b - K_b t).$$

Tables XI, XII, and XIII show the values for the three partially hydrolyzed acetates. The third column, the D.S. of tosyl, is calculated from the sulfur analysis alone, assuming that no deacetylation has taken place. The fourth column, Z_s, is calculated by subtracting the D.S. of iodine in the five-gram batch tosylations from the values in the third column. Strict accuracy would require that each

TABLE X

TOSYLATION-RATE STUDY
SULFUR CONTENT OF CELLULOSE ACETATES DURING TOSYLATION

Cellulose Acetate	Partially Esterified Acetates		Partially Hydrolyzed Acetates		
	A	B	C	D	E
Time, hours	Sulfur Content, %		Sulfur Content, %		
1	1.39	1.90	--	1.16	2.14
2	1.44	1.55	--	1.39	2.53
3	1.65	--	--	1.44	2.92
4	1.40	1.72	--	1.54	3.20
6	2.09	1.92	--	1.69	2.95
8	1.51	--	2.27	1.78	3.31
10	1.69	2.32	2.36	1.83	3.31
12	1.70	--	2.40	1.87	3.46[a]
24	1.42	--	2.60	2.06	3.56
48	1.69	1.61	2.70	2.18	4.02
96	1.22	--	2.82	2.39	4.24
144	1.34	1.26	2.94	--	4.32
192	1.32	--	2.94	--	4.22
240	--	1.62	2.86	--	4.29

[a] Sampled at 16 hours instead of 12.

TABLE XI

TOSYLATION-RATE STUDY
CELLULOSE ACETATE C

Time, hours	S, %	D.S. Tosyl[1]	Z_s[2]	$C_s - Z_s$[3]	$C_s/(C_s-Z_s)$
8	2.27	0.213	0.056	0.273	1.205
10	2.36	0.222	0.065	0.264	1.246
12	2.40	0.226	0.069	0.260	1.265
24	2.60	0.248	0.091	0.238	1.382
48	2.70	0.259	0.102	0.227	1.449
96	2.82	0.272	0.115	0.214	1.537
144	2.94	0.286	0.129	0.200	1.645
192	2.94	0.286	0.129	0.200	1.645
240	2.86	0.277	0.120	0.209	1.574

[1] D.S. tosyl $= \frac{267\ S}{3200 - 154\ S}$; See page 19.

[2] Z_s = D.S. tosyl - 0.157

[3] C_s = 3.000 - 2.514 - 0.157

TABLE XII

TOSYLATION-RATE STUDY
CELLULOSE ACETATE D

Time, hours	S,%	D.S. Tosyl[1]	Z_s[2]	$Q_s - Z_s$[3]	$Q_s/(Q_s-Z_s)$
1	1.16	0.101	—	—	—
2	1.39	0.123	—	—	—
3	1.44	0.128	—	—	—
4	1.54	0.137	0.001	0.430	1.002
6	1.69	0.152	0.016	0.415	1.038
8	1.78	0.161	0.025	0.406	1.062
10	1.83	0.166	0.030	0.401	1.075
12	1.87	0.170	0.034	0.397	1.086
24	2.06	0.189	0.053	0.378	1.140
48	2.18	0.201	0.065	0.366	1.178
96	2.39	0.223	0.087	0.344	1.253
144	2.47	0.231	0.095	0.336	1.283

[1] D.S. Tosyl = $\frac{264\ S}{3200 - 154\ S}$; See page 19.

[2] Z_s = D.S. Tosyl - 0.136. [3] Q_s = 3.000 - 2.433 - 0.136.

TABLE XIII

TOSYLATION-RATE STUDY
CELLULOSE ACETATE E

Time, hours	S,%	D.S. Tosyl[1]	Z_s[2]	$Q_s - Z_s$[3]	$Q_s/(Q_s-Z_s)$
1	2.14	0.197	—	—	—
2	2.53	0.238	0.007	0.329	1.021
3	2.92	0.280	0.049	0.287	1.171
4	3.20	0.312	0.081	0.255	1.318
6	2.95	0.284	0.053	0.283	1.187
8	3.31	0.325	0.094	0.242	1.387
10	3.31	0.325	0.094	0.242	1.387
16	3.46	0.342	0.111	0.225	1.493
24	3.56	0.354	0.123	0.213	1.577
48	4.02	0.411	0.180	0.156	2.154
96	4.24	0.439	0.208	0.128	2.625
144	4.32	0.450	0.219	0.117	2.872
192	4.22	0.437	0.206	0.130	2.585
240	4.29	0.446	0.215	0.121	2.777

[1] D.S. Ts = $\frac{264\ S}{3200 - 154\ S}$; See page 19.

[2] Z_s = D.S. Tosyl - 0.231. [3] Q_s = 3.000 - 2.433 - 0.231

sample be iodinated and analyzed, but Gardner and Purves (12) observed that tosylation of the primary hydroxyls is essentially complete after two hours. Analysis of each sample after this time should give the same D.S., and only the values in the table after 12 hours are of interest in the calculation of C_b.

The values for log $C_s/(C_s - Z_s)$ were plotted against time in Figure 3. The best straight line was drawn between the 24-hour point and succeeding points up to and including the point corresponding to maximum sulfur content. The points beyond this one have been disregarded because the substitution of tosyl groups by chlorine is known to take place slowly and is indicated by the diminishing sulfur content of these samples.

The intercept of this line with the ordinate is log C_s/C_b. From this value, C_b may be calculated. The D.S. of the more rapidly reacting hydroxyl, C_a, can be found by subtracting C_b from C_s. These values are listed in Table XIV. Similar calculations could not be carried out for the partially esterified acetates because the sulfur contents of the samples at various intervals fluctuated erratically, as may be seen from a glance at Table X.

TABLE XIV

DISTRIBUTION OF UNESTERIFIED HYDROXYLS

Cellulose Acetate	Partially Esterified Acetates		Partially Hydrolyzed Acetates		
	A	B	C	D	E
D.S. Acetyl	2.535	2.705	2.514	2.433	2.433
D.S. of C_6-OH	0.097	0.044	0.157	0.136	0.231
D.S. of C_3-OH	—	—	0.244	0.386	0.150
D.S. of C_2-OH	—	—	0.085	0.045	0.186

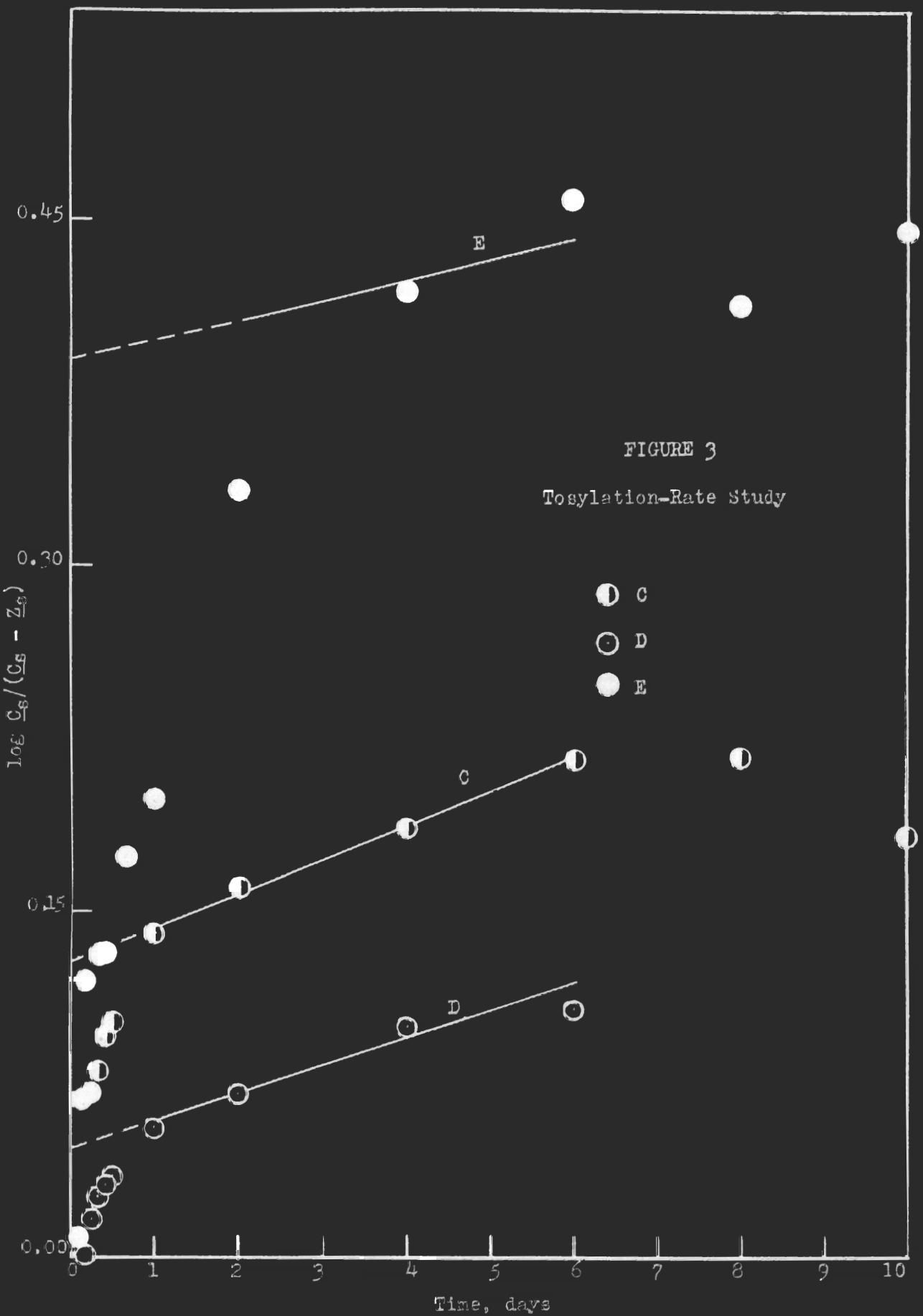


FIGURE 3

Tosylation-Rate Study

APPENDIX II

TABLE XV

TITRATION OF LEAD TETRAACETATE WITH 0.0912 N SODIUM THIOSULFATE

Cellulose Acetate	Blank	Partially Esterified Acetates A	B	Partially Hydrolyzed Acetates C	D	E
Time, hours						
12	4.087	3.959	4.089	3.849	3.768	3.716
24	4.152	3.963	4.096	3.938	3.876	3.469
36	4.158	3.940	4.119	---	3.814	3.379
48	4.085	3.840	4.062	3.765	3.711	3.736
80	4.077	3.769	4.055	3.652	3.594	3.582
120	4.124	3.680	3.980	3.668	3.389	3.412
200	4.090	3.585	4.034	3.424	3.534	3.393
360	4.000	3.398	3.973	3.520	3.349	3.307
Av.	4.097 ml.					

These values are graphed on Figure 4 (Acetates A, B, and C) and Figure 5 (Acetates D and E). The best straight line was drawn through the points for 80 to 360 hours and extrapolated to the ordinate. This intercept is the value for the volume of sodium thiosulfate solution equivalent to the lead tetraacetate consumed in oxidizing the glycol groups in each sample. These values are tabulated in Table VIII, page 33.

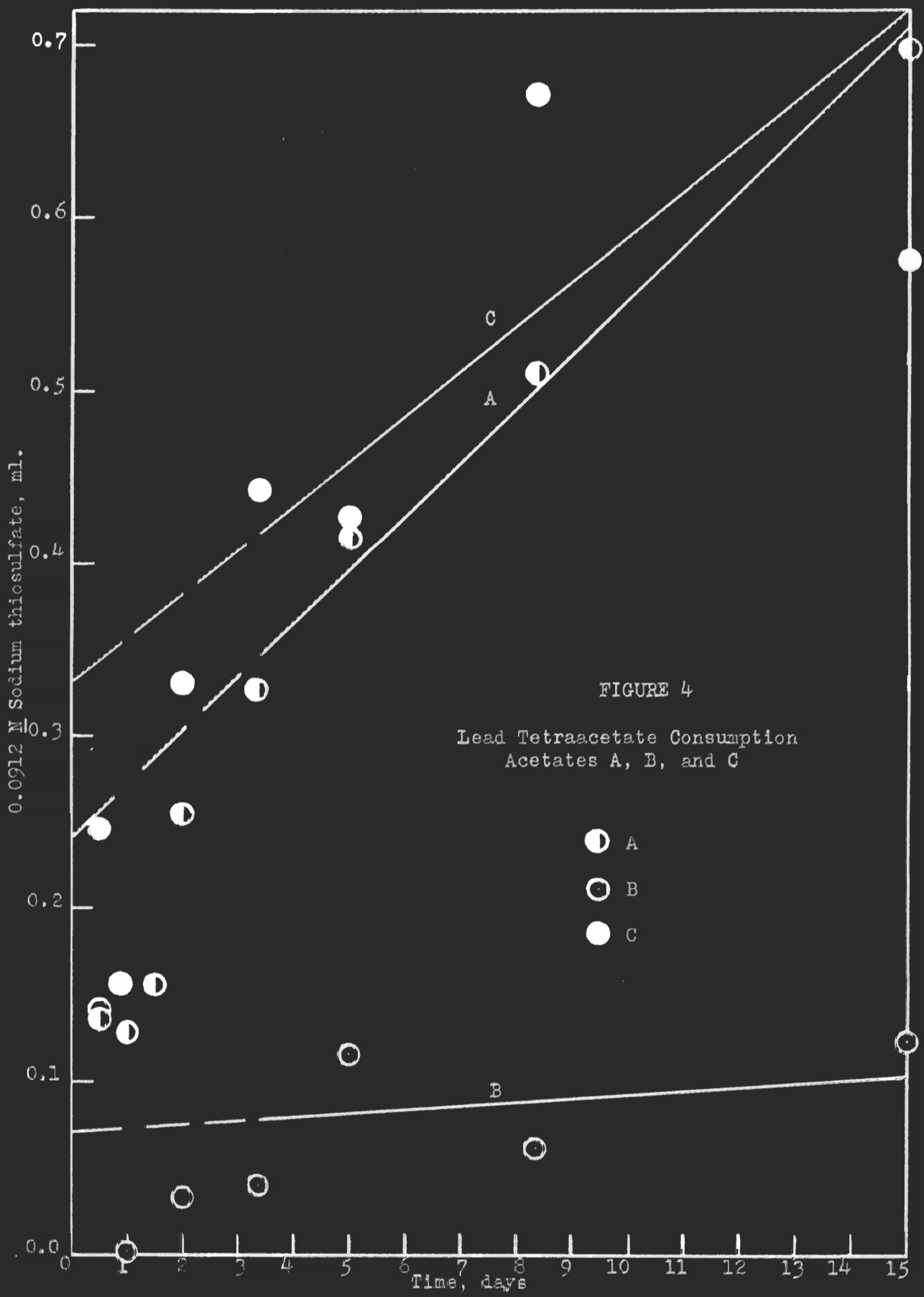


FIGURE 4

Lead Tetraacetate Consumption
Acetates A, B, and C

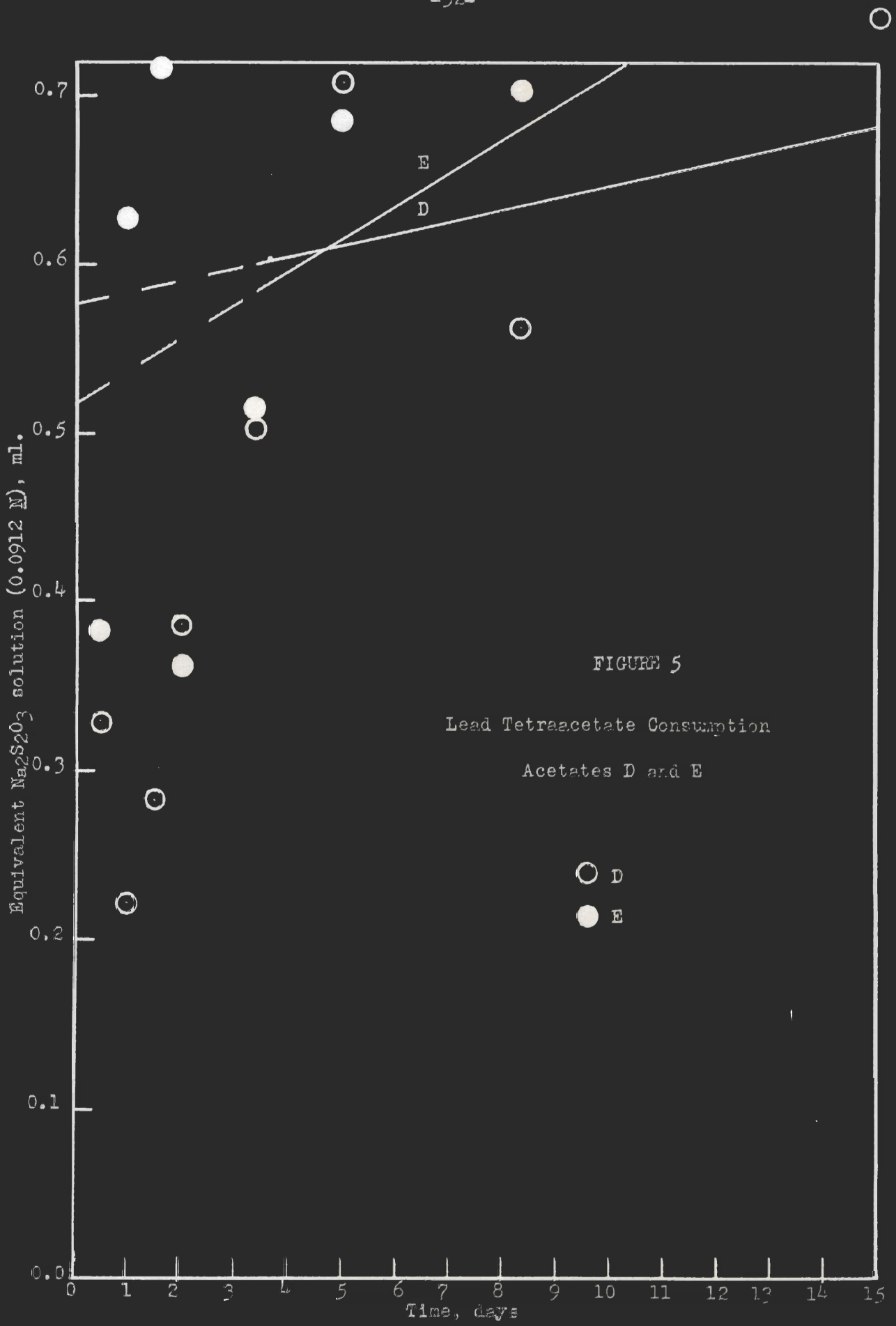


FIGURE 5

Lead Tetraacetate Consumption

Acetates D and E