[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY

THE ALKALINE OXIDATION OF CELLULOSE. I. MECHANISM OF THE DEGRADATIVE OXIDATION OF CELLULOSE BY HYDROGEN PEROXIDE IN PRESENCE OF ALKALI

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The alkaline oxidation of cellulose is a process of considerable economic importance. Most of the literature of oxidized cellulose, loosely termed oxycellulose, is of an empirical nature not subject to accurate chemical interpretation. The purpose of this investigation was to throw some light on the mechanism of the oxidation by an examination of the fragments obtained by hydrolysis of a partially oxidized cellulose. The oxidizing agent used was hydrogen peroxide. The oxidation was carried out at room temperature and in the presence of 3.4 *N* sodium hydroxide, thus approximating the conditions of the process of "aging" of alkali cellulose as in the manufacture of viscose.

INTRODUCTION

The action of oxidizing agents on cellulose results in products whose physical and chemical nature depend on the oxidizing agent used and, especially, on the acidity or alkalinity of the medium in which the oxidation is carried out. In particular it may be pointed out that in the presence of sodium hydroxide of 12% or higher concentration, cellulose undergoes a change recognized by an alteration of the x-ray diagram and by a pronounced change in physical properties (mercerization). It would not be unexpected, then, to find a difference in the mechanism of oxidation under these conditions.

Acidic oxidizing agents produce oxycelluloses which generally have marked reducing power. These oxycelluloses may have a degree of polymerization, when measured by viscosity of nitrated oxycellulose, not greatly different from that of the starting material. Most of them, however, are very sensitive to the action of alkalies, and are extensively degraded as the result of such action. Oxycelluloses prepared under alkaline conditions are usually nonreducing, and are resistant to the further action of alkali. Their degree of polymerization is generally considerably less than that of the starting material.

Davidson (1) has suggested that the oxidation of cellulose does not in general lead directly to rupture of the chain molecules but renders the linkages near the points of attack very susceptible to alkaline cleavage. This is the basic concept in later work on oxycellulose.

INFLUENCE OF THE NATURE OF THE OXIDIZING AGENT

There is considerable evidence that different oxidizing agents act in different ways on the cellulose. Thus, the action of potassium permanganate on a solution of cellulose in cuprammonium hydroxide leads to the formation of glucuronic

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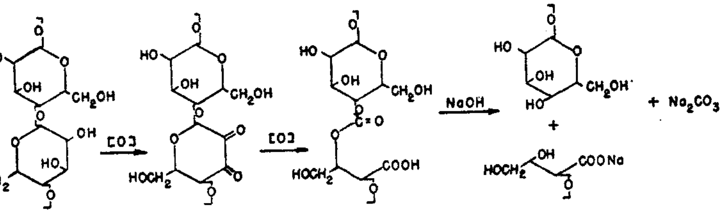
[1] Allied Chemical and Dye Corp. Fellow 1947–1948.

acid units, which appear to remain linked together (2). Glucuronic acid was obtained from the hydrolysate of cellulose so oxidized. The action of nitrogen dioxide on dry cellulose converts the primary alcohol groups to carboxyl groups without degradation (3), while periodic acid is said to oxidize only the secondary alcohol groups of carbon atoms 2 and 3 (4). Complete hydrolysis of the cellulose so oxidized yielded glyoxal and D-erythrose in about 20% of the theoretical yield.

With the exception of the cuprammonium hydroxide solution, the above oxidations were carried out in neutral or acid media and there is little or no direct evidence as to the course of oxidation in strongly alkaline solutions. It may be assumed either that a preliminary oxidation takes place, much as it does in acid media, this being followed by the action of alkali on the weak spot so formed, or that the alkali alters the structure of the cellulose in such a way as to create positions in the chain which are particularly sensitive to oxidation.

Several mechanisms have been proposed, but with little experimental evidence. Thus, Staudinger and Sohn (5) suggest that the two secondary alcohol groups are oxidized. The resulting carbonic ester linkage would be easily saponified by alkali, thus accounting for the rupture of the chain. If this is the mechanism, the hydrolytic products should contain erythronic or tartaric acid (see scheme 1).

1.



Heuser and Haskins (6) postulate a primary oxidation on the number 1 carbon atom with direct formation of a saponifiable ester linkage (scheme 2).

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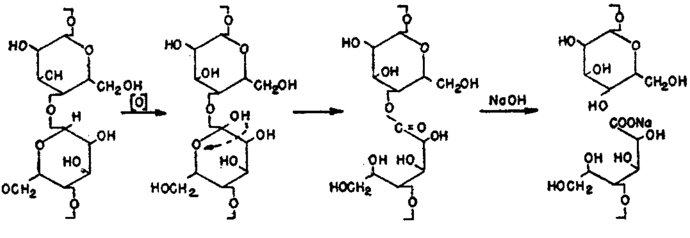
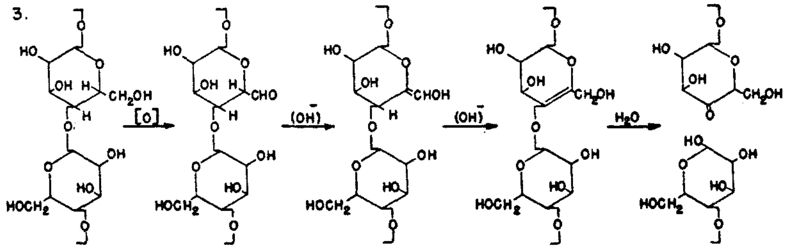


If this were the mechanism it should be possible to isolate gluconic acid or a compound derived from it from the products of hydrolysis of the oxycellulose.

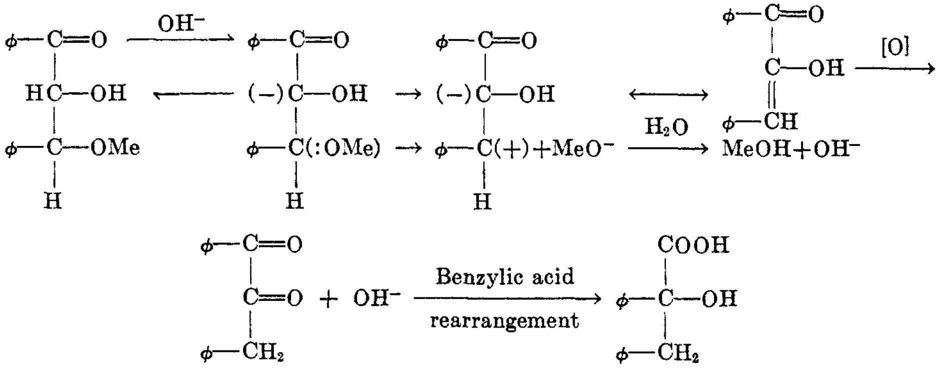
Ivanov and Kaversneva (7) explain the sensitivity of reducing oxycelluloses, in terms of the work of Gehrman, Kreider, and Evans (8), as resulting from an original oxidation of the primary hydroxyl group to an aldehyde group, followed by enolization and migration of the double bond in the presence of an alkali (8). The result would be a double bond between the 4 and 5 carbon atoms. This according to Gehrman, Kreider, and Evans causes the glycosidic linkage to be easily saponified (scheme 3).

3.



Another alternative explanation of the alkali sensitivity of reducing oxycellulose is that of an aldol dehydration.

Nicolet (9) found that α-hydroxy-β-methoxy-β-phenyl propiophenone rearranged in the presence of alkali to yield α,β-diphenyl lactic acid and proposed an aldol dehydration mechanism for this transformation. In terms of the mechanism proposed by Hauser and Breslow (10) for aldol dehydration, this rearrangment may be formulated as in 3a.

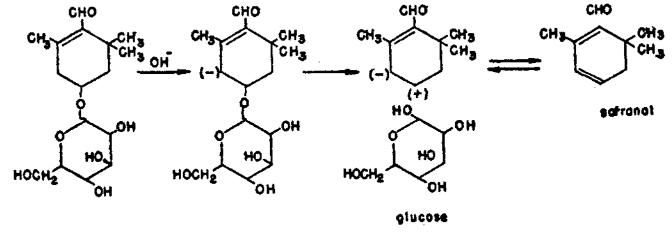


$$\begin{array}{ccccccccc} & & & & & & \phi\text{—C=O} & \\ \phi\text{—C=O} & \xrightarrow{OH^-} & \phi\text{—C=O} & & \phi\text{—C=O} & & | & [O] \\ | & & | & & | & & \text{C—OH} & \longrightarrow \\ \text{HC—OH} & \longleftarrow & (-)\text{C—OH} & \rightarrow & (-)\text{C—OH} & \longleftrightarrow & \| & \\ | & & | & & | & H_2O & \phi\text{—CH} & \\ \phi\text{—C—OMe} & & \phi\text{—C(:OMe)} & \rightarrow & \phi\text{—C(+)+MeO}^- & \longrightarrow & \text{MeOH+OH}^- & \\ | & & | & & | & & & \\ \text{H} & & \text{H} & & \text{H} & & & \end{array}$$

$$\begin{array}{cccc} \phi\text{—C=O} & & & \text{COOH} \\ | & & & | \\ \text{C=O} & + \;OH^- & \xrightarrow[\text{rearrangement}]{\text{Benzylic acid}} & \phi\text{—C—OH} \\ | & & & | \\ \phi\text{—CH}_2 & & & \phi\text{—CH}_2 \end{array}$$

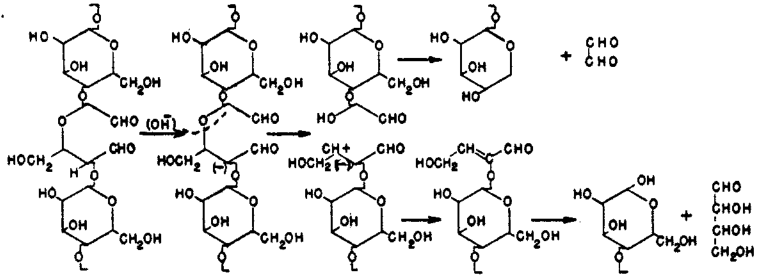
Helferich (11) has studied the behavior of various glycosides in alkali and found that, when the glycosidic group is on a carbon atom *beta* to a strong electron attracting group, the glycosidic linkage is cleaved by alkali. Thus glycosides of the type Gl-O-$CH_2(CH_2)_n$-CH_2NO_2 will reduce Fehling's solution only when n = 0. Similarly, picrocrocin yields safranal (12) on treatment with alkali, the *alpha,beta*-double bond making the *gamma* hydrogen atoms acidic Isbell (13) has interpreted the cleavage in the manner of scheme.4.

4.



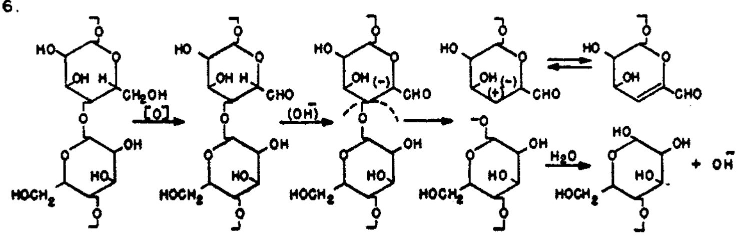
In a similar way the alkali sensitivity of periodate oxycellulose may be rather simply interpreted in terms of aldol dehydration.[2]

5.



The formation of glucuronic acid (2, 14) by air oxidation of cellulose in cuprammonium solution is indicative of the existence, at some time, of the uronaldehyde, and the degradation may be interpreted as in 6.

6.



In support of this mechanism Ivanov (15) has reported monotrityl cellulose to be stable towards atmospheric oxygen when air is passed through a suspension of monotrityl cellulose in cuprammonium hydroxide. On the basis of this evidence he concludes that oxidation of cellulose, at least by oxygen, must proceed by reaction with the primary hydroxyl. This is, however, a questionable conclusion since trityl cellulose is insoluble in cuprammonium hydroxide, is very difficult to wet, and is not, therefore, likely to react. Moreover, the assumption that the trityl group is always on the primary hydroxyl might be disputed.

DISCUSSION OF THE PROBLEM

The oxidation of cellulose in the presence of alkali is the process used industrially to lower the viscosity of solutions of cellulose derivatives. The primary interest in this study is, therefore, in the mechanism by which the cellulose chain is broken during such oxidation, rather than in the products formed by more extensive oxidation of the fragments. The plan, then, was to carry out a partial oxidation such, for example, as might be expected to lower the average degree of polymerization from 750 to about 50. It was planned to follow this oxidative degradation by hydrolysis of the oxidized cellulose, and to attempt to

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[2] The writers are indebted to Professors M. S. Newman and M. L. Wolfrom for suggesting the applicability of the aldol dehydration mechanism to the case of periodate oxycellulose.

find the fragments which represent the end groups. It should be clear that the amount of such end groups would not be very large as compared to the size of the original sample.

The cellulose used in this work was a bleached cotton linters whose intrinsic viscosity is 3.06, corresponding to a degree of polymerization of about 750. The oxidation was carried out by the action of hydrogen peroxide on cellulose steeped in 3.4 *N* sodium hydroxide solution. The insoluble portion of the oxycellulose so obtained was acetolyzed with acetic anhydride and sulfuric acid. The acetolysis product was then further degraded using hydrogen chloride in methanol. The hydrolysis was completed by the action of dilute hydrochloric acid. After removal of the hydrochloric acid, the acidic fraction was isolated using Amberlite ion exchange resins, since it was not generally possible to isolate so small a quantity as the barium salt by precipitation with alcohol. The acids so obtained were converted into the cadmium salts, and the latter were acetylated by the action of acetic acid saturated with hydrogen chloride (16). The acetylated acids were then chromatographed on silicic acid using a 5% solution of acetic acid in benzene as the developer. Crystalline D-arabonic acid tetraacetate was obtained. The water-soluble oxycellulose was hydrolyzed separately and D-arabonic acid was isolated as the acetate. The total quantity of D-arabonic acid obtained was equivalent to 172.5 mg. per hundred grams of cellulose oxidized.

Large amounts of carbon dioxide and formic acid, some oxalic acid and a small amount of lactic acid were found among the water-soluble oxidation products. These, however, are of no help in the understanding of the course of the reaction since they could be formed from highly degraded products.

In order to check the efficiency of the isolation procedure which was used, a recovery check was run on a solution containing 200 mg. of potassium D-arabonate and 10 g. of dextrose. Only 24% of the arabonic acid was isolated by use of the ion exchange resins. It is obvious, therefore, that the 172.5 mg. of arabonic acid actually isolated per 100 g. of cellulose oxidized was only a small fraction of the total arabonic acid produced by the oxidation.

Since glycosido-glucoses are known to be oxidized by alkaline hydrogen peroxide to give moderate yields of glycosido-arabonic acids, the quantity of D-arabonic acid obtained may be assumed to be an indication of the amount of reducing end groups in cellulosic material, though it is in no sense even an approximately quantitative relationship.

DISCUSSION OF THE RESULTS

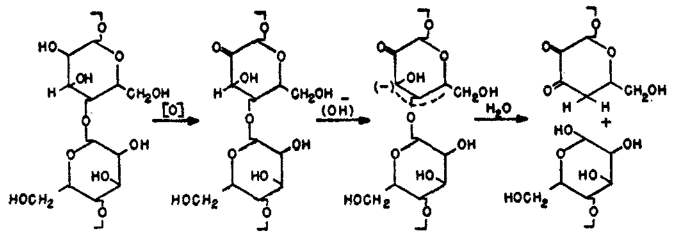
It is known from the work of Spoehr (17), Glattfeld (18), Glattfeld and Hanke (19), and Isbell (20), that moderate yields of glycosido-arabonic acids are obtained by oxidation of glycosido-glucoses with hydrogen peroxide in presence of alkali. It may then be assumed that the arabonic acid found among the products of hydrolysis of oxycellulose formed by the action of hydrogen peroxide in presence of alkali is a measure of the number of reducing end groups formed by the oxidative splitting of the cellulose chains, although it is in no sense a quantitative measure. From the intrinsic viscosity of cellulose in cuprammonium hydroxide, the degree of polymerization may be calculated. If the cellulose sample is fairly homogenous as to molecular weight distribution, the degree of polymerization represents, for our purposes, an acceptable estimate of the number of reducing end groups. Chemical cotton linters having a degree of polymerization of 750 would produce a theoretical yield of 135 mg. of arabonic acid per 100 g. of cellulose oxidized by alkaline hydrogen peroxide, if no splitting occurred. Since the method actually used in this investigation is capable of isolating at most a fourth of the arabonic acid produced by oxidation, and since the yield of glycosido-arabonic acids by oxidation of glycosido-glucoses is only moderate, the 174 mg. of arabonic acid isolated per 100 g. cellulose oxidized, is very suggestive of a mode of alkaline cleavage of the initial oxidation product such as to increase the number of free reducing glucose end groups. Thus mechanisms of alkaline oxidative degradation which require an increase in the number of reducing end groups are to be preferred to those which could not explain an increase.

The mechanism offered by Ivanov and the aldol dehydration scheme derived from the work of Helferich, Isbell and others both require an increase in the number of reducing end groups.

The alternative interpretations given below to explain the formation of new reducing end groups are consistent with the experimental results of this investigation.

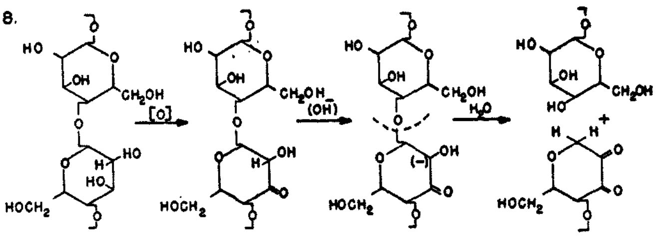
(a) Oxidation of the 2-secondary alcohol group (scheme 7).

7.



(b) Oxidation of the 3-secondary alcohol group (scheme 8).

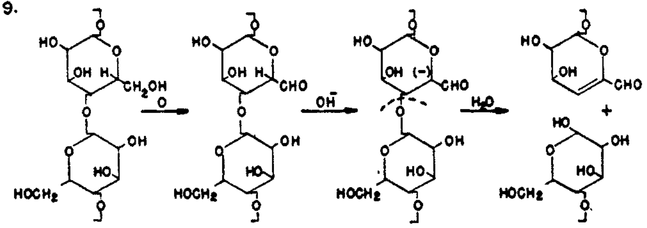
8.



The 3-keto derivative might also undergo rearrangement to the 2-keto form which may be cleaved as shown above.

(c) Oxidation of the primary alcohol group (scheme 9).

9.



In short, oxidation of any of the hydroxyl groups will produce a product which can readily undergo aldol dehydration.

EFFECT OF HYDROLYTIC AGENTS

In the course of this work several methods of hydrolysis of the oxycellulose were tried. The usual method, in which cellulose is treated with 72% sulfuric acid and the hydrolysis completed, after dilution, by warming, proved to be unsatisfactory because the sulfuric acid itself acts as an oxidizing agent.

EXPERIMENTAL

1. *Oxidation of cellulose with alkaline hydrogen peroxide.* Chemical grade cotton linter[8] (150 g., 5.8% moisture, intrinsic viscosity 3.06) was added to an oxidation mixture of 1500 ml. of carbonate-free 3.4 *N* sodium hydroxide and 150 ml. of 29.2% hydrogen peroxide, with protection from carbon dioxide. The flask was placed in a 20° constant temperature room. After eight days an additional 150 ml.-portion of 29.2% hydrogen peroxide was added. After a total time of oxidation of 31 days the reaction mixture was made slightly acidic with dilute sulfuric acid, and the oxycellulose was filtered and washed with distilled water until the filtrate was free of sulfate ions. After extracting most of the water with acetone there was obtained upon drying 119 g. of oxycellulose. Ash content was 0.13%.

2. *Examination of the water-soluble oxidation products.* Prior to acidification of the reaction mixture from the oxidation, the carbonate content was determined by acidifying a measured quantity of the solution and absorbing the carbon dioxide evolved in a standard Ascarite bulb absorption train. Based on the dry weight of the cellulose the carbon dioxide formed amounted to 0.0294 g. per gram of cellulose oxidized.

The filtrate and wash water fron the filtration of the oxycellulose, following acidification were concentrated under a vacuum to remove volatile acids. Distilled water was added to the residue and the vacuum distillation was repeated until the distillate was no longer acidic. After neutralization of the distillate with barium hydroxide, filtration, concentration, acidification, and redistillation, the formic acid content was determined, separately, by alkaline permanganate and by reduction of mercuric chloride (21). The two methods checked within less than one per cent. The amount of formic acid found was 7.6 g., or 0.054 g. per gram of cellulose oxidized.

The residue from the distillation of the volatile acids was freed of most of the sodium sulfate by addition of ethanol. Following removal of the ethanol, the nonvolatile, water-soluble products were extracted with ether in a continuous extractor. The ether-extractible acids were converted into zinc salts, and after much difficulty, 0.115 g. of a crystalline zinc salt was obtained which had approximately the composition of zinc lactate trihydrate:

Loss in weight on drying	19.3%
Calculated for zinc lactate trihydrate	18.4%
Zinc oxide, found	26.11%
Zinc oxide, calculated	27.35%

The material remaining after the ether extraction was treated with an excess of barium hydroxide and filtered. The precipitate so obtained was acidified with excess hydrochloric acid and filtered to separate the acids soluble in hydrochloric acid. This filtrate was again neutralized with barium hydroxide. The salt so obtained had a reducing value 96% of that calculated for barium oxalate. The acid regenerated from the barium salt gave a phenylhydrazine salt characteristic of oxalic acid.

The ether-insoluble, barium hydroxide-soluble material was acidified with dilute sulfuric acid and hydrolyzed at 80° for two days. After treatment with excess barium carbonate, filtration and concentration, the barium salts (2 g.) were precipitated by ethanol. One-fourth of these salts (0.50 g.) was converted to the free acids. The solution was passed through a 2.5 x 50 cm. column of analytical grade Amberlite IR-100 cation-exchanger to remove the barium, and the resin column was washed with distilled water until the filtrate was neutral. The barium-free solution was then passed slowly through the 2.5 x 50 cm. anion-exchanger of analytical grade Amberlite IR-4 to remove the acidic material from the neutral fraction. After washing the anion-exchanger with about 500 ml. of water, the acidic material was flushed from the column with 80 ml. of 5% ammonium hydroxide. The exchanger was then washed with distilled water, 500 ml., until the filtrate was no longer basic. The ammoniacal filtrate was then put through the regenerated cation-exchanger to remove the ammonia. Distilled water was run through the anion-exchanger until the filtrate was neutral. The glucose-free solution containing the acidic material was concentrated under vacuum to about 100 ml. and heated with excess cadmium carbonate at 50° for one day. After filtering and concentrating the solution, the cadmium salts were precipitated with ethanol and ether. The salts were then dried and acetylated with 5 ml. of acetic anhydride saturated with hydrogen chloride (21). After stirring the mixture for one hour at 0°, the acetylation was completed by heating at 50° for one hour. Excess acetic anhydride was removed under a vacuum and a few grams of ice was added. The acetylated products were isolated by extraction with chloroform, and dried with sodium sulfate. Chromatography of the acetylated material on a 70-cm. column of 3 silicic acid/1 Celite, using 250 ml. of 20 benzene/1 acetic acid developer, gave a column which was quite complex. Upon streaking with alkaline permanganate, there were three zones in the middle of the column, two faint and one sharp. There was, in addition, a zone at the very top and one near the bottom of the column. From the sharp middle zone there was obtained 66 mg. of crystalline material having the melting point 132–135°, and giving an undepressed melting point when mixed with a known sample of D-arabonic acid tetraacetate; literature (22) melting point, 135–136°. The rotation, $[\alpha]_D^{25}$ +31.1° (2.1% in chloroform), is in agreement with the literature value (21), $[\alpha]_D$ +32.5°, for D-arabonic acid tetraacetate. From the water-soluble fraction the amount of arabonic acid tetraacetate isolated amounts to 264 mg./141.3 g. cellulose oxidized or 93 mg. of arabonic acid/100 g. cellulose oxidized.

As will be shown later, sulfuric acid is capable of oxidizing as well as hydrolyzing cellulose. To show that the dilute sulfuric acid used in the hydrolysis did not produce the arabonic acid isolated, twenty grams of C.P. dextrose was dissolved in two liters of 1.5 *N* sulfuric acid and the solution was heated in an 80° oven for two days. After neutralizing with barium carbonate, the acidic material was isolated as described above. The amorphous cadmium salts were acetylated with acetic anhydride and hydrogen chloride (16). Chromatography of small quantity (108 mg.) of acetylated products so obtained on 3 silica/1 Celite, using 5% acetic acid in benzene as the developer, gave several zones. That no arabonic acid pentaacetate was present, was shown by running a comparative chromatogram of the same solution to which a small quantity of D-arabonic acid pentaacetate had been added. This gave rise to a new, well-defined zone in a predictable region of the chromatogram.

3. *Examination of the water-insoluble oxidation products. Isolation of* D*-arabonic acid following hydrolysis.* (a) *Hydrolysis by sulfuric acid.* On the basis of the work of Godman, Haworth, and Peat (23) it was thought that hydrolysis of the oxycellulose could be most conveniently effected by use of 72% sulfuric acid. With this method, however, the quantity

of barium salts obtained was much greater than seemed probable. In order to check the effect of 72% sulfuric acid on cellulose, the hydrolysis and isolation of the acids was repeated using chemical cotton linters. Eighteen grams of cotton linters was dissolved in 90 ml. of 72% sulfuric acid and allowed to stand at room temperature for six days. After dilution to two liters, the solution was placed in an oven at 80° for 36 hours. The resulting solution was stirred vigorously and carefully neutralized with two-thirds of the calculated quantity of barium hydroxide solution in such a manner as to avoid any local alkalinity. The remainder of the acid was neutralized with excess barium carbonate. After filtration, concentrating to 100 ml. and decolorizing, the barium salts were precipitated by pouring the solution into 500 ml. of boiling ethanol. After standing overnight in an ice-box the solution was decanted from the amorphous precipitate, which weighed 2.36 g., $[\alpha]^{26}_{D}$ +42.3° (H_2O, *c*, 5.6%). The salts were dissolved in a minimum quantity of water and reprecipitated with boiling methanol. After two additional reprecipitations to assure complete removal of glucose, the barium salts were dried. The rotation, $[\alpha]^{26}_{D}$ +45° (*c*, 4.6%), was measured in water. This material gave a slight test with Fehling's solution and a positive uronic acid test with naphthoresorcinol. A test for sulfur was negative. Analytical results indicate nothing more than that the material is probably a mixture of barium salts of aldonic and aldobionic acids.

Anal. Found: C, 30.1, 29.84; H, 4.76, 4.95; Ba, 21.95, 21.71.

No further attempt to identify these acids was made. The amount formed is surprising, and such as to show that 72% sulfuric acid oxidizes the cellulose. This fact throws strong doubt on the validity of any conclusions which might be made as a result of hydrolyzing oxycelluloses with 72% sulfuric acid. This method of hydrolysis was, therefore, abandoned.

(b) *Acetolysis as a means of degradation.* It is well known that cellulose can be degraded to cellobiose octaacetate by the combined action of acetic anhydride and sulfuric acid. It was thought that this method would be suitable for the preliminary degradation of oxycellulose.

An acetolysis mixture commonly used for the preparation of cellobiose octaacetate was used for the acetolysis of oxycellulose. Acetic anhydride, 100 ml., was cooled to 0° and 14 ml. of concentrated sulfuric acid was added slowly with stirring. Twenty grams of oxycellulose was broken into a coarse powder, and 92 ml. of the acetolysis mixture, cooled to 0° was added slowly. The cooled mixture was well mixed with a glass rod to prevent the formation of local warm spots, which cause extensive degradation, as shown by the development of a very dark brown color. After the oxycellulose was acetylated and a doughy mass formed, it was removed from the ice-bath and the reaction allowed to proceed with frequent stirring. The reaction was forced by placing the flask in a water-bath at 85° for half an hour. The thin, light brown solution resulting was poured on cracked ice. After an hour the water was saturated with salt to prevent emulsion formation and extracted four times with chloroform. After removal of the chloroform by evaporation the solids were dried in a vacuum desiccator.

The dried acetolysis product was dissolved in 500 ml. of 6% hydrogen chloride in absolute methanol. The methanolysis was carried out by refluxing the solution for one day. Concentration of the solution under a vacuum gave a sludge which was dissolved in sufficient water to give 500 ml. of a solution still containing considerable hydrochloric acid. After hydrolysis at 80° for two days, 30 g. of basic lead carbonate was added. The following day the lead chloride was removed and the solution saturated with hydrogen sulfide to remove the lead. After filtering, 20 g. of freshly precipitated silver carbonate was added and the chloride-free solution was filtered and saturated with hydrogen sulfide. After filtration, decolorization and aeration, the solution was treated with excess barium carbonate for one day at 50°, and filtered. Vacuum concentration of the filtrate gave a syrup, to which was added five volumes of absolute ethanol. So small an amount of insoluble material was deposited that this method of isolating the acidic fraction did not appear promising. The alcohol was removed under a vacuum and the syrup was diluted with distilled water. The acidic material was isolated by use of ion-exchange columns in a manner similar to that described above. The glucose-free solution of the acidic material was converted to the cadmium salts (0.146 g.). A 92% yield of crystalline glucose isolated from the neutral fraction indicates the completeness of the hydrolysis.

The cadmium salts of the acidic fraction of the oxycellulose hydrolysis were acetylated with 5 ml. of acetic anhydride saturated with hydrogen chloride as previously described. The acetylated acids (110 mg.) were separated by chromatography. The entire sample dissolved in chloroform was put on a 70-g. column of 3 silicic acid/1 Celite, using 400 ml. of 20 benzene/1 acetic acid as the developer. Three zones were found on streaking the column with alkaline permanganate. After removal of the stripe, the column was sectioned and the sections eluted with acetone and the material isolated by evaporation. The acetylated substances which had become fixed at the top of the column weighed 20 mg. and gave a positive uronic acid test with naphthoresorcinol. No crystalline products were isolated from this zone. This material could have been an aldobiuronic acid, since these acids are difficult to hydrolyze. The zone near the bottom of the column yielded 36 mg. of material which was not crystallized. This fraction gave a faint uronic acid test and is believed to be acetylated lactones.

The middle zone gave 52 mg. of amorphous material which was crystallized from hot toluene and petroleum ether solution to yield 38 mg. of crystalline material. The rotation of this material was measured in chloroform. $[\alpha]_D^{27}$ +33.4°, (*c*, 1.49%). On recovery of the material and recrystallization, a product was obtained which had m.p. 134–135°, mixed m.p., with an authentic sample of D-arabonic acid tetraacetate, 134–135°. Analysis gave C, 46.73; H, 5.68. Calc'd: C, 46.71; H, 5.43. Literature constants for D-arabonic tetraacetate, m.p. 135–136°, $[\alpha]_D$ +32.5°, $CHCl_3$. This amounts to 81 mg. arabonic acid/100 g. cellulose oxidized.

(c) *Check on oxidizing power of sulfuric acid in acetolysis.* Since it had been shown that sulfuric acid has an oxidizing effect on cellulose, the possible oxidizing action of the sulfuric acid in acetolysis was investigated by carrying out an acetolysis of cotton linters by the process described above.

Chromatography of the acetylated acidic material gave three zones. The very weak middle zone, however, was closer to the top than would be expected for D-arabonic acid tetraacetate. A portion of the acetylated products was mixed with a small amount of D-arabonic acid tetraacetate and the mixture chromatographed on a small silicic acid column, using 5% acetic acid in benzene as the developer. In addition to the three zones mentioned there was an additional strong zone in the position expected for the arabonic acid tetraacetate as determined by a blank run with arabonic acid tetraacetate only. This indicates the absence of D-arabonic acid tetraacetate in the acetylated acidic products from the cotton linter.

SUMMARY

1. D-Arabonic acid has been identified, in the form of the tetraacetate, as one of the products of the oxidation of cellulose by hydrogen peroxide in presence of strong alkali.

2. Several proposed mechanisms for the oxidation of cellulose have been discussed.

3. A mechanism has been proposed which is consistent with the behavior of β-alkoxycarbonyl compounds in alkali.

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