[CONTRIBUTION FROM THE INSTITUTE OF PAPER CHEMISTRY]

Nature of the Acid Degradation of Solutions of Cellulose Triacetate[1]

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This work was undertaken to learn the nature of the reactions occurring and the products formed when chloroform solutions of cellulose triacetate are refluxed with arylsulfonic acids in the presence of small amounts of alcohol or water. Three types of reaction occur—deacetylation, chain degradation and recombination of carbohydrate fragments. If large amounts of alcohol are present, the product is insoluble in water. As the alcohol present decreases, an increasing fraction of the product becomes water soluble. At around 2.5% ethanol (or 3% methanol), the product is entirely water soluble. Recombination takes place rapidly in the early stages of deacetylation. Chain breakage occurs more rapidly later. In the first stage of reaction the insolubility of the product is probably due to molecular size, but if the reaction is run 48 hours (to constant optical rotation), the difference between soluble and insoluble materials is not only a matter of size but also of structure, the soluble products being apparently more highly branched due to recombination. This work explains the alcoholytic and hydrolytic degradation of cellulose triacetate in chloroform, but the results will be valuable to chemists interested in other cellulose degradations, as they emphasize the complications that may arise due to recombination of the primary breakdown products.

When chloroform solutions of cellulose triacetate containing a little alcohol (or water) are acidified with an arylsulfonic acid and refluxed, the cellulose derivative precipitates as a gel which hardens on further refluxing. This material, when separated and deacetylated, is a carbohydrate, the properties of which vary with the amount of alcohol present. With large amounts of alcohol, a water-insoluble product is formed, but as the alcohol content of the original solution is decreased, an increasing fraction of the product can be dissolved in water until at 2.5% ethanol (or 3% methanol) the product is completely water soluble. Our investigations previously have been concerned only with the water-soluble portions and we have shown that the expected reactions of deacetylation and chain breakage are accompanied by recombination of carbohydrate fragments to form new glycosidic linkages.[2] The linkage between the aldehydic end-group (position 1) and the number 6 position of a glucose residue in another chain is the only one that has been proved definitely as this is a very stable linkage, but there is also evidence that other linkages are formed as well.

The final product differs a little according to whether the chloroform contains alcohols or water. In the presence of alcohols, there are alkyl groups at the ends of the chain; in the presence of water, reducing groups. We have interpreted this as evidence of alcoholysis and hydrolysis, respectively. It is impossible to rule out hydrolysis followed by alkylation in the reaction with alcohols, since traces of water inevitably are present.

In the work previously reported, we continued refluxing until constant optical rotation of the final product was reached, which is between one and two days. We now have studied the extent of the three competing reactions at various shorter times, measuring the acetyl content (deacetylation) and the methoxyl content (chain breakdown). The extent of the recombination reaction was estimated by paper chromatography of the hydrolyzate of the product. This technique is suitable because of the relatively slow rate of hydrolysis of 1–6 linkages, compared with the 1–4 linkages of the original chain. Gentiobiose may, therefore, be isolated from the partial hydrolysis products. Unfortunately, we have no means as suitable as this for detection of more labile linkages. The optical rotation data are consistent with the presence of 1–6 bonds. Table I and Fig. 1 show the results of this study.

The chromatograms show that even at the end of one hour, before the deacetylation has proceeded long enough to cause precipitation, there has been definite recombination as evidenced by the strong gentiobiose spot. Since recombination is not likely to occur until both deacetylation and chain breakage have begun, this shows that the recombination takes place rapidly and easily. It is possible, of course, for recombination to take place without either deacetylation or chain breakage, but it is not very probable.

Deacetylation is already well under way after one hour, with 30% of the acetyls split off, but the product is still chloroform-soluble. On the other hand, chain cleavage by methanolysis goes much faster in the later stages as measured by methoxyl content of the final product. Two points should be noted, however. The first point is that if chain cleavage occurs near the end, it will produce small fragments which, being mobile, may easily recombine and which being more soluble, may be lost during purification. In either case, the methoxyl content of the final product is prevented from being an exact measure of chain cleavage. The second point is that some hydrolysis has occurred as shown by the reducing power of the product. This is in line with the recent findings of Valley[3] that the initial step in the degradation of cellulose with alcoholic hydrogen chloride is hydrolytic (water is inevitably present, not only because of the difficulty of drying cellulose, but also because of the formation of water by the action of anhydrous acid on alcohol).

In previous work[2] the properties of the soluble material only were investigated. A comparison of the soluble and insoluble materials now has been made. Before discussing this comparison, however, some general observations on the solubility of the products should be mentioned.

First, there is a range of alcohol content in the

(1) Presented before the Division of Cellulose Chemistry at the 127th Meeting of the American Chemical Society, Cincinnati, Ohio, March 29–April 7, 1955.

(2) K. Ward, Jr., C. C. Tu and M. Lakstigala, THIS JOURNAL, **76**, 6102 (1954).

(3) R. B. Valley, Thesis, Institute of Paper Chemistry, 1955, accepted to *Textile Research J.* for publication.

TABLE I

YIELDS AND PROPERTIES OF METHYL GLYCOSIDES FROM METHANOLYSIS (3% METHANOL) OF CELLULOSE TRIACETATE IN CHLOROFORM

Methyl glycoside from refluxing, hr.	Yields, g. Before deacetylation Water sol.	Before deacetylation Water insol.	After deacetylation Water sol.	After deacetylation Water insol.	Acetyl content, % before deacetylation	Methoxyl content, % after deacetylation Water sol.	Methoxyl content, % after deacetylation Water insol.	$[\alpha]^{21-24}D$ after deacetylation Water sol.	Reducing power, mg. glucose/g., after deacetylation Water sol.	Reducing power, mg. glucose/g., after deacetylation Water insol.
1	..	22	..	15	30.90	..	0.2	....	..	2.4
2	..	20	..	14	22.70	..	.3	....	..	3.8
8	..	21	..	15	22.3	..	.5	....	..	3.5
16	20	..	5.0	12	10.43	3.1	1.0	+45.1°	4.8	3.1
24	18	..	2.5	13	3.09	2.4	1.1	+38.0	5.4	2.4
48	15	..	10.5	..	3.11	2.0	..	+69.3	7.2	3.3

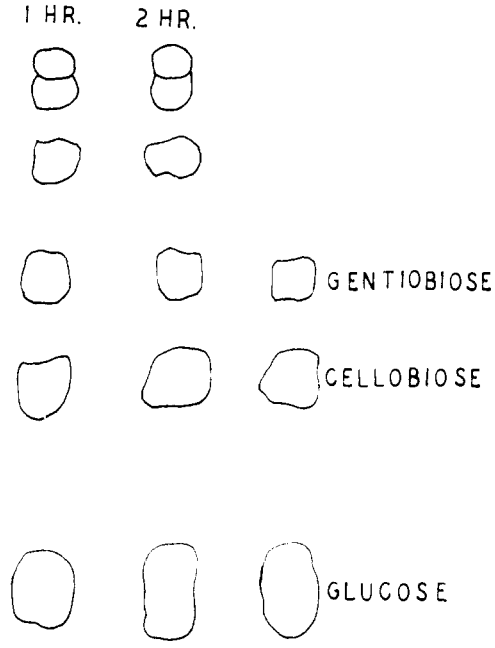

Fig. 1.—Chromatograms of the hydrolyzate of methyl glycoside.

alcoholyses where the final product is only partly soluble in water, as was stated earlier. It is worth noting again that over much of this range, the partly deacetylated product is water soluble and water insolubility is first evident after complete deacetylation. This odd effect is not new and is probably attributable to the disturbing effect of a few acetyl groups on the symmetry of the free hydroxyl distribution, just as partly methylated cellulose is soluble in water, while the cellulose itself is not.

Second, there are several ways of getting an insoluble product. There is the product obtained at short reaction times. There is the product obtained with large amounts of alcohol. Finally there is the insoluble portion of the partly soluble product obtained with moderate amounts of alcohol. We have studied this last product, because the soluble and insoluble portions have been formed under the same experimental conditions.

The results indicate that the differences in solubility correspond to differences both in molecular size and in molecular structure. It will be seen from Table II that the insoluble portions are several glucose units longer than the soluble portions, as estimated by the methoxyl content. These values have been corrected for the reducing power, a very small correction in any case, and probably give a good estimate of the number-average D.P.

TABLE II

DEGREE OF POLYMERIZATION OF METHYL GLYCOSIDES FROM CELLULOSE TRIACETATE

Methyl glycosides from alcoholysis, % methanol used	Degree of polymerization determined by Isothermal distn. of acetate	End group (MeO)	Visc. of acetate
2, water soluble	6	14	12
3, water soluble	7	11	12
4, water soluble	8	8	12
water insoluble	..	14	18
5, water soluble	..	6	..
water insoluble	..	12	17

Viscosity measurements are not exactly applicable, as these are partly branched polymers, but the apparent D.P. for the insoluble fraction is 18 as against 12 for the soluble fraction in the one example chosen. Isothermal distillation is also a doubtful method for this size of molecule; runs made on the acetates show a lower D.P. than by other methods, but it is probable that the acetates no longer correspond exactly in D.P. to the original material on account of possible changes during acetylation or fractional solubilities in purification.

That there must be differences in structure as well as in chain length is indicated by comparing the soluble material from the cook using 2% methanol with the insoluble material from the cook using 5% methanol. They are the same chain length but of quite different solubility. The nature of this difference has been established by comparing the chromatograms of hydrolyzates (with 0.1 *N* hydrochloric acid) of the soluble and insoluble products (Fig. 2). As the soluble portion is hydrolyzed, gentiobiose spots appear in the chromatogram from the start. These spots are approximately as strong as those of cellobiose and there are also unidentified spots in the disaccharide region. The insoluble portion behaves differently. Before hydrolysis it was extracted thoroughly with boiling water, as it contains a small amount of material which is soluble in hot and insoluble in cold water. The insoluble residue on hydrolysis gives strong spots for cellobiose but other disaccharides are absent or nearly so. The hot-water soluble extract gives very faint spots for gentiobiose and doubtful traces of other disaccharides than cellubiose. Even these faint indications may be due to adsorbed branched material.

These observations seem to indicate that recombination of small fragments produces increased solu-

bility in water as a result of branching while the linear chains remain water insoluble. Further evidence is found by closer study of the hydrolysis with 0.1 *N* hydrochloric acid of the soluble product.

If all the linkages were uniform one would expect a regular change in optical rotation as hydrolysis proceeds. This was not found.[2] Moreover, if the hydrolyzate is chromatographed on a charcoal column, the change of rotation with increasing D.P. is also irregular, as shown in Table III, whereas a homologous series of compounds would show a monotonic change.

TABLE III

SUGAR YIELDS AND THEIR PROPERTIES FROM CHARCOAL COLUMN OF THE HYDROLYZATE

Eluant, %	Amt., l.	Dry sugar yield, %	$[\alpha]^{22-28}D$ (*C*)	D.P. detd. by Iodometric titration of sugar	D.P. detd. by Isotherm distn. of sugar acetate
5 Ethanol	4.0	0.40	.....	..	..
15 Ethanol	4.0	1.10	+110° (1.1)	4	..
20 Ethanol	1.5	0.30	+ 84 (1.6)	4	..
25 Ethanol	4.0	.90	+ 88 (1.1)	6	5
30 Ethanol	2.0	.50	+ 97 (1.5)	8	..

We have shown that for comparable products, the insoluble portion is less branched, but whether this holds for the products formed at high alcohol concentrations we do not know. The insoluble portion produced after short cooks on the other hand is probably highly branched and the insolubility here seems to depend on the high D.P.

Experimental

Degree of Polymerization Determination. Isothermal Distillation.—The methyl glycosides were first converted to their acetates with a mixture of acetic anhydride, glacial acetic acid and anhydrous sodium acetate. The acetates were purified by dissolving in warm dioxane and precipitating with ice-water. This may involve some fractionation due to solubility of some portions and, in the case of the acetates of the water-insoluble glycosides, a small amount insoluble in hot dioxane. Each purified acetate was weighed and transferred into the isothermal distillation apparatus. About 2 ml. of chloroform was used as a solvent and cellobiose octaacetate as a reference compound. The determination was carried out in a constant temperature bath at 25° in the manner described by Clark.[4] The results are shown in Table II.

Viscosity Determination.—The acetates just described in 1% chloroform solution were used for viscosity measurements in an Ostwald–Cannon–Fenske type viscometer (A.S-T.M. 50) in a water-bath maintained at 25°. The reduced viscosity was used instead of the intrinsic, which seems justifiable at the low D.P.'s involved. *K* was estimated from Kraemer's data to be about 260.[5] The results are shown in Table II.

(4) E. P. Clark, *Ind. Eng. Chem. Anal. Ed.*, **13**, 820 (1941).

(5) E. O. Kraemer, *Ind. Eng. Chem.*, **30**, 1200 (1938).

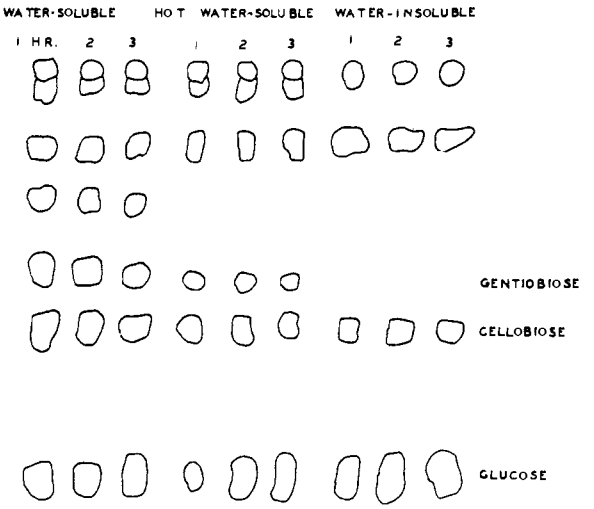

Fig. 2.—Chromatograms of the hydrolyzate of methyl glycoside.

End Group Determination.—Methoxyl contents of the prepared glycosides were determined in the usual manner. The results are shown in Table II.

Chromatographic Comparisons.—One gram of the water-insoluble material resulting from alcoholysis with 5% methanol was extracted with 2500 ml. of boiling water. The filtrate was concentrated to 100 ml. Precipitation occurred on addition of absolute ethanol and the precipitate was redissolved in 0.1 *N* hydrochloric acid to give a 3% solution. The residue was dissolved in 50% sulfuric acid and the solution was diluted and neutralized with barium carbonate. The neutralized solution was concentrated, dried and redissolved in 0.1 *N* hydrochloric acid as above. Another 3% solution of the water-soluble methyl glycoside was prepared as above. Each solution was hydrolyzed at 98 ± 1°. At one-hour intervals the hydrolyzate was spot-checked on a paper strip as previously described.[2] Three chromatograms are shown in Fig. 2.

Fractionation of the Hydrolyzate of the Water-soluble Polysaccharide.[1]—Ten grams of the water-soluble polysaccharide was dissolved in 330 ml. of 0.1 *N* hydrochloric acid. The procedures for this hydrolysis and for the chromatographic separation were reported previously by the authors. The isolation of gentiobiose from the 5% ethanol fraction was also reported at that time. The yields of sugar mixtures and the properties of various effluent fractions from the charcoal column, 61 by 411 mm., are shown in Table III.

Effect of Reflux Time on Products of Methanolysis.—A series of methyl glycosides was made by the methanolysis of cellulose triacetate in chloroform with 3% methanol. The methanolyses were conducted in the same manner as described by the authors[2] except that the refluxing times used were 1, 2, 8, 24 and 48 hours. The yields and properties of this series of methyl glycosides are shown in Table I.

Five-tenths gram of the glycoside resulting from one- and two-hour refluxing, respectively, was dissolved in 50% sulfuric acid. Each solution was diluted with water to 1 *N* sulfuric acid. Spot-checking was done for these two hydrolyzates. The result is shown in Fig. 1. A gentiobiose spot was found in both cases.

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