[CONTRIBUTION FROM THE FOREST PRODUCTS LABORATORY, FOREST SERVICE, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE ACTION OF CONCENTRATED HYDROCHLORIC ACID ON DIFFERENT CELLULOSES

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Introduction

When white spruce wood is hydrolyzed with dilute acid at atmospheric pressures, or higher, one of the reducing sugars produced is mannose.[3] Some investigators[4] have assumed that mannose is present in the wood as a mannan; others[5] consider it to be present as a part of the cellulose. Sherrard and Blanco[6] have further shown that in such a hydrolysis the quantity of sugar produced corresponds very closely with the quantity of cellulose removed. This would indicate that the mannose is present as a mannosecellulose. Recent investigation has brought to light the fact that mannose is contained in α, β and γ cellulose obtained from spruce cellulose prepared by the Cross and Bevan method. The same investigators[7] have demonstrated that no mannose is present in cotton, and also that the reagents involved in the isolation of the celluloses from white spruce are not responsible for its formation.

The fact that white spruce cellulose on hydrolysis yields considerable quantities of mannose and that cotton yields no mannose on hydrolysis was considered ample proof that considerable difference exists between these two celluloses. In order to investigate further any possible differences in celluloses from different woods it was decided to submit several to the action of concd. hydrochloric acid and to observe the rate of change of optical rotations. Accordingly, celluloses from 2 softwoods, white spruce and Douglas fir, and one hardwood, yellow birch, were prepared by the method of Cross and Bevan and compared with cotton which had received the same treatment.

Experimental Part

The 3 species of wood used in this investigation were ground and screened. Only that which passed through an 80-mesh and was retained by a 100-mesh sieve was used. The material was placed in alundum

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[2] Taken from a dissertation by A. W. Froehlke submitted to the University of Wisconsin in partial fulfilment of the requirements for the degree of Master of Science.

[3] THIS JOURNAL, **45**, 1008 (1923).

[4] Schorger, *J. Ind. Eng. Chem.*, **9**, 748 (1917).

[5] Bertrand, *Compt. rend.*, **129**, 1025 (1899).

[6] *J. Ind. Eng. Chem.*, **13**, 61 (1921).

[7] Ref. 3, p. 1012.

crucibles and extracted in a Soxhlet extractor with an equal mixture of alcohol and benzene for a period of 4 hours. The excess of solvent was removed by suction, the residual alcohol and benzene washed out with boiling water, and the extracted material then dried over a water-bath.

The cellulose samples were prepared from these by means of the Cross and Bevan process as modified by Schorger.[8]

The same process was duplicated in the case of raw, ginned cotton wool so that any variation in the hydrolysis curves for cotton and the wood celluloses could not be attributed to a variation in the preliminary preparation of the celluloses.

In order to bring cellulose into solution in hydrochloric acid it is necessary to increase the acid content to 40% or greater. This was accomplished by passing hydrogen chloride through ordinary concd. hydrochloric acid cooled to —10°. The acid so made was tightly stoppered in a glass-stoppered flask and maintained at a temperature of 0° or lower until used. The strength of the acid was determined by means of specific-gravity determinations. For this purpose an hydrometer calibrated between 1.180 and 1.240 was employed.

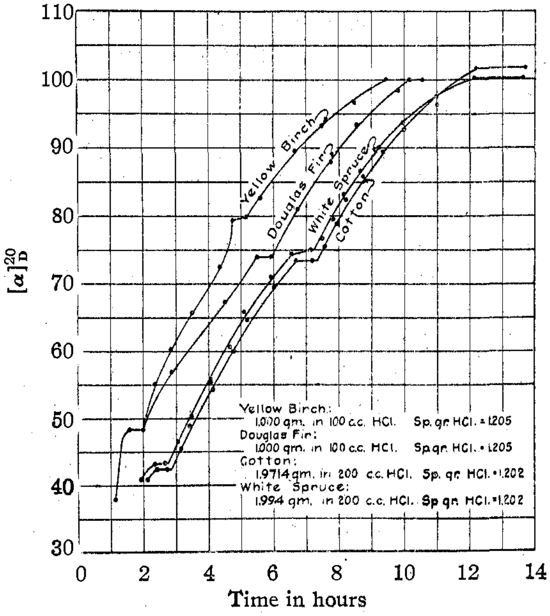

Fig. 1

It was found undesirable to use an acid of higher concentration because when the temperature of such an acid was raised from 0° to —20° considerable hydrogen chloride was evolved, making it unsafe to bring the acid to the required temperature in a closed flask.

Two hundred cc. of hydrochloric acid prepared as above was added to about 2 g. of the prepared cellulose in a glass-stoppered flask. The flask was tightly closed and the mass vigorously shaken until the cellulose completely dissolved.

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[8] Schorger, *J. Ind. Eng. Chem.*, **9**, 561 (1917).

In a preliminary experiment the curves of specific rotation plotted against the time showed a break common to the 4 celluloses at about the twelfth hour. Willstätter obtained a similar break between the second and third hours. The question immediately arose as to whether any relationship existed between the break in the curve obtained by Willstätter at the second hour and the break obtained in the curves of the hydrolysis of the 4 celluloses at the twelfth hour. Consequently, the 4 celluloses were hydrolyzed with a 41% hydrochloric acid and the course of hydrolysis followed from the first hour until a constant optical rotation was obtained; the following quantities of cellulose in 200 cc. of acid were used: 1.9714 g. of cotton cellulose, 1.9940 g. of white spruce cellulose, 2.0000 g. of Douglas fir cellulose, and 2.0000 g. of yellow birch cellulose. The cotton cellulose dissolved to a colorless solution in 20 minutes, which changed after 1.5 hours to a light straw-yellow, at about the fourth hour became much darker, and after 25 hours was light brown. The white spruce cellulose also required 20 minutes' shaking with the acid to complete its solution. This light brown solution became markedly deeper in color at about the fourth hour and after 25 hours the color was medium brown. The Douglas fir cellulose gave a colorless solution after 45 minutes' vigorous shaking. The particles before solution were very light brown while in contact with the acid. After 1.75 hours a trace of light yellow developed which became gradually darker. The yellow birch cellulose dissolved in 30 minutes to give a light brown solution.

The change in specific rotation that occurs with time is illustrated in the curves of Fig. 1. The position of the curve is greatly influenced by the strength of the acid used, the rate of hydrolysis increasing as the concentration of the acid is increased so that the effect of a stronger acid on the curve is to displace it to the left.

Willstätter showed that the specific rotation of a solution of pure glucose in fuming hydrochloric acid is much greater than in water. To repeat this work, a 1% glucose solution in hydrochloric acid and water at 20° was prepared, the initial rotation readings were immediately taken, and the mutarotation was followed until no further change was observable. After 4.5 hours the glucose acquired a constant specific rotation of 51.81° in water, while in the 41% hydrochloric acid this amounted to 100.16° after 3 hours. Assuming that glucose is the only sugar formed on hydrolysis of cellulose and that it is formed quantitatively, the yields from the 4 celluloses determined by the known formula, $C = \frac{100\alpha}{1.(\alpha)_D}$, were found to be cotton cellulose, 91.40%; white spruce cellulose, 90.58; Douglas fir cellulose, 90.10; and yellow birch cellulose, 90.10.

During the progress of the hydrolysis, samples were periodically removed from the flask, diluted, neutralized and the content of reducing sugar was determined by means of Fehling solution. These results are plotted in Fig. 2.

The first few 5cc. samples removed for analysis by reduction with copper became turbid when they were diluted to 20 cc. with water. A light precipitate of cellulose settled on standing, the amount of which gradually decreased until after the fifth hour dilution no longer caused precipitation of cellulose. Those samples, which became turbid were filtered before analysis.

No direct relationship is evident between the values obtained by the polariscope and those by reduction of Fehling solution. The curves obtained by the latter method are smooth and increase rapidly until the tenth hour. The reaction then becomes much slower and a maximum is reached only after about 25 hours. The values for dextrose obtained from the different celluloses by the reduction of Fehling solution are as follows:

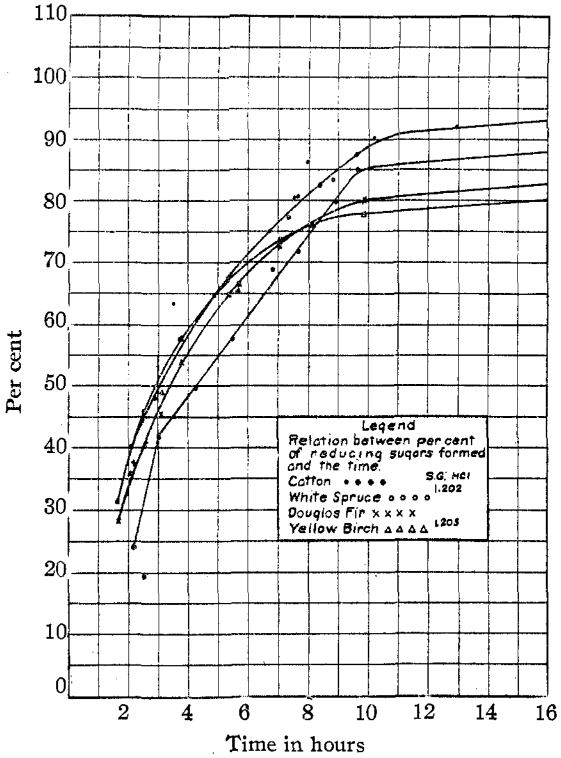

Fig. 2

Cellulose	White spruce	Cotton	Douglas fir	Yellow birch
Time, h., m.	22:55	22:50	25:20	25:20
Reducing sugar, %	97.8	93.9	87.57	85.60

Theory and Discussion

In the curves where specific rotations at 20° are plotted against time it is seen that those for spruce cellulose and cotton are practically identical regardless of the presence of mannose in the former. However, distinctly different curves were obtained for Douglas fir and yellow birch, the difference lying in the fact that the specific rotation of the yellow birch rises much more rapidly than that of any of the other celluloses used. A marked difference in the case of yellow birch was expected since it contains about 28% of pentosan[4] as compared with 5.5% and 9.5% for Douglas fir and white spruce, respectively. Further, the curves for all 3 wood celluloses are distinctly different from one another and with the exception of spruce cellulose are quite different from that for cotton.

An interesting relationship exists between all 4 curves. It will be noted that 2 breaks in the curve are common to each cellulose, the first break occurring at about the second hour, and the second one at about the sixth or seventh hour. Willstätter and Zechmeister[9] call attention to the first break in the curve for cotton as indicated between the second and third hour but neglected to take readings often enough between the seventh and eighth. They attribute the first break to the intermediate formation of cellobiose. This idea, however, is open to question. From a consideration of the last curves, showing optical rotation, apparently three reactions occur. These sharply defined stages of the reaction may indicate successive steps in the conversion of the cellulose to the final products or to secondary reactions of the products among themselves or with the hydrochloric acid. They may also be due to changes in the optical activity of the liberated sugars. It may also be assumed that from the start of the reaction 3 sugars are simultaneously formed. Under these circumstances the observed rotation would be the sum of the rotations of the individual sugars. If at some intermediate point along the curve the formation of one of the sugars ceases and its specific rotation becomes constant then a break in the curve would be produced such as was obtained experimentally. When it is assumed that 3 sugars act in this manner at 3 different points on the curve, then specific rotation curves would be produced having breaks identical in character with those obtained experimentally. On the other hand, instead of having several reactions taking place simultaneously, it would be entirely feasible to look upon the specific-rotation curves as resulting from a number of successive reactions. In this case the initial product would be a sugar whose rotation becomes constant after several hours, because after that time the sugar is no longer a reaction product. Just at this time another reaction results in which another sugar is formed. This reaction proceeds as in the case of the first sugar formed. If a third reaction of this nature occurs, then again a curve is produced having breaks corresponding to those obtained experimentally.

From the curves which illustrate the rate of formation of reducing sugars it may be seen that the amount of sugar formed gradually increases. The slope of these curves toward the end of the reaction is not as great as the slope during the initial course of the hydrolysis. This may be attributed to a slight reduction in the acid concentration of the solution. Although every precaution was taken to prevent any loss in the acid content of the cellulose solution during hydrolysis, it is recognized that in the

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[9] Willstätter and Zechmeister, *Ber.*, **46**, 2401 (1913).

frequent handling of the solution some loss in hydrogen chloride was involved, but it is believed that this loss was negligible.

Conclusion

The curves showing the specific rotation for celluloses from spruce, yellow birch, Douglas fir, and cotton in solution in concd. hydrochloric acid, exhibit marked differences, indicating a difference in either the primary or the secondary reactions, which in turn would point to a difference in the celluloses themselves.

A marked similarity was observed between the curves for cotton and white spruce celluloses. It is known that cotton hydrolyzes only to glucose, while a large percentage of the sugar formed by the hydrolysis of white spruce is mannose, which has a much smaller specific rotation than glucose, so that the solution of hydrolyzed white spruce should show a lower specific rotation than that of cotton cellulose. The curves for cellulose from Douglas fir and yellow birch are also similar in character, although the former contains 5.5% of pentosan while the latter contains as high as 28% of pentosan. This great variation in composition should cause a distinct difference in the specific rotations, but such is not the case, as may readily be seen from the curves.

In view of these facts we are forced to admit with Cunningham[10] that the optical method for determining the quantitative conversion of cellulose to sugar is of little value. It does, however, indicate that considerable differences exist between celluloses from different sources; otherwise, all the curves would be identical in shape.

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THE ISOSTERISM OF PHENYL ISOCYANATE AND DIAZOBENZENE-IMIDE

BY WALLACE H. CAROTHERS

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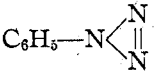
It was the purpose of the investigation the results of which are reported in this paper to test experimentally a prediction arising from the octet theory of the structure of atoms and molecules.

The structural formula of phenyl isocyanate is usually represented as $C_6H_5\text{—}N{=}C{=}O$ (1), and of diazobenzene-imide as $C_6H_5\text{—}N{=}N{\equiv}N$ (2), or as



$C_6H_5\text{—}N\!\left\langle\begin{matrix}N\\ \|\\ N\end{matrix}\right.$ (3). Applying the principles of the theory of atomic structure originated by G. N. Lewis[1] these would be $C_6H_5:\overset{..}{N}::C::\overset{..}{O}:$

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[10] Cunningham, *Trans. Chem. Soc.*, **113**, 173 (1918).

[1] Lewis, THIS JOURNAL, **38**, 762 (1916).