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A Recent Development in the Chemistry of Cellulose.

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Of the numberless bodies which now make up that department of chemical science which treats of the compounds of carbon comparatively few belong to the class to the consideration of which was originally applied the name "organic chemistry." In the early days of Wöhler, only those substances which occur organized in nature and which are formed in the animal and vegetable kingdoms only under the influence of a special, obscure agency called the vital force, were included in this classification. Among the few bodies which have hitherto resisted synthesis and which are as yet made only through the intervention of a vital force, are those which form the skeleton or framework of all vegetable tissues, and which are included under the generic term "cellulose." All plants, from the microscopic unicellular bacterium up to the giant conifers of the Yosemite Valley, are built up of cells, the envelopes or walls of which consist essentially of this organic compound, cellulose. From the earliest times, cellulose in its various forms has constituted the most important raw material used by man, either in its substantially pure state, as cotton or linen, or where it is associated with other more or less complex bodies in wood, bamboo, straw and other structures built up by the plant. For many years the commercial value of cellulose depended entirely upon its physical properties and the form in which it was obtained. When it became possible to modify the natural properties of this material by chemical treatment, its enormous economic importance was still further increased and its commercial value enhanced.

While the word "cellulose" may be used to include bodies of analogous composition having similar functions, it must not be

taken as signifying a simple, definite substance of unvarying properties. Just as we have wheat starch, potato starch and corn starch, varying in size and shape of granule, in viscosity and adhesiveness of the product made therefrom, etc., so, too, we have different forms of cellulose. Physically, these substances are, when freed from adhering waxes, resins and other incrusting materials, colorless, amorphous bodies capable of withstanding relatively high temperatures and soluble in none of the ordinary solvents. An ultimate analysis reveals the fact that cellulose is composed of carbon, hydrogen and oxygen in the proportions represented by the empirical formula $C_6H_{10}O_5$. This statement in no way, however, represents the true molecular complexity of the substance. Starch is represented by the same molecular proportion $C_6H_{10}O_5$. Superimposed upon what is probably a very complicated molecule in both of these substances, is what we call the colloidal state, a condition of matter of which we at present know almost nothing. In contradistinction to the sugars, the third closely allied member of the so-called carbohydrate group, we have in cellulose no clearly defined chemical or physical constants, such as melting point, boiling point, solubility relations, etc., to guide us. Although, as we shall find, the chemical reagents which act upon cellulose are not few, this action, unfortunately, is always accompanied by a more or less complete breaking down or splitting of the so-called cellulose aggregate. Through a study of those derivatives of cellulose and starch known as the bioses, where two $C_3H_5O_2$ groups combine with one molecule of water, Skraup, by means of a chlorine-acetyl compound, arrives at the conclusion that the simplest possible molecular weight of cellulose is 5508, while starch is 7440. This much, at least, is certain—that the forms of cellulose of which we have knowledge, are combinations of a large number of groups having the three elements in the proportion expressed by the formula $C_6H_{10}O_5$, and that, when undergoing chemical reaction, the more perfectly this complex or aggregate can be kept intact, the more valuable from a commercial point of view, are the resultant products.

A reaction which is common to all three members of the group of compounds, known as carbohydrates, viz., sugars, starches and cellulose, but which these substances show to a very unequal degree, is that of hydrolysis by dilute mineral acids. The sugars and starches are converted into bodies having an increased

percentage of hydrogen and oxygen, with the greatest ease, forming dextrose and levulose in the first case, and in the second a mixture of dextrose and other sugars. The enzyme diastase is also able to effect transformations of this character very easily. When we come to cellulose, however, we find a marked difference in the ease with which analogous reactions are brought about. Treatments which effect complete hydrolysis in the case of starch, has little or no effect upon cellulose. A different set of conditions are necessary to break up the cellulose aggregate and to add on the water necessary to form these simpler molecules or molecular complexes.

The earliest worker in this field to carry on systematic investigation and to obtain tangible results, seems to have been a Frenchman, Girard,* in 1881. By subjecting cellulose to the action of dilute sulphuric acid for several hours he obtained an easily pulverized mass, which he called cellulose hydrate and which he thought had the formula $(C_6H_{10}O_5)_2 \cdot H_2O$. A few years ago Stern† repeated this work and failed to get the results described by Girard. He found, however, that if cellulose be boiled with 5% sulphuric acid, a part is converted into dextrose while the major portion is simply disintegrated. This disintegration is due to the fact that certain portions of the cellulose fibre are more easily attacked than others, and as these portions are dissolved their removal causes the structure as a whole to fall to pieces. Since Stearn did not follow, in any case, the directions of Girard, it is not surprising that comparable results were not obtained. The fact remains that the product of such acid treatment shows physical properties not possessed by the original cellulose.

This hydrolysis may be carried to the point where practically a complete conversion of the cellulose into soluble and for a large part also fermentable sugars, takes place. On this fact is based the much-talked-of process for obtaining alcohol from wood, of Classen and others, where dextrose is first formed and then subsequently fermented.

A relatively large number of processes for making hydro-cellulose, differing in detail from the above, have been proposed, but they all result in a very friable powder in which the original

*Ann. de Chem. et Phys., 24, 350.

†Jour. Chem. Soc., 85, 336.

structural form of the cellulose is lost. They all seem to bear out the general formula $(C_6H_{10}O_5)_n \cdot H_2O$.

One of the more common methods used by investigators in the field of organic chemistry for determining the number of hydroxyl groups in a compound, is to substitute each one by an acetic acid radical, making a so-called ester. This esterification is usually effected by treating the hydroxyl-containing substance with acetyl chloride or acetic anhydride, with or without the presence of some condensing or esterifying agent, such as sodium acetate, zinc chloride or sulphuric acid. By separating the products of this reaction and then subjecting them to treatment with alcoholic potash, the acetyl groups may be split off and measured, and the number of hydroxyl groups determined.

A. N. P. Franchimont,* in 1882, while studying the problem of the constitution of cellulose, used this method. He found, however, that if the cellulose be treated with acetic anhydride without a condensing agent, the conditions necessary for the reaction were such that an almost complete disintegration of the cellulose aggregate resulted. However, by adding sulphuric acid to the reaction mixture, a hydrocellulose was formed and the esterification then took place with great ease. He points out that esters differing widely in solubility can be produced by varying the proportion of sulphuric acid. It is thus seen that Franchimont was the pioneer in this field of cellulose chemistry and opened up the way for the great amount of work which has recently been done upon this subject.

Lederer,** in his method for the production of the acetic acid esters of cellulose, provides for making hydrocellulose according to the method of Girard, and subsequently esterifying by acetic acid in the presence of a small quantity of sulphuric acid. Miles,† repeating the method of Franchimont, places the sulphuric acid in the reacting mixture and makes the hydrocellulose at the same time that the acetylation is effected. H. S. Mork,‡ working in conjunction with A. D. Little and the writer, found that by using the sulphonic acids of phenol or naphthiol, the reaction is more

*Rec. trav. chim. Pays-Bas., 18, 472.

**U. S. Patent, 654,988.

†U. S. Patent, 733,729.

‡U. S. Patent, 709,922.

easily controlled and a more uniform product obtained. Other investigators have proposed phosphoric acid, methyl sulphate and a variety of other hydrolyzing and condensing agents, without obtaining a materially different product. In all these cases, as in the original method of Franchimont, the resultant ester is dissolved by the reaction mixture and is recovered by precipitation therefrom in a large volume of water. The product of this procedure has been described as tetracetate of cellulose, and its appearance depends upon the way it is precipitated by water from its solution in acid. When saponified in the regular way with alcoholic potash, the product gives values corresponding to the tetracetate, although the yield corresponds to that of the tri-acetate calculated on the $C_6H_{10}O_5$ basis. Thus, 100 grams of carefully prepared cotton roving yields when acetylated with benzol-sulphonic acid, 168 grams of product, while that calculated for the tri-acetate is 177 grams and of the tetracetate considerably more. The saponification number is found to be about 705, while that calculated for the tri-acetate is 583 and that for the tetracetate 700.

Much light has been thrown upon this apparent discrepancy by a recent paper by Dr. H. Ost,* in which the analysis of these acetyl derivatives is discussed at length. Data are given which show that when the esters described above are saponified in the ordinary manner with alcoholic potash solution, acids other than acetic are formed, which, united with the potash, give an abnormally high saponification number. If the products of this saponifying action be mixed with sulphuric acid and the acetic acid distilled with steam, an amount of acid agreeing closely with that calculated for the tri-acetate is obtained. A method proposed by H. E. Perkin for determining the acetic groups in phenols was found by Ost to be especially applicable to the analysis of these products. It consists in gently heating the ester with 50% sulphuric acid solution for twenty-four hours or more, and then separating the acetic acid thus set free by distillation with steam. The figures obtained agree very closely with those calculated for cellulose tri-acetate, notwithstanding the fact that the products investigated were made by a number of different processes. The so-called cellulose tetracetate of Cross and Bevan, made by treating the cellulose recovered from the sulpho-carbonate reaction with

*Zeitschr. f. Angewandte Chem., 19—993.

magnesium acetate and acetyl chloride, was examined by this method by Perkin and Greene and found to be in reality the tri-acetate. Of course, it is possible that these products consist of a mixture of di- and tetracetates in such a proportion that the saponification equivalent is that of the tri-acetate, but while there are indications that di-acetates do exist in the mixture, the above supposition is quite improbable.

The fact noted by Franchimont that acetates of very different solubilities could be obtained by varying the amount of sulphuric acid employed in the reaction also lead to the development of a number of new cellulose derivatives.

There are unquestionably two separate reactions taking place simultaneously, the first being the production of the hydrocellulose by means of the acid, and the second the formation of the ester of this hydrocellulose by the acetic anhydride, accelerated by the presence of another acid or its equivalent. Taking up first the preparation of hydrocellulose, we find that the method proposed by Girard was to soak the well purified cellulose in a 3% sulphuric acid solution until saturated, press tightly between filterpapers and dry in the air. The paper thus treated was heated in a closed flask to 70° for three hours. The resultant product was a brittle, white mass which reduced Fehling solution slightly and was more deeply colored with fuchsin solution than before the treatment. Mork, in repeating this work, found the method very difficult to control, and very sensitive as regards the pressure on the cotton before drying, and the temperature and time of heating. By using too much acid or heating too long, a product is obtained which is probably the highly degraded cellulbiose of Skraup $(C_6H_{10}O_5)_2 \cdot H_2O$. Lederer has varied the method of Girard by substituting acetic acid for water, but obtained the same brittle mass, which soon fell to a structureless powder.

A very much more valuable product of uniform quality, as shown by Mork, can be prepared as follows: Into a mixture of 400 parts glacial acetate acid and 20 parts benzol-sulphonic acid are placed 100 parts of high-grade bleached cotton roving. This is allowed to remain until perfectly saturated with the liquid, when the mass is pressed until one-half of the liquid originally used has been recovered. The wet cotton, now holding 200 parts acetic acid and 10 parts benzol-sulphonic acid, is allowed to

stand at room temperature (15° to 20° C.) for about twelve hours. At the end of this period it will be found to have been converted into a highly reactive modification or form of cellulose which retains the original fibrous structure of the organic cellulose. When washed and dried the product is found to have increased in weight about 1.88% on the weight of the cotton used. This corresponds to the formula $(C_6H_{10}O_5)_6 \cdot H_2O$, which would require an increase in weight of 1.85%. This process admits of perfect control and produces a hydrocellulose in which the original cellulose has suffered little, if any degradation.

In the recent publication already referred to, Ost confirms these results, although he gives as the optimum conditions a somewhat greater proportion of acid to the cotton, and allows the mixture to stand for two days. From data obtained by the ultimate analysis of his product, Ost arrives, quite independently of Mork, at the same empirical formula $(C_6H_{10}O_5)_6 \cdot H_2O$. He confirms Mork's observations also, that too energetic treatment leads to a disintegration of the cellulose aggregate, forming products of much lower molecular weight containing a relatively larger quantity of water of hydrolysis.

All of these hydrocelluloses in the presence of the condensing agent react with ease with acetic anhydride, giving results which depend upon the extent of the hydration, the temperature of reaction and the time. Products may be made which are soluble in water alone, alcohol and water, acetone and water, acetone alone and chloroform alone. In obtaining the results given in the following table, cotton was treated with the hydrolyzing agent and acetic acid for the time given in the first column, and, without washing, was acted upon with acetic anhydride. The relative solubilities appear in the other columns, where *i* means insoluble, *ps* partially soluble, *g* gelatinized, and *s* soluble.

Cross and Bevan* have investigated an analogous series of substances and conclude that these compounds are the mixed esters of sulphuric acid and acetic acid. When a large amount of sulphuric acid calculated on the weight of the cotton was used, a material which was soluble in water was obtained, which contained the proportion of one sulphuric acid group for each $C_6H_{10}O_5$ group. By decreasing the amount of sulphuric acid the

*Ber., 38, 38 and 1859.

% Benzene Sulphonic Acid (on cellulose)	Time Preliminary	Temperature of Acetylation	Time of Acetylation	SOLUBILITY				
				Water	Ethyl Alcohol and Water	Acetone	Acetone and Water	Chloroform
1%—2%	None	80°—100°C.	1—2 hrs.			i.		s.
10%	24 hrs.	20°C.	24 hrs. 72 hrs.			i. i.	s. s.	p. s. s.
25%	24 hrs.	20°C.	24 hrs. 72 hrs. 96 hrs. 168 hrs.			p. s. p. s. p. s. p. s.	s. p. s.	i. p. s. s. s.
50%	24 hrs.	10°—15°C.	2 hrs. 15 hrs. 48 hrs.	s. g. i.				
50%	24 hrs.	5°—10°C.	96 hrs.		s.	s.	s.	i.

product was no longer soluble in water but was soluble in aqueous acetone and contained less sulphuric acid and more acetic acid groups. When a relatively small amount of sulphuric acid was present, the more normal acetone- and chloroform-soluble acetates were obtained. So far as I know, the analytical results given by the authors in support of these statements have not been confirmed by others, but the fact that by increasing the amount of sulphuric acid, products of radically different solubility may be obtained, confirms the work of Franchimont and Mork.

The technically valuable acetic acid ester of cellulose, however, is the tri-acetate, although as generally made, some di-acetate is present. The tri-acetate is easily soluble in chloroform while the di-acetate is much less so, being scarcely gelatinized. The increasing solubility in chloroform, due to the change of di- into the tri-acetate as the reaction proceeds, is shown in the following experiments:

Hydrocellulose made as above described was treated with acetic anhydride at 40° C., giving the following data:

Time	Solubility in Reacting Acids.	Solubility in Chloroform.
30 min.	Soluble	Insoluble
1½ hr.	"	Slightly soluble
4½ hr.	"	Very soluble

It will be noted that all of the acetic acid esters of cellulose, in contradistinction to the nitric acid esters, have been heretofore produced by methods which have involved, as a necessary consequence of their successful application, the complete breakdown and destruction of the physical form of the cellulose structure concerned in the reaction; that is, the product of the reaction is soluble in the reacting mixture. The great practical disadvantages incident to this simultaneous solution will be apparent. Among them may be mentioned the difficulty of control; the danger of local overheating which makes necessary the working of small batches; the necessity of precipitation in water to check the reaction; and the dilution, and to a considerable extent loss, of the reagents employed. It has been the goal of investigators in this field to produce an acetic acid ester of cellulose which will retain the structural form of the original cellulose in a way analogous to that of cellulose nitrate. This has been successfully done by H. S. Mork in the following manner:

100 parts hydrocellulose is prepared as has already been out-

lined, and while still moist with the hydrolyzing acid, is placed in a mixture of 300 parts acetic anhydride and 1200 parts benzol and allowed to stand at room temperature (15° to 20° C.) for about eighteen hours. When the reaction is complete, as ascertained by removing some of the product and determining its solubility in chloroform, acetone, or other appropriate solvents for the particular ester toward the manufacture of which the process has been directed, the mass is freed as far as possible from liquid, by whizzing in a hydro-extractor, and is then washed and dried. Among the important advantages offered by this process may be enumerated the complete control which results from the moderation of the rate of esterification by reason of the low temperature at which the same is conducted, coupled with the influence of the benzol, or its equivalent, in restraining the reaction; the ease of testing the progress of the process and of stopping it at any time desired; the large quantities of material which may be handled without endangering the quality of the product, and finally the ease of washing and drying the product in bulk.

The analysis of this product shows it to be the tri-acetate of cellulose, but differing from an analogous fibrous acetate which has been prepared by Strehlenert and Reubold,* in that it has apparently preserved the large molecular aggregate of the original cellulose. The material itself shows greater strength than the acetate of Strehlenert (which is described as being brittle); gives more viscous solutions than acetates hitherto prepared, and is so far as can be determined a superior product in all its properties.

The uses to which cellulose acetate may be put are at present limited by the expense of the material itself, incident to the cost of the necessary reagents and the relatively high price of its solvents. In general, it may be said that cellulose acetate can find technical application most readily where nitrocellulose, on account of its inflammability and low temperature of decomposition, cannot be employed. At present its most important use is in the electrical insulation of very fine wire, for which it has found an extended application in the hands of the General Electric Company at Lynn, Mass. A highly desirable quality of artificial silk and artificial horsehair can be made from the acetate, but for the present it is ruled out of the market by its cost of production.

*U. S. Patent, No. 812,098.