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Abstract

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NEW DATA ON THE RELATIONSHIP BETWEEN THE STRUCTURE OF POLYSACCHARIDES (CELLULOSE) AND THE DIRECTION OF CHEMICAL REACTIONS OCCURRING DURING THEIR THERMAL DECOMPOSITION

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In the present work we set ourselves the task of studying the influence of the structure of cellulose on the chemical processes occurring as a result of transformations of its molecule during thermal decomposition in vacuum. We carried out the investigation of the thermal decomposition of cellulose in vacuum mainly by the method of Pictet (^{1}) and Vein (^{2}), somewhat improved by us.

We studied the direction of the chemical processes during the thermal decomposition of cellulose as a function of physical structure (packing density) by determining the amount of 1,6-anhydro-1,5-glucopyranose (levoglucosan) formed in this process. This compound retains the empirical formula of the elementary unit of cellulose, but has a different position of the hydroxyl and of the oxygen bridge. Consequently, the quantitative yield of levoglucosan during the thermal decomposition of the macromolecule of cellulose requires preservation of its elementary unit. Proceeding from this, we assumed that, provided the functional groups of the elementary unit of cellulose are preserved, it is possible to have a constant yield of levoglucosan under standard conditions of thermal decomposition in vacuum, whatever chemical scheme may lead to its formation, i.e., through a stage of cellulose hydrolysis (^{3},^{4}) or by other schemes. The amount of levoglucosan formed directly indicates the direction of the chemical processes occurring during the thermal decomposition of cellulose.

It is well known that cellulose preparations identical according to X-ray structural analysis may differ very greatly in structure, characterized by different bond energies caused by different mutual arrangements of the molecules, conventionally termed the packing density of the polymer. Structural changes associated with disruption of intermolecular bonds are as yet amenable only to overall quantitative characterization. For this purpose calorimetry, sorption, hydrolyzability of the preparation, spectral analysis (in the infrared region), and

Fig. 1. Sorption and desorption isotherms of fiber at 20°: 1—initial cotton; 2—cellulose reprecipitated from a copper-ammonia solution; 3—cotton treated with 10% NaOH solution; 4—viscose staple fiber; a—sorption, b—desorption

Figure 1: Fig. 1. Sorption and desorption isotherms of fiber at 20°: 1—initial cotton; 2—cellulose reprecipitated from a copper-ammonia solution; 3—cotton treated with 10% NaOH solution; 4—viscose staple fiber; a—sorption, b—desorption

other methods are used. We also employed the methods of sorption and hydrolyzability to determine the influence of changes in the structure of cellulose preparations.

To obtain celluloses with different structural modifications (of chemically identical composition), we took as the initial preparation cotton cellulose obtained by the standard method of Corey and Gray ([5]), but with subsequent mild acid hydrolysis. To obtain celluloses with altered structure, we subjected it to various treatments: the initial preparation was dissolved in a copper-ammonia solution under conditions that maximally excluded oxidation processes, and was then precipitated from the solution in the form of a fine powder (according to the procedure described by us earlier ([6])).

The second route for obtaining celluloses with altered structure consisted in treating the initial preparation with 10% NaOH at 0° for 1 hour, followed by removal of the alkali and drying in air. As is known, with this treatment maximum swelling of the fiber is observed, dissolution

low-molecular-weight fractions, as well as dissolution of cellulose with the most damaged functional groups. As cellulose preparations with the most altered packing, hydrate-cellulose fibers in two modifications were taken: 1) highly oriented fibers (viscose cord) and 2) weakly oriented fibers (staple).

Changes in structure in the preparations obtained were characterized by the method of sorption and desorption isotherms (equilibrium moisture content) and by hydrolyzability. In addition, the indicated preparations were characterized by molecular weight and by the change in the functional groups of the elementary unit. The resulting characterization of the preparations is presented in Table 1 and in Fig. 1.

In all the preparations listed, the content of carbonyl and carboxyl groups was very insignificant, i.e., the elementary unit of the cellulose macromolecule was practically unchanged.

Fig. 1. Sorption and desorption isotherms of fiber at 20°: 1—initial cotton; 2—cellulose reprecipitated from a copper-ammonia solution; 3—cotton treated with 10% NaOH solution; 4—viscose staple fiber; *a*—sorption, *b*—desorption.

The amount of levoglucosan formed, obtained in the solid distillate ([7], [8]), was estimated by the increase in reducing substances. In separate experiments, levoglucosan was isolated in the form of a crystalline product, which was characterized by its angle of rotation and melting point, as well as by the properties of a derivative. The characteristics obtained agreed with literature data. On the basis of the investigation carried out, we consider it possible to draw the following conclusions: a change in the structure of cellulose, characterized by us by hydrolyzability and by

Table 1

Characteristics of cellulose preparations with different structures

No. of preparation	Method of treating the cellulose	General appearance of the cellulose	Properties of cellulose: degree of polymerization	Properties of cellulose: content of carbonyl groups, %	Properties of cellulose: content of carboxyl groups, %	Hydrolyzability of the sample	Yield of levoglucosan, %
1	Cotton cellulose treated according to Corey and Gray (5) and with 1% H_2SO_4 for 5 min at 100°	Normal fibrous structure	1000	0,04	0,51	5,21	60–63

No. of preparation	Method of treating the cellulose	General appearance of the cellulose	Properties of cellulose: degree of polymerization	Properties of cellulose: content of carbonyl groups, %	Properties of cellulose: content of carboxyl groups, %	Hydrolyzability of the sample	Yield of levoglucosan, %
2	Cellulose No. 1, dissolved in a copper-ammonia solution and isolated in the form of hydrate-cellulose	Fine powder	1000	0,11	0,073	10,76	14–15
3	Cellulose No. 1, treated with 10% NaOH at 0° for 1 hour	Normal fibrous structure	1200	0,013	0,07	9,55	36–37
4	Hydrate-cellulose fiber without additional orientation		380	0,03	0,14	23,5	4,0–4,5

No. of preparation	Method of treating the cellulose	General appearance of the cellulose	Properties of cellulose: degree of polymerization	Properties of cellulose: content of carbonyl groups, %	Properties of cellulose: content of carboxyl groups, %	Hydrolyzability of the sample	Yield of levoglucosan, %
5	Hydrate-cellulose fiber in the form of viscose silk with maximum orientation		400	0,065	0,17	23,2	4,8-5,0

sorption, sharply changes the direction of the chemical processes during the thermal decomposition of cellulose. With an increase in the hydrolyzability of the cellulose sample and the sorption of water, and with broadening of the hysteresis loop, the yield of levoglucosan decreases (cf. Table 1). For example, for the preparation of the original cotton fiber the hydrolyzability was 5 units, the equilibrium moisture content was minimal (curve 1), and the yield of levoglucosan was (60%) of the weight of the cellulose. For preparations No. 4 and No. 5 the hydrolyzability was 23.5 and 23.2 units, respectively, and the equilibrium moisture content increased (Fig. 1, 4); in this case the yield of levoglucosan was only 4–5%. Preparation No. 2 has an unchanged molecular weight in comparison with the original sample, as well as unchanged functional groups of the elementary unit, but as a consequence of a change in structure (curve 2, hydrolyzability 10.8). This preparation gave only 14% levoglucosan. Preparation No. 3, as a result of the conditions used for its preparation, was freed from low-molecular fractions of cellulose and practically contained no carboxyl groups; however, as a consequence of the change in structure, characterized by a hydrolyzability of 9.5 and an increased equilibrium moisture content, the yield of levoglucosan was only 36% of the original preparation (curve 3). It should be especially noted that both modifications of hydrate-cellulose fiber, possessing different degrees of orientation, are known to have similar sorption isotherms (9, 10) and hydrolyzability (11). Thus, the yield of levoglucosan cannot be compensated by increasing the degree of orientation of the chains in hydrate cellulose. The absence of a positive influence of the degree of orientation of the fiber on the yield of levoglucosan is apparently connected with the fact that the orientation carried out does not cause a significant increase in packing density.

The experimental data obtained show that a change in the density of arrangement of cellulose macromolecules causes a change in the direction of the chemical process of thermal decomposition of cellulose. From these data it follows that consideration of the chemical processes of thermal decomposition of cellulose solely on the basis of ideas about the structure of the individual molecule of the polymer is clearly insufficient. For high-molecular compounds, intermolecular bonds, the types of bonds, and their strength must be taken into account. A decrease in the packing density of macromolecules lowers the yield of levoglucosan and increases the yield of other products of the deep decomposition of cellulose. It may be supposed that an increase in the density of arrangement of cellulose macromolecules inhibits the side processes of hydrolysis and dehydration that arise during the formation of levoglucosan.

Thus, the structure of cellulose, characterized by packing density, is one of the principal factors determining the direction of the chemical reactions of its thermal decomposition.

It is of interest to trace the presence of the established regularity in the thermal decomposition of other high-molecular compounds.

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Note: Figure translations are in progress. See original paper for figures.