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Abstract

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CHEMISTRY

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THERMAL DECOMPOSITION OF CELLULOSE AND ITS STRUCTURE

(Presented by Academician V. A. Kargin on 29 VI 1957)

In studying the thermal decomposition of cellulose, in which the conditions of inaccessibility of the reagent to bonds in the more compacted regions are eliminated, we obtained data that make it possible to put forward a number of assumptions concerning both the mechanism of cellulose decomposition and its structure.

Cotton cellulose, treated under mild conditions according to Corey and Gray, was investigated, with an initial degree of polymerization (DP) of 2800 and 1500 (samples Nos. 1 and 2) and 700 (sample No. 3, obtained by mild hydrolysis of sample No. 2) (the DP was determined from the characteristic viscosity of the nitro derivative by the generally accepted method).

The investigation included the following stages: 1) carrying out the thermal decomposition of cellulose, 2) obtaining and analyzing the decomposition products, 3) determining the characteristics of the cellulose itself after a known heating time.

The thermal action on the cellulose was carried out in a quartz apparatus immersed in a block furnace and preheated to a constant temperature of 300°.

* Cellulose, dried to constant weight at 105° for 6 hr, was introduced over 30 sec into the quartz apparatus by means of a magnetic device.

After definite intervals of thermal action (5, 10, 20, 40, and 90 min), the experiment was stopped by lowering the furnace. The decomposition products were analyzed for the presence of levoglucosan by the previously described method (1); the remaining cellulose was analyzed. Nitro esters were obtained by the standard method in order to determine the degree of polymerization of the nitrocellulose (2). For samples subjected to thermal action for more than 40 min, repeated nitration was carried out to obtain cellulose nitrates most completely soluble in acetone (the nitrogen content corresponded to ~13.6%).

Figure 1

Figure 1: Figure 1

Preliminary investigations enabled us to choose a temperature of 300°, ensuring a significant yield of levoglucosan with a sufficiently slow process.

The method of carrying out the thermal decomposition of cellulose at one and the same temperature (300°)—continuously for 300 min, or stepwise over the same period—did not have a noticeable effect on the yield of levoglucosan, calculated with respect to the weight of the original cellulose; it amounted, respectively, to 44 and 46%. The experimental results obtained are expressed graphically in Fig. 1.

During the thermal decomposition of cellulose, at first there occurs a rapid decrease in the degree of polymerization, and for different cellulose preparations the course of the curves is different (Fig. 1, curves 1, 2, and 3). After 8-10 min, a certain critical point is reached at which all three curves merge into one, and the degree of polymerization reaches a constant value, of the order of 200; with further decomposition of the cellulose, only the amount of cellulose decreases, but the molecular weight of the residue remains unchanged.

As curve 4 shows, describing the dependence of the degree of decomposition of cellulose on the heating time, at the critical point the degree of decomposition reaches 8-4%. At the same time, the degree of decomposition is proportional to the heating time for all the samples studied.

The dependence of the yield of levoglucosan on the heating time (curves 5 and 6) shows that, after the critical value of time is reached, when the degree of polymerization reaches a value of the order of 200, the yield of levoglucosan rapidly increases and then reaches a constant value.

Fig. 1. Change in the degree of polymerization of cellulose (1-3), the percentage of decomposed cellulose (4), and the yield of levoglucosan (5, 6) during the thermal decomposition of cellulose as a function of heating time:
1 —DP-2800, 2 and 5 —DP-1500, 3 and 6 —DP-700, 4 —average for the three samples studied (DP-2800, 1500, and 700)

On the basis of the experimental data obtained, the following mechanism of cellulose decomposition may be envisaged. In the first period of the thermal decomposition of cellulose (up to the critical point), cleavage of the chain molecules occurs, with accumulation of fragments having a degree of polymerization of the order of 200. This means that the process of thermal decomposition of cellulose proceeds primarily in regions arranged periodically. During this period,

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* The experimental part for determining the DP was carried out by I. I. Nikolaeva.

the dehydration process predominates (the yield of levoglucosan is only 5-20%), leading to a profound change in the elementary unit and to the formation of readily volatile products. This process is analogous to the previously studied reaction of thermal decomposition of hydrated-cellulose fibers ([1]) and takes place in less compacted regions.

In the second period (after the critical point is reached), when the degree of polymerization has acquired a value of the order of 200 and the yield of levoglucosan has reached a constant value, thermal decomposition proceeds as a process of successive chemical transformation of the units of a fragment of the cellulose molecule, with detachment of the elementary unit, which, owing to internal isomerization, is converted into the monomeric compound—levoglucosan. The deg-

a degree of polymerization of 200 is preserved when the cellulose has decomposed by from 4 to 70-80%.

After the critical point, when the maximum dense packing has been reached, to which, apparently, corresponds the maximum removal of the less ordered (less compacted) part, the cellulose molecule decomposes without a change in the degree of polymerization. As Fig. 1 shows (curves 1, 2, 3), a degree of polymerization of 200 remains unchanged for 80 min at 300° in vacuum.

These facts make it possible to conclude that the detachment of a levoglucosan molecule from the chain molecule gives rise to an active center, which again causes internal isomerization of the next unit and the formation of a levoglucosan molecule. This process of chain decomposition of cellulose proceeds until all the units of the fragment have decomposed. Thus the process that has arisen in some chain molecule leads to its complete decomposition. The remaining molecules are not changed in the process.

The data obtained show the periodicity of the structure of the macromolecule of cotton cellulose from regions with different physical structure, which determines the chemical, thermal, and physical behavior not only of the macroscopic cellulose sample, but also of its individual molecule.

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