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Abstract

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ON THE MECHANISM OF THE THERMAL DECOMPOSITION OF CELLULOSE IN VACUUM AND THE FORMATION OF 1,6-ANHYDRO-1,5-GLUCOPYRANOSE–LEVOGLUCOSAN

(Presented by Academician I. N. Nazarov, June 7, 1957)

Until recently there has been no unambiguous explanation of the mechanism of formation, during the thermal decomposition of cellulose in vacuum, of 1,6-anhydro-1,5-glucopyranose–levoglucosan, a compound with the elemental composition of a unit of the structural unit of cellulose, but having a different position of the hydroxyl (at C_4 instead of C_6) and two oxygen bridges instead of one 1–5 bridge.

Irvine and Oldham (^{1}) proposed a mechanism for the formation of levoglucosan through an intermediate stage of hydrolysis of cellulose to glucose and dehydration of the latter.

This hypothesis found support in the reports of P. Karrer (^{2}) on the preparation of levoglucosan in high yield from β-*d*-glucose.

For a correct evaluation of existing concepts of the mechanism of formation of levoglucosan from cellulose, which represents a special case of the thermal depolymerization of polysaccharides to the monomer, we considered it necessary to carry out studies in order to obtain data for resolving the fundamental questions connected with the formation of levoglucosan from cellulose.

Such fundamental data are: 1) obtaining a stable yield of levoglucosan during the thermal decomposition of cellulose, 2) the possibility of formation of levoglucosan from β-*d*-glucose, 3) the influence of the physical structure of cellulose (packing density) on its thermal decomposition, 4) the influence of glucose on the process of levoglucosan formation from cellulose, 5) the influence of the magnitude of the degree of polymerization of cellulose.

As a result of systematic studies, while varying different physical factors, conditions were found (temperature, vacuum, and the properties of the cellulose) that make it possible to obtain, consistently, 55–60% levoglucosan.

The results obtained in studying the possibility of formation of levoglucosan from β-d-glucose under the optimum conditions for the thermal decomposition of cellulose are presented in Table 1. As is evident from the data in the table, the yield of levoglucosan amounts to only 5-6% of the glucose.

Table 1

Preparation of levoglucosan from β-d-glucose and cellulose during thermal decomposition in vacuum

Starting product	Yield of products, % of starting material: solid distillate	Yield of products, % of starting material: liquid distillate + dry residue	Yield of levoglucosan, % of starting product
β-d-Glucose	39–42	57	5–6
Cellulose	73–75	24	54–60
Levoglucosan	98.8	–	98.8

Studies of the thermal transformation of glucose show that the conversion of glucose into levoglucosan is possible, but the degree of conversion is very small —only 6%. Karrer' s data on the high yield of levoglucosan from β-d-glucose were not confirmed. The method we first applied for separating the products of the thermal decomposition of glucose by means of anionites made it possible to identify levoglucosan and to give an unambiguous answer regarding the possibility of levoglucosan formation and its amount.

Studies carried out with cellulose possessing different physical structures, characterized by packing density, were published by us earlier (^{3}).

The results obtained in the present investigation indicate a change in the direction of the chemical process of cellulose thermal decomposition depending on the packing of macromolecules in the actual sample. From these data it follows that the chemical processes of the thermal decomposition of cellulose cannot be considered solely on the basis of ideas about the structure of individual polymer molecules.

A decrease in the packing density of macromolecules leads to a decrease in the yield of levoglucosan and increases the yield of products of deep cellulose decomposition.

The facts of the low yield of levoglucosan from β-d-glucose (5-6%) and from readily hydrolyzable cellulose led us to the need to study the influence of the presence of glucose itself on the process of levoglucosan formation from cellulose. For this purpose glucose was introduced into the reaction system in an amount from 2 to 20% of the weight of the cellulose. The results are presented in Fig. 1.

As can be seen from Fig. 1, the introduction of glucose, irrespective of its amount, lowers the yield of levoglucosan to 30%.

Fig. 1. Effect of adding glucose to cellulose on the yield of levoglucosan

Since, in the thermal decomposition of the monomer (glucose), levoglucosan is not the main product, it also seemed necessary to study the effect of the degree of polymerization on the yield of levoglucosan during the thermal decomposition of cellulose. The results of these experiments are presented in Table 2.

Table 2

Effect of the degree of polymerization on the formation of levoglucosan

Degree of polymerization	Content of COOH groups per 100 glucose residues	Yield of decomposition products, in % of cellulose: solid distillate	Yield of decomposition products, in % of cellulose: liquid distillate and dry residue	Content of levoglucosan in tar by increase of specific rotation	Yield of levoglucosan in % of cellulose
1000	0.144	78	19.0	77.0	60.0
450	0.144	72	23.0	78.3	56.0
200	0.144	76	22.0	72.0	54.0
190	0.144	74	25.0	72.6	53.0
150	0.144	75	20.0	72.5	54.0
Cellobiose	–	25	–	–	3–4

As follows from the data of Table 2, changing the degree of polymerization in cellulose samples from 1000 to 150 has practically no effect on

formation of levoglucosan; its yield is 55–60%, provided that the physical structure remains unchanged.

To clarify the question of the influence of the minimum chain length on the formation of levoglucosan, studies were carried out on the thermal action on cellobiose in vacuum under the same conditions as in the decomposition of cellulose.

We found that the yield of paste-like distillate is 25%, and the yield of levoglucosan is only 3–4%, calculated on cellobiose (see Table 2).

The data obtained by us show that the basic elements of the hypothesis of levoglucosan formation through intermediate stages of cellulose hydrolysis to glucose and dehydration of glucose to levoglucosan are not confirmed experimentally and, consequently, the hypothesis itself is not correct.

On the basis of the facts presented, it should be considered that the mechanism of levoglucosan formation must include the following processes.

In regions with dense packing, the formation of levoglucosan proceeds predominantly. Here the processes of dehydration and hydrolysis are of only secondary importance. In regions with an altered structure, dehydration and hydrolysis proceed predominantly, leading to the formation of chemically modified and, possibly, thermally unstable glucopyranose units of the cellulose molecule. Therefore, cleavage of the 1,4-β-glucosidic bonds in this case does not lead to the formation of levoglucosan.

In our view, the isomerization process apparently includes migration of the hydrogen of the hydroxyl group from the 6th carbon to the oxygen atom at the 4th carbon atom and closure of the 1st carbon atom with the 6th carbon atom through this oxygen atom, with the formation of a five- and seven-membered ring while retaining the six-membered ring:

[[visible chemical structural scheme: cellulose chain fragment undergoing intramolecular isomerization and cle

According to the calculations of Reeves (4), the spatial arrangement of the atoms of the anhydroglucose unit favors the formation of the 1,6-anhydro ring, because the distance between the 1st and 6th carbon atoms is the smallest in comparison with any other pair of neighboring carbon atoms.

The decrease in the yield of levoglucosan upon addition of glucose to cellulose is apparently caused by the inhibiting action of the very active fragments of the glucose molecule on the isomerization of cellulose-chain fragments into levoglucosan, or by blocking of the radical center that arises as the first act in the process of levoglucosan formation.

It may be assumed that, for the formation of significant amounts of levoglucosan as a result of isomerization of the glucopyranose unit of cellulose, it is necessary to have a chain with a degree of polymerization sufficient to provide such a physical structure which, owing to blocking of the hydroxyl groups by hydrogen bonds, retards the process of dehydration and other side processes.

Conclusions. 1. The small yield of levoglucosan in the thermal decomposition of easily hydrolyzable cellulose, glucose, and cellobiose with added glucose rules out the possibility that intermediate stages of glucose formation and glucose dehydration to levoglucosan are present as intermediate stages in the formation of levoglucosan from cellulose.

These facts do not support the hydrolytic dehydration mechanism of levoglucosan formation that is widespread in the literature.

2. The formation of levoglucosan in substantial yield (55–60%) occurs only in the presence of a certain chain length in the cellulose macromolecule. It has been shown that, for a substantial yield of levoglucosan in the thermal decomposition of cellulose in vacuum, a compacted structure of cellulose is necessary.
3. The process of levoglucosan formation includes the decomposition of the cellulose molecule at the 1,4-β-glucosidic bonds and the subsequent isomerization of the resulting chain fragment into a levoglucosan molecule.

The main conclusions drawn in the study of cellulose may be extended to the thermal decomposition of other polysaccharides and also, probably, to other types of polymers.

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