Thermolytic reactions of cellulose
I. Dehydration reactions of cellulose

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Thermolytic reactions of cellulose have been studied by methods of thermal analysis and by the GC—MS analysis of products obtained from these reactions. It has been found that both 3,6-anhydride of D-glucose and 1,4:3,6-dianhydro-α-D-glucopyranose are formed during heating of cellulose in the temperature range 200—300 °C. It has been concluded that the dehydration reactions proceeding at that range of temperature lead to the dehydropolysaccharides formation. 3,6-Dehydration is supposed to be one of the possible dehydration reactions, which take place during heating of cellulose polymers.

Реакции термического разложения целлюлозы изучались при помощи методов термического анализа и анализа продуктов этих реакций посредством газовой хроматографии и масс-спектрометрии. Обнаружено, что 3,6-ангидрид D-глюкозы и 1,4:3,6-диангидро-α-D-глюкопираноза образуются во время нагревания целлюлозы в температурном интервале 200—300 °C. Пришлось к выводу, что реакции дегидратации протекающие в данном температурном интервале ведут к образованию дегидрополисахаридов. Предполагается, что 3,6-дегидратация является одной из возможных реакций дегидратации, которые происходят во время нагревания полимеров целлюлозы.

The thermolytic reactions of cellulose served as a subject to numerous studies, nevertheless some disagreement in the question of the primary product and in the mechanism of these reactions has been observed. In Scheme 1 it can be seen that a large number of thermolysis products have been considered. 1,6-Anhydro-β-D-glucopyranose *I* (levoglucosane) is regarded as the main reaction product. It has been assumed [1] that *I* is formed by the anhydrization of the primarily produced D-glucose *II*. In a number of studies [2, 3] the temporary formation of anhydrides *III* and *IV*, which should be subsequently transformed into the
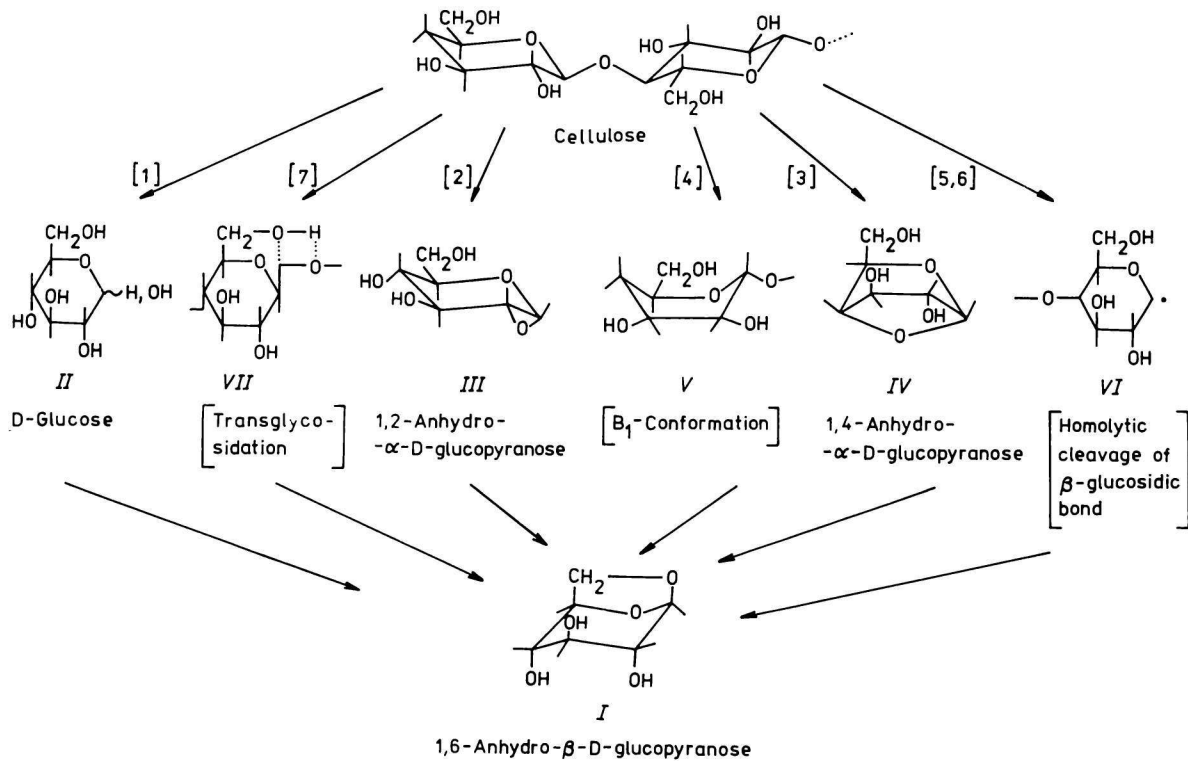
Scheme 1

The supposed reactions [1—7] leading to 1,6-anhydro-β-D-glucopyranose

product I, has been discussed. Some authors [4] refer to the importance of the conformational changes $(C \rightarrow B)$ of V that should precede the anhydrization. A very reasonable mechanism has been advanced by *Golova et al.* and *Kislitsyn et al.* [5, 6] who presuppose the homolytic scission of glycosidic bonds of the cellulose leading to the formation of radical structures VI being stabilized into the product I. *Shafizadeh* [7] contemplates upon the heterolytic cleavage of the glycosidic bond VII.

The main degradation reaction proceeding during cellulose thermolysis is thought to be depolymerization. However, in addition to depolymerization, the dehydration and thermooxidative reactions may go on during thermal degradation. These reactions may be applied particularly in the presence of acid-base catalysts. The primary products may also participate in the above reactions which give rise to a large number of secondary products. As a result, some of the products can be subsequently dehydrated intermolecularly. In this way the molecular mass of saccharides, that undergo dehydration, reincreases, which, at the same time, has an influence on the formation of the residue enriched by carbon after thermolysis (carbonization). *Kilzer* and *Broido* [3] reffered to the intermolecular dehydration, though the intramolecular dehydration of the cellulose chain is also possible. The dehydration proceeding on the C-2- and C-3-hydroxyl groups [8] or that of the primary hydroxyl group [9] can be expected. A review of thermolytic reactions of cellulose is given in [10].

Experimental

The cellulose sample used was the commercially available cellulose powder Whatman CF 11 (the ash content up to a maximum of 0.015 %). As GC-standards were used the following compounds: D-glucose (Lachema, Brno), m.p. 150 °C, 1,6-anhydro-β-D-glucopyranose, m.p. 178—180 °C and 3,6-anhydride of D-glucose, m.p. 120—122 °C prepared according to [11].

The cellulose sample (1 g) was thermolyzed in the nitrogen atmosphere in a quarz tube heated (10 °C min^{-1}) by the electric resistance furnace. The temperature was measured by a thermocouple (PtRh10—Pt) located in the sample. After the completion of thermolysis the sample was quickly cooled and reduced in the 0.5 M-NaBH$_4$ solution. The sample was then acetylated by the mixture consisting of the acetic anhydride and pyridine [12]. Before acetylation, methyl-β-D-arabinopyranoside (15 mg) had been added to the sample and used as an internal standard (ISTD) for the chromatographic analysis. After acetylation, the sample was filtrated and the excess of the acetylation mixture evaporated under nitrogen at 70 °C. The samples prepared in such a way were dissolved in CHCl$_3$ and sugars subjected to the GC—MS analysis as their alditol acetates.

For the separation of the reaction thermolysis products of cellulose the gas chromatography was used. The Hewlett—Packard model GC-5840 A, an instrument consisting of

glass columns (the length of 180 cm and the internal diameter of 2 mm) packed with 3 % SP-2340 on "Chromosorb WAW-DMCS 100/120 mesh" was used. The sample size was 1 μl and the nitrogen carrier gas flow rate was 30 ml min^{-1}. The temperature of the injection port was 250 °C and that of the FID detector 280 °C. The column temperature was programmed to 140—250 °C (10 °C min^{-1}).

To perform the analysis of the separated products of thermolysis, the mass spectrometry method was used. The equipment used was the Hewlett—Packard instrument, model MS 5985. Helium was used as a carrier gas (20 ml min^{-1}). The mass spectra were recorded during the whole time of the chromatographic separation; these were attained either by the EIMS (30 or 70 eV) or by the CIMS (200 eV) method. In the chemical ionization method methane was used as a reactant gas for soft ionization.

The thermal analysis was carried out on the equipment Thermoanalyzer 2 (Mettler). The employed cellulose sample (7—100 mg) was heated up to 600 °C at the heating rate of 10 °C min^{-1} either in the flow of nitrogen or in the air (7 l h^{-1}). The sensitivity of TG was 10 mg per scale, DTG — 1 mg/min, and of DTA — 50 μV per scale. A PtRh10—Pt thermocouple and freshly annealed Al$_2$O$_3$ as a standard for DTA were used.

Results and discussion

The thermoanalytical examination does not allow to obtain the complete information on the course of thermal decomposition of cellulose. Degradation of the cellulose chain was found to proceed even at temperatures lower than 200 °C. However, it cannot be related to the formation of volatile products, since no measurable mass loss exists (Fig. 1) at temperatures ranging between 100—250 °C; a drop in the polymerization degree to a respective value may be recorded only [13].

The high-molecular cellulose under atmospheric pressure begins to be thermally actively decomposed at the temperature of 250 °C (Fig. 1). With temperatures of above 300 °C the decomposition of it starts in a relatively high speed (1.84 mg min^{-1} at 325 °C). A thermolyzed cellulose leaves a small portion of the carbonaceous residue (5 %) at 600 °C. A rapid depolymerization of the cellulose chain proceeds only at the temperature higher than 300 °C. For the reactions running at temperatures in the range 250—300 °C one may assume that the activation energy (~140 kJ mol^{-1}) calculated according to the method [14] corresponds to the dehydration reaction. The chemism of this kind of dehydration has not been explicitly clarified so far.

The main volatile, low-molecular product in this stage (up to 250 °C) of thermal degradation of cellulose is water [15]. The increase of unsaturated bonds found as a result of the elimination of water molecules may be confirmed by the infrared analysis, the enhancement of the amount of added bromine, and by the increase of the water content in a distillate [16, 17]. These fact suggest that, besides the thermooxidative destruction of amorphous regions, only the dehydration takes place in this stage.
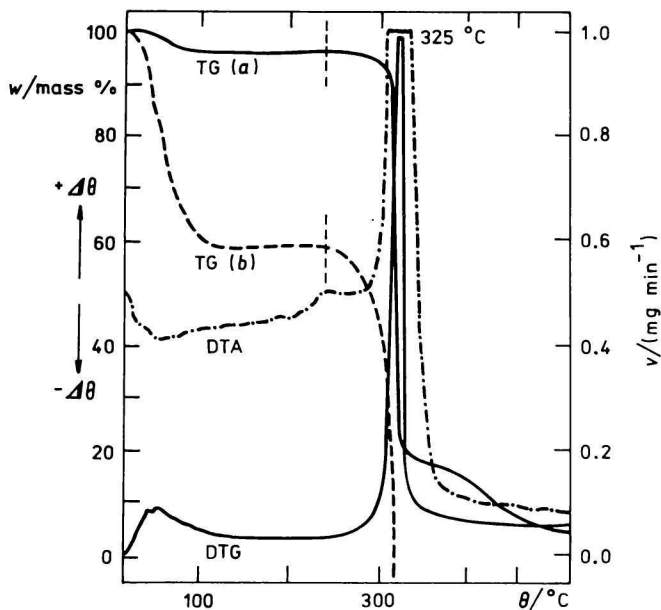
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Fig. 1. Thermograms of cellulose (10 °C min⁻¹, nitrogen, $m = 10$ mg).
TG (a) — 10 mg per scale.
TG (b) — 1 mg per scale; $\Delta w = 4.2$ mass %.

To clarify the chemism of the reactions which proceed during cellulose thermolysis in the temperature range 200—300 °C, the reaction mixture obtained in this way was subjected to the analysis. As indicated in Fig. 2, the following compounds were estimated *via* chromatographic separation and subsequent identification of separated products using mass spectrometry: *a*) 1,4:3,6-dianhydro-α-D-glucopyranose (0.22% out of the sample mass), *b*) ISTD, *c*) and *d*) 1,6-anhydrides of D-aldoses (2.0%), *e*) 3,6-anhydride of D-glucose (trace), *f*) D-glucose (0.06%).

From the results obtained (in the reaction mixture only two anhydrides with the molecular mass of 288.2 were determined) it can be concluded that 1,6-anhydrides are the essential primary products of cellulose thermolysis. In the reaction mixture, neither 1,2- nor 1,4-anhydrides of D-glucose were proved. The small amount of D-glucose *II* might appear due to the hydrolytic effect of water present in the sample, or to the chemical reaction of the released water. A major part of D-glucose formed could be dehydrated into 1,6-anhydrides under given conditions.

The new information obtained on examining the thermal degradation of cellulose is the determination of 3,6-anhydride of D-glucose *VIII*.

Based on the results achieved, the thermal decomposition of cellulose can be divided into two stages. At lower temperatures, mostly the dehydration reactions leading to the anhydrization of the cellulose chain occur. The main thermal
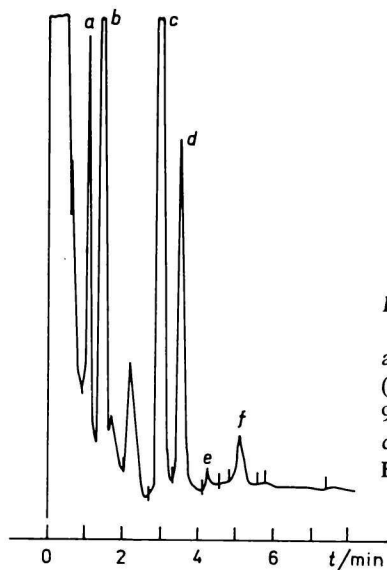
Fig. 2. Chromatogram of separated products from cellulose thermolysis.
a) 1,4:3,6-Dianhydride of D-glucose, EIMS data: m/e 186 (M), 143, 126, 114, 98, 69, CIMS data: m/e 187 (M + 1), 127, 99, 85, 69; b) ISTD — methyl-β-D-arabinopyranoside; c) and d) 1,6-anhydrides of D-aldoses; e) 3,6-anhydride of D-glucose, EIMS data: m/e 245, 229, 186, 169, 157, 112, CIMS data: m/e 333 (M + 1), 289, 273, 229, 169; f) D-glucose.

decomposition proceeding at temperature of above 300 °C is the depolymerization producing 1,6-anhydro-aldoses.

During the further step of the course of thermolysis, 3,6-anhydropolysaccharide may be cleaved by forming 3,6-anhydro-D-glucose *VIII*, or else 1,4:3,6-dianhydro-α-D-glucose *IX* (Scheme 2) may be originated. 1,4:3,6-Dianhydride *IX* was found in a relatively large quantity (the ratio of products *IX* and *II* is 3.67:1). On the other hand, the estimated amount of 3,6-anhydride *VIII* is substantially lower, which can be explained by the fact that the 3,6-anhydrization takes place chiefly in the polymeric chain; when the latter is cleaved, 1,4:3,6-dianhydride *IX* is formed.

It may be expected that the dehydration reactions presented above occur primarily in the amorphous regions of the cellulose. As was stated earlier [15, 17], the formation of double bonds was observed, however, the production of the anhydro cycles initiated by the reaction of the primary hydroxyl group (being the most reactive) as well as by the hydroxyl on C-3 lying in the *cis* position to C-6, cannot be excluded. In the amorphous regions where the (C-3—O—H ↔ O-5) intramolecular and the (C-6—O—H ↔ O-1 or C-6—O—H ↔ O-5) intermolecular bonds are not applied, the possibility of the C-3—O—C-6 anhydrization is real (Scheme 2). At higher temperatures, the indicated course of dehydration is possible also in the crystalline regions of the cellulose. However, here (at higher temperatures) the homolytic scission of glycosidic bonds is likely to take priority, and the radical structures developed *VI* (Scheme 1) undergo stabilization by forming the 1,6-anhydro cycle in accordance with the chemism proposed by
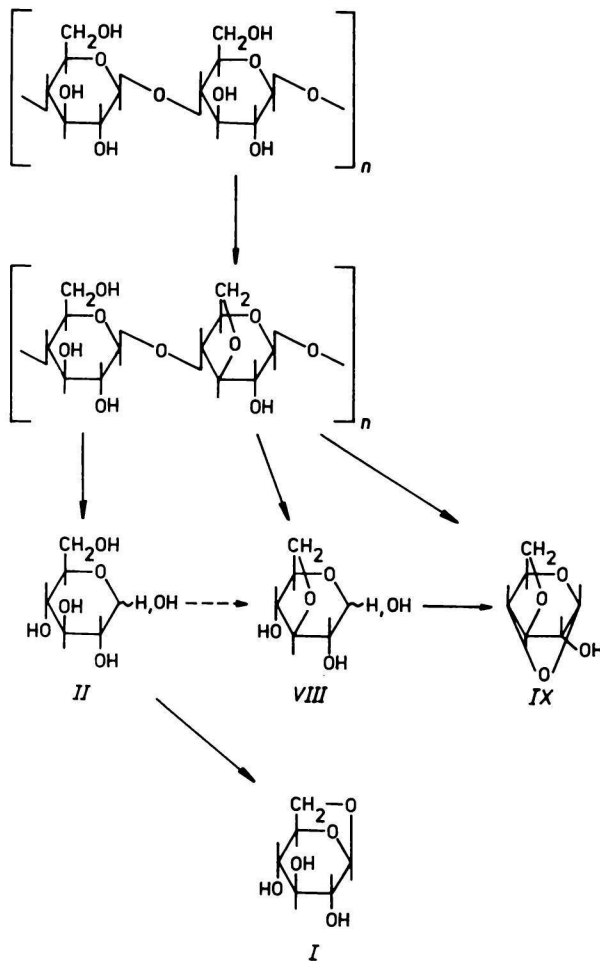
Scheme 2

Some dehydration reactions occurring during cellulose thermolysis

Kislitsyn [6]. In case that the 3,6-anhydro cycle was formed in the cellulosic chain, the rise of dianhydride *IX* after scission of the 1,4-β-D-glycosidic bonds might be observed, or the generated 3,6-anhydride *VIII* might continue in dehydrating into this product.

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