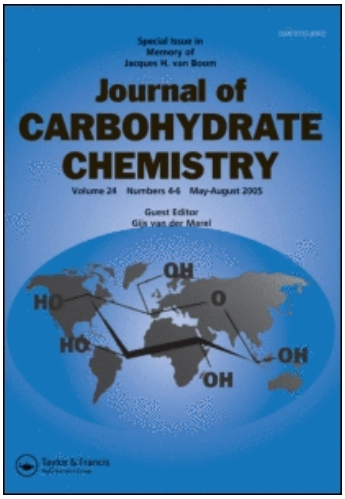

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Analytical Determination of 1,6-Anhydro-β-D-Glucopyranose and Kinetic Studies Under Hydrothermal Conditions

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ANALYTICAL DETERMINATION OF 1,6-ANHYDRO-ß-D-GLUCOPYRANOSE AND KINETIC STUDIES UNDER HYDROTHERMAL CONDITIONS

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ABSTRACT

1,6-Anhydro-ß-D-glucopyranose was identified for the first time in aqueous solutions obtained by hydrothermolysis of cellulosic matter. The identification and quantitative determination of the 1,6-anhydro-ß-D-glucopyranose, as well as of further degradation and conversion products, was accomplished by means of HPLC. For kinetic studies, 1,6-anhydro-ß-D-glucopyranose was degraded in aqueous solution under hydrothermal conditions in the range of 200-240°C. A kinetic model covering both formation and decomposition of 1,6-anhydro-ß-D-glucopyranose is proposed.

INTRODUCTION

The investigation of biomass as an energy source and a source of chemical raw materials has increased the attention paid to

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Dedicated to Professor O.Bobleter on the occasion of his 60th birthday.

Part of this work was presented at the XIIth International Carbohydrate Symposium, Utrecht, July 1-7, 1984.

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derivatives and degradation products of cellulose. In the course of enzymatic,[1,2] acid[3,4] or alkaline hydrolysis,[5,6] hydrothermolysis[7-10] or pyrolysis[11,12] studies of wood, straw or other cellulose-containing biomass, several compounds of considerable value occur which are difficult to produce by usual organic synthesis.

The hydrothermal degradation method of cellulosic matter was applied for the work described here. This process uses no chemicals other than pressurized water and dissolves hemicellulose and some of the lignin in the range 180-200 °C, cellulose at 260-290°C and the residual lignin at over 300 °C. This process yields oligosaccharides, monosaccharides, dihydroxyacetone, glyceraldehyde, methylglyoxal, hydroxymethylfurfural, furfural and phenylpropane derivatives.[13] Kinetic studies have been reported for the hydrothermal reaction when applied to disaccharides such as cellobiose, monosaccharides (e.g. glucose), the degradation of dihydroxyacetone, glyceraldehyde, methylglyoxal, and the formation of heterocyclic compounds (hydroxymethylfurfural and furfural).[9,10] It was shown that the hydrothermal process is not dependent on pH in the range 3-7 and alkaline, hydrothermal, and acidic hydrolysis are three individual processes with characteristic differences.[9] In this investigation it has been ascertained for the first time that 1,6-anhydro-ß-D-glucopyranose (levoglucosan) is formed during the hydrothermolysis of carbohydrates. This compound had been found mainly after pyrolysis of cellulosic materials. Shafizadeh[14] however showed that the qualitative and quantitative determinations of levoglucosan in such experiments were only possible with considerable analytical errors.

Investigations of 1,6-anhydro-ß-D-glucopyranose formation have been done mainly under acidic aqueous or under supercritical fluid conditions.[15,16] The present paper concentrates on improved analytical methods for 1,6-anhydro-ß-D-glucopyranose formed in aqueous solution under hydrothermal conditions, and a reaction kinetic study for the process.

1,6-Anhydro-ß-D-glucopyranose is of increasing interest in polymer chemistry due to the ability of this compound to form high-molecular weight stereoregular polysaccharides by cationic polymerization. High thermal stability polyurethanes and oligoethers of levoglucosan, used as epoxy-resin components,[17-19] have also been prepared.

RESULTS AND DISCUSSION

Characterization and isolation of 1,6-anhydro-ß-D-glucopyranose

By three different HPLC procedures, 1,6-anhydro- ß -D-glucopyranose and further degradation products were identified and determined quantitatively (with and without internal standard) after direct injection of the filtered hydrothermal degradation solutions.

In Fig.1 separations on different stationary HPLC phases are compared. The amino-bonded column material allows good separation of 1,6-anhydro-ß-D-glucopyranose from glucose and gluco-oligomers (d.p.= degree of polymerization 1 to 6).
In Fig.1(b) the Ca-loaded sulfonated ion exchanger (µ Spherogel, 7.5% Carbohydrate), shows clear separation of 1,6-anhydro-ß-D-glucopyranose from the monosaccharides glucose and fructose. The oligosaccharides up to a degree of polymerization of 4 are in a narrow range and further decomposition products, such as hydroxymethylfurfural and furfural, are eluted after approx. 28 and 32 minutes.

Using a column switching device, the gluco-oligomers can be determined up to d.p. 6 (Fig. 1c). To achieve this, a Ca-loaded ion exchange resin (HPX 42 C, Bio-RAD) and a Ca-loaded sulfonated polystyrene-divinylbenzene resin (8 µm, µ-Spherogel, 7.5% Carbohydrate cross linked) column were connected in series. With water as eluent, an HPLC analysis covering the gluco-oligomers up to d.p. 6 as well as the decomposition fragments took 48 min. Relatively high 1,6-anhydro-ß-D-glucopyranose concentrations (up

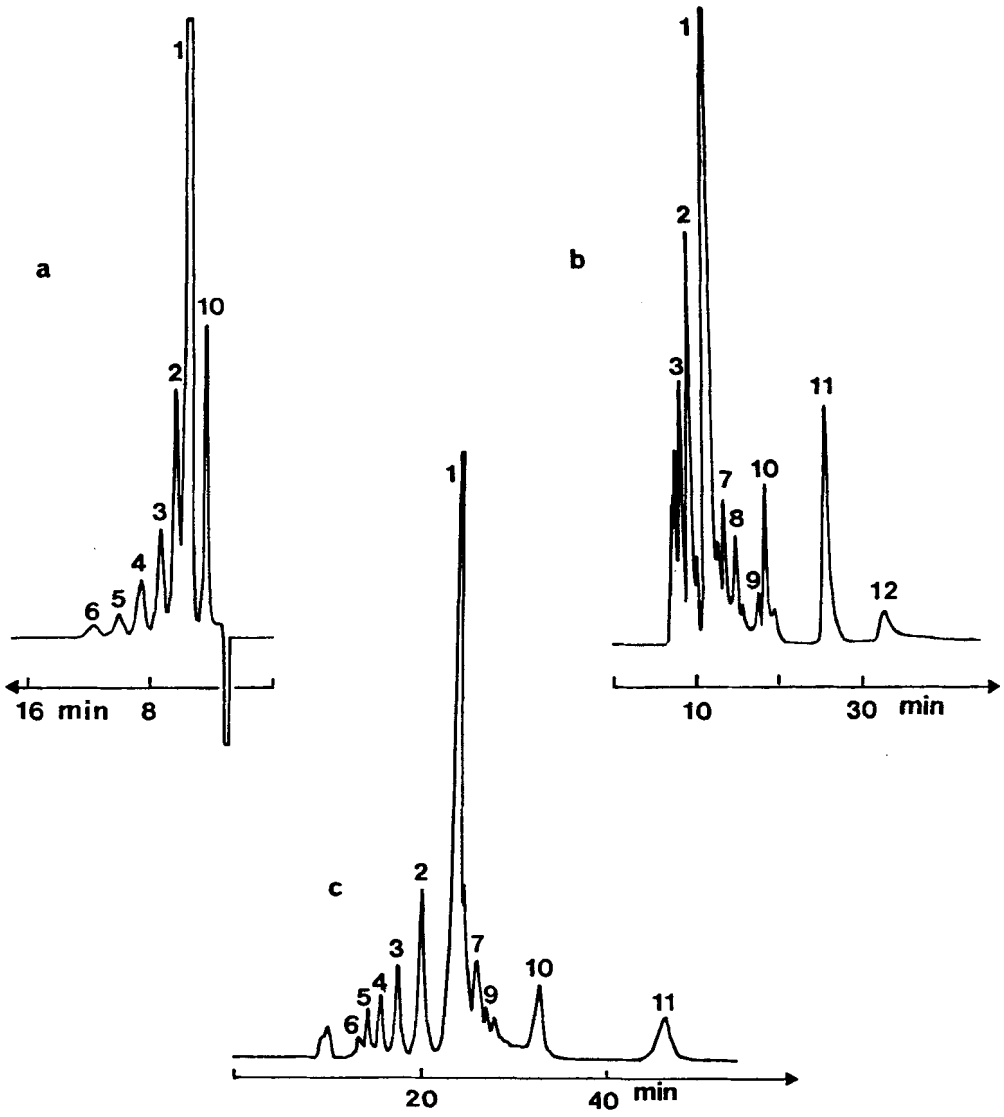

FIG.1 HPLC separations of 1,6-anhydro- ß -D-glucopyranose in hydrothermal degradation solutions; (a) by a amino-bonded phase column (T:23 °C; eluent: acetonitrile/water, 77/23; flow rate: 2mL/min; detector: r.i.). (b) by a Spherogel-Carbohydrate 7.5 % (85°C; eluent: water; flow rate: 0.6 mL/min; detector: r.i.). (c) by a series-connected system of an HPX 42 A and a Spherogel-Carbohydrate 7.5% (T:75°C; eluent: water; flow rate: 0.75 mL/min; detector: r.i.); 1..glucose, 2..cellobiose, 3-6...d.p. gluco-oligomers, 7..fructose, 8..glyceraldehyde, 9..dihydroxyacetone, 10..1,6-anhydro- ß -D-glucopyranose, 11..hydroxy-methylfurfural, 12..furfural

to 10 mg/mL) were obtained when wood or cotton were hydrothermally degraded and the solutions concentrated by reverse osmosis.

Kinetic studies

To obtain further information on the achievable yield of 1,6-anhydro-ß-D-glucopyranose (I) from biomass, kinetic studies involving hydrothermal degradation studies of this compound in the range 200-240°C (Fig.2-5), were undertaken. Among the reaction products, glucose (II) prevailed, with maximum yields of 40 %. Fructose (III), originating from a subsequent Lobry de Bruyn-van Ekenstein rearrangement, was found up to 8 % yield at 240°C, while mannose (IV) was below the detection limit of 0.1 mg/mL. In Fig. 6, hydroxymethylfurfural and furfural formation is shown; at 240° C the yields of these dehydration products equalled about 40 and 15% respectively.

The formation of 1,6-anhydro- ß -D-glucopyranose from cellulosic matter and its conversion pathways are outlined in Fig. 7.

The mathematical evaluation was based on the simplified reaction model of Fig. 8, from which the following equations were derived to describe the first order reactions:

$$\frac{d[I]}{dt} = -k_1[I] - k_7[I] + k_2[II] \quad (1)$$

$$\frac{d[II]}{dt} = -k_2[II] - k_3[II] + k_1[I] - k_5[II] + k_4[III] \quad (2)$$

$$\frac{d[III]}{dt} = -k_4[III] - k_6[III] + k_3[II] \quad (3)$$

After solving this equation system [20] the best fits are shown in Figs. 2 - 5 as full line curves. The rate constants k_1 to k_7 thus obtained are plotted versus 1/T in Fig. 9. The direct disintegration (k_1 and k_7) of 1,6-anhydro-ß-D-glucopyranose is relatively large; k_2 in the examined temperature range (200-240° C) small (Fig. 9).

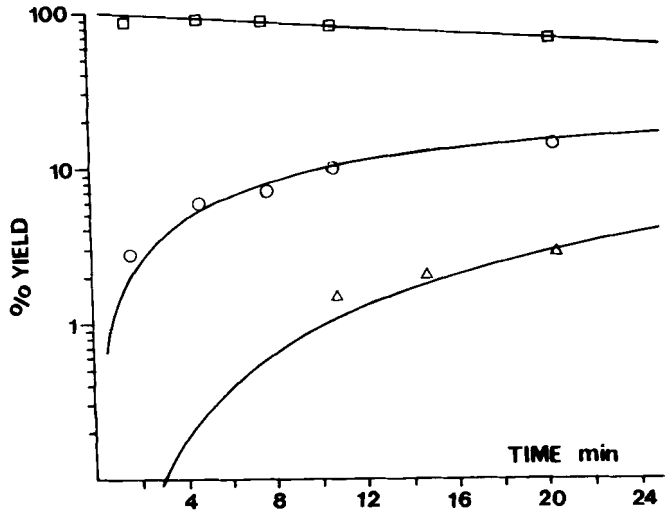

FIG.2 Hydrothermal treatment of 1,6-anhydro-ß -D-glucopyranose at 200°C, (□ 1.6.-anhydro-ß-D-glucopyranose, ○ glucose, △ fructose; plotted curves were calculated.)

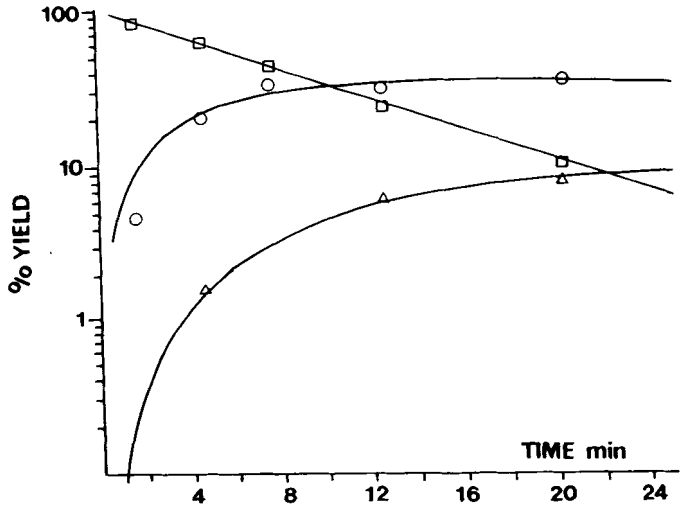

FIG.3 Hydrothermal treatment of 1,6-anhydro-ß -D-glucopyranose at 220°C, (■ 1.6.-anhydro-ß-D-glucopyranose, ○ glucose, △ fructose; plotted curves were calculated.)

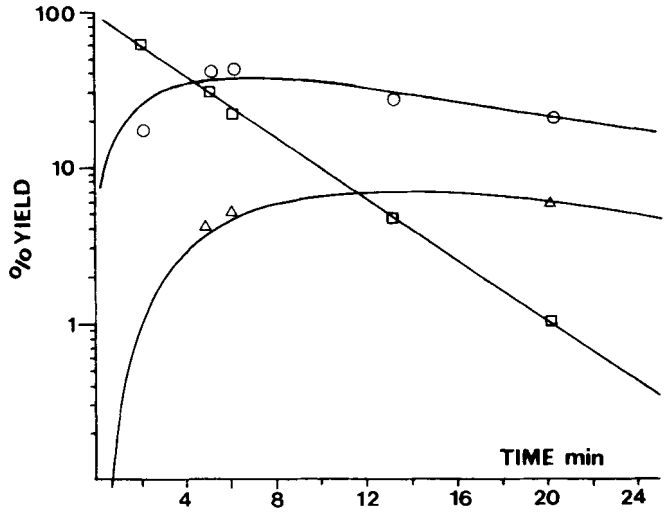

FIG.4 Hydrothermal treatment of 1,6-anhydro-β -D-glucopyranose at 230°C, (□ 1,6.-anhydro-β-D-glucopyranose, o glucose, △ fructose; plotted curves were calculated.)

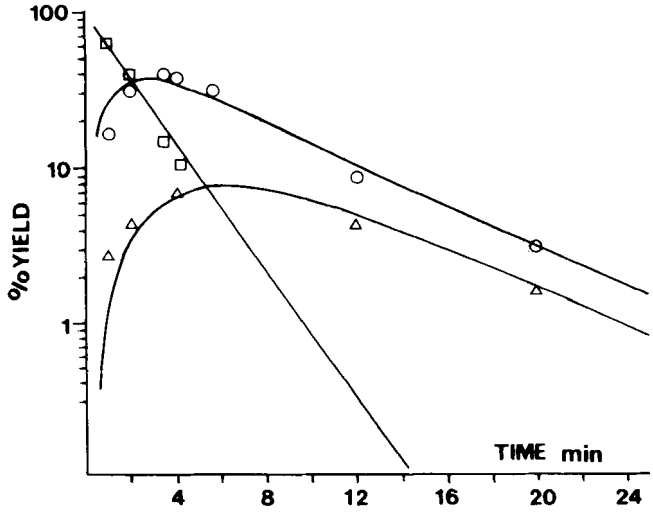

FIG.5 Hydrothermal treatment of 1,6-anhydro-β -D-glucopyranose at 240 ℃, (□ 1.6.-anhydro-β-D-glucopyranose, o glucose, △ fructose; plotted curves were calculated.)

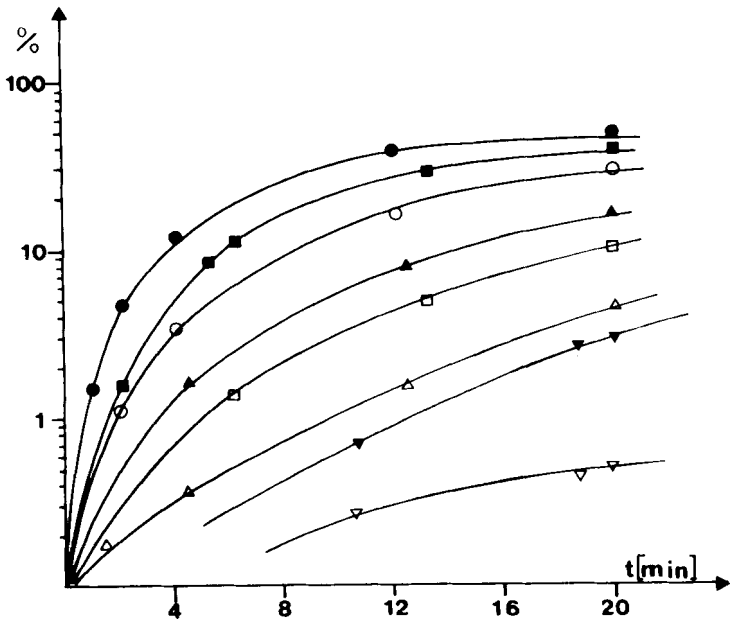

FIG.6 Hydroxymethylfurfural and furfural formation during the hydrothermal treatment of 1,6-anhydro-ß-D-glucopyranose in the range 200-240°C (hydroxymethylfurfural: ● 240°, ■ 230°, ▲ 220°, ▼ 200° furfural: ○ 240°, □ 230°, △ 220°, ▽ 200°C)

On the assumption that k_2 can be neglected, equation (1) becomes:

$$\frac{d[I]}{dt} = -k_1[I] - k_7[I] = -(k_1 + k_7)[I] \qquad (4)$$

where

$$k_1 + k_7 = k_{exp} \qquad (5)$$

In Table 1 the experimental rate constants (k_{exp}) are set against the computed ones (k_1+k_7). As they are in very good agreement with each other, Fig.8, though simplified, is obviously substantially correct.

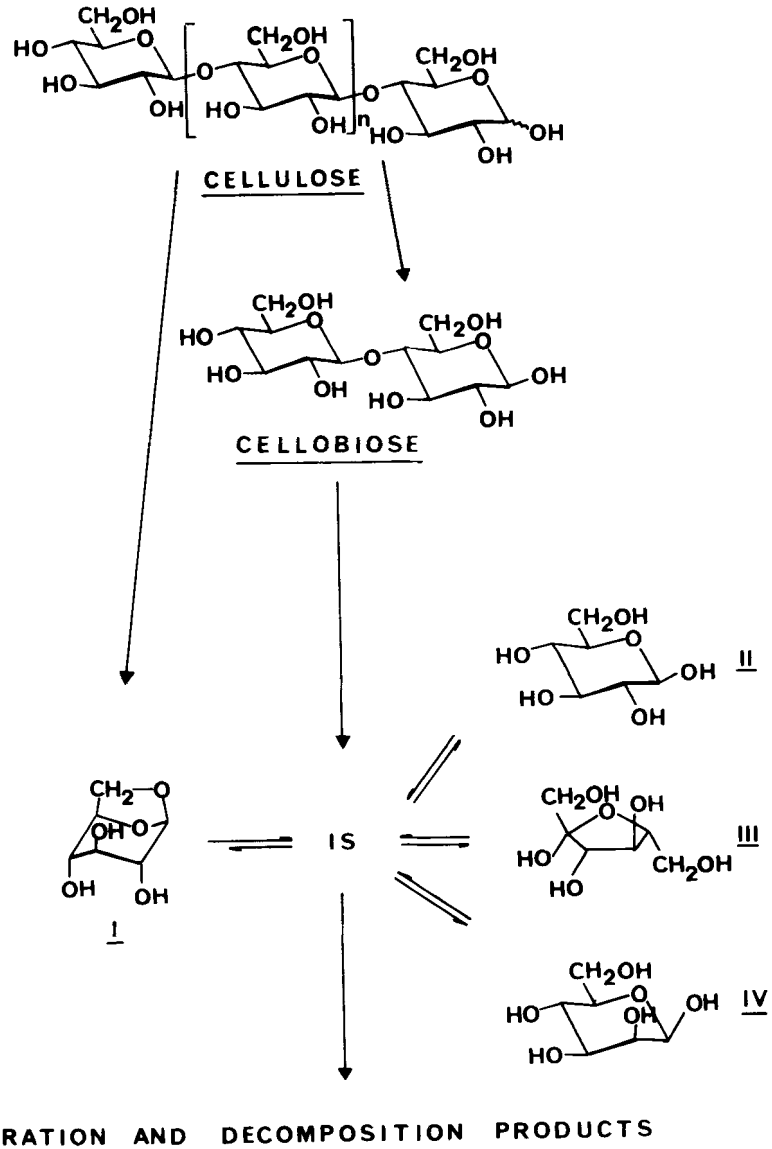

FIG. 7
Formation and conversion pathways of 1,6-anhydro-ß-D-glucopyranose (I) in the hydrothermal degradation of cellulose (IS=intermediate state, II=glucose, III=fructose, IV=mannose).

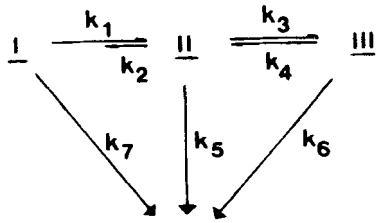

FIG. 8
Simplified reaction pathway for the kinetic study of the hydrothermal treatment of 1,6-anhydro-ß-D-glucopyranose (I). Glucose=II and fructose=III.

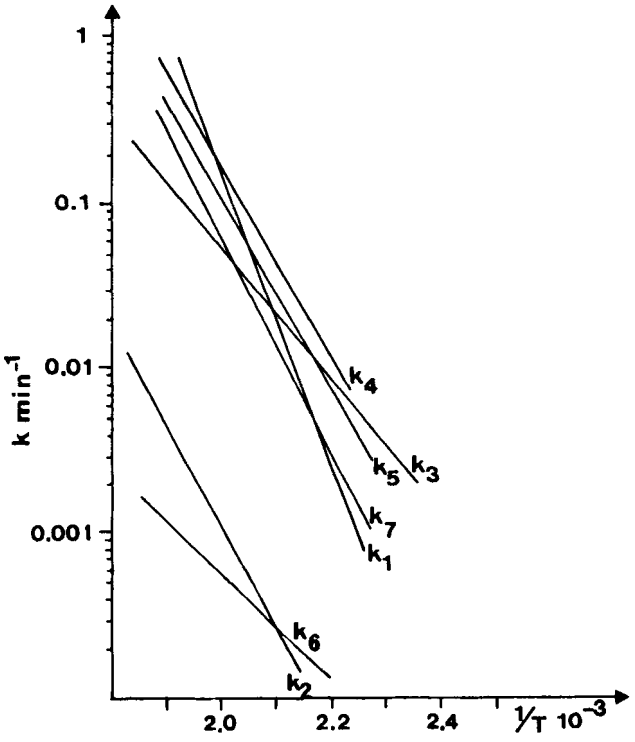

FIG.9 Arrhenius plots for the hydrothermolysis of 1,6-anhydro-ß-D-glucopyranose in the range 200-240 °C.

TABLE 1

Comparison of Experimental (kexp) and Calculated (k_1+k_7) Rate Constants of 1,6-anhydro-ß-D-glucopyranose

T (°C)	$k_{exp}\left[min^{-1}\right]$	$k_1+k_7\left[min^{-1}\right]$
200	0.019	0.020
220	0.109	0.110
230	0.230	0.230
240	0.480	0.480

1,6-anhydro-ß-D-glucofuranose could not be found up to our detection limit (0.01 mg/mL).

According to the Arrhenius equation an activation energy of 154 kJ/mol was computed for the hydrothermal disintegration reaction (k_{exp}) of 1,6-anhydro-ß-D-glucopyranose.

When the same hydrothermal reaction conditions were applied to degrade cellobiose or glucose at 240 °C 1,6-anhydro-ß-D-glucopyranose was formed in trace amounts only.

At this temperature the following order of stability towards hydrothermolysis (Fig.9) is observed:

cellulose > glucose > 1,6-anhydro-ß-D-glucopyranose > cellobiose

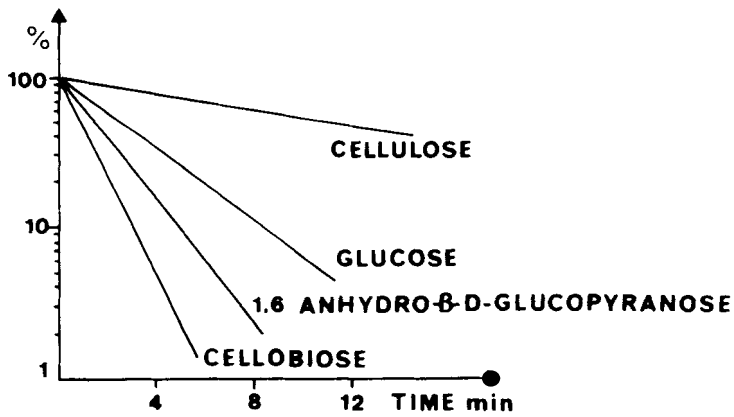

FIG.10 Stability of 1,6-anhydro-ß-D-glucopyranose as compared to cellulose, cellobiose and glucose [8] under hydrothermal reaction conditions (T:240°C).

Degradation of cellobiose and glucose (10 mg/mL each) at 280 °C (the temperature range suitable for cellulose hydrothermolysis) resulted in the formation of 0.23 and 0.60 mg/mL 1,6-anhydro-ß-D-glucopyranose respectively after one minute, so that the reaction pathway of Fig. 7, which states that 1,6-anhydro-ß-D-glucopyranose is also formed via cellobiose and glucose, is confirmed for hydrothermal reaction conditions. The alternative of a direct cleavage from cellulose end groups, as has been reported for pyrolysis,[14] can also be assumed in hydrothermal degradation.

1,6-anhydro-ß-D-glucopyranose can thus be obtained if it is removed quickly from the reaction zone in order to prevent it from being transformed into the more stable glucose.

Investigations using different celluloses are currently underway with the aim of achieving a preparative scale recovery of this product from the hydrothermal reaction media.

EXPERIMENTAL

Chromatographic methods

For analyses of hydrothermal solutions and separations of oligosaccharides, monosaccharides and degradation products high-performance liquid chromatography (HPLC) [13,21,22] was used, the columns being:

a) amino-bonded phase, Macherey & Nagel (eluent:acetonitrile/water, 77/23)
b) µ-Spherogel-Carbohydrate 7.5, Beckman,Inc., and
c) HPX 42 A, Bio-RAD, (eluent: HPLC grade water).

All compounds were detected by a differential refractive-index (r.i.) monitor (Altex Inc.).

The analysis of oligomeric sugars, monosaccharides, 1,6-anhydro-ß-D-glucopyranose and further degradation products in only one separation step was done by using a series connected

system of a Ca-loaded ion-exchange column (μ-Spherogel-Carbohydrate, Beckman,Inc., USA) and a Ag-loaded ion-exchange column (HPX 42A, Bio-RAD, CA,USA) and water as mobile phase.[23] The chromatographic conditions for each column system are given in the Figure 1 caption.

Sample preparation

Cellulose-containing material e.g. poplar wood without bark as used for the analytical examinations in Fig.1, was hydrothermally degraded at 290 °C in a dynamic apparatus.[8,24]

For kinetic studies the 1,6-anhydro-ß-D-glucopyranose (Sigma, U.S.A) solution (4mg/mL) was put into stainless steel autoclaves (180x 8 mm i.d.), and kept in an oil bath at 200-240 °C. After a predetermined period of time, the reaction was stopped by immersing the autoclave in an ice bath. The heating-up period, which was deducted from the total reaction time, was determined using a thermocouple placed inside the autoclave and was found to be 90 s at 240 °C. Some kinetic experiments were carried out in duplicate and the deviations were less than 5%.

Kinetic plots

For mathematical studies of the first order reaction equation system a Textronics computer system was used.

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