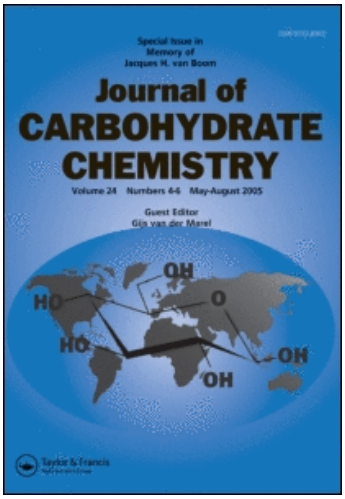

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HYDROLYSIS OF CELLOBIOSE IN DILUTE SULFURIC ACID AND UNDER HYDROTHERMAL CONDITIONS

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ABSTRACT

The sulfuric acid hydrolysis rate of cellobiose between pH 2 and 3 is directly proportional to the acid concentration. In good agreement with other authors, an activation energy of 133 kJ/Mol was found under these acidic conditions. The relation of the reaction rate constants for the glucose formation and glucose degradation (k_1/k_2) shows, in contrast to the hydrolysis of cellulose, little dependence on the temperature. Hydroxymethylfurfural, and to a lesser extent furfural, are glucose degradation products, which are also consumed but at a lower reaction rate than glucose.
At pH values between 3 and 4.7 (pure water) strong deviations of the hydrolysis rates were observed. The formation of organic acids decreases the pH but has no influence on the reaction rate. This fact indicates that hydrothermolysis follows a reaction mechanism different from that of acidic hydrolysis.

INTRODUCTION

Renewed interest in acid hydrolysis of carbohydrates arose in the western world after the "energy crisis" in 1973. GRETHLEIN [1]

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and SAEMAN [2] indicated that higher glucose yields can be obtained when cellulosic material is acidically hydrolysed at elevated temperatures. Over 60 % saccharification occurred by treating cellulose at 240 °C in a solution with 1 % H_2SO_4. However, the reaction period for reaching these optimum values, 10 to 20 seconds, was so short that the transformation of this process into technical dimensions was not realisable. In addition, the loss of 40 % of the carbohydrate raw material is too large for economical utilization.

Due to our extended work on hydrothermolysis of plant biomass, [3-6] we were especially interested in the region where acidic hydrolysis turns into hydrothermolysis. This region can best be analysed at relatively high temperatures and at low acid concentrations. For comparison, pure hydrothermal conditions also had to be investigated, whereby only water is added to the substrate. During this reaction small amounts of organic acids (e.g. acetic and formic acid) are formed, so that the reaction solution may reach pH 3 after a prolonged time without any addition of mineral acids. Cellobiose was used as the model compound.

A reasonable amount of literature [7-14] on mineral acid hydrolysis of this disaccharide and similar substances is available and therefore allows a comparison of the experiments which were carried out with sulfuric acid in this work.

RESULTS AND DISCUSSION

In the initial experiments the temperature dependence of the hydrolysis was studied, using 0.01 N sulfuric acid. The solutions

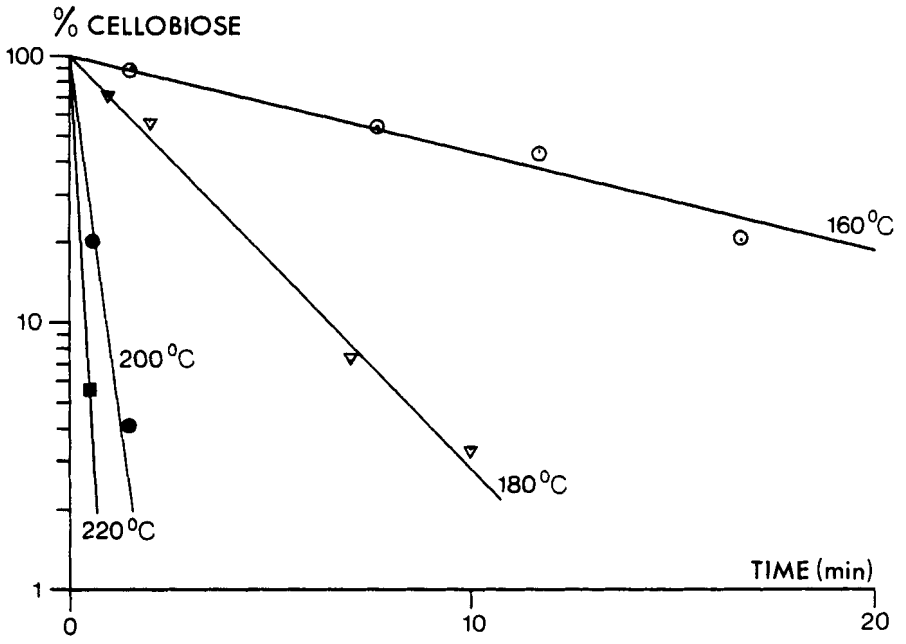

FIG.1 Acid hydrolysis of cellobiose; percentage of initial amount of cellobiose (10 mg/ml in 0.01 N sulfuric acid) as a function of time and temperature.

in the autoclaves contained 1% cellobiose. Fig. 1 shows that cellobiose hydrolysis follows first order kinetics.

The evaluation of the ARRHENIUS-diagram (Fig. 2) results in an activation energy E_a of

$$E_a = 133 \text{ kJ/Mol} \quad (31.7 \text{ kcal/Mol})$$

The corresponding frequency factor A is

$$A = 1.38 \times 10^{13} \text{ s}^{-1}.$$

These values are in good agreement with the results obtained by LINDBERG [10] (E_a = 138 kJ/Mol), who investigated the hydrolysis of cellobiose with 1 M sulfuric acid between 70 and 90 °C. It can be assumed that the formation and consumption of glucose (G) also

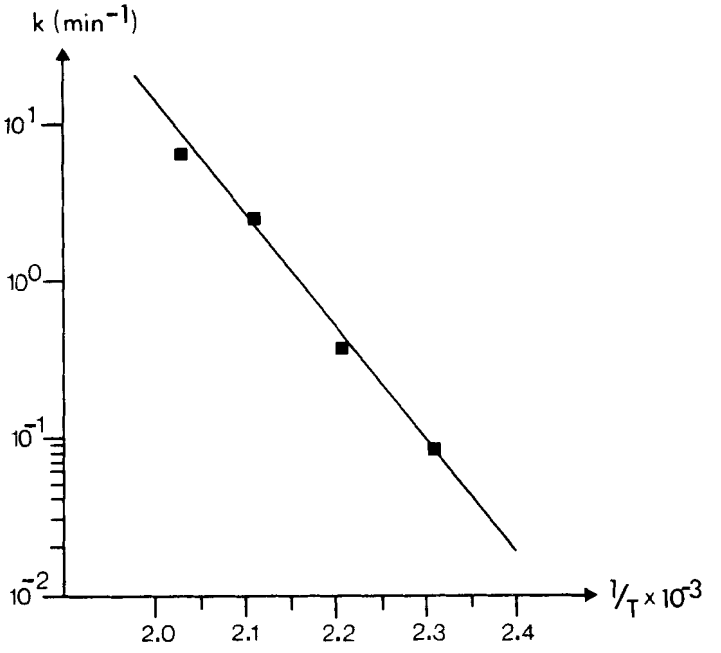

FIG.2 Arrhenius-plot of the acidic hydrolysis of cellobiose in 0.01 N sulfuric acid.

follow first order reactions:

$$CB \xrightarrow{k_1} G \xrightarrow{k_2} \text{degradation products} \qquad (1)$$

Under the conditions employed, at the beginning of the experiment only cellobiose (CB_o) but no glucose ($G_o = 0$ at $t = 0$) is in the solution. The following equation for the glucose build up as a function of the time t can be applied:

$$(G)_t = (C)_o \mu \frac{k_1}{k_1 - k_2} (e^{-k_1 t} - e^{-k_2 t}) + (G)_o e^{-k_2 t} \qquad (2)$$

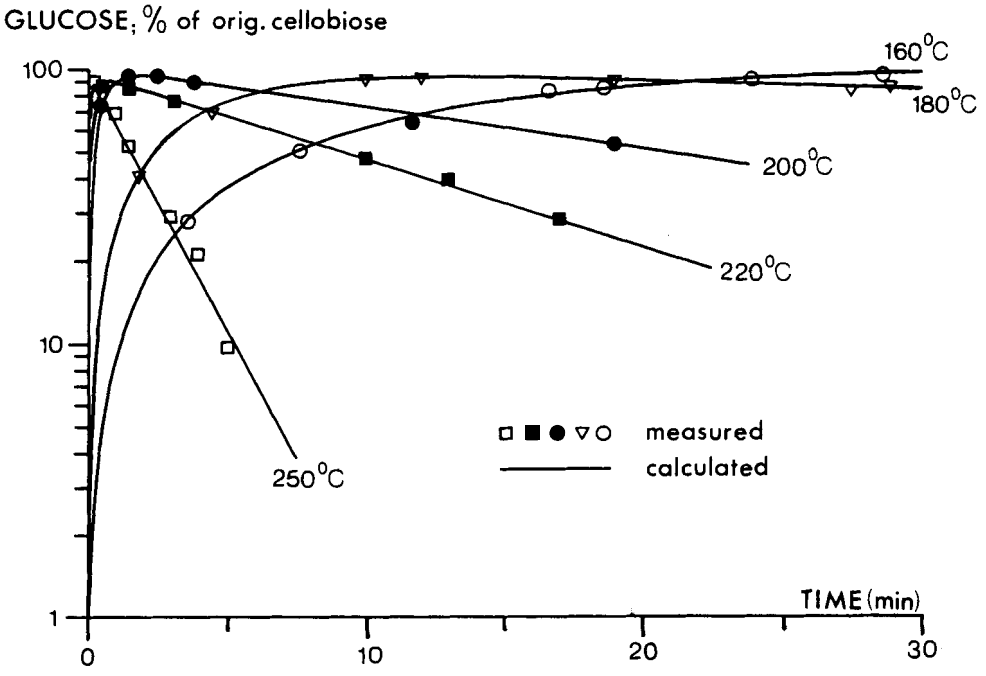

FIG.3 Formation of glucose in percentage of the original cellobiose (10 mg/ml in 0.01 N sulfuric acid) as a function of time and temperature (°C); the dots in the graph are measured values, the curves (solid lines) are calculated.

The symbol μ is the stoichiometric factor for the conversion of cellobiose to glucose.

In Fig. 3 the determined glucose is given as a function of time and temperature. The points are the results obtained by HPLC measurements and the plotted curves calculated with equation (2). It is obvious that the maxima of these curves are close to 100 %. This is to be expected when k_1 is much larger than k_2. Table 1 gives these reaction rate constants and their ratio for several temperatures. The k_1 values were evaluated from Fig. 1 and those

TABLE 1

Rate constants for the hydrolysis of cellobiose k_1 , the glucose decomposition k_2 and the ratio k_1/k_2 as a function of the reaction temperature using 0.01 N sulfuric acid

Reaction temperature (°C)	k_1 (min^{-1})	k_2 (min^{-1})	k_1/k_2
160	0.085	9.888×10^{-4}	85.96
180	0.356	4.427×10^{-3}	80.42
200	2.629	3.200×10^{-2}	82.16
220	6.393	7.415×10^{-2}	86.39

of k_2 resulted partially from Fig. 2 and were partially calculated using equation (2). The k_1/k_2 ratios stay within relatively narrow limits. The maxima in Fig. 3, however, indicate a slight decrease with increasing temperature. In contrast to this, SAEMAN [2] found a remarkable increase of the k_1/k_2 ratios when cellulose was hydrolyzed directly to glucose and hydrolysis rates were measured with increasing temperature. This divergence of behaviour is, however, not too surprising because acidic hydrolysis of cellulose is a heterogeneous reaction.

At the same time, it was of interest to investigate the degradation products which are formed from glucose. One of the major compounds is α-hydroxymethylfurfural (HMF). To a lesser extent, approximately one order of magnitude, furfural also occurs during acid treatment of these carbohydrates. In Fig. 4 the HMF and furfural amounts are plotted for different temperatures. By

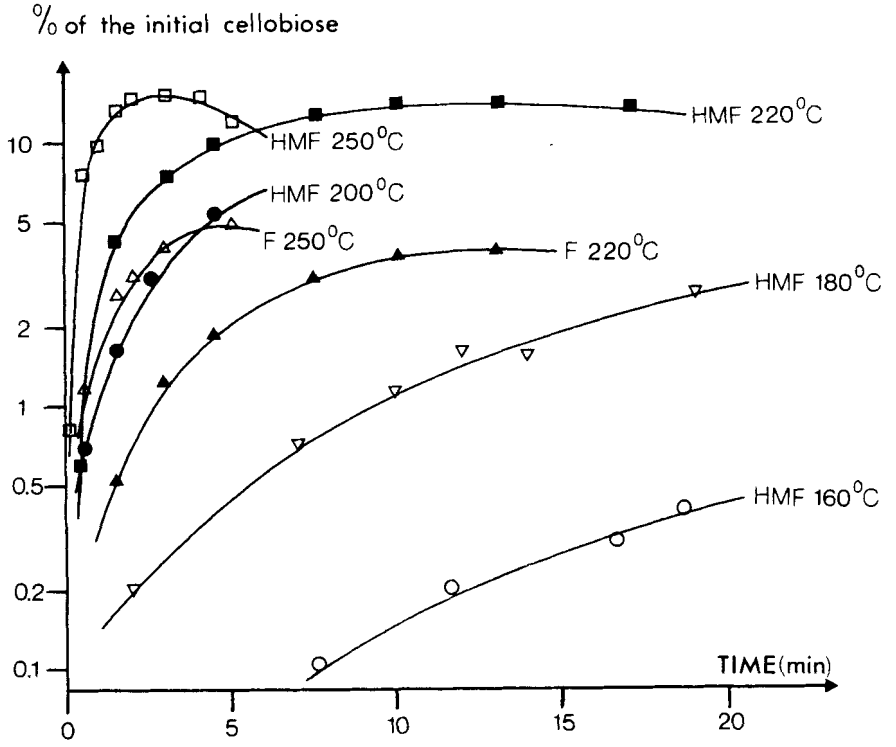

FIG.4 Formation of α-hydroxymethylfurfural (HMF) and furfural (F) as a percentage of the initial cellobiose (10 mg/ml in 0.01 N sulfuric acid) and as a function of temperature (°C) and time.

comparing Fig. 4 with Fig. 3, it can be shown that the stability of HMF is not decisively higher than that of glucose.

For the evaluation of the influence of acid concentration on the rate constants, a temperature of 200° C was chosen. In Fig. 5 the hydrolysis reaction of cellobiose is depicted with acid concentrations between 0.01 and 0.00 N H_2SO_4. Fig. 6 shows the formation of glucose during these reactions. The dependence of the acid concentration on the reaction rate of cellobiose can best be shown when the latter is plotted against the pH of the solution

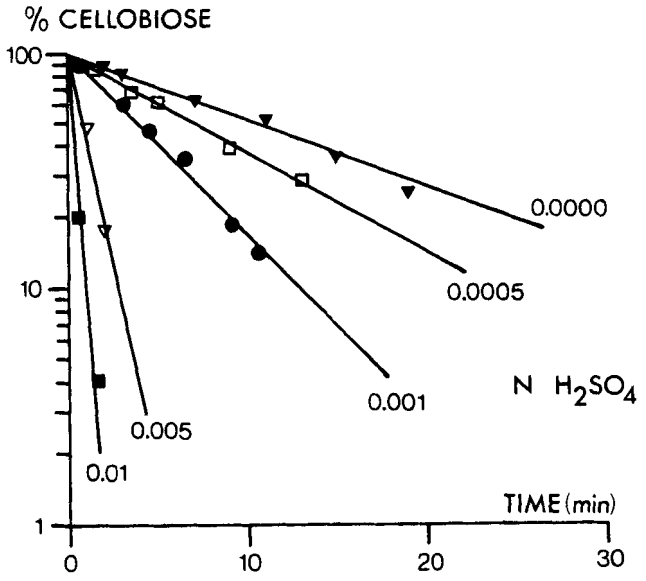

FIG.5 Acid hydrolysis and hydrothermolysis of cellobiose; percentage of initial cellobiose (10 mg/ml) as a function of time and acid concentration (N H_2SO_4); the reaction temperature was 200 °C.

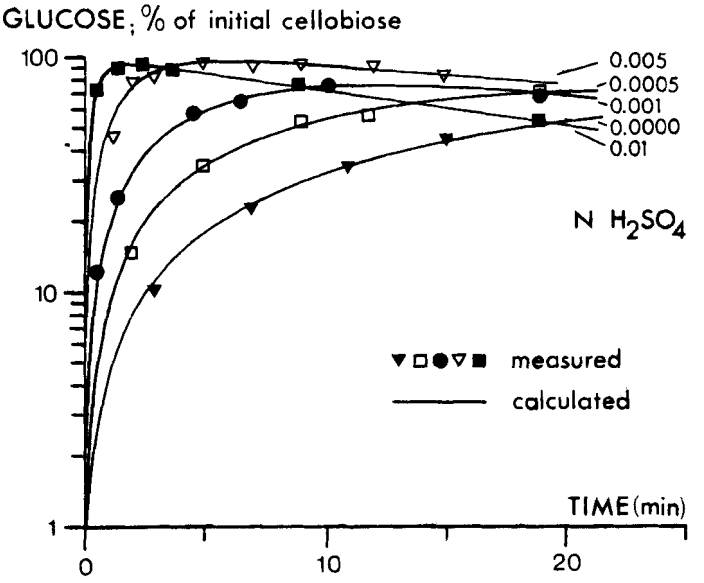

FIG.6 Formation of glucose as a percentage of initial amount of cellobiose (10 mg/ml) and as a function of time and acid concentration (N H_2SO_4) at a reaction temperature of 200 °C; the dots are measured values, the curves (solid lines) are calculated.

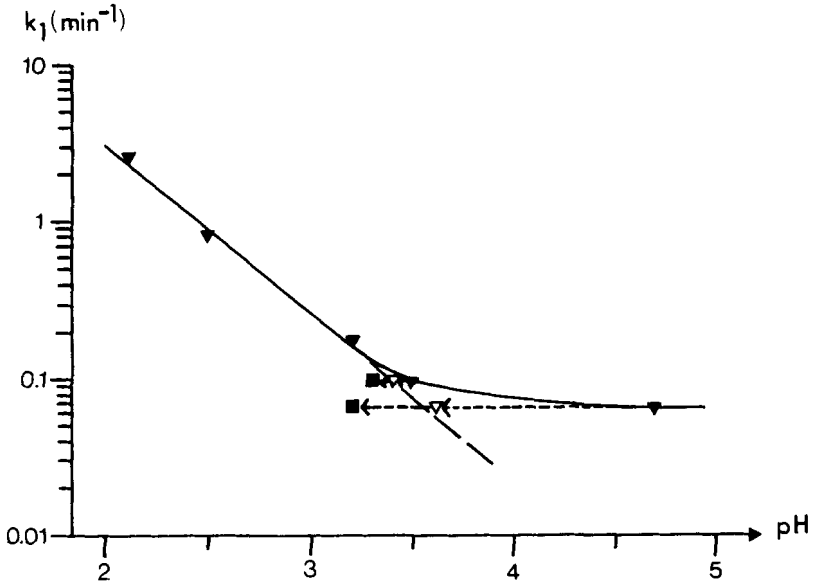

FIG.7 ZUCKER-HAMMETT-plot for the acid hydrolysis and hydrothermolysis of cellobiose at 200 °C; ▽ = pH after 50 % and ■ = pH after 90 % of cellobiose consumption.

(Fig. 7). Between pH 2 and 3 the expected slope with an approximate value of unity is obtained. This indicates an A-1 mechanism for the hydrolysis reaction. [11,14]

Within the pH range 2-3 the pH remains constant over the whole reaction period (see Table 2). However, between pH 3.2 and 4.7 the reaction behaviour clearly changes. Despite the fact that the reaction follows first order kinetics, the pH changes drastically during the reaction (Table 2). In this region the pH changes between 3 and 4.7 have obviously no influence on the reaction rate. This finding suggests that hydrothermolysis (occuring at a pH between 3.2 and 7) follows a distinctly different reaction mechanism than acid hydrolysis. In this connection the experiments

TABLE 2

Hammett acidity function H_o for dilute sulfuric acids [19] and pH values of cellobiose solutions in dilute sulfuric acids

Experiment No	Normality	H_o	pH measured		
			conversion rate of cellobiose		
			0 %	50 %	90 %
1	0.01	+ 2.06	2.1	2.1	2.1
2	0.005	+ 2.33	2.5	2.5	2.5
3	0.001	+ 3.02	3.2	3.2	3.2
4	0.0005	+ 3.4 ± 0.1	3.5	3.4	3.3
5	0.000	-	4.7	3.6	3.2

with an initial pH of 3.5 and 4.7 are of special interest. After a 50 % cellobiose consumption the pH decreased to such an extent that the experimental points fit into the linear part of the ZUCKER-HAMMETT-plot (Fig. 7). In the region of 50 to 90 % cellobiose transformation, the pH is already lowered so much that markedly higher reaction rates should occur. It was surprising , in contrast to earlier kinetic considerations, [21] that the first order reaction rate remained constant within experimental errors, in spite of this strong fall in pH. Also other results from our group indicate [15-17] that the hydrolysis of carbohydrates in the region of pH 3.2 to 7 is not governed by acid catalysis.

EXPERIMENTAL

Materials

Solutions containing 10 g beta-cellobiose (puriss.p.a. Fluka, Buchs, Switzerland) per litre were prepared. For purposes of comparison, certain solutions did not contain acid, whereas others were 0.01, 0.005, 0.001 and 0.0005 normal in sulfuric acid.

Hydrolysis

Small stainless steel autoclaves (188 x 8 mm I.D.) containing 4 cm^3 of the cellobiose solution were kept in an oil bath at temperatures between 160 and 250° C for a predetermined reaction period. The heating-up period was evaluated from a recorder diagram which registered the temperature in one of the autoclaves by means of a thermocouple. The maximum heating-up time was approximately 60 seconds. Immediately after the reaction the autoclaves were cooled in an ice bath.

Analysis

The carbohydrates were analyzed by HPLC, [18] using an amino-bonded phase column with acetonitrile-water (70:30 v/v) as eluent and a RI detector. The furfural decomposition products were measured on a RP-C_{18} column with methanol-water (70:30 v/v) as elution medium and an UV detector at 254 nm. [19]

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