Thermochimica Acta, 123 (1988) 255–261
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

DIFFERENTIAL SCANNING CALORIMETRY IN THE SACCHARIFICATION OF CELLULOSE *

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(Received 16 March 1987)

ABSTRACT

The kinetics of the acid hydrolysis of cellulosic materials were studied by differential scanning calorimetry, particularly regarding the dependence of the kinetic parameters and the enthalpy change on the crystallinity and moisture content of the cellulose samples.

The rate constant of the acid hydrolytic reaction increased with decreasing degree of crystallinity and increased with increasing moisture content of the sample. The heat of reaction increased with decreasing degree of crystallinity and with increasing initial moisture content of the sample.

INTRODUCTION

The acid hydrolysis of cellulosic materials has long been considered as a commercially feasible process for obtaining sugar solutions which are suitable for the production of industrial grade ethanol by fermentation.

We have reported that differential scanning calorimetry (DSC) is useful for estimating the yield of D-glucose formed in the acid saccharification of cellulose [1]. This paper describes the dependence of the kinetic parameters and the enthalpy change for the acid decomposition of cellulose on the crystallinity and the moisture content of the cellulose samples.

EXPERIMENTAL

Apparatus

The same apparatus as that described in our previous paper [1] was used. It consisted of a Perkin-Elmer DSC-C2 unit and a data station furnished with an optimal kinetic program. The sample holder, also described in our

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* Paper presented at the Sino-Japanese Joint Symposium on Calorimetry and Thermal Analysis, 5–7 November 1986, Hangzhou, People's Republic of China.

0040-6031/88/$03.50

previous paper, was of a type resistant to both high pressure and attack by acids.

Conditions

In all experiments, the initial acid concentration for the hydrolysis reaction was set at 3.8 wt.%, the weight ratio of sample to acid was set at about 1/4 and the scanning rate at 5 K min^{-1}.

Sampling

The samples used are specified as follows: cellulose powder B of Toyo Roshi Kaisha, 200-300 mesh, absolutely dry (COT); regenerated cellulose obtained by treating the above powder with a Schweizer solution, absolutely dry (RCO); powdery cellulose obtained by finely cutting filter paper, No. 5C of Toyo Roshi Kaisha, absolutely dry (FPI); powdery cellulose, same as FPI except that the moisture content is 2 wt.% (FPII); powdery celluose, same as FPI except that the moisture content is 9 wt.% (FPIII).

The moisture content was determined by weighing samples which had been dried after being kept in a desiccator at a definite humidity for a week.

RESULTS AND DISCUSSION

Figure 1 shows an example of the superimposition of DSC traces of COT and RCO. Kinetic parameters obtained using the kinetic program [1] from

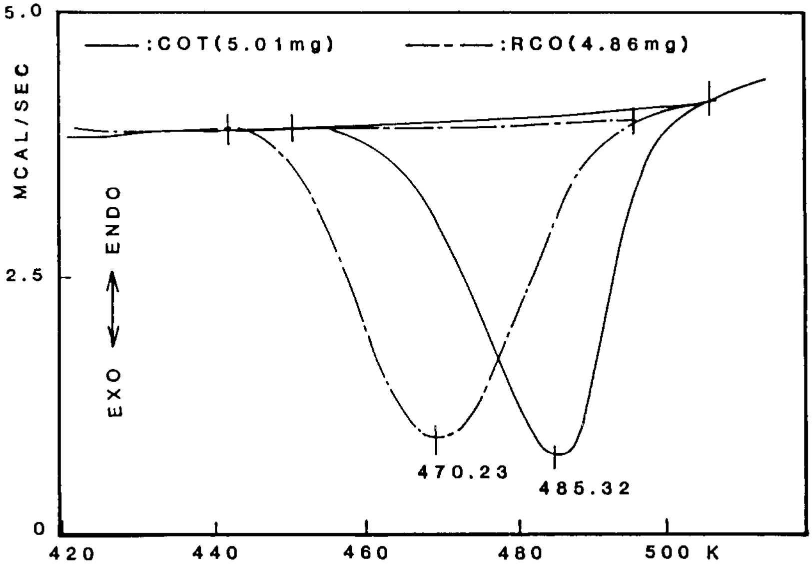

Fig. 1. DSC curves of cellulosic materials with sulphuric acid (3.8%) of several times the sample weight enclosed in a pressure-resistant gold-plated capsule.

TABLE 1

Kinetic data from DSC results (averaged values)

Sample	T_p [a] (K)	$-\Delta H$ [b] (kJ monomer^{-1})	ln K_0 [c] (s^{-1})	E_A [c] (kJ monomer^{-1})	n [c]
COT	495.4	104.6	58.71	249.5	1.0
RCO	473.6	122.6	53.25	223.3	1.4
FPI [d]	523.6	93.9	–	–	–
FPII	489.4	114.2	52.59	227.4	1.1
FPIII	480.9	141.0	37.451	166.1	1.0

[a] T_p, peak temperature of DSC curve.

[b] ΔH, enthalpy change.

[c] K_0, E_A and n are the frequency factor, activation energy and degree of reaction respectively in the Arrhenius equation.

[d] Calculation failure by taking the exotherm as a positive input in the ordinate.

TABLE 2

Calculated rate constants

Sample	$k_{443.16\ \mathrm{K}}$ (min^{-1})	$k_{453.16\ \mathrm{K}}$ (min^{-1})
COT	0.00167	0.00757
RCO	0.0107	0.0357
FPII	0.0015	0.0063
FPIII	0.0115	0.036

the DSC traces are given in Table 1. Table 2 gives the rate constants at definite temperatures, calculated using the parameters and assuming the Arrhenius equation. In order to speculate on the influence of the crystallinity and the moisture content on the rate constant, the ratios taken were those shown in Table 3.

Influence of crystallinity

Figure 2 shows X-ray diffraction patterns of COT and RCO. The pattern of COT is similar to that of linen or cotton, while the pattern of RCO is

TABLE 3

Ratios of rate constants

Sample rate constants	Ratio of rate constants	
	443.16 K	453.16 K
$k_{\mathrm{RCO}}/k_{\mathrm{COT}}$	6.4	4.7
$k_{\mathrm{FPIII}}/k_{\mathrm{FPII}}$	7.6	5.7

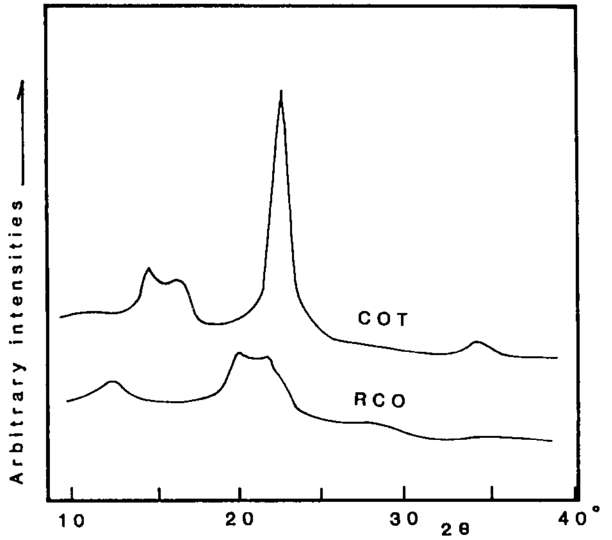

Fig. 2. X-ray powder diffraction patterns of COT and RCO.

similar to that of cupra rayon or viscous rayon [2]. The degree of crystallinity calculated by the integral intensity method [3] was 56% for COT and 41% for RCO.

We see from Table 3 that the rate constant for RCO is several times of that for COT at both temperatures (443.16 and 453.16 K). From this result, it is inferred that the rate constant increases with decreasing degree of crystallinity.

Influence of initial moisture content

From Table 3 it is seen that the rate constant for FPIII is several times as great as that for FPII. This suggests that the rate constant increases with increasing moisture content of the cellulosic samples.

Three samples of filter paper differing only in the moisture content (0%, 13%, 17%) were hydrolysed with 3.8 wt.% sulphuric acid (an amount several times the weight of the sample) in a miniature autoclave at 450 K for 20 min. Figure 3 shows the results of the liquid chromatography of the resulting solutions.

The peaks of refractive index S, F, A and G were found to be those of sulphuric acid, formic acid, acetic acid and D-glucose respectively. Peak D does not appear in refractive index but in UV absorption. It is presumed that F, A and D may be assigned to the decomposition products of D-glucose which is the intermediate product of the acid hydrolysis of cellulose. Table 4 gives the ratio of the peak area of each component to that of sulphuric acid. In the case of 0% moisture content, the value of G is the

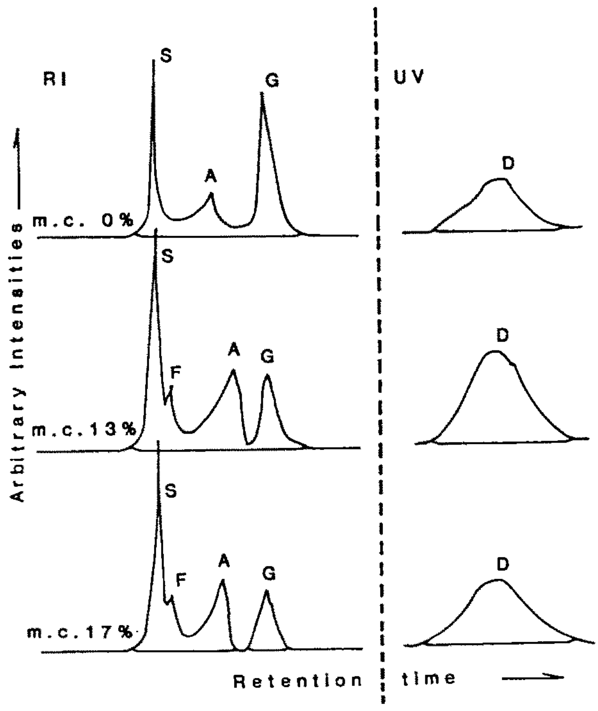

Fig. 3. Liquid chromatographs of the resulting solutions after hydrolysis of samples differing in moisture content (m.c.) in an autoclave at 450 K for 20 min.

largest but that of D is the smallest and peak F does not appear in the other cases. This suggests that the reaction of the sample with 0% moisture content goes rather slower than those of the others, assuming F would appear in an advanced stage of the decomposition of D-glucose. In the case of 13% moisture content, all the peaks are larger than those of the sample with 17% moisture content. Therefore the rate of reaction of the sample with 13%

TABLE 4

Peak ratios in liquid chromatographs of the solutions resulting after hydrolysis of cellulose in an autoclave

Sample water content (wt.%)	Ratio of peak area				
	S [a]	F [a]	A [a]	G [a]	D [b]
Retention time (min)	4.5	5.0	6.1	7.4	35.5
0	1	–	0.8	1.6	1.8
13	1	0.4	1.5	0.8	2.8
17	1	0.3	1.0	0.6	2.3

[a] Peak of refractive index.

[b] Peak of UV absorption (196 nm).

TABLE 5

Heat of hydrolysis of cellulose to D-glucose

Sample	ΔH (kJ monomer^{-1})
COT	35.6
ROC	17.6
FPI	46.3
FPII	26.0
FPIII	-0.8

moisture content must be larger than that of the 17% sample. Therefore, it was estimated that the rate of hydrolysis of cellulose was greatest in the sample with 13% moisture content, intermediate in the sample with 17% moisture content and least in the sample with 0% moisture content. It is suggested that water molecules involved in the cellulose structure accelerate the hydrolytic reaction but there might be an optimum moisture content which depends on a critical point at which water molecules are able to exist as bound water or free water in the cellulosic structure.

Enthalpy change

DSC traces of the acid hydrolysis of cellulosic materials show exothermic curves (Fig. 1). In Table 1, the heat of reaction of COT is smaller than that of RCO and those of the three samples which differ only in moisture content are as great and in the order FPI < FPII < FPIII, i.e. the heat of reaction seems to increase with an increase in the amorphous part of the sample and also with an increase in the initial moisture content. The heat of reaction can be assumed to include the heats of several decomposition reactions which might occur sequentially. Table 5 gives the heat of the first-stage reaction, cellulose → D-glucose, using the previous result for D-glucose, 140.2 kJ mol^{-1}. The result was obtained by subtracting the enthalpy change for D-glucose from the enthalpy change for the respective samples. The result shows that the heat of hydrolysis of cellulose to D-glucose is in most cases endothermic except in the case of FPIII and that the heat of hydrolysis is affected by the degree of crystallinity and the initial moisture content of the sample.

CONCLUSION

It would be inappropriate to try to draw conclusions from few experimental results. However, the results show that the rate and the heat of the acid hydrolysis of cellulose are affected not only by the degree of crystallinity but also by the initial moisture content of a cellulosic material.

ACKNOWLEDGEMENT

We are indebted to Dr. M. Yonemura for her support in the X-ray diffraction analysis.

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