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ACID HYDROLYSIS OF CELLULOSE IN A DIFFERENTIAL SCANNING CALORIMETER

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Differential scanning calorimetry was applied to the decompositions of cellulose and D-glucose with several concentration of sulfuric acid. The heat of reaction for cellulose was slightly less than that for glucose. It suggests that the heat of hydrolysis of the β-1,4-glucosidic linkage is endothermic.

The degree of reaction obtained by means of a commercial kinetic program was 1.1 ± 0.1, which was independent of the acid concentration for both cellulose and glucose.

The quantity of D-glucose produced by saccharification of cellulose was estimated using kinetic parameters obtained for cellulose and glucose, which were assumed to express the respective parameters for the successive first-order reactions cellulose to D-glucose, and glucose to decomposition products.

The kinetic treatment of the acid hydrolysis of cellulose has previously been performed in two ways: the kinetics of depolymerization in concentrated acid solution as a homogeneous phase reaction, and the kinetics of hydrolysis with dilute technical acid, assuming that the latter heterogeneous phase reaction can be approximated to the homogeneous one. In the latter case, it has been reported that the yield of D-glucose through acid hydrolysis of cellulose is controlled by the relative rates of the following reactions [1–7]:

$$\text{cellulose} \xrightarrow{k_1} \text{D-glucose} \xrightarrow{k_2} \text{products of glucose decomposition} \qquad (1)$$

Saeman [6] established the kinetics of wood saccharification in dilute acid at high temperature through isothermal experiments. He estimated the yield of D-glucose generated by the acid hydrolysis of cellulose, assuming that the first reaction in Eq. (1) can be described by the rate of decrease of the quantity of cellulose, and that the second one is equivalent to the decomposition of pure D-glucose. The above reactions have both been treated as first-order reactions since Saeman's experiment; although some modifications were proposed later, the reactions remained basically invariant. For example, separate kinetic parameters were given for the hydrolysis of the crystalline and the non-crystalline parts of cellulose [7].

On the other hand, instrumentation for thermal analysis at high pressure has been developed recently, in addition to the outstanding development of those for data analysis. At present, a pressure-resistant and acid-proof capsule for an extraordinary

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sample is offered by the Perkin–Elmer Corporation, which also supplies a kinetic program adaptable to the data station coupled with the differential scanning calorimeter.

We have applied these thermal analysis instruments to the kinetics of the acid hydrolysis of cellulose.

Experimental

Apparatus

The Perkin–Elmer DSC-2C and the "TADS" data station were employed with the high-pressure gold-plated capsule, Cat. No. 419-1760. The inner volume is approximately 45 μl. The limit of pressure is guaranteed up to 150 Bar.

Sampling

Filter paper for chemical analysis, No. 5C of Toyo Roshi Co., was used as a typical cellulose sample. A pulverized sample of a few mg was sealed in the capsule, together with a several-fold quantity of sulfuric acid, by means of the sealer. D-Glucose of Wako Junyaku Kogyo Co. (99.95% pure) was sampled in a similar way, for estimation of the second reaction in Eq. (1).

Procedure

The scanning was carried out mainly at 5 deg/min. The DSC curves obtained were treated with the kinetic program. The principle is as follows [8]:

If there is a simple chemical or physical conversion from A to B, the degree of conversion of A, x, and the rate of change with time, dx/dt, can be obtained via the following assumptions:

$$x = \frac{Q_{\text{partial}}}{Q_{\text{total}}} \tag{2}$$

$$\frac{dx}{dt} = k(1 - x)^n \tag{3}$$

where n expresses the degree of reaction, and Q_{partial} and Q_{total} are the heats generated in time t for intermediate and complete reaction, respectively. Both heats can be evaluated from the area under the DSC trace. k is the rate constant of the reaction, expressed by the Arrhenius equation

$$k = k_0 \exp\left(-\frac{E}{RT}\right) \tag{4}$$

where k_0, E, R and T are the frequency factor, the activation energy, the gas constant and the absolute temperature, respectively.

From Eqs (3) and (4), we have

$$\frac{dx}{dt} = k_0 \exp\left(-\frac{E}{RT}\right)(1-x)^n \tag{5}$$

Taking natural logarithms:

$$\ln\left(\frac{dx}{dt}\right) = \ln k_0 - \frac{E}{RT} + n \ln(1-x) \tag{6}$$

In order to obtain the three unknowns, k_0, E and n, multilinear regression is performed by using $\ln(dx/dt)$, $1/T$ and $\ln(1-x)$ as variables, known from the DSC trace through "TADS".

Results and discussion

Table 1 gives the direct experimental results. The data are rather few because of some difficulties in capsule sealing. C, m_s, m_a, T_p and Φ are the acid concentration, sample quantity, acid quantity, peak temperature of the DSC curve and scan rate, respectively. Q is the heat generated per unit weight of sample, not taking account of the weight of sulfuric acid, which only participates as the catalyst in the reaction.

Table 1 The experimental results

					FP			
C, wt.%	m_s, mg	m_a, mg	T_p, K	Q, J g^{-1}	k_0, min^{-1}	E, kJ mol^{-1}	n	Φ deg min^{-1}
3.4	4.28	19.39	482.5	871	$1.10 \cdot 10^{18}$	165.9	0.98	5
	1.73	9.41	480.1	744	$5.94 \cdot 10^{28}$	261.1	1.25	5
	1.78	16.80	480.2	677	$4.27 \cdot 10^{28}$	260.2	1.3	5
10	2.08	10.06	466.8	707	$1.57 \cdot 10^{29}$	257.7	1.25	5
63.6	4.79	15.01	424.3	711	$1.13 \cdot 10^{20}$	160.9	1.02	5
90	5.80	–	373.1	793	$7.73 \cdot 10^{15}$	113.5	1.11	5
	4.50	19.09	371.5	778	$2.61 \cdot 10^{18}$	130.3	1.37	5
					GL			
3.4	8.05	16.75	485.4	(810)	–	–	–	10
	5.90	25.51	471	795	$8.01 \cdot 10^{13}$	126.9	0.98	5
	6.14	–	472.5	723	$3.22 \cdot 10^{16}$	165.8	1.11	5
10	6.54	13.14	461.8	723	$2.95 \cdot 10^{15}$	151.7	1.04	5
63.6	7.35	13.92	417.4	666	$9.75 \cdot 10^{18}$	151.2	1.23	5
90	12.82	–	396.0	(798)	–	–	–	2.5
	7.02	10.14	394.0	1032	$1.09 \cdot 10^{18}$	135.5	1.25	5
	8.95	22.46	385.5	691	$1.39 \cdot 10^{17}$	125.3	1.11	5

Bracketed values in the Table were obtained by extrapolation of the DSC trace broken by steam leaking. Dashes in the m_a column signify unknown values, due to acid leakage on sample sealing. Dashes in the columns for the kinetic parameters indicate 'impossible to calculate', due to a break in the DSC trace.

Figure 1 shows DSC curves for cellulose and D-glucose as a function of acid concentration. The effect of the acid concentration is outstanding in the case of cellulose, in contrast with that for glucose. It suggests that the hydrolysis of cellulose can be described as a kind of prototropic reaction [9].

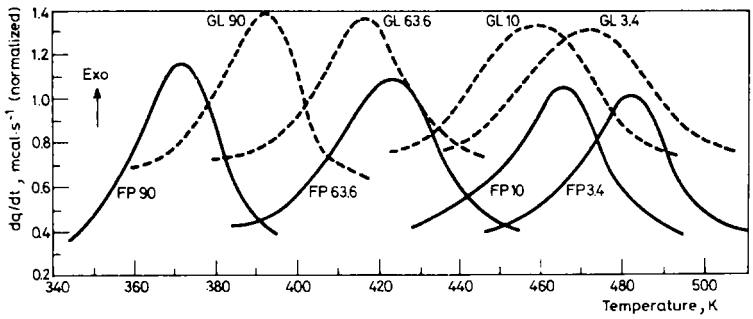

Fig. 1 DSC curves at various acid concentrations; scan rate 5 deg/min. —— filter paper, — — — D-glucose. The numbers express acid concentration in %

Heat of hydrolysis of cellulose

The heat of reaction, Q, averaged over all the cases, not taking account of the acid concentration, is 756±20 J/g for cellulose and 777±37 J/g for D-glucose. The deviations express the standard deviation. If we take the heat of reaction for cellulose, Q_c, with glucose unit instead of the monomer unit, we have

$$Q_c = 136.3 \pm 3.8 \text{ kJ/mol} \tag{7}$$

$$Q_g = 140.0 \pm 6.6 \text{ kJ/mol} \tag{7'}$$

where Q_g denotes the heat of decomposition of D-glucose, converted mainly into levulinic acid and formic acid [10]. The fluctuations in the values from Eqs (7) and (7') are so large that we have

$$Q_c \cong Q_g \tag{8}$$

The actual decomposition process of cellulose may be complicated, but Q_c may be expressed schematically by the sum of the heat of hydrolysis of cellulose and the heat of decomposition of glucose:

$$Q_c = Q_{\text{hyd.}} + Q_g \tag{9}$$

where

$$\frac{1}{\nu}(C_6H_{10}O_5)_\nu + H_2O \rightarrow C_6H_{12}O_6 + Q_{hyd.} \quad (10)$$

and

$$C_6H_{12}O_6 \rightarrow \text{decomposed glucose} + Q_g \quad (11)$$

From Eqs (8) and (9), we see that

$$Q_{hyd.} \ll Q_g \quad (12)$$

However, if we optimalistically assume that the central values of Q_c and Q_g differ significantly, we have

$$Q_{hyd.} = Q_c - Q_g = -3.8 \text{ kJ/mol} \quad (13)$$

Since cellulose is assumed to be a long-chain polymer of D-glucose linked by β-1,4-glucosidic bonds, the heat of hydrolysis of cellulose corresponds to the heat of hydrolysis of the β-1,4-glucosidic linkages. Then if $\Delta H_{\beta 1,4}$ stands for the enthalpy change:

$$\Delta H_{\beta 1,4} = -Q_{hyd.} \cong 3.8 \text{ kJ/mol} \quad (14)$$

This means an endothermic reaction. This is in contrast with the result for the heat of hydrolysis of the α-1,4-glucosidic linkage in starch, where the enthalpy change determined enzymatically was exothermic [11]:

$$\Delta H_{\alpha 1,4} \cong -4.2 \text{ kJ/mol} \quad (15)$$

This work was non-isothermal, and the experimental errors are beyond discussion. A large-scale test at room temperature, however, supported the endothermic result. That is, when 10 g filter paper was dissolved in 200 g 90% sulfuric acid in a Dewar vessel, the temperature fell by several degrees, while a similar test for glucose showed an initial temperature elevation of several degrees during several minutes.

Kinetics

The kinetic parameters obtained with the above program through "TADS" are given in Table 1. The degree of reaction, n, was 1.1 ± 0.1 for both cellulose and glucose. The values of k_0 and E display considerable scatter. However, the rate constants calculated for the k_0 and E pairs fall in an appropriate range, as shown by Table 2.

Table 3 gives the average values of the rate constants at several temperatures in the case of $C = 3.4\%$, compared with literature values obtained by extrapolating the acid concentration or temperature in the empirical formulae. The rate constants for both cellulose and glucose are well characterized, with their temperature-dependence, and the values agree with those from the literature, in spite of the fact that Q and Q_g are not very different from each other. The reason is that not the absolute heat values, but the ratio, $Q_{partial}/Q_{total}$, features in the kinetic treatment.

Table 2 Fluctuation of rate constant of cellulose decomposition ($C = 3.4\%$)

T, K	k (exp. 1), min^{-1}	k (exp. 2), min^{-1}	k (exp. 3), min^{-1}	Averaged, min^{-1}
443.2	0.0115	0.0129	0.0117	0.0120
453.2	0.0360	0.0614	0.0551	0.0509
463.2	0.0879	0.273	0.243	0.201
473.2	0.322	1.136	1.010	0.823

Table 3 Rate constants compared with literature values (acid concentration 3.4 wt.%)

T, K	$k_{cellulose}$, min^{-1}			$k_{glucose}$, min^{-1}		
	this work	ref. 1	ref. 2*	this work	ref. 1	ref. 2
443.2	0.012	0.015	0.018	0.038	0.046	0.048
453.2	0.051	0.036	0.053	0.091	0.10	0.11
463.2	0.20	0.081	0.15	0.22	0.22	0.24
473.2	0.82	0.18	0.40	0.56	0.46	0.51

* Douglas fir.

ref. 1: T. Kobayashi, Mokuzai Shingikai Hōkoku, 1 (1952) 1.

$$k_{FP} = 1.57 \cdot 10^{14} \cdot C^{1.42} \cdot \exp(-34000/RT), \quad C = 2\text{–}32\%,\ T = 373.2\text{–}423.2\ K$$

$$k_{GL} = 6.50 \cdot 10^{13} \cdot C^{1.19} \cdot \exp(-32000/RT), \quad C = 1\text{–}32\%,\ T = 373.2\text{–}423.2\ K$$

ref. 2: J. F. Saeman, Ind. Eng. Chem., 37 (1945) 43.

$$k_{DF} = 1.73 \cdot 10^{19} \cdot C^{1.34} \cdot \exp(-42900/RT), \quad C = 0.4\text{–}1.6\%,\ T = 443.2\text{–}463.2\ K$$

$$k_{GL} = 1.86 \cdot 10^{19} \cdot C^{1.02} \cdot \exp(-32700/RT), \quad C = 0.4\text{–}1.6\%,\ T = 443.2\text{–}463.2\ K$$

The good result leads us to assume that the rate constants for cellulose and glucose express k_1 and k_2 in Eq. (1), respectively. We also assume $n = 1$. The yield of the intermediate material in a successive first-order reaction, z, the glucose yield in this case, is given by Eq. (16) [12]:

$$z = \frac{k_1}{k_2 - k_1}[\exp(-k_1 t) - \exp(-k_2 t)] \tag{16}$$

The optimum time, t_m, which gives the maximum value of z, z_m, can be obtained via $dz/dt = 0$. Then:

$$t_m = \frac{1}{k_2 - k_1}(\ln k_2 - \ln k_1) \tag{17}$$

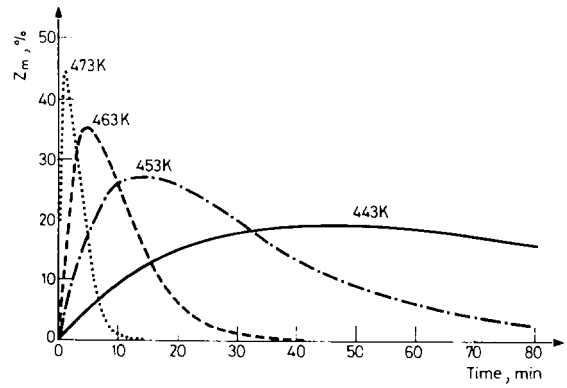

Fig. 2 Glucose yield with time at $C = 3.4\%$ (in calculation)

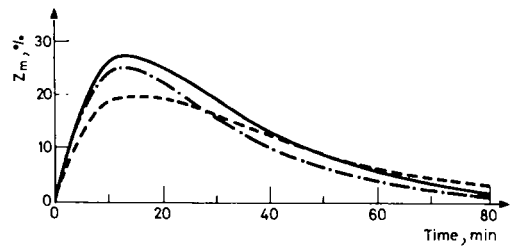

Fig. 3 Calculated values of glucose yield at 453.2 K and $C = 3.4\%$, compared with the literature results. —— this paper, – – – Kobayashi [4], – · – Saeman [6] (Douglas fir)

and

$$z_m = k_1 \exp(-k_2 t_m) = (k_r)^{\frac{1}{1-k_r}} \tag{18}$$

where

$$k_r = \frac{k_1}{k_2}, \quad \text{but} \quad k_r \neq 1.$$

Table 4 gives the results of calculation. In dilute acid, and especially at $C = 3.4\%$, z_m increases considerably with temperature. The higher the temperature, the shorter the time, i.e. the same results as found by Saeman. Figure 2 shows the glucose yield vs. time at several temperatures in the case of $C = 3.4\%$. Figure 3 shows the yield at 453.2 K, compared with literature values calculated from the formulae in Table 3.

As shown by Table 4, the extremely concentrated acid leads to a very high glucose yield. The result is supported by the fact that the potential glucose content in cellulose is usually analyzed with sulfuric acid over 72%. In this case, the temperature-dependence is opposite to that in the more dilute acid. That is, the lower the tem-

Table 4 Glucose yield estimated from the experimental results

C, wt.%	T, k	k_1, min^{-1}	k_2, min^{-1}	k_r, k_1/k_2	t_m, min	z_m, %
3.4	443.2	0.012	0.038	0.32	37	19
	443.2	0.051	0.091	0.56	13	27
	463.2	0.20	0.22	0.91	4.7	35
	473.2	0.82	0.56	1.5	1.6	44
10	433.2	0.0043	0.034	0.06	70	9
	443.2	0.021	0.090	0.23	21	15
	453.2	0.12	0.32	0.38	4.9	20
	463.2	0.37	0.59	0.63	2.1	29
63.6	383.2	0.004	0.010	0.40	150	22
	393.2	0.016	0.037	0.43	40	23
	403.2	0.066	0.145	0.46	10	24
	413.2	0.211	0.426	0.50	3.3	25
90	310	$5.1 \cdot 10^{-4}$	$5.3 \cdot 10^{-6}$	96	$1.3 \cdot 10^{4}$	95
	330	$8.6 \cdot 10^{-3}$	$2 \cdot 10^{-4}$	43	560	90
	350	0.11	$4.8 \cdot 10^{-3}$	23	33	85
	370	1.0	0.084	12	2.7	80

perature, the higher the yield. This suggests that the difference in activation energy between the first and second reactions changes the sign in the acid concentration range 63.6–90%.

If the kinetic parameters of the first and second reactions are given by k_{01}, E_1, and $k_{02}, E_2, k_1/k_2 = k_r$ can be expressed by the following equation,

$$k_r = \frac{k_{01}}{k_{02}} \exp\left(-\frac{E_1 - E_2}{RT}\right) \tag{19}$$

Then if $E_1 > E_2$, k_r increases with temperature, while if $E_1 < E_2$, k_r decreases with temperature. We see that z_m increases with k_r through Eq. (18). The temperature-dependence of z_m therefore depends upon $E_1 \lesseqgtr E_2$. The activation energy values obtained were plotted in relation to acid concentration and straight lines were tentatively drawn, as shown in Fig. 4. An intersection of the lines appears in the acid concentration range 63.6–90%, which agrees with the expected boundary.

Some problems

In this paper, some difficulties arise in the discussion of the kinetics of such a complicated reaction as the acid hydrolysis of cellulose, not excluding the experimental difficulties.

i) *Non-isothermal conditions.* In the kinetics, non-isothermal conditions do not play the primary role in principle; this is due to the employment of the Arrhenius equation, which is valid for isothermal conditions. In order to overcome this weakness,

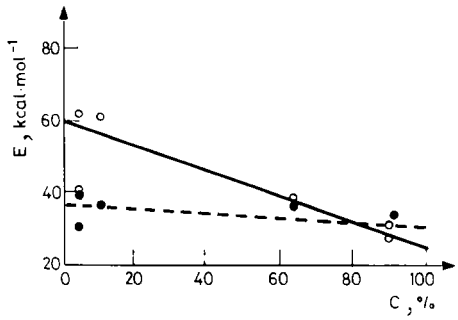

Fig. 4 Activation energies and acid concentration. —— cellulose, — — — D-glucose

we usually have to take a number of DSC traces at different scanning rates, Φ. In this paper, we were not able to obtain enough data by changing Φ. Further, the reaction is not simple. The glucose decomposition products, levulinic acid and formic acid, further decompose step by step to carbon, water and other products during the DSC scan. Thus, the area under the DSC trace refers to the sum of all the heats generated in many successive reactions. It must be noted, however, that Q_c and/or Q_g do not vary with the acid concentration up to 5 deg/min. This means that the two reactions progress in a similar way, even if the acid concentration changes, but at the same scan rate. Schematically, therefore, we have

$$A \rightarrow B \rightarrow C \rightarrow D \rightarrow E \rightarrow \ldots \text{ for cellulose, and}$$

$$B \rightarrow C \rightarrow D \rightarrow E \rightarrow \ldots \text{ for glucose.}$$

Here, many stages, D, E, and so on, can be incorporated after stage C, in so far as we are interested particularly in product B.

The approximation holds that

$$A \rightarrow B \rightarrow C \text{ for cellulose, and}$$

$$B \rightarrow C \text{ for glucose.}$$

ii) $k_{\text{cellulose}} \neq k_1$. Since $Q_{\text{hyd.}} \ll Q_g$, the DSC trace for cellulose reflects the state of decomposition of glucose produced from cellulose. It does not demonstrate the degree of decrease of the quantity of cellulose directly. As shown in Fig. 1 and Table 1, however, the peak temperature of the DSC trace for cellulose varies greatly with the concentration of the acid hydrolysis catalyst, as expressed by k_1. The characteristics of the first reaction are revealed not in the heat quantity, but on the temperature scale. This may be the reason why the kinetic program give adequate values of the rate constant for cellulose. Basically, however, the cellulose trace should be solved as the superposition of two steps: the decomposition of cellulose and the decomposition of glucose. The real k_1 may be larger than $k_{\text{cellulose}}$ (here k_1) because the decomposition heat of the glucose formed from cellulose should appear after the glucose production.

Conclusion

It is a notable result that kinetic analysis of the DSC curves for the decompositions of cellulose and glucose with acid gives a similar result to that obtained on ordinary isothermal acid hydrolysis, as regards estimation of the glucose yield from the saccharification of cellulose.

It suggests that estimation of the yield of the intermediate in other successive first-order reactions is possible by employing a differential scanning calorimeter.

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Zusammenfassung – Die Zersetzung von Cellulose und D-Glucose durch Schwefelsäure unterschiedlicher Konzentration wurde mittels DSC untersucht. Die Reaktionswärme ist bei Cellulose etwas geringer als bei Glucose, was zeigt, daß die Hydrolyse der β-1,4-Glucosidbindung ein endothermer Vorgang ist. Der mittels eines kommerziellen kinetischen Programms erhaltene Reaktionsgrad beträgt 1.1 ± 0.1 und erwies sich sowohl bei Cellulose als auch bei Glucose als unabhängig von der Säurekonzentration. Die durch Verzuckerung von Cellulose gebildete Menge an D-Glucose wurde unter Verwendung von für Cellulose und Glucose erhaltenen kinetischen Parametern bestimmt, für die angenommen wurde, daß sie die entsprechenden Parameter der Folgereaktionen erster Ordnung Cellulose → D-Glucose und Glucose → Zersetzungsprodukte darstellen.

Резюме – Методом дифференциальной сканирующей калориметрии проведено изучение разложения целлюлозы и Д-глюкозы. Теплота реакции разложения целлюлозы была немного меньше, чем для глюкозы. Это заставляет предполагать, что теплота реакции гидроли-

за β-1,4-глюкозидного звена является ендотермической. Степень реакции для глюкозы и целлюлозы, вычисленная с помощью доступной кинетической программы, была равной 1.1 ± 0.1 и была независимой от концентрации кислоты. Количество Д-глюкозы, полученной осахариванием целлюлозы, было оценено на основе кинетических параметров, полученных для целлюлозы и глюкозы и которые были приняты, чтобы выразить соответствующие параметры для параллельно протекающих реакций первого порядка превращения целлюлозы до глюкозы и разложения глюкозы.