The Heterogeneous Character of the Dilute Acid Hydrolysis of Crystalline Cellulose. III. Kinetic and X-Ray Data

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SYNOPSIS

Thirteen prehydrolyzed samples of cellulose, including native, mercerized, and regenerated materials were hydrolyzed in 1% and 1.5% sulfuric acid at 160, 170, and 180°C. Pseudo first-order rate constants and weight average degrees of polymerization were determined for each sample. For all cellulose samples, data from several experiments were used to determine the dependence of the rate of hydrolysis on sulfuric acid concentration. The results obtained in this study indicate that Sharples' end-attack model is consistent with kinetic data for the hydrolysis of cellulose II samples, but is not applicable to the hydrolysis of cellulose I samples. X-ray diffraction analyses indicated that, for native and mercerized cellulose samples, structural changes during dilute acid hydrolysis are not significant. However, data for rayon indicated that such changes may need to be taken into account in analysis of the reaction kinetics.

INTRODUCTION

Saccharification of cellulose is of interest to researchers concerned with the development of alternative sources of liquid fuels since glucose, the product of cellulose hydrolysis, is an important intermediate for fermentation to ethanol and other chemicals. Previous researchers[1] have indicated that the dilute acid hydrolysis of cellulose is the process with the greatest potential for commercialization. The results reported in this paper focus on the kinetics of the dilute acid hydrolysis process and on the questions of whether or not changes in the crystalline structure of the residual cellulose accompany the hydrolysis reaction.

Because cellulose is not soluble in dilute acid, the dilute acid hydrolysis of cellulose is a heterogeneous reaction. Many researchers have studied this reaction under a variety of conditions.[2-11] For both cellulose I and cellulose II, these researchers have reported that the dilute acid hydrolysis can be modeled as a pseudohomogeneous, first-order reaction. In addition, it has been reported that celluloses with the same crystalline morphology, but obtained from different sources, hydrolyze at widely different rates. In order to be able to model the production of glucose from different sources of cellulose without the necessity for independently studying the hydrolysis of each substrate, it would be desirable to have a mathematical model of the dilute acid hydrolysis which could be used to explain the observed first order kinetics and provide a framework for correlating kinetic data for a variety of cellulosic substrates.

Sharples[6,7] has proposed a model for the dilute acid hydrolysis of cellulose which explained the first order kinetics and the fact that different rates are obtained for celluloses from different sources. In a previous paper,[1] we reported kinetic data (rate constants and activation energies) for the dilute acid hydrolysis of a variety of cellulosics and examined the applicability of Sharples' model. We reported that Sharples' end-attack model is consistent with kinetic data for cellulose II samples, but is not appropriate for characterizing the reactions of cellulose I samples.

The present paper extends our previous study of the dilute acid hydrolysis of cellulose to a wider range of reaction conditions. In particular, the present paper focuses on the effects of reaction temperature

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and acid concentration. The activation energy and dependence of the reaction rate on acid concentration are reported. Since some researchers[12] have reported that the conformation of a cellulose substrate changes during the homogeneous hydrolysis reaction and since Atalla et al.[13] have also indicated that cellulose can experience a conformation change when treated with various solvents, we also used X-ray diffraction analyses to assess whether or not structural changes occur in the residual crystalline cellulose during dilute acid hydrolysis.

EXPERIMENTAL

Prehydrolyzed cellulose samples were subjected to batch hydrolysis in 1% and 1.5% sulfuric acid for varying lengths of time at 160, 170, and 180°C. For each of the hydrolyzed samples, both the total weight loss and the cellulose weight loss (based on sugar analysis[14]) were determined. The experimental methods for mercerization, prehydrolysis, batch hydrolysis, and size exclusion chromatography used in this study are the same as those employed in the second paper in this series.[1] The cellulosic materials used for the hydrolysis experiments were the same as those used previously. In addition, four other samples: two cotton linters, microcrystalline cellulose, and spruce were also hydrolyzed in 1% sulfuric acid. Table I indicates the various samples employed and their characteristics.

X-Ray Diffraction Analysis

The crystallographic structures of the cellulose samples were examined by a Scintag computer automated X-ray diffractometer operated in the Bragg–Brento mode with $CuK\alpha_1$ radiation ($\lambda = 1.5405$ Å). Alpha quartz and silicon crystals were used as internal standards. The relative angular positions of the X-ray beam source, the sample holder, and the detector were calibrated before each operation of the X-ray instrument. Reflection data were obtained from the powdered samples of the various types of cellulose from $2\theta = 10$–$30°$ at a step size of $0.05°$. The rate of data collection was $0.5°/min$. The total scanning time was ca. 40 min.

RESULTS AND DISCUSSION

Kinetic Studies of the Acid Hydrolysis of Cellulose

Representative semilog plots of the cellulose weight loss data for a cotton sample hydrolyzed in 1.5% sulfuric acid at each reaction temperature are shown in Figure 1. In the present study, an extent of hydrolysis corresponding to a weight loss of more than 70% of the original cellulose was employed. The data indicate that the rate at which the cellulose component loses weight obeys pseudo-first-order kinetics even when more than 70% of cellulose component has been hydrolyzed. First-order rate constants for each of the prehydrolyzed samples (determined from linear regression analyses of the data) are listed in

Table I   Data for Cellulosic Samples Hydrolyzed in 1% H_2SO_4 at 160, 170, and 180°C[a]

Species	DP_w	$2/b$	Rate Constant (min^{-1})			Activation Energy (kcal/mol)
			$k_{160°C}$	$k_{170°C}$	$k_{180°C}$	
Cotton	171.3 ± 12	170.4	0.00220	0.00541	0.01897	42.0
Ramie	188.3 ± 7	187.5	0.00180	0.00465	0.01502	41.4
Linen	164.1 ± 8	163.2	0.00335	0.00904	0.02739	40.9
α-Cellulose	98.4 ± 2	97.0	0.00649	0.01706	0.05009	39.8
Cotton linter 1	124.7 ± 2	123.6	0.00307	0.00822	n.a.	37.6
Cotton linter 2	164.3 ± 9	163.2	0.00215	0.00511	0.01569	38.8
Microcrystalline cellulose	118.0 ± 1	116.8	0.00453	0.01358	0.04282	43.8
Spruce cellulose	81.0 ± 4	79.4	0.00709	0.02048	0.05955	41.5
Merc. cotton	75.3 ± 5	73.6	0.00285	0.00715	0.02249	40.2
Merc. ramie	99.8 ± 5	98.4	0.00222	0.00562	0.01599	38.5
Merc. linen	101.7 ± 3	100.3	0.00227	0.00519	0.01601	38.1
Merc. α-cellulose	44.8 ± 1	42.2	0.00494	0.01205	0.04170	41.5
Rayon	16.7 ± 1	12.0	0.02621	0.07221	0.24310	43.4

[a] DP_w values reported in this table are the average of the values obtained from nine reaction conditions. The values reported for $2/b$ were calculated from eq. (3) using the average DP_w values.
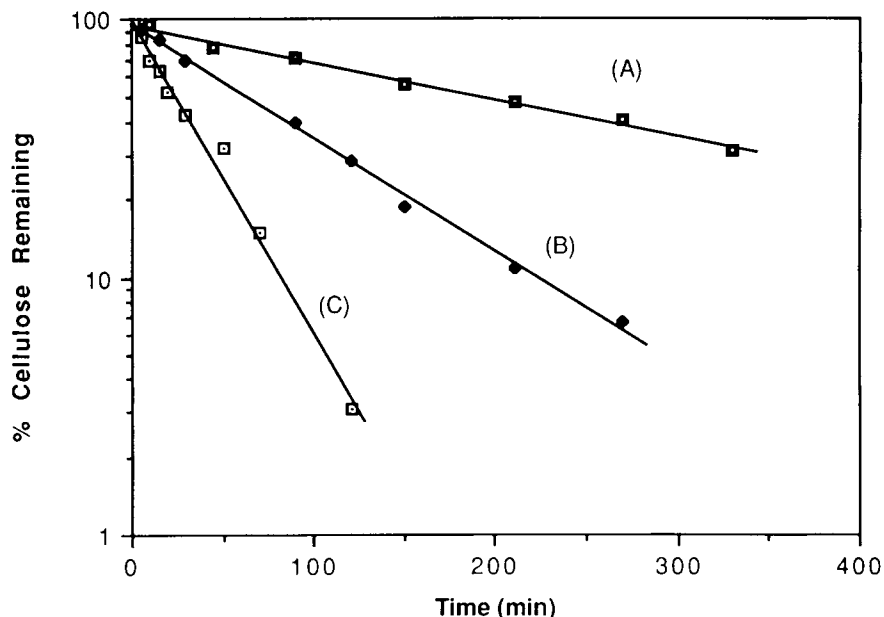
Figure 1   Semilog plots of weight loss data for the cellulose component of cotton hydrolyzed in 1.5% H_2SO_4 at (A) 160, (B) 170, and (C) 180°C.

Tables I and II. As noted in two previous studies[1,15] in our laboratory and another report in the literature,[5] mercerization of cotton and ramie enhances their rates of hydrolysis. However, identical treatments of linen and α-cellulose have the opposite effect. The data in Table II indicate that, for ramie and mercerized ramie hydrolyzed at 160°C in 1.5% sulfuric acid, the rate constant for ramie is larger than that for mercerized ramie, which is contrary to what we have observed in previous studies under somewhat different experimental conditions. Examination of the rate constants of these two samples at the two other temperatures investigated (170 and 180°C) indicates that the mercerized ramie hydro-

lyzes somewhat faster than the conventional ramie (by 17.8 and 9.4%, respectively). At 160°C the difference in the rate constants for ramie and mercerized ramie is sufficiently small that the deviations from conclusions drawn from previous studies can be attributed to experimental uncertainties (see the comparison of experimental and calculated rate constants shown in Table IV).

For the reaction conditions used in this study, a 10°C increase in temperature causes the rate constant to increase by a factor of 2.9. This value is comparable to the corresponding values reported by Foster and Wardrop[4] (2.8) and a previous paper[1] in this series (3.1). Marchessault and Ranby[16] have

Table II   Data for Cellulosic Samples Hydrolyzed in 1.5% H_2SO_4 at 160, 170, and 180°C

	Rate Constant (min^{-1})			Activation Energy (kcal/mol)
Species	$k_{160°C}$	$k_{170°C}$	$k_{180°C}$	
Cotton	0.00328	0.01010	0.02822	42.0
Ramie	0.00293	0.00791	0.02431	41.2
Linen	0.00420	0.01323	0.03994	43.9
α-Cellulose	0.00897	0.02803	0.08005	42.7
Merc. cotton	0.00485	0.01377	0.03115	36.3
Merc. ramie	0.00288	0.00932	0.02659	43.3
Merc. linen	0.00367	0.00767	0.02380	36.4
Merc. α-cellulose	0.00634	0.01914	0.05757	43.0
Rayon	0.03978	0.11410	0.28210	38.2

indicated that, for homogeneous hydrolysis in concentrated phosphoric acid, the rate of hydrolysis of wood is approximately twice that for cotton linters. Our data indicate that the rate of hydrolysis of α-cellulose is about 2.8 times that for cotton cellulose.

Tables I and II contain values of the activation energy calculated from the rate constants for hydrolysis at different temperatures in 1% and 1.5% sulfuric acid. The average (based on all samples) value of the Arrhenius activation energy was 40.7 ± 2.4 kcal/mol. This value is very close to that reported in the previous study (42.0 ± 3.1 kcal/mol). The average activation energy for the cellulose I samples was 41.3 ± 1.9 kcal/mol, while that for the cellulose II samples was 39.9 ± 2.8 kcal/mol. Since the difference between these two values is not very significant in statistical terms, some question exists as to whether the indicated difference between the activation energies for the cellulose I and cellulose II samples is meaningful.

The dependence of the rates of hydrolysis of various samples of cellulose on the acid concentration can be calculated by combining data for the rate constants obtained in this study with those reported for the reaction in 2% H_2SO_4. The dependence of the rate of hydrolysis on acid concentration and temperature can be expressed as

$$k = k_0[H^+]^n \exp(-E/RT) \qquad (1)$$

where k is the pseudo-first-order rate constant (min^{-1}), k_0 is the Arrhenius preexponential factor (min^{-1}), n is the order of the reaction with respect to $[H^+]$, $[H^+]$ is the hydrogen ion concentration

(%), E is the activation energy for the reaction (cal/mol), R is the gas constant (1.987 cal/mol K), and T is the absolute temperature (K).

The acidity of the contents of the reactor, $[H^+]$, is dependent on many factors: the concentration of acid solution employed, the neutralizing capacity of the substrate (ash content), and the extent of the secondary ionization of sulfuric acid. Since less than 1% of the bisulfate ion dissociates under the conditions usually employed for hydrolysis of cellulose,[17] one may treat this system as if only the first ionization of H_2SO_4 occurs. The neutralizing capacity differs from substrate to substrate. The ash contents of the prehydrolyzed cellulose samples used in this study are negligible (ranging from 0 to 0.03%). Ash contents were determined using ASTM method No. D1102.[18] Conner et al.[19] have indicated that the low-ash material can be prepared by washing the high-ash material with a dilute solution of HCl. Since the prehydrolyzed samples were prehydrolyzed in constant boiling HCl, it is not surprising that most of the ash is removed during the prehydrolysis step.

Saeman[2] reported that the value of n for cellulose from Douglas fir was 1.34 when $[H^+]$ was taken as the percent acid concentration. The corresponding value reported by Bhandari et al.[10] for cellulose contained in corn stover was 2.74. The value of n reported by Conner et al.[19] for Douglas-fir lignocellulose was 1.218 when $[H^+]$ was taken as the molal concentration of acid. These researchers assumed that the same value applies to the hydrolysis of lignocellulose from southern red oak. In our regression analyses we treated the data assuming that the values of both n and the activation energy were the

Table III Comparison of Experimental and Calculated Rate Constants for Hydrolysis in 1% H_2SO_4

| Sample | $k_0 \times 10^{-18}$ (min^{-1}) | 160°C | | 170°C | | 180°C | |
		k_{exp} (min^{-1})	k_{cal} (min^{-1})	k_{exp} (min^{-1})	k_{cal} (min^{-1})	k_{exp} (min^{-1})	k_{cal} (min^{-1})
Cotton	0.6220	0.00220	0.00216	0.00541	0.00625	0.01897	0.01727
Ramie	0.5246	0.00180	0.00182	0.00465	0.00527	0.01502	0.01457
Linen	0.8926	0.00335	0.00310	0.00904	0.00897	0.02739	0.02478
α-Cellulose	1.6907	0.00649	0.00587	0.01706	0.01699	0.05009	0.04694
Cotton linter 1	0.8502	0.00307	0.00295	0.00822	0.00855	n.a.	0.02361
Cotton linter 2	0.5621	0.00215	0.00195	0.00511	0.00565	0.01569	0.01561
Microcrystalline cellulose	1.3959	0.00453	0.00485	0.01358	0.01403	0.04282	0.03815
Spruce cellulose	2.0739	0.00709	0.00720	0.02048	0.02084	0.05955	0.05758
Mercerized cotton	0.7954	0.00285	0.00276	0.00715	0.00799	0.02249	0.02208
Mercerized ramie	0.5974	0.00222	0.00207	0.00562	0.00600	0.01599	0.01659
Mercerized linen	0.6014	0.00227	0.00209	0.00519	0.00604	0.01601	0.01670
Mercerized α-cellulose	1.2918	0.00494	0.00448	0.01205	0.01298	0.04170	0.03587
Rayon	7.1409	0.02621	0.02479	0.07221	0.07177	0.24310	0.19830

Table IV Comparison of Experimental and Calculated Rate Constants for Hydrolysis in 1.5% H_2SO_4

Sample	160°C		170°C		180°C	
	k_{exp} (min^{-1})	k_{cal} (min^{-1})	k_{exp} (min^{-1})	k_{cal} (min^{-1})	k_{exp} (min^{-1})	k_{cal} (min^{-1})
Cotton	0.00328	0.00347	0.01010	0.01005	0.02825	0.02777
Ramie	0.00293	0.00293	0.00791	0.00848	0.02431	0.02342
Linen	0.00420	0.00498	0.01323	0.01442	0.03994	0.03985
α-Cellulose	0.00897	0.00944	0.02803	0.02732	0.08005	0.07548
Mercerized cotton	0.00485	0.00444	0.01377	0.01285	0.03115	0.03551
Mercerized ramie	0.00288	0.00333	0.00932	0.00965	0.02659	0.02667
Mercerized linen	0.00367	0.00336	0.00767	0.00972	0.02380	0.02685
Mercerized α-cellulose	0.00634	0.00721	0.01914	0.02088	0.05757	0.05768
Rayon	0.03978	0.03986	0.11410	0.11541	0.28210	0.31883

same for all samples. The data were analyzed using the regression procedure in the SAS statistical package. The value of n obtained in this manner is 1.172 ± 0.043. The corresponding value of the activation energy is 40.6 ± 0.5 kcal/mol. The Arrhenius preexponential factor k_0 was also determined for each sample. In these regression procedures, $[H^+]$ was taken as the percent sulfuric acid concentration.

By inserting the values of n and activation energy obtained from statistical treatment, eq. (1) can be rewritten as

$$k = k_0[H^+]^{1.172}\exp(-40600/RT) \qquad (2)$$

The calculated value of k_0 for each sample is listed in Table III. With these k_0 values and eq. (2), one can predict first-order rate constants for hydrolysis in dilute sulfuric acid. The experimental first-order rate constants obtained for the reaction conditions

employed in our studies and those calculated from eq. (2) by SAS are also tabulated in Tables III, IV, and V. The overall, average difference between the rate constants determined experimentally and those calculated by eq. (2) is approximately ±7%. For mercerized linen, the average difference between the experimentally determined and calculated rate constants (approximately ±13%) is significantly higher. The reason why mercerized linen exhibits this larger difference is not known. It may be due to the fact that the commercial linen used in these experiments had a significantly larger lignin content (even after mercerization) than the other cellulosics studied. However, the fact that the original linen does not exhibit this same trend would seem to rule out the hypothesis that the lignin content may be the source of the larger difference between the experimental and calculated rate constants for the mercerized linen.

Table V Comparison of Experimental and Calculated Rate Constants for Hydrolysis in 2% H_2SO_4[a]

Sample	150°C		160°C		170°C	
	k_{exp} (min^{-1})	k_{cal} (min^{-1})	k_{exp} (min^{-1})	k_{cal} (min^{-1})	k_{exp} (min^{-1})	k_{cal} (min^{-1})
Cotton	0.00146	0.00160	0.00592	0.00486	0.01358	0.01408
Ramie	0.00146	0.00135	0.00446	0.00410	0.01157	0.01189
Linen	0.00208	0.00229	0.00799	0.00698	0.02085	0.02021
α-Cellulose	0.00441	0.00434	0.01107	0.01322	0.03676	0.03827
Mercerized cotton	0.00209	0.00204	0.00667	0.00622	0.01698	0.01801
Mercerized ramie	0.00164	0.00153	0.00517	0.00467	0.01423	0.01352
Mercerized linen	0.00151	0.00154	0.00584	0.00470	0.01642	0.01301
Mercerized α-cellulose	0.00325	0.00332	0.01003	0.01010	0.03141	0.02924
Rayon	0.01781	0.01834	0.04480	0.05580	0.18220	0.16170

[a] Experimental data are from a previous paper.[1]

Figure 2 contains a plot of the calculated rate constants versus the experimental rate constants. Examination of this plot indicates that the mathematical model developed from the statistical analysis can be used to predict the rate constant for the dilute sulfuric acid hydrolysis of cellulose. Inspection of the plot indicates that several points are not very close to the correlation line. Further inspection reveals that these points all correspond to the rayon sample. This observation may indicate that the mathematical expression of eq. (2) cannot be used to predict the rate constants for the hydrolysis of rayon to a high degree of accuracy. Possible reasons for this discrepancy will be discussed later. A plot of the calculated rate constants versus experimental rate constants which omits data points correspondent to the rayon samples is indicated in Figure 3. This plot confirms that eq. (2) can be used to predict the rate constants with a high degree of accuracy for the dilute sulfuric acid hydrolysis of all the cellulose samples investigated except rayon.

Size-Exclusion-Chromatography Analysis

The SEC analysis used in this study is basically the same as that employed in the previous investigation. The universal calibration technique employing polystyrene standards was used.[20] The Mark–Houwink coefficients used in this work were $K = 0.0112$ and $\alpha = 0.72$ for polystyrene in tetrahydrofuran (THF)[21] and $K = 0.0053$ and $\alpha = 0.84$ for cellulose tricarbanilate (CTC) in THF.[22].

The basic hypothesis on which the end-attack model of Sharples[6,7] is based is that differences in
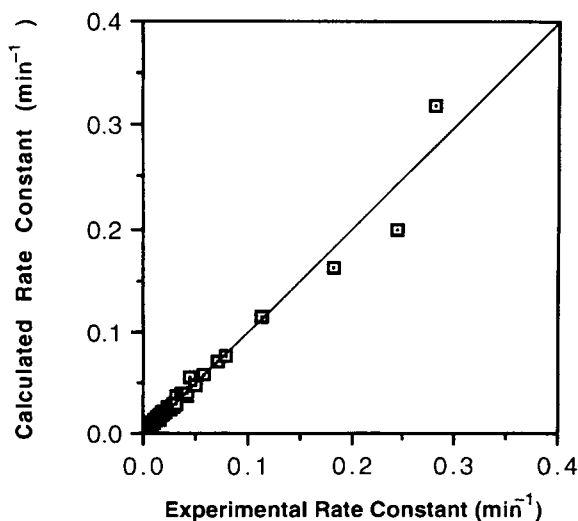
Figure 2 Comparison of experimental and calculated rate constants.
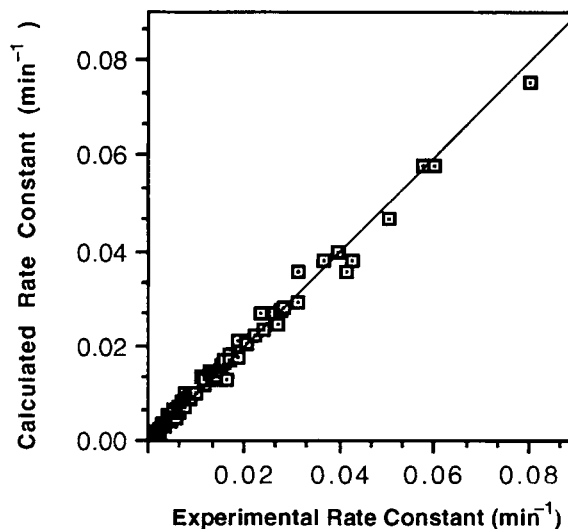
Figure 3 Comparison of experimental and calculated rate constants (data points for rayon excluded).

the rates of hydrolysis of cellulosic materials result from differences in the degrees of polymerization of these materials. In terms of this model, the relationship which should exist between the rate constant k and weight average degree of polymerization DP_w is

$$\frac{1}{k} = \left(\frac{\rho}{4B}\right)\left(\frac{2}{b}\right) = \left(\frac{\rho}{4B}\right)\left[DP_w - \frac{2S^2}{(DP_w + 2S)}\right] \quad (3)$$

where ρ is the density of cellulose, B is an intrinsic rate constant, b is the distribution constant, and S is the solubility limit.

The average degree of polymerization (DP_w) from the SEC analysis and values of $2/b$ calculated from eq. (3) for cellulose samples hydrolyzed in dilute sulfuric acid are listed in Table I. The solubility limit S was taken to be 9 in accordance with Sharples' suggestion,[6] although Atalla[23] has pointed out that the solubility limit should be smaller than 9. Since the calculation of $2/b$ is very insensitive to the value of S employed when S is much smaller than the degree of polymerization, no correction was deemed necessary.

Plots of $1/k$ versus $2/b$ are shown in Figures 4 and 5 for cellulose I and cellulose II samples hydrolyzed in 1% H_2SO_4, respectively. Corresponding plots for cellulose samples hydrolyzed in 1.5% H_2SO_4 are shown in Figures 6 and 7. These plots again indicate that only in the case of the cellulose II samples do the plots go through the origin as required by Sharples' model. Since cellulose I and cellulose II
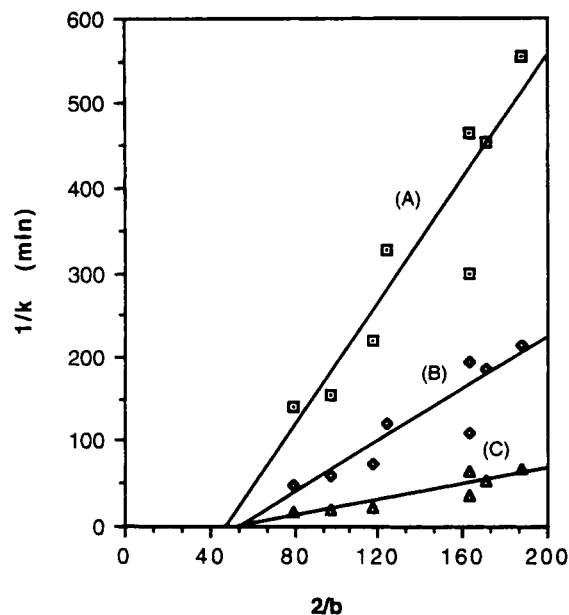
Figure 4   Plots of $1/k$ versus $2/b$ for cellulose I samples hydrolyzed in 1% H_2SO_4 at (A) 160, (B) 170, and (C) 180°C.
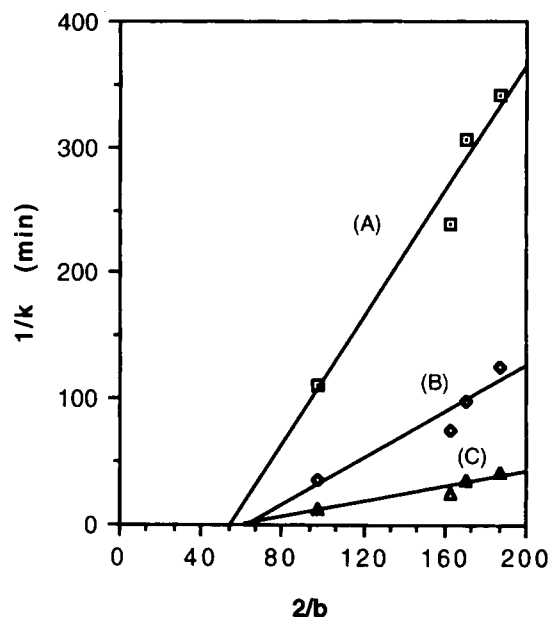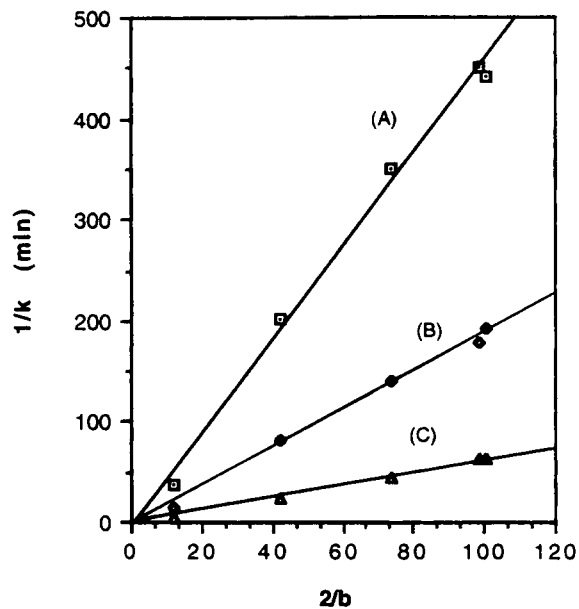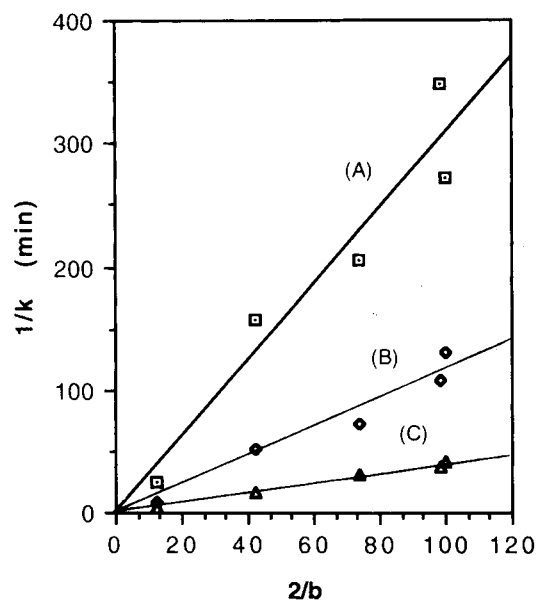

Figure 6   Plots of $1/k$ versus $2/b$ for cellulose I samples hydrolyzed in 1.5% H_2SO_4 at (A) 160, (B) 170, and (C) 180°C.

polymorphs have different chain configurations and hydrogen bonding patterns, it is not unexpected that the data from the cellulose I samples and cellulose II samples show different linear relationships. However, for Sharples' model to apply, the straight lines have to pass through the origin. None of the plots

for the cellulose I samples goes through the origin. These data indicate that Sharples' model is consistent with data for the dilute acid hydrolysis of the cellulose II, but not with data for the hydrolysis of the cellulose I samples. This observation is consistent with data reported in previous papers.[1,15]

Figure 5   Plots of $1/k$ versus $2/b$ for cellulose II samples hydrolyzed in 1% H_2SO_4 at (A) 160, (B) 170, and (C) 180°C.

Figure 7   Plots of $1/k$ versus $2/b$ for cellulose II samples hydrolyzed in 1.5% H_2SO_4 at (A) 160, (B) 170, and (C) 180°C.
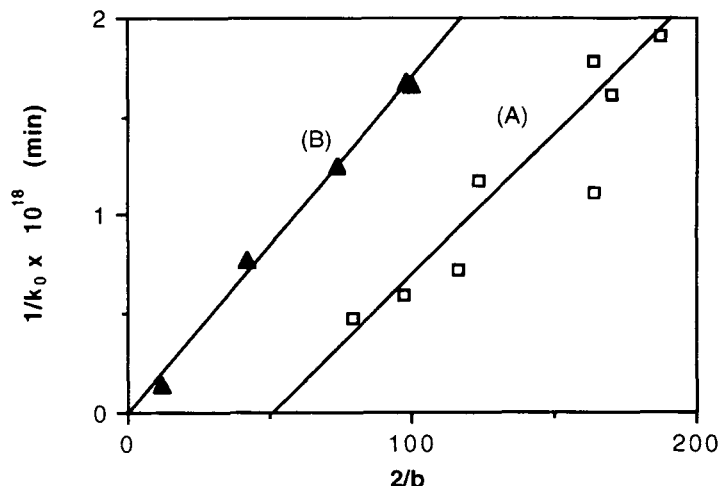
Figure 8   Plots of $1/k_0$ versus $2/b$ for (A) cellulose I and (B) cellulose II samples.

Instead of using the pseudo-first-order rate constants to prepare plots of $1/k$ versus $2/b$, one could employ Arrhenius preexponential factors k_0 (see Fig. 8). In calculating values of k_0 for use in this plot, it was assumed that the values of activation energy and n are the same for all samples. The trends for hydrolysis of the cellulose I and cellulose II samples still hold. The straight line for the data for hydrolysis of the cellulose II samples goes through the origin as predicted by Sharples' model. However, the plot of the data for the cellulose I samples does not seem to go through the origin. To predict the rate of hydrolysis of a specific cellulose II sample in dilute sulfuric acid, one needs only to measure its weight average degree of polymerization. After the degree of polymerization is determined, the Arrhenius preexponential factor k_0 can be determined from Sharples' model; then the reaction rate constant can be calculated from equation (2).

Investigation of the data for cellulose I samples shown in Figure 8 indicates that if linen is excluded from this plot, one can draw a straight line through the other samples, although the straight line does not follow Sharples' model and some scatter is evident. Examination of the plots shown in Figures 4 and 6 also indicates that in most cases, the data points for linen deviate from the correlation line significantly. Once again, the lignin content in linen may play an important role. Wood[24] has reported that the lignin content of the linen used in this study increased from 4% to 17% when the prehydrolyzed linen was hydrolyzed to an extent of 66% weight loss. This increase of lignin content may complicate the analysis of the kinetic data since all the other native cellulosic materials employed in this study

are very pure with respect to cellulose content. By excluding the linen sample from the data analysis, one should be able to find a relationship between the Arrhenius preexponential factors k_0 and the degrees of polymerization for cellulose I samples if ex-
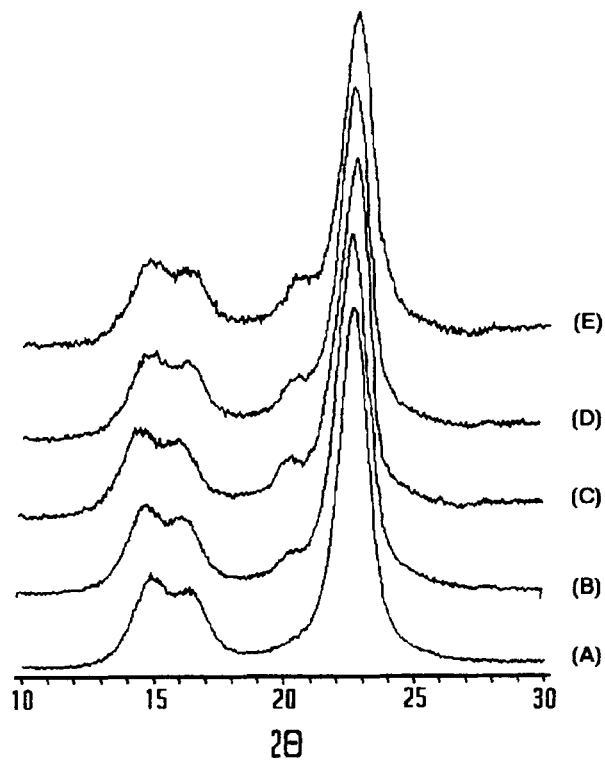

Figure 9   X-ray diffractograms of ramie hydrolyzed in 1.5% H_2SO_4 at 180°C: (A) prehydrolyzed sample; (B) 7% weight loss; (C) 38% weight loss; (D) 57% weight loss; (E) 72% weight loss.

perimental data are available for additional samples of cellulose I. With the development of this linear relationship and the same approach to predicting the rate constants for cellulose II samples employed above, one can predict the rate constants for cellulose I samples via determinations of their degrees of polymerization.

X-Ray Diffraction Analysis

Ellefsen and co-workers[12] have reported that a new crystalline modification of cellulose, cellulose x, is formed when cellulose is dissolved in concentrated phosphoric acid or hydrochloric acid for some time and then precipitated from the solution. Atalla et al.[13] have indicated that the structure of a cellulosic material may change when it is treated with various solvents at high temperatures. In order to investigate whether or not reaction rates are influenced by changes in structure during the hydrolysis process (e.g., cellulose II → cellulose IV), X-ray diffraction analyses were used to investigate whether the structures of cellulosic materials change during hydrolysis. Prehydrolyzed and hydrolyzed ramie, mercer-
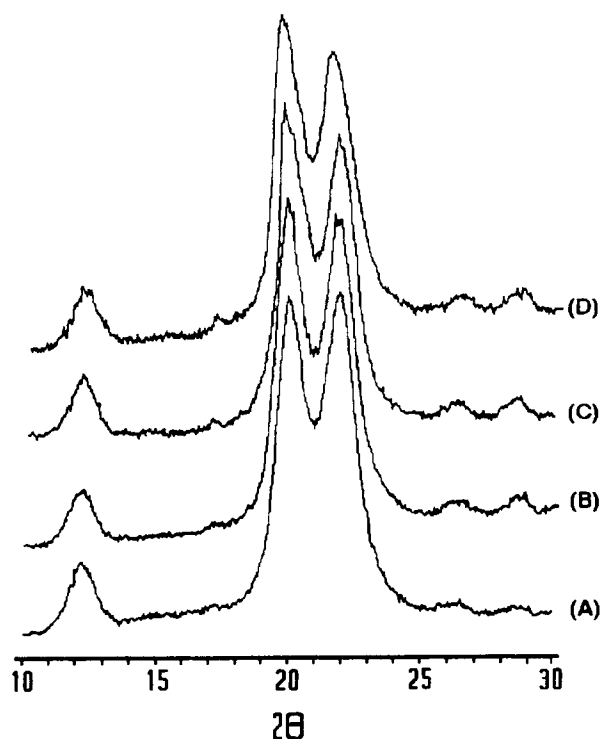

Figure 11   X-ray diffractograms of rayon hydrolyzed in 1.5% H_2SO_4 at 180°C: (A) prehydrolyzed sample; (B) 21% weight loss; (C) 31% weight loss; (D) 45% weight loss; (E) 64% weight loss.

Figure 10   X-ray diffractograms of mercerized linen hydrolyzed in 1.5% H_2SO_4 at 180°C: (A) prehydrolyzed sample; (B) 29% weight loss; (C) 48% weight loss; (D) 63% weight loss.
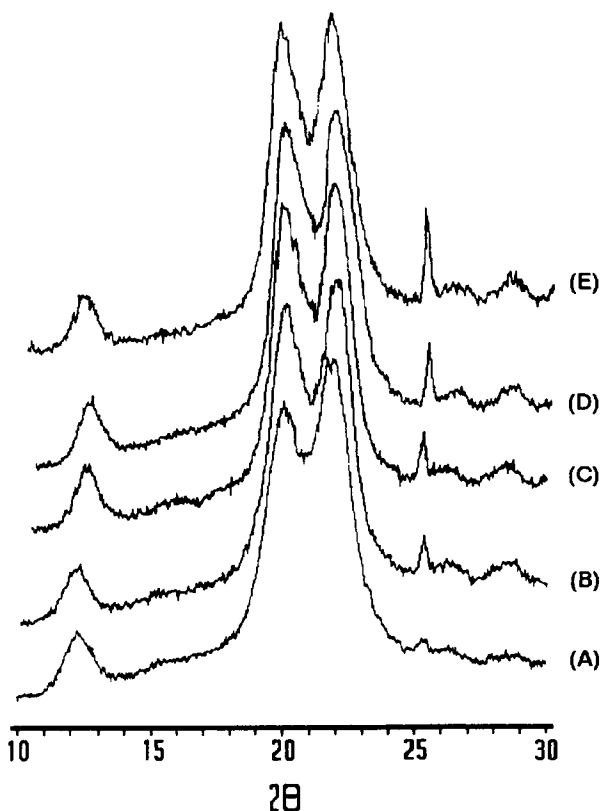
ized linen, and rayon were taken as representatives of native, mercerized, and regenerated celluloses, respectively. Native cellulose is characterized by a cellulose I structure, while both mercerized and regenerated celluloses possess the cellulose II structure.

X-ray diffractograms of ramie, mercerized linen and rayon at various extents of weight loss are shown in Figures 9, 10, and 11, respectively. Inspection of Figure 9 indicates that a small peak ($10\bar{1}$) develops at ca. 20.5° when the prehydrolyzed ramie sample is hydrolyzed. Although this feature indicates the occurrence of structural change during hydrolysis, the $10\bar{1}$ peak is very small. Hence the extent of the structural change is not significant. Typical X-ray diffractograms of various cellulose structures are shown in Figures 12[13] and 13.[12] Comparison of the data in Figure 9 with these diffractograms indicates that the highly hydrolyzed ramie still retains a cellulose I structure. No evidence for a cellulose IV structure is observed in the data for the hydrolyzed ramie samples.
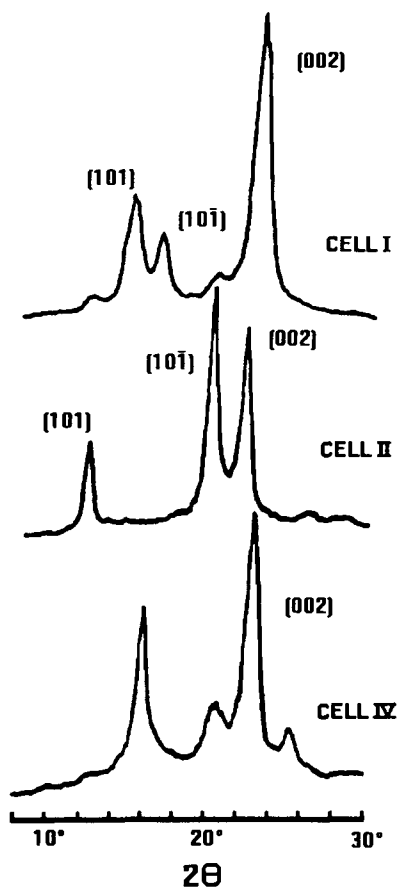
Figure 12 Diffractograms of high crystallinity samples of cellulose I, II, and IV. The cellulose I sample contains a small residue of cellulose II. All samples correspond to a low DP cellulose. (Adapted from Atalla et al.,[13] p. 471, reprinted by courtesy of Marcel Dekker, Inc.)

In the diffractograms of a very pure, crystalline cellulose II structure, the intensity of the 101 peak should be larger than that of the 002 peak. Examination of the data in Figure 10 for the prehydrolyzed mercerized linen reveals that the two peaks are of comparable intensity. As the hydrolysis time increases, the intensity of the 002 peak decreases relative to that of the 10$\bar{1}$ peak. This observation may indicate that in the mercerized sample of linen, there is some residual cellulose I, which hydrolyzes faster than the cellulose II which constitutes the bulk of the sample. This explanation is consistent with the values of the rate constants for linen and mercerized linen. Comparison of the diffractograms in Figure 10 with those in Figure 14[12] reveals that the amount of cellulose I residue present in the prehydrolysed mercerized linen is very small (< 10%). Hence the kinetics of the hydrolysis of mercerized samples

should not be complicated to any significant extent by the occurrence of structural rearrangements. As in the case of the ramie sample, there was no indication of the formation of a cellulose IV structure for the highly hydrolyzed mercerized linen.

The diffractograms of prehydrolyzed and hydrolyzed rayon are shown in Figure 11. Because no peak characteristic of cellulose IV appears at ca. 16°, it is apparent that no cellulose IV is formed. As the hydrolysis time increases, a very sharp peak develops at ca. 25.5°. This peak may be attributed to an impurity present in the initial sample. Since the intensity of the impurity peak increases as the hydro-
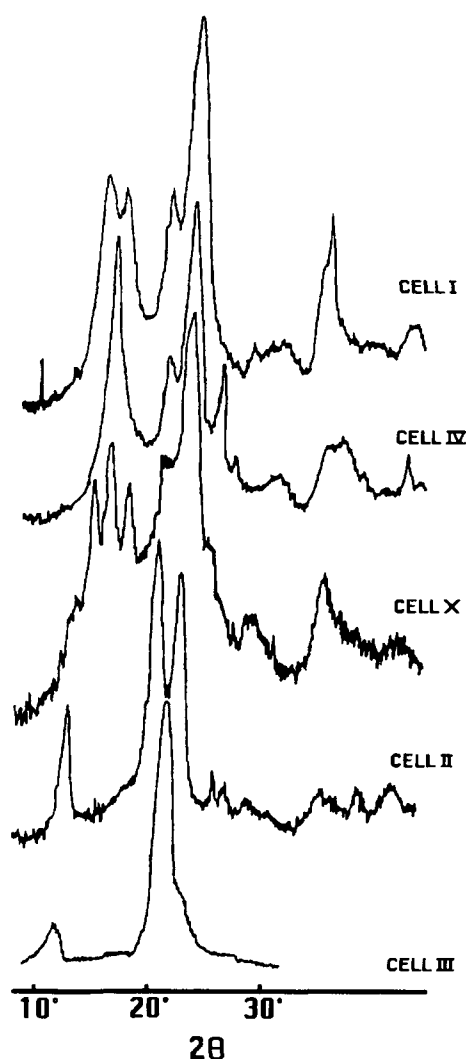

Figure 13 X-ray diffractograms of different modifications of cellulose. (Adapted from Ellefsen and Tonnesen,[12] reprinted by permission of the copyright owner, John Wiley & Sons, Inc., © 1971.)
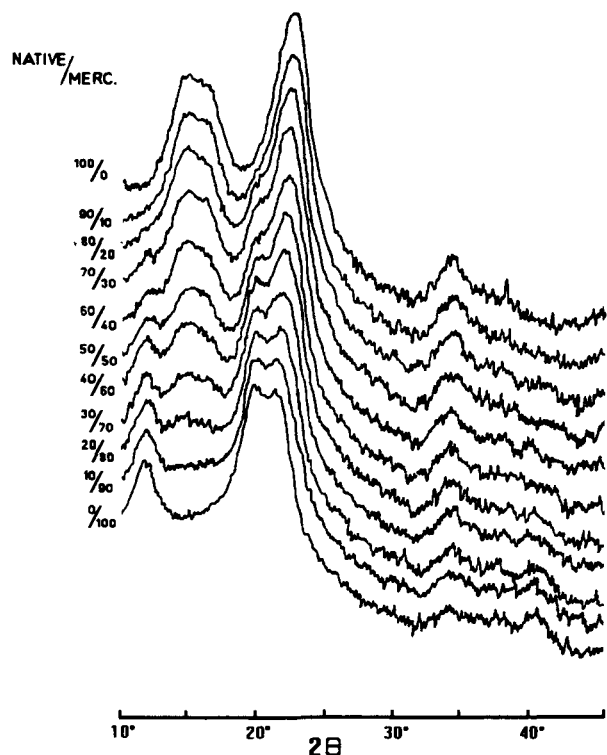
Figure 14 X-ray diffractograms of prepared mixtures of native and mercerized grade wood pulp. (Adapted from Ellefsen and Tonnesen,[12] reprinted by permission of the copyright owner, John Wiley & Sons, Inc., © 1971.)

lysis time increases, it is evident that the impurity is insensitive to hydrolysis. From the relative intensities of the $10\bar{1}$ and 002 peaks of the prehydrolyzed rayon sample and from a comparison of the diffractograms in Figure 11 with those in Figure 14, it appears that rayon sample contains more cellulose I residue than does the mercerized linen sample. The hydrolysis rate constants determined for rayon should thus actually correspond to those for a structure representing a combination of cellulose I and cellulose II structures. Since cellulose I and cellulose II derived from the same source do not hydrolyze at the same rate, the presence of this cellulose I residue may affect the kinetics of the hydrolysis of the rayon samples. The rayon sample used in this study is a commercial product, and no information regarding its origins or the regeneration process employed is available. Hence there is no way that the rate constant data for rayon can be corrected to account for the presence of cellulose I residue. The fact that rayon is a mixture of cellulose I and cellulose II might be one reason that eq. (2) cannot predict the hydrolysis rate constants for rayon very well.

CONCLUSIONS

The conclusion drawn in the previous study that the hydrolysis behavior of cellulose II samples is consistent with Sharples' end-attack model is again confirmed. Differences in the rates of hydrolysis of cellulose II samples result from differences in the degrees of polymerization of these samples. Sharples' model is not appropriate for use with cellulose I samples. In these samples the degree of polymerization is not the only factor which influences the rates of hydrolysis of celluloses from different sources. Statistical treatment of the kinetic data provides a general mathematic expression for the pseudo-first-order rate constants as a function of acid concentration and temperature. This mathematical model can be used to predict the rate constants of the samples used in this study under various reaction conditions. X-ray diffraction analyses indicate that for native and mercerized celluloses no kinetically significant structural changes occur during dilute acid hydrolysis.

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