KINETICS OF ALKALINE THERMOCHEMICAL DEGRADATION OF POLYSACCHARIDES TO ORGANIC ACIDS

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INTRODUCTION

Very little research has been done to explore commercial application of the thermochemical degradation of polysaccharide materials to organic acids in alkaline solution. Much of the work on alkaline degradation of polysaccharides has been conducted at 100°C or lower to investigate mechanisms of degradation, reaction termination and the effects of molecular structure (1-4). However, little conversion of polysaccharides to acids occurs at these low temperatures. Most investigations at higher temperatures have involved study of the alkaline pulping process at approximately 170°C (5,6), where polysaccharide degradation is limited and not desired. Chesley et al. (7) proposed a commercial method for producing formic, acetic, glycolic and lactic acids from cellulosic materials. However, optimum process parameters were not clear, kinetic data was not obtained, additional acids were not identified, and most of the starting polysaccharide material was not accounted for. More recent work has provided additional information on the thermochemical degradation of cellulose to organic acids at reaction conditions of practical interest (8,9). However, no additional organic acids were identified, and the acid production data was difficult to interpret because of long heat-up times. No data has been reported for the important polysaccharide, starch, at reaction conditions of practical interest.

The object of this study was to obtain and compare kinetic data for the thermochemical degradation of starch and cellulose to organic acids in alkaline solution. Reaction conditions leading to substantial or complete degradation in short times were selected so that the results could have practical application to the production of organic acids. Data for the formation of seven identified acids were also collected to allow determination of reaction conditions leading to optimum yields. The reaction system used in a previous study (8) was modified to allow rapid attainment of reaction temperatures, thus making kinetic data more easily analyzed.

EXPERIMENTAL

Materials

Starch used in experiments was commercial, food-grade starch (CPC International Inc. Englewood Cliffs, NJ) having a moisture content of 13%. Cellulose was purchased commercially as a highly purified, finely powdered product (Cellulay-Cellulose, United States Biochemical Corp., Cleveland, OH) and had a moisture content of 6%.

Formic acid (88%) (Fisher Scientific Co., Fair Lawn, NJ), glacial acetic acid (J. T. Baker Chemical Co., Phillipsburg, NJ), glycolic acid, L(+)-lactic acid (grade L-1), DL-α-hydroxybutyric acid (sodium salt), α-hydroxyisobutyric acid and DL-α-hydroxyvaleric acid (sodium salt) (Sigma Chemical Co., St. Louis, MO) were used as standards in HPLC and GC analyses. Glutaric acid (Mallinckrodt, Inc., St. Louis, MO) was used as an internal standard in the GC analyses. Boron trifluoride (14% in propanol) (Eastman Kodak Co., Rochester, NY) was used as a derivatizing agent to produce propyl esters of the organic acids for GC analyses.

Reactions

All reactions were performed under nitrogen in a 1-L magnetically stirred autoclave equipped with a cooling coil (Model AFP 1005, Autoclave Engineers, Erie, PA). Each experiment was run by first adding 167g of aqueous solution containing 10g of NaOH to the autoclave and heating the sealed autoclave to the desired temperature plus 5-10°. A well-mixed slurry of 10g of starch or cellulose (moisture free) in 85g of water was then added to an adjacent Kuentzel vessel (Vessel KD-19.3-SS11, Autoclave Engineers, Erie PA) which had tubing with a ball valve leading from its bottom to the stirred autoclave. The tubing extended through the head of the stirred autoclave to below the surface of the alkaline solution. After addition of the starch or cellulose slurry, the Kuentzel vessel was quickly sealed and connected to a nitrogen cylinder. The Kuentzel vessel was pressured to 100 psi above the pressure in the stirred autoclave, and the starch or cellulose slurry was injected into the hot alkaline solution in the stirred autoclave by opening the ball valve. The resulting solution volume was 250ml and it contained 10g of starch or cellulose (0.25M based on glucose monomer) and 10g of NaOH (1.00N). This solution dropped below the target reaction temperature for a short time, but returned to the desired temperature in 1-3 min. The reaction was timed from the moment of injection.

Experiments were conducted at temperatures between 180 and 300°C, and the reactants were held at the selected temperature for varying times to determine the effect of reaction time. The temperature dropped quickly upon flow of water through the cooling coil and removal of the autoclave heater. The time required to cool the reactants to below 100°C was 5-15 min.

After cooling to room temperature, the autoclave was opened and the reaction products were suctioned out. In the case of cellulose, any unreacted material appeared as a solid residue in the reaction solution. Any residue was filtered from the reaction solution and then extracted with water. The filtrate was combined with extract, and an aliquot of the combined solution was titrated for total organic acids. The solid residue was dried at 40°C for 24 hr. in a forced-air oven and then at 98°C for 24 hr. in a vacuum oven. In the case of starch, any unreacted starch was soluble in the alkaline product solution. An aliquot of the solution was titrated for total acids. Unreacted

starch was precipitated quantitatively with acetone (10). A 5.0g aliquot of the product solution was neutralized with 2.0N HCl to pH 7 and 25ml of acetone was added. After sitting overnight, the starch precipitate was separated by centrifugation, washed with 20ml of a 1:3 acetone-water solution, separated again by centrifugation, and finally dried in the same manner as for cellulose solid residue.

High-Performance Liquid Chromatography

Filtered product solutions from reactions with starch and cellulose were analyzed using a Waters Associates high-performance liquid chromatograph model ALC 201 equipped with a refractive index detector model R-401 (Waters Associates, Milford, MA) to identify water-soluble products. This was accomplished by matching retention times of product compound peaks with retention times of standards. A 300 mm x 7.8 mm Aminex HPX-87H organic acid analysis column (Bio-Rad Laboratories, Richmond, CA) was used. Elution was carried out at 60°C using 0.002N H_2SO_4 at a flow rate of 0.5 ml/min. Data acquisition from the chromatographic system was by the Hewlett-Packard integrating recorder model 3388A (Hewlett Packard Co., Palo Alto, CA).

Gas Chromatography

To verify the compounds identified by HPLC, both standards and product solutions were converted to their propyl esters with BF_3-propanol according to the method of Salwin and Bond (11). Analysis of the esterified compounds was performed on a Hewlett Packard 5880A gas chromatograph equipped with a flame ionization detector and a bonded Superox FA (Alltech Assoc., Inc. Deerfield, IL) fused-silica capillary column (25m x 0.25mm I.D., 0.2 µm film thickness). The temperature program was 100°C to 240°C at 5°C/min and 10 min at 240°C. The injector temp was 225°C and the detector temp was 300°C. Carrier flow (He) was 1.0 ml/min. Injection volume was 1µl with a split ratio of 80:1.

RESULTS AND DISCUSSION

Degradation of Starch and Cellulose

An analysis of the data was performed to determine whether starch and cellulose degradation in alkaline solution could be described by second-order kinetics according to the equations:

$$\text{polysaccharide} + N\cdot\text{alkali} \longrightarrow \text{products} \qquad 1)$$

$$\frac{dC_p}{dt} = -k_a C_p C_a \qquad 2)$$

$$\ln \frac{C_a}{C_p} = \ln M + C_{p_o}(M-N)k_a t \qquad 3)$$

$$M = C_{a_o}/C_{p_o} \qquad 4)$$

$$N = (C_{a_o} - C_a)/(C_{p_o} - C_p) \qquad 5)$$

where k_a is the reaction rate constant for starch or cellulose in alkaline solution, C_p is the concentration of starch or cellulose, C_{p_o} is the concentration of starch or cellulose at t=0, C_a is the concentration of alkali, C_{a_o} is the concentration of alkali at t=0, t is the reaction time, and N is the stoichiometric reactant ratio between hydroxide ion and polysaccharide.

The catalytic effect of the hydroxide ion would normally be represented as part of the reaction rate constant (k_a) for each temperature, because catalyst concentration normally remains constant. However, in the case of alkaline degradation of starch or cellulose, organic acids are produced which are converted to their salts by the alkali present, thus reducing the hydroxide ion concentration. Therefore, it seemed that this degradation reaction could be represented by second-order kinetics, with the hydroxide ion concentration determined by the stoichiometry of conversion of starch or cellulose to organic acids.

Figures 1 and 2 show experimental data plotted according to Equation 3 on semilogarithmic graphs to determine applicability of second-order kinetics. The linear plots indicate that the results conform to second-order kinetics quite well. Table I shows the reaction parameters determined for each temperature plotted in Figures 1 and 2.

Table I. Reaction Parameters for Alkaline Degradation

	Starch		Cellulose	
T	N	k_a	N	k_a
°C		liter/mole min.		liter/mole min
180	1.44	0.0026	2.09	0.0034
200	1.17	0.0243	1.85	0.0194
220	1.16	0.1334	1.71	0.1189
240	1.16	0.3733	1.59	0.6000

Interestingly, although $M = C_{a_o}/C_{p_o} = 4.0$ for both starch and cellulose, extrapolating the data plotted in Figures 1 and 2 back to t = 0 gives M = 5.0 for starch and M = 4.6 for cellulose. Thus, M increased from 4.0 to 5.0 for starch and 4.6 for cellulose in very little or no time instead of the expected finite time. Considering that M eventually reaches infinity for the systems studied, this represents a small fraction of more easily degraded polysaccharide. The results of this paper apply to the more resistant fractions of starch and cellulose, which constitute the bulk of those polysaccharides.

Figure 3 shows the reaction rate constants determined from the slopes of the lines in Figures 1 and 2 plotted against the reciprocal of absolute temperature on a semilogarithmic graph. The slope of the line through the points allows determination of the reaction activation energy according to the Arrhenius equation: $k = k_o\ e\ \exp(-E/RT)$. The value of E determined in this manner is 39,500 calories/mole, which appears to apply equally well to the degradation of starch or cellulose.

Production of Organic Acids

The values of N calculated for starch and cellulose shown in Table I reveal that as these polysaccharides were degraded by alkali, a smaller number of organic acid molecules were formed from each glucose monomer in starch compared to cellulose. This means that the organic acids produced initially from starch had a greater molecular weight than those produced from cellulose. This is illustrated clearly in Figure 4, which shows equivalents of organic acids produced from the degradation of starch or cellulose as a function of time. Although starch and cellulose degrade at the same rate, the rate of total organic acid formation was less for starch, and fewer equivalents of organic acids were produced in a given time from starch than from cellulose. The relative difference decreased as the temperature increased, and at higher temperatures the difference in total equivalents of organic acids produced disappeared at short times. A maximum concentration of approximately 0.45 equivalents/L of total organic acids was produced for both starch and cellulose for the reaction systems studied. Apparently, in starch degradation, the initially larger molecules of organic acids eventually break down into a larger number of smaller organic acids. Therefore, the total organic acid formation for starch ultimately equals that for cellulose. Since the starting concentration of starch and cellulose was 0.25 mol/L based on the glucose monomer, the average equivalent weight for the organic acids produced is (0.25)(180)/(0.45) = 100g/eq. This assumes that all the polysaccharide material degrades to acids.

The HPLC chromatograms of the alkaline degradation products of starch and cellulose were quite similar. Based on retention times of standards, formic, acetic, glycolic, lactic, 2-hydroxybutyric and 2-hydroxyvaleric acids were identified. The GC chromatograms of the propyl esters of the starch and cellulose chromatograms were also quite similar. Since GC gave much better separation of degradation products than HPLC, the GC chromatograms were used to calculate the yields of glycolic, lactic, 2-hydroxybutyric and 2-hydroxyvaleric acids. Formic and acetic were hidden under the GC solvent peak; thus, their yields were determined from the HPLC chromatograms. In addition, 2-hydroxyisobutyric, which was hidden under the HPLC lactic peak, was identified and quantified with GC. Tables II and III give the maximum yields of these acids at several temperatures. The corresponding times at temperatures to achieve maximums are included in the headings.

Table II. Maximum Organic Acid Yields from Degradation of Starch in Alkaline Solution

	Yields[1] %			
	240°C 30 min[2]	260°C 30 min	280°C 20 min	300°C 5 min
Formic	10.5	10.9	10.5	10.2
Acetic	1.6	1.9	2.3	2.1
Glycolic	3.4	4.5	5.3	5.6
Lactic	16.9	17.5	19.1	19.0
2-Hydroxybutyric	2.3	2.9	3.6	3.6
2-Hydroxyisobutyric	2.4	2.6	2.7	2.5
2-Hydroxyvaleric	1.1	1.4	1.6	1.3
Total	38.2	41.7	45.1	44.3

[1]Based on starting dry weight of starch

[2]Maximum not yet attained

Table III. Maximum Organic Acid Yields from Degradation of Cellulose in Alkaline Solution

	Yields[1] %			
	240°C 32 min	260°C 18 min	280°C 6 min	300°C 3 min
Formic	10.8	10.9	10.7	10.2
Acetic	1.6	1.9	1.7	1.7
Glycolic	4.6	4.8	5.5	5.2
Lactic	19.8	19.9	20.4	18.5
2-Hydroxybutyric	3.4	3.3	3.5	3.4
2-Hydroxyisobutyric	2.1	2.1	2.1	1.9
2-Hydroxyvaleric	1.3	1.6	1.4	1.3
Total	43.6	44.5	45.3	42.2

[1]Based on starting dry weight of cellulose

Consistent with the results for rates of total acids produced shown in Figure 4, it took a longer time to reach the maximum yields starting with starch compared to cellulose. The maximum yields of the identified product acids at each temperature were quite similar for starch and cellulose starting materials. The time required to reach the maximum yields decreased as temperature increased. The trade-off is the higher operating pressure at higher temperature. The total yields of the identified acids appear to reach an optimum at approximately 280°C for both starch and cellulose.

The similarity in maximum yields for the identified product acids from starch and cellulose suggests similar or identical reaction pathways. The slower rate for acid formation from starch could be explained by dissolved starch polymer or partially degraded starch polymer interfering with additional degradation of initial conversion products. The greater ease with which starch polymer dissolves in alkaline solution compared to cellulose is consistent with this possibility.

Although significant amounts of other organic acids are produced, lactic acid is the major product for the reaction conditions studied. As well as having numerous direct uses, lactic acid has the potential of being an important intermediate in the production of other valuable products (12, 13). Preliminary economic analysis indicates that production of lactic acid from alkaline degradation of cellulose has economic merit (9). It is also conceivable that all the hydroxy acids produced could be used together without separation to produce polyester materials.

CONCLUSIONS

Starch and cellulose can both be thermochemically degraded in alkaline solution to water soluble compounds of relatively low molecular weight. (A parallel study examines more completely the nature of these compounds (14).) Both starch and cellulose degradation processes can be described by second-order kinetics, with the hydroxide ion concentation determined by the stoichiometry of polysaccharide conversion to organic acids. The thermochemical degradation activation energy in alkaline solution for both starch and cellulose is 39,500 calories/mole.

The production of organic acids from starch proceeds more slowly than from cellulose. Ultimately, however, the yields of acids are quite similar from both. Formic, acetic, glycolic, lactic, 2-hydroxybutyric, 2-hydroxyisobutyric and 2-hydroxyvaleric acids are produced in significant amounts. The maximum yield of lactic acid is approximately 20%, and the maximum sum total yield of all identified acids is approximately 45% for the conditions investigated.

Increasing the yields of the desirable acids produced from the thermochemical, alkaline degradation of polysaccharides will require additional understanding of the reaction mechanisms and kinetics involved. Additional research should also proceed to determine the effect of other bases and supplementation of alkali catalysis by other catalytic materials.

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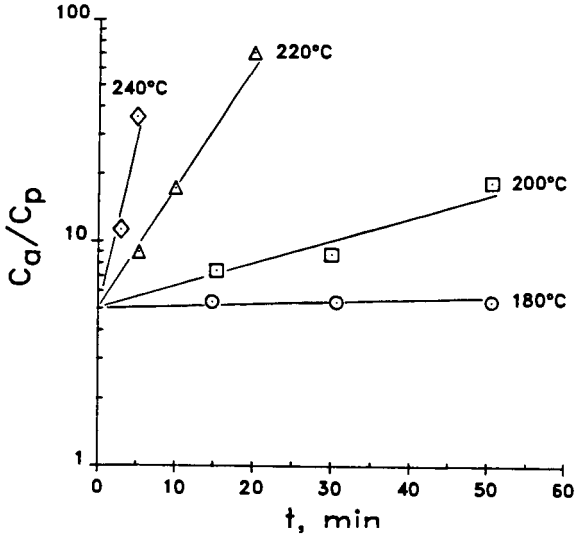

Figure 1. Effect of time on thermochemical degradation of starch in alkaline solution according to Eq. 3.

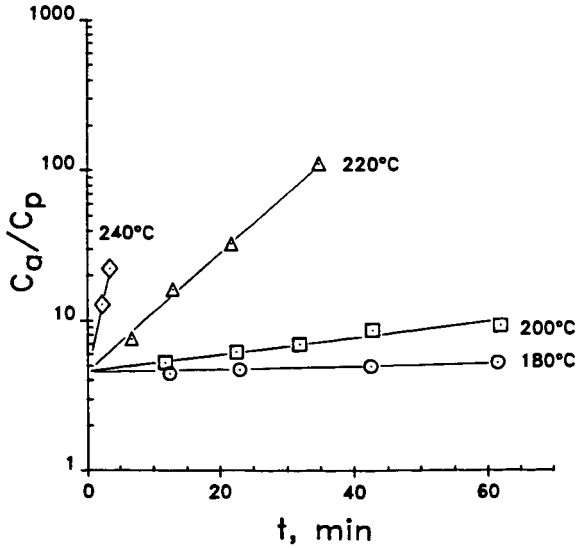

Figure 2. Effect of time on thermocnemical degradation of cellulose in alkaline solution according to Eq. 3.

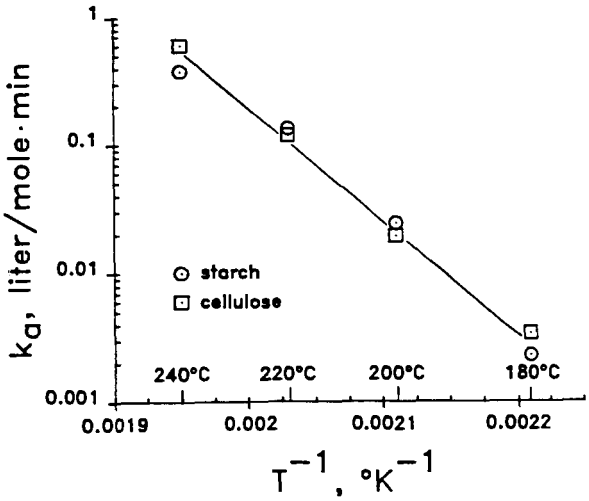

Figure 3. Relation of second-order reaction rate constants for starch and cellulose to temperature according to Arrhenius equation.

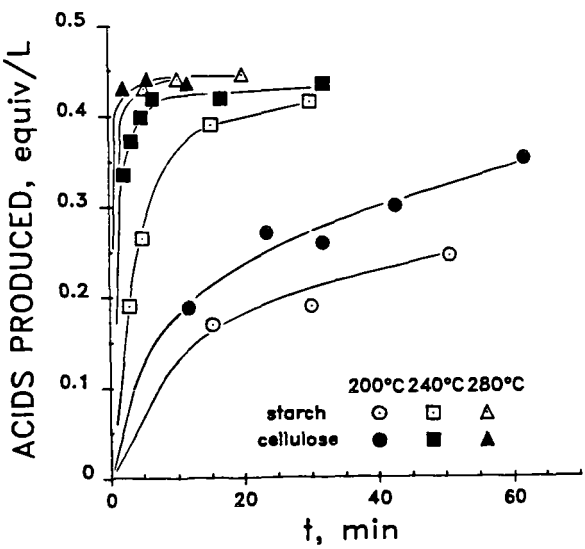

Figure 4. Effect of time on organic acid production from thermochemical degradation of starch and cellulose in alkaline solution.