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Influence of carboxyl group on the acid hydrolysis of cellulose

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Abstract Cellulose isolated from wood is more susceptible than cotton cellulose to homogeneous hydrolysis in phosphoric acid. The influence of carboxyl group introduction at the C6 position on the hydrolysis rate of cellulose in 82.5% phosphoric acid was studied as a model of the oxidation of cellulose during pulping. The rate constant of hydrolysis for dissolving pulp was larger than that of cotton cellulose at temperatures of 25°–35°C. Mercerized cotton cellulose was partially oxidized regioselectively at the C6 position by a free radical system using 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO). The oxidized cellulose was obtained at a range of 1.7–12.7 mEq carboxyl content per 100g of cellulose. The hydrolysis rate of the oxidized cellulose samples accelerated with increasing carboxyl content in the samples.

Key words Hydrolysis of cellulose · Phosphoric acid · TEMPO

Introduction

Cellulose isolated from wood is more susceptible to homogeneous hydrolysis in phosphoric acid than is cotton cellulose.^{1,2} The electron-withdrawing groups, such as carboxyl groups, introduced to the C6 position of cellulose during pulping are thought to accelerate the hydrolysis of cellulose. The carboxyl group seems to form an activated part (*a* bond in Fig. 1) in glycosidic linkages, where hydrolysis is rapidly catalyzed.

Lindberg³ studied the hydrolysis of low-molecular-weight model compounds such as pseudocellobiouronic acids in sulfuric acid instead of phosphoric acid. Usuda et al.⁴ studied the hydrolysis of cellulosic substances oxidized with nitrogen dioxide. However, the influence of carboxyl groups introduced regioselectively at the C6 position of cellulose on the hydrolysis rate is not known.

Isogai^{5,6} developed the method for preparing polyglucuronic acid mediated with 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) free radical. Their method is advantageous in respect to highly regioselective introduction of the carboxyl groups at the C6 position to cellulose. The regioselectively oxidized celluloses should be useful for studying the influence of the carboxyl group on the hydrolysis of cellulose.

In this study we prepared regioselectively oxidized samples with a range of carboxyl contents from mercerized cotton cellulose using the method of TEMPO free radical oxidation. Here we discuss the influence of the carboxyl group on the hydrolysis rate of cellulose.

Experiments**Materials and reagents**

Commercial grade dewaxed cotton for absorbents (Hakuzo Medical, Osaka, Japan) and dissolving pulp (Nippon Paper Industries, Tokyo, Japan) were used as the cellulose samples. Before hydrolysis the dissolving pulp was defiberized and freeze-dried. Reagent grade 85% phosphoric acid was used for hydrolysis. TEMPO free radical was obtained from Tokyo Kasei Kogyo (Tokyo, Japan). All the other reagents were reagent grade.

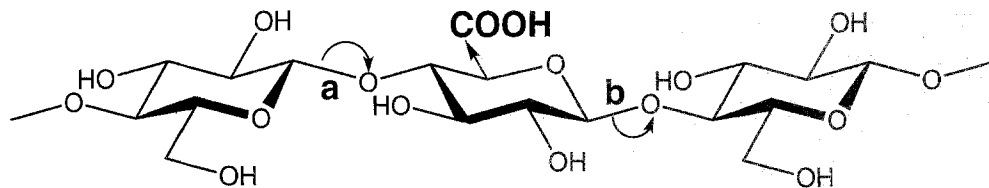
Preparation of oxidized cellulose

Cotton cellulose was mercerized by suspending it in 17.5% NaOH for 1h, followed by washing with distilled water (about pH6) until the washings became about pH 6. The

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Fig. 1. Hypothesis of the inductive effect^{1,2}



a: activated, b: stabilized

TEMPO oxidation was carried out according to the method of Isogai.^{5,6} KBr was used instead of NaBr. All reagents were 1/64, 1/48, and 1/32 of the amount sufficient to prepare polyglucuronic acid; that is, the TEMPO used was 1.6×10^{-4} to 3.1×10^{-4} equivalent (eq.) of primary alcohol, KBr 5.9×10^{-3} to 1.2×10^{-2} eq., and NaClO 1.6×10^{-2} to 3.1×10^{-2} eq. Ten samples containing different carboxyl contents (1.7, 2.6, 3.1, 3.5, 6.7, 7.6, 8.0, 9.6, 12.4, 12.7 mEq carboxyl group in 100 g cellulose) were prepared by varying the amounts of reagent used and the reaction time (11–210 min). The oxidized celluloses were freeze-dried before hydrolysis.

Determination of carboxyl content

The carboxyl content was determined by titrating with calcium acetate solution.⁷

Hydrolysis

The rate of hydrolysis was followed by measuring solution viscosity. An Ostwald-type viscometer (efflux time for water was 10 s at 20°C) was used. The phosphoric acid solution for hydrolysis was prepared by adding one part distilled water to five parts 85% phosphoric acid. The efflux time of this solvent was about 90 s at 30°C. The efflux time was reproducible within 0.1 s on repeated runs.

To the weighed cellulose samples in an Erlenmeyer flask was added 85% phosphoric acid. The suspension was then shaken until a homogeneous solution was obtained. The cellulose/solution ratio was 2 mg/ml for cotton cellulose and 4 mg/ml for dissolving pulp. The solution was diluted with distilled water to prepare the 82.5% phosphoric acid solution. The solution was then filtered through a G3 sintered glass filter.

When hydrolysis proceeds as a homogeneous first-order reaction, the rate constant k and specific viscosity η_{sp} can be approximately related by

$$\Delta(1/\eta_{sp}) = kt \quad (2mKW)$$

where t is the reaction time, m is the molecular weight of the anhydrous glucose unit (162), K is a constant ($2.77 \times 10^{-5} \text{ dl} \cdot \text{g}^{-1}$), and W is the amount of solute (g) in 1 dl of solution. Thus, the value of k can be evaluated from the slope ($k/2mKW$) of the regression line between $1/\eta_{sp}$ versus t .

Table 1. Carboxyl content and rate constants for cotton cellulose and dissolving pulp

Sample	Carboxyl content (mEq/100g cellulose)	$k \times 10^8 \text{ (s}^{-1}\text{)}$		
		25°C	30°C	35°C
Cotton cellulose	2.0	2.41	5.53	12.1
Dissolving pulp	4.3	2.76	6.63	16.4

k , rate constant

Results and discussion

Marchessault and Rånby^{1,2} reported that the hydrolysis rate of cellulose originating from wood is larger than that of cotton cellulose at temperatures of 20–40°C. Similar results were obtained by Usuda et al.⁴

Table 1 shows the carboxyl content and rate constants for cotton cellulose and dissolving pulp. The dissolving pulp with a higher content of carboxyl group was hydrolyzed 1.1–1.4 times faster than cotton cellulose at temperatures of 25–35°C. The position of the carboxyl group in the dissolving pulp is not easily determined, although a carboxyl group in the repeating glucose unit is likely to be present at C6. Thus, oxidized celluloses with a carboxyl group at the C6 position of cellulose can be used to clarify the relation of the carboxyl group content and the hydrolysis rate. The cellulosic samples containing a range of the carboxyl groups were prepared by TEMPO oxidation.

Figure 2 shows the changes in carboxyl content of the cotton cellulose as a function of the oxidation time with TEMPO. The carboxyl content appears to level off within about 2 h, and the final carboxyl content was determined by the quantity of the oxidizing reagent. A total of 10 oxidized cellulosic samples, as described in the experimental section, were obtained. TEMPO oxidation is a useful method for preparing a wide range of oxidized cellulosic samples. The carboxyl content could be controlled by the reaction time and the amount of oxidizing reagents. In the present study, samples with 1.7–12.7 mEq of carboxyl content per 100 g cellulose (0.27–2.0 glucuronic acids per 100 glucose units) were selected. This is because both the cotton cellulose and dissolving pulp used had relatively low carboxyl content (2.0 and 4.3 mEq, respectively). Oxidized cellulose with a much higher carboxyl content did not dissolve in 85% phosphoric acid.

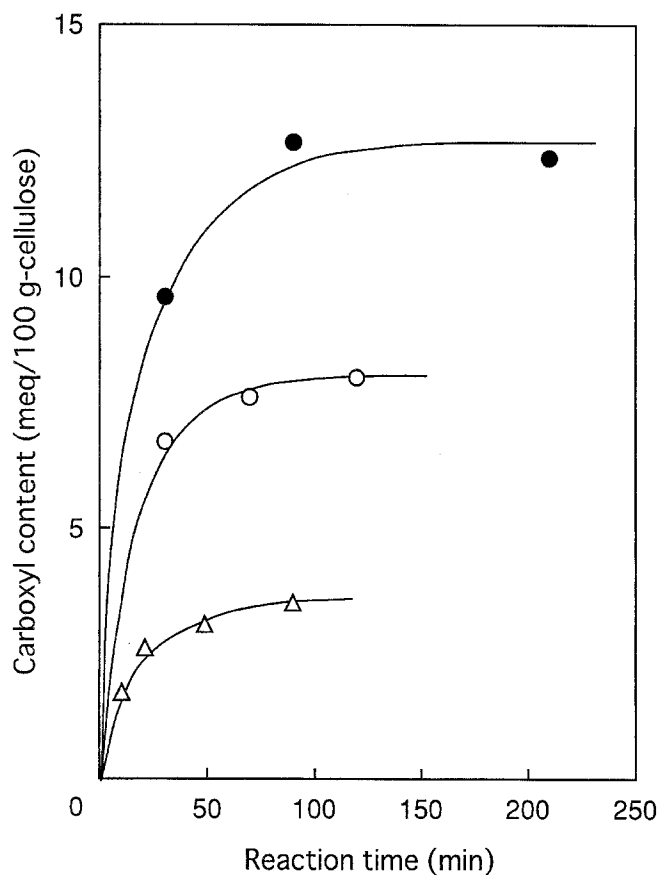


Fig. 2. Changes in carboxyl content. *Triangles*, 1/64; *open circles*, 1/48; *filled circles*, 1/32 of the amount of reagents sufficient to obtain polyglucuronic acid

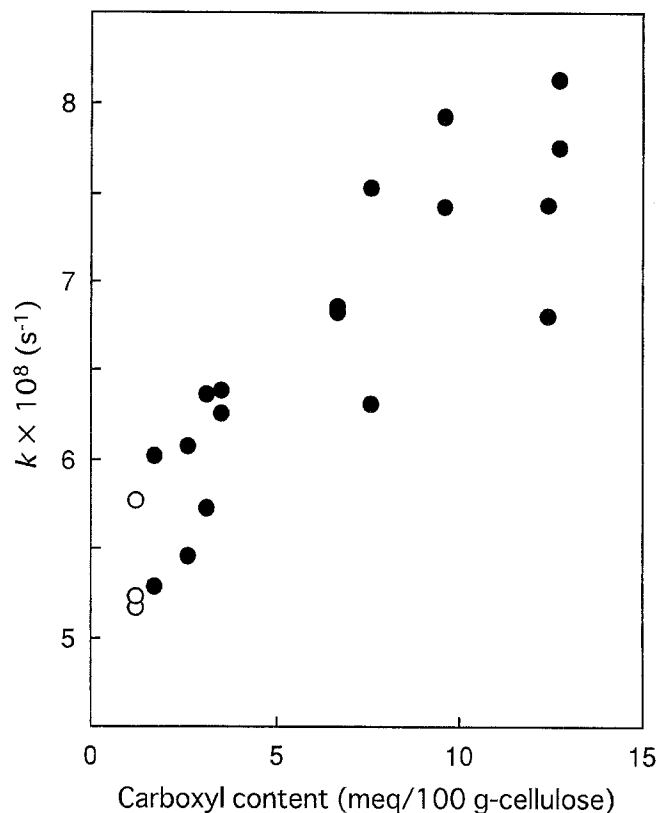


Fig. 3. Relation between hydrolysis rate and content of carboxyl groups. *Open circles*, mercerized cellulose; *filled circles*, oxidized cellulose

Figure 3 shows the relation between the hydrolysis rates and carboxyl content of oxidized cellulose and mercerized cellulose. The hydrolysis was performed at 30°C. The results clearly indicate that the hydrolysis rate increases linearly with an increase in carboxyl content.

Lindberg³ reported that a carboxyl group at the C6 position does not accelerate the reaction from the hydrolysis of cellobiouronic acid, cellobiose, and pseudocellobiouronic acid in sulfuric acid. The difference between Lindberg's and our results may be explained by the hydrolysis conditions, especially the acid used. In fact, Nakano and Rånby⁸ reported that methylglucuronic acid and methylglucoside in concentrated phosphoric acid are hydrolyzed with a reaction mechanism different from that in dilute sulfuric acid.

Furthermore, Usuda et al.⁴ reported that the hydrolysis rate of cellulose oxidized by nitrogen dioxide does not increase even if the carboxyl content increases from 2.4 to 18.0 COOH mEq/100 g cellulose. Because the selectivity of nitrogen dioxide oxidation is lower than that of TEMPO oxidation, the oxidation may occur not only at the C6 position but also at the C2 and C3 positions.⁹

The activation energy of oxidized cellulose decreased with an increase in the content of carboxyl groups (Fig. 4).

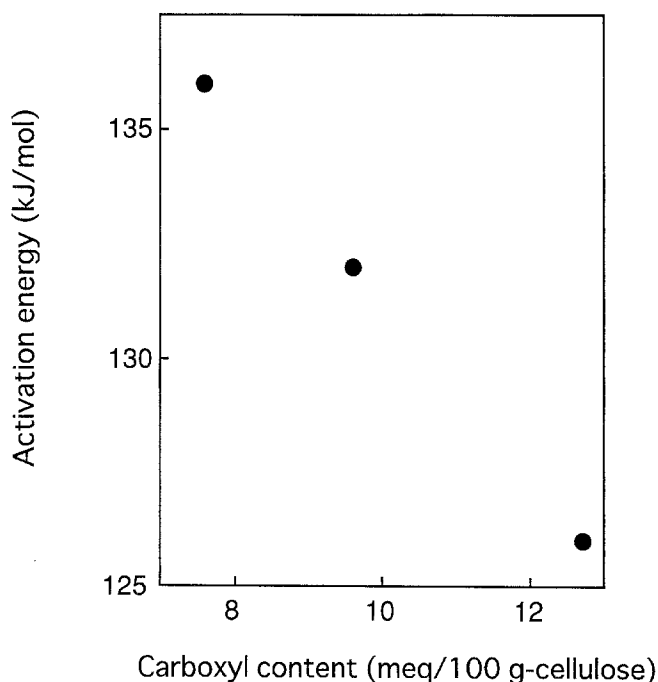


Fig. 4. Relation between activation energy and content of carboxyl groups in oxidized cellulose

Conclusions

Dissolving pulp contained more carboxyl groups than cotton cellulose; and the former in concentrated phosphoric acid at 25°, 30°, and 35°C was hydrolyzed at a higher rate than the latter. Regioselectively oxidized celluloses with a range of carboxyl concentrations could be prepared by the method of TEMPO free radical oxidation. The greater substitution with carboxyl groups resulted in a higher hydrolysis rate of oxidized celluloses in phosphoric acid. These results can form the groundwork for the difference in hydrolysis rates between cotton cellulose and dissolving pulp.

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