Hydrolysis of Cellulose Fiber in the Presence of 12-Tungstosilicic Acid

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Synopsis

Hydrolysis of cellulose fiber in the presence of 12-tungstosilicic acid was investigated, and the acid was found to show a higher catalytic activity than did hydrochloric acid at the same concentration of acid, although the ratio of the activities of 12-tungstosilicic acid to hydrochloric acid depended on the concentration. The influence of the ionic strength on the reaction rates was examined, and it was believed that the difference in the ionic strength between 12-tungstosilicic acid and hydrochloric acid at the same concentration of acid was one of reasons for the higher catalytic activity of 12-tungstosilicic acid. From the examinations of change in degree of polymerization of the cellulose fiber with the hydrolysis and adsorption behavior of 12-tungstosilicic acid by the cellulose fiber, it was found that 12-tungstosilicic acid, in spite of its bulky structure, easily penetrated into the amorphous region of the cellulose fiber, as does hydrochloric acid, and catalyzed the hydrolysis of glucoside bond there.

INTRODUCTION

The effective use of cellulosic materials as renewable resources has been recognized to be important and hydrolyses of cellulose in the presence of acids or enzyme to glucose, which can be converted into, for example, ethanol with a fermentation process,[1] have been investigated. In the processes, however, the lower yield of glucose in the hydrolysis process, usually up to 50% has been found to cause a bottleneck. In order to solve the problems efforts have been offered.

Catalyses in the presence of a heteropolyacid have been a subject of numerous investigations and effective catalyses have been reported.[2] We have been interested in the hydrolysis of carbohydrates in the presence of a heteropolyacid, and have already found its catalytic activity on the hydrolysis of soluble carbohydrates to be higher than that of hydrochloric acid.[3,4] In the present experiment, the catalytic activity of 12-tungstosilicic acid (a typical Keggin type heteropolyacid) on the hydrolysis of cellulose fiber is examined, and some factors affecting it are discussed.

EXPERIMENTAL

Materials. Pine bleached sulfite pulp was disintegrated and used as a cellulose fiber. All other reagents, including 12-tungstosilicic acid, $H_4SiW_{12}O_{40}$ (from Wako Pure Chemical Co., Tokyo), were used without further purification.

Measurements of Hydrolysis Behavior. About 1 g of cellulose fiber was added to 50 mL of acid solution and kept at 100 or 60°C in a shaking thermostat. After a specific time the reaction mixture was filtered with a

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sintered glass filter and washed with water throughly. The residual cellulose fiber was dried in vacuum and weighed to determine the weight loss caused by hydrolysis, then used for determination of degree of polymerization, DP, according to the measurement of viscosity with the Cu-ethylene diamine method.[5] The filtrate of the reaction mixture was passed through an Amberlite IRA-45 column to remove acid, followed by fractionation of the soluble products according to the ion-exchange chromatography method previously reported.[4]

Adsorption of 12-Tungstosilicic Acid by Cellulose Fiber. About 0.5 g of cellulose fiber was added to 10 mL of 12-tungstosilicic acid aqueous solution and kept at 10°C. After 12 h the supernatant liquid was taken out and dried to determine the concentration of 12-tungstosilicic acid. From the difference in the amounts of 12-tungstosilicic acid in the original and in the supernatant liquid, the amount of 12-tungstosilicic acid adsorbed by the cellulose fiber was calculated, and it was evaluated according to the Langmuir's adsorption isotherm.

RESULTS AND DISCUSSION

Hydrolysis of cellulose is a typical specific acid catalysis and proceeds as follows:
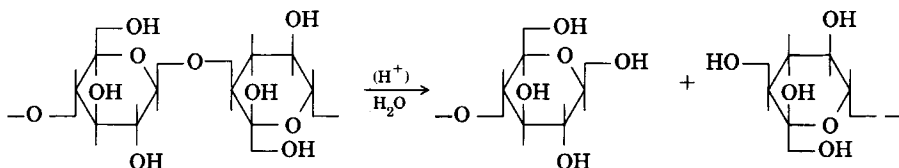
12-Tungstosilicic acid was used as a catalyst, and the catalytic activity on the hydrolysis of cellulose fiber was compared with that of hydrochloric acid. The 12-tungstosilicic acid is a typical Keggin type heteropolyacid and is known to have a form like a ball with a diameter of about 10 Å.[6]

First, the decrease in weight of cellulose fiber with the hydrolysis was examined. Figure 1 shows the plots of residual weight of the cellulose fiber against the reaction time. In the upper figure, the weight of cellulose fiber is found to decrease more in the presence of 12-tungstosilicic acid than in the presence of hydrochloric acid at the same acid concentrations. The lower figure shows the plots of the logarithm of the residual weight against the reaction time, and fairly good straight lines are obtained, except for early stage of the reaction. This result means that the decrease rates of the weight apparently follow pseudo-first-order kinetics. The pseudo-first-order rate constant, k_1, was calculated from the slope of each straight line obtained. The result is tabulated in Table I, where the higher catalytic activity of 12-tungstosilicic acid over that of hydrochloric acid is clearly shown. For both catalysts, furthermore, the value of k_1 is found to increase faster than the increase in acid concentration: For example, in the presence of 12-tungstosilicic acid, the value of k_1 at 1.5N is about 8.7 times larger than that at 0.5N. It is well known that in the higher range of acid concentration the activity coefficient of the hydronium ion increases with an increasing acid
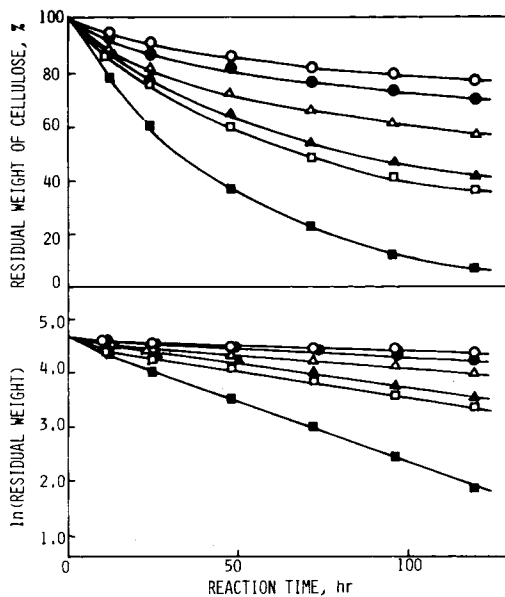
Fig. 1. Decrease in residual weight of cellulose fiber with hydrolysis in the presence of 12-tungstosilicic acid (●,▲,■) or hydrochloric acid (○,△,□), with reaction time, at 100°C. Acid concentration (○,●) $0.5N$; (△,▲) $1.0N$, (□,■) $1.5N$. Cellulose concentration, $0.123M$ as glucose unit.

concentration.[7] The change in k_1 value with an increasing acid concentration was compared with that of activity coefficient of the hydronium ion. Figure 2 shows the plots of logarithm of k_1's and activity of hydronium ion for hydrochloric acid against the logarithm of stoichiometric concentration of the acids. For hydrochloric acid the dependences of k_1 and the activity on the stoichiometric concentration are found to be very similar, which suggests that the k_1 value predominantly depends on the activity of the hydronium ions. For 12-tungstosilicic acid, however, the dependence of k_1 value on the stoichiometric concentration is found to be greater than that for hydrochloric acid. We had found that the activity of hydronium ion of 12-tungstosilicic acid was lower than that of hydrochloric acid at the same stoichiometric concentration, and its increase with the increasing concentration was also lower than that of hydrochloric acid,[4] although the accurate values had not been evaluated. Therefore, for the hydrolysis in the presence of 12-tungstosilicic acid it is inferred that factors other than the activity of hydronium ion also influence on the reaction rate.

12-Tungstosilicic acid is a tetrabasic acid with an ionic strength about

TABLE I

Pseudo-First-Order Rate Constants, k_1's, for the Hydrolysis of Cellulose Fiber in the Presence of 12-Tungstosilicic Acid (SiW) or Hydrochloric Acid (HCl) at 100°C

	SiW			HCl		
Concn (N)	0.5	1.0	1.5	0.5	1.0	1.5
k_1 (10^{-6}s^{-1})	0.75	2.16	6.62	0.54	1.27	2.41
Ratio	1	2.9	8.7	1	2.3	4.4
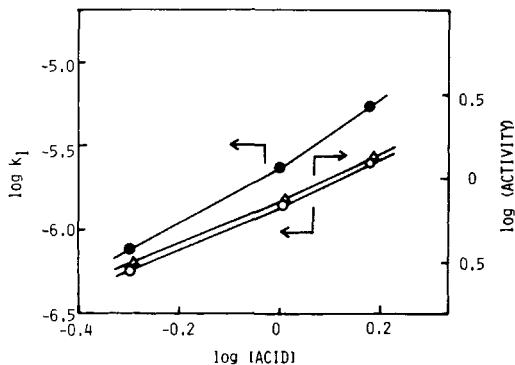
Fig. 2. Comparison of dependence of k_1's in the presence of 12-tungstosilicic acid ($\bullet$) or hydrochloric acid ($\bigcirc$), and activity ($\triangle$) of hydronium ion of hydrochloric acid, on stoichiometric concentration of acid.

2.5 times higher than that of hydrochloric acid at the same normality. Then the effect of ionic strength on k_1 was investigated for the hydrolysis of cellulose in the presence of hydrochloric acid. Figure 3 shows the changes in k_1 with addition of aluminium chloride or sodium chloride to the reaction system. In the upper figure, at the same molar concentration, aluminium chloride is found to enhance the k_1 more than sodium chloride. In the lower figure, at the same ionic strength, however, both inorganic additives are found to enhance the k_1 to a similar degree. Furthermore, comparing theses k_1's with that of hydrolysis of cellulose in the presence of 12-tungstosilicic acid at the same acid concentration and ionic strength, the k_1's are found to be reasonably close, although the latter is still slightly larger than the
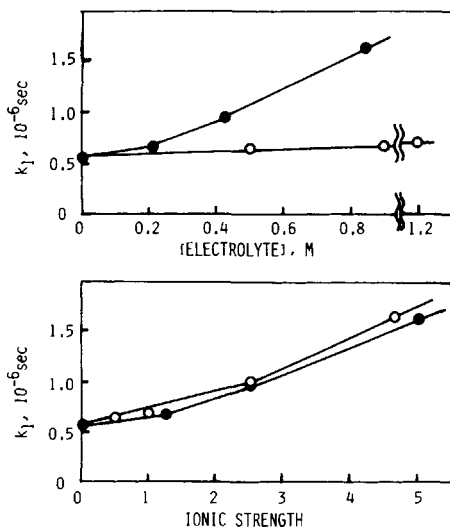

Fig. 3. Influence of addition of aluminium chloride ($\bullet$) or sodium chloride ($\bigcirc$) on k_1 for hydrolysis of cellulose in the presence of hydrochloric acid. Hydrochloric acid concentration, $0.5N$.

former. Therefore, it is believed that the difference in the ionic strength between hydrochloric acid and 12-tungstosilicic acid at the same acid concentration is one of the reasons for the higher catalytic activity of 12-tungstosilicic acid.

Soluble products of the hydrolysis of cellulose fiber were analyzed. The reaction mixture was filtered, the filtrate was passed through an Amberlite IRA-45 column to remove acid, and then fractionated by the ion-exchange chromatography described by Khym and Zill.[8] Figure 4 shows the fractionation curves of the soluble products expressed as reducing sugar. It is found that, with both hydrochloric acid and 12-tungstosilicic acid, over 90% of the soluble products was recovered as glucose (second peak) and 1–2% as oligosaccharides (first peak). There was no significant difference between the ratios of glucose percent to oligosaccharides percent in the presence of hydrochloric acid and of 12-tungstosilicic acid, although the total amount of soluble products for the former catalyst system is slightly less than that for the latter catalyst system.

Changes in DP of residual cellulose fiber with the hydrolysis was investigated. Figure 5 shows the plots of DP against the reaction time at 60°C. The DP's are found to decrease rapidly in a short time in the early stage. Although in the early stage the decrease in DP with the hydrolysis in the presence of 12-tungstosilicic acid shows a tendency to be slightly larger than that in the presence of hydrochloric acid at the same reaction time, the DP's after long reaction time, the so-called level-off DP's, however, show no significant difference from each other depending on the acid. This result suggests that the heteropolyacid, in spite of its bulky structure, easily penetrate into the amorphous region of the cellulose fiber just as does hydrochloric acid and catalyze the hydrolysis of glucoside bond there.

Adsorption behavior of 12-tungstosilicic acid by cellulose fiber was investigated. The ○ plot in Figure 6 shows the relationship between the amount of adsorbed 12-tungstosilicic acid and the concentration of 12-tungs-
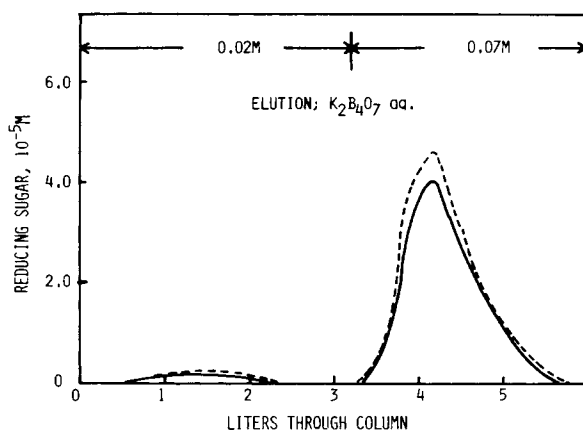

Fig. 4. Fractionation curves of soluble products of hydrolysis of cellulose in the presence of 12-tungstosilicic acid (- - - - - -) or hydrochloric acid (—), with ion-exchange chromatography. Column; Dowex 1 (borated), 1.54 cm² × 30 cm, flow rate 3.6 mL/min.
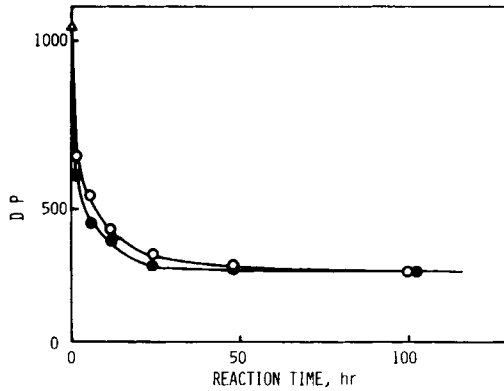
Fig. 5. Decrease in DP of cellulose fiber with hydrolysis in the presence of 12-tungstosilicic acid (●) or hydrochloric acid (○), at 60°C. Acid concentration, 1.0N.

tosilicic acid in the bulk solution, and a curve is obtained. These data were evaluated according to the Langmuir's adsorption isotherm:

$$\frac{c}{a} = \frac{1}{K \cdot A_s} + \frac{1}{A_s} \cdot c \tag{1}$$

where A_s is a constant value which corresponds to the saturated adsorption amount, c is the concentration of 12-tungstosilicic acid in the bulk solution, K is the stability constant, and a is the quantity of adsorption. The △ plot in the figure shows the Langmuir plot of the adsorption data, and a fairly good straight line is obtained, meaning that the adsorption behavior follows the Langmuir's adsorption isotherm. From the straight line obtained the parameters of the equation were calculated: As was 0.29 mol/unit mol as glucose, which was rather a high value considering that the crystalline region of the cellulose fiber is unaccesible, whereas K was about 0.18 L/
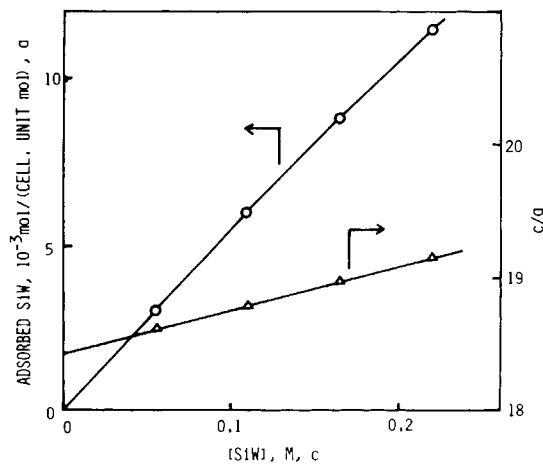

Fig. 6. Adsorption behavior of 12-tungstosilicic acid (SiW) by cellulose fiber (○) and its Langmuir plot (△), at 10°C.

unit mol, which was a lower value than expected. These values suggest that 12-tungstosilicic acid easily penetrates into the amorphous region of the cellulose fiber, although the affinity of the 12-tungstosilicic acid to the cellulose fiber is rather weak.

References

1. For example, *Hydrolysis of Cellulose: Mechanisms of Enzymatic and Acid Catalysis*, Adv. Chem. Ser. No. 181, R. D. Brown, Jr., and L. Jurasek, Eds., American Chemical Society, Washington, DC, 1979; R. Katzen, *Proceedings of the Conference on Chemical Feedstock Alternatives*, Van Antwerpen, Ed., American Inst. Chem. Engineers, New York, 1977.

2. K. Nomiya, T. Ueno, and M. Miwa, *Bull. Chem. Soc. Jpn.*, **53**, 1827 (1980); Y. Izumi and K. Hayashi, *Chem. Lett.*, **1980**, 787; K. Matsuo, K. Urabe, and Y. Izumi, *Chem. Lett.*, **1981**, 1315.

3. K. Arai and Y. Ogiwara, *Makromol. Chem. Rapid Commun.*, **4**, 181 (1983).

4. K. Arai and Y. Ogiwara, *J. Appl. Polym. Sci.*, **29**, 3087 (1984).

5. S. M. Neale and R. Waite, *Trans. Faraday Soc.*, **39**, 261 (1941).

6. J. F. Keggin, *Nature*, **131**, 908 (1933); *Proc. Roy. Soc.*, **A144**, 75 (1934).

7. H. S. Harned and R. W. Ehlers, *J. Am. Chem. Soc.*, **55**, 2179 (1933).

8. J. X. Khym and L. P. Zill, *J. Am. Chem. Soc.*, **76**, 209 (1952).