

Hydrolysis of Dextrin in the Presence of 12-Tungstosilicic Acid

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Synopsis

Hydrolysis of dextrin in the presence of 12-tungstosilicic acid was investigated, and the acid was found to show an approximately two times higher catalytic activity than did hydrochloric acid. From the comparison of degree of dissociation of 12-tungstosilicic acid with that of hydrochloric acid, examination of the influence of the ionic strength on the reaction rates, analysis of the reaction products, and evaluation of activation parameters of the reaction, it was assumed in conclusion that the higher catalytic activity of 12-tungstosilicic acid resulted from a "concentration effect" due to the complex formation of the heteropolyanions with dextrin molecules, and from the effect of its higher ionic strength, but not from the effect of direct participation of the heteropolyanion to the elementary reaction process.

INTRODUCTION

Catalyses in the presence of a heteropolyacid have been the subject of numerous investigations, and effective catalyses, such as oxidation of olefins,¹ hydration of olefins,² polymerization of benzyl alcohols,³ and alcoholysis of epoxides,⁴ have been reported. We have been interested in the hydrolysis of carbohydrates in the presence of a heteropolyacid, and have already found its higher catalytic activity on the hydrolysis of sucrose than that of hydrochloric acid.⁵ In the present experiment, the catalytic activity of 12-tungstosilicic acid (Keggin-type heteropolyacid⁶) on the hydrolysis of dextrin was examined in comparison with that of hydrochloric acid, and some factors affecting it were discussed.

EXPERIMENTAL

Materials. Commercially available dextrin was purified by pouring a 20% aqueous solution into fivefold volume of methanol to cause it to precipitate. The number-average molecular weight of the purified dextrin, estimated by the method of end-group determination, was 66. All other reagents, including 12-tungstosilicic acid, $H_4SiW_{12}O_{40}$ (from Wako Pure Chemical Co., Tokyo), were used without further purification.

Measurement of Reaction Rate. Dextrin aqueous solution (10 mL of 0.5M as anhydroglucose unit) was added to 90 mL of 12-tungstosilicic acid or hydrochloric acid aqueous solution of a given concentration, and the mixture was kept at a given temperature in a thermostat. Then 2-mL aliquots of the reaction mixture were taken out at intervals and were passed through an Amberlite IRA-45 column to remove the acid. Of each effluent, 300 mL was recovered, and the amount of reducing sugar was determined according to the method of Somogyi.⁷ The amount of reducing sugar was

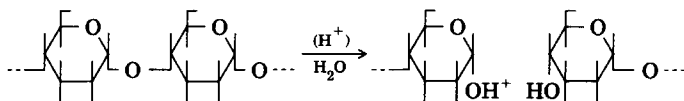
plotted against the reaction time, and the pseudo-first-order rate constant was calculated from the slope of the straight line thus obtained.

NMR Study. NMR spectra were obtained with an analytical NMR spectrometer (Nichiden-Varian Co., Varian A-60D, 60 MHz) at various concentrations of 12-tungstosilicic acid or hydrochloric acid in water, the chemical shifts of water-proton being measured. Sodium 3-trimethylsilylpropane-sulfonate was used as a reference.

Fractionation of the Reaction Products. More 2-mL aliquots of the reaction mixture were taken out at intervals and passed through an Amberlite IRA-45 column, and then 300 mL of each effluent recovered was concentrated to 50 mL. The concentrated solution was fractionated by the ion-exchange chromatography described by Khym and Zill⁸; the concentrated solution was added to boric acid solution, and the mixture was adsorbed on a Dowex 1 column, which had been converted to the borate form. Elution was carried out with potassium tetraborate solutions, first of 0.02M and then 0.07M. The effluent fractions (25 mL each) were analyzed for the amount of anhydroglucose unit by the phenol-sulfuric acid method.⁹ The column size and flow rate were 1.54 cm² × 30 cm and 3.6 mL · min⁻¹, respectively. Recovering yields of the anhydroglucose unit with the fractionation were in the range of 85 ± 5%.

RESULTS AND DISCUSSION

Hydrolysis of dextrin, a typical specific acid catalysis, proceeds as follows:



The reaction rate, average cleavage rate of glucoside bond, can usually be evaluated by a determination of the amount of reducing sugar yielded at intervals. In the present reaction system, however, the heteropolyanion in the reaction mixture was found to make the direct application of the usual determination method impossible. Thus, at first, the elimination of the heteropolyanion from the reaction mixture was examined, and it was found that the heteropolyanion was completely eliminated by passing the reaction mixture through an Amberlite IRA-45 (weak-base-type ion exchanger) column, while the reducing sugar in the reaction mixture was almost perfectly recovered, under the condition mentioned in the experimental section; passing the reaction mixture through an Amberlite IRA-400 (strong-base-type ion exchanger) column made the perfect recovery of the reducing sugar difficult. Figure 1 shows an elution histogram for reducing sugar of a mixed solution of glucose and 12-tungstosilicic acid with an Amberlite IRA-45 column, and it is found that about 98% of the reducing sugar is recovered with recovering 300 ml of effluent under the present elution condition, with no elution of heteropolyacid.

Thus, aliquots of the reaction mixtures of dextrin hydrolysis in the presence of 12-tungstosilicic acid or hydrochloric acid were taken out at intervals and passed through an Amberlite IRA-45 column, and then offered to the

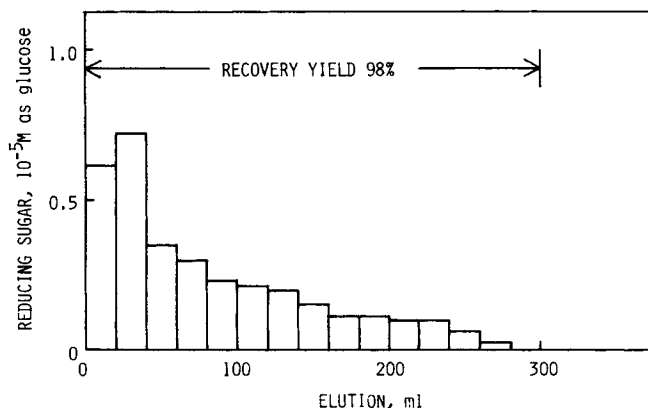


Fig. 1. An elution histogram for reducing sugar of a mixed aqueous solution of glucose and 12-tungstosilicic acid, with an Amberlite IRA-45 column. Mixed solution: [glucose] = 0.05M; [12-tungstosilicic acid] = 0.03N; 2 mL. Column length: 80 mm. Column diameter: 12 mm. Flow rate: 3.0 mL · min⁻¹.

determination of the amount of reducing sugar in it, according to the method of Somogyi.⁷ Figure 2 shows the changes in the amount of reducing sugar in the reaction mixture in the presence of various concentration of 12-tungstosilicic acid, with reaction time. It is found in the figure that the amount of reducing sugar begins to increase after a certain reaction time, depending on the concentration of 12-tungstosilicic acid; in the case of reaction in the presence of hydrochloric acid such a delay of the reaction was not found. The delay of the reaction is inferred to indicate that the formation of a preferable complex for the reaction needs a certain time in the present reaction system. However, after a certain reaction time depending on the concentration of 12-tungstosilicic acid, each reaction reaches a steady state

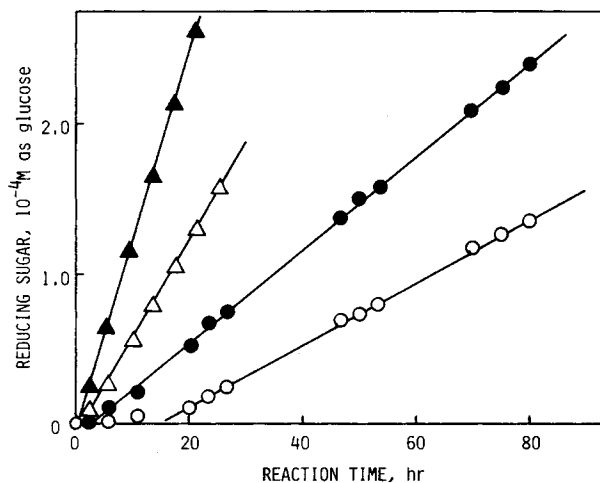


Fig. 2. Increase in the amount of reducing sugar in the reaction mixture of dextrin hydrolysis in the presence of various concentrations of 12-tungstosilicic acid, with reaction time, at 70°C; [dextrin] = 0.05M as anhydroglucose unit; [12-tungstosilicic acid] (N): (○) 0.05; (●) 0.10; (△) 0.20; (▲) 0.30.

and shows a proportional increase in the amount of reducing sugar with the reaction time. From the slope of the straight line thus obtained, the pseudo-first-order rate constant k_1 , was calculated.

Figure 3 shows dependence of the k_1 value on the acid concentration for the reactions in the presence of 12-tungstosilicic acid or hydrochloric acid. It is found that for each plot k_1 increases proportionally with an increasing acid concentration and that 12-tungstosilicic acid shows about two times higher catalytic activity than hydrochloric acid at the same acid concentration as equivalent per liter, N , for both examinations at 60°C and 70°C.

Although similar higher catalytic activity of heteropoly acid have found in many reactions, the reason for the higher catalytic activity is not always evident. For example, Izumi et al.² proposed a new reaction mechanism for the hydration reaction of olefins to explain the higher catalytic activity, in which the heteropolyanion participates in the formation of reaction intermediate. For the present reaction, a specific acid catalysis, however, such a participation of the anion to the reaction process is hardly assumed to be reasonable. Accordingly, in order to find the reason why 12-tungstosilicic acid shows a higher catalytic activity than hydrochloric acid, some experiments were carried out.

First, the proton magnetic resonance shifts of water-proton in the presence of 12-tungstosilicic acid or hydrochloric acid at various concentrations were measured. It has been established that the chemical shift of the proton magnetic resonance is concentration-dependent in the solutions of electrolytes which yield hydrogen-containing ions. The chemical exchanges average the chemical shifts in the proton resonance position over the different chemical species, and the averaged shifts observed are correlated with the dissociation of the solute.¹⁰ Figure 4 shows the plots of the difference,

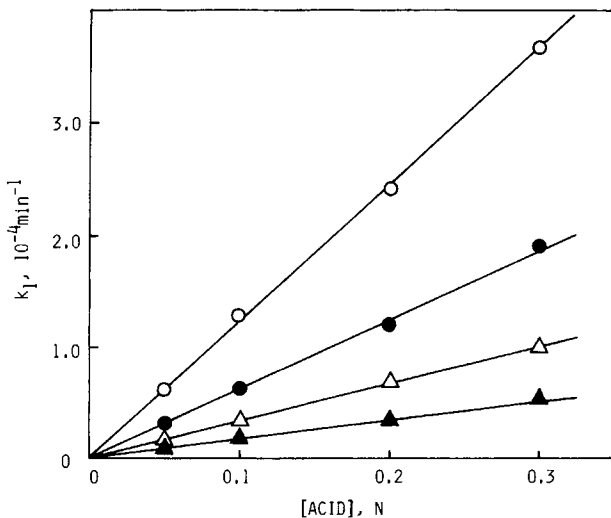


Fig. 3. Dependence of first-order rate constant k_1 of dextrin hydrolysis in the presence of 12-tungstosilicic acid or hydrochloric acid; [dextrin] = 0.05M as anhydroglucose unit: (○) 12-tungstosilicic acid at 70°C; (●) hydrochloric acid at 70°C; (△) 12-tungstosilicic acid at 60°C; (▲) hydrochloric acid at 60°C.

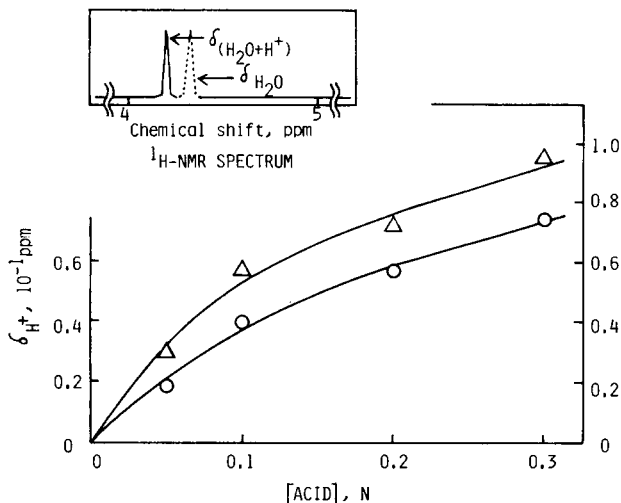


Fig. 4. Plots of the difference, δ_{H^+} , of averaged chemical shifts between the acid solution, $\delta_{(\text{H}_2\text{O}+\text{H}^+)}$, and pure water, $\delta_{\text{H}_2\text{O}}$, against acid concentration, for the proton magnetic resonance shifts of water proton of 12-tungstosilicic acid (○) and hydrochloric acid (△) solutions.

δ_{H^+} of averaged chemicals shifts between an acid solution, $\delta_{(\text{H}_2\text{O}+\text{H}^+)}$, and pure water, $\delta_{\text{H}_2\text{O}}$ (see Fig. 4) against acid concentration in normality. It is found that hydrochloric acid solution shows a higher value of δ_{H^+} than 12-tungstosilicic acid solution at the same concentration as acid in normality, indicating that the degree of dissociation of hydrochloric acid is higher than that of 12-tungstosilicic acid. Therefore, the difference in the degree of dissociation of the acids is believed to influence rather preferably the reaction in the presence of hydrochloric acid than that in the presence of 12-tungstosilicic acid.

The influence of ionic strength of the reaction system on k_1 was examined. 12-Tungstosilicic acid is a polyacid with an ionic strength about 2.5 times higher than that of hydrochloric acid, and the higher ionic strength was assumed to be one of reasons for the higher catalytic activity of 12-tungstosilicic acid. Table I shows the comparison of k_1 in the presence of 12-tungstosilicic acid with that in the presence of hydrochloric acid at the same ionic strength adjusted by addition of sodium chloride. It is found that,

TABLE I
Comparison of First-Order Rate Constant k_1 of Dextrin Hydrolysis in Presence of 12-Tungstosilicic Acid with that in Presence of Hydrochloric Acid at Same Ionic Strength μ , Adjusted by Addition of Sodium Chloride, at 70°C

[Acid] (N)	Acid	μ	k_1 (10^{-5} min^{-1})
0.1	$\text{H}_4\text{SiW}_{12}\text{O}_{40}$	0.25	11.7
	HCl	0.10	6.1
	HCl + NaCl	0.25	6.6
0.3	$\text{H}_4\text{SiW}_{12}\text{O}_{40}$	0.75	34.5
	HCl	0.30	16.9
	HCl + NaCl	0.75	21.7

although k_1 in the presence of hydrochloric acid increases with addition of sodium chloride, it is still clearly lower than that in the presence of 12-tungstosilicic acid at the same ionic strength. Therefore, it is believed that the difference in the ionic strength between hydrochloric acid and 12-tungstosilicic acid at the same concentration as acid is certainly one of reasons for the higher catalytic activity of 12-tungstosilicic acid, but cannot be the only reason for it.

Change in the distribution of degree of polymerization (DP) of dextrin with hydrolysis in the presence of 12-tungstosilicic acid was examined and compared with that in the presence of hydrochloric acid. Figures 5 and 6 show fractionation curves of the hydrolysis products in the presence of 12-tungstosilicic acid and hydrochloric acid, respectively, by ion-exchange column chromatography. Three peaks are shown in each figure, being attributed to the fractions with DP of 66-3, 2, and 1. It is found that the increase in the tailing fraction (with mediate DP) of the first peak with reaction time is less in the presence of 12-tungstosilicic acid, while the increase in the second and the third peaks (with DP of 2 and 1) with reaction time is more. This result suggests that the dextrin hydrolysis in the presence of 12-tungstosilicic acid proceeds in a less random manner than that in the presence of hydrochloric acid; as a manner that some dextrin molecules are locally hydrolyzed to molecules with DP of 2 or 1, whereas the others are less affected. This result, associated with the fact that accomplishment of steady state of the reaction needs a certain time depending on the concentration of heteropolyacid, may suggest that the reaction proceeds via formation of a certain complex between the heteropolyacid and the substrate. Keggin-type heteropolyacid has a bulky ionic crystal structure, oxygen atoms being placed periphery,⁶ and the structure is stable even in water under the condition used in the present experiment¹¹; a heteropolyanion can be regarded as a ball with a diameter of about 10 Å, covered

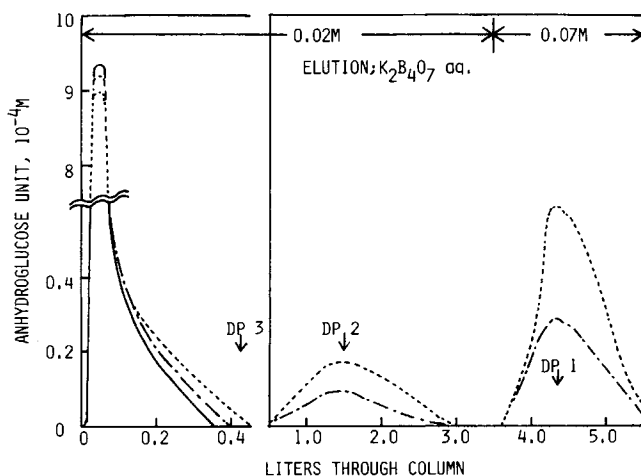


Fig. 5. Fractionation curves in terms of anhydroglucose units of dextrin hydrolysis product in the presence of 12-tungstosilicic acid with the ion-exchange chromatography, at reaction times 0 (—), 40 (— · —), and 80 (---) h; [dextrin] = 0.05M as anhydroglucose unit; [12-tungstosilicic acid] = 0.10N.

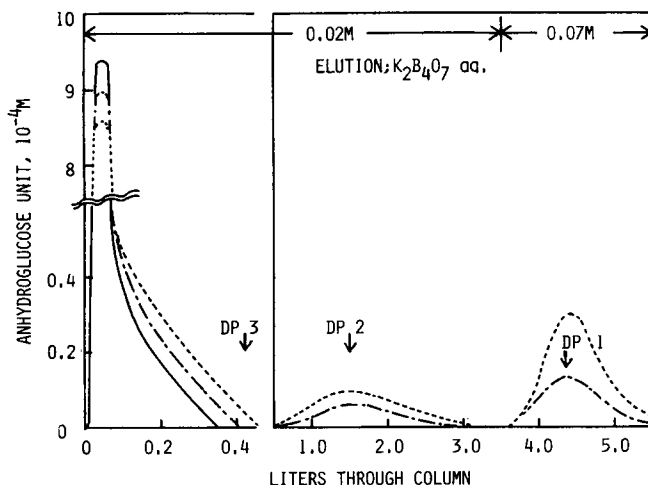


Fig. 6. Fractionation curves in terms of anhydroglucose units of dextrin hydrolysis product in the presence of hydrochloric acid with the ion-exchange chromatography, at reaction times 0 (—), 40 (— · —), and 80 (---)h; [dextrin] = 0.05M as anhydroglucose unit; [hydrochloric acid] = 0.10N.

by 36 oxygen atoms. These oxygen atoms are assumed to be possible to interact with hydroxyl groups in the substrate molecules, leading to the formation of a complex. If this assumption is true, the higher catalytic activity of 12-tungstosilicic acid can be explained by a "concentration effect" of the substrate that the substrate is concentrated near periphery of the heteropolyanion where hydronium ions also interact with the anion, not considering the direct participation of the heteropolyanion to the elementary reaction process.

Temperature dependence of k_1 's was examined. Figure 7 shows Arrhenius plots of k_2 's, calculated as k_1 divided by concentration of acid in normality, of dextrin hydrolysis in the presence of 12-tungstosilicic acid or hydrochloric

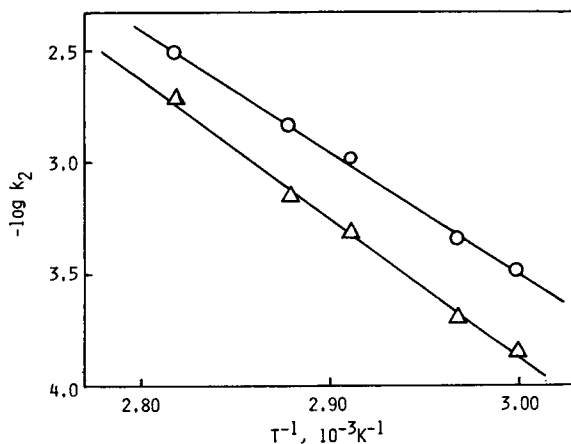


Fig. 7. Arrhenius plots of second-order rate constant k_2 of dextrin hydrolysis in the presence of 12-tungstosilicic acid (○) and hydrochloric acid (△).

TABLE II
 Activation Parameters of Dextrin Hydrolysis in Presence of 12-Tungstosilicic Acid or Hydrochloric Acid, at 70°C

Acid	ΔG^\ddagger (kcal · mol ⁻¹)	ΔH^\ddagger (kcal · mol ⁻¹)	ΔS^\ddagger (e.u.)
H ₄ SiW ₁₂ O ₄₀	27.7	24.9	-8
HCl	28.1	26.8	-4

acid, and Table II shows the activation parameters calculated therefrom. Enthalpy of activation is seen to be about 2 kcal · mol⁻¹ less in the presence of 12-tungstosilicic acid than in the presence of hydrochloric acid. It is well known that, in the acid hydrolysis of carbohydrates, increase in ionic strength of the reaction system leads to lowering enthalpy of activation for the reaction, especially at a range of higher ionic strength, as well as increase in reaction rate.¹² In the present experiment, however, the difference in enthalpy of activation between reaction systems in the presence of 12-tungstosilicic acid and in the presence of hydrochloric acid, resulted from the difference between their ionic strengths, is calculated to be up to 0.5 kcal · mol⁻¹ in the range of the present reaction condition. Therefore, again for the lowering of enthalpy of activation of about 2 kcal · mol⁻¹, it is suggested that there are other effective factors than ionic strength. In some reactions, it has been found that the formation of a complex between the catalyst and the substrate leads to lowering of enthalpy of activation, as well as increasing of the reaction rate.¹³ Therefore, the lower enthalpy of activation of the reaction in the presence of 12-tungstosilicic acid may support the formation of a complex between the acid and the dextrin.

From these results, it is assumed in conclusion that the higher catalytic activity of 12-tungstosilicic acid resulted from a "concentration effect" due to the complex formation of the heteropolyanions with dextrin molecules, and from the effect of its higher ionic strength, but not from the effect of direct participation of the heteropolyanion to the elementary reaction process.

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