

Preparation of Copoly(vinyl Alcohol–Styrenesulfonic Acid) Resin and Its Catalytic Activity on Hydrolysis of Carbohydrates. IV. Hydrolysis of Dextrin in Mixtures of Organic Solvents with Water

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Synopsis

The reaction rates of dextrin hydrolysis in the presence of copoly(vinyl alcohol–styrenesulfonic acid) resin in mixtures of dimethyl sulfoxide and dioxane with water were measured and compared with those in the presence of Amberlite 120B. In the case of Amberlite 120B the second-order rate constant, k_2 , of the reaction decreased continuously with increasing vol % of the organic solvents, whereas in the case of the copolymer resin it passed a minimum and increased again at the higher vol % range. The influence of blocking of the hydroxyl groups in the copolymer resin by formalization on the catalysis was investigated. The increase in k_2 in the higher vol % range of the organic solvent was suppressed with the blocking, and the interactions between hydroxyl groups in the substrate and the copolymer resin was confirmed to play an important role for the increase in the k_2 in the higher vol % range of the organic solvents. Temperature dependence of k_2 was also examined, and the increase in k_2 in the higher vol % range of the organic solvents was found to be due to pronounced decreases in enthalpy of activation, suggesting that the increase might be resulted from the enhancement of interactions between the substrate and the catalytic copolymer resin.

INTRODUCTION

Some investigations have been made on the solvent effect on the rate enhancement of the reactions in the presence of a synthetic polymer catalyst, which have some interactions with the substrates, and homogeneous hydrolysis of dextrin in the presence of copoly(vinyl alcohol–vinylsulfonic acid) in the mixtures of some organic solvents with water was also reported.¹ In this work, in succession to previous works,^{2–5} the rates of heterogeneous hydrolyses of dextrin in the presence of copoly(vinyl alcohol–styrenesulfonic acid) resin were measured in mixtures of dimethyl sulfoxide (DMSO) and of dioxane with water, in order to obtain more information about the mechanism of the catalysis.

EXPERIMENTAL

Materials

Commercially available reagent grade DMSO and dioxane were used without further purification. Other reagents were purified with the method previously reported.^{3,6}

Preparation of the Catalyst Copolymer Resin

Catalyst copolymer resins were prepared and characterized with the method previously reported.⁴

Measurement of Hydrolysis Rate

An aqueous solution of dextrin and the catalyst copolymer resin were added to a mixture of an organic solvent with water, and kept at a given temperature in a thermostat. The reaction rates were estimated with the method previously reported,³ and second-order rate constants, k_2 's, with respect to the concentrations of substrate and catalyst, not considering the content of water in the reaction mixtures, were calculated from the rates.

Formalization of the Catalyst Copolymer Resin

Formalization of the hydroxyl groups in the catalyst copolymer resin was carried out with the method of Fujimoto et al.,⁷ and the degree of formalization of the product was determined with the method of Sakurada et al.⁸

RESULTS AND DISCUSSION

First, changes in k_2 's of dextrin hydrolyses in the presence of copoly(vinyl alcohol-styrenesulfonic acid) resin, poly(styrenesulfonic acid) resin, or Amberlite 120B (commercial sulfonic acid type cation exchanger, H⁺ form) in the mixtures of organic solvents with water, with increasing vol % of the organic solvents were examined. Figures 1 and 2 show the relationships between the vol % of the organic solvents and k_2 in the mixtures of DMSO and dioxane with water, respectively. It can be seen in each figure that k_2 of the reaction in the presence of the catalyst copolymer decreases in the lower vol % range of the organic solvent, goes through a minimum at a certain composition, and then increases with increasing organic solvent in the higher vol % range, whereas k_2 in the presence of poly(styrenesulfonic acid) resin or Amberlite 120B continuously decreases. The decrease in k_2 's in the presence of the catalyst copolymer resin at a lower vol % range of organic solvent and in the presence of Amberlite 120B

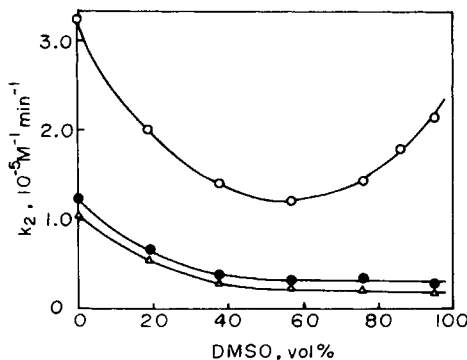


Fig. 1. Second-order rate constants, k_2 's, of dextrin hydrolyses in mixture of DMSO with water in the presence of copoly(vinyl alcohol-styrenesulfonic acid) resin no. 1 (vinyl alcohol unit, 12.6 mol %) (O) poly(styrenesulfonic acid) resin (●) or Amberlite 120B (Δ) at 70°C.

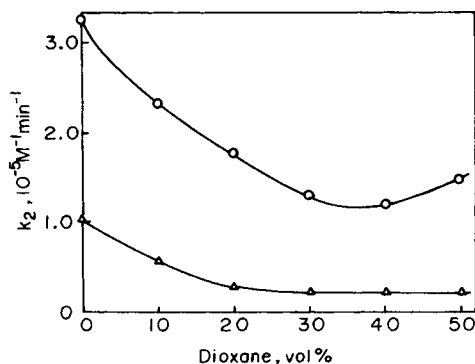


Fig. 2. Second-order rate constants, k_2 's, of dextrin hydrolyses in mixture of dioxane with water in the presence of copoly(vinyl alcohol-styrenesulfonic acid) resin no. 1 (vinyl alcohol unit, 12.6 mol %) (O) or Amberlite 120B (Δ) at 70°C.

and poly(styrenesulfonic acid) resin are presumably due to the nucleophilic behavior of the DMSO and dioxane to the decrease in the amount of water as a reactant in the reaction mixtures, and to the dielectric property of the mixed solvents. The increases in k_2 in the presence of the catalyst copolymer resin at a higher vol % range of the organic solvents qualitatively agree with those obtained previously in the hydrolysis of dextrin in the presence of the similar homogeneous catalyst copolymer in mixtures of organic solvents with water.¹ Considering the discussion about the changes in k_2 in the homogeneous reaction system, the enhancement of the interactions between hydroxyl groups in the substrate and the catalyst copolymer resin may be proposed to be an important factor for increase in k_2 also in this case.

In order to confirm this proposition, the influence of blocking of the hydroxyl groups in the catalyst copolymer resin on the catalysis was investigated. Figure 3 shows the changes in the k_2 's of the dextrin hydrolyses in the mixture of DMSO with water in the presence of the copolymer resins, after partial blocking hydroxyl groups in the copolymer resins by formalization. It can be seen that the increase

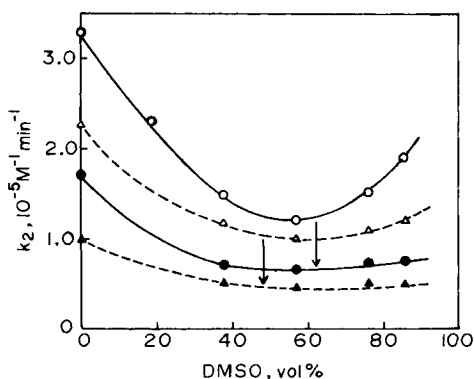


Fig. 3. Changes in second-order rate constants, k_2 's, of dextrin hydrolyses in mixture of DMSO with water in the presence of copoly(vinyl alcohol-styrenesulfonic acid) resins nos. 2 and 3 (vinyl alcohol unit, 13.0 and 8.6 mol %), with blocking hydroxyl groups of the copolymers by formalization at 75°C: (—○—) Copolymer resin no. 1; (—●—) formalized copolymer resin no. 1 (degree of formalization, 61%); (—Δ—) copolymer resin no. 2; (—▲—) formalized copolymer resin no. 2 (degree of formalization, 47%).

in k_2 's in the higher vol % range with increasing vol % of DMSO is suppressed with the blocking, although the k_2 's decrease in any vol % range of DMSO. This result suggests that the hydroxyl groups in the catalyst copolymer resin play an important role for the increase in k_2 in a higher % range of DMSO, presumably due to the enhancement of interactions between hydroxyl groups in the substrate and the copolymer resin.

Temperature dependence of the k_2 's in the mixtures of DMSO with water was examined. Figures 4 and 5 show the k_2 's in the mixture of DMSO with water at various temperatures in the presence of the catalyst copolymer resin and Amberlite 120B, respectively. Arrhenius plots of these data give good straight lines as shown above. Activation parameters were calculated from the plots and summarized in Table I. It can be seen that enthalpies of activation, ΔH^\ddagger 's, with the copolymer resin decrease with increasing vol % of DMSO, especially at the higher vol % range of DMSO whereas k_2 's increase. The same tendency was

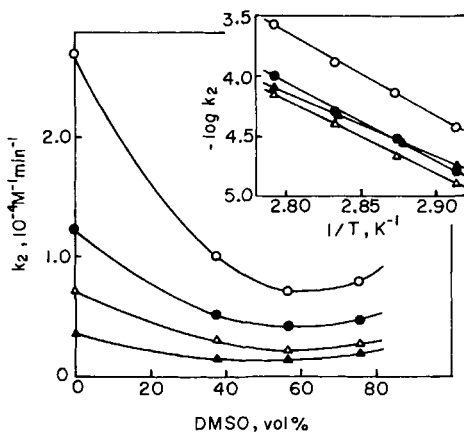


Fig. 4. Temperature dependence of second-order rate constants, k_2 's of dextrin hydrolysis in mixture of DMSO with water in the presence of copoly(vinyl alcohol-styrenesulfonic acid) resin no. 1 (vinyl alcohol unit, 12.6 mol %). Temperature ($^{\circ}\text{C}$): (O) 85; (●) 80; (Δ) 75; (\blacktriangle) 70.

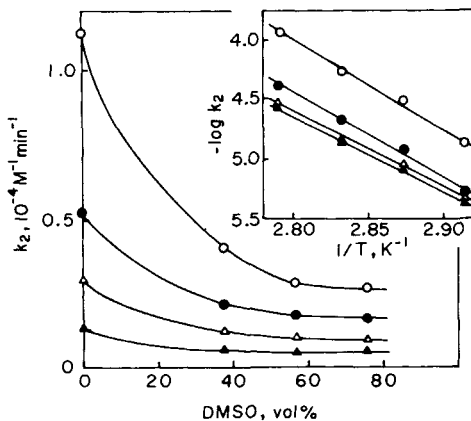


Fig. 5. Temperature dependence of second-order rate constants, k_2 's, of dextrin hydrolysis in mixture of DMSO with water in the presence of Amberlite 120B. Temperature ($^{\circ}\text{C}$) (O) 85; (●) 80; (Δ) 75; (\blacktriangle) 70.

TABLE I
 Activation Parameters of Dextrin Hydrolysis Reaction in Mixture of DMSO with Water in
 Presence of Copolymer Resin and Amberlite 120B at 75°C^a

Catalyst DMSO, vol%	Copolymer resin				Amberlite 120B			
	0	38	57	76	0	38	57	76
ΔG^\ddagger	29.91	30.51	30.76	30.59	30.51	31.15	31.31	31.36
ΔH^\ddagger	30.9	28.7	28.2	23.5	33.5	31.8	28.7	28.4
ΔS^\ddagger	3	-5	-7	-20	9	2	-8	-9

^a ΔG^\ddagger and ΔH^\ddagger are in kcal mol⁻¹ and ΔS^\ddagger in entropy units.

found in the mixture of dioxane with water, although the data were rather scattered. The rate enhancement of dextrin hydrolysis by introducing poly(vinyl alcohol) sequences into the catalyst resin has also been found to result from a decrease in ΔH^\ddagger ,⁵ and the similarity of the changes in ΔH^\ddagger may also support the proposition that the increase in k_2 of the present reaction in the higher range of the organic solvents was a result of enhancement of interactions between the substrate and the catalyst copolymer resin.

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