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Specific Effects in Acid Catalysis by Polymeric Sulfonic Acids in the Hydrolysis of Some Carboxylic Esters[1]

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The catalytic effects of polymeric sulfonic acids in ester hydrolysis in aqueous acetone were inferior to that of hydrochloric acid. However, the hydrolysis rate was accelerated by increasing the water content of acetone-water mixtures, and, in a water solution, polymeric sulfonic acids were much more effective catalysts. Furthermore, the catalytic efficiency of polymeric sulfonic acid in ester hydrolysis in water increased with the length of the ester molecule. The polymeric sulfonic acid with a strong hydrophobic character was more effective; 69% sulfonated polystyrenesulfonic acid, for example, hydrolyzed methyl hydrogen azelate in water over five times more rapidly than hydrochloric acid. The specificity thus obtained suggests that, in the hydrolysis of electrically-neutral esters in water, ester molecules are concentrated in the neighborhood of the polymer by the hydrophobic interaction between catalyst and substrate. Besides, in the hydrolysis of aliphatic esters catalyzed by polyvinylsulfonic acid in 50% aqueous acetone, there was a linear relationship between the reciprocal of the rate constant and the intrinsic viscosity of the polymer, while in the case of polystyrenesulfonic acid hardly such any relationship was found. These remarkably different behaviors of the two kinds of polymer catalysts should be attributed to the difference in the expansion of the polymer chain in solutions.

The acid-catalyzed hydrolysis of esters by polymeric sulfonic acids, as previously reported by others,[2] has been carried out mostly in heterogeneous systems with cross-linked sulfonated polystyrene resins. Therefore, there is some difficulty in estimating and discussing precisely the catalytic activity relating to the molecular structure of the polymer in solutions.

It is the aim of the present paper to report on the specific behavior of water-soluble polymeric sulfonic acids in the hydrolysis of esters in various medium compositions of the homogeneous solution. The sulfonic acids were prepared by different polymerizing processes from their respective monomers, except sulfonated polystyrene sulfonic acid. Polymeric sulfonic acid is a strong polybasic acid comparable to sulfuric acid and protons are considered to be localized along the polymer chain. Hence, the proton density in solutions may be locally concentrated, unlike as in mineral acid. It may, therefore, be expected that if an interaction between the polymer catalyst and a substrate occurs, this interaction can be specifically changed according to the characteristics of the substrate and the outer solution used.

Experimental

Monomers.—Sodium vinylsulfonate was prepared from sodium β-bromoethanesulfonate and sodium hydroxide by modifying the patent directions.[3] To 60 g. of sodium β-bromoethanesulfonate 29 g. of 40% sodium hydroxide was vigorously stirred drop by drop. During the addition the temperature was kept below 50°C. Further stirring was continued until the temperature fell to room temperature, and then the reaction mixture was neutralized with concentrated hydrochloric acid at 0—5°C. After large portions of sodium bromide had been filtered, an equal volume of alcohol was added to the filtrate at 0°C. Sodium vinylsulfonate was thus precipitated and filtered off. The yield was 24 g. (65% of the theoretical amount).

Potassium *p*-styrenesulfonate was prepared by the method of Wiley and Reed.[4] To 65 ml. of chlorosulfonic acid at 0—5°C, there was added, drop by drop, 27.5 ml. (0.2 mol.) of β-bromoethylbenzene, which had been prepared according to the directions of Whitmore.[5] After 30 min. the reaction mixture was poured onto ice with stirring in order to precipitate the sulfonyl chloride, which was then washed with ice water and taken up in ether. The ether solution was washed with dilute sodium bicarbonate and dried. The residue remaining on the evaporation of the ether was dissolved in 70 ml. of cold 95% ethanol. To this solution there

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[1] Dissertation submitted by Oh-Kil Kim in partial fulfillment of the requirement for the Ph. D. degree in the Graduate School of The University of Tokyo.

[2] a) V. C. Haskell and L. P. Hammett, *J. Am. Chem. Soc.*, **71**, 1284 (1949); b) C. W. Davies and G. G. Thomas, *J. Chem. Soc.*, **1952,** 1607; c) P. Riesz and L. P. Hammett, *J. Am. Chem. Soc.*, **76**, 992 (1954); d) C. H. Chen and L. P. Hammett, ibid., **80**, 1329 (1958).

[3] D. B. P. 836491, Farbwerker Hoechst, *Chem. Abstr.*, **47**, 2766 (1953).

[4] R. H. Wiley and S. F. Reed, Jr., *J. Am. Chem. Soc.*, **78**, 2171 (1956).

[5] F. C. Whitmore, C. H. Herr, D. G. Clarke, C. S. Rowland and R. W. Schiessler, ibid., **67**, 2059 (1945).

was slowly added a solution of 45 g. of potassium hydroxide in 200 ml. of 95% ethanol. This reaction mixture was refluxed for one hour and filtered. The solid thus collected was washed with an additional 100 ml. of hot ethanol and filtered. The combined filtrates were cooled to -20°C to precipitate the crude product. This crude product was dissolved in a minimum quantity of hot water and filtered. The filtrate was extracted with benzene and cooled to precipitate the product. A final recrystallization from 95% ethanol gave 13 g. (30% yield) of potassium *p*-styrenesulfonate.

The polymerizations of sodium vinylsulfonate and potassium *p*-styrenesulfonate were carried out with three different methods.

Poly(sodium vinylsulfonate) was obtained as follows:

a) PVSH(A): Five grams of sodium vinylsulfonate in 4.9 ml. of water was poured into an ampoule, chilled in ice, and evacuated to about 2 mmHg; the evacuation and pressuring with nitrogen were repeated, and then the ampoule was sealed. The polymerization was carried out by exposing the mixture to a ^{60}Co source yielding about 2×10^5 r./hr. for 72 hr. at 0°C. The resulting stickey solid was dissolved in 30 ml. of water and precipitated by adding 45 ml. of methanol. Treating the gummy precipitate with methanol yielded 3.5 g. (70% conversion) of a straw-colored polymer after it had been dried in vacuo over phosphorus pentoxide. The intrinsic viscosity*1 of the polymer was 12.8, and the molecular weight*1 was 20000.

b) PVSH(R)6): Twelve grams of a 50% sodium vinylsulfonate solution (6 g. of sodium vinylsulfonate) containing 0.075 g. of potassium persulfate and 0.023 g. of sodium bisulfite was poured into an ampoule; the ampoule was evacuated and pressured repeatedly with nitrogen, and then sealed. The ampoule was tumbled in a bath at 18°C for 72 hr. The resulting viscous oil was dissolved in 30 ml. of water and precipitated with 45 ml. of methanol; 4.08 g. of a polymer was obtained after drying in vacuo over phosphorus pentoxide. The intrinsic viscosity was 7.20, and molecular weight was 12000.

c) PVSH(S): Five grams of the finely-powdered and dried crystalline sodium vinylsulfonate was sealed in an ampoule and exposed to a ^{60}Co source yielding about 2.5×10^5 r./hr. for 72 hr. at room temperature. The irradiated crystals, after precipitation with 70% aqueous methanol in the usual fashion to remove the monomer, gave 2.5 g. of a polymer. The intrinsic viscosity and the molecular weight of the polymer were 1.70 and 3000 respectively.

Poly(potassium *p*-styrenesulfonate) was obtained as follows:

a) PSSH(A): Four grams of potassium *p*-styrenesulfonate in 16 ml. of water was poured into an ampoule. Polymerization was carried out in the same manner as in PVSH(A). After exposure to γ-radiation for 72 hr. at room temperature, the polymer formed was precipitated from 70% aqueous dioxane. Drying the precipitates in vacuo over phosphorus pentoxide, yielded 2.5 g. of a polymer. The intrinsic viscosity*2 of the polymer was 42.0.

b) PSSH(R)7): Five grams of potassium *p*-styrenesulfonate in 15 ml. of water was taken into an ampoule, and then a solution of 1.35 g. of potassium persulfate (2.66% based on the monomer) and 0.66 g. of sodium bisufite (1.34% on the monomer) in 2 ml. of water was added as an initiator. The ampoule was then evacuated and sealed in the usual fashion. The polymerization was carried out under tumbling in a bath at 18°C for 72 hr. The resulting viscous oil was precipitated from 70% aqueous dioxane; 3.2 g. of polymer was obtained after drying in vacuo over phosphorus pentoxide. The intrinsic viscosity was 30.7.

c) PSSH(S): Five grams of finely-powdered and dried crystalline potassium *p*-styrenesulfonate was sealed in an ampoule and exposed to a ^{60}Co source yielding about 2.5×10^5 r./hr. for 72 hr. at room temperature. The irradiated crystals yielded 2.3 g. of polymer after it had been precipitated with 75% aqueous methanol and dried according to the usual manner. The intrinsic viscosity was 18.09. All the sodium and potassium polymer sulfonates were completely converted into free acids by passing them through a column of cation exchange resin in hydrogen form, such as Amberlite IR-120.

The sulfonation of polystyrene was carried out using the addition-compound of sulfur trioxide and dioxane by the method described by Signer and his co-workers.8) The addition-compound was easily formed by the addition of one mole of sulfur trioxide to one mole of dry dioxane. To the finely-divided suspension of the adduct, consisting of 20 g. of sulfur trioxide and 26 ml. of dioxane in 140 ml. of dichloroethane, a solution of polystyrene ($\overline{M}_w=15\times10^4$) in 140 ml. of dichloroethane was added in one portion; then the mixture was agitated for several minutes. The sulfonation proceeded to 69% after the mixture had stood at 20°C for 24 hr. The reaction was stopped by the addition of water. The polymer was dissolved easily in water and neutralized with sodium hydroxide. The sulfonated polymer salt was dialysed to remove sulfuric acid through a semipermeable membrane by keeping it in distilled water. The specific conductivity of the outer solution dropped below $3\times10^{-5}\cdot\text{ohm}^{-1}\cdot\text{cm}^{-1}$ after a period of one month. The dialysed sulfonated polymer salt was converted into free acid through the ion exchange resin in hydrogen form in the usual method. The degree of the sulfonation of polystyrene was determined by both gravimetric and elementary analyses of the sulfur atom. The two results corresponded satisfactorily.

Other Reagents.—The esters and acetone were obtained commercially (except methyl hydrogen succinate, methyl hydrogen glutarate and ethyl hydrogen adipate) and were further fractionated in a thirty-inch column of glass helices. Methyl hydrogen succinate was prepared according to the procedure of Cason,9) by

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*1 The value of intrinsic viscosity of poly(sodium vinylsulfonate) was determined in 0.5 N sodium chloride solution at 20°C and the molecular weight was calculated by K. Dialer and R. Kerber, *Makromol. Chem.*, **17**, 56 (1956).

*2 The value of intrinsic viscosity of poly (potassium *p*-styrenesulfonate) was determined in 2 N sodium hydroxide solution at 20°C.

6) D. S. Breslow and A. Kutner, *J. Polymer Sci.*, **27**, 295 (1958).

7) R. H. Wiley, N. R. Smith and C. C. Ketterer, *J. Am. Chem. Soc.*, **76** 720 (1954).

8) R. Signer, A. Demagistri and C. Müller, *Makromol. Chem.*, **18/19**, 139 (1956).

9) J. Cason, "Organic Syntheses," Coll. Vol. 3, 169 (1945).

the reaction of succinic anhydride and methanol (m. p. 57—58°C). Methyl hydrogen glutarate was prepared by the reaction of glutaric anhydride and methanol using the method described by Harris¹⁰⁾ (b. p. 158—165°C/23 mmHg). Methyl hydrogen adipate was prepared from adipic acid and methanol according to the procedure of Morgan and Walton¹¹⁾ (b. p. 128°C/30 mmHg). The methyl hydrogen azelate was a gift of the Soda-Perfumery Co., Ltd.

Procedures.—The initial concentrations of esters and acid catalysts were adjusted to 0.2 mol./l. in acetone (or 0.05 mol./l. in water) and 0.08 N in water respectively. Three or four samples were used in each run, and each reaction mixture was made up of 4 ml. of the initially-adjusted ester in acetone (or water) and an equal volume of aqueous acid. The reaction mixtures were placed in 10 ml. glass-stoppered bottles suspended in a thermostat controlled to 45±0.01°C. The reaction was followed by withdrawing samples from the bath at suitable intervals, and by titrating the acid present with 0.05 N standard sodium hydroxide, using a phenolphthalein indicator. The first-order rate constants were calculated using the expression:

$$k=\frac{2.303 \log a/(a-x)}{(\text{Catalyst})\ t}$$

where a is the initial ester concentration; x is the concentration of acid formed after time t, and (Catalyst) is the concentration of added polymeric sulfonic acid or hydrochloric acid. The catalytic efficiency, q, was defined as the ratio of the specific rate of hydrolysis catalyzed by polymeric sulfonic acid to that catalyzed by hydrochloric acid.

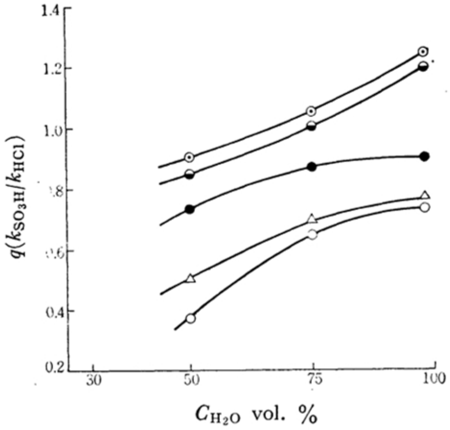

Fig. 1. Catalytic efficiencies of polymeric sulfonic acids for ethyl acetate in various mixtures of water and acetone at 45°C:
●, PVSH(S); △, PVSH(R); ○, PVSH(A); ⊙, PSSH(S); ◓, PSSH(A).

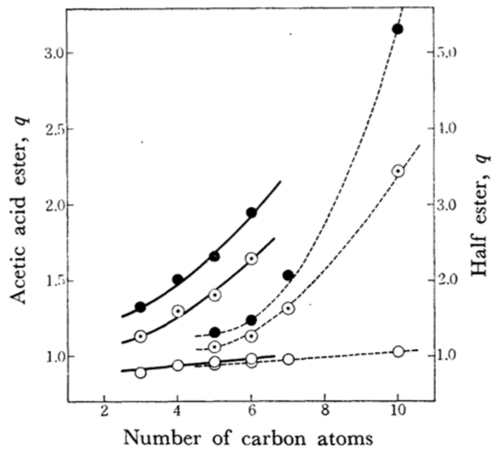

Fig. 2. Catalytic efficiencies of polymeric sulfonic aicds as a function of the chain length of acetic acid ester (solid line) and half ester (dotted line) hydrolyzed in water at 45°C (acid and ester concentrations are fixed at 0.04 and 0.025 mol./l., except 0.015 for phenyl acetate and 0.012 for methyl hydrogen azelate, respectively). Points on solid line are for methyl-, ethyl-, n-propyl-, n-butyl- and phenyl acetate and on dotted line are methyl hydrogen succinate, glutarate, adipate and azelate in increasing order:
●, (PS)SH (69%); ⊙, PSSH(S); ○, PVSH(S).

Results and Discussion

The catalytic effects of cross-linked sulfonated polystyrene resins are supposed to be appreciably different from those of water-soluble polymeric sulfonic acids because of cross-linking and particle size. The effects of particle size and cross-linking reported by Haskell and Hammett²ᵃ⁾ and Davies and Thomas²ᵇ⁾ suggested that the outer layers of the resin particles are responsible for much of the catalytic effect, the diffusion of non-electrolytes towards or away from the center of the particles being a slow process.

The results obtained in the present hydrolysis showed several new aspects by eliminating the complicating factors. The catalytic effects of polyvinylsulfonic acid (PVSH) and polystyrenesulfonic acid (PSSH) (polymerized by different methods) on the hydrolysis in 50% (v./v.) aqueous acetone were inferior to that of hydrochloric acid, especially PVSH, as is illustrated in Table I. The hydrolysis rate was, however, found to be accelerated by the increasing of volume % water in acetone-water mixtures. The hydrolysis rates measured in the presence of varying acetone concentrations are plotted in Fig. 1. In a water solution polymeric sulfonic acids were much more efficient than hydrochloric acid. This tendency is apparent in polystyrenesulfonic acid. The catalytic efficiency, q, of polymeric sulfonic acids, especially partially-sulfonated polystyrene ((PS)SH), in ester hydrolysis in water increased with the

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10) S. A. Harris, D. E. Wolf, R. Mozingo, G. E. Arth, R. C. Anderson, N. R. Easton and K. Folkers, *J. Am. Chem. Soc.*, **67**, 2098 (1945).

11) G. T. Morgan and E. Walton, *J. Chem. Soc.*, **1933**, 91.

TABLE I. THE RATES OF HYDROLYSIS OF ESTERS CATALYZED BY HYDROCHLORIC ACID, POLYVINYLSULFONIC ACIDS AND POLYSTYRENESULFONIC ACID HAVING DIFFERENT MOLECULAR WEIGHT IN 50% (v./v.) AQUEOUS ACETONE AT 45°C

$k \times 10^3$ (l. mol^{-1} min^{-1})

Acid	[η]	Et. Ac.	Et. *n*-Bu.	Et. *n*-Capro.	Et. Ph. Ac.
PVSH(S)	1.7	14.62	7.23	5.10	5.06
PVSH(R)	7.2	9.51	5.12	2.61	3.29
PVSH(A)	12.8	7.30	3.79	1.84	2.03
PSSH(S)	15.3	18.09	8.01	5.22	6.26
PSSH(R)	30.7	—	7.21	5.27	5.96
PSSH(A)	42.0	16.80	7.16	5.12	5.92
(PS)SH (69%)	—	18.32	9.03	7.39	7.36
HCl		19.84	9.28	7.31	7.30

TABLE II. THE RATE DIFFERENCE IN THE HYDROLYSIS OF ESTERS DIFFERING ONLY IN ESTER CONCENTRATION IN AQUEOUS SOLUTION

$k \times 10^3$ (l. mol^{-1} min^{-1})

Ester	Me. Ac.		Et. Ac.		Me. H. Adip.		Me. H. Azel.
Acid	0.1	0.025	0.1	0.025	0.1	0.025	0.012 (mol./l.)
(PS)SH	42.59	46.85	49.02	51.01	44.58	50.87	128.02
PSSH(S)	39.04	40.10	44.66	44.63	32.44	37.52	77.53
PVSH(S)	30.38	31.94	32.67	32.22	20.53	22.10	25.60
PVSH(A)	27.68	29.10	26.14	26.85	15.45	16.57	16.27
HCl	35.49	33.02	36.31	33.56	22.07	23.02	23.93

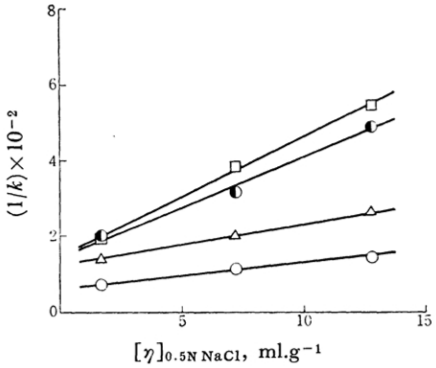

Fig. 3. Relation between hydrolysis rate of esters with PVSH and its intrinsic viscosity in 50% aq. acetone at 45°C:
○, ethyl acetate; △, ethyl *n*-butyrate;
◐, ethyl phenylacetate, □, ethyl *n*-caproate.

number of carbon atoms in the ester, as is shown in Fig. 2. The catalytic efficiency, *q*, of PVSH is closest to unity for every ester, while that of (PS)SH (69%), for example, is more than five for methyl hydrogen azelate. This contrasts remarkably with the reaction in aqueous acetone. The specificity thus obtained suggests that in aqueous acetone, because of the preferential solvation of the organic solvent with the polymer, hardly any interaction between the polymer and the ester occurs, while in water the hydrophobic interaction between the polymer catalyst and the substrate may become predominant and increase apparently with an increase in the hydrophobic character of the ester and the polymer molecule, such as (PS)SH (69%). Accordingly, it may result in an increase of the ester concentration in the neighborhood of the polymer chain by the hydrophobic interaction. Thus, the rate difference in PVSH and PSSH under these conditions should be attributed mainly to the hydrophobic character of the molecule.

The above interpretation is supported by the facts that cross-linked sulfonated polystyrene resin absorb organic solvents preferentially rather than esters in the mixed solvents, while esters or organic acids in a water solution are positively adsorbed on the resin in proportion to the length of the carbon atoms.[12]

Furthermore, the catalytic activity of PVSH in the hydrolysis of several aliphatic esters depends on the molecular weight of the polymer catalyst in 50% aqueous acetone more distinctly than it does in water. There was a linear relationship between the reciprocal of the rate constant and the intrinsic viscosity of the polymer, while hardly any such relationship was detectable in the presence of PSSH and (PS)SH (69%). A plot of $1/k$ against [η] is shown in Fig. 3.

It is believed that the remarkably different catalytic behaviors of these two kinds of polymers are due to the difference in the expansion of polymer chains in solutions and to the hydrophobic interaction between catalyst and substrate. The molecules of PVSH in solutions, especially in aqueous acetone, are not appreciably expanded as compared to those of PSSH. Since the expansion is subject to steric

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[12] C. W. Davies and G. G. Thomas, *J. Chem. Soc.*, **1951**, 2624.

restraints as the molecular weight of PVSH increases, the localized protons along the polymer chain result in confinement within an extremely limited region in the reaction system, thereby making the molecular weight of PVSH responsible for the reduction of the catalytic activity. This interpretation is supported by the observation that the catalytic effects of PVSH, in cases where the molecular weight was below 2000, were much the same as those of hydrochloric acid.

Although there is another view that the distance between sulfonic acid groups on the polymer chain may also be responsible for the catalytic activity, this is contradicted by the fact that the catalytic behavior of sulfonated isotactic polystyrene sulfonic acid (70% sulfonation) was nearly the same as that of the atactic one ((PS)SH (69%)). The hydrolysis rate constants with the former under the conditions shown in Table I were 17.12×10^{-3} for ethyl acetate and 6.08×10^{-3} for ethyl *n*-caproate. Moreover, the hydrolysis rates of esters with polymeric sulfonic acid in water were affected, to some extent, by the ester concentration. The results of some experiments are shown in Table II. The decrease in catalytic activity occurring when the concentration ratio of the ester to the polymer catalyst increased may be related to the reduction of the overall hydrolysis of esters as a result of a lack of an active site on the polymer. The above results suggest the presence of hydrophobic interaction between the polymer catalyst and the ester.