

Hydrolysis of Polymeric Esters with Long Chain Alkyl- and Alkylbenzene Sulfonic Acids

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Water soluble samples of partially acetylated polyvinyl alcohol are hydrolyzed in aqueous solution using long chain alkyl- and alkylbenzene sulfonic acids as catalyst, and the rates of hydrolysis with these catalysts are compared with those found with hydrochloric acid. When such a comparison is made at an equivalent acid concentration, octyl sulfonic acid is found to show nearly the same rate of hydrolysis as that with hydrochloric acid, whereas, in the case of hydrolysis with longer alkyl- and alkylbenzene sulfonic acids such as dodecyl- and dodecylbenzene sulfonic acids, much higher rates are observed. These higher rates of hydrolysis may be attributed to higher local concentrations of the long chain sulfonic acid in the neighborhood of polymer molecules as a result of hydrophobic attractions between the substrate and the catalyst molecule. Some quantitative discussions are also given.

1. INTRODUCTION

In a previous paper¹⁾, we have described studies concerning the homogeneous hydrolysis of low molecular weight esters with polymeric sulfonic acids such as polyvinyl sulfonic acid, copolymers of vinyl sulfonic acid and styrene and sulfonated polystyrene *etc.*

In aqueous solution of a polymeric sulfonic acid, hydrogen ions, which contribute to the hydrolysis, are localized only in the neighborhood of the polymer molecule, while, in dilute solution, there is a region where no hydrogen ions responsible for the hydrolysis exist; consequently the hydrolysis may take place only in the neighborhood of the polymer molecule. When esters of longer alkyl chains such as butyl acetate are hydrolyzed with partially sulfonated polystyrene, the ester molecules are bound by hydrophobic interactions between the benzene ring and the alkyl group. This results in a higher concentration of ester in the neighborhood of polymer molecule. In such a case, the rate of hydrolysis with a polymeric sulfonic acid is more than ten times greater than that with hydrochloric acid. When no ester molecules exist around the polymeric catalyst, no difference is found between the rates of hydrolysis by the polymeric catalyst and by hydrochloric acid.

The present paper concerns the reverse case, *i. e.*, the homogeneous hydrolysis of polymeric esters with low molecular weight sulfonic acids such as long chain alkyl- and alkylbenzene sulfonic acid. Although no changes in the macroscopic rate of hydrolysis are observed if the sulfonic acid molecules are distri-

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buted homogeneously throughout the reaction system, we would expect a much higher rate of hydrolysis if the sulfonic acid would be bound by a polymer substrate which would result in higher hydrogen ion concentration around the polymer substrate.

2. EXPERIMENTAL

Materials

Since polyvinyl acetate is insoluble in water and is unsuitable for our purpose, partially acetylated samples of polyvinyl alcohol (PVA) have been prepared according to a method developed in our Laboratory²⁾. PVA was dissolved in a suitable mixture of acetic acid and water, and heated to 40°C for acetylation using 0.1N hydrochloric acid as a catalyst. After several hours of heating acetylation equilibrium was attained. Degrees of acetylations of the samples employed in the present study ranged between 9.21 and 35.6 mole%, and DP's of the parent PVA were 170, 1410 and 5000.

For comparison commercially available ethyl- and ethylene acetate and monoacetin were used as low molecular substrates.

Octyl-, dodecyl-, hexadecyl- and octadecyl sulfonic acid catalysts were prepared and purified by conventional method. Dodecylbenzene sulfonic acid was obtained by hydrolyzing commercial dodecylbenzene sodium sulfonate.

General Procedure

Hydrolysis of esters with sulfonic acids has been carried out in aqueous solution unless otherwise specified; control experiments were always made under identical experimental conditions using hydrochloric acid catalyst. The procedure of hydrolysis was followed by titration with 0.1N-NaOH.

The reaction rate was computed according to the following pseudomonomolecular equations:

$$\frac{dx}{dt} = kb(a - x) \quad (1)$$

$$k = \frac{2.303}{tb} \log \frac{a}{a - x} \quad (2)$$

where a is initial ester concentration in moles/lit., b equivalent concentration of sulfonic acid, and x concentration of free carboxyl groups after time t .

The catalyst effect is quantitatively expressed by r indicating the ratio of the constant k for a sulfonic acid to that for hydrochloric acid: $r = k/k_{HCl}$. As we have pointed out in our previous papers³⁾, Eq. (1) does not describe the course of the hydrolysis of polyvinyl acetate. However k obtained from eq. (1), which increases with hydrolysis, has been used as the initial rate constants for comparison.

As is well-known and further confirmed by our experiments, alkyl- and alkylbenzene sulfonic acids and hydrochloric acid exhibit in aqueous solution nearly the same pH when compared at the same equivalent concentration. Therefore, if sulfonic acid is not bound to the substrate, r must be near unity.

When sulfonic acid is bound to a substrate, a larger value of r is expected.

3. RESULTS AND DISCUSSION

Influence of the Concentration of Dodecylbenzene Sulfonic Acid on r

Two PVA samples with different degrees of acetylation (23.3 and 33.6mole%) have been used for hydrolysis in aqueous solution of dodecylbenzene sulfonic acid of various concentrations. Results are shown in Fig. 1 together with those

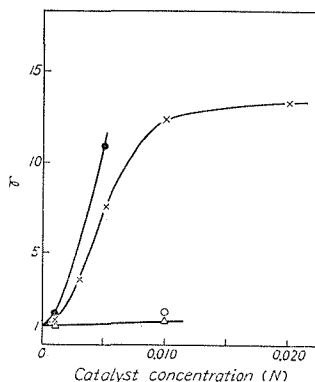


Fig. 1. Hydrolysis of partially acetylated PVA's and some low molecular esters with dodecylbenzene sulfonic acid (Substrate conc. : 0.30 g/100 cc ; temp. : 80°C).

× part. acetyl. PVA (23.3 mole%) △ monoacetin, ethylacetate
● part. acetyl. PVA (33.6 mole%) ○ ethylene diacetate

for ethyl acetate, ethylene diacetate and monoacetin. In a very dilute sulfonic acid solution r is near unity for all substrates tested. With increasing acid concentration, r increases remarkably with acetylated PVA's but the increase is very slight when the substrate is a low molecular weight acetate. The largest value of r in Fig. 1 is 14 ; this implies that dodecylbenzene sulfonic acid is 14 times more reactive than hydrochloric acid.

When the substrate is a polymer ester, the ester groups are bound to polymer molecules, and the hydrolysis cannot take place in a region between polymer molecules, as has already been mentioned.

If hydrochloric acid is distributed homogeneously throughout the reaction mixture, the rate of hydrolysis with HCl can be expressed by

$$R_{HCl} = \kappa \frac{M_{HCl}}{V} \cdot \frac{M_E}{V_p} V_p \quad (3)$$

where κ is a constant, V and V_p are total volume of the reaction mixture and effective volume around the substrate where hydrolysis can actually take place, respectively, and M_{HCl} and M_E are the amount of hydrochloric acid and of ester group, respectively. Equation (3) may be rewritten as

$$R_{HCl} = \kappa \frac{M_{HCl}}{V} \frac{M_E}{V} V. \quad (4)$$

Eq. (4) expresses that the overall rates of hydrolysis with polymer and with

low molecular weight ester are equal although in the former case the reaction occurs only in the neighborhood of a polymer molecule.

When long chain alkyl- or alkylbenzene sulfonic acid catalyst is used, part of the ester may be bound to a polymeric substrate. Assuming that the rate of the hydrolysis may be described by the same rate constant as in the case of hydrolysis with hydrochloric acid, the relative rate constant may be expressed as follows :

$$r = \frac{k}{k_{HCl}} = \frac{R}{R_{HCl}} = \frac{M_{s,p}}{V_p} \cdot \frac{V}{M_{HCl}} \quad (5)$$

where $M_{s,p}$ is the bound amount of the acid.

Since under our experimental conditions $M_{HCl} = M_s$ (M_s is total amount of the acid), Eq.(5) may be reduced to

$$r = \frac{M_{s,p}}{V_p} \cdot \frac{V}{M_s} \quad (6)$$

Therefore r is the ratio of acid concentration in the effective volume over the homogeneous distribution of the acid.

Results in Fig. 1 suggest that the binding of acids to polymeric substrate is negligible in very dilute solution but increases rapidly with increasing concentration until saturation.

Eq.(6) is applicable to any low molecular weight substrate, if the binding of acid to substrate occurs. In fact larger values of r obtained with low molecular weight substrates at higher acid concentrations shown in Fig. 1 suggest that the substrate-polymer binding does occur. We have found that butyl acetate shows similar behavior to acetylated PVA in hydrolysis with dodecylbenzene sulfonic acid.

Hydrolysis with Various Sulfonic Acids

Experiments have been carried out with acetylated PVA's of different degrees

Table 1. Hydrolysis of acetylated PVA and some low molecular esters with various sulfonic acids. (Conc. of acetylated PVA : 0.30g/100cc ; conc. of low molecular ester : 0.0120M.)

Catalyst	Catalyst conc. (N)	Temp. (°C)	r for the following substrates				
			Mono-acetin	Ethylene-diacetate	Acetylated PVA		
					9.21*	23.3*	33.6*
Octyl s. a.	0.010	40	—	—	1.1	1.1	1.3
Dodecyl s. a.	0.0050	50	—	—	10.4	9.3	10.8
Dodecyl s. a.	0.010	40	1.1	1.3	12.5	13.5	12.4
Hexadecyl s. a.	0.0010	50	—	—	6.2	—	14.1
Hexadecyl s. a.	0.0025	50	—	—	19.6	18.3	26.3
Hexadecyl s. a.	0.0050	50	1.9	—	19.3	20.0	30.0
Hexadecyl s. a.	0.010	40	—	—	7.6	19.1	22.1
Octadecyl s. a.	0.0050	50	—	—	9.1	21.8	28.4
Dodecyl b. s. a.	0.0050	50	—	—	19.3	16.7	19.9
Dodecyl b. s. a.	0.010	40	1.5	1.9	20.7	20.6	20.7

* Degree of acetylation in mole%

of acetylation and low molecular acetates using octyl-, dodecyl-, hexadecyl-, octadecyl- and dodecylbenzene sulfonic acids as catalyst. Experimental conditions and results are summarized in Table 1. For acetylated PVA's all sulfonic acids except octyl sulfonic acid show very large r -values; the largest r in Table 1 is 30. In the case of octyl sulfonic acid, acid is not bound by substrate. This conclusion is supported, as will be later shown, by viscometric study. The degree of acetylation has no serious effect upon r for dodecyl- and dodecylbenzene sulfonic acid while for hexadecyl- and octadecyl- sulfonic acid r increases with increasing degree of acetylation. The value of r for low molecular weight substrates is expectedly near unity in all cases.

Influence of Degree of Polymerization of Acetylated PVA on r

All acetylated PVA's employed in the foregoing experiments had the degree of polymerization (DP) of 1410. The influence of degree of polymerization on r has been studied. Although acetylated PVA's of different DP's should have the same degree of acetylation, however, the samples having somewhat different degrees of acetylation (35.6, 33.6 and 27.0 mole%) were only available. As shown in Table 2, the effect of r on the DP of acetylated PVA is negligible. Consequently $M_{s,p}/V_p$ is almost independent of DP. This can also be explained by a sulfonic acid-polymer bond.

Table 2. Influence of degree of polymerization of acetylated PVA on r (Substrate conc. : 0.3g/100cc ; catalyst conc. : 0.010N ; temp. : 40°C).

DP	170	1410	500
Degree of acetylation	35.6	33.6	27.0
r	16.0	20.7	16.9

Influence of Temperature and Organic Solvent on r

The molecular motion of sulfonic acid increases with increasing temperature, and r is expected to decrease because the amount of bound acid is smaller under these conditions. Experiments have been carried out at 40° and 80°C employing dodecyl-, hexadecyl- and dodecylbenzene sulfonic acid as catalysts (see Table 3). As expected with dodecyl- and dodecylbenzene sulfonic acid, r decreased with rising temperature, whereas it increased with hexadecyl sulfonic acid. The reason for the latter case is not yet completely clear but it is probably due to the unstable colloidal nature of the solution.

When an organic liquid is added to the reaction mixture the hydrophobic attraction between substrate and catalyst is depressed and r drops to unity as is shown in Table 4.

Interaction between Polymeric Substrate and Long Chain Sulfonic Acids

It is well-known⁴⁾ that surface active agents are bound in aqueous solutions to polymers such as PVA, polyvinyl pyrrolidone, polypropylene glycol and polyethylene glycol. We have also carried out viscometric experiments to show the binding of long chain alkyl- and alkylbenzene sulfonic acids to acetylated and

Table 3. Influence of reaction temperature on r . (Substrate conc. : 0.3g/100cc)

Catalyst	Degree of acetyl. (mole%)	Catalyst conc. (N)	Reaction temp. (°C)	r
Dodecyl s. a.	24.6	0.010	40	13.5
"	"	0.010	80	3.6
"	"	0.020	40	19.1
"	"	0.020	80	2.5
Dodecyl b. s. a.	10.6	0.010	40	20.7
"	"	0.010	80	14.4
"	24.6	0.010	40	21.6
"	"	0.010	80	12.4
"	"	0.020	40	22.4
"	"	0.020	80	13.3
"	33.6	0.005	40	19.9
"	"	0.005	80	10.8
Hexadecyl s. a.	10.6	0.010	40	7.6
"	"	0.010	80	44.1
"	24.6	0.010	40	19.1
"	"	0.010	80	42.8

Table 4. Effect of organic solvents on r . (Degree of acetylation of acetylated PVA : 10.6 mole% ; substrate conc. : 0.30g/100cc ; catalyst conc. : 0.010N ; temp. 40°C).

Catalyst	r for the following systems	
	Dioxane-water (3 : 7)	Acetone-water (3 : 7)
Dodecyl s. a.	1.20	1.26
Hexadecyl s. a.	0.96	1.06
Dodecyl b. s. a.	—	1.19

Table 5. Viscosity of aqueous solution of mixtures of sulfonic acids and partially acetylated (23.3 mole%) PVA, (Conc. of sulfonic acid : 0.010N ; polymer conc. : 0.30g/100cc ; temp. : 30°C)

Solution	η rel
Water+octyl sulfonic acid	1.000
Water+part. acetyl. PVA	1.211
Water+octyl s. a.+part. acetyl. PVA	1.211
Water+dodecyl sulfonic acid	1.000
Water+dodecyl s. a.+part. acetyl. PVA	1.318
Water+dodecylbenzene sulfonic acid	1.000
Water+dodecyl b. s. a.+part. acetyl. PVA	1.501
Water+PVA	1.249
Water+dodecyl b. s. a.+PVA	1.375

unacetylated PVA. Results are shown in Table 5.

Octyl sulfonic acid of near unity r -value is apparently not bound to acetylated PVA. This acid exhibited no viscosity change when added to aqueous

polymer solution. Dodecyl- and dodecylbenzene sulfonic acid having large r -values exhibited large relative viscosity increases when added to aqueous solutions of acetylated and unacetylated PVA. These observations strongly support our model of polymer-substrate bonds. To show that acetylated PVA behaves like a polyelectrolyte when a surface active agent is bound to the polymer, η_{sp}/c was determined at various polymer concentrations in aqueous dodecylbenzene sulfonic acid solutions. As shown in Table 6, η_{sp}/c increases with decreasing polymer concentration and behaves like a polyelectrolyte.

Table 6. Concentration dependence of η_{sp}/c of partially acetylated (23.3 mole%) PVA in a dilute solution of dodecylbenzene sulfonic acid. (Conc. of sulfonic acid: 0.010*N*; temp. : 30°C)

Conc. of part. acetyl. PVA	1.0	0.50	0.30	0.15
η_{sp}/c	0.972	1.17	1.67	2.50

REFERENCES

- (1) I. Sakurada, Y. Sakaguchi, T. Ono, and T. Ueda, to be published in *Makromolekulare Chemie*.
- (2) K. Kuroyanagi, and I. Sakurada, *Kobunshi Kagaku*, **6**, 419 (1949).
- (3) I. Sakurada, K. Ohashi, and S. Morikawa, *J. Soc Chem. Ind., Japan*, **46**, 1287, 1290, 1293 (1942).
- (4) S. Saito, *Kolloid-Z.*, **133**, 12 (1953) ; **154**, 19 (1957) ; **158**, 120 (1958) ; **165**, 162 (1959).