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The Alcoholysis of Polyvinyl Acetate*

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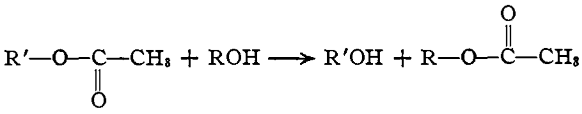
That polyvinyl acetate undergoes ester exchange under the influence of various catalysts has been reported by previous investigators, for example, Blaikie and Crozier,[1] but to date there are no quantitative kinetic data of this reaction. In the present paper the results of kinetic studies of the methanolysis of polyvinyl acetate in the presence of hydrogen chloride and sodium hydroxide as catalysts are reported. Although we refer to the deacetylation of polyvinyl acetate in absolute methanol as an alcoholysis reaction, it may also be considered an ester exchange reaction, as indicated in the following equation



$$R'—O—\underset{\underset{O}{\|}}{C}—CH_3 + ROH \longrightarrow R'OH + R—O—\overset{\overset{O}{\|}}{C}—CH_3$$

in which R'OH represents polyvinyl alcohol and ROH, methyl alcohol. Kinetic studies of such ester interchanges in anhydrous media involving small molecules are available for comparison. From these studies it can be ascertained what differences, if any, are produced in kinetic behavior when one of the molecules is a polymer. When investigating ester interchange with simple organic esters, *e. g.*, esters of aliphatic alcohols in which R and R' are closely related members of a homologous series, it is often difficult to isolate quantitatively the reaction products. Therefore, indirect physical methods have usually been employed for following the course of the reaction. In the alcoholysis of polyvinyl acetate, however, direct isolation of the polymer can be employed to follow the course of the reaction up to about 50% completion. The samples of polymer thus isolated may be analyzed for their vinyl acetate content by chemical means.

Recently, Lee and Sakurada[2] investigated the saponification of polyvinyl acetate by sodium hydroxide, using a methanol–water mixture as a solvent, and followed the progress of the reaction by determination of the disappearance of sodium hydroxide. The data indicated a bimolecular reaction whose rate constant agreed with those for the saponification of monomeric vinyl acetate and ethyl acetate under the same conditions. Skrabal[3] has suggested an alternative mechanism to account for the results of Lee and Sakurada in which methyl acetate is formed by ester interchange between methyl alcohol and polyvinyl acetate, and the methyl acetate is then saponified by the alkali. Since the reaction was followed by alkali consumption, there are insufficient data to determine which of the two processes is the rate-determining factor. Skrabal's proposed mechanism, however, would explain the correspondence between the apparent saponification rate of polyvinyl acetate and those of the simpler esters. In our experiments on the methanolysis of polyvinyl acetate, no complications similar to those encountered in the work just mentioned are possible, since the deacetylation of polyvinyl acetate was directly followed by isolation and analysis of the partially deacetylated polyvinyl esters.

Experimental

Preparation of Materials

Dry Methanol.—The dry methanol was prepared by refluxing 4.5 l. of commercial synthetic methanol over magnesium methylate prepared from 50 g. of magnesium turnings, in an all-glass reflux outfit for two hours. The methanol was then distilled in an all-glass distilling apparatus with a 15-in. Vigreux column. The portion boiling between 64.3 and 64.5° was collected. The specific gravity of the product agreed well with the accepted value in the International Critical Tables. As a further check, a sample of the methanol was analyzed for water content by an adaptation of Fischer's method.[4] Duplicate analyses by this method of liquids such as methanol should not differ by more than one unit in the second decimal in the range of 0 to 1%, using a 20-g. sample. Water was absent within the accuracy of the method.

Polyvinyl Acetate.—Polyvinyl acetates ranging in degree of polymerization between 150 and 900 monomeric units were prepared by the method of McDowell and Kenyon.[5] The polymers used in acid-catalyzed alcoholysis experiments were reprecipitated from acetone into hot water and again steamed to remove contaminants still remaining,

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[1] K. G. Blaikie and R. N. Crozier, *Ind. Eng. Chem.*, **28**, 1155 (1936).

[2] S. Lee and I. Sakurada, *Z. physik. Chem.*, **184A**, 268 (1939).

[3] A. Skrabal, *ibid.*, **185A**, 390 (1939).

[4] K. Fischer, *Angew. Chem.*, **48**, 394 (1935).

[5] W. H. McDowell and W. O. Kenyon, THIS JOURNAL, **62**, 415 (1940).

particularly benzoic acid. For both alkaline- and acid-catalyzed experiments, the polymers were dried for ten days in a Majonnier oven at 60° under a vacuum of 27 to 28 in. (700 mm.) of mercury. Weighings made after the ninth and tenth days of drying were constant. The samples were stored over anhydrous calcium chloride.

Four analyses of the dried polyvinyl acetate using the modified Fischer method gave an average moisture content of 0.05% by weight, the highest value of the four analyses being 0.1%. When dealing with solid materials such as a polymer, in which homogeneous sampling is difficult, closer checks on duplicate determinations might not be expected.[5a] The degree of polymerization (D. P.), *i. e.*, the average number of monomeric units in the polymeric chain, was determined in acetone solution by the viscosimetric method at a concentration of 0.1 g. of polymer per 100 cc. of solution.[5a] The Staudinger constant of 2.6×10^{-4} was employed to convert the specific viscosity into the corresponding degree of polymerization.

In all the experiments except those involving a study of the effect of molecular weight, polymers of relatively low degree of polymerization were employed to reduce viscosity effects to a minimum.

Catalysts.—The alkaline catalyst was prepared by dissolving 25 g. of sodium hydroxide in 2500 cc. of dry methanol and filtering through an asbestos mat to remove carbonate. The acid catalyst was prepared by passing dry hydrogen chloride into dry methanol maintained at −9°. Samples were not stored for more than a few hours to avoid possible errors introduced by slow esterification of the methyl alcohol by the hydrogen chloride.

General Procedure for Alcoholysis

The general procedure of acid alcoholysis was as follows: A known weight of polyvinyl acetate (25 g. in those experiments where the concentration of polymer was not varied) was dispersed with shaking in 400 cc. of dry methanol. When dispersion was complete, the tightly stoppered flask was immersed in a bath thermostatically maintained at 30.00 ± 0.05° to establish equilibrium between the contents of the flask and the bath. The catalyst, made up to a volume of 200 cc. with dry methanol, was then added under constant mechanical stirring. In experiments at 30° the catalyst solution was at room temperature when added. However, in experiments at 10 or 50° the catalyst solution was brought to the bath temperature before addition. After being stirred for a minute, 25 cc. of solution was pipetted from the mixture, added to about 100 cc. of 70:30 methanol–water and titrated with 0.500 *N* sodium hydroxide solution with phenolphthalein indicator. The alcoholysis mixture was stirred for a total of five minutes and the reaction was then allowed to proceed with no further stirring in the tightly stoppered flask. At suitable intervals, samples were removed and immediately precipitated with agitation in tap water at about 35°. Before the last sample was taken, another 25-cc. portion of the reaction mixture was titrated to determine the change in catalyst concentration during reaction. The precipitated samples were washed with tap water until acid free and dried for five days in small aluminum dishes in a Majonnier oven at 60° under a vacuum of 27 to 28 in. (700 mm.) of mercury. At this time, successive weighings, twenty-four hours apart, were constant.

It has been shown by other investigators[6] that the alcoholysis reaction is very sensitive to slight changes in the moisture content of the reaction mixture. We realized that moisture might be introduced by contact with the atmosphere during the steps of mixing the components and removing the samples following the technique described in the preceding paragraph. Therefore, before this method was adopted, a comparative series was run in which contact of the reaction mixture with the moisture of the atmosphere was excluded during these steps. The form of the reaction curve obtained was identical with that of the curve obtained using the experimental technique described. In each new series of experiments a duplicate of a previous experiment was included as a control to be sure that no serious experimental errors, such as improper catalyst concentration or absorption of moisture from the air, had been introduced. If a control had shown any substantial deviation, the accompanying series would have been rerun, but no significant deviations were encountered.

The procedure for alkaline alcoholysis was substantially the same as for acid alcoholysis except for certain modifications in concentration. Fifteen grams of polyvinyl acetate was dispersed in 470 cc. of dry methanol. When this mixture had come to temperature equilibrium with the bath, the catalyst and a sufficient amount of methanol to bring the volume of the reaction mixture to 525 cc. were added. After being stirred for one minute, a portion was removed by pipet, added to 100 cc. of 70:30 methanol–water, and titrated with standard acid. Samples were removed at suitable intervals and precipitated in water at 35° which had been slightly acidified with hydrochloric acid. Acidification aided precipitation and washing.

The bath temperatures of 10, 30 and 50° were thermostatically controlled to a variation of ±0.05°.

Analysis of Samples

One-half gram of the polyvinyl ester was dispersed in 20 cc. of Eastman Kodak Co. grade pyridine, usually at room temperature. Dispersion may be accelerated, however, and, with samples of low acetate content, aided, by warming to 55°. An excess of standard potassium hydroxide in methyl alcohol was pipetted into the flask. After heating the solution at 55° for one hour, 100 cc. of distilled water was added and the samples were left at room temperature for approximately sixteen hours. During this time the polyvinyl alcohol which precipitated during hydrolysis either dissolved completely or became swollen. Excess alkali was titrated with standard hydrochloric acid. From the alkali consumed, the vinyl acetate content of the polymer was calculated.

Using this procedure, commercial polyvinyl acetates and those made in these Laboratories could be analyzed with a reproducibility of approximately 0.1 cc. of 0.5 *N* alkali per half-gram sample and with a deviation from the calculated value within 1%. All analyses were made in duplicate and averaged. The analytical values are given in terms of mole per cent. calculated from the weights of the monomeric units, *i. e.*, vinyl acetate 86 and vinyl alcohol 44.

(5a) We wish to thank the Industrial Laboratory for the moisture determinations and Dr. P. T. Newsome and Mr. R. H. Wagner, of these Laboratories, for the viscosity measurements.

(6) H. Dawson, *J. Chem. Soc.*, **99**, 3 (1911).

Results

When polyvinyl acetate is alcoholyzed with acidic or basic catalysts in methanol, a mixed polymer, or hydrolyzed polyvinyl acetate, is formed which contains both hydroxyl and acetyl groups. As the ratio of hydroxyl to acetyl groups increases, the alcoholyzed acetate becomes increasingly water-susceptible, passing through a stage at which it is swollen and somewhat water-soluble, ultimately reaching complete water-solubility. Because of the difficulty of isolating samples which had been alcoholyzed to incipient water-solubility, the alcoholyses were followed, in most cases, only to the point at which about 50 mole per cent. of the acetyl groups was removed. Up to this point, the recovery is substantially quantitative.

The results of typical experiments are summarized in Table I. For brevity, the analytical values of subsequent experiments are not tabulated, but only the constants of the reactions are given.

TABLE I

REPRESENTATIVE ALCOHOLYSIS EXPERIMENTS

Acid-catalyzed (run no. 110)

N_{acid} = 0.695; temp., 30.00 ± 0.05°; concn. polymer. 0.468 monomeric moles/l.; D. P., 272

Time, min.	Vinyl alcohol			
	Wt. % (z)	Mole % (x)	$z^{0.5}$	$x^{0.5}$
4	2.31	4.42	1.52	2.10
8	6.09	11.27	2.47	3.35
13	13.41	23.19	3.67	4.83
18	24.95	39.33	4.99	6.26
22	35.09	51.30	5.92	7.16
25	42.71	59.22	6.53	7.70

Base-catalyzed (run no. 18)

N_{base} = 1.838 × 10^{-2}; temp., 30.00 ± 0.05°; concn. polymer, 0.332 monomeric moles/l.; D. P., 365

Time, min.	Vinyl alcohol			
	Wt. % (z)	Mole % (x)	$z^{0.5}$	$x^{0.5}$
6.5	2.9	5.5	1.70	2.34
12	6.5	11.7	2.55	3.42
18	12.1	21.1	3.48	4.59
24	19.4	32.0	4.40	5.65
30	28.9	44.0	5.38	6.63

Figure 1 shows the experimental data as weight per cent. of polyvinyl alcohol (z) and as mole per cent. (x) *versus* time of alcoholysis (t). These data can be expressed as a linear relationship (Fig. 2) by using the empirical equations

$$\sqrt{x} = mt \qquad (1)$$

$$\sqrt{z} = m't \qquad (1a)$$

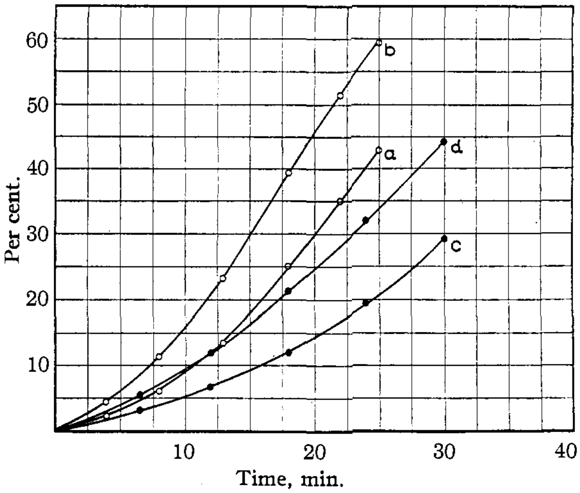


Fig. 1.—Typical alcoholysis experiments: (a) weight per cent. of polyvinyl alcohol (z) formed *vs.* time, acid-catalyzed; (b) mole per cent. of polyvinyl alcohol (x) formed *vs.* time, acid-catalyzed; (c) weight per cent. of polyvinyl alcohol (z) formed *vs.* time, base-catalyzed; (d) mole per cent. of polyvinyl alcohol (x) formed *vs.* time, base-catalyzed.

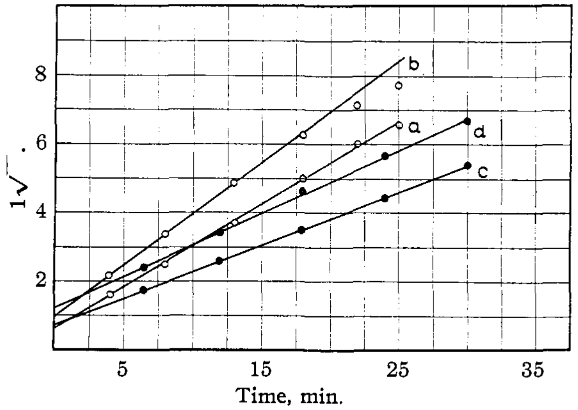


Fig. 2.—Typical alcoholysis experiments: (a) $\sqrt{z}$ *vs.* time, acid-catalyzed; (b) $\sqrt{x}$ *vs.* time, acid-catalyzed; (c) $\sqrt{z}$ *vs.* time, base-catalyzed; (d) $\sqrt{x}$ *vs.* time, base-catalyzed.

In subsequent work, the concentration of polyvinyl alcohol is expressed in terms of mole per cent. This relationship of the square root of the mole per cent. of polyvinyl alcohol *versus* time appears valid over a range of at least 30% completion. The slope m forms a convenient means by which the velocities may be compared, since it represents an average value in which all the data in a given experiment are weighted equally. If $y(x_0x)$ represents the absolute concentration of polyvinyl alcohol units at any time, and x_0 represents the original concentration of polyvinyl acetate, both in monomeric moles per liter, the relationship between the absolute instantaneous velocity, dy/dt, and m is obtained as

$$dy/dt = 2\,\frac{mx_0\sqrt{x}}{100} \qquad (2)$$

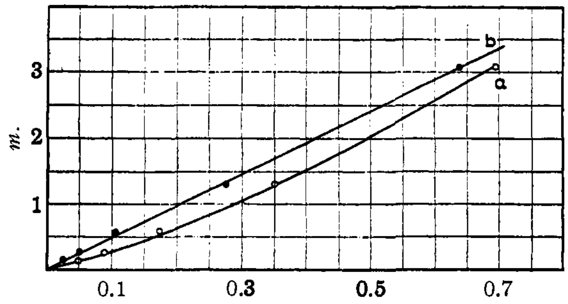


Fig. 3.—The effect of acid catalyst concentration on reaction rate: (a) N; (b) $N^{1.22}$.

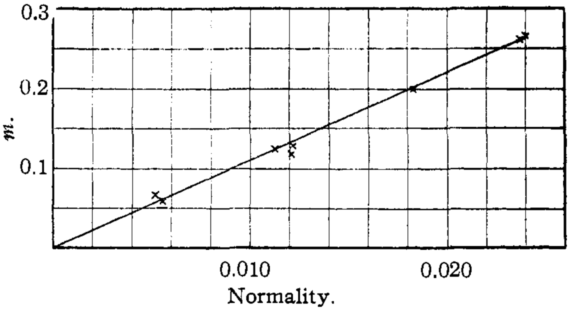


Fig. 4.—Effect of basic catalyst concentration on the reaction rate.

Formally, the quantity m may be regarded as a function of all the variables. In the tabulation of results, comparisons of relative velocities are effected by means of a characteristic quantity K, obtained by dividing m by the catalyst concentration $N_{b(ase)}$ in the base-catalyzed alcoholysis and $N^{1.22}_{a(cid)}$ in the acid-catalyzed alcoholysis. The reason for using a value $N^{1.22}$ in the case of the acid alcoholysis will be explained later.

Effect of the Catalyst Concentration on the Rate of Reaction.—Results of the study of the effect of catalyst concentration on the reaction rate are shown in Tables IIa and IIb and Figs. 3 and 4.

TABLE II

EFFECT OF CATALYST CONCENTRATION ON RATE OF REACTION

a. ACID-CATALYZED ALCOHOLYSIS

Temp., 30.00 ± 0.05°. Concn. of polymer in monomeric moles/l. (x_0) = 0.468; degree of polymerization (D. P.), 272

Run no.	N_{acid}	m	$N^{1.22}_{acid}$	$K = m/N^{1.22}$
106	0.0490	0.011	0.0252	0.438
107	.0888	.0250	.0521	.480
108	.1738	.0570	.1183	.482
109	.351	.132	.2788	.474
110	.695	.308	.6415	.479

b. BASE-CATALYZED ALCOHOLYSIS

Temp., 30.00 ± 0.05°; concn. of polymer in monomeric moles/l. (x_0) = 0.332; degree of polymerization (D. P.), 365

Run no.	$N_{base} \times 10^3$	m	$K = m/N_{base}$
24	5.23	0.067	12.8
23	5.5	.062	11.3
20	11.3	.125	11.1
19	12.1	.118	9.8
49	12.2	.132	10.8
18	18.3	.199	10.9
25	23.7	.262	11.1
26	24.0	.267	11.1

The values of the normalities are averages of titrations at the beginning and the end of the reaction. In the acid-catalyzed samples there was no appreciable change in catalyst concentration during the reaction. In the base-catalyzed reactions, a decrease of approximately 10% usually occurred. In the base-catalyzed alcoholysis (Fig. 4), the relationship between m (Eq. 1) and alkali concentration in terms of normality is linear. The slope is shown in Table IIb as a characteristic quantity of K_b, equivalent to m/N_b. When the data of Table IIa are plotted in a similar manner (Fig. 3), a linear function is not obtained, but, when $N_a^{1.22}$ is used in place of N_a, a straight line passing through the origin results.

In Tables IIIa and IIIb, the results of studies of effect of molecular size upon the rate of reaction are summarized.

TABLE III

EFFECT OF DEGREE OF POLYMERIZATION OF POLYVINYL ACETATE ON RATE OF REACTION

a. ACID-CATALYZED ALCOHOLYSIS

Temp., 30.00 ± 0.05°; concn. of polymer in monomeric moles/l. (x_0) = 0.468

Expt.	D. P.	N_{acid}	m	K_a
118	692	0.1848	0.0636	0.488
119	381	.1222	.0360	.469
120	272	.2170	.0738	.488
121	147	.1851	.0500	.392

b. BASE-CATALYZED ALCOHOLYSIS

Temp., 30.00 ± 0.05°; concn. of polymer in monomeric moles/l. (x_0) = 0.332

Expt.	D. P.	$N_{base} \times 10^2$	m	K_b
49	365	1.218	0.132	10.8
50	520	1.228	.1245	10.2
51	870	1.213	.1270	10.5

The results of experiments made to ascertain dependence of the alcoholysis rate on the initial concentration of polyvinyl acetate are tabulated in Tables IVa and IVb.

The results of experiments to determine the dependence of velocity of alcoholysis on temperature are tabulated in Tables Va and Vb.

TABLE IV

EFFECT OF POLYMER CONCENTRATION ON RATE OF REACTION

a. ACID-CATALYZED ALCOHOLYSIS

Temp., 30.00 ± 0.05°; degree of polymerization (D. P.), 272

Run no.	Concn. polymer, x_0	m	N_{acid}	K_a
111	0.235	0.155	0.3672	0.513
112	.466	.138	.3633	.474
113	.90	.123	.347	.448
114	1.7	.104	.3363	.395

b. BASE-CATALYZED ALCOHOLYSIS

Temp., 30.00 ± 0.05°; degree of polymerization (D. P.), 365

Run no.	Concn. polymer, x_0	m	$N_{base} \times 10^3$	K_b
43	0.332	0.1185	10.8	10.9
44	.44	.147	13.4	10.9
45	.62	.135	13.4	10.1
46	1.05	.1125	13.4	7.7

In experiments 44, 45, and 46, the high resin concentration made it impossible to titrate the samples for catalyst content. A known amount of base was therefore used and the sodium hydroxide concentration calculated.

TABLE V

EFFECT OF TEMPERATURE ON RATE OF REACTION

a. ACID-CATALYZED ALCOHOLYSIS

Concn. of polymer in monomeric moles/l. (x_0) = 0.468; degree of polymerization (D. P.), 272

Run no.	Temp., °K.	N_{acid}	m	K_a	log ($K \times 10^2$)
115	283	0.231	0.0160	0.0957	0.981
116	303	.167	.0485	0.431	1.634
117	323	.166	.193	1.725	2.237

b. BASE-CATALYZED ALCOHOLYSIS

Concn. of polymer in monomeric moles/l. (x_0) = 0.332; degree of polymerization (D. P.), 365

Run no.	Temp., °K.	m	$N_{base} \times 10^2$	K_b
60	283	0.14	5.4	2.6
61	283	0.146	6.14	2.4
	303[a]	...	...	11.05[a]

[a] Average, see Table IIb.

In alkaline alcoholysis, experiments were run at 10 and 30°. From the average values of these results, the velocity appeared to double with each 10° increase in temperature. In acid-catalyzed alcoholysis, the change of K_a with temperature follows the Arrhenius temperature dependence equation, as shown in Fig. 5. The reaction rate approximately doubled for each 10° increase in temperature within the limits investigated. Upon substituting the respective values of K in the Arrhenius equation, values for the energy of activation of 13,000 calories for the base-catalyzed alcoholysis and 13,200 calories for the acid-catalyzed alcoholysis were calculated.

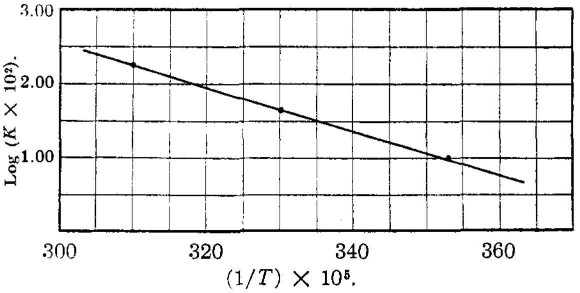
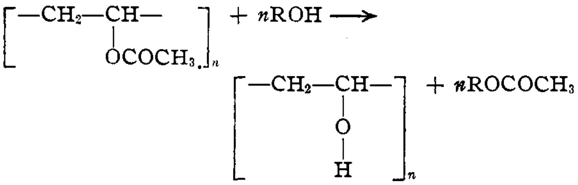


Fig. 5.—The dependence on temperature of the acid-catalyzed reaction.

Discussion

Polyvinyl acetate is generally believed to be a long-chain molecule of recurring monomeric units and is thus an ester of a high molecular weight linear polyhydric alcohol (polyvinyl alcohol). It must be borne in mind that any given sample of polymer contains a distribution of chains of different lengths, the measured D. P. of which represents an average value. A partially deacetylated product possesses a distribution not only of chain lengths, but also, possibly, of molecules containing various relative quantities of hydroxyl and acetyl groups. It is assumed in this treatment that, for any given degree of deacetylation, the ratio of hydroxyl to acetyl groups on most of the chains is close to the average obtained by analysis. Since the ester groups are dependent units along the chain, the essential over-all reaction may be represented in terms of the simple monomeric units, as follows



$$\left[-CH_2-\underset{\displaystyle OCOCH_3}{\underset{|}{CH}}-\right]_n + nROH \longrightarrow \left[-CH_2-\underset{\displaystyle H}{\underset{|}{\underset{\displaystyle O}{\underset{|}{CH}}}}-\right]_n + nROCOCH_3$$

Though rupture of the chains appears to accompany the deacetylation of polyvinyl acetate,[5] the present study is probably not appreciably affected by such a phenomenon.

Studies of the alcoholyses of simple esters, several of which have been carried out heretofore,[7] indicate that the reaction may be regarded as dependent upon the first powers of the concentration of ester groups and of the acidic or basic catalyst, respectively. In the system dealt with here, however, it was found that the course of the reaction could not be represented in terms of any simple kinetic model. Under any given set

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[7] S. Kolhatkar, *J. Chem. Soc.*, **107**, II, 921 (1915).

of initial conditions the course of the reaction appears to be autocatalytic, *i. e.*, the absolute velocity of the reaction increases continuously up to about 40 mole per cent. completion. One of the products of the reaction, methyl acetate, is excluded as the autocatalyst, as a result of qualitative experiments in which the material was found to depress the velocity when present in large concentrations. Since similar curves were obtained for acidic and basic catalysis, it appears that the factors influencing the rate during the course of the reaction are related to the degree of deacetylation of the polymer rather than to external causes. The increase in the hydroxyl content may cause a change in the solvent–solute relationship which produces an increase in rate as the reaction progresses.

An explanation of the behavior just noted may also be found by considering the reaction to be stepwise. Thus, the velocity of the reaction under any given set of initial conditions may be represented by the formula

$$dy/dt = rk_1(P_r) + (r - 1)(k_2)(P_{r-1}) + \ldots + (r - n)(k_{n+1})(P_{r-n}) \quad (3)$$

where dy/dt is the instantaneous rate of production of polyvinyl alcohol in monomeric moles per liter per unit time, P_r is the concentration of unreacted polymer, r is the number of acetyl groups initially present in the average polymeric molecule, and P_{r-n} is the concentration of polymer from which have been removed n acetyl groups. If it is assumed that the representative quantities k_n are functions of n, it is readily seen that dy/dt may increase continuously throughout the initial portion of the reaction, if $k_1 < k_2 \ldots k_n < k_{n+1}$. This scheme also imposes the condition that the rate will decrease rapidly during the latter stages of reaction. In this connection it will be observed from Figs. 1b and 1d that such a decrease appears to begin near 40% completion of the reaction. Changes of k_n due to steric effects often have been noted in other investigations of alcoholysis[8] and hydrolysis[9] of esters of polybasic acids.

Yamasaki[10] has shown that each ester radical of triacetin has an equal rate of hydrolysis at 35° with hydrochloric acid catalysis. In addition to the difficulties of comparing a hydrolysis reaction with an alcoholysis, triacetin is an ester of a 1,2-glycol, while polyvinyl acetate is an ester of a 1,3-glycol[11] which may introduce steric effects of the residual ester groups.

It has been suggested that the apparent autocatalytic cause of the reaction is due to the presence of a small amount of moisture in the reactants which depresses the rate of deacetylation in the early stages and which disappears as the reaction proceeds. Assuming that the shape of the reaction curve is in part a consequence of the presence of water, the process by which it disappears must involve a positive catalysis by acid and base, respectively, in approximately the same power dependence as that of the main reaction. It would seem improbable from kinetic considerations that the rate of disappearance of water in the cases of acidic and basic catalysis, respectively, would be such as to balance the alcoholysis reaction so that the net observed results in the respective cases would be similar. Furthermore, the course of the reaction conforms to the same empirical equation at all of the temperatures investigated. This implies that the temperature coefficients of the alcoholysis and the assumed reaction leading to the disappearance of water must be nearly the same. This seems rather unlikely. Unless water is consumed by other impurities present, no reaction is apparent to account for its disappearance.

In preliminary experiments, not reported in this paper, using commercial polyvinyl acetate and methanol without further drying, reaction curves similar to those of the carefully dried materials were obtained, though the reaction velocity was less. If it is assumed that ROH_2^+ is a more active catalyst for the alcoholysis than is H_3O^+, a uniformly depressed reaction rate would be expected when small amounts of water are present.

Other aspects of the reaction present no similar abnormalities. Figure 4 shows that the velocity of alcoholysis depends on the first power of the alkali concentration (the concentration of the base was always small enough to consider that the activity coefficient was essentially equal to 1). In the case of the acid-catalyzed alcoholysis (Fig. 3), however, the rate seems proportional to a fractional power of the concentration of hydrogen chloride. While previous investigations[8] of similar alcoholytic processes have shown that rates

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[8] Z. Patel and H. Watson, *J. Indian Inst. of Science*, **16A**, 55 (1933).

[9] *E. g.*, A. Skrabal and E. Singer, *Monatsh.*, **40**, 363 (1919); **41**, 339 (1920).

[10] E. Yamasaki, THIS JOURNAL, **42**, 1455 (1920); see also J. Meyer, *Z. Elektrochem.*, **13**, 485 (1907).

[11] C. S. Marvel and C. E. Denoon, Jr., THIS JOURNAL, **60**, 1045 (1938).

depend on approximately the first power of acid concentration, there are numerous instances of other acid-catalyzed reactions in which the dependence has been found to be complex.[12]

Except for one instance which appears anomalous, the data in Tables IIIa and IIIb indicate no significant change in velocity caused by variation of chain length. This constitutes further support for the earlier assumption that degradation of the chain during the reaction is without appreciable effect in so far as the kinetics of alcoholysis are concerned. According to equation (2), the rate of appearance of polyvinyl alcohol divided by the initial concentration of polymer (x_0) at any given value of x should be a constant. Tables IVa and IVb show that this condition is approached in dilute solutions. With increasing polymer concentration, there is a well-defined downward drift of the values of K. Since an over-all change in concentration of eightfold causes only about a 25% change in the relative rate of alcoholysis, it may be concluded that the deviations in more concentrated solutions of the polymer are due to secondary causes.

From Fig. 5 it is seen that the data conform to the Arrhenius equation. It thus appears likely that all of the rate constants K_n appearing in the scheme represented by equation (3) have approximately the same dependence on temperature.

Summary

1. The alcoholysis of polyvinyl acetate in absolute methanol has been studied, using both hydrogen chloride and sodium hydroxide as catalysts.

2. The reaction possesses apparent autocatalytic characteristics, which may be due either to an autocatalytic or to a stepwise nature.

3. The reaction rate is dependent on the first power of the concentration of the basic catalyst, and on the 1.22 power of the concentration of the acidic catalyst.

4. The reaction rate is further dependent upon approximately the first power of the polymer concentration, independent of the molecular weight of the polymer, and responds to temperature changes according to the Arrhenius equation.

5. A qualitative explanation of these relationships is suggested.

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[12] See, *e. g.*, H. Dawson and F. Powis, *J. Chem. Soc.*, **103**, II. 2135 (1913).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Oxidation Products of $\Delta^{9,10}$-Octalin

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This work was initiated for the purpose of finding a suitable method of preparing the octalone-1 which has been designated by Hückel and Naab[1] as the $\Delta^{9,10}$-isomer. In addition it was planned to prepare intermediates such as $\Delta^{9,10}$-octalol-1 which, along with the known 9,10-dihydroxydecalin, may be converted by dehydration into different isomeric hexahydronaphthalenes. The latter are of interest as model compounds for the many natural products which contain this diene system.

For the preparation of $\Delta^{9,10}$-octalin the method of Linstead *et al.*[2,3] was followed although certain modifications which appear to be essential were made. The method consists of the dehydration of β-decalol and isomerization of the resulting octalin by means of phosphoric acid and phosphoric anhydride. The yield of $\Delta^{9,10}$-octalin from β-decalol was 78%. Although we have obtained the known blue nitroso chloride derivative[3c] of $\Delta^{9,10}$-octalin from our product, the possibility that small amounts of isomers are present[2] is by no means excluded.

The desired octalone-1 has been obtained by the action of nitrous acid on 9-amino-$\Delta^{4,10}$-octalin and by the chromic acid oxidation of $\Delta^{9,10}$-octalin.[1] More recently it has been made by cyclization of γ-(Δ^1-cyclohexenyl)-butyric acid.[4] We have obtained the same substance in 45% over-all yield by the following series of reactions. The oxidation of $\Delta^{9,10}$-octalin with selenium dioxide in the presence of acetic anhydride at 5° gave the acetate of $\Delta^{9,10}$-octalol-1 (II) in 65% yield. Hydroly-

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[1] Hückel and Naab, *Ann.*, **502**, 136 (1933).

[2] Linstead, Wang, Williams and Errington, *J. Chem. Soc.*, 1136 (1937).

[3] Other methods for the preparation of $\Delta^{9,10}$-octalin: (a) Nametkin and Gaglow, *Ber.*, **62**, 1570 (1929); (b) Durland and Adkins, THIS JOURNAL, **61**, 429 (1939); (c) Hückel, Danneel, Schwartz and Gercke, *Ann.*, **474**, 121 (1929).

[4] Nenitzescu and Przemetzky, *Ber.*, **74**, 676 (1941).