

1234

The Kinetics of the Heterogeneous Hydrolysis of Poly(vinyl formate) and of Poly(vinyl formate-co-stearate)*

EDMUND F. JORDAN, JR., and WILLIAM S. PORT, *Eastern Regional
Research Laboratory, † Philadelphia 18, Pennsylvania*

In a previous paper,¹ the preparation and the properties of poly(vinyl alcohol-co-stearate) were described. The practical success in the preparation rested on the ability of the formate segments in poly(vinyl formate-co-stearate) to be hydrolyzed selectively when suspended in a dilute solution of a strong acid. The kinetics of the hydrolysis of the formate and of the stearate) segments in this copolymer under these conditions were therefore studied. In the course of the study, the activation energies, the frequency factors, and the entropies and free energies of activation for the hydrolyses, and the effect of the stearate content on these constants were determined. A comparison was also made between these constants and those calculated from data in the literature for model compounds.

The hydrolysis of an ester is a reaction whose rate is dependent on the concentration of three molecular species, and if the concentration of each of these species were permitted to vary, the reaction would be expected to follow third-order kinetics, i.e.:

$$-\frac{d(\text{RCO}_2\text{R}')}{dt} = \frac{d(\text{RCO}_2\text{H})}{dt} = k_3(\text{RCO}_2\text{R}')(\text{H}_2\text{O})(\text{H}_3\text{O}^+) \quad (1)$$

If, however, as in the present experiments (where RCO_2H is HCO_2H), hydrolysis is carried out heterogeneously in a large excess of water, and if the diffusion rate of water is constant, the concentration of water and ester may be assumed to be constant and eq. (1) reduces to a pseudo-first-order reaction:

$$\frac{d(\text{HCO}_2\text{H})}{dt} = k_f(\text{H}_3\text{O}^+) \quad (2)$$

If a strongly ionized acid is added in such concentration that the change in the hydrogen ion concentration due to the hydrolysis of the ester is

* This paper was presented at the Fall Meeting of the American Chemical Society, New York, N. Y., September 13, 1957. It is Part XII in the series "Polymerizable Derivatives of Long-Chain Fatty Acids." Paper XI is ref. 1.

† One of the Laboratories of the Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

negligible, the hydrogen ion concentration becomes constant and eq. (2) becomes a pseudo-zero-order reaction and integrates to:

$$(\text{HCO}_2\text{H})_t = k_a t \quad (3)$$

where $(\text{HCO}_2\text{H})_t$ is the concentration of formic acid at time t , and k_a is the reaction rate constant at the particular acid concentration, $(\text{H}_3\text{O}^+)_a$, of the experiment. The first-order constant k_f is related to k_a in that it is a partially reduced reaction rate constant, i.e.:

$$k_f = \frac{k_a}{(\text{H}_3\text{O}^+)_a} \quad (4)$$

In a similar fashion, the hydrolysis of stearate segments is given by:

$$\frac{d(\text{C}_{17}\text{H}_{35}\text{CO}_2\text{H})}{dt} = k_s (\text{H}_3\text{O}^+) \quad (5)$$

$$(\text{C}_{17}\text{H}_{35}\text{CO}_2\text{H})_t = k'_a t \quad (6)$$

$$\frac{k'_a}{(\text{H}_3\text{O}^+)_a} = k_s \quad (7)$$

EXPERIMENTAL

Poly(vinyl formate) and copolymers of vinyl formate and vinyl stearate were prepared and purified by the techniques previously reported.¹ Samples of these polymers were obtained as irregular, porous flakes of dimensions approximately $1.5 \times 1.5 \times 0.5$ cm.

For the analytical methods used in the kinetic studies, advantage was taken of the experimentally observed condition that the formic acid obtained on hydrolysis entered almost entirely into the water phase, whereas the stearic acid produced remained occluded in the polymer. A new polymer sample was used for each time interval. Samples were placed into graduates and 75.0 g. of 0.01–0.2 *M* hydrochloric acid was added to each graduate. (The molarity of the hydrochloric acid was determined analytically.) An air condenser was used to close the graduate which was then heated in a thermostatically controlled bath at a temperature in the range of 65–97°C. At the end of a predetermined period, the graduate was removed from the bath, the sample was well stirred, and a 10.00 ml. aliquot of the supernatant liquid was taken and titrated with standard alkali. The acid content in excess of the hydrochloric acid originally present thus corresponded to the formate segments hydrolyzed. The residual polymer was then separated, and it was cut into small pieces and extracted three times with 100 ml. refluxing acetone to recover the hydrolyzed stearic acid. (The final extraction was preceded by overnight storage in acetone at room temperature.) Formic acid was removed by repeated evaporation with acetone until no odor of formic acid could be detected. Final traces of

formic acid were removed by azeotropic distillation with chloroform. The residual stearic acid was then dissolved in ethanol and titrated with standard alkali.

RESULTS AND DISCUSSION

The general conformance of the hydrolysis of the formate and stearate groups to zero-order kinetics at given acid concentrations is shown in Figures 1 and 2 for a copolymer containing 3 mole-% vinyl stearate. A

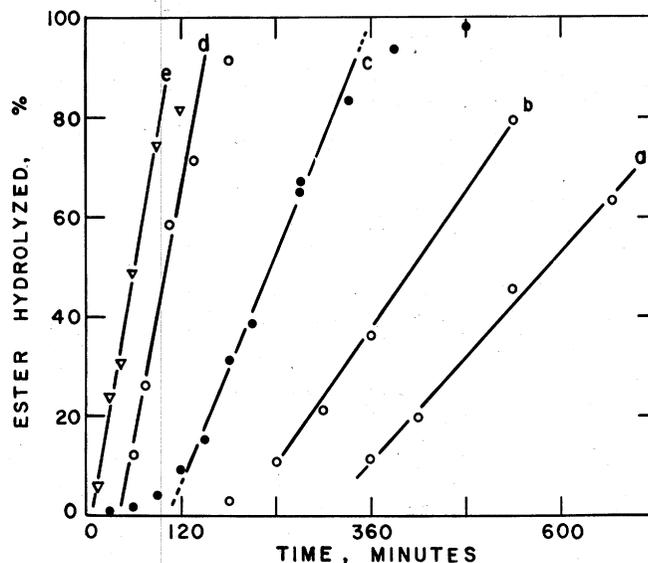


Fig. 1. Hydrolysis of a copolymer of vinyl formate containing 3 mole-% vinyl stearate. Removal of formate segments: (a) at 66°C., 0.1781 *M* HCl; (b) at 75.5°C., 0.0933 *M* HCl; (c) at 75.5°C., 0.1776 *M* HCl; (d) at 85.5°C., 0.1787 *M* HCl; (e) at 96.5°C., 0.1845 *M* HCl.

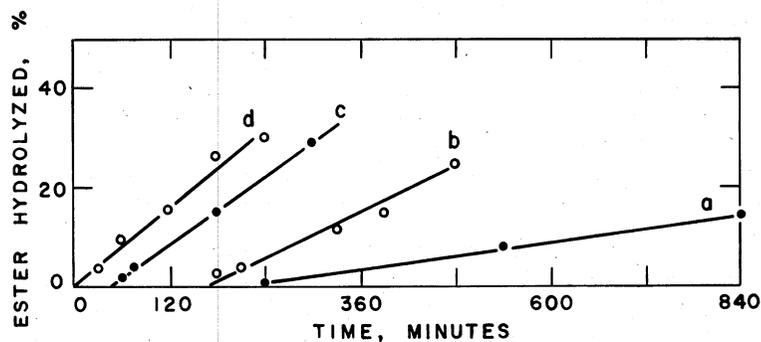


Fig. 2. Hydrolysis of a copolymer of vinyl formate containing 3 mole-% vinyl stearate. Removal of stearate segments: (a) at 75.5°C., 0.0933 *M* HCl; (b) at 75.5°C., 0.1776 *M* HCl; (c) at 85.5°C., 0.1787 *M* HCl; (d) at 96.5°C., 0.1845 *M* HCl.

linear relationship between the per cent of ester hydrolyzed and time pertains for the major portion of the hydrolysis period. However, as may be seen, for example, from Curve *c* in Figure 1, there are two periods of deviation from the linear relationship. During the first 15% of the hydrolysis the rate increases with time and in the final 15% of the hydrolysis the rate drops off. The duration of the early period deviation varies inversely with the hydrochloric acid concentration and with temperature. A possible explanation of the early period deviation is that complete diffusion of catalyst acid and water into the polymer has not yet occurred and that not all the polymer chains are contributing to hydrolysis. Hence, the rate of hydrolysis appears to be low in this initial period.

The later deviation is not understood; it is possible that the decreased rate is due to the rate of reversal of the hydrolysis becoming significant as the concentration of formic acid increases. There is also some experimental evidence for retention of formic acid by the polymer. Direct analysis of the residual polymer corresponding to the samples at 330 and 390 minutes (Curve *c*, Figure 1), after the extraction with acetone to remove the stearic acid, showed 2.5 and 0.9% formate contents, respectively. This would seem to indicate that the hydrolysis has proceeded to 97.5 and 99.1%, respectively. It is possible, however, that small amounts of polymers having high formate contents were extracted by the acetone and that, therefore, the per cent hydrolyses indicated in the figure are correct, but a change in the rate of hydrolysis had occurred.

If there be a real decrease in the rate of hydrolysis of the formate segments when the hydrolysis exceeds about 80% this must be taken into account in any application of the data to arrive at an optimum time for a practical preparation of the vinyl alcohol copolymers. For example, the optimum time may be selected on the basis of an arbitrarily predetermined maximum concentration for residual formate segments (e.g., 2%). From Curve *c* in Figure 1, therefore, if the decreased rate of hydrolysis is considered to be real, the optimum time using 0.1776 *M* hydrochloric acid at 75.5°C. is approximately 8 hours. If the zero-order rate data alone be used (i.e., the decrease in the rate of hydrolysis be considered to be only apparent), the optimum time would be approximately 6 hours. In any

TABLE I
Effect of the Catalyst Acid Concentration on the Rate Constants for the Hydrolysis of Poly(vinyl formate-co-stearate)^a

	75.5°C.		85.5°C.	
	[HCl], mole/l.	0.1776	0.0933	0.1787
K_a , %/min.	0.431	0.241	1.08	0.505
K_f , min. ⁻¹	2.43	2.59	6.06	5.46
K_a' , %/min.	0.0556	0.0247	0.104	0.0522
K_s , min. ⁻¹	0.319	0.264	0.593	0.565

^a Copolymer containing 3 mole % vinyl stearate.

technological use of the rate data, due consideration must be made, of course, for the initial period.

The test of the validity of eqs. (4) and (7) for the system under investigation is shown in Table I.

Thermodynamic Constants of the Activated Complex for the Hydrolysis of Poly(vinyl esters)

In Table II, there is compiled the rate data for hydrolysis at temperatures in the range 65.5–86.5°C. The least squares method² was used to calculate the slope and intercept of the line best fitting these data. Figures 3 and 4 illustrate the deviation of the experimental data from the least squares straight line. From the slope, the activation energy, E , in the Arrhenius equation was calculated; the probability-frequency factor, $\log PZ$, is numerically equal to the intercept. On the assumption³ that E equals enthalpy of activation, ΔH^\ddagger , the entropy of activation, ΔS^\ddagger , and the free energy of activation, ΔF^\ddagger , were calculated from the equations $PZ = (RT/Nh) e^{\Delta S^\ddagger/R}$ and $\Delta F^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$. The variation of the Arrhen-

TABLE II
Pseudo First-Order Reduced Rate Constants for the Hydrolysis of Vinyl Formate Copolymers

Temp., °C.	Reduced reaction rate constants	
	k_f	k_s
	0 Mole-% vinyl stearate	
65.5	3.62	
75.0	6.07	
75.5	6.50	
86.5	11.95	
	3 Mole-% vinyl stearate	
66	0.937	0.156
75.5	2.43	0.319
75.5	2.59	0.264
85.5	6.06	0.593
85.5	5.46	0.565
	5 Mole-% vinyl stearate	
66	1.062	0.120
76.5	2.19	0.219
86	4.67	0.485
	10 Mole-% vinyl stearate	
66	0.635	0.0810
75.5	1.38	0.156
85.5	3.21	0.297

ius constants (E and PZ) and ΔS^\ddagger and ΔF^\ddagger with stearate content for the hydrolysis of copolymers of vinyl formate and vinyl stearate are shown in Table III.

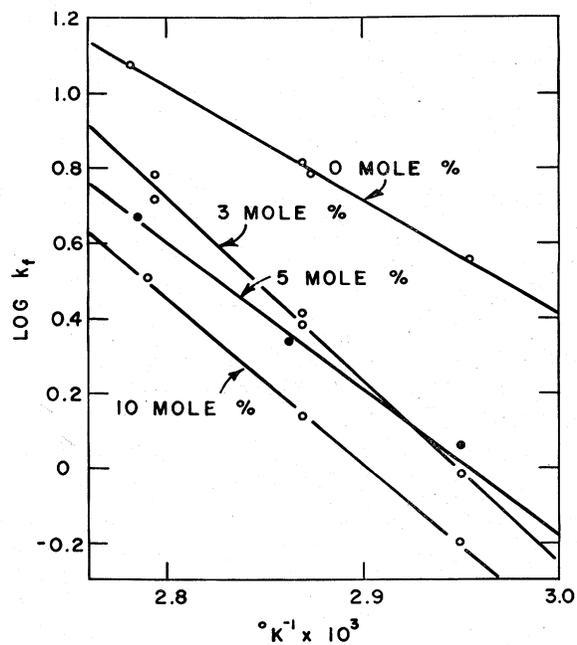


Fig. 3. Effect of temperature on the first-order reaction rate constant for the hydrolysis of formate segments in copolymers of vinyl formate and vinyl stearate.

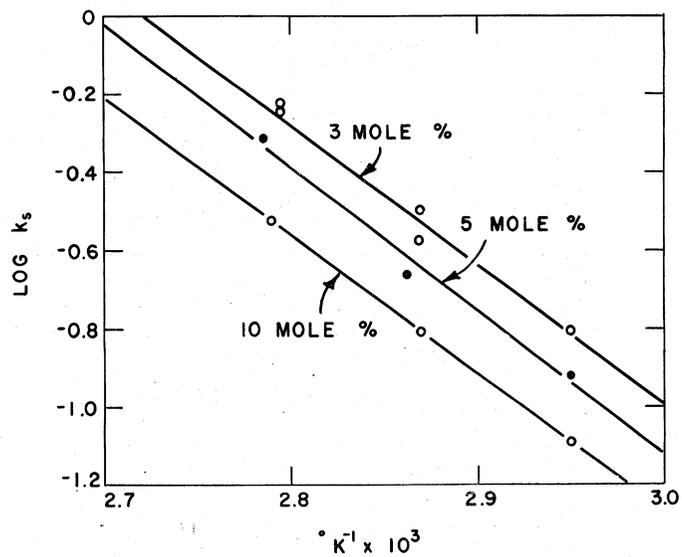


Fig. 4. Effect of temperature on the first-order reaction rate constant for the hydrolysis of stearate segments in copolymers of vinyl formate and vinyl stearate.

TABLE III
Thermodynamic Constants of the Activated Complex in the First-Order Hydrolysis of Vinyl Formate Copolymers

Vinyl stearate, mole-%	Hydrolysis of formate segments				Hydrolysis of stearate segments			
	E , kcal./mole	log PZ	ΔS^\ddagger , ^a cal./deg. mole	ΔF^\ddagger , ^a kcal./mole	E , kcal./mole	log PZ	ΔS^\ddagger , ^a cal./deg. mole	ΔF^\ddagger , ^a kcal./mole
0	13.77	9.45	-23.76	22.05	—	—	—	—
3	22.21	14.31	-1.52	22.73	16.36	9.73	-22.45	24.19
5	17.85	11.52	-14.26	22.82	16.74	9.85	-21.91	24.37
10	20.07	12.73	-8.72	23.11	16.09	9.28	-24.51	24.63
Isopropyl formate ^b	13.82	9.80	-22.15	21.53	—	—	—	—
Isopropyl acetate ^b	—	—	—	—	16.69	9.84	-21.96	24.34
Poly(vinyl acetate) ^c	—	—	—	—	13.28	11.11	-16.14	18.91

^a At 75.5°C.

^b Constants calculated from data in ref. 4.

^c 1.22-Order acid-catalyzed methanolysis. Calculated from data in ref. 6.

The variation of the stearate content has a marked effect on the entropy of activation for the complex formed in the hydrolysis of the formate segments. If the limited data are typical of a continuous pattern, the entropy change appears to pass through a maximum at about 3 mole-%, through a minimum at about 5 mole-%, and then appears to rise again. A smaller variation is noted in the entropy of activation for the hydrolysis of stearate segments as the vinyl stearate content changes. The change in the free energy of activation for the hydrolysis of both formate and stearate segments increases to a small extent as the stearate content increases.

It is interesting to compare (Table III) the entropy and free energy of activation for the hydrolysis of the formate and stearate segments with the corresponding constants for isopropyl formate and acetate which, because of their formal similarity to the secondary ester segments of the copolymer, may serve as approximate model compounds. The data from which these constants were calculated were taken from Palomaa.⁴ That an acetate can be used as a valid model for the much longer-chain stearate is admittedly a gross assumption, but it gains some support from the work of Taft⁵ who showed that the free energy reaction constants f for the hydrolysis of acetates, propionates, and butyrates are approximately the same (0.820, 0.678, 0.694, respectively) as compared with formates (0.394).

The fact that the entropies and free energies for the hydrolysis of the ester segments in the polymers are so very nearly equal to those for the model compounds suggests that the configuration of the complex and the driving force for the hydrolyses of the homopolymers are independent of the degree of polymerization. Disturbance of the structure of poly(vinyl formate) by

copolymerization increases the probability of the formation of the activated complex as indicated by the sharp increase in the entropy of activation as the stearate groups are introduced.

It is also of interest to compare the hydrolysis and alcoholysis of a poly(vinyl ester). Minsk, Priest, and Kenyon⁶ studied the homogeneous methanolysis of poly(vinyl acetate) under both acidic and basic catalysis. They showed that the reaction rate is dependent on the first power of the concentration of the basic catalyst and on the 1.22 power of the acidic catalyst. A qualitative explanation for the unusual order of the acid catalyzed reaction was offered in which the rate constant for methanolysis was assumed to vary with the acetyl content of the polymer. From their data on the temperature dependence of the reaction rate constant, E , $\log PZ$, ΔS^\ddagger , and ΔF^\ddagger , for the acid-catalyzed methanolysis were calculated and are listed in Table III.

Anomalous Kinetics at Approximately 95°C.

It was found that at approximately 95°C. the reduced reaction rate constants for hydrolysis of both the formate and stearate groups differed from the values predicted on the basis of the Arrhenius constants. This is shown in Table IV. It was found further that eq. (4) does not apply (i.e., $k_a/(\text{H}_3\text{O}^+)_a$ is not constant) although its equivalent for stearate groups [Eq. (7)] holds somewhat better. The reduced reaction rate constant increases as the concentration of catalyst acid decreases. The effect is more marked with the formate than with the stearate groups. Practically,

TABLE IV
Anomalous Reaction Rate Constants for Hydrolysis
at Approximately 95°C.

Temp., °C.	[HCl], mole/l.	k_a , %/min.	k_f		k'_a , %/min.	k_s	
			Found	Calc. ^a		Found	Calc. ^a
0 Mole-% vinyl stearate							
96.5	0.0195	1.32	67.5	19.84			
96.5	0.0948	1.18	12.4	19.84			
96.5	0.1837	2.08	11.3	19.84			
3 Mole-% vinyl stearate							
96.5	0.0189	0.812	43.0	14.20	0.0129	0.684	1.13
95.5	0.0938	0.667	7.10	13.10	0.0635	0.675	1.07
96.5	0.1845	0.910	4.92	14.20	0.133	0.722	1.13
5 Mole-% vinyl stearate							
94.5	0.0189	0.340	18.0	8.94	0.175	0.925	0.928
96	0.1783	1.67	9.35	8.08	0.114	0.640	0.845
10 Mole-% vinyl stearate							
96	0.0190	0.291	15.3	7.02	0.0161	0.845	0.543
96.5	0.0895	0.835	9.30	7.28	0.0460	0.514	0.559
96.5	0.1776	0.735	4.15	7.28	0.0835	0.470	0.559

^a From E and $\log PZ$ in Table III.

there is an advantage toward obtaining a differential hydrolysis in conducting the hydrolysis at a high temperature and a low acid concentration.

The authors are indebted to Drs. C. Roland Eddy and Constantine Ricciuti for valuable discussions.

References

1. E. F. Jordan, W. E. Palm, D. Swern, L. P. Witnauer, and W. S. Port, *J. Polymer Sci.*, **32**, 33 (1958).
2. J. F. Kenney, *Mathematics of Statistics*, Van Nostrand, New York, 1947, p. 149.
3. S. Glasstone, *Textbook of Physical Chemistry*, Van Nostrand, New York, 1946, pp. 1103-4.
4. M. H. Palomaa, E. G. Salmi, J. I. Jansson, and T. Sala, *Ber.*, **68B**, 303 (1935).
5. R. W. Taft, Jr., *J. Am. Chem. Soc.*, **74**, 2729 (1952).
6. L. M. Minsk, W. J. Priest, and W. O. Kenyon, *J. Am. Chem. Soc.*, **63**, 2715 (1941).

Synopsis

The rate of hydrolysis of formate and stearate segments from poly(vinyl formate) and from poly(vinyl formate-co-stearate) suspended in dilute aqueous hydrochloric acid was studied. Evidence was presented to show that the hydrolysis follows pseudo-first-order kinetics. The Arrhenius constants and the entropies and free energies of activation for the hydrolysis of formate and stearate groups from copolymers containing 0, 3, 5, and 10 mole-% vinyl stearate were calculated from the partially reduced reaction rate constants at three temperatures. For the hydrolysis of formate segments, ΔS^\ddagger is markedly affected by the stearate content, whereas the variation in ΔF^\ddagger is small. Variations in vinyl formate content have smaller effects on the thermodynamic constants of the activated complex for the hydrolysis of the stearate segments. At approximately 95°C., some anomalous kinetic behavior was observed.

Résumé

La vitesse d'hydrolyse de segments formiques et stéariques obtenu aux dépens de formiate de polyvinyle et de copolymère de formiate et stéarate de vinyle suspendus dans une solution aqueuse diluée d'acide chlorhydrique a été étudiée. On montre expérimentalement que l'hydrolyse suit une cinétique d'ordre unitaire apparent. Les constantes d'Arrhenius, les entropies et énergies libres d'activation de l'hydrolyse des groupes formiques et stéariques au sein de copolymères contenant 0, 3, 5 et 10 moles-% de stéarate de vinyle ont été calculées au départ des constantes de vitesse partiellement réduite de réactions à trois températures. Pour l'hydrolyse de segments formiques, ΔS^\ddagger est fortement affectée par la teneur en unité stéarique, alors que la variation de ΔF^\ddagger est faible. Des variations de la teneur en ester formique n'exercent que peu d'effets sur les constantes thermodynamiques du complexe activé de l'hydrolyse des segments stéariques. A environ 95°C, on a observé certains effets cinétiques anormaux.

Zusammenfassung

Die Hydrolysegeschwindigkeit von Format- und Stearatsegmenten aus Poly(vinylformat) und aus Poly(vinylformat-co-stearat), welches in verdünnter wässriger Salzsäure suspendiert war, wurde untersucht. Es wurde Evidenz gegeben, die zeigt, dass die Hydrolyse einer Kinetik pseudo-erster Ordnung folgt. Die Arrheniuskonstante und die Entropien und freien Aktivationsenergien für die Hydrolyse von Format- und Stearatgruppen aus Copolymeren, die 0, 3, 5 und 10 Mol% Vinylstearat enthielten, wurden aus teilweise reduzierten Reaktionsgeschwindigkeitskonstanten bei drei Temperaturen

berechnet. Für die Hydrolyse von Formatsegmenten wird ΔS^\ddagger erheblich durch den Stearatgehalt verändert, während die Variation von ΔF^\ddagger klein ist. Variationen des Vinylformatgehaltes haben kleinere Wirkungen auf die thermodynamischen Konstanten des aktivierten Komplexes für die Hydrolyse der Stearatsegmente. Bei ungefähr 95°C wurde ein etwas anomales kinetisches Verhalten beobachtet.

Received October 11, 1957