

KINETIC STUDIES IN ESTER HYDROLYSIS

Part IV. Alkaline Hydrolysis of Ethyl Acetate in Mixed Solvents*

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INTRODUCTION

In the previous part we have presented the results of our investigations on acid hydrolysis of ethyl acetate in dioxan-water and acetone-water systems. The interesting results obtained therein and also the fact that there are still some aspects of the mechanism of the reaction which require elucidation, made it worth while studying alkaline hydrolysis of the ester in the same series of solvent mixtures.

The abstract of a paper by Huang and Hsieh⁴ on the saponification of methyl acetate indicated that the reaction rate increased with increasing dioxane content of the solvent and that the rate constant varied linearly with the mole-fraction of dioxane. This evidently means that the reaction velocity is increased by a decrease in dielectric constant. Moelwyn-Hughes⁵ has cited this work while dealing with ion-dipole reactions. Glasstone, Laidler and Eyring,³ on the other hand, have treated alkaline hydrolysis as a reaction between dipoles and have used the results of Fairclough and Hinshelwood² on benzoic esters in alcohol-water mixtures to demonstrate the linear variation of $\log k$ with $\frac{D-1}{2D+1}$, which is characteristic of dipole-dipole reactions. Reaction velocity is found to be decreased by decrease of dielectric constant. It is easily seen that these two treatments with their respective experimental evidences run counter to each other. This situation calls forth fresh attempts to throw more light on the mechanism of the reaction and the influence of solvent on the reaction rate. In the present study, an effort has been made to vary the dielectric constant over a wide range, but high percentages of organic solvent had to be excluded owing to the limitations imposed by the very low solubility of sodium hydroxide in such media.

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RESULTS AND DISCUSSION

A summary of the results obtained are presented in Tables I and II and Figs. 1 and 2 show the variations of k -values with solvent composition.

TABLE I

Second order velocity constants in dioxan-water mixtures

Solvent composition volume % dioxan	Temperature in degrees Centigrade			
	30		40	
	Dielectric constant	$k \times 10^2$	Dielectric constant	$k \times 10^2$
0	(76.8)	16.20	73.12	28.12
10	67.76	16.67	64.49	28.45
20	58.80	12.79	56.84	26.17
30	50.43	11.22	47.05	22.01
40	41.80	10.07	39.54	18.72
50	33.51	8.583	31.66	16.01
60	25.53	7.434	24.11	13.61

TABLE II

Velocity constants in acetone-water mixtures

Solvent composition volume % acetone	Temperature in degrees Centigrade			
	30		40	
	Dielectric constant	$k \times 10^2$	Dielectric constant	$k \times 10^2$
0	(76.8)	16.20	73.12	28.18
10	72.31	15.48	68.95	28.96
20	67.75	13.99	64.60	24.02
30	62.70	11.51	59.80	19.50
40	57.60	9.791	54.99	16.47
50	51.98	7.952	49.62	13.27
70	39.53	6.483	37.69	10.37

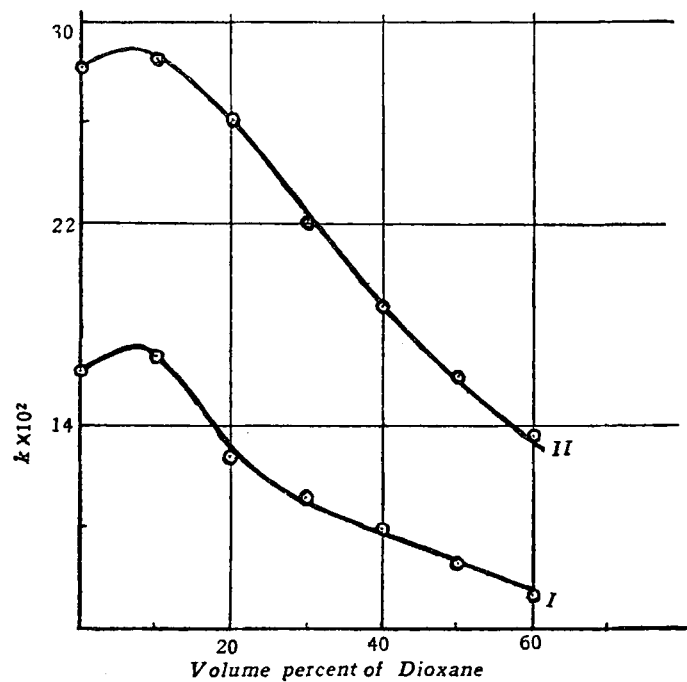


FIG. 1. Variation of velocity with composition I—30° C ; II—40° C. (Alk. Hydr.)

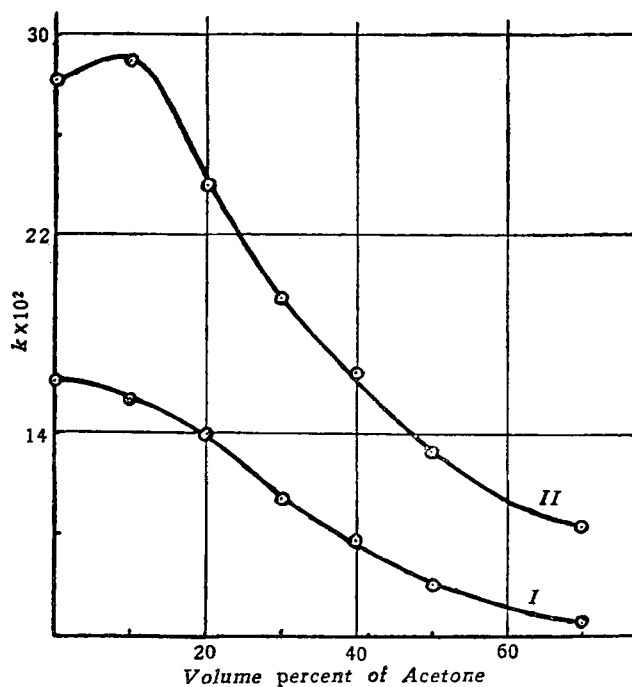


FIG. 2. Velocity composition curves for Acetone-Water Mixtures I—30° C ; II—40° C (Alk. Hydr.)

With both solvent mixtures, it is observed that there occurs a maximum in the region of 10% organic solvent excepting in the case of acetone-water mixtures at 30° C. where there is a progressive reduction in reaction rate with increasing amounts of organic solvent. The behaviour here observed in dioxane-water mixtures differs from that found by Huang and Hsieh in the following important respects:—

(i) Instead of a continuous increase with increasing amount of dioxane (*i.e.*, with decreasing dielectric constant), the velocity constant begins the fall when the dioxane content exceeds a certain value. (ii) Also, the composition range over which the velocity increases is found to be much smaller.

The variation observed seems to suggest that the reaction is one between ion and dipole in compositions below 10% and between dipole and dipole for compositions above 10%, if dielectric constant is considered to be the major factor affecting the reaction rate. Since there can be no doubt about the indispensability of the hydroxyl ion for the formation of the transition complex, the remarkable change in trend of the rate constant necessitates a detailed examination of the exact role of the water molecule in alkaline hydrolysis. All aspects of the problem will be more fully considered in Part V.

While recognising the limitations of observations at only two temperatures, it is nonetheless useful to compute the parameters of the arrhenius rate equation. The experimental activation energies and the frequency factors are given in Table III.

TABLE III
Activation energies and frequency factors

Volume % of organic solvent	Dioxane Water		Acetone Water	
	E Kilocal.	Frequency factor Log ₁₀ PZ	E Kilocal.	Frequency factor Log ₁₀ PZ
0	10.42	6.73	10.42	6.73
10	13.78	9.08	11.80	7.70
20	13.48	8.83	10.18	6.49
30	12.69	8.21	9.93	6.22
40	12.19	7.79	9.79	6.06
50	11.74	7.41	9.95	5.86
60	11.39	7.09
70	8.84	5.19

Excepting for the sharp increase when the solvent composition changes from 0% to 10% organic solvent, variations of both E and PZ values with composition are quite gradual. Fig. 3 shows that unlike in the case of acid hydrolysis the variations in activation energy in the two series of solvents are quite similar.

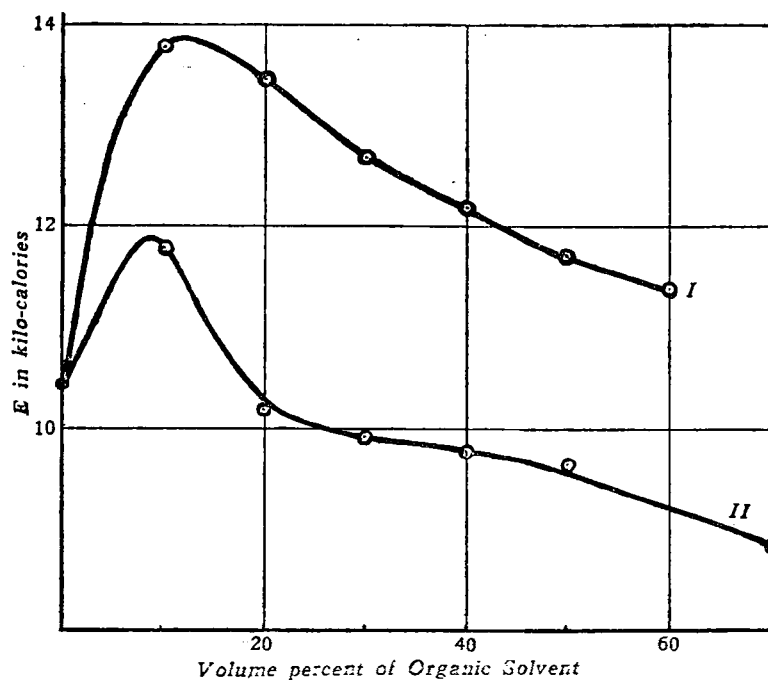


FIG. 3. Variation of E with composition

- I. Dioxane-Water Mixtures
- II. Acetone-Water Mixtures

Fig. 4 illustrates the variation of $\log PZ$ values with composition and brings out the remarkable parallelism between and trends of E and PZ values. Fairclough and Hinshelwood have shown, from statistical considerations, that the frequency factor (PZ) is a function of the characteristic frequency of the bond involved in a reaction and obtained a linear relationship between $\log_{10} PZ$ and $1/\sqrt{E}$ in a number of cases. Davis and Evans have observed a similar behaviour in the case of several aliphatic esters, the substituents being responsible for changes in activation energy. Fig. 5 shows the plots of $1/\sqrt{E}$ against $\log_{10} PZ$ for the present investigation. It is seen that they yield fairly linear plots. Combining these observations, it seems as though the behaviour referred to is independent of the agency (substituent or solvent

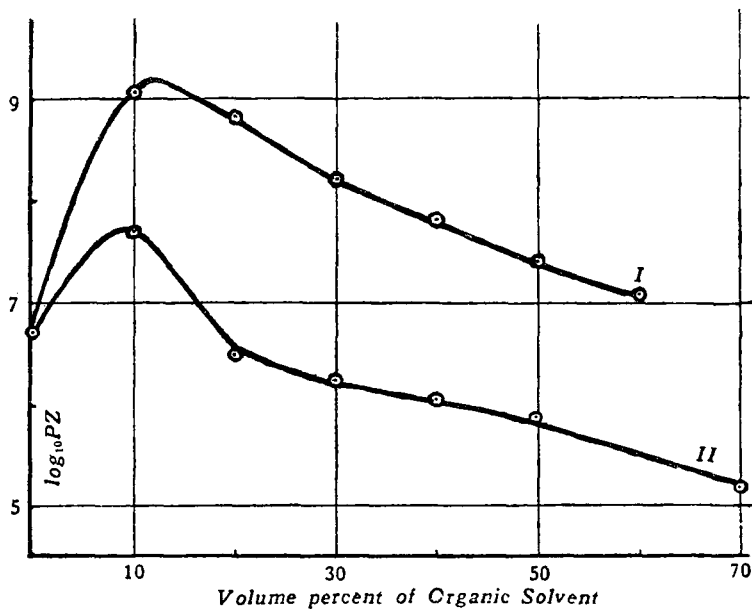


FIG. 4. Variation of log PZ with composition
 I. Dioxane-Water Mixtures
 II. Acetone-Water Mixtures

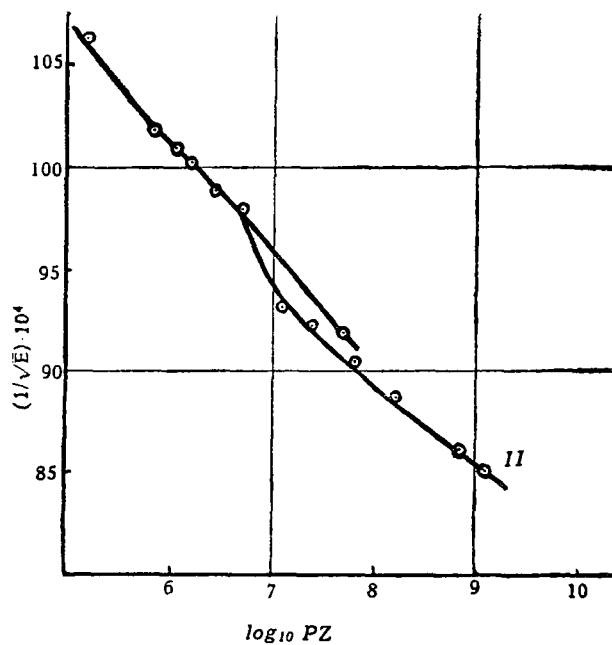


FIG. 5. Alk. Hydr.—log PZ — $1/\sqrt{E}$ curves
 I. Acetone-Water Mixtures
 II. Dioxane-Water Mixtures

change) that brings about changes in energies of activation and offers further support to the interpretation given by Fairclough and Hinshelwood.

EXPERIMENTAL

The materials used in the study were purified by the same procedure as described in the previous part.

Velocity Measurements.—The reaction vessels used were 100 ml. or 50 ml. Pyrex reaction bottles with specially ground stoppers. They were tested for evaporation losses by putting acetone in them and keeping for a month. The loss in weight was found to be negligible.

Owing to the fastness of the reaction, it had naturally to be studied at lower temperatures than in the case of acid hydrolysis and hence the temperature control possible was much better, the fluctuations being within $\pm 0.005^\circ \text{C}$.

Ester solutions were prepared as described in Part III.

The alkaline hydrolysing agent was prepared in a similar way. The requisite amount of a previously standardised sodium carbonate-free sodium hydroxide solution required to make 100 ml. of N/10 solution was run into the appropriate volume of organic solvent taken in a 100 ml. standard flask and enough water added to bring the level a little below the neck. After allowing sufficient time (with occasional shaking) for the contents to attain room temperature, the solution was made up to the mark with water and well shaken.

The flasks containing ester solution and the hydrolysing agent were immersed in the thermostat and left for four hours for attainment of temperature equilibrium. The strength of the alkali solution was then determined by titration in order to evaluate the solvent expansion correction. The same correction was also applied to the ester solution. 50 ml. (or 25 ml.) of the alkali solution were transferred by means of a standard pipette into a 100 ml. (or 50 ml.) reaction bottle which was also kept immersed in the bath. After allowing a little more time to compensate for slight temperature changes, 50 ml. (or 25 ml.) of the ester solution were added to the alkali solution with a standardised rapid delivery pipette. The bottle was stoppered, taken out, well shaken and returned to the bath as quickly as possible. The instant of half-delivery of the ester solution was taken as zero time. The reaction was followed by withdrawing 10 ml. (or 5 ml.) samples of the reaction mixture and running them into 10 ml. (or 5 ml.) lots of N/20 HCl and titrating the excess of acid against N/40 barium hydroxide,

with bromo-thymol blue as indicator. Time was noted by a standardised stop-watch graduated to 0.2 sec. A second stop-watch of the same quality was employed for determining the reaction times for the samples accurately. Just before taking a reading, the second stop-watch was started at a definite time read in the first one. The second watch was stopped at the instant of half-delivery of the sample and the reading noted. The sum of the two gave the time for the particular sample. Half-deliveries were marked on the pipettes with a vibro tool. Typical runs are given in Tables IV and V.

The velocity constants were calculated from the equation for a second order reaction.

$$k(a-b)t = 2.303 \left[\log_{10} \frac{b}{a} + \log_{10} \frac{a-x}{b-x} \right],$$

TABLE IV

Alkaline hydrolysis of ethyl acetate in acetone-water mixtures at 30° C.

Vol. % acetone	Strength of alkali	Strength of ester	Titre of 10 ml. of acid used for stopping reaction							
				Time in sec. t	96.0	213.8	327.0	437.5	580.0	695.4
0	0.0497 N	0.0475 N	20.15	Titre of reaction mixture V_t	8.55	11.35	14.25	15.10	16.20	16.65
				t	89.0	214.2	327.0	441.0	562.6	692.4
10	0.0499 N	0.0474 N	20.20	V_t	8.05	12.15	14.05	15.02	16.00	16.50
				t	92.0	210.0	329.8	445.6	579.8	723.0
20	0.0497 N	0.0476 N	20.20	V_t	7.70	11.60	13.80	14.90	15.75	16.55
				t	103.2	208.8	332.2	447.8	572.0	719.2
30	0.0497 N	0.0476 N	20.15	V_t	7.45	10.72	13.15	14.25	15.10	16.00
				t	73.5	213.0	327.5	435.0	552.1	648.9
40	0.0497 N	0.0486 N	19.70	V_t	5.60	9.85	12.13	13.30	14.15	14.80
				t	93.0	200.0	303.0	441.5	587.0	727.8
50	0.0496 N	0.0490 N	20.20	V_t	5.70	9.05	11.30	12.00	14.10	15.20
				t	77.2	187.0	296.4	409.4	521.2	652.6
70	0.0495 N	0.0486 N	20.20	V_t	4.00	7.45	9.70	11.30	12.50	13.40
				t						

TABLE V

Alkaline hydrolysis of ethyl acetate in dioxan-water mixtures at 30° C.

Vol. % dioxan	Strength of alkali	Strength of ester	Titre for acid used (10 ml.) to stop reaction							
				<i>t</i>	96.0	213.8	327.0	437.5	580.0	695.4
0	0.0497 N	0.0475 N	20.15	Titre for V_t 10 ml. of reaction mixture	8.55	11.35	14.25	15.10	16.20	16.65
				<i>t</i>	86.0	182.0	269.3	362.4	450.8	550.0
10	0.0503 N	0.0489 N	19.70	<i>t</i>	7.65	11.10	13.0	13.95	14.50	15.50
				V_t	90.3	181.2	275.0	384.4	478.4	585.4
20	0.0497 N	0.0487 N	19.70	<i>t</i>	7.45	10.55	12.55	13.80	14.60	15.35
				V_t	100.2	180.6	260.5	350.3	435.0	561.8
30	0.0498 N	0.0489 N	20.60	<i>t</i>	7.72	10.40	12.50	13.70	14.45	15.53
				V_t	94.2	175.6	281.2	364.0	445.0	550.6
40	0.0481 N	0.0493 N	20.60	<i>t</i>	7.30	10.10	12.55	13.65	14.35	15.40
				V_t	84.0	166.0	246.8	397.8	470.2	..
50	0.0495 N	0.0486 N	20.65	<i>t</i>	5.75	8.75	10.70	12.30	13.65	..
				V_t	91.5	190.5	306.2	404.2	439.9	633.2
60	0.0497 N	0.0495 N	19.70	<i>t</i>	5.25	8.20	10.55	11.75	12.65	13.55
				V_t						

where a and b are alkali and ester concentrations and x the fraction hydrolysed at time t . Values of $\log_{10} \frac{a-x}{b-x}$ were plotted against t and k -values calculated from the slope of the straight lines obtained. This procedure for calculation eliminated any error in the noting of zero time. Fig. 6 gives a sample of the plot of $\log_{10} \frac{a-x}{b-x}$ against t .

SUMMARY

The alkaline hydrolysis of ethyl acetate in dioxane-water and acetone-water mixtures have been studied. The trend of the reaction rate shows a maximum in the region of 10% organic solvent except in the case of acetone-water mixtures at 30° C. A close parallelism is observed in the variations

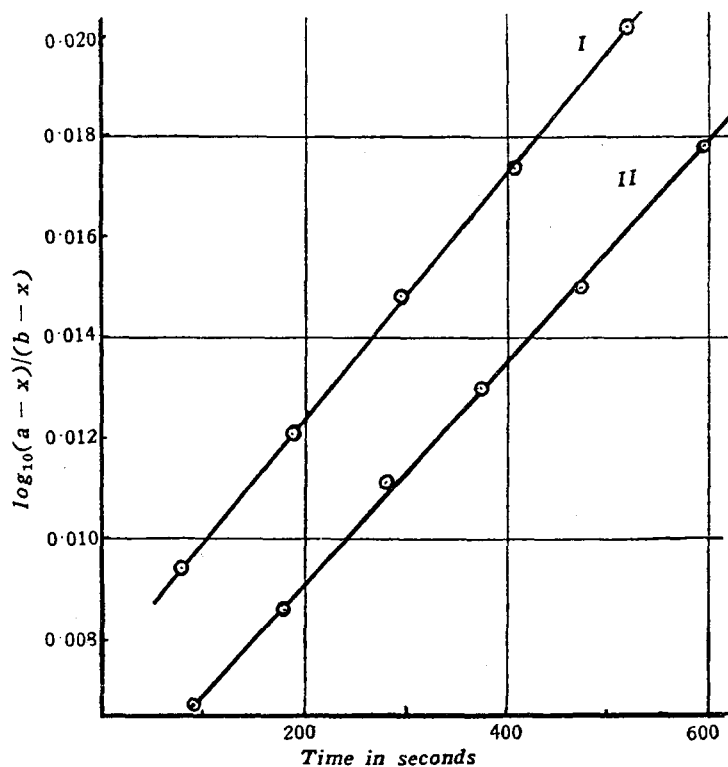


FIG. 6. 30° C. Alk. Hydr.
I. 70% Acetone ; II. 40% Dioxane.

of both E and \log_{10} PZ values in the two series of solvent mixtures. Also, the PZ values have a marked tendency to follow changes in energies of activation.

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