

KINETIC STUDIES IN ESTER HYDROLYSIS

Part IX. The Hydrolysis of Ethyl Acetate in Dioxan-Water Systems

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INTRODUCTION

IN the previous Part (VIII) we reported the abnormalities in acid hydrolysis of ethyl acetate in water to which small additions of acetone were made. The present report deals with similar studies in which the organic solvent added is dioxan. Here too, it was observed in Part IV^{2a} that small additions of organic solvent might not conform to the expected correlation for an ion-dipole reaction. Differences from the acetone-water system should, however, be expected for two reasons. The changes in dielectric constant for small additions of dioxan may not be appreciable as the change in water content is only of the order of 3 moles per cent. Unlike acetone, dioxan can provide two centres for the association of the proton but the hydrogen bond is weaker in the ether oxygen. If the dielectric constant is to exert a dominant influence, while a drift in the Arrhenius activation energy was anticipated earlier, this drift may not be large and the individual value may be expected to be close enough almost within the limits of experimental error. This drift may be even eliminated if by suitable addition of a neutral salt, dielectric constant changes are reduced still further.

DISCUSSION OF RESULTS

The experimental results obtained are presented in Tables I and II while typical runs are given in the experimental part.

If one were to take only individual values and compare them, as anticipated, activation energy values are confined to a narrow range. The difference between the extreme values of 0.8 kilocalories, however, is outside the range of experimental error. Reckoning by standard statistical procedures for errors arising from temperature variations, analytical accuracy and errors in the measurement of time, values may be considered accurate to within 250 calories. The pronounced trend with a maximum value for the addition of about 6% by volume of dioxan (1.2 moles %) is clearly noticed in Fig. 1.

TABLE I
Rate constants and Arrhenius Parameters for the reaction

Dioxan in mixture		k_2 values at temperatures $\times 10$			E K. Cals.	Log_{10}PZ
% By volume	Mole fraction	30° C.	35° C.	40° C.		
0	0	1.617 1.620*	1.862	2.817 2.812*	10.53	6.69
2	0.004288	1.649	1.929	2.882	10.60	6.80
4	0.008712	1.682	1.968	2.944	10.62	6.83
6	0.01347	1.699	2.009	3.030	10.97	7.09
8	0.01834	1.735	2.013	3.079	10.88	7.03
10	0.02344	1.671	1.961	2.851	10.14	6.49
10*	..	1.667*	..	2.845*

* Values taken from Part IV for comparison. All values of rate constants are in moles/litre, seconds⁻¹.

TABLE II
Rate constants in dioxan-water mixtures in the presence of
0.0444 M potassium acetate

% Dioxan by volume	k_2 values at temperatures			E K. Cals.	Log_{10}PZ
	30° C.	35° C.	40° C.		
0	0.1642	0.2142	0.2914	10.92	7.04
2	0.1668	0.2281	0.2986	11.07	7.13
4	0.1746	0.2341	0.3132	11.10	7.20
6	0.1682	0.2281	0.3016	11.10	7.18
8	0.1666	0.2158	0.2969	10.96	7.08
10	0.1652	0.2027	0.2849	10.34	6.62

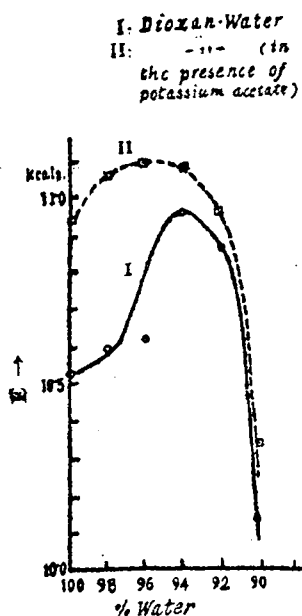


FIG. 1

The Fairclough-Hinshelwood correlation between the two Arrhenius parameters is also maintained in this region as may be seen from Fig. 2.

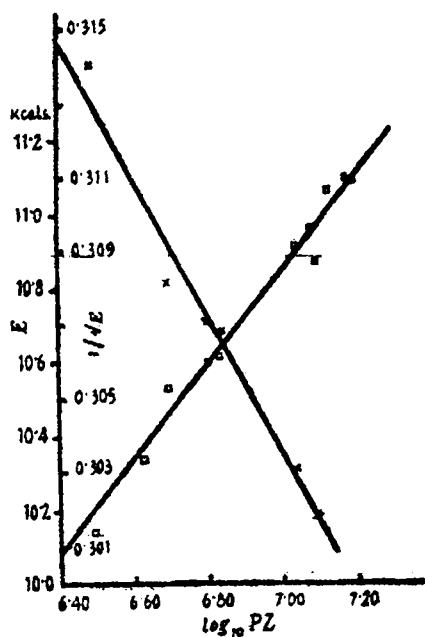


FIG. 2

The deviation from the normal dielectric constant-activation energy expected from the Kirkwood relationship⁵ which appeared probable in the earlier part is thus confirmed in this solvent mixture also. The immediate effect of adding dioxan is presumably a disturbance of the quasicrystalline tetrahedral distribution of the water molecules which participate in the second stage of the reaction. Since the reactant in the first stage is also the solvated hydroxyl ion, the intervention of the dioxan disturbs also the solvation shell expected for this ion; it has been noticed¹ that both hydrogen and hydroxyl ions are solvated in aqueous systems with a distribution of water molecules as in water itself. This alters both the entropy of activation and the energy of activation that is actually observed. The effect of the dielectric constant of the environment becomes pronounced as the molefraction of water is reduced and the later additions of dioxan correspond to such correlation as reported in the earlier work.

Unequivocal evidence for neutral salt action in ester is not available.³ The addition of an acetate to the system introduces the minimum of disturbance of the environment with acetanion as a product of the reaction. When present in quantities of the same order as the reactants but somewhat larger, in the initial stages, no change in the ionic strength may be expected and the principal effect is the one caused by a change in the dielectric constant of the medium. The influence of this changed environment is noticed in the results presented in Table II. The drift in the absence of added acetate is eliminated and the Arrhenius activation energy as well as the frequency factor becomes constant in the experimental region within the limits of experimental error. With increasing concentration of the organic solvent, addition of an acetate appears to be practically without effect as may be noticed in the system containing 10% by volume of dioxan (2.2 moles %). For a complete analysis of the position, values of activities of the reacting ions are necessary and are at present lacking. The need for this is clearly shown by the trend in the rate constant values presented in the table with an apparent maximum at 4% by volume of dioxan with added acetate (as against the maximum at 6% by volume in its absence). Again extreme values differ by an amount beyond the limits of experimental error.

While both acetone-water systems and dioxan-water systems confirm the anticipated deviations, a comparison of the abnormal regions in the two systems brings out certain differences. Acetone addition leads to a reaction rate change which is less than dioxan addition even though the dielectric constant can be expected to be higher. At the higher temperature the rate constants tend to approach each other especially when one considers the molefraction of water (Fig. 3).

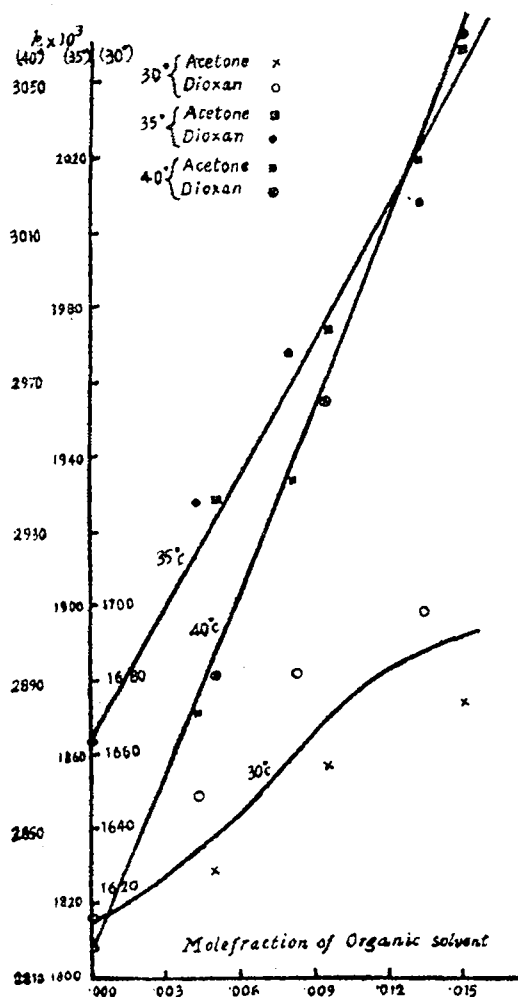


FIG. 3

The initial addition of dioxan or acetone alters the rate primarily by the disturbance of the quasicrystalline structure of the aqueous environment. This is clearly noticed in the increased values of entropy of activation in the initial stages as shown in Table III.

TABLE III

% Water by volume	100	98	96	94	92	90
Entropy of activation at 30° C.	26.07	26.44	26.89	26.89	26.66	25.24

TABLE IV
The alkaline hydrolysis at 30° C.

% Dioxan by Volume	Titre of 10 ml. HCl	Concentration		Time in sec. $t_{1/2}$	Titre value of aliquots			
		OH'	Ester					
0	19.50	0.02469 N	0.02584 M	92.0 $t_{1/2}$	271.9 10.75	477.5 13.30	751.9 15.1	1440 17.0
2	20.30	0.02529 N	0.024265 M	82.45 $t_{1/2}$	260.0 7.75	445.6 12.45	656.6 14.20	914.5 15.50
4	17.60	0.02595 N	0.02587 M	110.0 $t_{1/2}$	288.8 8.75	497.3 11.25	815.2 13.20	1132. 14.20
6	19.10	0.02595 N	0.02321 M	116.4 $t_{1/2}$	220.1 7.25	387.6 10.15	606.4 12.05	816.3 13.20
8	19.20	0.02557 N	0.02760 M	115.1 $t_{1/2}$	319.0 11.00	484.7 12.85	719.1 14.85	1018 16.10
10	19.30	0.02615 N	0.02625 M	140.5 $t_{1/2}$	331.8 10.40	511.3 12.50	913.2 14.85	1153 15.60

TABLE VI
Alkaline hydrolysis of ethyl acetate in dioxan-water at 40° C.

% Dioxan by Volume	Titre of 10 ml. —————→		Concentration of		Ester	Titre value of aliquots								
	HCl	OH'	OH'	Ester		<i>t</i> sec. <i>V_t</i>	<i>t</i> sec. <i>V_t</i>	<i>t</i> sec. <i>V_t</i>	<i>t</i> sec. <i>V_t</i>	<i>t</i> sec. <i>V_t</i>	<i>t</i> sec. <i>V_t</i>			
0	20.35	0.02627	0.02322	0.02322		79.90 6.70	274.0 12.50	420.3 14.20	712.0 15.80	905 16.00				
2	18.45	0.02672	0.02448	0.02448		83.7 6.40	263.3 11.50	417.2 13.20	627.1 14.40	911.3 15.25				
4	19.90	0.02730	0.02265	0.02265		74.6 5.50	249.4 11.15	413.5 13.15	772.0 14.85	981.8 15.30				
6	19.25	0.02726	0.02645	0.02645		80.1 6.85	271.1 12.70	485.8 14.90	776.0 16.20	888.5 16.50				
8	19.85	0.02643	0.02476	0.02476		84.9 6.90	283.6 12.75	487.4 14.85	728.4 16.05	1003 16.75				
10	19.85	0.02730	0.02353	0.02353		75.9 5.35	223.8 10.60	394.4 13.05	654.7 14.65	924.8 15.45				

TABLE VII
The hydrolysis of ethyl acetate in the presence of potassium acetate
 (The concentration of potassium acetate was 0.0444 M in all cases)

Temp. ° C.	% Dioxan by Volume	Concentration of		Titre of		Concentration of		Titre of		Concentration of			
		OH'	Ester	HCl	10 ml.	OH'	Ester	HCl	10 ml.	OH'	Ester		
		30				35				40			
0	19.10	0.0257	0.0262	19.10	0.0259	0.0254	20.35	0.0263	0.0232				
2	19.20	0.0247	0.0254	18.60	0.0270	0.0261	18.45	0.0267	0.0245				
4	19.10	0.0256	0.0245	19.30	0.0261	0.0224	19.90	0.0273	0.0227				
6	17.75	0.0255	0.0244	19.15	0.0262	0.0246	19.25	0.0273	0.0265				
8	17.90	0.0251	0.0263	18.40	0.0259	0.0233	19.05	0.0264	0.0248				
10	19.10	0.0248	0.0248	20.95	0.0264	0.0265	19.85	0.0273	0.0235				
0	<i>t</i> sec. <i>V_t</i>	117.3 4.85	326.1 10.25	533 12.65	785 14.40	1060 15.40	1254 15.90						
2	<i>t</i> sec. <i>V_t</i>	107.2 5.25	274.6 10.10	465.8 12.50	682.2 14.15	1244 16.15							
30° C.	4	<i>t</i> sec. <i>V_t</i>	108.8 4.60	475.4 11.85	658.2 13.25	1084 15.00	1301 15.50						
	6	<i>t</i> sec. <i>V_t</i>	105.2 3.80	316.6 8.95	527.1 11.25	725.4 12.60	1037 13.65	1324 14.30					
35° C.	0	<i>t</i> sec. <i>V_t</i>	107.0 5.10	319.0 10.85	506.8 13.05	793.8 14.75	1069 15.65						
	6	<i>t</i> sec. <i>V_t</i>	110.2 5.10	290.8 10.30	506.0 12.85	968.4 15.10	1373 15.95	1739 16.45					
40° C.	0	<i>t</i> sec. <i>V_t</i>	79.9 6.70	274.0 12.50	420.3 14.20	712.0 15.80	906.1 16.30	1292 17.00					

The increased reaction rate in the region of small additions of organic solvents has then to be accounted for by the differences in the solvation of the proton and the transition state and the relative stability of the proton-oxygen bond. The anomalies have been noticed in the physical properties of these mixed solvents which are considered in a separate communication.

EXPERIMENTAL

The experimental technique was the same as in the previous Part. The dioxan used was a sample purified by the method of Eigenberger⁴ the final purification being by fractional freezing. The physical constants of the solvent used were as follows:—

B.P. 100.5–100.8° C.; Density: d_4^{25} 1.02802; Refractive Index n_D^{25} 1.4202. Carbonate-free sodium hydroxide was used, freshly prepared each time and standardised before each experiment. The reaction was followed by changes in hydroxide ion concentration followed titrimetrically using an electrometric method employing the Serfass circuit indicated in the previous part. The temperature of the thermostat was maintained at the chosen level within a margin of 0.01° by electronic control together with efficient centrifugal stirring of bath.

Typical experimental runs are presented in Tables IV, V, VI and VII.

SUMMARY

The kinetics of the hydrolysis of ethyl acetate by hydroxyl ions in dioxan-water systems also shows the same anticipated deviations from the Kirkwood picture of ion-dipole reactions. For small additions of organic solvents, more than the dielectric constant, the mole fraction of water and the changes in the environment of the transition state appear to be more significant. This is indicated by the reaction in the presence of acetate ions. The results are compared with those in acetone-water systems.

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