

# KINETIC STUDIES IN ESTER HYDROLYSIS

## Part VII. Solvent Influences

BY S. V. ANANTAKRISHNAN, F.A.Sc.

(Department of Chemistry, Madras Christian College, Tamburam)

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IN earlier parts of the series we had reported in these *Proceedings*, the results of our studies on the hydrolysis of ethyl acetate in different solvent mixtures and of other esters in 60% dioxan.<sup>2, 3</sup> It is necessary at this stage to consider the extent and probable manner in which the solvent affects this reaction as a preliminary to further studies. In spite of the limitations in using experimental Arrhenius parameters, the value of these, nevertheless, provides us with a convenient criterion for comparisons, though, as will be noticed further in this note, this is not always feasible. Both activation energies and frequency factors may be modified by dielectric constant as well as the viscosity of the solvent. Further, very often, the two parameters show changes in the same direction and no single physical property can be expected to show any proper correlation in the case of pure solvents. The use of solvent mixtures enables attention being directed to one physical constant while all others are kept invariant or nearly so. This has been attempted in Parts I, IV and V (*loc. cit.*).

In all our previous reports, the results presented related to solvents of constant composition, primarily because of the ease of preparing these solvent mixtures. Where polar solvents are involved, as has invariably been the case, both dielectric constant and viscosity change with temperature and for comparisons in a 'constant' electrical environment, a better choice is to consider rate constant under iso-dielectric conditions. As an approximation, this may be done by graphical interpolation of our earlier data. The results of such interpolation is presented in Table I.

The inadequacy of dielectric constant as a criterion for distinguishing between ion dipole and dipole-dipole reactions was noticed in the earlier parts, where deviations from the two accepted correlations for such reactions were noticed. The position is shown in still greater relief by comparing the iso-dielectric rate constants presented here. Even using only the narrow range from dielectric constant 75 to 45, the abnormalities

TABLE I. *Acid Hydrolysis of Ethyl Acetate*  
*First Order Rate Constants in Iso-dielectric Solvent Mixtures*

Dielectric constant	T: 35° C. $k_1 \times 10^4$	45° C. $k_1 \times 10^4$	50° C. $k_1 \times 10^4$	
<i>A. Dioxan-Water system</i>				
74.93	2.806	6.35	14.0	
66.13	2.625	6.30	13.7	
57.32	2.582	6.05	13.3	
40.67	2.163	5.06	11.7	
24.82	1.614	3.97	8.77	
10.34	1.096	2.77	6.12	
5.40	1.147	3.33	6.38	
<i>B. Acetone-Water system</i>				
70.63	2.587	6.27	13.85	
66.17	2.331	5.75	12.92	
56.29	1.817	4.46	10.00	
44.99	1.367	3.12	7.00	
32.12	0.937	2.30	5.00	
25.22	0.965	2.35	5.17	
<i>C. Glycerol-Water system</i>				
Dielectric constant	T: 35° C. $k_1 \times 10^4$	42° C. $k_1 \times 10^4$	50° C. $k_1 \times 10^4$	60° C. $k_1 \times 10^4$
69.60	2.557	3.09	8.400	14.40
63.50	2.945	5.41	9.13	17.59
57.20	3.226	6.20	10.25	23.05
48.20	2.581	5.10	10.50	20.70

are well brought by comparing the rates at the two temperatures common to the three solvent mixtures. This is shown in Figs. 1 and 2 below.

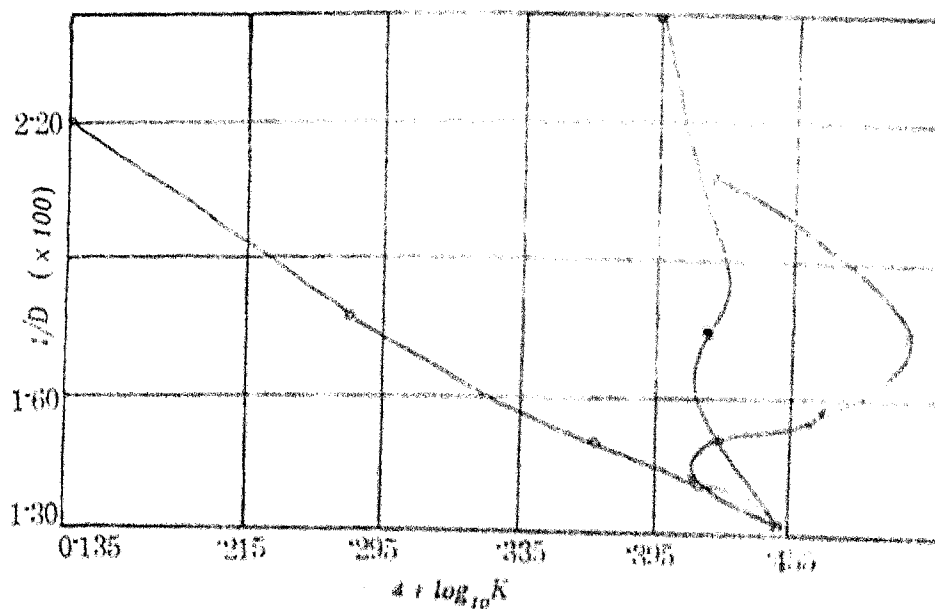


FIG. 1. Ordinate  $4 + \log_{10} k$ . Abscissa  $100 - 1/D$ . Points on ordinate, 0.135, 0.215, 0.295, 0.335, 0.395, 0.415. Points on abscissa, 1.30, 1.60, 1.90, 2.20.

x — Glycerol-water. ● — Dioxan-water. ○ — Acetone-water.

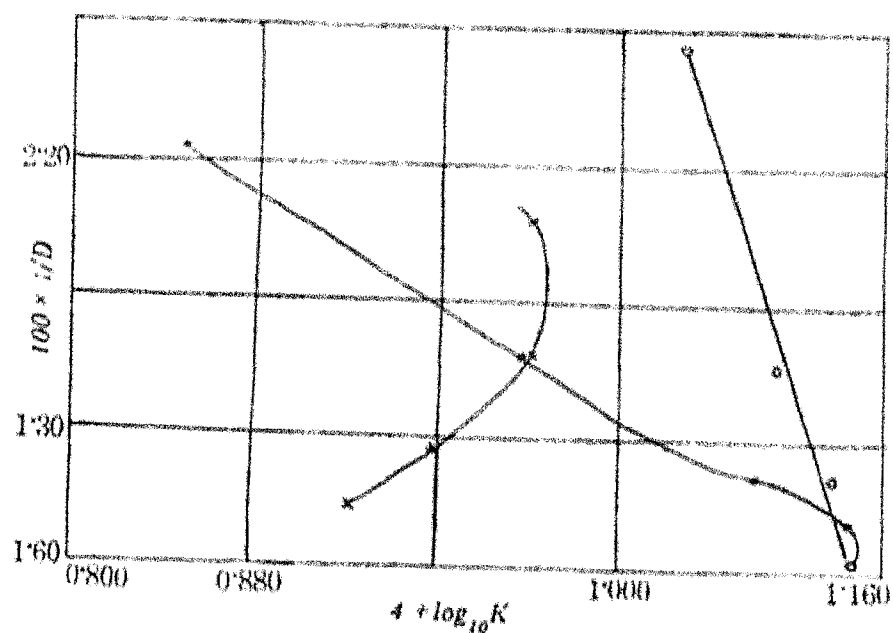


FIG. 2. Co-ordinates and points as in Fig. 1. Figures on Ordinate, 0.800, 0.880, 0.940, 2.000, 1.160. Abscissa as in Fig. 1.

In the case of isocomposition mixtures, a strict linearity between logarithm of rate constant and reciprocal of temperature was observed so that the two Arrhenius parameters could be calculated. The change to iso-dielectric conditions, however, gives us curves which show considerable deviations from linearity, which can be attributed to various causes, some of which are considered later in this note. It is none the less useful to compare the curves and these are presented in Figs. 3, 4 and 5 below.

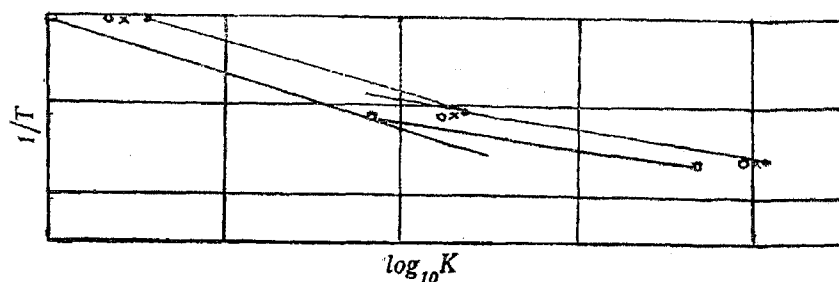


FIG. 3

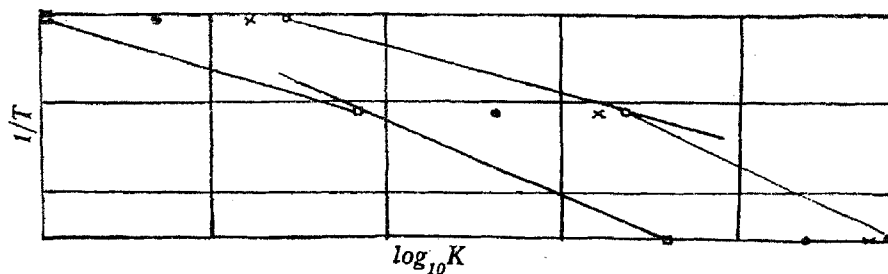


FIG. 4

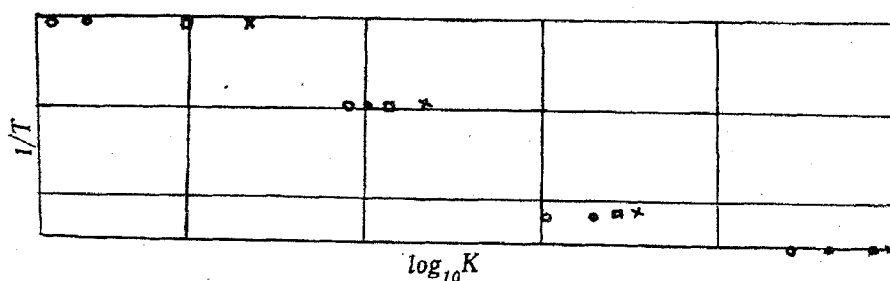


FIG. 5

FIGS. 3, 4 and 5. Abscissa  $1/T$ , Ordinate  $\log_{10} k$ .

FIG. 3. Dioxan-water; FIG. 4. Acetone-water; FIG. 5. Glycerol-water.

We may now turn our attention to alkaline hydrolysis in mixed solvents. Rate constants for iso-dielectric conditions may be obtained by analogous methods. The results are collected in Table II.

TABLE II. *Iso-dielectric Second Order Rate Constants in Alkaline Hydrolysis of Ethyl Acetate in Mixed Solvents*

Dielectric constant	$k_2$ at 30° C. · 10 <sup>5</sup>	$k_2$ at 40° C. · 10 <sup>7</sup>
A. <i>Dioxan-Water</i> system		
76.8 (water)	1.63	2.80
67.75	1.67	2.88
58.80	1.28	2.67
50.43	1.13	2.32
41.80	1.01	1.98
33.51	0.86	1.64
25.53	0.74	1.41
B. <i>Acetone-Water</i> system		
72.31	1.55	2.85
67.75	1.40	2.87
62.70	1.15	2.30
57.60	0.98	1.96
51.98	0.80	1.48
39.53	0.65	1.11

As with acid hydrolysis, here also, no clear correlation between dielectric constant and rate constant is found and we have the same abnormality on the initial addition of the organic solvent to water.

It is recognised that the reactivity of a compound is influenced by the state of polarisation as well as the polarisability of the bond which is primarily involved in the change. The former is essentially a constant while polarisability is liable to changes in the environment. In an earlier communication,<sup>1</sup> it has been shown that there is a close correlation between the characteristic frequency and the logarithm of rate constant and the analysis showed that in ester hydrolysis, one has to consider the carbon-oxygen bond polarisability. If changes in solvent composition alter this one may expect a change in the frequency with change in solvent. No data are, however, available to test this. Some information may be expected by a slightly different approach.

Ingold and coworkers<sup>1</sup> have shown from a study of the rate constants of acid and alkaline hydrolysis of a series of aromatic esters that there is a close correlation between the ratio of the two rate constants and the dipole

moment of the compound. In our present study, using only a single ester namely, ethyl acetate, no change in dipole moment is to be expected but changes in polarisation are not ruled out. A comparison of the two rate constants may thus be expected to give us useful information. So long as we restrict comparison to values at the same temperature, experimental values can be directly used. In the case of acid hydrolysis, these values have to be computed from the known temperature relationships in solvents of constant composition and to this extent the results are only approximate. The values obtained are given in Table III.

TABLE III. *Ratio of the Rate Constants of Alkaline and Acid Hydrolysis of Ethyl Acetate in Solvents of Different Composition*

% Organic solvent in mixture	30° C.		40° C.	
	Dioxan-Water	Acetone-Water	Dioxan-Water	Acetone-Water
0		810		910
10	670	800	730	980
20	690	800	800	900
30	490	1,725	815	850
40	670	935	810	1,000
50	1,075	1,170	1,280	1,325
60	825	910	980	925

At neither of the temperatures can a definite trend be indicated for either solvent. Generally, the ratios in the case of acetone-water tends to be higher than those of dioxan-water and at higher temperatures, the two ratios approach each other.

Several causes may contribute to the observed variations. The activity of the hydrogen and hydroxyl ions may not be the same in the different solvents. The reactant is essentially a solvated proton in acid hydrolysis and the dimensions of this solvated ion will depend on which solvent is associated with the ion during the reaction. The frequency factor which is governed by the dimensions of the ion as well as the viscosity of the solvent will show changes under these conditions. But these cannot account for the extent of change and apparent vagaries obvious from the tables. The most significant factor is likely to be the environment of the reactant molecules.

While the hydronium ion and possibly even the ethyl acetate molecule may be considered approximately spherical, the hydrogen ion solvated by

acetone or dioxan molecules will have different shapes and conditions analogous to those of anisotropic liquids can arise locally. A proper analysis of the reaction requires a knowledge of the potential  $\phi$  in the environment, which in its turn is related to the total polarisation. It is not feasible to calculate this at present for mixed solvents. Variations have to be expected with composition arising from two principal causes. As a consequence of interionic attraction, one has to expect the polarised ester molecule to be surrounded by an atmosphere of solvated ions. While the larger dimensions of the organic solvents facilitate a certain amount of close packing, the hydronium ion will have to be differently distributed. At lower temperatures this structural factor is not negligible while a rise in temperature minimises the influence. Consequently, at higher temperatures, the ratio of the rate constants of acid and alkaline hydrolysis approaches the same value in corresponding solvent compositions. A fuller understanding is possible only after further work with variations in all the parameters involved and with a larger number of esters.

#### SUMMARY

The data obtained in earlier work have been recalculated to give the rate constants under iso-dielectric conditions. These results clearly show that specific solvent effects are present in both acid and alkaline hydrolysis. There is a possible change in the polarisation of the ester molecule with composition in which structural changes in the liquid state presumably play a part.

#### REFERENCES

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