

KINETIC STUDIES IN ESTER HYDROLYSIS

Part II. The Influence of Solvent on the Reaction

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THOUGH correlation between reaction in the gas phase and reactions in solution has been noticed, it is fairly established that a solvent exerts considerable influence on the course of reactions. A solvent may be termed "inert" if it is unassociated, nonpolar and chemically "saturated" and there is no difference in the rate of a reaction whether in gaseous phase or in solution. Such solvents are, however, of very limited application and are unsuitable for reactions of the type under investigation. Qualitative relationship has been established between the velocity constant of bimolecular reactions and the dielectric constant, cohesion and viscosity of the solvent.^{6, 7} Using solvents of "similar type", Evans and Jenkins¹ obtain for the alkaline hydrolysis of benzoic esters the relation

$$E = E_B + E_X/\epsilon_{20},$$

where E_B is the bond energy, $E_X/\epsilon_{20} = E_R$ the repulsion energy and ϵ the dielectric constant of the medium. The extent of solvent influence will naturally depend on the ratio E_R/E and will be small if the ratio is too small a fraction. The solvent effect has also been thoroughly studied only in a few cases.

Now, molecules in general may exert influences on one another and, when within molecular distances from one another, there must be a pronounced change in the potential energy curves. This effect must be especially noticeable in solution. Consequently the first effect that might be observed is a difference in the energy of activation. It is also noticed that where E changes with solvent, PZ of the reaction velocity equation changes concurrently.

In Part I, the influence of substituent on the parameters of the Arrhenius equation has been considered and in the present communication attention is directed to solvent influences. Since it was considered desirable to alter both viscosity and dielectric constant, glycerol was chosen as the medium, varying amounts of water being added to alter both these physical properties.

The choice of this solvent, however, imposed a severe restriction on the choice of esters on account of their low solubility in glycerol-water systems but this does not affect the validity of the conclusions arrived at.

Three esters have been studied in four different concentrations of glycerol and at four different temperatures. For comparison, the relevant results of Part I in 60% dioxan and values calculated from the data of Hinshelwood² for 60% alcohol are also included. The results are summarised in Tables I-VII.

TABLE I

Hydrolysis of Ethyl Acetate

Medium	Temperature in °C.	Time for % reaction in minutes				$k_1 \times 10^5$
		5	10	20	40	
20% Glycerol	35	33.0	70.0	141.0	319.0	25.57
	42	20.0	39.0	78.0	177.0	47.54
	50	10.0	20.0	40.0	87.0	90.33
	60	4.5	9.5	19.0	42.0	190.1
40% Glycerol	35	30.0	61.0	125.0	290.0	29.45
	42	15.0	31.0	67.0	160.0	56.45
	50	9.5	19.25	37.5	88.0	96.79
	60	3.5	7.75	16.5	39.75	235.7
60% Glycerol	35	25.0	54.0	115.0	288.0	32.25
	42	11.0	28.0	63.0	169.0	60.22
	50	7.0	16.0	35.0	95.0	108.4
	60	3.5	8.0	18.0	47.0	208.4
80% Glycerol	35	34.0	69.0	146.0	..	25.81
	42	18.0	38.0	80.0	..	47.26
	50	9.0	19.0	40.0	..	93.46
	60	5.0	8.0	20.0	..	193.6

TABLE II

Hydrolysis of Ethyl Propionate

Medium	Temperature in °C.	Time for % reaction in minutes				$k_1 \times 10^5$
		5	10	20	40	
20% Glycerol	35	38.0	72.0	138.0	307.0	26.31
	42	16.0	34.0	75.0	170.0	49.27
	50	9.5	20.5	40.5	93.5	88.84
	60	4.5	9.75	19.5	45.5	186.9
40% Glycerol	35	32.0	62.0	120.0	284.0	30.80
	42	17.0	35.0	72.0	178.0	51.13
	50	9.5	20.0	40.5	94.0	90.33
	60	4.5	9.0	19.0	47.0	193.6
60% Glycerol	35	28.5	57.0	124.5	321.0	30.10
	42	15.0	31.5	67.5	195.0	57.06
	50	7.5	15.5	35.0	94.0	110.6
	60	4.5	9.75	19.0	55.5	193.6
80% Glycerol	35	36.0	72.0	147.0	..	25.09
	42	15.0	33.0	80.0	..	48.40
	50	10.0	22.0	46.0	..	83.39
	60	4.0	9.5	21.0	..	180.7

TABLE III
Hydrolysis of Ethyl Chloracetate

Medium	Temperature in °C.	Time for % reaction in minutes				$k_1 \times 10^5$
		5	10	20	40	
20% Glycerol	35	45.0	99.0	201.0	450.0	17.82
	42	27.0	54.0	112.0	249.0	32.65
	50	17.0	32.0	62.0	135.0	58.28
	60	8.0	16.0	30.0	66.0	117.9
40% Glycerol	35	42.0	89.0	177.0	397.0	20.53
	42	25.0	50.0	100.0	226.0	36.13
	50	13.0	26.0	52.0	120.0	71.32
	60	7.0	13.0	26.5	61.0	142.7
60% Glycerol	35	39.0	78.0	157.0	381.0	23.16
	42	21.0	45.0	96.0	225.0	38.72
	50	11.5	23.0	48.0	117.0	77.43
	60	7.0	13.0	25.0	61.0	142.6
80% Glycerol	35	37.0	79.0	156.0	384.0	23.16
	42	21.0	42.0	90.0	240.0	43.01
	50	12.0	25.0	50.0	130.0	73.23
	60	6.0	12.0	24.0	62.0	150.5

TABLE IV
Values of k_1 , E , and Log PZ for Ethyl Acetate in Different Solvents

Solvent	$k_1 \times 10^5$ at 42°	E	Log PZ
20% Glycerol	47.54	16,620	8.2377
40% Glycerol	56.45	15,870	7.7559
60% Glycerol	60.22	14,370	6.7853
80% Glycerol	47.26	17,100	8.5798
60% Dioxane	24.41	16,930	8.1761
60% Alcohol	17.37*	16,200	7.5665

* The value is at 39°·8 and is taken from Hinshelwood and Timm (2).

TABLE V
Values of k_1 , E and Log PZ for Ethyl Propionate in Different Solvents

Solvent	$k_1 \times 10^5$ at 42°	E	Log PZ
20% Glycerol	49.27	15,880	7.7243
40% Glycerol	51.13	15,250	7.3010
60% Glycerol	57.06	13,900	6.4771
80% Glycerol	48.4	16,130	7.8692
60% Dioxan	19.93	15,960	7.3802

TABLE VI
Values of k_1 , E and Log PZ for Ethyl Monochloracetate in Different Solvents

Solvent	$k_1 \times 10^5$ at 42°	E	Log PZ
20% Glycerol	32.65	15,160	7.0414
40% Glycerol	36.13	15,790	7.5682
60% Glycerol	38.72	14,650	6.8325
80% Glycerol	43.01	15,310	7.2553
60% Dioxan	15.05	16,640	7.7993
60% Alcohol	13.48*	15,300	6.9017

* The value is at 39°·8 and is taken from Hinshelwood and Timm (2).

TABLE VII

Solvent	Viscosity in centipoises at 30° C.	Time (mins.) taken for 10% reaction at 35° C.		
		Ethyl Acetate	Ethyl Propionate	Ethyl Chloracetate
20% Glycerol	1.36	70	72	99
40% Glycerol	2.73	61	62	89
60% Glycerol	7.31	54	57	78
80% Glycerol	34.92	69	72	79
60% Dioxan	1.63	138	162.5	202
60% Alcohol	1.69	406*	..	445*

* The values are at 24°·86 and are taken from Hinshelwood and Timm (2).

An examination of the tables brings out clearly that both the composition of the solvent and the nature of the ester influence the reaction. Some abnormalities are also noticeable, *e.g.*, an apparently fast reaction in 60% glycerol as compared with other concentrations of glycerol.

The most important influence that must be considered is that of the solvent on the parameters of the reaction velocity equation. It is clear that for the same reaction both E and PZ vary considerably and are affected to different degrees. The change in value of E is of the order of 2.8 kilocalories which is beyond the limits of experimental error while that in PZ is even more significant, being several powers of ten.

Following Hinshelwood and Fairclough⁴ $\log PZ$ may be plotted against $\frac{1}{\sqrt{E}}$ (Fig. 1). The curves are not linear and extrapolation to $\frac{1}{\sqrt{E}} = 0$ gives for PZ values several powers of ten greater than that corresponding to

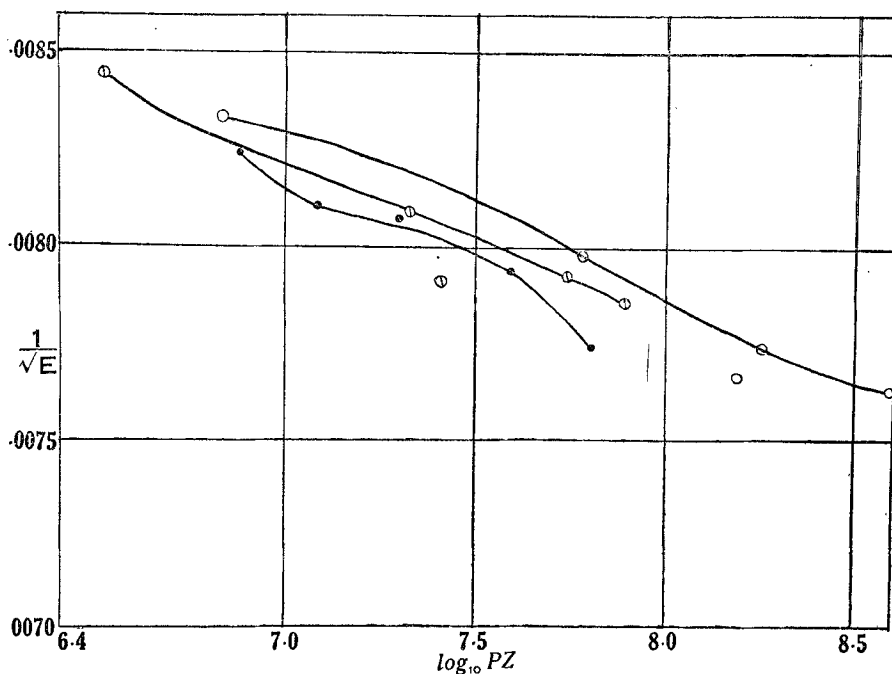


FIG. 1

a gas collision number with $P = 1$. At the same time the close correlation between E and PZ may be seen from the linear character of the E — $\log PZ$ curve (Fig. 2).

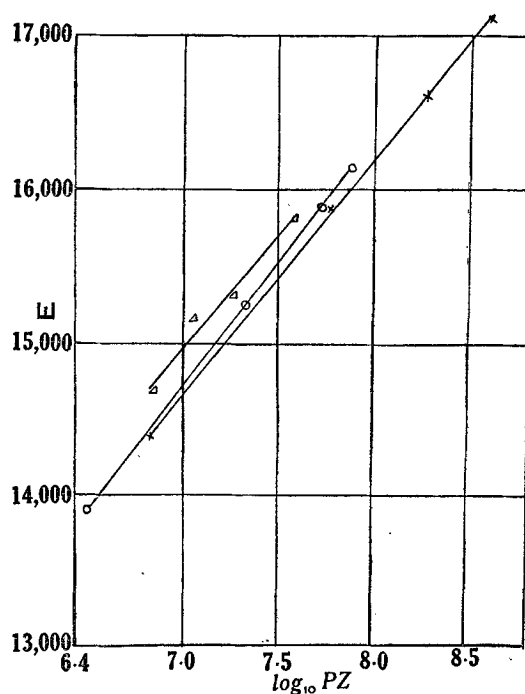


FIG. 2

- Ethyl Acetate
- × Ethyl Propionate
- Δ Ethyl Chloracetate

Now the whole process can be visualised as involving the principal factors of activation, deactivation and completion of the chemical change. Jowett⁵ has shown that the collision frequency in a liquid system exceeds that in a gaseous system and in the derivation of the correction factor the viscosity term appears in the numerator

$${}_1Z_s = \frac{3 \pi \eta \sigma}{2m_1}$$

when ${}_1Z_s$ is the number of collisions which a solute molecule of mass m_1 and diameter σ makes during one second in a medium of viscosity η .

If every collision were effective and if viscosity were to be the primary factor, one may expect the reaction in 80% glycerol to be the fastest in the present series, whereas the reaction appears fastest in 60% glycerol and the velocity in 80% glycerol is not very different from that in 20% glycerol, though the viscosity is 24 times greater. Considering the ionic nature of the reaction, the dielectric constant of solvent may be expected to greatly

influence the speed of the reaction. With glycerol-water systems, we have consequently to take into account changes in both dielectric constant and viscosity with composition. Data on the dielectric constant of mixtures of glycerol and water are not available but data on variations of viscosity with composition and with temperature are available. The latter alone is inadequate for drawing any quantitative deductions, which must therefore be postponed to a later date. A qualitative comparison is, however, possible. Within the small temperature range investigated, the change in dielectric constant is only about 10% assuming the mixture law to be valid for glycerol-water systems. On the other hand, in the same range, the viscosity changes fourfold, the value at 60° being only a fourth of the value at 35°. The two influences probably work in opposite directions and one may expect a point of maximum velocity in changing from 0% glycerol to 100% glycerol. The position of this maximum will naturally shift with temperature and will vary with the nature of the ester. These changes can be observed in two ways:—(1) plotting the time taken for a definite percentage of the reaction (say 20%) against the composition of the medium (Fig. 3), and (2) plotting change of E with composition of the medium (Fig. 4).

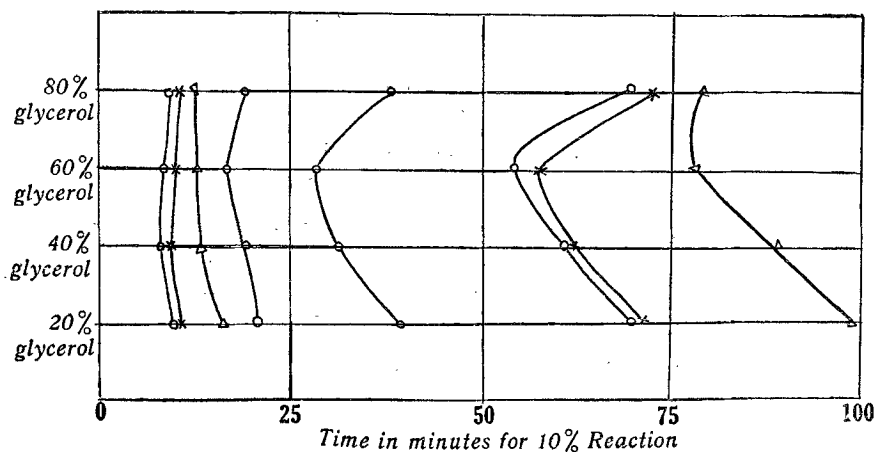


FIG. 3.

- O Ethyl Acetate
- x Ethyl Propionate
- Δ Ethyl Chloracetate

It will be noticed from Fig. 3 that a parabolic curve is obtained which flattens out with increase of temperature, the position of maximum velocity shifting from about 60% glycerol at 35° C. to 40% glycerol at 60° C. A more complete picture is possible only with larger temperature ranges and intermediate compositions for the medium.

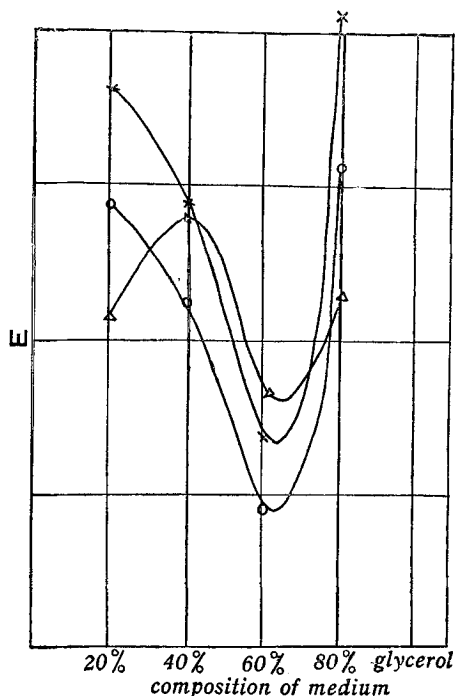


FIG. 4

Fig. 4 brings out another aspect. Ethyl acetate and ethyl propionate are affected in the same way by change of solvent. Except for a slight displacement, the shape of the curve is the same, the reaction showing a minimum value of E in the 60% glycerol region. Chloroacetic ester on the other hand appears to behave differently, the curve showing a maximum and a minimum. This difference is probably only one of degree and an explanation is possible only after a more complete investigation of the change with intermediate glycerol concentrations in the solvent. These will form the subject of a later communication. The solvent influences the reaction both by increasing Z and by providing a polar environment that facilitates the breaking up of the transition-complex.

It is interesting to compare also, the velocity of the reaction in glycerol-water with that in dioxan-water and alcohol-water systems. The reaction is slowest in alcohol though the dielectric constant of alcohol is much greater than that of dioxan and the viscosity is slightly greater (Table VII). This must be attributed to the fact that ethyl alcohol is also a product of reaction and the presence of an environment of alcohol molecules stabilizes the transition complex. Since the rate-determining step involves the

breaking up of this complex, an apparently slow reaction is the result. In dioxan, this complication is absent and the reaction is much faster. Both these solvents have a lower dielectric constant and a much lower viscosity than glycerol-water systems and the comparatively faster reaction is easily understandable. Noteworthy also is the fact that though 20% glycerol is less viscous than either 60% dioxan or 60% alcohol, the reaction in that solvent is faster. The difference must be traced to the higher dielectric constant. Mention may be made here of the peculiar solvent influence in the pyridine methyl iodide reaction in mixed solvents.³

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Experimental

The experimental procedure was similar to that described in Part I. Glycerol (bidistilled, s.g. 1.23 for analysis, Kahlbaum) was used without further purification).

Summary

The kinetics of acid hydrolysis of ethyl acetate, ethyl propionate and ethyl chloracetate in glycerol-water system has been studied. Both viscosity and dielectric constant influence the reaction and a close correlation of the parameters of the reaction velocity equation is noticed.

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