

# KINETIC STUDIES IN ESTER HYDROLYSIS

## Part XIII. The Alkaline Hydrolysis of Benzene Dicarboxylic Esters and the Half Ester of Succinic Acid—A Study of Consecutive Reactions and the Mechanism of Half Ester Hydrolysis

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IN the previous part<sup>9</sup> one of us had reported the results of studies on esters of succinic acid which made it necessary to investigate the phthalic esters as also the half ester of succinic acid. These are reported in the present communication.

### EXPERIMENTAL

The esters and solvents used were purified by standard techniques. The preparation of the half ester required the use of well-steamed vessels and a distillation at the lowest possible temperature to avoid disproportionation into the free acid and the diester. All rate studies were as before with the difference that the reaction has been studied mostly at a constant ionic strength of 0.01 unless indicated otherwise. The constancy of ionic strength was designed to minimise the effect of the diacid ion produced during the reaction. Rate constants for the first and second stage in the dibasic esters were evaluated by the Frost and Schwemer method.<sup>5</sup> The physical constants of the esters used were as under:—

Ester	Boiling Point or Melting Point	$n_D^{30}$	Dipole moment
Diethyl Orthophthalate	.. 295° C. (b.p.)	1.4977	2.40
Dibenzyl Phthalate	.. 42.5 (m.p.)	..	2.12
Diethylterephthalate	.. 44.0 (m.p.)	..	2.30
Ethylhydrogensuccinate	.. 172° C./42 mm.	1.4299	..

## DISCUSSION OF RESULTS

Any analysis of dibasic ester hydrolysis has to take into account the relative rates of the first and second step of the consecutive reactions as also the environmental influences on each of these. The relevant results are presented in Tables I and II below.

TABLE I  
*The hydrolysis of esters of dibasic acids in dioxan water mixtures*

Compound	% Dioxan by Volume	Temperature ° C.						
		30			35		40	
		$k_1$	$k_2$	$k_1/k_2$	$k_1$	$k_1/k_2$	$k_1$	$k_1/k_2$
Diethyl Phthalate	50	0.01485	0.00247	6.00	0.02080	5.94	0.02870	5.87
	60	0.01192	0.00230	5.18	0.01701	5.11	0.02390	5.03
	70	0.01020	0.00219	4.66	0.01480	4.61	0.02124	4.58
Dibenzyl Phthalate	50	0.02421	0.00403	6.00	0.03361	5.92	0.04618	5.84
	60	0.01986	0.00383	5.19	0.02799	5.09	0.03901	5.00
	70	0.01705	0.00360	4.74	0.02427	4.62	0.03407	4.53

TABLE II  
*The hydrolysis of esters of dibasic acids in acetone water mixtures*

Compound	% Acetone	Temperature ° C.						
		30			35		40	
		$k_1$	$k_2$	$k_1/k_2$	$k_1$	$k_1/k_2$	$k_1$	$k_1/k_2$
Diethyl Phthalate	50	0.01272	0.00205	6.20	0.0184	6.11	0.02624	6.03
	60	0.00946	0.00189	5.00	0.0139	4.95	0.02012	4.90
	70	0.00814	0.00175	4.65	0.0122	4.59	0.01803	4.53
Dibenzyl Phthalate	50	0.01865	0.00309	6.04	0.02681	5.95	0.03810	5.87
	60	0.01591	0.00298	5.34	0.0232	5.29	0.03320	5.19
	70	0.01181	0.00285	4.14	0.01739	4.11	0.02530	4.02
Diethylterephthalate	50	..	..	..	0.1472	2.78	0.2090	2.74
	60	..	..	..	0.1112	2.25	0.1609	2.22
	70	..	..	..	0.0976	2.12	0.1442	2.16

The results clearly show that the influence of the solvent on the first as well as the second stage of the hydrolysis is the same. The mechanism of the second stage cannot then be very different from that of the first. The changes in the alcohol part of the ester have very little effect on the rates while increasing the distance between the carboxyl groups leads to nearly theoretical values for the relative rates. The reaction is slowed down by decrease in the dielectric constant of the environment at all temperatures while the temperature effect on the ratios of the two rates is slight.

A proper analysis, however, cannot be made on these alone. The Arrhenius parameters or the thermodynamic constants can be expected to give better information while different theoretical approaches can be compared by estimates of the distances of closest approach. There is also the need for a clarification as to whether the second stage is an ionic interaction between two bodies carrying a negative charge or whether this is an ion dipole reaction. The study of the half ester comes in handy for this. Unless steps are taken to ensure constancy of ionic strength, there will be a change in the ionic strength of the reacting system as the reaction proceeds. The relevant data on these are collected together in Tables III, IV and V.

The Arrhenius parameters confirm the view that the difference between the first and second stage of the hydrolysis cannot be widely different. The small difference can be readily accounted for. The transmission of the electrical effects of the carboxyl ion is quite noticeable in the phthalates and the greater distance in the para isomer leads to negligible effect by the charge in the half ester. This is readily seen from the fact that the difference in activation energies are beyond the limits of experimental error in the ortho esters, as well as the para compound but the difference corresponds to less than 0.02 electron volts. A further indication is provided by the other features of the reaction. Both stages are affected by changes in the dielectric constant of the environment in the same direction ruling out any change of mechanism. A crucial test is provided by the estimates of the dimensions of the reaction complex. Scatchard has shown that the rate constants are related to the molecular dimensions by the equation

$$\ln k' = \ln k'_{\substack{k=0 \\ D=\infty}} - \frac{Z_A Z_B e^2}{DkTr} + \frac{Z_A Z_B e^2}{DkT} \cdot \frac{K}{1 + a_i K}$$

where the reactants are ionic while Laidler and Landskroner have shown that for an ion dipole reaction of the type of ester hydrolysis a suitable topology can be assumed for the transition state which leads to an expression which predicts a linear relation between  $\ln k$  and  $1/D$ .<sup>7</sup>

TABLE III

*The alkaline hydrolysis of ethyl hydrogen succinate in water*

Concentration of ester: 0.005001 M; Concentration of OH' 0.004999 M							
Mean ionic strength ..	0.01050	0.020459	0.010974	0.011283	0.011593	0.012109	0.01263
Rate Constant ..	0.1036	0.1068	0.1053	0.1063	0.1053	0.1057	0.1057
In the presence of 0.005036 moles of KCl							
Mean ionic strength ..	0.01545	0.01565	0.01596	0.01622	0.01668	0.01697	0.01750
Rate Constant ..	..	..	0.1260 (mean value)		..	..	..

Both sets of reaction were at the same temperature 40° C.

TABLE IV

*Thermodynamic constants and Arrhenius parameters for the reaction*

(Suffixes 1 and 2 refer to the first stage and second stage)

Compound	% Dioxan or Acetone	E <sub>1</sub>	E <sub>2</sub>	ΔH <sub>1</sub>	ΔH <sub>2</sub>	log PZ <sub>1</sub>	log PZ <sub>2</sub>	ΔS <sub>1</sub>
Diethyl Phthalate	Dioxan							
	50	12.42	12.87	11.81	12.26	7.1261	6.6722	-26.01
	60	13.11	13.68	12.50	13.07	7.5286	7.1671	-24.16
	70	13.82	14.16	13.21	13.55	7.9723	7.5465	-22.13
	Acetone							
	50	13.65	14.18	13.04	13.57	7.9458	7.5386	-22.25
	60	14.22	14.60	13.61	13.99	8.2330	7.7980	-20.94
	70	15.43	15.49	14.82	14.88	9.0264	8.3049	-17.31
Dibenzyl Phthalate	Dioxan							
	50	12.17	12.71	11.58	12.10	7.1564	6.7680	-25.87
	60	12.73	13.39	12.12	12.78	7.4750	7.2370	-24.41
	70	13.050	13.88	12.44	13.27	7.6380	7.5672	-23.67
	Acetone							
	50	13.47	13.96	12.86	13.35	7.9823	7.5562	-22.09
	60	13.87	14.38	13.26	13.77	8.2049	7.8426	-21.07
	70	14.35	14.92	13.74	14.31	8.6502	8.1984	-19.03
Diethyl Terephtha- late	Acetone							
	50	13.43	13.92	12.82	13.31	8.6937	8.5963	-18.82
	60	14.13	14.42	13.52	13.91	9.0661	8.9946	-17.13
	70	14.97	15.18	14.36	14.57	9.6094	9.4237	-14.64

All E and ΔH values are in kilocalories while ΔS values are in entropy units.

TABLE V  
Molecular distances for reaction by different methods for half-ester hydrolysis

Compound		Scatchard <sup>10</sup>	Laidler <sup>7</sup>	Lamer <sup>8</sup>	Ingold <sup>6</sup>
Diethyl Succinate	D ..	76.88	2.90	0.03764	..
	A ..	20.76	3.00	..	..
Dibenzyl Succinate	D ..	134.2	2.85	0.03794	..
	A ..	16.85	3.00	..	..
Diethyl Phthalate	D ..	58.68	2.90	..	19.86–48.74*
	A ..	13.31	3.20	..	..
Dibenzyl Phthalate	D ..	149.10	2.85	..	19.43–48.99*
	A ..	24.60	3.00	..	..
Diethyl Terephthalate	A ..	34.22	2.90	0.09797	34.89–282.1*

\* Values indicate variations with the proportion of organic solvent.

D values in aqueous dioxan.

A values in aqueous acetone.

Scatchard values are based on the slope of

$$\log k - \frac{1}{D} \text{ graph}$$

for a reaction between ions where the slope equals

$$-\frac{e^2 z_a z_b}{2.303 r k T}$$

Laidler values are based on the method indicated by Laidler and Landskröner for ion dipole reactions.

Lamer values are on the collision theory using the equation

$$\log_{10} \sigma = \frac{1}{2} \log_{10} K_{\infty} - \frac{1}{2} \log_{10} \frac{60N}{1000} - \frac{1}{4} \log_{10} \left[ 8\pi RT \frac{(M_A + M_B)}{M_A M_B} \right] + \frac{E_0}{2 \times 2.303 RT}$$

Ingold values are based on the method indicated by Ingold and Gane on cyclic esters.

For the monoesters the mean radius of the reaction zone works to about 3 Å and it is noticed that the same value is reached in the half-ester hydrolysis as well. This clearly indicates that the half-ester hydrolysis is one requiring the same ion-dipole mechanism as the monocarboxylic esters or the first stage of the diesters. The values calculated on the basis of Ingold's method lead to abnormal figures varying with the solvent composition, indicating that they refer to the solvated transition state and further studies are expected to show the extent to which this value will help in estimating the degree of

solvation. The greater dispersal of charges in the transition state will lead to a greater degree of solvation with apparently larger dimensions and since Ingold's approach is one primarily taking electrostatic forces alone, the observed values are not inconsistent. It is, however, not correct to assume the values to be that of the unsolvated complex.

The correctness of the rate constants by treating the system of consecutive reactions is also shown by the observations with the sodium ethyl succinate.

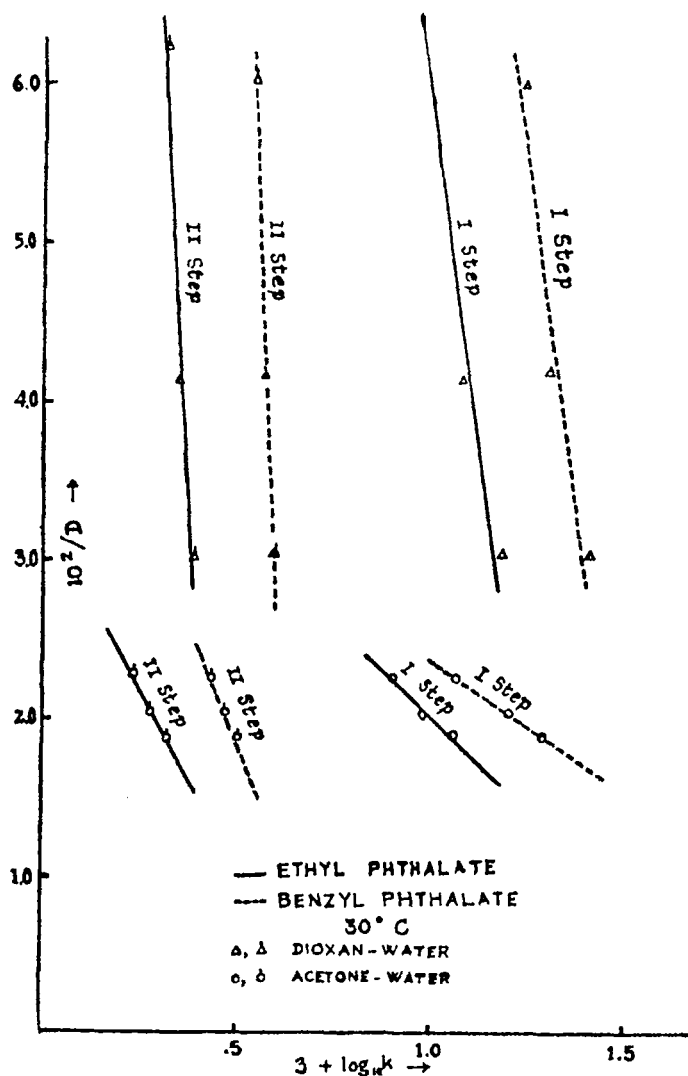


FIG. 1.

The rate constant obtained is within the limits of experimental error the same by both methods for the second stage of the diester.

The reaction presents another interesting facet of the role of solvent in the reaction. The ion dipole mechanism requires a linear relationship between rate constant and the reciprocal of the dielectric constant. This can be readily seen to be the case (Fig. 1). Fairclough and Hinshelwood<sup>4</sup> have shown that there is in general a correlation between the two parameters of the Arrhenius rate equation. While this is an indication of the role of environment, unlike the influence of substituents, greater variations can be expected. It will be readily noticed from Fig. 2 that specific differences

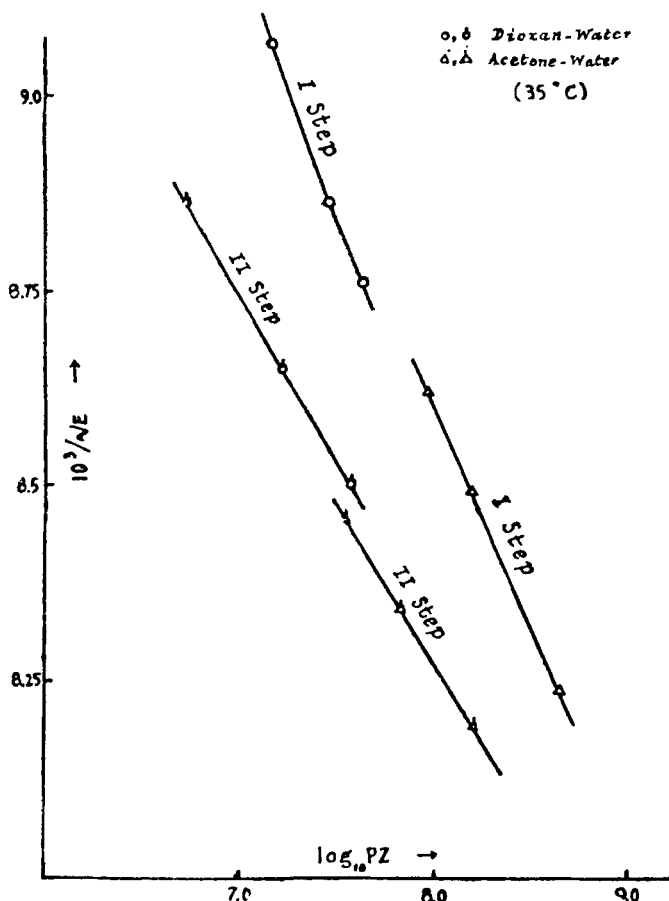


FIG. 2. Benzyl phthalate.

are by no means unusual. Within a single system of solvent mixtures the trends are comparable but change of the components of the mixture brings about changes in this aspect as well. In the present studies, we have been

dealing with a system in which water is itself one of the reactants. A comparison of the rates as a function of the mole fraction of water is of some interest and we do find such a correlation (Fig. 3).

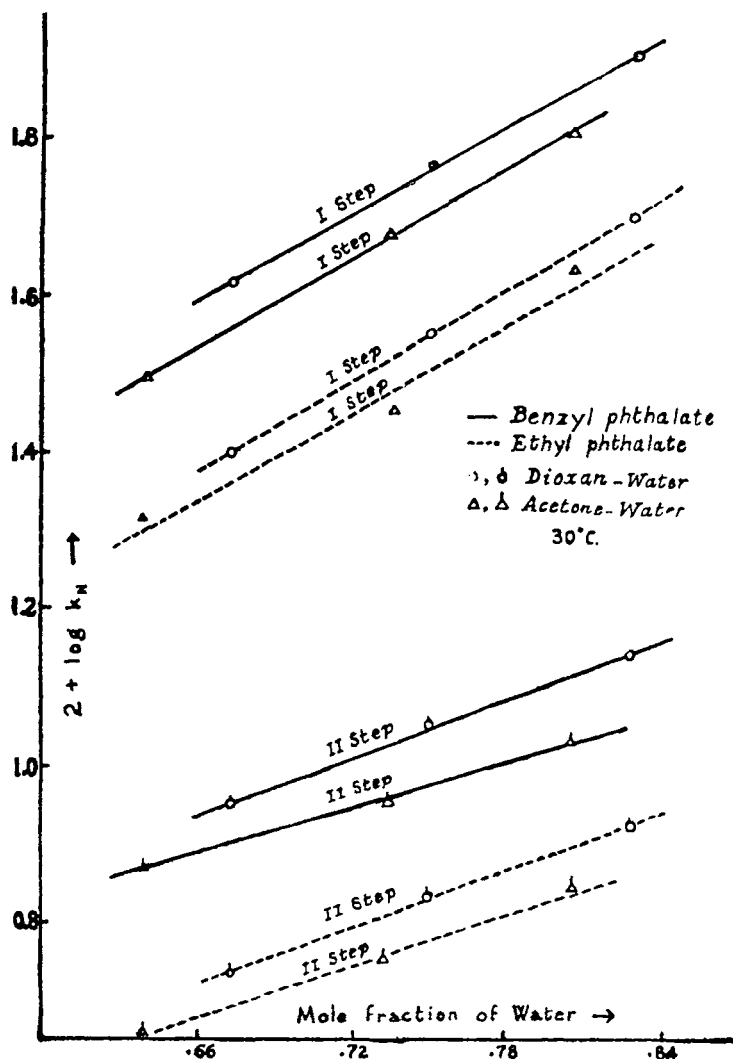


FIG. 3.

Some of our earlier observations<sup>1, 2, 9</sup> have shown this aspect of the problem in systems where there is only a small addition of an organic solvent but in the region where the changes in mole fraction water is not very large, it is generally expected that the Kirkwood correlation is adequate. We find that even here the picture is not adequate. The reaction is one in which



the solvated hydroxyl ion has to participate and a second molecule of water also enters into the picture. It has been established that the hydroxyl ion is surrounded by water molecules tetrahedrally<sup>3</sup> and in the current mechanism of the ester hydrolysis this fits in conveniently. While any hydrogen bonding between the oxygen atoms of dioxan and of water is bound to be weak, the forces associating water with acetone are bound to be stronger so that the activation energies for the reaction in acetone can turn out to be higher. This is our observation in the results presented earlier. In the region where the mole fraction of water is low, the structure breaking process needed for the reaction can be seen also in the pre-exponential term of the rate equation.

An aspect of solvent influence that has to be considered is the extent to which the reaction is diffusion controlled. A serious difficulty in any precise theoretical treatment of solvent influence is the need to introduce structural effects of the type mentioned in the foregoing paragraph. Further work is necessary before a proper treatment is possible but the trend is quite clear.

#### SUMMARY

The study of hydrolyses of the diesters of benzene dicarboxylic acids as a consecutive reaction and of the sodium salt of the half ester in mixed solvents clearly indicates that both in the first and in the second stage the reaction is only of the ion-dipole type. Calculations of the dimensions of the reactant species show that the most reasonable values are given by the Laidler approach while the Ingold calculations probably give the dimensions of the solvated transition state.

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