

KINETIC STUDIES IN ESTER HYDROLYSIS

Part X. The Alkaline Hydrolysis of Some Benzoic Esters in Mixed Solvents

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INTRODUCTION

IN earlier parts of this series were reported the results of studies on a number of aliphatic esters and in particular of ethyl acetate in a variety of solvent compositions. Specific solvent influences were noticeable in which dielectric constant was only one of the factors and abnormal features were noticed where the organic solvent component in the aqueous system was a small fraction of the mixture.¹ It appeared necessary to study some aromatic esters as well as the esters of polybasic acids. The present report presents the results of studies with some benzoic esters.

EXPERIMENTAL

The solvents used were purified as in earlier parts while the esters were invariably freshly purified and distilled before use. The physical constants of the esters are given below:

Ethyl benzoate b.p. 212.9° C.	n_D^{30} 1.5028	Dipole moment 1.95
<i>o</i> -Nitro Ethyl benzoate b.p. 173.0/18 mm.	n_D^{30} 1.5211	„ „ 3.79
<i>p</i> -Nitro Ethyl benzoate m.p. 57°		„ „ 3.84
Benzyl benzoate b.p. 323°	n_D^{30} 1.5641	„ „ 2.08

(All the physical constants were measured using the samples purified for the experiment. Dipole moment values refer to benzene solutions.)

The course of the reaction was followed by standard procedures, analysing aliquot parts. Freshly standardised dilute ammonia solutions were used for estimating excess acid used for chilling the reaction mixture and a screened indicator composed of neutral red and methylene blue was used. Temperature control was accurate to 0.02° C. in the range studied and was periodically checked.

DISCUSSION OF RESULTS

Unlike the studies with ethyl acetate, the range of solvent compositions that could be used was limited by solubility of the reactants. In every instance, strict second order rate constants could be got and the graph of $\log(a-x)/(b-x)$ against time was linear within the limits of experimental error (Fig. 1). The relevant rate constant data are presented in Table I.

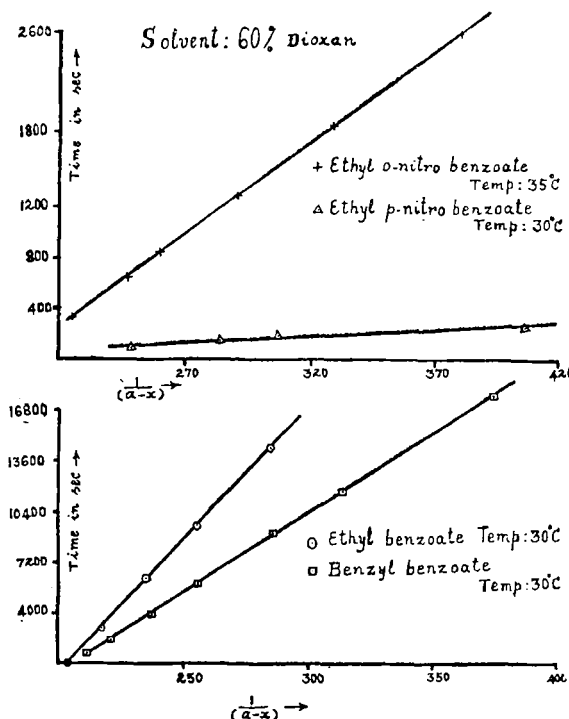


FIG. 1

It will be noticed that in all the instances, the reaction rate decreases with a decrease in dielectric constant, indicating repulsive interactions of the ion-dipole system if one is to assume what is not true, that free energies of hydration of the ion as well as of the transition state are unimportant. At the concentrations of reactants used, the Debye-Huckel limiting law is applicable and no serious error is introduced in applying the Kirkwood approximation.⁴

In dealing with mixed solvents, one has to choose between iso-composition and iso-dielectric conditions for comparisons. Svirbeley and Warner¹ object to the use of isocomposition data as such and use the relation.

$$E_D = E_{app} + R \left[\frac{\log K}{\partial D} \right]_T \frac{\partial D}{\partial \left(\frac{1}{T} \right)}$$

TABLE I A

Ester	Solvent composition % dioxan v/v	Temperature °C.						
		30		35		40		
		Conc. of reactants $\times 10^3$	$k_1 \times 10^3$	Conc. of reactants $\times 10^3$	$k_2 \times 10^3$	Conc. of reactants $\times 10^3$	$k_3 \times 10^3$	
Ethyl benzoate	..	40	5.005	9.72	8.560*	13.50	4.926	18.50
	..	50	4.908	7.42	8.532*	10.40	5.012	14.50
	..	60	5.026	5.95	8.521*	8.50	5.138	12.00
	..	70	5.192	5.08	8.516*	7.40	5.202	10.05
<i>o</i> -Nitro ethyl benzoate	..	40	5.017	$k_2 \times 10^2$ 10.87	5.025	14.41
	..	50	5.139	8.35	5.039	11.20
	..	60	4.957	6.84	5.024	9.26
	..	70	5.035	5.97	5.028	8.17
<i>p</i> -Nitro ethyl benzoate	..	60	5.146	5.821	5.208	7.960
	..	70	5.108	5.023	5.012	6.963
Benzyl benzoate	..	50	5.109	12.11	5.426	$k_2 \times 10^3$ 16.80	5.099	$k_3 \times 10^3$ 23.14
	..	60	5.047	9.92	5.229	14.00	5.008	19.50
	..	70	5.001	8.52	5.014	12.30	4.826	17.03

TABLE I B

The alkaline hydrolysis of benzyl benzoate in acetone-water system

Solvent composition Acetone% v/v	Temperature ° C.					
	30		35		40	
	Conc. of reactants $\times 10^3$ M	k_2 $\times 10^3$	Conc. of reactants $\times 10^3$ M	k_2 $\times 10^3$	Conc. of reactants $\times 10^3$	k_2 $\times 10^3$
50	4.824	9.31	4.926	13.40	5.209	19.04
60	5.226	7.95	5.014	11.57	5.129	16.50
70	5.098	5.901	5.024	8.70	4.999	12.69

Note.—The concentration of the hydroxide used was practically the same as that of the ester except those marked * where the OH' concentration was about 0.001 M higher. All rate constants are in units of moles/litre, sec.⁻¹

The degree of linearity in the graph of the reciprocal of temperature against the logarithm of the rate constants in the present studies indicate that apparently the correction term is not appreciable and we are justified in using the more convenient isocomposition data in Table II.

Laidler and Eyring⁵ have shown that in the alkaline hydrolysis of ethyl benzoate in alcohol-water systems, the empirical relationship reported by Evans and Polanyi² $T\Delta S = \alpha\Delta H + \beta$ holds good. While our results show clearly that the trends in both ΔH and ΔS appear to be similar, the expected linear relationship is not satisfactory. Apparently, where non-hydroxylic solvents are present, the solvation of the reactant species as well as the transition state are influenced to different degrees by the dielectric constant in the microscopic region as well as the topology of the transition state. The results, however, bring out the Fairclough-Hinshelwood relationship between the two Arrhenius parameters.³ Even here, we have to treat each compound separately in a given solvent pair and changes in solvent pair systems also alter the individual values though the trend for a given compound may be maintained.

For an ion-dipole reaction, assuming a solvent continuum, it has been shown that the rates and activation energies involve functions of the dipole moments of the reacting species. The reaction centre in these esters is the COOR group and substituents in the benzene ring can modify the group

TABLE II

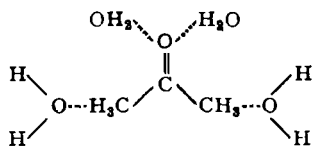
Ester	Solvent dioxan vol.%	E k.cals.	ΔH k.cals.	\log_{11} PZ	ΔS e.u.
Ethyl benzoate ..	40	12.220	11.608	6.800	-27.51
	50	12.760	12.148	7.300	-25.17
	60	13.230	12.618	7.600	-23.84
	70	13.950	13.338	7.760	-23.11
<i>o</i> -Nitro ethyl benzoate	40	10.800	10.818	6.696	-27.97
	50	11.260	10.648	6.908	-27.01
	60	11.610	10.998	7.070	-26.26
	70	12.010	11.398	7.293	-25.24
<i>p</i> -Nitro ethyl benzoate	60	11.570	10.948	8.102	-21.54
	70	12.280	11.668	8.552	-19.47
Benzyl benzoate ..	50	12.470	11.858	7.066	-26.27
	60	12.790	12.178	7.220	-25.59
	70	13.280	12.678	7.508	-24.25
	Acetone water system % Acetone by vol.				
	50	13.550	12.938	7.737	-23.21
	60	13.960	13.348	7.964	-22.17
	70	14.530	13.918	8.250	-20.91

moment by altering the apparent charge on the carbon of the carbonyl. The introduction of the nitro group can then be expected to reduce the activation energy for the reaction as is actually found to be the case. The position in the benzene ring does not appear to make any serious difference to the activation energy but as may be expected, there is a pronounced difference in the entropy of activation. The value is considerably higher with

the ortho-nitro compound. The proximity of the negative end of the N-O dipole hinders the approach of the OH⁻ ion from certain directions. Alteration of the alkoxy group is not without effect and the replacement of the ethyl by benzyl leads to a slight reduction in the activation energy following the trend of the dipole moment.

Turning to solvent influence on the reaction, both rates and activation energies follow the trend in the dielectric constant with rates decreasing and activation energies increasing as the water content decreases.

It has been observed with ethyl acetate hydrolysis that abnormalities are noticed only for small additions of the organic solvent to water while in the region of compositions used in the present study, the characteristic correlation of Kirkwood⁴ between Dielectric constant and rates holds good. The one compound studied in both dioxan-water and acetone-water system shows again the differences noticed in earlier parts. The reaction in acetone is consistently slower. The activation energy as well as the entropy of activation are also much higher and beyond the limits of experimental error. The difference has to be traced to the specific property of acetone in forming a solvated molecule of the type



so that the system as a whole has to use also the extra energy for rupture of the bond between water and acetone in addition to the normal energy needed for the reaction. The increase in value of the entropy of activation is also consistent with this structure breaking part of the mechanism.

SUMMARY

The alkaline hydrolysis of some benzoic esters in dioxan-water mixtures as well as that of benzyl benzoate in acetone-water has been studied. The observations indicate a group influence consistent with the ease of formation of the transition state by interaction between the hydroxyl ion and the carbonyl group of the ester in the rate determining step. The influence of dielectric constant is what might be expected for an ion-dipole reaction but specific solvent influences cannot be excluded.

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