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Kinetics and Solvent Effects in the Acid Hydrolysis of Potassium Ethyl Malonate in Dioxane—Water and Acetone—Water Mixtures

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With 1 Figure

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The acid-catalysed hydrolysis of potassium ethyl malonate in presence of $0.05N$-HCl in water and in dioxane—water as well as acetone—water mixtures containing up to about 90% by weight of the organic solvent was studied over the temperature range 30–55 °C. The reaction rate decreases continuously with decreasing water content of the solvent mixtures until it reaches a minimum at about 80% dioxane and increases again. The isocomposition activation energy shows only slight changes with solvent composition. The kinetics of the reaction was investigated from the viewpoints of solvent composition, water concentration and dielectric constant. The radii and thermodynamic parameters of the activated complex were calculated and discussed. The conclusions drawn show that the reaction is better treated as an ion—dipole rather than an ion—ion interaction.

Introduction

The kinetics of half-ester hydrolysis, particularly the base-catalysed reaction, has received considerable interest, but still the type of interaction is not yet established[1–6]. On the other hand, only little work has been done on the kinetics of acid-catalysed hydrolysis of dicarboxylic esters[7] or their half-esters[8]. In the present investigation the kinetics of the acid hydrolysis of potassium ethyl malonate is reported in an attempt to present a comprehensive study of the effect of solvents on the kinetics of the half-ester hydrolysis. Since medium effects play a distinct role among the factors governing the rate of hydrolysis, the reaction was studied in two aqueous solvents namely, the non-polar solvent dioxane, and the dipolar aprotic solvent acetone. The solvent compositions represent an extensive series ranging from pure water up to about 90% by weight of the organic solvent over which the dielectric constant, solvating power and proton availability of the medium changes widely.

Experimental

Materials

The ester was prepared from diethyl malonate according to the method described before[9] and was estimated to be 99% pure by complete hydrolysis with excess of KOH and back titration with HCl.

Dioxane was purified by acidifying with HCl and refluxing under N_2 followed by distillation from KOH and drying over Na metal then distilled[10] from $SnCl_2$.

Acetone was purified by refluxing with pure $KMnO_4$, distilled and dried over K_2CO_3 [10]. The screened indicator used in the titration technique was prepared by mixing equal volumes of 0.1% solution of methylene blue and neutral red in absolute ethanol[7].

Reaction Mixtures and Kinetic Procedure

Binary mixtures of organic solvents and water were prepared on a weight basis. The concentration of the catalysing acid was 0.05*M*-HCl in all mixtures. The hydrolysis was carried out in glass-stoppered flasks except for temperatures above 40 °C in presence of acetone as solvent where the reaction was carried out in small Pyrex glass ampoules to prevent any change of solvent composition due to evaporation. The reaction rates were determined by titrating samples at different time intervals against standard NaOH solution using the screened indicator mentioned above. Titres at completion of reaction were obtained by heating aliquots in sealed ampoules at 65 °C for several days, then contents were followed by titration until a constant reading consistent with the calculated value was obtained.

Results and Discussion

The first-order rate constants for the acid hydrolysis of potassium ethyl malonate in water and in dioxane—water as well as acetone—water mixtures at 30–55 °C were calculated from the slopes of the linear plots of log $a/(a - x)$ against time, t. The reaction followed the first-order rate law up to about 75%. The rate constants at different temperatures and solvent compositions are collected in Tables 1 and 2 together with the respective activation energies.

Dependence of Rate on Temperature

The isocomposition activation energy, E_c, remains more or less constant, i.e., independent of solvent composition within the experimental error. According to the absolute reaction rate theory[11] this can be explained if one assumes that the effect of solvation of reactants balances that of the activated state. A similar observation was previously found in the acid hydrolysis of ethyl hydrogen maleate and some homologous esters in dioxane—water and acetone—water mixtures[8] as well as in some monocarboxylic esters in ethanol—water mixtures[12].

Table 1. *Observed Rate Constants and Activation Energies for the Acid Hydrolysis of Potassium Ethyl Malonate in Dioxane—Water Mixtures*

Solvent composition		$k' \cdot 10^6$, min^{-1}					E_c, kcal/mole
dioxane, wt%	$[H_2O]$, moles/l	30°	35°	40°	45°	55°	
0.00	55.52	84	118	171	272	597	15.36
15.30	47.28	68	95	154	199	461	15.36
30.32	39.23	56	71	120	174	364	15.36
40.11	33.91	46	66	101	151	345	15.58
50.05	28.39	40	55	85	126	295	15.63
69.55	17.38	27	40	59	87	182	15.76
79.51	11.70	24	36	54	79	162	15.84
89.62	5.92	30	47	67	105	227	15.84

Table 2. *Observed Rate Constants and Activation Energies for the Acid Hydrolysis of Potassium Ethyl Malonate in Acetone—Water Mixtures*

Solvent composition		$k' \cdot 10^6$, min^{-1}				E_c, kcal/mole
acetone, wt%	$[H_2O]$, moles/l	30°	35°	40°	45°	
0.00	55.52	84	118	171	272	15.36
7.96	50.12	73	102	152	224	14.90
16.16	45.06	59	91	135	205	14.68
28.84	37.49	46	69	109	155	15.09
42.55	29.38	33	51	83	115	15.03
57.18	21.17	27	44	70	96	15.36
67.85	15.47	23	35	56	78	15.36
79.39	9.60	16	26	40	56	15.36

Influence of Solvent Composition on the Rate

The variation of rate with the organic solvent content in dioxane—water and acetone—water can be seen from Tables 1 and 2. It is evident that the rate diminishes continuously with decreasing water concentration until about 20% water, in dioxane—water mixtures, after which the rate increases as the dioxane content is further increased. This minimum in rate can be attributed to the coincident maximum in the acidity function of the mixed solvent near this composition[13], where the catalytic effect of the medium on both sides of the minimum is essentially different. A similar trend is expected to take place in acetone—water mixtures if rate measurements were taken in media containing more than 80% by wt. of acetone. However, due to the low boiling point of acetone, such measurements could not be made conveniently without appreciable error.

The rate can also be expressed as a function of water concentration by plotting log k' against log $[H_2O]$. The rate shows a marked increase as the concentration of water is increased and linear plots are obtained in water rich media. Deviations from linearity are observed in media of relatively low water contents. The slope of the linear portions is unity for all temperatures confirming that the rate is first order with respect to water.

Effect of Dielectric Constant on the Rate

The reaction is enhanced by increase in the dielectric constant. According to *Laidler* and *Eyring*[14], for reactions between two dipoles, a linear relationship between log k' and $(D - 1)/(2D + 1)$ is to be expected, provided the non-electrostatic terms are small enough to be neglected. Investigation over large areas of solvent compositions has, however, shown serious deviations from linearity[15]. On the other hand, according to the electrostatic theories of *Laidler* and *Landskroener*[16], *Moelwyn-Hughes*[17] and *Kilpi*[18], ln k' should vary linearly with $1/D$.

Graphical applications of the different electrostatic interaction theories for ion—dipole as well as dipole—dipole treatments showed that the best linear plots are obtained when log k' is plotted as a function of D[15] as shown in Fig. 1. Departures from linearity at low dielectric constants are more evident when log k' is plotted against $1/D$. The linearity at high dielectric constant is however still preserved. Deviations from linearity are probably due to preferential solvation, or solvent sorting, of the activated complex by water, with the higher dielectric component of the solvent mixtures[14].

The nature of half-ester hydrolysis is still a matter of controversy. While some investigators state that the alkaline hydrolysis is an ion—ion interaction[1–3], others hold the view that it is an ion—dipole interaction[19–22]. However, the acid hydrolysis reaction in the present study, based on dielectric constant effects can better be treated as an ion—dipole interaction, in which the ester molecule represents the actual dipole, rather than a dipole—dipole interaction between the ester and water molecules. On this basis, the radius of the activated complex can be calculated[11, 16] using the slopes of the linear portion of log k' against $1/D$ plots. The value obtained is 4.3 Å in dioxane—water and 3.8 Å in acetone—water mixtures. This difference could be explained if one assumes that the organic solvent molecule plays a role in solvation of the transition state, specially in media of high contents of the organic solvent. The dioxane molecule, being larger than the acetone molecule will therefore give a larger radius of the activated complex in dioxane—water than in acetone—water mixtures. *Svirbely* and *Mador*[2a] calculated the value of r^* for the alkaline hydrolysis of potassium ethyl malonate in water as well as dioxane—water mixtures. Their value was found to be 4.8 Å, in agreement with the present value.

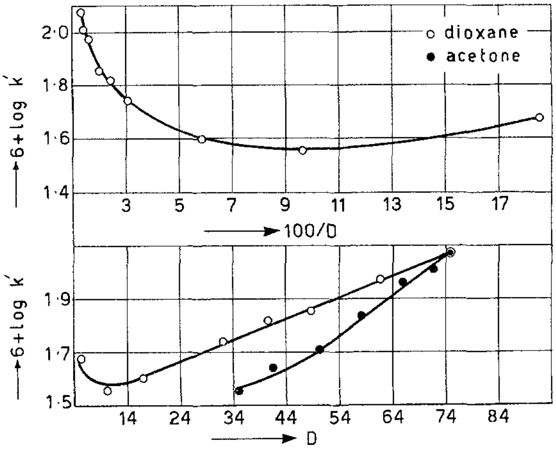

Fig. 1. Dependence of reaction rate on the dielectric constant of the solvent

Rate and Thermodynamic Parameters

The thermodynamic parameters ΔF^*, ΔH^* and ΔS^* of activation provide a suitable means for studying the properties of the activated complex and the solvating power of the medium. These data are compiled in Table 3. The value of ΔF^* shows an increase as the organic solvent content of the reaction mixture increases. On the other hand, ΔH^*, in the case of dioxane—water mixtures, remains almost constant up to about 30%, then fluctuations in its value take place. However, in acetone—water mixtures it shows a non-linear decrease up to about 40% then remains constant in acetone-rich media. The entropy of activation, ΔS^*, which shows a non-linear trend with solvent composition, has a highly negative value, in concordance with the A_{Ac2} mechanism[23] involved. This trend reveals explicitly the important role of specific solvation effects which result in non-random distribution of solvent molecules[24]. In other words, there will be a higher degree of order in the strongly hydrogen-bonded system as the relative concentrations of the solvent components change, and consequently the preferential solvation of the activated complex by water would undoubtedly vary. The changes, therefore, in the enthalpies and entropies of activation will arise mainly from relative changes in the solvation of the reactants and of the activated complex.

Table 3. *Thermodynamic Parameters of Activation and Frequency Factors at 40 °C*

a) Dioxane—Water Mixtures

Parameter	Dioxane, wt%							
	0.00	15.30	30.32	40.11	50.05	69.55	79.51	89.62
ΔF^*, kcal/mole	26.20	26.27	26.42	26.51	26.63	26.86	26.93	26.79
ΔH^*, kcal/mole	14.74	14.74	14.74	14.96	15.01	15.14	15.22	15.22
$-\Delta S^*$, cal/mole deg	36.62	36.84	37.33	36.91	37.14	37.45	37.42	36.97
$\log A$	5.21	5.17	5.06	5.15	5.10	5.29	5.05	5.15

b) Acetone—Water Mixtures

Parameter	Acetone, wt%							
	0.00	7.96	16.16	28.84	42.55	57.18	67.85	79.39
ΔF^*, kcal/mole	26.20	26.27	26.34	26.50	26.65	26.76	26.89	27.11
ΔH^*, kcal/mole	14.74	14.28	14.06	14.47	14.41	14.74	14.74	14.74
$-\Delta S^*$, cal/mole deg	36.62	38.32	39.23	39.32	39.11	38.41	38.82	39.52
$\log A$	5.21	4.84	4.43	4.83	4.67	4.82	4.73	4.58

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