MEDIUM EFFECT ON ALKALINE HYDROLYSIS OF DIPHENIC ACID MONOMETHYL ESTER

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The alkaline hydrolysis of diphenic acid monomethyl ester was studied in mixtures of water with methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, tert-butyl alcohol, and acetone. The dependences of the rate constant on the concentration of the nonaqueous component at different temperatures were obtained and the activation parameters at an isodielectric composition of the reaction medium were determined. The influence of the ionic strength on the reaction rate in the mentioned media was studied and conclusions were drawn as to the role of specific interactions between the reacting ions in the kinetics and mechanism of the studied reaction.

During alkaline hydrolysis of monoesters of dicarboxylic acids, electrostatic interactions between the ester anion and OH^- ion play a role and at the same time there are some effects that cannot be elucidated within the scope of the electrostatic theory of ionic reactions. Certain deviations from the theory were observed in studying the effect of supporting electrolytes in aqueous medium[1-4]. It turns out that nonelectrostatic interactions are still more important if the alkaline hydrolysis is followed in a mixture of water with a nonaqueous solvent[5-10]. The specific effect of the nonaqueous component is attributed to desolvation of the OH^- ion[5] or to changes in the solvation spheres of the ester and activated complex[6-10]. In mixed solvents, specific effects of supporting electrolytes play a role similarly as in aqueous medium[3,11].

Our aim was to obtain informations about the effect of the nonaqueous component of the medium and of supporting electrolytes on the rate and thermodynamic activation parameters for the alkaline hydrolysis of diphenic acid monomethyl ester, and thus to contribute to the elucidation of the role of both electrostatic and nonelectrostatic interactions in ionic reactions in solutions.

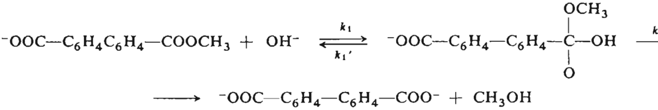
EXPERIMENTAL

Diphenic acid monomethyl ester was prepared from the acid anhydride[12]. Carbonate-free sodium hydroxide was prepared on Dowex 2X8 ion exchanger (200—400 mesh)[13]. Absolute ethyl alcohol was obtained by means of sodium and the fraction boiling at 78·0—78·5°C was used.

Propyl alcohol, methyl, isopropyl, and tert-butyl alcohol, and acetone were distilled prior to use. The reaction was followed by titration[2]. The starting concentrations of the reactants were identical and the rate constant was calculated as $k = (1/(a - x) - 1/a)/t$, where a denotes initial concentration of hydroxide and monoester, resp. The dependence of $1/(a - x)$ on time was linear for all the studied media. The relative error of the rate constant did not exceed 3%. The activation enthalpy and entropy were determined from the temperature dependence of the rate constants in the range 50—70°C with an accuracy of ±2 kJ/mol and ±7 J/mol K, respectively.

RESULTS AND DISCUSSION

The alkaline hydrolysis of diphenic acid monomethyl ester is a reaction between two ions of equal charge, which proceeds by the $B_{Ac}2$ mechanism[14] according to the following scheme:



$$^{-}OOC{-}C_6H_4C_6H_4{-}COOCH_3 + OH^- \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} {}^{-}OOC{-}C_6H_4{-}C_6H_4{-}\underset{O}{\overset{OCH_3}{C}}{-}OH \xrightarrow{k_2}$$

$$\longrightarrow {}^{-}OOC{-}C_6H_4{-}C_6H_4{-}COO^- + CH_3OH \qquad (A)$$

According to the simple electrostatic theory, the rate constant of reaction (*A*) should decrease with decreasing relative permittivity ε_r according to the equation[15]

$$\log k_{\varkappa \to 0} = \log k^{\infty}_{\varkappa \to 0} - z_A z_B e^2 / kT\varepsilon_r r\,, \qquad (1)$$

where z_A and z_B denote charge numbers, e electron charge, k Boltzmann's constant, T absolute temperature, and r critical interionic distance. It is seen from Table I that the dependence of $\log k$ on $1/\varepsilon_r$ is linear only for the mixtures of water with methyl alcohol or ethyl alcohol. The value of r calculated from Eq. (*1*) is 0·3 nm for the former and 0·5 nm for the latter mixtures. These different values suggest that also in these mixtures the specific interactions play a role during the studied reaction. If the reaction course were controlled only by electrostatic interactions, the value of r would not depend on the reaction medium and the rate constants would be equal for equal relative permittivities. The specific effect of the solvent was manifested in a similar way during alkaline hydrolysis of ethyl and propyl acetates[16-18].

In other solvents, the rate constant decreases with increasing mole fraction of the nonaqueous component x_2 (*i.e.*, decreasing ε_r) up to $x_2 = 0{\cdot}15 - 0{\cdot}20$ and then it increases. A similar dependence was observed also during alkaline hydrolysis of *o*-phthalic acid monomethyl ester[13]; the corresponding logarithm of the rate constant shows a linear correlation with that for the alkaline hydrolysis of diphenic acid monomethyl ester in mixtures of water with propyl alcohol or acetone (Fig. 1). Such a linear correlation holds also in the case of other binary solvents except for water–tert-butyl alcohol mixtures. These correlations suggest that similar specific solvent effects come into play during alkaline hydrolysis of both esters.

With respect to the mechanism through which the reaction proceeds Eq. (*A*) we can assume the formation of an intramolecular hydrogen bond in the activated complex (Fig. 2) similarly as in the dissociation of dicarboxylic acids[19,20]. The formation of such a complex lowers the probability of a reversible decomposition of the activated complex to the starting substances. The intramolecular hydrogen bond is then made possible by the mutual orientation of the benzene nuclei of the studied monoester[20]. The described stabilization of the activated complex is possible only if the reactants are at least partially desolvated. In media where the free carboxyl group is hydrated (solvated), the probability of formation of an intramolecular hydrogen bond is smaller. The results suggest that in aqueous methanol or ethanol the water molecule in the solvation sphere of the carboxyl group can be replaced by an alcohol molecule. The activated complex cannot be stabilized and the addition of these alcohols into the reaction system influences the reaction rate mainly through a change in the relative permittivity. In other studied solvents, the decrease of the reaction rate is due to a change in the relative permittivity only at low concentrations of the cosolvent. With an increasing concentration of the nonaqueous component ($x_2 > 0{\cdot}1$), the carboxyl group becomes gradually dehydrated, whereby the conditions become favourable for the stabilization of the activated complex.

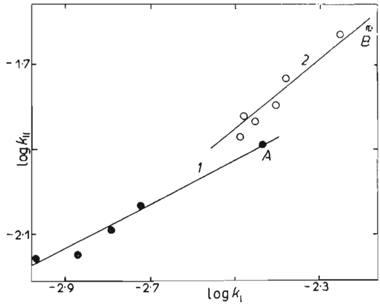


FIG. 1

Correlation Between Logarithms of Rate Constants for Alkaline Hydrolysis of Diphenic Acid Monomethyl Ester (log k_I) and *o*-Phthalic Acid Monomethyl Ester (log k_{II})

1 Water–propyl alcohol at 60°C; 2 water–acetone at 50°C; points *A* and *B* correspond to the rate constants in water.

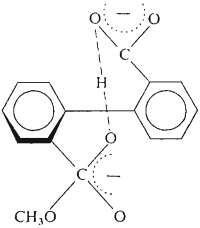


FIG. 2

Stabilization of Activated Complex by Intramolecular Hydrogen Bond

TABLE I

Dependence of the Rate Constant, Activation Enthalpy $\Delta H^{\ddagger}$ and Activation Entropy $\Delta S^{\ddagger}$ for Alkaline Hydrolysis of Diphenic Acid Monomethyl Ester on Mole Fraction of Nonaqueous Component at 60°C

[Ester] = [NaOH] = 0·01 mol/dm^3.

x_2	$k \cdot 10^3$ dm^3 mol^{-1} s^{-1}	$\Delta H^{\ddagger}$ kJ mol^{-1}	$\Delta S^{\ddagger}$ J mol^{-1} K^{-1}
	Methyl alcohol		
0·039	5·17	56·0	—121
0·082	4·05	60·6	—109
0·131	2·78	57·7	—123
0·183	2·17	67·7	— 93
0·301	1·00	—	—
	Ethyl alcohol		
0·027	5·69	52·7	—130
0·058	4·82	54·8	—125
0·093	3·30	—	—
0·133	2·66	56·5	—125
0·180	2·09	59·7	—111
0·236	1·60	—	—
	Propyl alcohol		
0·021	5·24	—	—
0·046	3·60	54·3	—128
0·074	2·93	—	—
0·107	2·57	58·7	—118
0·146	2·30	—	—
0·192	2·30	63·1	—106
0·317	3·63	68·1	— 87
	Isopropyl alcohol		
0·021	5·39	—	—
0·046	4·45	50·2	—139
0·073	3·39	—	—
0·106	2·78	56·4	—124
0·145	2·50	—	—
0·190	2·50	60·2	—114
0·314	4·05	69·7	— 81

TABLE I
(*Continued*)

x_2	$k \cdot 10^3$ $\mathrm{dm^3\,mol^{-1}\,s^{-1}}$	$\Delta H^{\neq}$ $\mathrm{kJ\,mol^{-1}}$	$\Delta S^{\neq}$ $\mathrm{J\,mol^{-1}\,K^{-1}}$
	Tert-butyl alcohol		
0·017	5·43	—	—
0·037	3·64	52·7	—132
0·060	3·20	—	—
0·086	2·96	58·1	—120
0·120	2·60	—	—
0·155	2·60	59·4	—116
0·263	5·06	63·9	— 97
	Acetone		
0·022	5·27	—	—
0·047	4·16	—	—
0·076	3·96	—	—
0·108	3·53	—	—
0·147	3·23	—	—
0·200	3·33	—	—
0·314	5·66	—	—

The activation energy and entropy values in dependence on ε_r in various media are summarized in Table II. (The values of ε_r are corrected for the temperature dependence.) According to the electrostatic theory, the activation energy of the reaction between ions of equal polarity should increase with decreasing ε_r. The theoretical dependence of the activation energy on relative permittivity has the form[15]

$$\Delta E_A = -z_A z_B e^2 \, \Delta\varepsilon_r / \varepsilon_{r1}\varepsilon_{r2} r \, , \qquad (2)$$

where $\Delta\varepsilon_r = \varepsilon_{r,2} - \varepsilon_{r,1}$ and other symbols have the same meaning as in (*1*). If we set $r = 0{\cdot}3$ nm in aqueous methanol and 0·5 nm in aqueous ethanol, the value of ΔE_A is in the given interval of relative permittivities smaller than the accuracy of determination of the activation energy. Accordingly, in these two solvents the experimental activation energy should not change with ε_r, which was however observed only in aqueous ethanol. In aqueous methanol the activation energy increases more than the theory predicts, in other solvents it decreases with decreasing relative permittivity. Hence, a qualitative agreement with the theory was attained only in mixtures of water with ethanol or methanol.

The fact that no unique isokinetic temperature was found in any of the solvents used suggests that the effect of the nonaqueous component on the alkaline hydrolysis of the monoester is complex. (The isokinetic temperature was determined by the criterion of two temperatures[21].)

We studied also the effect of ionic strength adjusted with NaCl (Table III) and $BaCl_2$ (Table IV) in the mixed solvents. The dependence of the rate constant on the ionic strength adjusted with NaCl is given as

$$\log k = \log k_0 + 2Az_Az_B\sqrt{I}/(1 + aB\sqrt{I})\,, \qquad (3)$$

where A and B are Debye–Hückel constants and a is the distance of closest approach of the ions. The value of a was chosen so as to attain an agreement between the theore-

TABLE II

Dependence of Activation Energy E_A and Activation Entropy $\Delta S^{\neq}$ for Alkaline Hydrolysis of Diphenic Acid Monomethyl Ester on Relative Permittivity in Various Solvents

ε_r	E_A kJ mol^{-1}	$\Delta S^{\neq}$ J mol^{-1} K^{-1}
	Methyl alcohol	
62·5	87·8	—36
60·6	89·4	—28
58·8	91·1	—25
57·1	96·6	— 9
	Ethyl alcohol	
62·5	72·6	—77
58·8	74·0	—77
55·5	75·0	—74
50.0	75·0	—77
	Propyl alcohol	
58·8	69·8	—91
50·0	69·8	—92
37·0	62·7	—113
31·2	52·7	—114
	Isopropyl alcohol	
58·8	68·1	— 92
50·0	66·9	—100
37·0	58·5	—126
31·2	52·7	—142
	Tert-butyl alcohol	
58·8	73·2	— 79
50·0	73·2	— 82
31·2	57·3	—131
23·8	49·7	—148
—	—	—

TABLE III

Dependence of Rate Constant for Alkaline Hydrolysis of Diphenic Acid Monomethyl Ester on Ionic Strength Adjusted with NaCl in Mixed Solvents at 60°C

[Ester] = [NaOH] = 0·01 mol/dm^3

I mol dm^{-3}	$k \cdot 10^3$ dm^3 mol^{-1} s^{-1}
Methyl alcohol, $x_2 = 0{\cdot}183$	
0·04	2·36
0·07	2·47
0·12	2·66
0·22	3·02
0·32	3·30
0·52	3·64
Methyl alcohol, $x_2 = 0{\cdot}301$	
0·04	1·13
0·07	1·30
0·12	1·43
0·22	1·60
0·32	1·80
Propyl alcohol, $x_2 = 0{\cdot}046$	
0·04	3·88
0·07	4·16
0·12	4·45
0·22	4·87
0·32	5·34
Tert-butyl alcohol, $x_2 = 0{\cdot}037$	
0·04	3·94
0·07	4·33
0·12	4·60
0·22	5·13
0·32	5·53
Tert-butyl alcohol, $x_2 = 0{\cdot}155$	
0·04	3·30
0·07	4·24
0·12	5·00
0·17	5·40
0·22	5·86
Propyl alcohol, $x_2 = 0{\cdot}192$	
0·04	2·72
0·07	3·09
0·12	3·51
0·17	3·79
0·22	4·00
Isopropyl alcohol, $x_2 = 0{\cdot}046$	
0·04	4·85
0·07	5·13
0·12	5·43
0·22	6·07
0·32	6·69
Isopropyl alcohol, $x_2 = 0{\cdot}190$	
0·04	3·13
0·07	3·57
0·12	4·16
0·17	4·53
0·22	4·73
—	—
Acetone, $x_2 = 0{\cdot}047$	
0·04	4·50
0·07	4·87
0·12	5·34
0·22	6·00
0·32	6·20
Acetone, $x_2 = 0{\cdot}200$	
0·04	4·23
0·07	4·78
0·12	5·28
0·17	5·77
0·22	6·23

tical and experimental slopes of the dependence $\log k = f(I)$; it decreases with decreasing relative permittivity (Table V), *i.e.*, the effect of the ionic strength on the reaction rate becomes more marked at lower values of ε_r. The influence of the solvent on the primary salt effect can be attributed to a change in the solvation sphere

TABLE IV

Dependence of Rate Constant for Alkaline Hydrolysis of Diphenic Acid Monomethyl Ester on Ionic Strength Adjusted with $BaCl_2$ in Mixed Solvents at 60°C
[Ester] = [NaOH] = 0·01 mol/dm^3.

I mol dm^{-3}	$k \cdot 10^3$ dm^3 mol^{-1} s^{-1}
Methyl alcohol, $x_2 = 0{\cdot}183$	
0·023	2·37
0·030	4·06
0·040	5·33
0·050	6·67
Propyl alcohol, $x_2 = 0{\cdot}046$	
0·023	5·50
0·030	6·78
0·040	8·33
0·050	10·6
Propyl alcohol, $x_2 = 0{\cdot}192$	
0·023	5·00
0·030	11·3
0·40	17·2
0·050	23·4
Isopropyl alcohol, $x_2 = 0{\cdot}046$	
0·023	6·00
0·030	7·53
0·040	9·78
0·050	11·8
Acetone, $x_2 = 0{\cdot}047$	
0·023	6·22
0·030	8·11
0·040	9·88
0·050	11·8
Isopropyl alcohol, $x_2 = 0{\cdot}190$	
0·023	5·33
0·030	11·1
0·040	20·2
0·050	25·0
Tert-butyl alcohol, $x_2 = 0{\cdot}037$	
0·030	5·33
0·023	7·45
0·040	8·78
0·050	10·3
Tert-butyl alcohol, $x_2 = 0{\cdot}155$	
0·023	5·22
0·030	9·45
0·040	15·2
0·050	18·9
—	—
Acetone, $x_2 = 0{\cdot}200$	
0·023	5·55
0·030	14·3
0·040	23·2
0·050	38·7

of the reactants. The lowering of ε_r is favourable for the formation of ion pairs M^+–ester$^-$ (Me^+ is a metal cation), which with respect to a decrease of electrostatic repulsion forces between the ester and OH^- ions causes an acceleration of the reaction. The values of a in (*3*) were obtained higher than in the case of alkaline hydrolysis of *o*-phthalic acid monomethyl ester[11], which can be related to the distance between the reaction center and the center of the negative charge in the monoester molecule.

TABLE V

Values of Parameter a according to Eq. (*3*) at Different Relative Permittivities at 60°C

Medium	ε_r	a nm
Water–methyl alcohol	55·0	0·68
Water–methyl alcohol	48·1	0·58
Water–propyl alcohol	58·1	0·72
Water–propyl alcohol	39·4	0·66
Water–isopropyl alcohol	58·3	0·69
Water–isopropyl alcohol	39·3	0·59
Water–tert-butyl alcohol	54·4	0·69
Water–tert-butyl alcohol	32·0	0·55
Water–acetone	59·7	0·67
Water–acetone	43·5	0·57

TABLE VI

Ratio of Rate Constants for Alkaline Hydrolysis of Diphenic Acid Monomethyl Ester in Water and Mixed Solvents as Function of Mole Fraction x_2 of Nonaqueous Component

$t = 60°C$, $I = 0{\cdot}04\ \mathrm{mol/dm^3}$.

Nonaqueous comp.	x_2	$(k_{\mathrm{H_2O}}/k_{\mathrm{mix}})_{\mathrm{NaCl}}$	$(k_{\mathrm{H_2O}}/k_{\mathrm{mix}})_{\mathrm{BaCl_2}}$
Propyl alcohol	0·046	1·87	1·12
Propyl alcohol	0·192	2·68	0·57
Isopropyl alcohol	0·046	1·50	1·01
Isopropyl alcohol	0·190	2·33	0·49
Tert-butyl alcohol	0·037	1·85	1·13
Tert-butyl alcohol	0·155	2·20	0·65
Acetone	0·047	1·62	1·00
Acetone	0·200	1·74	0·43

In the presence of $BaCl_2$, the rate constant increases with the ionic strength much more markedly than with NaCl. Besides that, the influence of $BaCl_2$ on the rate constant becomes stronger with decreasing value of ε_r, which can be illustrated by the ratio of rate constants at equal ionic strength $I = 0{\cdot}04\ \text{mol/dm}^3$ adjusted with NaCl and $BaCl_2$ in water and in the mixed solvents (Table VI). While the ratio of the rate constants, k_{H_2O}/k_{mix}, increases with the concentration of the nonaqueous component in the presence of NaCl, it decreases in the presence of $BaCl_2$. The effect of Ba^{2+} ions on the rate constant of the studied reaction can be compared with the effect of Ba^{2+}, Ca^{2+}, and Tl^+ ions on the rate of alkaline hydrolysis of monoesters of aliphatic acids[22] forming in the transition state chelates with these ions, whereby the activated complex is stabilized. The formation of a chelate with the monomethyl ester of diphenic acid is naturally less probable than in the mentioned cases with respect to the size of the assumed chelate ring. The ratios of the rate constants in Table VI suggest rather an association of the Ba^{2+} ion with the monoester ion, for which the conditions are more favourable in media with a higher content of the nonaqueous component.

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