

INFLUENCE OF MEDIUM ON ALKALINE HYDROLYSIS OF SUCCINIC ACID MONOMETHYL AND MONOPROPYL ESTERS

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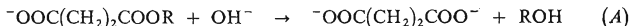
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The kinetics of alkaline hydrolysis of succinic acid monomethyl and monopropyl esters were studied in mixed aqueous-nonaqueous media at various temperatures and ionic strengths. The results of measurements are discussed in terms of electrostatic and specific interactions between the reactants and other components of the reaction mixture. The kinetic parameters in the media under study are related to the influence of the cosolvent on the solvation sphere of the reactants.

New findings about the properties of liquid binary mixtures led to a more intense study of the reaction kinetics in mixed solvents. A number of specific effects was observed, which can be attributed to changes in the solvation sphere of the reactants or activated complex or to changes in the solvent structure^{1,2}. In studying the influence of the nonaqueous component of the solvent on the alkaline hydrolysis of esters, the attention was focussed on water-dimethylsulphoxide mixtures³⁻¹⁰. Further work revealed that the specific effects connected with changes of the solvation sphere of the reactants and activated complex can be observed also in other mixed solvents^{4,11,12}. At a certain limiting concentration of the nonaqueous component, x_2^* , water has a most ordered structure¹³. Extrema of the dependences of the activation enthalpy and entropy on the mole fraction of the nonaqueous component were been often observed at this concentration¹.

Our aim was to obtain data about the influence of the nonaqueous component of the solvent and of the supporting electrolytes on the rate and thermodynamic activation parameters of the reaction:



and to contribute to the elucidation of the role of specific interactions connected with the change of the solvation spheres of the reactant and activated complex.

EXPERIMENTAL

Sodium salts of succinic acid monomethyl and monopropyl esters were prepared by mixing the corresponding alcoholates in an alcoholic solution with an equivalent amount of the acid anhydride, allowing to stand for 15 min at room temperature, filtering, and evaporating to crystallization. The sodium salt which separated after cooling was recrystallized from an aqueous solution. Carbonate-free sodium hydroxide was prepared on a Dowex 2X8 ion exchanger, 200—400 mesh¹¹. Acetone, methyl alcohol, propyl alcohol, isopropyl alcohol, ethyl alcohol, and tert-butyl alcohol were of reagent grade and redistilled prior to use.

The reaction was followed titrimetrically by determining the concentration of OH^- ions in samples taken from the reaction mixture tempered to within $\pm 0.05^\circ\text{C}$ at chosen time intervals. The apparatus was described in ref.¹⁴, the titrating agent was 0.025M-HCl, and phenolphthalein was used as an indicator. Equal starting concentrations of the reactants were used (0.005M-NaOH and 0.005M ester); the rate constant obeyed the equation $k = 1/t(1/(a-x) - 1/a)$, where a is the initial concentration of the hydroxide (and of the ester). The dependence of $1/[\text{OH}^-]$ on the time was linear in all cases, the relative error of the rate constant not exceeding 3%. The activation enthalpy was determined with an accuracy to within $\pm 2 \text{ kJ/mol}$ and activation entropy to within $\pm 7 \text{ J mol}^{-1} \text{ K}^{-1}$.

RESULTS AND DISCUSSION

The dependence of the rate constant, activation enthalpy and activation entropy on the concentration of the nonaqueous component is given in Table I. It varies with the kind of the solvent used, an evidence for the presence of specific interactions in the studied systems. The dependence of the rate constant on the mole fraction of tert-butyl alcohol and isopropyl alcohol passes through a maximum approximately at the concentration x_2^* (0.05). The maximum decreases with increasing temperature (Fig. 1). At higher alcohol concentrations, the reaction rate in the case of isopropyl alcohol does not change, but in the case of tert-butyl alcohol it increases beginning from the concentration $x_2 = 0.12$, similarly to the alkaline hydrolysis of *o*-phthalic¹¹ and diphenic¹⁵ acid monomethyl esters. The maximum on the curve $\log k = f(x_2)$ is apparently related to the influence of the nonaqueous component on the water structure and hence on the solvation sphere of the reactants. Compounds which support the water structure can to a certain extent bind water from the solvation sphere. Desolvated ions are more reactive than solvated ones, whereby the

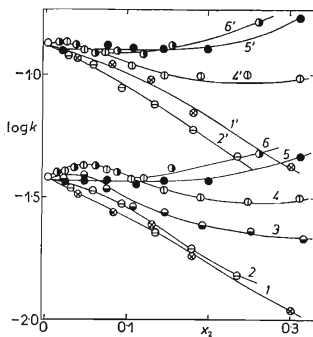


FIG. 1

Dependence of Logarithm of Rate Constant for Alkaline Hydrolysis of Succinic Acid Monomethyl Ester on Mole Fraction of Nonaqueous Component

1 aqueous methyl alcohol; 2 aqueous ethyl alcohol; 3 aqueous propyl alcohol; 4 aqueous isopropyl alcohol; 5 aqueous acetone; 6 aqueous tert-butyl alcohol; 20°C. 1'–6' same solvents but at 30°C.

observed increase of the reaction rate can be explained. The decrease of the maximum on the curve $\log k = f(x_2)$ at higher temperatures can be attributed to a perturbation of the water structure by heat.

The influence of electrolytes on the reaction rate in the medium water-isopropyl alcohol is illustrated by Table II, which includes the effect of 0.5M-N(CH₃)₄Br 0.5M-NaCl, and 0.5M-NaClO₄. The latter salt has a structure-breaking effect weakening the hydrogen bonds in water, whereas tetraalkylammonium salts act in the opposite sense (structure making effect)¹⁶⁻¹⁸. The structure breaking effect of NaClO₄ acts against the structure making effect of isopropyl alcohol at concentrations near x_2^* and this results in a decrease of the reaction rate. This interpretation is favoured by the fact that the difference in the reaction rates measured in the presence of NaClO₄ and (CH₃)₄NBr is largest at a mole fraction of isopropyl alcohol equal to 0.047, which is approximately the value of x_2^* at which the number of associated water molecules is largest and the structure breaking effect of perchlorate is most marked.

The influence of the cosolvent on the reaction kinetics in solution is due mainly by its effect on the solvation sphere of the reactants. To realize the reaction, it is necessary for the reactants to release at least partly their solvation spheres¹⁰. In mixed aqueous-nonaqueous media, the nonaqueous component can favour the desolvation. A cosolvent with a large molecule cannot replace water in the solvation sphere of the carboxyl and ester groups, which are in such a medium not solvated. Thus it is possible to explain to some extent the differences among kinetic parameters in isodielectric mixtures of water with nonaqueous components. On the other hand, the properties of the solvated reactant molecule or its part play a role in the desolvation, or replacement of water molecules by the molecules of the nonaqueous component. The results of kinetic measurements suggest that the solvation sphere of the ionized group is less influenced by the change of water structure due to the cosolvent than the solvation sphere of the ester group. However, this assumption cannot be verified by mere analysis of electrostatic forces. In the first case, we have to deal with forces of the type ion-dipole acting between the solvated group and the water molecules, in the second case with forces of the type dipole-dipole. The potential energy of interaction between a univalent ion and a dipole with a dipole moment p_1 is given as

$$U_{i-d} = ep_1 \cos \vartheta / 4\pi\epsilon, \quad (1)$$

$$U_{d-d} = -p_1 p_2 / 2r^2 \pi\epsilon. \quad (2)$$

Since the hydrated ion is an anion (COO⁻), the dipole moment of water is oriented so that¹⁹ $\cos \vartheta \ll 1$ and $U_{i-d} / U_{d-d} = r \cdot e \cdot \cos \vartheta / 2p_2 \ll 1$. The energy of electrostatic interaction of water molecules with the monoester can be near the ester group comparable or larger than near the COOH group. The character, mainly size of sub-

TABLE I

Dependence of Rate Constant, Activation Enthalpy ΔH^\ddagger and Activation Entropy ΔS^\ddagger for Alkaline Hydrolysis of Succinic Acid Monomethyl Ester on Mole Fraction of Nonaqueous Component

0.005M-NaOH, 0.005M ester, 20°C.

x_2	$k \cdot 10^2$ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	ΔH^\ddagger kJ mol^{-1}	ΔS^\ddagger $\text{J mol}^{-1} \text{K}^{-1}$
Water	3.76	45.3	-116
Methyl alcohol			
0.039	3.28	46.8	-113
0.082	2.77	49.6	-104
0.130	2.47	47.7	-112
0.181	1.84	49.2	-109
0.301	1.09	48.4	-116
Ethyl alcohol			
0.027	3.58	44.4	-120
0.058	3.35	43.0	-126
0.093	2.96	40.6	-135
0.134	2.33	42.5	-130
0.180	1.93	41.5	-135
0.236	1.53	39.6	-144
Isopropyl alcohol			
0.021	3.94	45.8	-115
0.046	4.23	38.7	-138
0.073	4.08	39.2	-137
0.106	3.77	37.2	-144
0.145	3.40	38.2	-142
0.190	3.20	40.1	-136
0.249	3.03	41.5	-131
0.314	3.20	40.1	-136
Tert-butyl alcohol			
0.017	3.97	43.9	-121
0.037	4.17	42.0	-127
0.060	4.20	38.2	-140
0.086	3.97	41.0	-131
0.120	3.80	42.0	-128
0.155	4.07	42.0	-128
0.263	4.80	43.5	-121

TABLE I
(Continued)

x_2	$k \cdot 10^2$ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	ΔH^\ddagger kJ mol^{-1}	ΔS^\ddagger $\text{J mol}^{-1} \text{K}^{-1}$
Acetone			
0.022	3.67	45.1	-117
0.047	3.67	42.0	-123
0.076	3.65	44.9	-118
0.108	3.57	46.3	-114
0.147	3.70	46.4	-113
0.200	3.70	47.2	-110
0.314	4.67	46.3	-111
Propyl alcohol			
0.021	3.73	—	—
0.046	3.87	—	—
0.074	3.41	—	—
0.107	2.89	—	—
0.146	2.75	—	—
0.192	2.45	—	—
0.252	2.28	—	—
0.317	2.13	—	—

TABLE II

Dependence of Rate Constant for Alkaline Hydrolysis of Succinic Acid Monomethyl Ester on Concentration of Isopropyl Alcohol in the Presence of 0.5M-NaCl, 0.5M-NaClO₄, or 0.5M-(CH₃)₄NBr

0.005M-NaOH, 0.005M ester, 20°C.

x_2	$k \cdot 10^2, \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$		
	NaCl	NaClO ₄	(CH ₃) ₄ NBr
Water	5.14	4.80	5.33
0.022	6.07	5.60	6.13
0.047	6.50	5.83	6.60
0.076	6.60	6.42	6.73
0.108	6.50	6.44	6.90

stituent R plays apparently an important role in solvation of the COOR group. Thus, it is possible to explain the different course of the dependence $\log k = f(x_2)$ in the medium of aqueous acetone or aqueous isopropyl alcohol in the case of alkaline hydrolysis of succinic acid monomethyl or monopropyl ester. In the other case, the rate constant decreases monotonously with the mole fraction of these cosolvents (Table III).

TABLE III

Dependence of Rate Constant for Alkaline Hydrolysis of Succinic Acid Monopropyl Ester on Mole Fraction of Nonaqueous Component
0.005M-NaOH, 0.005M ester, 30°C.

x_2	$k \cdot 10^2$ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	x_2	$k \cdot 10^2$ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
Acetone		Isopropyl alcohol	
0.000	2.30	0.021	2.07
0.022	2.20	0.046	1.92
0.047	2.11	0.073	1.74
0.076	1.98	0.106	1.50
0.108	1.90	0.145	1.34
0.147	1.84	0.190	1.13
0.200	1.74	0.314	0.958
0.314	1.67	—	—

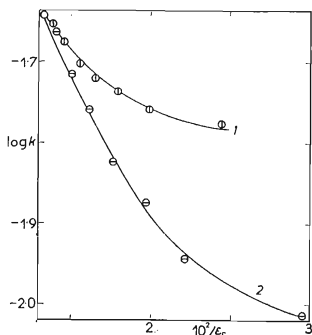


FIG. 2

Influence of Relative Permittivity on Alkaline Hydrolysis of Succinic Acid Monopropyl Ester

1 Aqueous acetone; 2 aqueous isopropyl alcohol; 30°C.

The increase of the rate of alkaline hydrolysis of succinic acid monomethyl ester at higher concentrations of acetone or tert-butyl alcohol can be elucidated so that desolvation of the COOH group is favourable for stabilization of the activated complex by an intramolecular bond. The most stable intramolecular hydrogen bond is formed²⁰ with such dicarboxylic acids whose carboxyl groups are 0.25 nm apart. With the monopropyl ester of succinic acid, obviously no hydrogen bond can be formed owing to the volume of the ester group. The reaction course is controlled

TABLE IV

Dependence of Rate Constant for Alkaline Hydrolysis of Succinic Acid Monomethyl Ester on Ionic Strength Adjusted by NaCl in Mixed Solvents
0.005M-NaOH, 0.005M ester, 20°C.

I mol dm ⁻¹	$k \cdot 10^2$ dm ³ mol ⁻¹ s ⁻¹	I mol dm ⁻³	$k \cdot 10^2$ dm ³ mol ⁻¹ s ⁻¹
Water		0.11	5.32
0.01	3.76	0.21	5.81
0.03	3.98	0.31	5.92
0.06	4.18	Acetone $x_2 = 0.200$	
0.11	4.53	0.03	4.50
0.21	4.92	0.06	5.24
0.31	5.00	0.11	5.65
Methyl alcohol $x_2 = 0.181$		0.16	5.92
0.03	2.02	0.21	6.17
0.06	2.16	Isopropyl alcohol $x_2 = 0.046$	
0.11	2.30	0.03	4.60
0.21	2.48	0.06	5.20
0.31	2.67	0.11	5.47
Methyl alcohol $x_2 = 0.301$		0.21	5.92
0.03	1.21	0.31	6.34
0.06	1.37	Isopropyl alcohol $x_2 = 0.190$	
0.11	1.45	0.03	4.07
0.21	1.61	0.06	4.86
0.31	1.71	0.11	5.37
Acetone $x_2 = 0.047$		0.16	5.96
0.03	4.47	0.21	6.20
0.06	4.87	—	—

mainly by electrostatic interactions, and the rate constant decreases with decreasing relative permittivity of the medium (Fig. 2).

In mixtures of water with methanol and ethanol, the rate constant of alkaline hydrolysis of the monomethyl ester decreases with increasing alcohol concentration probably because the water molecule in the solvation sphere is replaced by an alcohol molecule and the activated complex cannot be stabilized by an intramolecular hydrogen bond.

Thermodynamic activation parameters were calculated from the temperature dependence of the rate constants. Activation enthalpy and entropy in the water-alcohol mixtures pass through a minimum near x_2^* . A similar minimum was found earlier¹² in alkaline hydrolysis of esters and is apparently related to a change in the solvent structure. The activation energy for isodielectric mixtures was calculated from the temperature dependences of the rate constants corrected for an equal value of the relative permittivity. It is independent of the dielectric constant except for the water-methanol mixtures, where it increases with decreasing relative permittivity, this increase being much larger than the theoretical²¹. This is also an evidence for the important role of the specific effect of the alcohol in alkaline hydrolysis of succinic acid monomethyl ester.

The influence of ionic strength on the rate constant in water and its mixtures with methyl or isopropyl alcohol and acetone (Table IV) can be expressed as

$$\log k = \log k_0 + 2Az_A z_B \sqrt{I}/(1 + aB \sqrt{I}), \quad (3)$$

TABLE V

Values of Parameter a at which the Experimental Slope of the Dependence $\log k = f(I)$ is Equal to the Theoretical $2Az_A z_B$ According to Eq. (3) in Media with Different Relative Permittivity at 20°C

Medium	ϵ_r	a nm	$2Az_A z_B$
Water	80.4	0.914	1.009
Water-methyl alcohol	66.9	0.917	1.330
Water-methyl alcohol	59.6	0.840	1.579
Water-acetone	72.4	0.665	1.179
Water-acetone	53.0	0.745	1.884
Water-isopropyl alcohol	70.1	0.825	1.234
Water-isopropyl alcohol	48.2	0.637	2.173

where A and B denote constants of the Debye-Hückel theory of strong electrolytes, z_A and z_B are charge numbers of the reactants, and a is the distance of closest approach, by whose proper choice an agreement between the theoretical and experimental slopes was achieved. The values of a are given in Table V; they are almost the same in water as in aqueous methanol with a higher value of ϵ_r , whereas in other mixed solvents they depend on the kind of the nonaqueous component, apparently owing to a specific effect of the cosolvent.

The influence of the ionic strength on alkaline hydrolysis of monomethyl esters of succinic and terephthalic acids²² is smaller than with analogous esters of *o*-phthalic²³ and diphenic acids¹⁵. This difference can be related to the distance of the COO^- group bearing the charge center from the ester group, where the reaction proceeds. Similarly, barium chloride has a lesser influence on the studied reaction than on the alkaline hydrolysis of methyl esters of aromatic dicarboxylic acids. This can be illustrated by the ratio of rate constants in the presence and without BaCl_2 , k_{BaCl_2}/k . Its values are, respectively, 1.26, 1.41, 1.65, and 2.07 for monomethyl esters of succinic, terephthalic²², diphenic²², and *o*-phthalic acids²² in the case of 0.01M- BaCl_2 in water. The ratio of the rate constants increases with decreasing relative permittivity, but not so considerably as with the monomethyl esters of *o*-phthalic and diphenic acids. These results suggest that the acceleration of the reaction in the presence of Ba^{2+} ions is due to the formation of ion pairs Ba^{2+} -ester⁻, whereas with the monoesters of *o*-phthalic, diphenic, oxalic, and malonic acids²⁴ the activated complex is probably stabilized by the formation of a chelate.

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