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**ALKALINE HYDROLYSIS OF METHYL HYDROGEN MALONATE  
IN WATER-ORGANIC SOLVENTS**

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Kinetics of alkaline hydrolysis of methyl hydrogen malonate in water-methanol, water-dioxane, water-tert-butyl alcohol and water-ethylene glycol mixtures was examined. The values of the transfer functions of the activated complex  $\delta_m\mu^\ddagger$  from water to the first two mixed media were calculated from the measured solubilities of tetrabutylammonium hydrogen malonate, the activation Gibbs energies and the known values of transfer functions for tetrabutylammonium and hydroxide ions. Some conclusions concerning the effect of a nonaqueous component of the solvent on solvation of the reactants and the activated complex have been drawn from the experimental data obtained.

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Alkaline hydrolysis of monoesters of malonic acid together with other monoesters of dicarboxylic acids has been examined in the past and reported in several papers<sup>1-8</sup> dealing with the effect of ionic strength and specific interionic interactions on rate and activation parameters both in aqueous and aqueous-nonaqueous mixtures. Results of these papers corroborated only partly conclusions of electrostatic theory of ionic reactions. Some experiments showed that ions of the supporting electrolyte form a complex with the monoester ion<sup>1</sup>, whilst formation of ion pairs in other reaction systems had to be presumed<sup>3,5</sup>. The Olson-Simonson effect<sup>9</sup> was observed<sup>2</sup> when adjusting the ionic strength with supporting electrolytes of various charge type. Investigation of alkaline hydrolysis in aqueous-nonaqueous mixture revealed that only in some cases the relative permittivity of the solvent is decisive for the values of experimental kinetic parameters. Dependence of the reaction rate constant on the mole fraction of nonaqueous cosolvent showed the changes of kinetic data to be first of all caused by reorganisation of solvation shells of reactants<sup>7</sup>. As found<sup>8</sup>, the electrostatic and nonelectrostatic effects could be mutually compensated. In connection with the importance of solvation and preferential solvation for reactions in mixed solvents it seemed useful to investigate the effect of the nonaqueous component on both the solvation of the reactants and the activated complex. This problem has been successfully solved for the solvolysis of tert-butyl chloride in water-alcohol mixtures<sup>10</sup> on the basis of investigating the dependence of thermodynamic transfer functions on the mole fraction of the nonaqueous cosolvent. Similar procedure

has been employed when analysing the solvent effect on kinetics of many substitution and redox reactions<sup>11</sup>.

The aim of this study was to elucidate the effect of solvation of both the reactants and the activated complex on the kinetics and mechanism of alkaline hydrolysis of methyl hydrogen malonate by analysis of the effect of nonaqueous solvent component on the kinetic parameters.

## EXPERIMENTAL

Sodium salt of monomethyl malonate was prepared according to<sup>12</sup>. Carbonate-free sodium hydroxide was obtained from sodium chloride solution by passing through a Dowex 2×8 (0.074–0.038 mm grain size) column converted in an OH<sup>(-)</sup> form with 2 mol dm<sup>-3</sup> NaOH; the concentration of NaCl corresponded to 0.25 mol dm<sup>-3</sup> NaOH column outflow. The NaOH solution was standardized by titration with potassium hydrogen phthalate and the absence of chlorides was proved by AgNO<sub>3</sub> reagent. All nonaqueous solutions employed, *i.e.* methanol, dioxane, tert-butyl alcohol, ethylene glycol of *p.a.* grade were distilled prior to use. For solubility measurements, necessary for calculation of the Gibbs transfer energy of the monoester anion, the less soluble tetrabutylammonium salt was used instead of the well soluble sodium salt; it was prepared from the sodium salt by shaking its aqueous solution with tetrabutylammonium iodide dissolved in dichloromethane. Tetrabutylammonium methyl malonate was precipitated from the dichloromethane layer with ether. Its solubility in water was determined by shaking the solid in excess in a thermostated cell, until saturation was attained. A filtered defined volume of the saturated solution was dried to constant weight. The experimental solubility values are the averages of 2–3 independent runs, the relative error of their mean value did not exceed 3%.

Hydrolysis of the monoester was conductometrically monitored using a semi-automatic bridge BM 484 (Tesla, Czechoslovakia) by the procedure described in<sup>8</sup>. The reaction systems were thermostated to ±0.005 K. Experimental values of the rate constants are the averages of at least four independent runs. Their relative error for aqueous medium did not exceed 1%, the single relative errors for the mixed medium were maximally 2%.

## RESULTS AND DISCUSSION

The values of experimental rate constants of alkaline hydrolysis of methyl hydrogen malonate in aqueous media and in binary aqueous–nonaqueous mixtures are listed in Table I. As found, the experimental rate constant decreases with the increasing amount of the nonaqueous component, *i.e.* with the decrease of relative permittivity in all media under investigation excepting water–dioxane mixtures this being in line with the conclusions of electrostatic theory of ionic reactions<sup>13</sup>. Moreover, in aqueous methanol the dependence of the logarithm of rate constant on the reciprocal relative permittivity value is linear; this allows in this case to use equation (1) for calculating the critical interionic distance of reacting ions,  $r_0$ .

$$\ln(k/k_0) = -z_A z_B e^2 / 4\pi\epsilon_0 \epsilon_r r_0, \quad (1)$$

where  $z_A = z_B = 1$  is the charge number of reacting ions and the other symbols have their usual meaning. The  $r_0 = 0.106$  nm holds for the given experimental conditions. Not as good accordance with theory was found for the dependence of activation parameters upon mole fraction of the nonaqueous cosolvent. Data presented in Table II show that only results from aqueous dioxane media, where the activation enthalpy increases with the decreasing relative permittivity as corresponding to electrostatic interactions between ions with an equal charge sign, are in accordance

TABLE I

Rate constants of alkaline hydrolysis of sodium methyl malonate in binary aqueous–nonaqueous mixtures  $c_{\text{ester}} = c_{\text{NaOH}} = 0.005 \text{ mol dm}^{-3}$

$T, \text{K}$	$x_2$	$10^2 k$ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	$T, \text{K}$	$x_2$	$10^2 k$ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
methanol			tert-butyl alcohol		
303.84	0	5.39	303.84	0.0209	5.18
	0.0470	4.06		0.0457	4.80
	0.0999	2.72		0.0759	4.63
	0.1599	1.71		0.1133	4.59
313.71	0.2284	1.11	313.71	0.0209	9.47
	0	10.39		0.0457	8.34
	0.0470	7.67		0.0759	7.81
	0.0999	4.94	322.62	0.1133	7.38
	0.1599	2.98		0.0209	15.91
322.62	0.2284	1.73	0.0457	13.49	
	0	17.99	0.0759	12.02	
	0.0470	13.03	0.1133	11.34	
	0.0999	8.39		dioxane	
	0.1599	5.08	303.84	0.0229	4.27
0.2284	2.72	0.0502		3.86	
ethylene glycol				0.0831	4.32
303.84	0.0346	3.34		0.1235	5.72
	0.0747	2.88		313.71	0.0229
	0.1216	2.76	0.0502		7.67
313.71	0.0346	7.37	0.0831		9.07
	0.0747	6.15	0.1235	13.42	
322.62	0.0346	15.81	322.62	0.0229	14.59
	0.0747	13.22		0.0502	13.42
				0.0831	16.46
				0.1235	26.62

with conclusions of the theory. On the other hand, dependence of the experimental rate constant upon the relative permittivity of the medium is not in agreement with the theory. Most controversial with the electrostatic theory is the fact that the rate constant values in isodielectric mixtures, containing various nonaqueous cosolvents are not equal. It is obvious that in addition to electrostatic interactions between the reacting ions the non-electrostatic factors play a noticeable role in the investigated system. Solvation of both the reactants and the activated complex and its changes associated with alterations in the composition of the solvent can be of an especial importance. To understand the specific cosolvent effects on the kinetic parameters of reactions it proved convenient to divide the aqueous binary mixtures

TABLE II

Activation parameters of alkaline hydrolysis of sodium methyl malonate in binary aqueous–nonaqueous mixtures

$x_2$	$\Delta H^\ddagger$ , kJ mol <sup>-1</sup>	$\Delta S^\ddagger$ , J K <sup>-1</sup> mol <sup>-1</sup>
0	49.8	-105
methanol		
0.0470	48.1	-113
0.0999	46.3	-123
0.1599	44.9	-131
0.2284	36.1	-164
tert-butyl alcohol		
0.0208	46.3	-117
0.0457	42.4	-131
0.0759	38.9	-143
0.1133	36.7	-150
dioxane		
0.0229	50.7	-104
0.0502	51.7	-102
0.0831	55.7	-88
0.1235	64.4	-59
ethylene glycol		
0.0346	64.9	-60
0.0747	63.6	-65

into typically aqueous (TA) and typically nonaqueous (TNA) ones on the basis of excess thermodynamic functions  $\Delta G^E$ ,  $\Delta H^E$  and  $\Delta S^E$  (ref.<sup>14</sup>). Of the studied mixtures, water–methanol, water–tert-butyl alcohol and water–dioxane belong to TA mixtures, ethylene glycol is an example for the solvent forming TNA mixtures with water. Nature of the cosolvent had in this case only a small effect on kinetic parameters of the reaction. A more significant effect could be observed in connection with the activation enthalpy, which reached a greater value in water–ethylene glycol mixtures; than in other media under study having comparable mole fraction of the nonaqueous cosolvent (Table II). Since the transfer functions of some ions for mixtures of water with methanol and dioxane are known, it was easy to calculate the transfer function of the activated complex for the examined reaction. The change of rate constant with the solvent composition can be expressed by means of activation Gibbs energy using equation (2), where  $\delta_m$  is the solvent operator<sup>14</sup> and  $x_2$  is the mole fraction of cosolvent.

$$\delta_m \Delta G^\ddagger = \Delta G^\ddagger(x_2) - \Delta G^\ddagger(x_2 = 0) = -RT \ln (k_{x_2=0}/k_{x_2}) \quad (2)$$

The change in Gibbs activation energy with the transfer from water into a binary solvent mixture of mole fraction  $x_2$  of the nonaqueous cosolvent is at the same time given by expression (3), where  $\mu^\ddagger$ ,  $\mu^\ominus$  ( $C_4H_5O_4^-$ ),  $\mu^\ominus(OH^-)$  are the standard chemical potentials of the activated complex, monoester and hydroxide anions, respectively.

$$\delta_m \Delta G^\ddagger = \delta_m \mu^\ddagger - [\delta_m \mu^\ominus(C_4H_5O_4^-) + \delta_m \mu^\ominus(OH^-)]. \quad (3)$$

The quantity  $\delta_m \mu^\ominus(C_4H_5O_4^-)$  was estimated from solubility measurements of tetrabutylammonium methyl malonate in water and in water–methanol and water–dioxane mixtures (Table III). Providing the ratio of activity coefficients of salts in water and

TABLE III

Solubility  $S$  of tetrabutylammonium methyl malonate in water–methanol and water–dioxane at 298.2 K

$x_2$	$S$ , mol dm <sup>-3</sup>	$x_2$	$S$ , mol dm <sup>-3</sup>
0	0.0743		
	Methanol		Dioxane
0.0470	0.1193	0.0229	0.1669
0.0999	0.1618	0.0502	0.3529
0.1599	0.2303	0.0831	0.7166
0.2284	0.3375	0.1235	0.7498

in mixed solvents equals one, relation (4) holds for the transfer function of tetrabutylammonium salt,  $\delta_m\mu^0$  (ester), where  $S_0$ ,  $S_x$  are the solubilities of the salt in water, and in the solvent mixture, respectively.

$$\delta_m\mu^0 \text{ (ester)} = 2RT \ln (S_0/S_x). \quad (4)$$

Since the transfer function of the electrolyte equals to the sum of contribution of the separate ions, *i.e.*  $\delta_m\mu^0$  (ester) =  $\delta_m\mu^0(\text{C}_4\text{H}_5\text{O}_4^-)$  +  $\delta_m\mu^0(\text{Bu}_4\text{N}^+)$ , relation (5) holds for the Gibbs activation energy, and the transfer function for the activated complex  $\delta_m\mu^\ddagger$  can be calculated from equation (5).

$$\delta_m \Delta G^\ddagger = \delta_m\mu^\ddagger - [\delta_m\mu^0 \text{ (ester)} - \delta_m\mu^0(\text{Bu}_4\text{N}^+) + \delta_m\mu^0(\text{OH}^-)]. \quad (5)$$

Values reported in<sup>15,16</sup> were employed for transfer functions of the tetrabutylammonium cation  $\delta_m\mu^0(\text{Bu}_4\text{N}^+)$  and the hydroxide anion  $\delta_m\mu^0(\text{OH}^-)$ . Values of transfer functions for water-methanol and water-dioxane mixtures are listed in Table IV. The transfer function for the initial state  $\delta_m\mu^0$  (i.s.) is the sum of transfer functions of the monoester and hydroxide anions. From the transfer functions some conclusions concerning the effect of the nonaqueous cosolvent on the solvation of the reactants and the activated complex<sup>17</sup> can be drawn. Data summarized in Table IV reveal that the hydroxide anions are destabilized by addition of a nonaqueous cosolvent in the whole region of water-methanol and water-dioxane mixtures ( $\delta_m\mu^0(\text{OH}^-) > 0$ ) studied. Analysis of the solvent effect on the rate of the alkaline hydrolysis, consisting in separation into reactant and activated complex effects (Fig. 1a, b) provided evidence for the assumption that desolvation of the hydroxide anion plays a more significant role when compared with that of the ester anion. Both the initial state and the activated complex are destabilized by addition of the nonaqueous component in a mixed solvent; in the water-methanol mixture a greater destabilization of the activated complex ( $\delta_m\mu^\ddagger > \delta_m\mu^0$  (i.s.)) was found; in water-dioxane the activated complex and the initial state are destabilized approximately to the same extent ( $\delta_m\mu^\ddagger \approx \delta_m\mu^0$  (i.s.)). Comparison of transfer functions for both mixtures showed at the same time that the effect of dioxane upon solvation of the reactants and the activated complex is far greater than the effect of methanol. Destabilization of the initial state, predominantly due in both cases to desolvation of the hydroxide anion, leads in water-dioxane mixtures to an enhancement of the rate constant at mole fractions greater than 0.05. In water-methanol mixtures of a low content of methanol the ester ion is stabilized; at higher concentrations of methanol a destabilization takes place and grows greater with the content of nonaqueous component. From the values presented in Table IV it can be concluded that the decrease in rate constant is, in this case, due to a more significant effect on the activated complex and less to its affect on the initial state. The role of the activated complex from the viewpoint of

TABLE IV

Gibbs energy ( $\text{kJ mol}^{-1}$ ) of transfer of the ester ion  $\delta_m \mu^\ominus(\text{A}^-)$ , hydroxide ion  $\delta_m \mu^\ominus(\text{OH}^-)$ , activated complex  $\delta_m \mu^\ddagger$ , initial state  $\delta_m \mu^\ominus(\text{i.s.})$ , and activation Gibbs energy  $\delta_m \Delta G^\ddagger$  for alkaline hydrolysis of sodium methyl malonate at 298.2 K in aqueous–nonaqueous mixtures

$x_2$	$\delta_m \mu^\ominus(\text{A}^-)$	$\delta_m \mu^\ominus(\text{OH}^-)$	$\delta_m \mu^\ominus(\text{i.s.})$	$\delta_m \mu^\ddagger$	$\delta_m \Delta G^\ddagger$
Methanol					
0.0470	-0.39	0.61	0.22	0.89	0.67
0.0999	0.25	1.30	1.55	3.19	1.64
0.1599	0.94	2.15	3.09	5.88	2.79
0.2284	1.84	3.16	5.00	8.70	3.70
Dioxane					
0.0229	-0.16	3.90	3.74	4.34	0.60
0.0502	-0.23	7.71	7.47	8.33	0.86
0.0831	-0.49	11.10	10.61	11.26	0.65
0.1235	2.19	14.10	16.29	16.40	0.11

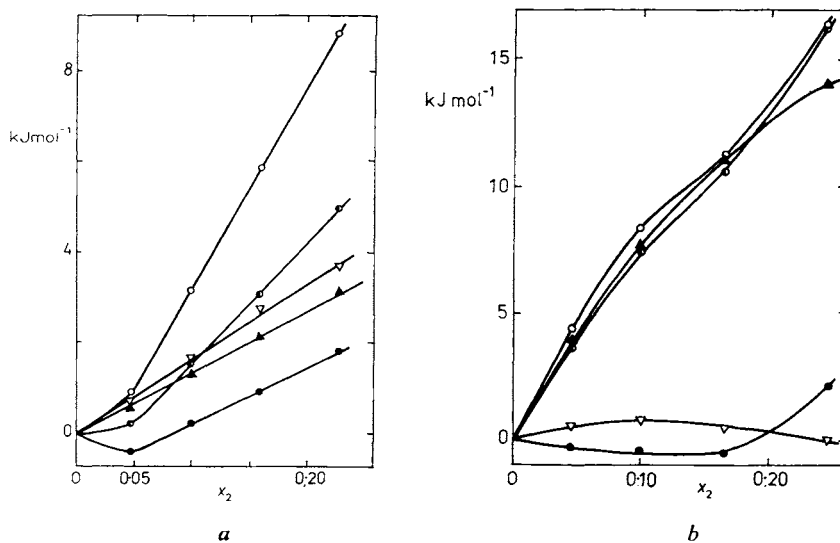


FIG. 1

Alkaline hydrolysis of methyl sodium malonate in mixtures: *a* water–methanol, *b* water–dioxane at 298.2 K; The dependence of transfer function on mole fraction of the nonaqueous cosolvent for ester ion  $\bullet$   $\delta_m \mu^\ominus(\text{C}_4\text{H}_5\text{O}_4^-)$ , hydroxide ion  $\blacktriangle$   $\delta_m \mu^\ominus(\text{OH}^-)$ , initial state  $\bullet$   $\delta_m(\text{i.s.})$ , activated complex  $\circ$   $\delta_m \mu^\ddagger$ , and activation Gibbs energy  $\nabla$   $\delta_m \Delta G^\ddagger$ .

its interaction with polar solvent molecules has been emphasized by the fact that the alkaline hydrolysis of the ester or monoester proceeds by the  $B_{AC}2$  mechanism *via* a tetrahedral intermediate, which has a higher charge than the starting monoester. Also the negative value of the activation entropy found in mixtures with all cosolvents employed can obviously be in connection with the preceding statement.

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