

Alkaline hydrolysis of methyl hydrogen fumarate in water—alcohol mixed solvents

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Kinetics of alkaline hydrolysis of methyl hydrogen fumarate were examined in water—methanol and water—ethanol at 298.2 K. The values of transfer functions of the activated complex from water to the mixed media were calculated from the measured solubilities of the acid ester, the activation Gibbs energies, and the known values of transfer functions for hydrogen and hydroxide ions. The results of the analysis of medium effect on the solvation of the initial and transition state depend significantly on the method used for the evaluation of the transfer functions of individual ions.

Исследована кинетика щелочного гидролиза монометилового эфира фумаровой кислоты в смесях вода—метиловый спирт и вода—этиловый спирт при 298,2 К. На основании установленных величин растворимости эфира кислоты, свободной энергии активации и известных чисел переноса ионов водорода и гидроксила были вычислены числа переноса активированного комплекса для перехода из воды в смешанную среду. Результаты анализа влияния растворителя на сольватацию исходного и промежуточного состояния в значительной мере зависят от метода, использованного для расчета чисел переноса отдельных ионов.

The kinetics of alkaline hydrolysis of methyl hydrogen maleate and methyl hydrogen fumarate were investigated in paper [1] dealing with the effect of temperature, ionic strength, and relative permittivity with the aim of obtaining information on electrostatic and nonelectrostatic contributions to the activation energy of these reactions. In a mixed solvent the solvation and preferential solvation of the initial and transition state play an important role. The corresponding information can be obtained in particular by means of the thermodynamic transfer functions of reactants $\delta_m\mu_r^\circ$ and activated complex $\delta_m\mu^\ddagger$, together with the activation Gibbs energy of transfer $\delta_m\Delta G^\ddagger$ [2, 3]. A quantum-chemical calculation of interaction energies of OH^- ion with the components of a mixed solvent showed their good correlation with the transfer functions [4]. The presence of specific nonelectrostatic interactions is also demonstrated by the different reaction rates in isodielectric mixtures containing various nonaqueous cosolvents [4, 5]. Application of thermodynamic transfer functions represents a way to interpret the measured effect of the solvent on kinetics and mechanism

of reactions in mixed solvents. It is not a problem to use this procedure to analyze the reactions of electroneutral molecules because the transfer functions of such species can be obtained with sufficient accuracy. In the ionic reactions, however, the main problem is the evaluation of the transfer functions of individual ions. These values often depend on the procedure used. The separation of the transfer Gibbs energy of an electrolyte into the contribution of the cation and anion is enabled only by the introduction of extrathermodynamic assumptions. One of the most used procedures is based on the TATB (tetraphenyl arsonium tetraphenyl boride) assumption. According to this assumption the transfer Gibbs energy of both tetraphenyl arsonium cation and tetraphenyl boride anion is the same [6], *i.e.* the following equation holds

$$\delta_m \Delta G_{\text{Ph}_4\text{As}^+}^\circ = \delta_m \Delta G_{\text{Ph}_4\text{B}^-}^\circ = \frac{1}{2} \delta_m \Delta G_{\text{Ph}_4\text{AsPh}_4\text{B}}^\circ \quad (1)$$

Using this assumption numerous transfer functions of ions were evaluated [7, 8]. Another method used for the evaluation of ionic transfer functions is based on the Born theory of ion—solvent interactions [9, 10]. The discrepancies between the values obtained by these methods are an object of discussion [11].

The aim of the present study was to contribute to the elucidation of the effect of solvation of the reactants and the activated complex on the alkaline hydrolysis of methyl hydrogen fumarate by analysis of the effect of the nonaqueous component of the solvent on kinetic parameters.

Experimental

Methyl hydrogen fumarate was prepared according to [12]. The sodium salt was obtained by the neutralization of methanolic solution of acid ester with methanolic NaOH (*viz.* [1]). Kinetic measurements were carried out with the sodium salt, for solubility measurements the less soluble methyl hydrogen fumarate was used. Carbonate-free sodium hydroxide was prepared as in [13]. Hydrolysis of the acid ester was conductometrically monitored using a semi-automatic bridge BM 484 (Tesla, Czechoslovakia) by the procedure described in [1]. The solubility was determined by shaking the solid in excess with the solvent in a thermostatted cell at 298.2 K, until saturation was attained. A filtered defined volume of the saturated solution was dried to constant mass. The experimental solubility values are the averages of three independent runs, the relative error of mean value did not exceed 3 %.

Results and discussion

The values of experimental rate constants of alkaline hydrolysis of methyl hydrogen fumarate in aqueous media and in binary aqueous—alcohol mixtures

Table 1

Rate constants of alkaline hydrolysis of methyl hydrogen fumarate in mixed media as a function of mole fraction x_2 of nonaqueous component
 $c(\text{ester}) = c(\text{NaOH}) = 0.005 \text{ mol dm}^{-3}$, temperature 298.2 K

Methanol		Ethanol	
x_2	k $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	x_2	k $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
0	0.296 ± 0.018		
0.046	0.206 ± 0.004	0.033	0.235 ± 0.005
0.100	0.149 ± 0.010	0.072	0.197 ± 0.007
0.160	0.099 ± 0.004	0.117	0.151 ± 0.010
0.229	0.059 ± 0.009	0.170	0.085 ± 0.004

are listed in Table 1. The results are the averages of 3—6 independent kinetic runs. The experimental rate constant decreases with the increasing amount of the nonaqueous component, which is in line with the conclusions of electrostatic theory of ionic reactions. The dependence of the logarithm of rate constant on the reciprocal relative permittivity is in accord with eqn (2) linear [14] (Fig. 1).

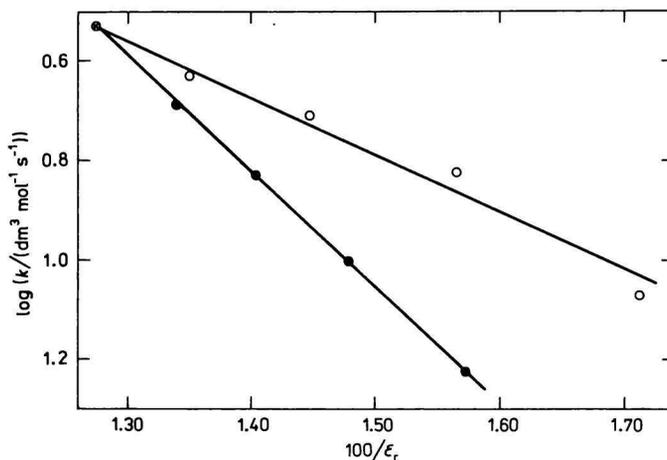


Fig. 1. $\log k$ as a function of the reciprocal value of relative permittivity at 298.2 K. ● Methanol; ○ ethanol.

The critical interionic distances, however, evaluated by means of eqn (2), differ significantly from each other (0.105 nm for the medium water—methanol, 0.212 nm for water—ethanol).

$$\log \frac{k}{k_0} = - \frac{z_A z_B e^2}{4\pi \epsilon_0 \epsilon_r k T r_0} \quad (2)$$

The symbols k , k_0 , z_A , z_B , e , r_0 , k , ε_0 , T stand for the rate constant at given relative permittivity, and for $\varepsilon_r = \infty$, the charge numbers of reacting ions, electron charge, critical interionic distance of reacting ions, the Boltzmann constant, permittivity of vacuum, and temperature, respectively.

Besides the above-mentioned difference in the critical interionic distances, the value of r_0 in the medium water—methanol is unreasonably small. The insertion of macroscopic relative permittivity into the relationship (2) may be considered as one of reasons explaining the evaluated value of this critical interionic distance. The actual value of ε_r can be lowered in the vicinity of reacting ions as a result of dielectric saturation [15]. In our case, however, the product of ionic charges is low, and both reacting ions are anions. In the proximity of anions the dielectric saturation is not so great as around the cations, and the relative permittivity varies less [16—18].

Information on solvation, stabilization and destabilization of the initial state, and activated complex can be obtained by means of thermodynamic transfer functions. The change of rate constant with the solvent composition, expressed by the mole fraction x_2 of nonaqueous cosolvent, is related to the activation Gibbs energy by eqn (3), where δ_m is the solvent operator [19]

$$\delta_m \Delta G^\ddagger = -RT \ln \frac{k_{x_2}}{k_{x_2=0}} \quad (3)$$

The change in activation Gibbs energy on going from water to mixed solvent $\delta_m \Delta G^\ddagger$ is related to the transfer functions of reactants $\delta_m \mu^\circ(\text{C}_5\text{H}_5\text{O}_4^-)$, $\delta_m \mu^\circ(\text{OH}^-)$, and that of the activated complex $\delta_m \mu^\ddagger$ by eqn (4)

$$\delta_m \Delta G^\ddagger = \delta_m \mu^\ddagger - [\delta_m \mu^\circ(\text{C}_5\text{H}_5\text{O}_4^-) + \delta_m \mu^\circ(\text{OH}^-)] \quad (4)$$

The quantity $\delta_m \mu^\circ$ has been calculated from solubilities of the methyl ester in investigated solvents. The relation (5) holds for the transfer function of the methyl ester $\delta_m \mu^\circ(\text{C}_5\text{H}_6\text{O}_4)$, where S_0 , S_x are the solubilities in water and in the solvent mixture, respectively

$$\delta_m \mu^\circ(\text{C}_5\text{H}_6\text{O}_4) = 2RT \ln \frac{S_0 \gamma_0}{S_x \gamma_x} \quad (5)$$

γ_0 , γ_x are the activity coefficients of the methyl ester in investigated solvents, and it was assumed that their ratio equals one. The solubility values together with the values of transfer functions are listed in Table 2. The values of transfer functions of H^+ and OH^- ions in water—methanol mixtures evaluated with the application of TATB assumption [7] differ substantially from the values calculated by the procedure described in [9, 20]. Whereas the transfer function $\delta_m \mu^\circ(\text{OH}^-)$, evaluated on the basis of TATB assumption, changes only very

Table 2

Solubility S of methyl hydrogen fumarate, Gibbs energy of transfer of the ester ion $\delta_m\mu^\circ(\text{A}^-)$, hydroxide ion $\delta_m\mu^\circ(\text{OH}^-)$, activated complex $\delta_m\mu^\ddagger$, initial state $\delta_m\mu^\circ(\text{i.s.})$, and activation Gibbs energy $\delta_m\Delta G^\ddagger$ for alkaline hydrolysis of methyl hydrogen fumarate in water—alcohol mixtures at 298.2 K

x_2	$\frac{S}{\text{mol dm}^{-3}}$	$\frac{\delta_m\Delta G^\ddagger}{\text{kJ mol}^{-1}}$	$\delta_m\{\mu^\circ(\text{A}^-)\}$	$\delta_m\{\mu^\circ(\text{OH}^-)\}$	$\delta_m\{\mu^\circ(\text{i.s.})\}$	$\delta_m\{\mu^\ddagger\}$	$\delta_m\{\mu^\circ(\text{A}^-)\}$	$\delta_m\{\mu^\circ(\text{OH}^-)\}$	$\delta_m\{\mu^\circ(\text{i.s.})\}$	$\delta_m\{\mu^\ddagger\}$
				TATB				Wells		
Methanol										
0	0.092									
0.046	0.132	0.899	-2.06	-0.05	-2.11	-1.21	-1.28	0.72	-0.56	0.34
0.100	0.169	1.702	-3.42	-0.15	-3.57	-1.87	-1.77	1.56	-0.21	1.49
0.160	0.174	2.701	-3.60	-0.15	-3.75	-1.05	-1.05	2.51	1.46	4.16
0.229	0.202	3.978	-4.25	0	-4.25	-0.27	-0.65	3.67	3.02	6.99
Ethanol										
				<i>a</i>						
0.033	0.144	0.572	-2.66	0.62	-2.04	-1.47	-1.00	2.35	1.35	1.92
0.072	0.178	1.009	-3.77	1.50	-2.27	-1.26	-0.16	5.21	5.05	6.06
0.117	0.208	1.669	-4.20	2.58	-1.62	0.05	1.43	8.41	9.84	11.51
0.170	0.259	3.094	-5.92	4.33	-1.59	1.50	2.00	11.01	13.01	16.10

a) Evaluated from the values of ionic product of water [21] and from the values of $\delta_m\mu^\circ(\text{H}^+)$ [8].

little with the content of methanol (Fig. 2a), the same transfer function, as given in [20], increases substantially under equal conditions. Because of this discrepancy the dependence of transfer functions of initial state $\delta_m\mu^{\circ}(\text{i.s.})$ and activated complex $\delta_m\mu^{\ddagger}$ on the methanol content differs essentially, too. It can be seen from Fig. 2a that the degree of stabilization of initial state in all investigated media is greater than in water ($\delta_m\mu^{\circ}(\text{i.s.})$ in the whole investigated interval of methanol content decreases). On the other hand, the activated complex is less stabilized, and little destabilized at higher contents of methanol.

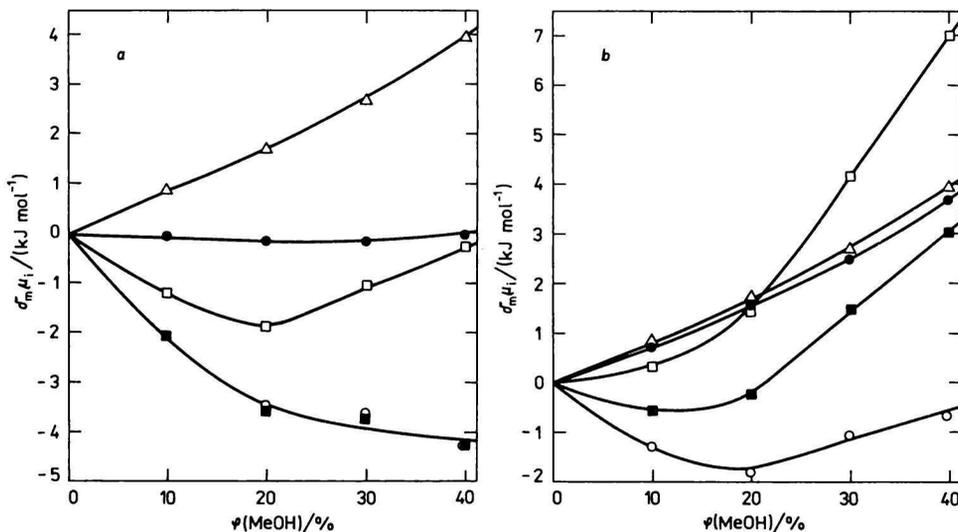


Fig. 2. Alkaline hydrolysis of methyl hydrogen fumarate at 298.2 K in water—methanol mixture: the dependence of transfer functions on volume fraction of the nonaqueous cosolvent for ester ion $\circ \delta_m\mu^{\circ}(\text{A}^-)$, hydroxide ion $\bullet \delta_m\mu^{\circ}(\text{OH}^-)$, initial state $\blacksquare \delta_m\mu^{\circ}(\text{i.s.})$, activated complex $\square \delta_m\mu^{\ddagger}$, and activation Gibbs energy $\Delta \delta_m\Delta G^{\ddagger}$.

a) Evaluated on the basis of TATB assumption; b) according to Wells.

The observed rate constant decrease with increasing mole fraction of nonaqueous component is due largely to a stabilization of the initial state, whereas according to [19] the alteration of the rate constant (resp. $\delta_m\Delta G^{\ddagger}$) is influenced in a series of alkaline hydrolyses just by the destabilization of OH^- ion, the value of $\delta_m\mu^{\circ}(\text{OH}^-)$ being in water—methanol mixtures positive [9, 22]. The course of the curves in Fig. 2b reflects the pronounced destabilization of the activated complex in the whole experimental interval of concentration of nonaqueous component, whereas the initial state is a little stabilized at the least content of methanol, at higher contents destabilization of the initial state takes place. The

reason for the decrease of the experimental rate constant is to be looked for in the different stabilization and/or destabilization of the initial state and the activated complex.

In the medium water—ethanol the transfer functions of OH^- ion, obtained by both procedures, increase with the content of nonaqueous component, the difference of the values of $\delta_m\mu^\circ(\text{OH}^-)$ is, however, also in this case considerable (Fig. 3a, 3b). The greatest difference exists in the course of the transfer function of initial state $\delta_m\mu^\circ(\text{i.s.})$, the course of transfer function of transition state $\delta_m\mu^\ddagger$ is similar, in particular at higher contents of ethanol. The course of rate constant dependence on ethanol content may be again explained by the differences in transfer functions $\delta_m\mu^\circ(\text{i.s.})$ and $\delta_m\mu^\ddagger$.

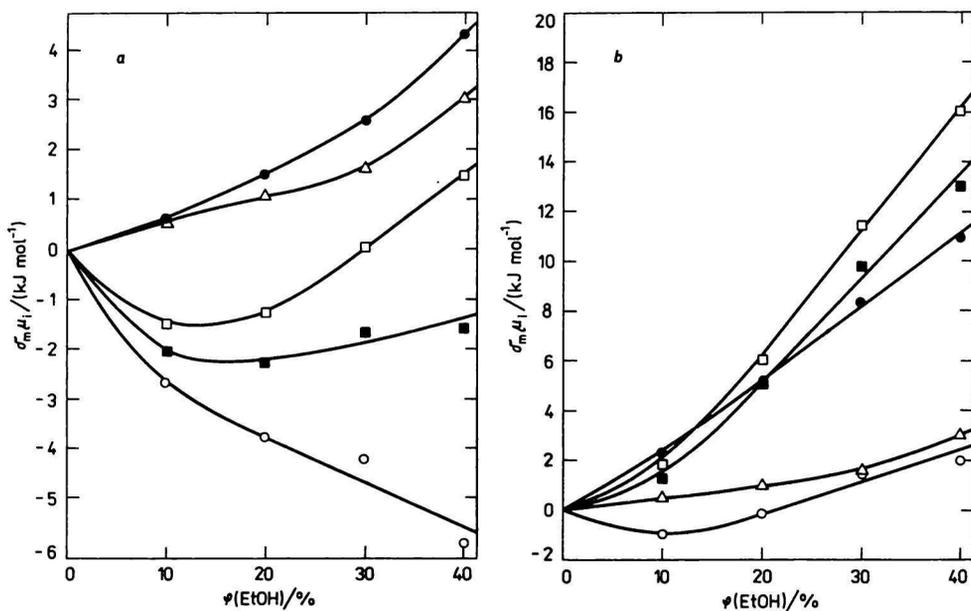


Fig. 3. Alkaline hydrolysis of methyl hydrogen fumarate at 298.2 K in water—ethanol mixture: the dependence of transfer functions on volume fraction of the nonaqueous cosolvent for ester ion \circ $\delta_m\mu^\circ(\text{A}^-)$, hydroxide ion \bullet $\delta_m\mu^\circ(\text{OH}^-)$, initial state \blacksquare $\delta_m\mu^\circ(\text{i.s.})$, activated complex \square $\delta_m\mu^\ddagger$, and activation Gibbs energy \triangle $\delta_m\Delta G^\ddagger$.

a) Evaluated on the basis of TATB assumption; b) according to Wells.

From the observations described above it can be concluded that the unambiguous interpretation of the solvent effect on reaction rate is also hindered in the system studied by the necessity of introducing the extrathermodynamic assumptions for evaluation of transfer functions of individual ions. Even the

generally accepted TATB assumption did not seem to guarantee the reliable values of these quantities. In [23] the different volume of tetraphenyl arsonium cation and tetraphenyl boride anion is considered as a reason for the possible difference in their transfer functions. Further it is clear that the different solvation of a cation and anion by the molecules of a polar solvent [16] can be another reason for the asymmetry of $\text{Ph}_4\text{AsPh}_4\text{B}$.

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