

Kinetics of alkaline hydrolysis of the monomethyl ester of terephthalic acid in mixed aqueous-organic solvents

V. HOLBA and J. BENKO

*Department of Physical Chemistry, Faculty of Natural Sciences,
Komenský University, CS-842 15 Bratislava*

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Komenský University, Bratislava*

The kinetics of alkaline hydrolysis of the monomethyl ester of terephthalic acid was investigated in aqueous and mixed aqueous-nonaqueous media. The experimental results are appreciated from the view-point of the influence of ionic strength and relative permittivity of the solvent on kinetic parameters. A significant influence of specific interactions of supporting electrolytes and nonaqueous cosolvents on the reaction has been revealed.

Изучалась кинетика щелочного гидролиза монометилового эфира терефталевой кислоты в водной и смешанных водно-неводных средах. Экспериментальные результаты оцениваются с точки зрения влияния ионной силы и относительной диэлектрической проницаемости растворителя на кинетические параметры. Было обнаружено значительное влияние специфических взаимодействий электролитов-носителей и неводных соразтворителей на ход реакции.

The alkaline hydrolysis of the monoesters of dicarboxylic acids represents a group of model reactions convenient for studying the influence of reaction medium on kinetic parameters. Formerly, the influence of ionic strength [1—3] as well as the influence of the ions of supporting electrolyte [4—6] was investigated in detail. It results from these studies that the influence of supporting electrolyte cannot be satisfactorily explained solely on the basis of electrostatic forces operating between the ions of reaction system. The experimental kinetic parameters are affected by the structure of monoester as well as by the character of supporting electrolyte. The study of these reactions in mixed solvents has shown that the relative permittivity of medium determines the course of reactions only in some nonaqueous cosolvents [7—10]. The specific properties of solvent manifest themselves mainly by the ability of solvent to solvate the starting substances and activated complex. A convincing observable manifestation of the existence of

nonelectrostatic factors consists in unequal values of rate constants in isodielectric aqueous-nonaqueous solvents containing different nonaqueous cosolvents. The alkaline hydrolysis of the monomethyl ester of terephthalic acid was previously investigated from the view-point of the influence of ionic strength on the rate and activation parameters, while a special attention was paid to the influence of barium ions. In measuring the rate of this reaction, electrolytes of different charge type were used for adjusting the ionic strength in order that it might be possible to estimate to which extent the Olson—Simons effect [11, 12] manifested itself. The influence of composition of solvent on kinetic parameters of alkaline hydrolysis of this monoester has not been hitherto investigated. In this paper, the results of measurements of the rate and activation parameters of alkaline hydrolysis of the monomethyl ester of terephthalic acid in mixed aqueous-nonaqueous media in the presence of sodium and barium chloride are described with the aim to appreciate the role of electrostatic and specific nonelectrostatic interactions affecting the course of reaction.

Experimental

The monomethyl ester of terephthalic acid was prepared from its dimethyl ester by partial hydrolysis according to the procedure described in paper [11]. Carbonate-free sodium hydroxide was prepared by means of the ion exchanger "DOWEX 200—400 mesh" [8]. Other chemicals used were anal. grade reagents. The reaction was investigated by titrimetric determination of the nonconsumed hydroxide in the samples taken from the reaction system in certain time intervals (for a more detailed description of experiments see paper [2]). The initial concentrations of reactants were equal and the experimental rate constant was calculated according to the relationship valid for reactions of the second-order $k = (1/t)[1/(c_0 - c) - 1/c_0]$ where c_0 is the initial concentration. The dependence of $1/(c_0 - c)$ on time was linear in all investigated media. The relative error of rate constant did not exceed 3 %. The activation parameters were determined from the temperature dependence of experimental rate constant in the temperature range 20—40 °C. Their accuracy was $\pm 2 \text{ kJ mol}^{-1}$ for activation enthalpy and $\pm 7 \text{ J mol}^{-1} \text{ K}^{-1}$ for activation entropy.

Results and discussion

Influence of ionic strength

The results of measurement concerning the influence of ionic strength adjusted by sodium chloride on alkaline hydrolysis of the monomethyl ester of terephthalic acid in aqueous medium are presented in paper [11]. In the present study, the

influence of ionic strength adjusted by sodium chloride and barium chloride on that reaction in mixed aqueous-nonaqueous media was investigated. The results of these measurements are given in Table 1. It ensues from this table that the rate constant increases with ionic strength in all investigated cases, which is in harmony with prediction of the electrostatic theory for ions with equal sign of charge. The obtained data were evaluated by using eqn (1) which was convenient for all investigated media in the sense that relationship $\log \{k\} = f[\{I\}^{1/2}/(1 + \{I\}^{1/2})]$ was linear

$$\log \frac{k}{k^0} = \frac{2Az_Az_B\{I\}^{1/2}}{1 + \{I\}^{1/2}} \quad (1)$$

The symbols k , k^0 , A , and z_Az_B in this equation stand for the rate constant at ionic strength I , the rate constant at zero ionic strength, the Debye—Hückel constant, and the product of charge numbers of reacting ions, respectively. In our case, $z_A = z_B = 1$, the value of the constant A depends on temperature and relative permittivity of reaction medium and $\{I\}$ is the numerical value of ionic strength in mol dm^{-3} . The value of experimental slope of the straight line $\log \{k\} = f(I)$ according to eqn (1) is dependent on the composition of solvent as well as on the electrolyte used for adjusting the ionic strength. The dependence on composition may be, to a certain extent, explained by the fact that the Debye—Hückel constant includes the relative permittivity, while the dependence of the product $2Az_Az_B$ on the character of supporting electrolyte is a manifestation of specific interactions between ions of the reaction system. Like in the hydrolysis of other monoesters [4—6, 8—12], the reaction rate for the monomethyl ester of terephthalic acid is greater in the medium of barium chloride than in the medium of sodium chloride at equal ionic strength. The specific effect of barium ions as well as some multivalent cations and the Tl^+ ions is to be explained by the formation of a monoester—barium complex with chelate bond [4]. As for the monomethyl terephthalate anion, such structure is very little probable owing to steric reasons. Other way in which cations can affect the kinetics of alkaline hydrolysis of monoester is the formation of ion pairs, e.g. $(\text{monoester})^-$, Ba^{2+} . If a part of monoester anions is bound in ion pairs, the repulsive electrostatic forces between reactants decrease. The formation of ion pairs is more probable in the medium with lower relative permittivity. In harmony with this fact, the experimental slope of the relationship (1) is greater for barium chloride as supporting electrolyte in the medium of *tert*-butyl alcohol (+3.12) with mole fraction of cosolvent 0.155 (relative permittivity $\epsilon_r = 42.6$) than in the medium of propyl alcohol (+1.25) with mole fraction of cosolvent 0.192 ($\epsilon_r = 48.5$). The found difference between experimental slopes is, however, too great and cannot be explained only by that difference between relative permittivities of the used mixed solvents, from which it results that the solvent affects the reaction rate in a specific way.

Table 1

Rate constants of alkaline hydrolysis of the monomethyl ester of terephthalic acid as a function of ionic strength I , adjusted by means of sodium and barium chloride, and of mole fraction x_2 of nonaqueous solvent component
 $c(\text{ester}) = c(\text{NaOH}) = 0.005 \text{ mol dm}^{-3}$, temperature $20.0 \text{ }^\circ\text{C}$

$I/(\text{mol dm}^{-3})$	$k \cdot 10^2/(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	$I/(\text{mol dm}^{-3})$	$k \cdot 10^2/(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$
Water—propyl alcohol		$x_2 = 0.192, \text{BaCl}_2$	
$x_2 = 0.046, \text{NaCl}$		0.02	0.98
0.03	3.66	0.03	1.02
0.06	3.87	0.04	1.13
0.11	4.10	Water— <i>tert</i> -butyl alcohol	
0.21	4.35	$x_2 = 0.155, \text{NaCl}$	
0.31	4.52	0.03	0.99
$x_2 = 0.192$		0.06	1.09
0.03	2.08	0.11	1.21
0.06	2.39	0.16	1.27
0.11	2.55	0.21	1.30
0.16	2.72	$x_2 = 0.155, \text{BaCl}_2$	
0.21	2.89	0.02	1.28
—	—	0.03	1.50
—	—	0.04	1.75

Influence of nonaqueous component of solvent

The values of rate constants and thermodynamic activation parameters of the investigated reaction in mixed aqueous-nonaqueous media are given in Table 2. The values of rate constant, activation enthalpy, and activation entropy for aqueous medium under equal conditions are $5.25 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, 51.8 kJ mol^{-1} , and $-93 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. It results from this table that the reaction rate decreases with increasing content of nonaqueous component of the solvent in all investigated cases. This fact is in agreement with the electrostatic theory because ions with alike charges are involved in this reaction. Similarly, the negative value of activation entropy [13] is consistent with this theory. From the view-point of arrangement of the activated complex and its closest surroundings, the decrease in entropy is in connection with the increased charge of the activated complex when compared with starting ions. The degree of orientation of the polar molecules which constitute the solvation shell of the activated complex increases in stronger electric field. This interpretation corresponds to the reaction mechanism according to which the alkaline hydrolysis of esters is a bimolecular reaction [14] (mechanism $B_{AC}2$). Fig. 1 represents the logarithm of the relative rate constant as a function of the reciprocal value of relative permittivity. This relationship ought to be linear according to the following equation

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

where e , r_0 , k , ϵ_0 , and T are electron charge, critical interionic distance of reacting ions, the Boltzmann constant, permittivity of vacuum, and temperature, respectively. As evident from this figure, eqn (2) is appropriate for all cosolvents used in lower concentrations (*i.e.* higher values of ϵ_r) except methyl alcohol. The fact that the relationship $\log \{k\} = f(1/\epsilon_r)$ is not linear in the water—methyl alcohol medium even at low concentrations of nonaqueous cosolvent may be due to comparable dimensions of the H_2O and CH_3OH molecules. In this case, both components may participate in the formation of the solvation shell in which they can substitute each other if the composition of solvent changes. The influence of methyl alcohol on solvation or desolvation of reactants is evidently more important in relation with the kinetics of the investigated reaction than its influence on relative permittivity of the reaction medium. The specific nonelectrostatic influence is also in operation in the media of other cosolvents used. That is especially evident if one compares the reaction rates in isodielectric mixtures. The linear sections of the relationships in Fig. 1 enabled us to calculate the critical interionic distances by means of eqn (2). These distances are 0.32 nm (water—dioxan), 0.22 nm (water—*tert*-butyl alcohol), 0.19 nm (water—*isopropyl* alcohol), and 0.13 nm (water—*propyl* alcohol). These values also indicate that the role of nonelectrostatic interactions is not negligible in this case. The physical significance of r_0 in eqn (2)

Table 2

Rate constants, activation enthalpies, and activation entropies of alkaline hydrolysis of the monomethyl ester of terephthalic acid as a function of mole fraction x_2 of nonaqueous solvent component
 $c(\text{ester}) = c(\text{NaOH}) = 0.005 \text{ mol dm}^{-3}$, temperature 20.0 °C

	$\frac{k \cdot 10^2}{\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$	$\frac{\Delta H^\ddagger}{\text{kJ mol}^{-1}}$	$\frac{\Delta S^\ddagger}{\text{J mol}^{-1} \text{ K}^{-1}}$		$\frac{k \cdot 10^2}{\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$	$\frac{\Delta H^\ddagger}{\text{kJ mol}^{-1}}$	$\frac{\Delta S^\ddagger}{\text{J mol}^{-1} \text{ K}^{-1}}$
Water—methyl alcohol				Water—isopropyl alcohol			
0.039	4.98	48.7	-103	0.106	1.64	41.0	-138
0.082	3.67	43.5	-123	0.145	1.05	47.6	-121
0.130	2.33	50.2	-109	0.190	0.75	44.6	-115
0.181	1.36	48.7	-114	Water— <i>tert</i> -butyl alcohol			
0.301	0.52	49.6	-118	0.017	4.82	46.0	-112
Water—propyl alcohol				0.037	4.17	40.6	-132
0.021	4.72	44.9	-116	0.060	2.43	39.6	-140
0.046	3.35	40.6	-134	0.086	1.50	43.9	-129
0.074	1.85	43.0	-131	0.120	1.01	50.5	-114
0.107	1.11	46.0	-125	0.155	0.80	54.4	-99
0.146	0.73	51.1	-111	Water—dioxan			
0.192	0.53	53.3	-99	0.019	4.30	47.3	-107
Water—isopropyl alcohol				0.040	3.30	47.3	-112
0.022	5.10	44.9	-116	0.065	2.51	50.4	-104
0.046	4.07	41.0	-130	0.094	1.80	49.8	-109
0.073	2.77	39.9	-138	—	—	—	—

consists in the fact that this quantity is the sum of radii of the ions which make up the activated complex [15]. It results from these values that r_0 is significantly dependent on the used cosolvent despite of the fact that the sum of radii of the ions constituting the activated complex is constant.

The influence of temperature and relative permittivity of medium may be characterized by the coefficients $a(T) = d \ln \{k\} / d(1/T)$ or $a(\epsilon_r) = d \ln \{k\} / d(1/\epsilon_r)$ which are compared with the ratio of absolute temperature to relative permittivity T/ϵ_r [16]. According to the electrostatic theory of ionic reactions, it ought to be valid for the reactions between ions with alike charge $a(T)/a(\epsilon_r) > T/\epsilon_r$, which was fulfilled for all investigated media in our case. The following relationship may be derived from the theory for the coefficient $a(T)$ [16].

$$a(T) = -\frac{1}{R} [\Phi_1(r_0) + \Phi_2(r_0)] \quad (3)$$

where R is the gas constant, $\Phi_1(r_0)$ nonelectrostatic molar energy and $\Phi_2(r_0)$ electrostatic molar energy for which it holds

$$\Phi_2(r_0) = \frac{z_A z_B e^2}{4\pi\epsilon_0\epsilon_r r_0(1 + \kappa a_i)} \exp[\kappa(d_i - r_0)] \quad (4)$$

The symbols κ , d_i , and r_0 stand for reciprocal value of the radius of ionic atmosphere according to the Debye—Hückel theory of strong electrolytes, contact distance, and critical interionic distance in activated complex, respectively. Other symbols have the usual meaning. By extrapolating to zero ionic strength (*i.e.* $\kappa = 0$), eqn (4) gets simplified and we may write for electrostatic energy

$$\Phi_2(r_0)_{\kappa=0} = \frac{z_A z_B e^2}{4\pi\epsilon_0\epsilon_r r_0} \quad (5)$$

which was approximately valid for experimental conditions of this work. By using $\Phi_2(r_0)_{\kappa=0}$, the nonelectrostatic potential $\Phi_1(r_0)$ may be calculated. This calculation was carried out on the basis of the experimental values obtained with water—*tert*-butyl alcohol mixtures. The value of 0.3 nm which is reasonable in this case with respect to radii of the reacting ions was substituted for the critical interionic distance. The calculated values of energies and their ratios are given in Table 3. It results from this table that the nonelectrostatic energy is considerably greater than the electrostatic one in the whole investigated interval of relative permittivities of the solvent (*i.e.* at all investigated concentrations of cosolvent). Furthermore, it results from the calculated values that the ratio Φ_1/Φ_2 depends on the concentration of cosolvent. A higher value of this ratio at greater mole fraction of *tert*-butyl alcohol indicates a more important role of nonelectrostatic factors in this medium. Further more detailed conclusions, however, meet with difficulties in relation with the calculation of the electrostatic term Φ_2 . According to eqn (5), the value of this

Table 3

Nonelectrostatic (Φ_1) and electrostatic (Φ_2) molar energy corresponding to alkaline hydrolysis of the monomethyl ester of terephthalic acid in water—*tert*-butyl alcohol mixtures
 $\Delta H^\ddagger = 39.6 \text{ kJ mol}^{-1}$, $r_0 = 0.3 \text{ nm}$

ϵ_r	$10^4 \cdot (\Phi_1)/(\text{J mol}^{-1})$	$10^3 \cdot (\Phi_2)/(\text{J mol}^{-1})$	$(\Phi_1)/(\Phi_2)$
71.4	3.37	6.48	5.20
64.5	3.30	7.18	4.59
58.8	3.23	7.87	4.10
54.0	3.16	8.57	3.69
50.0	3.09	9.26	3.33
43.5	2.95	10.6	2.78

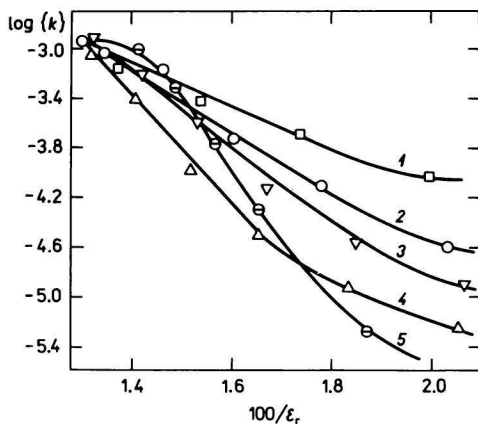


Fig. 1. $\log \{k\}$ as a function of the reciprocal value of relative permittivity.

1. Water—dioxan, 2. water—*tert*-butyl alcohol, 3. water—*isopropyl* alcohol, 4. water—*propyl* alcohol, 5. water—*methyl* alcohol; temperature 20 °C.

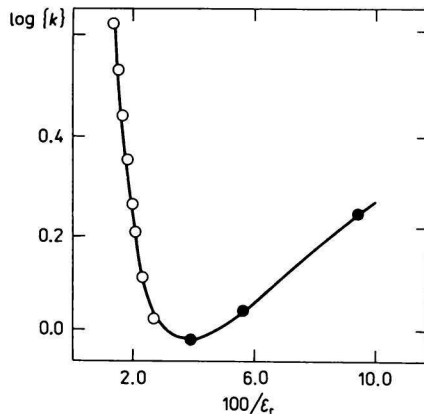


Fig. 2. $\log \{k\}$ as a function of the reciprocal value of relative permittivity in water—dioxan mixtures.

Empty circles — values obtained in this work; full circles — values taken from paper [18]. Temperature 25 °C.

term depends on relative permittivity and critical interionic distance r_0 for which the above-mentioned equal value was substituted at all values of ϵ_r . The effective value of r_0 may, however, vary with composition of the solvent. It is confirmed by the known nonlinearity of the relationship $\log \{k\} = f(1/\epsilon_r)$ which is almost always observed at lower values of relative permittivity of reaction medium [17] and was observed in our case, too (Fig. 1).

Besides the data given in Table 2, we determined the values of rate constants for the water—dioxan medium at 298 K in order to compare them with the results

published in paper [18] the authors of which investigated the alkaline hydrolysis of the dimethyl ester of terephthalic acid in the water—dioxan medium at the above temperature. Because of limited solubility of dimethyl ester in the medium with low concentration of dioxan, the authors of paper [18] give the values of rate constants for the ϵ_r interval 25.82—10.70. Owing to good solubility of the sodium salt of monomethyl ester in aqueous and mixed aqueous-nonaqueous media, we were able to complete the relationship $\log \{k\} = f(1/\epsilon_r)$. The results of these measurements together with the values taken from paper [18] are represented in Fig. 2. It is obvious from this figure that the relationship goes through the minimum so as it was expected by the authors of papers [18] and [19]. Thus the conclusions of the cited papers dealing with the mechanism of alkaline hydrolysis of esters have been unambiguously confirmed. As for the region of relative permittivities exceeding the value of ϵ_r corresponding to the minimum, the ions with alike charges, *i.e.* anion of monoester and hydroxyl ion react in the rate-determining step (Fig. 2). In media with relative permittivity smaller than the value of ϵ_r corresponding to the minimum of the plot (*i.e.* $\epsilon_r < 25$) the hydroxyl ion reacts with the ion pair (monoester)⁻—cation or even with higher associates of the monoester anion with cations of the reaction system. The results obtained by investigating the alkaline hydrolysis of the monomethyl ester of phthalic, diphenic, and terephthalic acid in the presence of barium chloride in mixed aqueous-nonaqueous media [20] are in good agreement with this interpretation. The ratio of rate constants in the presence and absence of BaCl₂, $\beta = k_{\text{BaCl}_2}/k$, has the value of 1.52 for the monomethyl ester of phthalic acid in aqueous medium, in the medium water—propyl alcohol ($x_2 = 0.192$) it is $\beta = 7.0$, and in the medium water—*tert*-butyl alcohol ($x_2 = 0.155$) it is $\beta = 5.25$. As for the monomethyl ester of diphenic acid in equal media, it is $\beta = 1.43, 5.25, \text{ and } 6.35$, and for the alkaline hydrolysis of the monomethyl ester of terephthalic acid under equal conditions we obtain $\beta = 1.25, 1.85, \text{ and } 1.76$. A considerable dependence of β on the composition of solvent in the first two foregoing cases and its small dependence on this composition for the monomethyl ester of terephthalic acid is in relation with the stabilization of the activated complex by the formation of a Ba²⁺—(monoester)⁻ chelate. It concerns those esters in which the relative position of the carbonyl and ester groups is favourable for the formation of a chelate structure like in alkaline hydrolysis of the monoesters of aliphatic dicarboxylic acids [4]. Such stabilization is not possible for steric reasons in case of the monomethyl ester of terephthalic acid. As the formation of chelate is supported by dehydration for which mixed aqueous-nonaqueous solvents provide good conditions, the value of β depends on the composition of solvent especially in those cases in which a chelate can arise.

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