

# Kinetics of alkaline hydrolysis of phthalic, isophthalic, and terephthalic acid monomethyl esters

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Temperature dependence of kinetic parameters of the alkaline hydrolysis of phthalic, isophthalic, and terephthalic acid monomethyl esters was studied by conductometric method. The relation was derived for the calculation of rate constant from the time dependence of the conductivity of the reaction mixture, which is valid for ionic reactants with equal initial concentrations. On the basis of temperature dependence of the activation enthalpy, the mechanism of the investigated reactions is discussed.

Кондуктометрически исследованы кинетические параметры щелочного гидролиза монометилвых эфиров фталевой, изофталевой и терефталевой кислот в зависимости от температуры. Выведена формула для расчета константы скорости из зависимости электропроводности реакционной системы от времени, имеющая силу для ионных реагентов с одинаковой исходной концентрацией. На основании зависимости энтальпии активации от температуры обсуждается возможный механизм реакций.

Alkaline hydrolysis of esters of carboxylic acids belongs to relatively frequently investigated reactions. Most often, the course of the reaction is studied by titration of nonreacted hydroxide in withdrawn samples [1—7]. The relative error of rate constants, thus determined, lies mostly within the interval 1 to 3 %. Disadvantages of this method are high labouriosity and considerable consumption of chemicals. Other physicochemical methods have been also used in kinetic studies of these reactions, including the stopped flow method for quickly proceeding hydrolysis [1, 8—11]. A high precision has been attained by Cleve in a conductometric kinetic study of hydrolysis of halogene substituted esters of carboxylic acids as the first-order reactions [12—16]. A formula for the calculation of the second-order

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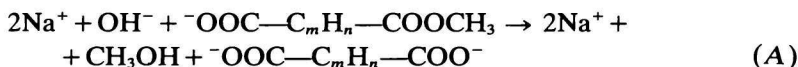
reaction rate constants for the reaction of acetic acid ethyl ester and sodium hydroxide was given by *Guggenheim* [17]. However, it is necessary to know the conductivity of the reaction mixture at the start of the reaction  $G_0$  and in equilibrium  $G_\infty$ . The same applies also in calculation of the second-order reaction rate constants of alkaline hydrolysis of esters [18–22].

The aim of our study was to evaluate the second-order reaction rate constants with possibly lowest experimental error for the alkaline hydrolysis of phthalic, isophthalic, and terephthalic acid monomethyl esters in order to obtain information about temperature dependence of the activation enthalpy. The conductometric method, adjusted in the way that the knowledge of  $G_0$  and  $G_\infty$  was unnecessary, has been found most suitable for the present study.

### Experimental

Sodium salts of phthalic, isophthalic, and terephthalic acid monomethyl esters were prepared according to the methods given in [2], [23, 24], and [5], respectively. Carbonate-free sodium hydroxide stock solution ( $c_0 = 0.125 \text{ mol dm}^{-3}$ ) was prepared according to [3].

The reaction of sodium salt of dicarboxylic acid monomethyl ester with sodium hydroxide can be expressed by the equation



The conductivity of the system can be expressed as the sum of conductivities due to single ions. For the time  $t = 0$  and  $t = \infty$  the following relations can be written

$$G_0 = 2G_0(\text{Na}^+) + G_0(\text{OH}^-) + G_0(\text{E}^-) \quad (1)$$

$$G_\infty = 2G_\infty(\text{Na}^+) + G_\infty(\text{A}^{2-}) \quad (2)$$

$\text{E}^-$  is monoester anion and  $\text{A}^{2-}$  is dicarboxylic acid anion. The contribution of sodium cations to total conductivity is constant during the reaction and, consequently,  $G_0(\text{Na}^+) = G_\infty(\text{Na}^+)$ . The molecules of methanol are practically nondissociated and, consequently, they do not contribute to total conductivity. For the conductivity of the reaction system at  $0 < t < \infty$  the relation (3) is valid

$$G_t = 2G_0(\text{Na}^+) + \frac{c^0 - x}{c^0} [G_0(\text{OH}^-) + G_0(\text{E}^-)] + \frac{x}{c^0} G_\infty(\text{A}^{2-}) \quad (3)$$

$c^0$  is the initial concentration of reactants and  $x$  is the concentration of products at the time  $t$ . After rearrangement, using eqn (2), we obtain

$$G_t = G_\infty + \frac{c^0 - x}{c^0} [G_0(\text{OH}^-) + G_0(\text{E}^-) - G_\infty(\text{A}^{2-})] \quad (4)$$

The ratio  $(c^0 - x)/c^0$  can be substituted by  $(G_t - G_\infty)/(G_0 - G_\infty)$  and for  $G_t$  it results

$$G_t = G_\infty + \frac{G_t - G_\infty}{G_0 - G_\infty} [G_0(\text{OH}^-) + G_0(\text{E}^-) - G_\infty(\text{A}^{2-})] \quad (5)$$

The term  $G_0(\text{OH}^-)$   $(G_t - G_\infty)/(G_0 - G_\infty)$  expresses the contribution of  $\text{OH}^-$  ions to total conductivity at time  $t$ , i.e.  $G_t(\text{OH}^-)$ . After rearrangement of the relation (5) we obtain

$$G_t(\text{OH}^-) = (G_t - G_\infty) \cdot \left( 1 + \frac{G_\infty(\text{A}^{2-}) - G_0(\text{E}^-)}{G_0 - G_\infty} \right) \quad (6)$$

For  $t=0$  and  $t=\infty$  the relation (6) acquires the form (7) and (8), respectively

$$G_0(\text{OH}^-) = G_0 - G_\infty + G_\infty(\text{A}^{2-}) - G_0(\text{E}^-) \quad (7)$$

$$G_\infty(\text{OH}^-) = 0 \quad (8)$$

By means of relations (6–8) the concentrations of reactants in the course of reaction can be expressed if it is assumed that the conductivity is a linear function of concentration. The relations (9) and (10) are valid, where  $\beta_1$  and  $\beta_2$  are proportionality constants.

$$x = \beta_1 [G_0(\text{OH}^-) - G_t(\text{OH}^-)] = \beta_1 (G_0 - G_t) \cdot \left( 1 + \frac{G_\infty(\text{A}^{2-}) - G_0(\text{E}^-)}{G_0 - G_\infty} \right) \quad (9)$$

$$c^0 - x = \beta_2 [G_t(\text{OH}^-) - G_\infty(\text{OH}^-)] = \beta_2 (G_t - G_\infty) \cdot \left( 1 + \frac{G_\infty(\text{A}^{2-}) - G_0(\text{E}^-)}{G_0 - G_\infty} \right) \quad (10)$$

For the calculation of the second-order reaction rate constant at the equal initial concentrations of reactants, the well-known relations (11) and (12) hold

$$k = \frac{1}{t} \left( \frac{1}{c^0 - x} - \frac{1}{c^0} \right) \quad (11)$$

$$k t c^0 = \frac{x}{c^0 - x} \quad (12)$$

Using eqns (9) and (10), assuming  $\beta_1 = \beta_2$ , one obtains from eqn (12)

$$k t c^0 = \frac{G_0 - G_t}{G_t - G_\infty} \quad (13)$$

The relation (13) is identical with the relation given by *Guggenheim* [17] for the reaction of neutral molecule ( $\text{CH}_3\text{COOC}_2\text{H}_5$ ) with monovalent anion ( $\text{OH}^-$ ), where neutral molecule ( $\text{C}_2\text{H}_5\text{OH}$ ) and monovalent anion ( $\text{CH}_3\text{COO}^-$ ) are being formed. The present derivation gives evidence that this relation can be used also for

the reaction of two monovalent anions ( $^-\text{OOC}-\text{C}_m\text{H}_n-\text{COOCH}_3$  and  $\text{OH}^-$ ), where neutral molecule ( $\text{CH}_3\text{OH}$ ) and divalent anion ( $^-\text{OOC}-\text{C}_m\text{H}_n-\text{COO}^-$ ) are being formed.

The relation (13) can be arranged so that it enables to calculate the rate constants from conductivity data without knowing the values of  $G_0$  and  $G_\infty$ . From eqn (13) one can write for  $G_0$

$$G_0 = ktc^0(G_t - G_\infty) + G_t \quad (14)$$

If the relation (14) is written for times  $t_1$  and  $t_2$  it can be rearranged to

$$G_{t_1} - G_{t_2} = kc^0(t_2G_{t_2} - t_1G_{t_1}) - (t_2 - t_1)G_\infty kc^0 \quad (15)$$

From the slope of graphical dependence  $G_{t_1} - G_{t_2} = f(t_2G_{t_2} - t_1G_{t_1})$ , which is according to eqn (15) linear for constant time interval  $t_2 - t_1$ , the rate constant of the investigated reaction can be calculated.

The method used for the kinetic measurements was the same as described in [25]. The magnitude of the time interval  $t_2 - t_1$  was chosen between 0.4 and 0.9  $t_{1/2}$ ; within this interval the values of rate constants have not been affected. All rate constants in the present study have been calculated by the least-square method (correlation coefficients of the corresponding linear dependences were not less than 0.9999) and they represent the average from three or more independent measurements with the relative error less than 0.9 %. Temperature dependences of rate constants have been evaluated by means of Multiple Linear Regression program from software package of Hewlett—Packard 9821 A calculator.

## Results and discussion

Rate constants of phthalic, isophthalic, and terephthalic acid monomethyl ester hydrolysis are given in Table 1. Temperature dependences were evaluated according to [26]. Three-parameter dependence

$$\ln \{k\} = A/T + B \ln \{T\} + C \quad (16)$$

was used. Activation parameters of the reactions under study were calculated from the parameters  $A$ ,  $B$ , and  $C$  using relations (17—21) [27] and are given in Table 2 together with the activation parameters of alkaline hydrolysis of maleic acid monomethyl ester, calculated by the same method from data in paper [25].

$$A = -\Delta H_0^\ddagger/R \quad (17)$$

$$B = \Delta C_p^\ddagger/R + 1 \quad (18)$$

$$C = (\Delta S_0^\ddagger - \Delta C_p^\ddagger) / R + \ln \{k/h\} \quad (19)$$

$$\Delta H_T^\ddagger = \Delta H_0^\ddagger + \Delta C_p^\ddagger T \quad (20)$$

$$\Delta S_T^\ddagger = \Delta S_0^\ddagger + \Delta C_p^\ddagger \ln \{T\} \quad (21)$$

Table 1

Rate constants of alkaline hydrolysis of terephthalic acid monomethyl ester (I), ( $c^0(\text{est}) = c^0(\text{NaOH}) = 5 \times 10^{-3} \text{ mol dm}^{-3}$ ), isophthalic acid monomethyl ester (II), ( $c^0(\text{est}) = c^0(\text{NaOH}) = 1 \times 10^{-2} \text{ mol dm}^{-3}$ ), and phthalic acid monomethyl ester (III), ( $c^0(\text{est}) = c^0(\text{NaOH}) = 1 \times 10^{-2} \text{ mol dm}^{-3}$ )

in terms of temperature

I		II		III	
$\frac{T}{\text{K}}$	$\frac{10^2 k}{\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{10^2 k}{\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{10^2 k}{\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$
288.13	4.094	288.13	2.690	308.15	0.4192
290.68	4.979	290.63	3.237	310.65	0.4986
293.12	5.907	293.15	3.887	313.15	0.5984
295.66	7.064	295.68	4.669	315.65	0.7084
298.15	8.567	298.13	5.606	318.15	0.8366
300.69	10.13	300.67	6.707	320.60	0.9956
303.14	12.13	303.17	8.119	323.13	1.168
305.69	14.56	305.65	9.685	325.61	1.381
308.17	17.44	308.15	11.51	328.11	1.603
310.65	20.68	310.66	13.80	330.71	1.907
313.15	24.40	313.15	16.27	333.15	2.220
315.63	28.71			335.66	2.622
318.11	34.03			338.15	3.005
				340.61	3.517
				343.15	4.092

Table 2

Activation parameters for alkaline hydrolysis of monomethyl esters of terephthalic (I), isophthalic (II), phthalic (III), and maleic acid (IV)

	$\frac{\hat{T}}{\text{K}}$	$\frac{\Delta H^\ddagger}{\text{kJ mol}^{-1}}$	$\frac{-\Delta S^\ddagger}{\text{J K}^{-1} \text{ mol}^{-1}}$	$\frac{\Delta C_p^\ddagger}{\text{J K}^{-1} \text{ mol}^{-1}}$	$\frac{-d\Delta H_T^\ddagger/dT}{\text{J K}^{-1} \text{ mol}^{-1}}$	$\frac{\Delta C_p^\ddagger - d\Delta H_T^\ddagger/dT}{\text{J K}^{-1} \text{ mol}^{-1}}$
I	303.12	51.5	92	162	41	203
II	300.64	61.8	98	206	38	244
III	325.65	54.5	113	43	44	87
IV	306.80	55.4	97	-39	37	-2

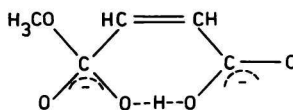
Owing to the change of temperature, the relative permittivity of medium is changed and this causes the change of activation energy with temperature, which can be expressed according to [28] by the relation

$$\frac{dE_A^*}{dT} = \frac{N_A z_A z_B e^2 L^2 \bar{T}}{4\pi\epsilon_0 \epsilon_r r_0} \left\{ \frac{3}{2} r_0 \left[ \frac{2N_A I e^2}{\epsilon_0 \epsilon_r k \bar{T}} \right]^{1/2} \left[ 1 - \frac{1}{2} \left( \frac{1 - L\bar{T}}{L\bar{T}} \right)^2 \right] - 1 \right\} \quad (22)$$

$z_A$  and  $z_B$  are the charge numbers of reacting ions,  $r_0$  is critical interionic distance (the value  $r_0 = 0.3$  nm was used for all monoesters),  $I$  is ionic strength,  $L = (\partial \log \epsilon_r / \partial T)_p$  is Abegg's constant ( $L(\text{H}_2\text{O}) = 4.63 \times 10^{-3} \text{ K}^{-1}$ ),  $\bar{T}$  is the median of the temperature interval studied, and  $k$  is Boltzmann's constant. Considering the validity of the relation  $\Delta H^* = E_A - RT$ , the change of the activation enthalpy in terms of temperature due to the change of  $\epsilon_r$  ( $d\Delta H_{\epsilon_r}^*/dT$ ) can be also expressed by the relation (22). During the reaction (A) the ionic strength is being changed. The value  $2.5 c^0$ , which corresponds to the half-time of the reaction was taken as the contribution of reactants to the ionic strength.

The values of  $\Delta C_p^* - d\Delta H_{\epsilon_r}^*/dT$  (Table 2) were calculated, which represent the changes of the activation enthalpy not influenced by temperature dependence of the relative permittivity. The highest values of these differences were found for terephthalic acid monomethyl ester (I) and isophthalic acid monomethyl ester (II) (Table 2) in accordance with the highest effect of temperature on activation enthalpy of the corresponding reactions. The dependence of the rate constant on temperature is influenced mainly by temperature effect on solvation of the reactants. As the temperature increases, the strength of solvation shells decreases and it leads to gradual increase of rate constant values with temperature.

The values of differences  $\Delta C_p^* - d\Delta H_{\epsilon_r}^*/dT$  for phthalic acid monomethyl ester (III) and maleic acid monomethyl ester (IV) were considerably lower than for I and II. The increase of rate constant with increasing temperature is in case of III less pronounced than for I and II, in case of IV it was even slowed down. Considering that alkaline hydrolysis of esters of carboxylic acids takes place by  $B_{AC}2$  mechanism, this phenomenon can be explained by the stabilization of the activated complex due to the formation of the intramolecular hydrogen bond. This is possible for steric reasons in case of III and IV only,



similarly as it is observed in the process of dissociation of dicarboxylic acids [29]. In the stabilized complex, the probability of reversible decomposition to starting substances is lowered. During the reaction of IV the stabilization of the activated

complex by hydrogen bond practically compensates the effect of temperature on solvation shells of the reactants. In the reaction of *III*, which was studied at higher temperatures, the temperature effect on solvation shell dominates, as the strength of hydrogen bond with increasing temperature decreases in both, activated complex and solvation shell. Similar stabilization of the activated complex is assumed in case of the alkaline hydrolysis of phthalic and diphenic acid mono-methyl esters, particularly in mixed solvents, where nonaqueous component lowers the strength of the solvation shells of reactants and thus the probability of the intramolecular hydrogen bond formation in the activated complex increases [3, 6]. More precise measurements indicate that the stabilized activated complex can be formed also during alkaline hydrolysis of maleic and phthalic acid monomethyl esters in water medium and its effect on reaction rate decreases with increasing temperature.

The rate constants found by conductometry (this paper) are in relatively good agreement with those obtained by titration method [2, 5]. Considerably lower experimental error attained by conductometric method enables to get information on reactions studied, not accessible by the titration method.

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