KINETICS OF ALKALINE HYDROLYSIS OF DIPHENIC AND TEREPHTHALIC ACID MONOMETHYL ESTERS

Vladislav HOLBA, Ján BENKO and Jana KOZÁNKOVÁ
Faculty of Natural Sciences,
Comenius University, 816 50 Bratislava

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The dependence of the rate constant of alkaline hydrolysis of diphenic acid monomethyl ester and terephthalic acid monomethyl ester on ionic strength and temperature was studied together with the specific influence of some electrolytes on the reaction rate. Thermodynamic activation parameters extrapolated to zero ionic strength and critical interionic distances of reacting ions were calculated from the temperature dependences of the rate constants.

Alkaline hydrolysis of monoesters of dicarboxylic acids was shown to be a suitable reaction for the comparison of the electrostatic theory of ionic reactions with experiments. Reactions of this type were studied by many authors[1-6]. It turned out that the theory of Brönsted and Bjerrum is applicable especially if uni-univalent electrolytes are used to adjust the ionic strength, although also in this case a small specific effect of cations and anions of the supporting electrolyte is observed[4]. A stronger specific effect of univalent cations was found in studying the influence of ionic strength on the rate of alkaline hydrolysis of cyclohexylphthalate in a medium of aqueous dimethyl sulphoxide[3]. In the presence of supporting electrolytes with a divalent cation, the reaction rate increased much more than the theory of the primary salt effect predicts. Especially marked is the influence of Ba^{2+} ions on the rate of hydrolysis of the monomethyl ester of *o*-phthalic acid, which we studied in detail[4,5].

The aim of the present work was to study the effect of ionic strength and the specific effect of base electrolytes on the rate and activation parameters of the alkaline hydrolysis of the monomethyl esters of diphenic and terephthalic acids with the object to obtain information about the relation between their structure and the ion interactions in the reaction system.

EXPERIMENTAL

Monomethyl ester of diphenic acid was prepared from its anhydride, which was added to an equivalent amount of an alcoholic solution of sodium methanolate. The mixture was allowed to react for 15 min. The sodium salt of the monomethyl ester was after evaporation of the solvent dissolved in water and the filtered solution was precipitated with 5% HCl to give the monomethyl ester. We calculated for the formula $C_{15}H_{12}O_4$ (256·26) 70·3% C, 4·7% H and found 69·5% C, 4·7% H. The solution was prior to measurement neutralized with an equivalent quantity of sodium hydroxide.

Monomethyl ester of terephthalic acid was prepared from its dimethyl ester, 100 g of which was dissolved in 1 000 ml of acetone and heated to boil under reflux. An equivalent quantity of an alcoholic solution of sodium hydroxide was added into the hot liquid under stirring, the precipitate was filtered off and dried, dissolved in water and filtered. The filtrate was precipitated with 5% HCl to give the monomethyl ester, which was purified by two-fold crystallization from a 2 : 1 mixture of acetone and ethanol. Its sodium salt, obtained by reacting with sodium hydroxide, was recrystallized from water. We calculated for the formula $C_9H_7NaO_4$ (202·14) 53·5% C, 3·4% H and found 53·2% C, 3·4% H.

Carbonate-free sodium hydroxide was prepared on a Dowex 2X8 ion exchanger (200—400 mesh)[7]. Other chemicals were of reagent grade (Lachema, Brno). The method of measurements was described earlier[7]. Starting concentrations of the reactants were the same in both reactions investigated, the dependence of $1/[OH^-]$ on time was linear and from its slope the rate constant was calculated. The relative error of the rate constant in both reactions did not exceed ±3%.

RESULTS AND DISCUSSION

The rate constants for the alkaline hydrolysis of monomethyl esters of diphenic and terephthalic acids at various ionic strengths (adjusted by NaCl) and temperatures are summarized in Tables I and II. The dependence of the rate constants on ionic strength was in both cases evaluated with the use of the following equations:

$$\log k = \log k_0 + 2Az_Az_B \sqrt{(I)}/(1 + \sqrt{I}) , \qquad (1)$$

$$\log k = \log k_0 + 2Az_Az_B \sqrt{(I)}/(1 + aB \sqrt{I}) , \qquad (2)$$

$$\log k = \log k_0 + 2Az_Az_B \sqrt{I}/(1 + aB \sqrt{(I)}) + CI , \qquad (3)$$

$$\log k_0' = \log k_0 + CI , \qquad (4)$$

where $\log k_0'$ is given by the equation[8]

$$\log k_0' = \log k - 2Az_Az_B \sqrt{I}/(1 + aB \sqrt{(I)}) , \qquad (5)$$

A and B are constants of the Debye–Hückel theory, a denotes distance of closest approach of ions, and C empirical constant.

The dependence of the rate constant on ionic strength is in both cases in accord with Eq. (1), although the slope of the straight line is much smaller than $2A$ ($z_Az_B = 1$). The agreement was better with the use of Eq. (2) where $aB > 1$. The values of this product and the distance of closest approach are given in Table III, whence it follows that the parameter a, which is to be adjusted in Eq. (2) to make the experimental slope of the dependence of $\log k$ on $\sqrt{(I)}/(1 + aB \sqrt{I})$ equal to the theoretical value of $2A$, is in the studied temperature range smaller for the alkaline hydrolysis of diphenic acid monomethyl ester than for the other case. For comparison,

TABLE I

Dependence of Rate Constant of Alkaline Hydrolysis of Diphenic Acid Monomethyl Ester on Ionic Strength Adjusted by NaCl and on Temperature

$c_{ester} = c_{NaOH} = 0{\cdot}01$ mol/l.

t °C	I mol l^{-1}	$k \, . \, 10^2$ l mol^{-1} s^{-1}	t °C	I mol l^{-1}	$k \, . \, 10^2$ l mol^{-1} s^{-1}
50	0·02	0·38	70	0·02	1·23
50	0·05	0·42	70	0·05	1·41
50	0·10	0·47	70	0·10	1·58
50	0·20	0·53	70	0·20	1·68
50	0·30	0·55	70	0·30	1·88
50	0·40	0·59	70	0·40	1·91
50	0·50	0·59	70	0·50	1·99
60	0·02	0·69	75	0·02	1·64
60	0·05	0·74	75	0·05	1·87
60	0·20	0·85	75	0·10	2·06
60	0·30	0·93	75	0·20	2·27
60	0·40	0·99	75	0·30	2·29
60	0·50	1·00	75	0·40	2·55
—	—	—	75	0·50	2·60

TABLE II

Dependence of Rate Constant of Alkaline Hydrolysis of Terephthalic Acid Monomethyl Ester on Ionic Strength Adjusted by NaCl and on Temperature

$c_{ester} = c_{NaOH} = 0{\cdot}005$ mol/l.

t °C	I mol l^{-1}	$k \, . \, 10^2$ l mol^{-1} s^{-1}	t °C	I mol l^{-1}	$k \, . \, 10^2$ l mol^{-1} s^{-1}
15	0·01	3·88	25	0·01	7·75
15	0·04	4·19	25	0·04	8·50
15	0·19	4·75	25	0·19	9·88
15	0·29	4·98	25	0·29	10·6
15	0·39	5·13	25	0·39	10·9
15	0·49	5·24	25	0·49	11·2
20	0·01	5·25	30	0·01	10·7
20	0·04	5·69	30	0·04	11·9
20	0·19	6·58	30	0·19	13·7
20	0·29	6·93	30	0·29	14·5
20	0·39	7·12	30	0·39	15·0
20	0·49	7·33	30	0·49	15·4

the value of a corresponding to the alkaline hydrolysis of *o*-phthalic acid monomethyl ester is equal to 0·45 nm at 60°C (ref.[4]).

The influence of ionic strength on the studied reactions is shown in Fig. 1. It is seen that the dependence of log k'_0 on I according to Eqs (*4*) and (*5*) for different values of aB is linear for aB = 3·12 and 2·03 for the alkaline hydrolysis of monomethyl esters of terephthalic and diphenic acids, respectively; in both cases the value

TABLE III

Parameter a, Measured and Theoretical Slope of the Dependence of log k on $\sqrt{(I)}/(1 + aB\sqrt{I})$, (Eq. (*2*)) at Various Temperatures

t, °C	α_{teor}	α_{exp}	a, nm	Ba
		Diphenic acid monomethyl ester		
50	1·075	1·071 ± 0·022	0·65	2·17
60	1·099	1·099 ± 0·034	0·69	2·22
70	1·125	1·129 ± 0·036	0·60	2·03
75	1·139	1·130 ± 0·069	0·64	2·18
		Terephthalic acid monomethyl ester		
15	1·002	1·002 ± 0·052	1·06	3·47
20	1·009	1·008 ± 0·047	0·95	3·12
25	1·018	1·018 ± 0·045	0·85	2·79
30	1·044	1·045 ± 0·052	0·96	3·19

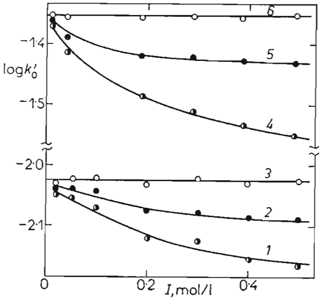

FIG. 1

Dependence of log k'_0 on Ionic Strength Adjusted by NaCl for Alkaline Hydrolysis of Monomethyl Esters of Diphenic *1*—*3* and Terephthalic *4*—*6* Acids

1 aB = 1·00; *2* aB = 1·50; *3* aB = 2·03; *4* aB = 1·00; *5* aB = 2·00; *6* aB = 3·12. *1*—*3* 60°C; *4*—*6* 20°C.

of C (slope of the straight lines) is close to zero. From the comparison of the dependences of the rates of both studied reactions with a similar dependence for *o*-phthalic acid monomethyl ester it follows that the influence of ionic strength on these reactions is the smaller the more distant is the reaction center from the center of the negative charge, *i.e.*, the more distant is the esterified carboxyl group from the ionized carboxyl group. A similar conclusion follows from the analysis of the dependence of rate constants of alkaline hydrolysis of aliphatic dicarboxylic acids monoesters on ionic strength[2,15].

Barium chloride has an especially marked influence on the rate of the studied reactions (Table IV). This can be expressed by the ratio of the rate constants in the presence and in the absence of Ba^{2+} ions, k_{BaCl_2}/k. At a ionic strength of 0·05M, adjusted by $BaCl_2$, the values of this ratio are 2·07, 1·65, and 1·41 for the monomethyl esters of *o*-phthalic (ref.[4]), diphenic, and terephthalic acids, respectively. This decreasing order can be attributed to the formation of a chelate of the monoester with Ba^{2+} ions, whereby the activated complex is stabilized similarly as was observed in hydrolysis of monoesters of aliphatic dicarboxylic acids[6]. With respect to the space configuration, the monomethyl ester of terephthalic acid cannot form a chelate with Ba^{2+} ions, therefore in this case the ratio of k_{BaCl_2}/k is smallest.

The influence of some other base electrolytes on the rate of alkaline hydrolysis of the monomethyl ester of diphenic acid is shown in Table V; the specific effect of uni-univalent electrolytes can be discussed in terms of the solvation of OH^- ions with respect to the fact[9] that only desolvated OH^- ions can react in alkaline hydrolysis of esters. By comparing the effect of uni-univalent electrolytes with that of sodium sulphate it can be concluded that the reaction rate depends mainly on the concentration of the supporting electrolyte cation, *i.e.*, that the Olson–Simonson's effect takes place[10]. Hence, the reaction rate in the medium of sodium hexacyanoferrate should be smallest. The measured value of the rate constant, which is in this medium higher than in the presence of sodium sulphate, can be attributed to a change in ionic strength, which is smaller than calculated from the analytical concentration because of association of Na^+ with $Fe(CN)_6^{4-}$ ions[11].

Activation energies at various ionic strengths were calculated from the temperature dependence of the rate constants. According to the equation[12]

$$E_A = E_A^0 + 3{\cdot}34 z_A z_B \sqrt{I}\,, \qquad (6)$$

the activation energy should in the studied interval of ionic strength adjusted with an uni-univalent electrolyte increase by 1·9 KJ/mol. This, however, is in the range of experimental errors (±2 kJ/mol). A larger change was observed when the ionic strength was adjusted by barium chloride: the value of E_A increased from 54·9 kJ/mol at 0·001M-$BaCl_2$ to 61·4 kJ/mol at 0·07M-$BaCl_2$. This change is larger than according to Eq. (*6*). From the rate constants extrapolated to zero ionic strength according

TABLE IV

Dependence of Rate Constants of Alkaline Hydrolysis of Monomethyl Esters of Diphenic and Terephthalic Acids on Ionic Strength Adjusted by $BaCl_2$

t °C	I mol l^{-1}	$k \cdot 10^2$ l mol^{-1} s^{-1}	t °C	I mol l^{-1}	$k \cdot 10^2$ l mol^{-1} s^{-1}
		Monomethyl ester of diphenic acid			
50	0·023	0·43	70	0·023	1·38
50	0·030	0·50	70	0·030	1·74
50	0·040	0·54	70	0·040	1·95
50	0·050	0·60	70	0·050	2·22
60	0·023	0·74	75	0·023	1·90
60	0·030	0·90	75	0·030	2·16
60	0·040	0·99	75	0·040	2·46
60	0·050	1·14	75	0·050	3·06
		Monomethyl ester of terephthalic acid			
20	0·013	5·90	20	0·040	7·40
20	0·020	6·27	20	0·110	8·10
20	0·030	6·97	—	—	—

TABLE V

Rate Constants of Alkaline Hydrolysis of Diphenic Acid Monomethyl Ester in the Presence of Various Electrolytes

$c_{ester} = c_{NaOH} = 0{\cdot}01$ mol/l, $t = 60$°C.

Electrolyte	I mol l^{-1}	$k \cdot 10^2$ l mol^{-1} s^{-1}	Electrolyte	I mol l^{-1}	$k \cdot 10^2$ l mol^{-1} s^{-1}
LiCl	0·50	1·09	NaI	0·62	1·03
KCl	0·50	1·09	$NaClO_4$	0·62	1·03
NaCl	0·62	1·07	NaF	0·62	1·10
NaBr	0·62	0·99	$BaCl_2$	0·05	1·14
$NaNO_3$	0·62	1·09	$SrCl_2$	0·05	1·23
$(CH_3)_4NBr$	0·62	1·03	Na_2SO_4	0·62	0·89
$(C_2H_5)_4NBr$	0·62	0·95	$Na_4Fe(CN)_6$	0·62	0·95

to Eq. (2), the extrapolated values of the activation energy, activation entropy, and frequency factor A_0 were calculated (Table VI). The extrapolated probability factor P_0 was calculated as $P_0 = A_0/Z$, where Z is the collision factor. The value of P_0 is also given by the equation[13]

$$P_0 = \exp\left(-z_A z_B e^2 L/\varepsilon_r k r_0\right), \qquad (7)$$

where e denotes the electron charge, $L = -\mathrm{d}\log\varepsilon_r/\mathrm{d}T$ is Abegg's constant ($4\cdot63 \,.\, 10^{-3}\,\mathrm{K}^{-1}$ for water), k Boltzmann's constant, and r_0 critical interionic distance in the activated complex. The values of r_0 calculated from this equation (Table VI) are much too small, similar to the case of alkaline hydrolysis of other monoesters of organic dicarboxylic acids. They did not much change even when the collision frequency was set equal to $6\cdot2 \,.\, 10^9\,\mathrm{l\,mol^{-1}\,s^{-1}}$, which is usual for solutions[14], rather than the value of $2 \,.\, 10^{11}\,\mathrm{l.\,mol^{-1}\,s^{-1}}$, calculated for the gaseous phase. A possible explanation may be that Eq. (7) involves only electrostatic interactions, while other interactions between the reacting particles are neglected. Other results of the present work suggest that mainly such effects play an important role which are related to solvation of the reactants or of the activated complex and – in the presence of barium chloride – also to the formation of its chelate with the monoester.

TABLE VI

Activation Parameters for Alkaline Hydrolysis of Monomethyl Esters of Diphenic (*I*) and Terephthalic (*II*) Acids Extrapolated to Zero Ionic Strength

Ester	E_A^0 kJ mol^{-1}	A_0 s^{-1}	$\Delta S_0^{\ddagger}$ J mol^{-1} K^{-1}	Z l mol^{-1} s^{-1}	P_0	r_0 nm
I	54·4	$2\cdot14 \,.\, 10^6$	—124	$2 \,.\, 10^{11}$	$1\cdot07 \,.\, 10^{-5}$	0·097
				$6\cdot2 \,.\, 10^9$	$3\cdot45 \,.\, 10^{-4}$	0·14
II	50·4	$4\cdot10 \,.\, 10^7$	—105	$2 \,.\, 10^{11}$	$2\cdot05 \,.\, 10^{-4}$	0·11
				$6\cdot2 \,.\, 10^9$	$6\cdot47 \,.\, 10^{-3}$	0·19

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