

THE EFFECT OF IONIC STRENGTH ON THE ALKALINE HYDROLYSIS OF SODIUM ETHYL SUCCINATE AND SODIUM ETHYL GLUTARATE

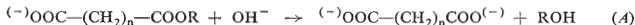
V. HOLBA and M. RIEVAJ

*Department of Physical Chemistry,
Comenius University, 801 00 Bratislava*

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Kinetics of alkaline hydrolysis of sodium ethyl succinate and sodium ethyl glutarate was examined at different concentrations of sodium perchlorate and at several different temperatures. The rate constants determined were used to calculate the dependence of thermodynamic activation parameters on ionic strength and temperature. The results are compared with theoretical relations derived for the reactions between ions.

During alkaline hydrolysis of monoesters of dicarboxylic acids, a positive primary kinetic salt effect is observed, which indicates that the rate determining step is the reaction of the anion of the monoester with hydroxyl ion (*A*). Rates of similar reactions have frequently been



determined in dependence on the dielectric constant of solvent, ionic strength, or on concentration of added electrolytes of different charge type and of different atomic radius of their cation¹. On further investigation it has been found that the rate of reaction (*A*) is influenced by the character of added electrolytes, specific effect being dependent above all on the cation used. The effect of ionic strength, or of concentration of added electrolyte, on thermodynamic activation parameters of these reactions has not yet been systematically investigated. Some results indicate, however, that the character of the dependence of activation energy on ionic strength may be one of the criteria of the occurrence of non-electrostatic interactions, and that especially in the reactions of the likely charged ions².

In this work we examined the dependence of thermodynamic activation parameters on ionic strength, which was adjusted by sodium perchlorate, with the aim to obtain further information on the kinetics of alkaline hydrolysis of monoesters of dicarboxylic acids and to confront these data with the relations derived on the basis of electrostatic theory of ionic reactions^{3,4}.

EXPERIMENTAL

Monoethyl ester of succinic acid (*I*) was prepared according to the procedure described in lit.⁵, monoethyl ester of glutaric acid (*II*) was obtained according to lit.⁶. For *I*, $\text{C}_5\text{H}_{10}\text{O}_4$ (146.1) calculated: 49.25% C, 6.90% H; found: 49.35% C, 6.90% H. For *II*, $\text{C}_7\text{H}_{12}\text{O}_4$ (160.2) calculated: 52.48% C, 7.54% H; found: 52.5% C, 7.55% H. The other chemicals used were of analytical purity grade.

Kinetic measurements. To a solution of *I* (*II*), placed in a polyethylene flask, was added such volume of sodium hydroxide solution which ensured equimolar concentrations of both reactants after neutralization of the monoethyl ester. All the solutions were warmed to reaction temperature prior to mixing. The hydrolysis proper was followed titrimetrically, by determining the concentration of the free hydroxide. The titration was carried out in nitrogen atmosphere; thymol blue was used as indicator. The apparatus was described in a previous work⁷. At the higher temperatures (55–70°C), at which the hydrolysis of *I* is comparatively fast, the procedure was modified in the following way. The sample, taken from the reaction mixture by means of cooled pipette, was introduced into a solution of potassium hydrogen phthalate, which was in excess to the sodium hydroxide present in the sample. This stopped the reaction⁸, and excess hydrogen phthalate was retitrated by sodium hydroxide. With *II*, the above procedure was used for the whole temperature range investigated. As initial concentrations of the reactants were the same (0.005 mol/l in both cases), the rate constant was calculated according to the relation $k = 1/t[1/(a-x) - 1/a]$, where *a* is the initial concentration of the hydroxide or of the respective monoethyl ester. In all the cases examined the dependence of $1/[\text{OH}^-]$ on time was linear. Each rate constant listed is the average of three or four independent measurements, the relative error in the determination being in the case of *I* as a rule less than 1.5 per cent, exceptionally 1.5 to 2 per cent. With *II*, the accuracy of the measurements was even better (the relative error 1.2, exceptionally 1.2–1.6 per cent). The error in determination of activation energy was calculated by the procedure described in the work⁹ and its value was 2.5 and lesser than 2 per cent for the reaction of *I* and *II*, respectively.

RESULTS AND DISCUSSION

The values of rate constants determined at different temperatures and ionic strengths are presented in Table I. These data were used to calculate the values of activation energy and activation entropy in dependence on ionic strength (Table II). The dependence of experimental rate constant *k* on ionic strength *I* at individual temperatures was evaluated according to Eq. (1). The values of temperature-dependent constant *A* were taken from tables^{10,11}. The values of $\log k_0$ and *B*

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

were calculated by means of $\log k'_0$ defined as

$$\log k'_0 = \log k - 2Az_Az_B\sqrt{I}/(1 + \sqrt{I}), \quad (2)$$

the product of the ionic charges z_Az_B being, here, equal to 1. According to Eq. (2) it follows that

$$\log k'_0 = \log k_0 + BI. \quad (3)$$

Relation (1) is usually valid for the reactions of the reactants of identical charge ($z_A = z_B = 1$) up to the ionic strength of 0.1 mol/l. Under this condition, the dependence of $\log k'_0$ on ionic strength should be linear, which is the case for both

TABLE I

Dependence of Rate Constant of Hydrolysis of Sodium Ethyl Succinate (*I*) and Sodium Ethyl Glutarate (*II*) on Temperature and Ionic Strength

Concentration of the esters and NaOH was 0.005 mol/l.

$t, ^\circ\text{C}$	$I, \text{mol/l}$	$k, \text{lmol}^{-1} \text{min}^{-1}$		$t, ^\circ\text{C}$	$I, \text{mol/l}$	$k, \text{lmol}^{-1} \text{min}^{-1}$	
		<i>I</i>	<i>II</i>			<i>I</i>	<i>II</i>
20	0.01	1.25	1.96	30	0.06	2.87	4.22
20	0.02	1.30	2.06	30	0.08	2.99	4.39
20	0.03	1.37	2.16	30	0.10	3.11	4.58
20	0.04	1.43	2.22	35	0.01	3.31	4.68
20	0.06	1.47	2.32	35	0.02	3.48	5.00
20	0.08	1.53	2.38	35	0.03	3.68	5.24
20	0.10	1.57	2.47	35	0.04	3.81	5.44
25	0.01	1.75	2.63	35	0.06	3.96	5.69
25	0.02	1.87	2.81	35	0.08	4.14	5.82
25	0.03	1.95	2.96	35	0.10	4.32	6.07
25	0.04	2.02	3.02	40	0.01	4.45	6.15
25	0.06	2.06	3.11	40	0.02	4.73	6.55
25	0.08	2.12	3.20	40	0.03	4.94	6.84
25	0.10	2.20	3.32	40	0.04	5.15	7.16
30	0.01	2.42	3.58	40	0.06	5.45	7.47
30	0.02	2.59	3.72	40	0.08	5.66	7.85
30	0.03	2.70	3.90	40	0.10	5.87	8.19
30	0.04	2.80	4.06	—	—	—	—

TABLE II

Dependence of Activation Energy E_A (kcal/mol) and Entropy (cal/mol K) of Hydrolysis of *I* and *II* on Ionic Strength (mol/l)

<i>I</i> mol/l	<i>I</i>		<i>II</i>	
	E_A	ΔS^\ddagger	E_A	ΔS^\ddagger
0.01	11.57	-22	10.44	-25
0.02	11.66	-21	10.49	-24
0.03	11.74	-21	10.49	-24
0.04	11.75	-21	10.65	-24
0.06	11.89	-20	10.73	-23
0.08	12.01	-20	10.87	-23
0.10	12.04	-20	10.93	-22

reactions (Figs 1 and 2). Eq. (3) was used in both cases for estimating temperature dependence of k_0 and B . The values of constant B (1/mol) for temperatures 20, 25, 30, 35, and 40°C were found to be successively for I: -0.5705 , -0.6627 , -0.5603 , -0.4221 , and -0.4033 ; for II: -0.5341 , -0.6337 , -0.4918 , -0.4826 , and -0.3685 . By using extrapolated rate constants, extrapolated values of thermodynamic activation parameters were determined (Table III).

In addition to the temperature region given in Table I, both reactions were also examined at a broader range of temperatures (15–70°C), using two different ionic strengths (0.080 and 0.100 mol/l.) Already with the attained accuracy of the measurements Arrhenius dependence shows distinct curvature. After dissecting the temperature interval to two regions, we have determined for each the values of activation energies. These are presented in Table IV. According to the theory³, the coefficient ($\partial E_A/\partial T$) for the reactions of likely charged ions in an aqueous medium should be negative. The positive value observed in both reactions examined indicates the presence of the effects which do not originate from electrostatic interactions between reacting ions.

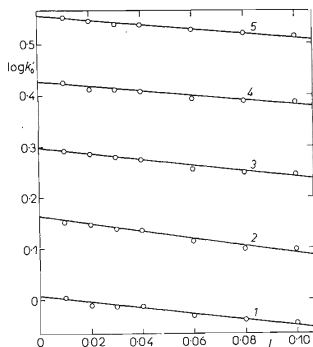


ABB. 1

Dependence of $\log k'_0$ on Ionic Strength Calculated According to Eq. (3) for Hydrolysis of Sodium Ethyl Succinate

Points represent experimental data, straight lines were calculated by the least squares method. 1 20°C, 2 25°C, 3 30°C, 4 35°C, 5 40°C.

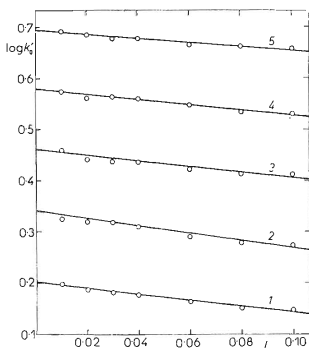


FIG. 2

Dependence of $\log k'_0$ on Ionic Strength Calculated According to Eq. (3) for Hydrolysis of Sodium Ethyl Glutarate

Points represent experimental data, straight lines were calculated by the least squares method 1 20°C, 2 25°C, 3 30°C, 4 35°C, 5 40°C.

TABLE III
Values of Thermodynamic Activation Parameters for *I* and *II* Extrapolated to Zero Ionic Strength

Quantity	<i>I</i>	<i>II</i>
E_A^0 , kcal/mol	11.33	10.14
A^0 , s ⁻¹	$4.8 \cdot 10^6$	$9.8 \cdot 10^5$
P^0 , mol/l	$2.4 \cdot 10^{-5}$	$4.9 \cdot 10^{-6}$
ΔS^\ddagger , cal/mol K	-23	-26

TABLE IV
Dependence of Activation Energy E_A (kcal/mol) of the Reaction of *I* and *II* on Temperature at Constant Ionic Strength *I* (mol/l)

<i>I</i>	<i>t</i> , °C	E_A for	
		<i>I</i>	<i>II</i>
0.01	15-40	11.57	10.44
	45-70	12.15	10.92
0.08	15-40	12.01	10.87
	45-70	12.61	11.45

The dependence of Arrhenius activation energy on ionic strength was estimated also according to Moelwyn-Hughes theory of ionic reactions³, yielding relation (4), where E_A^0 is the activation energy extrapolated to zero ionic strength. According to Eq. (4)

$$E_A = E_A^0 + 800z_A z_B \sqrt{I} \quad (\text{cal/mol}) \quad (4)$$

the activation energy of the reaction of the ions whose $z_A z_B = 1$ should increase with the square root of ionic strength, the coefficient $dE_A/d\sqrt{\mu}$ being equal to 800. In both cases under study the activation energy is a linear function of $\sqrt{\mu}$, having the form (5) and (6) for *I* and *II*, respectively.

$$E_A = 11.33 \pm 0.53 + (2.33 \pm 0.12)\sqrt{I}, \quad (5)$$

$$E_A = 10.15 \pm 0.12 + (2.43 \pm 0.23)\sqrt{I}. \quad (6)$$

It is noteworthy that the value of $dE_A/d\sqrt{I}$ is in both cases three times as great as the theoretical value. The activation entropy is in both cases negative throughout the region of ionic strengths examined. This is again in qualitative agreement with the theory of ionic reactions⁴, according to which the activation entropy of the reaction of ions with charges z_A and z_B is expressed by Eq. (7), where e is the electron charge, D is the dielectric constant, r is interionic distance in the activated complex, k is

$$\Delta S^\ddagger = -(z_A z_B e^2 / D r k T) (\partial \ln D / \partial \ln T)_p \quad (7)$$

Boltzmann constant, and T is Kelvin temperature. The determined values of ΔS^\ddagger fit the relation (7) (Tables II and III) providing that r equals approximately to 1 Å. A similar result is also obtained on using extrapolated value of probability factor P^0 , extrapolated to zero ionic strength, in calculation of interionic distance. According to the electrostatic theory it holds³ that

$$P^0 = \exp(-z_A z_B e^2 L / D k r), \quad (8)$$

where L is Abbeig constant and the other symbols have the same meaning as in Eq. (7). After numerical substitution, Eq. (8) gives for sodium ethyl succinate the value of r equaling to 0.9 Å and for sodium ethyl glutarate the value of 0.8 Å. These values are however substantially smaller than the values obtained for the reactions of the reactants with similar radii and with the charge $z_A = z_B = -1$. Similarly, the extrapolated values of probability factor P^0 (Table III) are from 10 to 100 times smaller than the values common for the reactions involving the ions with the same product of charges³. Observed deviations may be partly explained in terms of electrostatic theory. As already shown, Eq. (8) does not describe well the systems consisting of more complex ions¹². Along with ion-ion interaction, in these cases it is necessary to consider also ion-dipole interaction, which may significantly contribute to over-all energy. Observed phenomena may also be interpreted in terms of specific, non-electrostatic factors, for example, electrolyte-solvent interactions, which in the system under study could be perchlorate ion-water interaction, in view of appreciable "structure-breaking" effect of perchlorate^{13,14}.

Obtained results thus conform with the experience that non-electrostatic interactions are important especially in reactions of likely charged ions¹⁵.

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