

# Kinetics of alkaline hydrolysis of the monoethyl ester of adipic acid

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The kinetics of alkaline hydrolysis of the monoethyl ester of adipic acid have been investigated as a function of temperature and ionic strength. The results of measurements are discussed in terms of the primary kinetic salt effect. The applicability of electrostatic theory to the calculation of critical interionic distances of the reacting ions is discussed. The evaluation of experiments leads to the conclusion that the course of reaction is affected not only by electrostatic but also by nonelectrostatic interactions between the components of the reaction system.

Была исследована кинетика щелочного гидролиза моноэтилового эфира адипиновой кислоты в зависимости от температуры и ионной силы. Результаты измерений обсуждаются с точки зрения кинетического первичного солевого эффекта. Обсуждается применимость электростатической теории для расчета критических межйонных расстояний реагирующих ионов. Истолкование экспериментов ведет к заключению, что на ход реакции оказывают влияние не только электростатические, но и неэлектростатические взаимодействия между компонентами реакционной системы.

The rate-determining step in the alkaline hydrolysis of the monoesters of dicarboxylic acids is a reaction of the anion of acid ester with the hydroxide ion



This reaction is a model reaction suited for the verification of the theories of ionic reactions. The reactions of type (A) of different monoesters were investigated as a function of ionic strength or concentration of the supporting electrolytes with different charges and ionic radii [1]. The influence of the cations of supporting electrolytes on the rate of hydrolysis of the monoethyl ester of adipic acid was thoroughly investigated [2—4]. The authors adjusted the ionic strength with various electrolytes and found out an especially remarkable effect of the tetraalkyl ammonium salts [3]. The influence of ionic strength on the thermodynamic activation parameters of alkaline hydrolysis of the monoethyl ester of oxalic, malonic, succinic, and glutaric acid was studied in [5, 6].

The present study is based on the investigation of the influence of temperature and ionic strength on the hydrolysis of the monoethyl ester of adipic acid and its aim is to obtain the data necessary for the calculation of kinetic parameters by using the relationships ensuing from the electrostatic theory of ionic reactions and thus to contribute to elucidation of the character of interactions among reactants by evaluating these parameters.

### Experimental

The monoethyl ester of adipic acid was prepared according to [7].

For  $C_8H_{14}O_4$  calculated: 55.13% C, 8.10% H; found: 55.1% C, 8.2% H.

All other chemicals used were anal. grade. The kinetic measurements were carried out as follows: Such amount of sodium hydroxide was added into a solution of the monoethyl ester of adipic acid placed in a polyethylene vessel that, on neutralizing the acid ester, the concentrations of both reactants were equal ( $0.005 \text{ mol l}^{-1}$ ). Simultaneously, the volume of sodium chloride needed for adjusting ionic strength was added. Before mixing, all solutions were thermostated to the required temperature ( $\pm 0.1^\circ\text{C}$ ). The hydrolysis itself was followed titrimetrically by determining the concentration of free hydroxide in the samples successively taken after reaction start. Nitrogen from a pressure gas vessel was applied to sampling and bubbling through the sample during titration. An apparatus described in more detail earlier [5, 6] was used in these experiments.

### Results and discussion

As the initial concentrations of reactants were equal, the rate constant could be calculated according to the following equation

$$k = \frac{1}{t} \left( \frac{1}{a-x} - \frac{1}{a} \right) \quad (1)$$

$a$  is the initial concentration of hydroxide or monoester. At all ionic strengths and temperatures investigated, the dependence  $1/[\text{OH}^-]$  on time was linear, which pointed out that the investigated reaction proceeded as a reaction of the second order. The small change in ionic strength due to the transformation of the reacting monoester with the charge  $-1$  into the anion of adipic acid with the charge  $-2$  did not manifest itself in the course of reaction. The relative error of the rate constant did not exceed  $\pm 3\%$ . The dependence of rate constant on ionic strength was evaluated by the use of eqns (2—6). The values of rate constants for different temperatures and ionic strengths are given in Table 1.

$$\log k = \log k_0 + \frac{2A z_A z_B \sqrt{I}}{1 + \sqrt{I}} \quad (2)$$

$$\log k = \log k_0 + \frac{2A z_A z_B \sqrt{I}}{1 + \sqrt{I}} + CI \quad (3)$$

$$\log k'_0 = \log k - \frac{2A z_A z_B \sqrt{I}}{1 + \sqrt{I}} \quad (4)$$

$$\log k'_0 = \log k_0 + CI \quad (5)$$

$$\log k = \log k_0 + \frac{2A z_A z_B \sqrt{I}}{1 + Ba \sqrt{I}} \quad (6)$$

Table 1

Rate constants of alkaline hydrolysis of the monoethyl ester of adipic acid as a function of temperature and ionic strength

$$c_{\text{ester}} = c_{\text{NaOH}} = 0.005 \text{ mol l}^{-1}$$

$t$ °C	$I$ mol l <sup>-1</sup>	$10^2 k$ l mol <sup>-1</sup> s <sup>-1</sup>	$t$ °C	$I$ mol l <sup>-1</sup>	$10^2 k$ l mol <sup>-1</sup> s <sup>-1</sup>
25	0	2.66 <sup>a</sup>	35	0	4.90 <sup>a</sup>
25	0.010	3.25	35	0.010	5.96
25	0.045	3.61	35	0.045	6.55
25	0.070	3.80	35	0.070	6.76
25	0.100	3.95	35	0.100	7.15
30	0	3.35 <sup>a</sup>	40	0	6.58 <sup>a</sup>
30	0.010	4.28	40	0.010	8.03
30	0.045	4.58	40	0.045	8.96
30	0.070	4.83	40	0.070	9.13
30	0.100	5.33	40	0.100	9.96

a) Values extrapolated by means of eqn (5).

In calculating the quantity  $\log k'_0$  [8], the values tabulated for individual temperatures [9] were inserted as the constant  $A$  according to the Debye—Hückel theory and the formal product of charge numbers, *i.e.* +1 was substituted for the product  $z_A z_B$ . The plot  $\log k = f[\sqrt{I}/(1 + \sqrt{I})]$  according to (2) was linear in the range of experimental errors and the plot  $\log k'_0$  vs.  $I$  according to (5) as well. However, it has been found that the experimental slope of the straight line corresponding to eqn (2) ( $\alpha_{\text{exp}} = d \log k / d f(I)$ ) is at all temperatures used considerably smaller than the expected theoretical value  $2A$  (Table 2). The dependence of  $\log k'_0$  on ionic strength is also linear in accordance with eqn (5). The constant  $C$  depends on temperature and its values are  $-0.866$ ,  $-0.600$ ,  $-1.11$ , and

Table 2

Variation of the theoretical and experimental slope of the straight line  $\log k = f[\sqrt{I}/(1 + \sqrt{I})]$  with temperature

$t$ °C	$\alpha_{\text{theor}}$	$\alpha_{\text{exp}}$
25	1.023	0.57
30	1.032	0.55
35	1.042	0.49
40	1.052	0.52

$1.30 \text{ l mol}^{-1}$  at temperatures 25, 30, 35, and 40°C, respectively. The dependence  $\log k = f(I)$  according to eqn (6) has been plotted for various values of the parameter  $a$  (Fig. 1). As seen, the slope of the straight line attains the theoretical value  $2A$  if the value of 1 nm is inserted for  $a$ . The results of measurements of alkaline hydrolysis of the monoethyl esters of oxalic, malonic, succinic, and glutaric acid [5, 6] enable to calculate the values of the parameter  $a$ . Thus we obtain the value of 0.31 nm for the monoethyl ester of oxalic acid and 0.55 nm for the other above-mentioned monoethyl esters. A comparison of these values with the value valid for monoethyl ester of adipic acid (1 nm) leads to the conclusion that the distance of the closest approach is related with the size of the ion of monoester.

Eqns (2) and (5) were used for the calculation of the rate constants extrapolated to zero ionic strength at individual experimental temperatures. Though the values extrapolated according to eqn (2) were somewhat different from the values obtained by extrapolating according to eqn (5) (cf. [10]), the plot  $\log k_0 = f(1/T)$  was in both cases a straight line with equal slope. From the temperature dependence of the extrapolated rate constants, the extrapolated value of activation energy was obtained ( $E_A^0 = 48.2 \text{ kJ mol}^{-1}$ ). In this way, the extrapolated value of activation entropy based on the collision theory ( $\Delta S^\ddagger = -60 \text{ J mol}^{-1} \text{ K}^{-1}$ ) as well

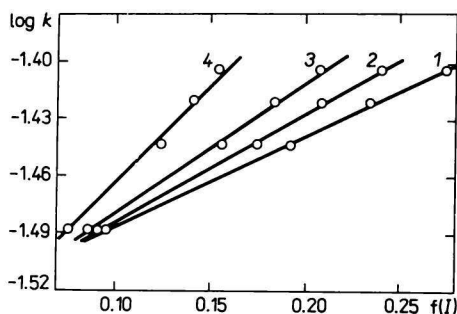


Fig. 1.  $\log k$  as a function of  $\sqrt{I}/(1 + Ba\sqrt{I})$ .  
 1.  $Ba = 0.4835$ ; 2.  $Ba = 1$ ; 3.  $Ba = 1.656$ ;  
 4.  $Ba = 3.312$ .

as extrapolated value based on the theory of absolute reaction rates ( $\Delta S_0^\ddagger = -122 \text{ J mol}^{-1} \text{ K}^{-1}$ ) was obtained [11]. For the extrapolated rate constant  $k_0$ , activation energy  $E_A^0$ , and frequency factor  $A_0$ , it holds

$$k_0 = A_0 \exp \left( -\frac{E_A^0}{RT} \right) \quad (7)$$

On inserting the corresponding values, the mean value of frequency factor extrapolated to zero ionic strength can be obtained ( $A_0 = 7.27 \times 10^6 \text{ s}^{-1}$ ). By using the known value of  $A_0$ , the extrapolated value of steric factor  $P_0$  may be calculated from the relation  $P_0 = A_0/Z$ . It has been revealed that the collision factor  $Z$  shows the value of  $2 \times 10^{11} \text{ l mol}^{-1} \text{ s}^{-1}$  for most reactions in gaseous phase [12] whereas the value of  $6.2 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$  [13] is to be used for reactions in solution. On inserting the last mentioned value, we obtain  $P_0 = 1.17 \times 10^{-3}$ . In the scope of the electrostatic theory of ionic reactions, the following expression may be derived for  $P_0$  [11]

$$P_0 = \exp \left( -\frac{z_A z_B e^2 L}{\epsilon_r k r_0} \right) \quad (8)$$

where  $L = -d \ln \epsilon_r / dt$ ,  $k$ ,  $e$ ,  $\epsilon_r$ , and  $r_0$  are the Abegg constant (its value for water is  $4.63 \times 10^{-3} \text{ K}^{-1}$ ), the Boltzmann constant, charge of electron, relative permittivity of medium, and critical interionic distance of reacting ions, respectively. If we substitute the value of the product of charge numbers of reacting ions, *i.e.* +1 for  $z_A z_B$  and the macroscopic relative permittivity of water (78.54 at 25°C) for  $\epsilon_r$ , we obtain  $r_0 = 0.146 \text{ nm}$ . This value is small with respect to the size of reacting ions. The derivation of eqn (8) is based on the simplifying assumption according to which the electrostatic contribution is the only contribution to activation energy. Nevertheless, it is evident that nonelectrostatic interactions may be also in operation in the reaction of the investigated ion of monoester. It is also impossible to neglect the fact that the hydroxide ion attacks the group  $-\text{COOC}_2\text{H}_5$ , while the centre of charge is in different site of the ion of monoester. In a similar case, the authors [14] did not succeed in interpreting the measured values only on the basis of electrostatic interactions even if the ion—dipole interaction was included. Another possibility of obtaining a greater and therefore more probable value of critical interionic distance by means of eqn (8) consists in introducing the microscopic relative permittivity of water instead of its macroscopic value. In a strong electrostatic field such as a field in the vicinity of ion, an electric saturation takes place. This saturation results in a decrease in relative permittivity of the medium which surrounds the ion [15—17]. The value of 11.46 must be substituted for relative permittivity in order that eqn (8) may give, for instance, the value of  $r_0$  equal to 1 nm which is necessary for the parameter  $a$  in eqn (6) to afford the slope of the straight line in Fig. 1 to be equal to 1.023. Such a low relative permittivity is

exhibited by water in a very strong electrostatic field, for instance, in the field in the close vicinity of small multivalent cations. On the other hand, the electric saturation in the vicinity of anions is relatively small and the relative permittivity of water in the proximity of these ions practically reaches its macroscopic value [15, 16]. Thereby, the permittivity rapidly increases with the distance from ion. At the distance of about 1 nm, its local value is only little different from the macroscopic value, even in the neighbourhood of cations [17, 18]. Because of these facts, eqn (8) cannot supply a reasonable value of critical interionic distance even by using a correction for relative permittivity, which speaks against a pure electrostatic interpretation of interactions in the rate-determining step of the investigated reaction.

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