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Polarographic Study of Aminoalkyl Esters of αβ-Unsaturated Acids and Their Reactions

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The review is devoted to the polarographic study of the reactions of aminoalkyl esters of αβ-unsaturated acids: electrochemical reduction, hydrolysis (including hydrolysis in a two-phase system), partition, and isomerisation. Detailed polarographic characteristics and equations for the polarographic wave and the kinetics and equilibria of the reactions using the limiting polarographic current are presented. The corresponding analytical applications of the method are considered. The kinetics and mechanisms of the processes are discussed from the standpoint of the structure of the electrical double layer, the acid-base properties of the aminoalkyl esters, and intramolecular hydrogen bonds in conjunction with correlation analysis. A comparison is made with data obtained by pH-stat and spectrophotometric methods. The bibliography includes 166 references.

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I. INTRODUCTION

Interest in aminoalkyl esters of αβ-unsaturated acids has been aroused comparatively recently and for this reason we shall consider briefly the problems concerning the applications of these esters and also the methods for their synthesis.

Aminoalkyl methacrylates and acrylates, monomers with functional groups, are used in the manufacture of a wide variety of polymeric materials: synthetic rubbers[1], rubber suitable for the manufacture of tyres[2], latexes[3], vulcanising agents for rubbers[4-9], fibreglass[10-18], anionic polyelectrolytes and polyampholytes[19-25], coatings[26-33], modified cellulose materials[34-37], and physiologically active polymers[38-42]. Certain other applications of the esters have also been described[43-53].

The following methods are used to synthesise esters of methacrylic and acylic acids containing in the alkoxy-radical a tertiary amino-group or a secondary amino-group with a t-alkyl or aryl substituent at the nitrogen atom[51-53]. (1) Esterification of aminoalcohols by unsaturated acids. The use of this method is limited owing to the necessity to remove from the required monomers an admixture of the salt of the initial acid and the amino-alcohol and also owing to the inadequate yields of the monomers. (2) Acylation of aminoalcohols by acid chlorides. The latter method is more universal and makes it possible to obtain high yields of the methacrylate and acrylate derived from a wide variety of aminoalcohols. However, owing to the low availability and high cost of acid chlorides, the applications of this method are as a rule limited to preparative laboratory syntheses.
(3) Transesterification of lower unsaturated acid esters with aminoalcohols. Because of the low cost of the initial methacrylate and acrylate esters, their high purity and stability, and also the comparatively simple technology and high yields of the required monomers, this method is most widely used in practice. Alkaline metal, alkaline earth metal, and titanium alkoxides are used as effective process catalysts.

Methacrylates and acrylates containing in the alkoxy-group a primary amino-group or a secondary amino-group with unbranched or only slightly branched alkyl residues at the nitogen atom are as a rule obtained in the form of hydrochlorides by the interaction of acid chlorides with aminoalcohol hydrochlorides.

The aminoalkyl methacrylate and acrylate esters discussed in this review were obtained mainly by trans-esterification (method 3) and from acid chlorides.

In connection with the expanding use of aminoalkyl esters of αβ-unsaturated acids, studies of the physicochemical properties of these compounds and the development of highly sensitive physicochemical methods for their determination are assuming increasing importance. This review is devoted to this problem and is concerned mainly with results obtained by the polarographic method: polarographic studies of the hydrolysis, isomerisation, and partition reactions and polarographic methods for the determination of the aminoalkyl esters. A number of important advantages of the polarographic method for the investigation of the kinetics and equilibria of the above reactions are noteworthy: (1) the possibility of recording kinetic curves without sampling; (2) the comparatively simple solution of the problem of the maintenance of a constant pH and ionic strength owing to the high sensitivity of the method, etc.

Since the polarographic method yields at the same time valuable information about the mechanism of the electrochemical reduction of the test compounds, these data have also been included in the review. Compared with methacrylate and acrylate esters without an amino-group in the alkoxy-moiety, the corresponding aminoalkyl esters are of considerable interest as regards their electrochemical behaviour, since, depending on the pH of the solution, they can exist in both protonated and non-protonated states. This factor makes it possible to investigate the intramolecular catalysis in the hydrolysis of the aminoalkyl esters as a function of the pH.

II. POLAROGRAPHIC CHARACTERISTICS AND THE MECHANISM OF ELECTROCHEMICAL REDUCTION

For comparison, we shall consider in this section also certain data referring to unsaturated acid esters without an amino-group in the alkoxy-moiety.

The possibility of the polarographic reduction of esters with $\alpha\beta$-conjugated double bonds (the carbonyl and ethylene bonds) was demonstrated for the first time in relation to methyl methacrylate[54]. The reduction wave of methyl methacrylate ($E_{1/2} = -1.92$ V; here and henceforth the potentials are quoted relative to the normal calomel electrode) was obtained in the presence of lithium chloride or tetramethylammonium iodide in 25% ethanol as the supporting electrolyte.

Data have been published[55-62] on the reduction of methacrylates without an amino-group in the alkoxy-moiety using non-aqueous and mixed solvents. The polarographic behaviour of methacrylates with substituents other than amino-groups in the alkoxy-moieties has been discussed[63,64]. The reduction involves the ethylene bond with formation of isobutyrate esters[55-57]:

$$CH_2=C(CH_3)-C\overset{O}{\underset{OR}{<}} + 2e + 2H^+ \rightarrow CH_3-CH(CH_3)-C\overset{O}{\underset{OR}{<}} \quad (1)$$

The reduction of methacrylates and acrylates containing an alkylamino-group has been studied[65-72] in both aqueous buffer solutions[65-67,71] and using non-aqueous solvents (alcohol, dimethylformamide[68-70]). The polarographic characteristics of acrylate and methacrylate esters in various supporting electrolytes are presented in Tables 1 and 2. To facilitate the comparison, the limiting current constant I_{lim} is defined as the limiting current divided by the characteristic of the capillary; the dimensions of I_{lim} are μA litre mole^{-1} mg$^{-2/3}$ s$^{1/2}$. The limiting current constant undivided by the capillary characteristic is denoted henceforth by Klim.

The reduction of aminoalkyl methacrylates is irreversible like that of methacrylates containing alkoxy-moieties without an amino-group[63]; the slopes of the $E - \lg[\bar{i}/(\bar{i}_d - \bar{i})]$ straight lines is 75–85 mV for neutral buffer solutions and 60–67 mV for alkaline solutions[66,71].

In studies on the reduction of a number of aminoalkyl acrylates and methacrylates in dimethylformamide it was noted[70] that the limiting current constant is smaller approximately by a factor of two than in a protic solvent. However, the addition of proton donors (water, phenol, propargyl alcohol) to dimethylformamide leads to an increase of the limiting current to values approximately equal to those in a protic solvent (Table 1). In consequence of the differences between the properties of the free radicals formed in the first stage of the reduction of monomers, under these conditions the limiting current for the methacrylates reaches constant values at much lower concentrations of proton donors than for acrylates (see below)[57]. The increase of the limiting current in the presence of proton donors has been explained[70] by the fact that in non-aqueous dimethylformamide the process stops at the stage involving the formation of radical-anions,

$$CH_2=C(CH_3)COOR + e \rightarrow \dot{C}H_2-\bar{C}(CH_3)COOR, \quad (2)$$

which probably dimerise subsequently. The one-electron mechanism of the reduction of methacrylates in an aprotic medium (dimethylformamide) has been confirmed[62] for methyl methacrylate.

In the presence of proton donors, the radical-anion is protonated[70]:

$$\dot{C}H_2-\bar{C}(CH_3)COOR + HA \rightarrow \dot{C}H_2-CH(CH_3)COOR \quad (3)$$

which facilitates subsequent reduction. Calculation of the number of electrons involved in the reaction by the Il'kovich equation using the diffusion coefficients for compounds of a similar type showed that the reduction process involves the addition of two electrons[58,65,69]. However, in the case of the dimethacrylate derived from triethylene glycol the limiting currents in both anhydrous dimethylformamide and in the presence of proton donors are almost the same[74], which indicates the absence of the radical-anion protonation stage. This finding has been explained[74] by the possible amination of the radical-anion (or the dimeric biradical) by the tetraalkylammonium cations from the supporting electrolyte.

Table 1. The polarographic characteristics of the reduction of acrylate and methacrylate esters [A=CH_2=CHC(=O)–; M=CH_2=C(CH_3)C(=O)–; 25°C].

Compound	0.05 M $(C_2H_5)_4NI$ in dimethylformamide					0.05 M $(C_2H_5)_4NI$ in CH_3OH		
	$-E_{1/2}$, V	I_{lim} DMF	I_{lim} 1 M (DMF + H_2O)	I_{lim} 8 M (DMF+phenol)	References	$-E_{1/2}$, V	I_{lim}	References
A—$OCH_2CH_2N(CH_2—CH=CH_2)_2$	2.081	2.17	2.34	4.46	70	—	—	—
M—$OCH_2CH_2N(CH_2—CH=CH_2)_2$	2.253	2.07	3.45	4.08	70	—	—	—
A—$OCH_2CH_2N(C_2H_5)_2$	2.118	—	2.16	4.34	70	—	—	—
M—$OCH_2CH_2N(C_2H_5)_2$	2.269	—	3.84	4.70	70	2.07	5.60	69
A—OCH_2CH_2N⟨⟩	2.087	1.47	—	—	57	—	—	—
M—OCH_2CH_2N⟨⟩	2.260	3.91	—	—	57	2.04	5.56	69
A—OCH_3	—	—	—	—	—	1.83*	3.23*	56
M—OCH_3	—	—	—	—	—	1.92*	2.60*	56
M—OC_2H_5	—	—	—	—	—	1.94**	2.53**	56
M—$OCH_2—CH=CH_2$	—	—	—	—	—	1.97*	2.75**	56
A—OC_4H_9	2.111	—	1.77	5.00	70	—	—	—
M—OC_4H_9	2.252	—	3.50	5.50	70	2.02**	2.08**	56

* In 0.02 M $(C_2H_5)_4NI$.
** In 0.1 M Li_2SO_4; 10% CH_3OH.

Table 2. The polarographic characteristics of the reduction of methacrylate esters [$M=CH_2=C(CH_3)C\overset{O}{\diagup\!\!\diagdown}$; 25°C; aqueous solution]

No.	Compound	pK_a^*	pH 7.40, universal buffer (Li^+), ionic strength 0.05			pH ~ 12 (LiOH); ionic strength 0.02		
			$-E_{1/2}$, V	I_{lim}	References	$-E_{1/2}$, V	I_{lim}^{**}	References
1	$M—OCH_2CH_2N(CH_2CH=CH_2)_2$	6.93	—	—	—	1.976	—	65
2	$M—OCH_2CH_2N(CH_3)CH_2CH=CH_2$	7.39	—	—	—	1.956	2.35	65
3	$M—OCH_2CH_2N(CH_3)_2$	7.94	1.666	3.60	65	1.934	2.87	65
4	$M—OCH(CH_3)CH_2N(CH_3)_2$	7.96	1.678	3.46	65		—	65
5	$M—OCH_2CH_2N(CH_3)C_4H_9$	8.28	1.632	3.43	65	1.926	2.35	65
6	$M—OCH(CH_3)CH_2N(C_2H_5)_2$	8.65	1.645	3.35	65			
7	$M—OCH_2CH_2N(C_2H_5)_2$	8.66	1.645	3.50	65	1.912	2.76	65
8	$M—OCH_2CH_2N(C_3H_{7}\text{-iso})_2$	8.77	1.713	3.30	65			
9	$M—OCH_2CH_2NHC(CH_3)_3$	9.12	1.775	3.20	65	1.898	2.68	65
10	$M—OCH_2CH_2C\equiv N$	—	—	—	—	1.885	2.62	63
11	$M—OCH_2C\equiv CH$	—	—	—	—	1.908	2.62	63
12	$M—OCH_2CH_2N^+(CH_3)_3$	—	—	—	—	1.743	—	63
13	$M—OCH_2CH_2Cl$	—	—	—	—	1.930	2.78	63
14	$M—OCH_2C_6H_5$	—	—	—	—	1.951	2.89	63
15	$M—OCH_2CH_2OCH_3$	—	—	—	—	1.963	2.62	63
16	$M—OCH_2CH_2OC_2H_5$	—	—	—	—	1.963	2.62	63
17	$M—OCH_3$	—	—	—	—	1.968	2.76	63
18	$M—OC_2H_5$	—	—	—	—	1.973	2.62	63
19	$M—OC_4H_9$	—	—	—	—	1.993	2.70	63

* K_a are the acid dissociation constants of the aminoesters taken from the literature[72,73].
** The currents I_{lim} in the alkaline pH range were found by extrapolation to zero time[71].

The protonation of the radical-anion observed in the presence of proton donors is evidently very rapid, since the values of $E_{1/2}$ and K_{lim} for methacrylates and acrylates without an amino-group in the molecules are independent of the pH (pH 7.5–12.5).[57]

The limiting current for the reduction of aminoalkyl methacrylates in an aqueous buffer solution at a pH close to that of the neutral medium is diffusional[65,71] (the slope of the $\lg i_{lim} - \lg H_{Hg}$ straight lines is 0.5; temperature coefficient 0.95–1.37% per degree), as for methacrylates without an amino-group in the alkoxy-moiety[63]. The values of $E_{1/2}$ and K_{lim} in the range pH < 8.5–9.5 are almost independent of the pH; $E_{1/2}$ is also independent of the concentration of the aminoalkyl ester and $\bar{i}_{lim}$ is directly proportional to its concentration.

In the alkaline pH range (pH > 8.5–9.5), the reduction process has a kinetic mechanism[66] (the slope of the $\lg \bar{i}_{lim} - \lg H_{Hg}$ straight lines is 0.26–0.39; temperature coefficient 2.5–3.9% per degree), which may in fact explain the decrease of the limiting current constant (Table 2). The kinetic mechanism of the reduction process in alkaline solution has been accounted for[66] by the influence on this reaction of the protonation of the neutral aminoalkyl ester molecule (at the nitrogen atom) preceding the electrochemical stage proper. The limiting current for the analogous esters without an amino-group remains diffusional also in the alkaline pH range[63]. The protonation of aminoalkyl esters proceeds in a very thin reaction layer at the surface of the electrode[66]. Under these conditions, the main proton donors are hydronium ions; on the other hand, with increase of pH and the acid dissociation constant of the aminoalkyl ester (K_a), water molecules may also be involved in the protonation stage[66]. In the region of kinetic waves, K_{lim} decreases with increasing pH and $E_{1/2}$ shifts towards negative values.

The following mechanism of the above electrode process has been proposed[66]:

$$\begin{array}{ccccc} & \xleftarrow{e\ (III)} & RN & \overset{(I)}{\underset{H^+}{\rightleftarrows}} & RNH^+ \xrightarrow{e\ (II)} \\ & & \uparrow \text{diff.} & & \uparrow \text{diff.} \\ & & RN & \rightleftarrows & RNH^+ \end{array}, \qquad (4)$$

including the occurrence in the general case of simultaneous reactions involving the reduction of the non-protonated (RN) and protonated (at the nitrogen atom; RNH^+) forms of aminoalkyl esters. In the region of the rise in the wave, there is then also electrochemical inhibition (the process is irreversible) in both simultaneous electron transfer stages.

Like methacrylates without an amino-group[63,75] and aminoalkyl esters of other acids[76], aminoalkyl methacrylates[66,71] are adsorbed on the mercury electrode[66,71]; however, at potentials more positive by 0.4–0.5 V than the half-wave potential, they are desorbed[66]. Bearing in mind the high negative reduction potential of aminoalkyl methacrylates, the influence of their adsorption on the chemical electrode reactions can probably be neglected.

In alkaline solutions (pH ≥ pK_a) the simultaneous reduction reactions (II) and (III) take place [mechanism (4)]. If only reactions (I) and (II) occur (slow protonation), they are described by the kinetic equation[77]

$$E_{1/2} = \frac{RT}{\alpha n_a F} \ln \frac{10^{-3} n \bar{S} F k_{el}^0}{K_{lim}} + \Psi_1 \left(\frac{\alpha n_a - 1}{\alpha n_a} \right) + \frac{RT}{\alpha n_a F} \ln [H^+] + \frac{RT}{\alpha n_a F} \ln \frac{\bar{i}_d}{\bar{i}_{lim}}, \qquad (5)$$

where α is the transfer coefficient, n_a the number of electrons involved in the potential-determining reaction, $\bar{S}$ the surface area of the mercury drop (in cm^2), k_{el}^0 the rate constant for the electrochemical stage (in $cm\ s^{-1}$) and Ψ_1 the potential in the outer Helmholtz plane.

When only reaction (III) takes place [mechanism (4)], $E_{1/2}$ is given by the equation[78]

$$E_{1/2} = \frac{RT}{\alpha n_a F} \ln \frac{10^{-9} n \bar{S} F k^0_{el}}{K_{lim}} + \Psi_1. \qquad (6)$$

It follows from Eqns. (5) and (6) that in alkaline solutions (αn_a = 0.8–0.9) in the presence of Li^+(LiOH) the relative influence of reactions (I) and (II) will be greater than in a solution at the same pH but in the presence of the $(Alk)_4N^+$ cation (the Ψ_1 potential is more negative in the case of Li^+).[79] The observed shift of $E_{1/2}$ towards negative values (Fig. 1) with increase of K_a in 0.02 M LiOH solution has therefore been explained[66] by the dominant influence on $E_{1/2}$ of the term of Eqn. (5) containing K_a.

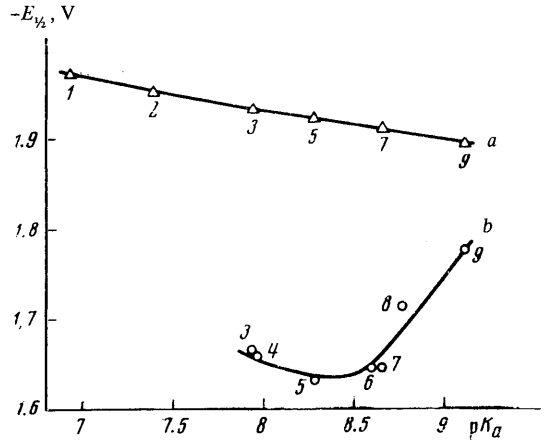


Figure 1. Variation of $E_{1/2}$ with the acid dissociation constants of aminoalkyl esters[66]: *a*) 0.02 M LiOH; *b*) universal buffer solution with LiOH + 0.03 M LiCl (pH 7.4; ionic strength 0.05). The numbers against the symbols correspond to the numbers of the esters in Table 2.

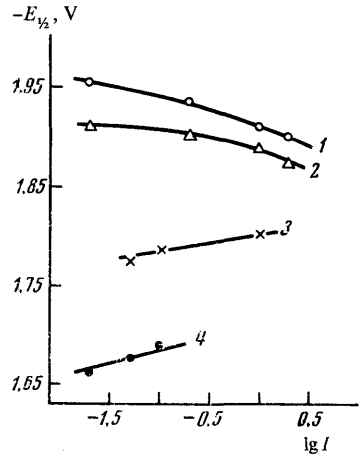


Figure 2. Variation of $E_{1/2}$ with the ionic strength I of the supporting electrolyte[66]; 0.02 M LiOH + LiCl; 1) M–$OCH_2CH_2N(C_2H_5)_2$; 2) M–$OCH_2CH_2N(CH_3)(CH_2{=}CH{-}CH_2)$; universal buffer solution with LiOH + LiCl (pH 7.4); 3) M–$OCH_2CH_2NHC(CH_3)_3$; 4) M–$OCH_2CH_2N(CH_3)_2$ (M = $CH_2{=}C(CH_3)C(=O)$ throughout).

An increase of the ionic strength of an alkaline solution (pH 12) leads[66] to a shift of $E_{1/2}$ towards less negative values (Fig. 2), as for esters with other uncharged alkoxy-groups[63]. The replacement of Li^+ by $(Alk)_4N^+$ in these solutions also greatly facilitates the reduction of the aminoalkyl esters (Fig. 3). The observed phenomena have been explained[66] by the increasing influence of reaction (III) [mechanism (4)] as a result of its acceleration due to the decrease of the absolute value of the Ψ_1 potential[79]. According to Eqn. (6), the change in the rate constant for the electrochemical stage k^0_{el} in solutions with $(Alk)_4N^+$ assumes a considerable importance.

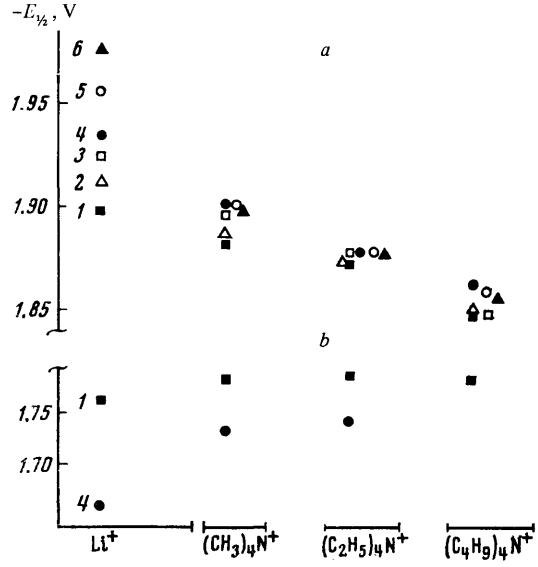


Figure 3. Variation of $E_{1/2}$ with the nature of the cation (Kt^+) of the supporting electrolyte[66]: *a*) 0.02 M KtOH; *b*) universal buffer solution with the corresponding KtOH (pH 7.4; ionic strength 0.02): 1) M–$OCH_2CH_2NHC(CH_3)_3$; 2) M–$OCH_2CH_2N(C_2H_5)_2$; 3) M–$OCH_2CH_2N(CH_3)C_4H_9$; 4) M–$OCH_2CH_2N(CH_3)_2$; 5) M–$OCH_2CH_2N(CH_3)CH_2{-}CH{=}CH_2$; 6) M–$OCH_2CH_2N(CH_2{-}CH{=}CH_2)_2$.

As in the case of methacrylates without an amino-group[64], the values of $E_{1/2}$ for aminoalkyl esters in a non-protonated form are displaced towards less negative values with increase in the size of the cation of the indifferent electrolyte (Fig. 3):

$$Li^+;\ (CH_3)_4N^+;\ (C_2H_5)_4N^+;\ (C_4H_9)_4N^+.$$

This is qualitatively consistent with the corresponding shift of the Ψ_1 potential[80,81] but the displacement of $E_{1/2}$ exceeds the value expected as a result of the Ψ_1-effect[82] and depends to a considerable degree on the size of the substituent in the ester molecule. This has been explained[64] on the basis of the concept[79,83] of specific interactions of the organic depolariser in tetraalkylammonium salt solutions where the electrolyte cation is adsorbed (this leads to the formation of a cationic complex in the adsorption layer). As a result of this interaction, the depolariser is "drawn into" the double layer by the

strongly adsorbed tetraalkylammonium cation, which leads to an additional acceleration of the electrode process and a positive shift of $E_{1/2}$.

When the pH approaches the value of pK_a, reactions (I) and (II) predominate [mechanism (4)] for partly protonated aminoalkyl esters, and, taking into account the quasidiffusional wave, $E_{1/2}$ is expressed by the following equation under these conditions[84]:

$$E_{1/2} = \frac{RT}{\alpha n_a F} \ln \frac{10^{-3} n \bar{S} F k^0_{el}}{K_{lim}} + \Psi_1 \left(\frac{\alpha n_a - 1}{\alpha n_a} \right) + \frac{RT}{\alpha n_a F} \ln \frac{[H^+]}{K_a + [H^+]} \quad (7)$$

It follows from Eqn. (7) that, when the nature of the aminoalkyl ester changes, $E_{1/2}$ begins to experience the opposite influence of K_a in addition to the influence of k^0_{el}. As a result of this, the plot of $-E_{1/2}$ against pK_a passes through a minimum[66] (Fig. 1).

For fully protonated aminoalkyl esters (pH $\ll$ pK_a), $E_{1/2}$ corresponding to the diffusional wave is described by the following equation[78] [reaction (II) in mechanism (4)]:

$$E_{1/2} = \frac{RT}{\alpha n_a F} \ln \frac{10^{-3} n \bar{S} F k^0_{el}}{K_{lim}} + \Psi_1 \left(\frac{\alpha n_a - 1}{\alpha n_a} \right). \quad (8)$$

In this pH range, the half-wave potential $E_{1/2}$ virtually ceases to depend on the pH of the solution[66] (Fig. 4). The considerable positive shift of $E_{1/2}$ with decrease of pK_a (pH 7.4) (Fig. 1) can be explained by the polarising influence of the substituents in the protonated aminoalkyl esters, which becomes enhanced owing to the intramolecular hydrogen bond (see below).

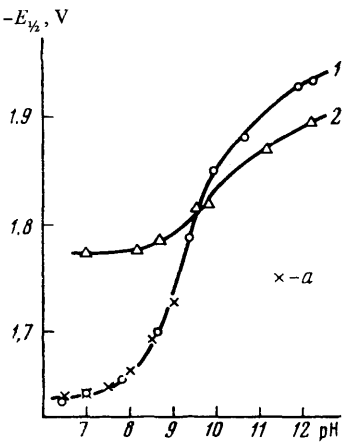


Figure 4. Variation of $E_{1/2}$ with pH of the universal buffer solution (LiOH) [66] [ionic strength 0.02 (+ LiCl)]: 1) M–$OCH_2CH_2N(C_2H_5)_2$ (pK_a = 7.94); 2) M–OCH_2CH_2. .$NHC(CH_3)_3$ (pK_a = 9.12); *a*) points calculated by Eqn. (7).

When Li^+ is replaced by $(Alk)_4N^+$ in the indifferent electrolyte in neutral buffer solutions at pH 7.4 (in contrast to alkaline solutions at a pH 12), $E_{1/2}$ for the aminoalkyl esters shifts towards negative values (Fig. 3),[66] which is consistent with Eqns. (7) and (8) (αn_a = 0.7–0.8). A similar influence of the indifferent electrolyte has been observed for an aminoalkyl ester with a quaternary nitrogen atom [$-CH_2CH_2N^+(CH_3)_3$], which is also consistent with the theory[80]. $E_{1/2}$ for protonated aminoalkyl esters[66] and the ester with a quaternary nitrogen atom[63] shifts in the same direction with increasing ionic strength [Eqns. (7) and (8)].

A tendency towards a negative shift of $E_{1/2}$ with increase of the molecular weight of methacrylates (methyl, ethyl, and butyl methacrylates) as been noted[61], which the authors explained by the positive inductive effects of the alkyl group, increasing from the methyl to the butyl group. This leads to an increase of electron density at the vinyl bond and hinders its reduction. This question has been examined qualitatively[63] on the basis of the correlation equation[85]

$$\Delta E_{1/2} = \rho^*_\pi \sigma^*_R, \quad (9)$$

where ρ^*_π is the constant defining the sensitivity of $E_{1/2}$ for the given group of compounds to the influence of the solvent and σ^*_R is the Taft constant. A satisfactory correlation has been obtained in the range of values of σ^*_R from –0.13 to 0.8, characterised by the following parameters: $\rho^*_\pi = 0.114 \pm 0.008$; $S = \pm 0.007$; $r = 0.977$. Since the ester with a non-protonated amino-group does not deviate from the general correlation, this permitted the conclusion[63] that the inductive effect of the non-protonated amino group has a dominant influence on the electrochemical activity of the aminoalkyl esters and made it possible to explain the small experimental negative shift[69,86] of $E_{1/2}$ following the introduction of an alkylamino-group into the alkoxy-moiety of acrylates and methacrylates.

$E_{1/2}$ for the ester derived from β-trimethylammoniumethanol was found to deviate[63] from the $E_{1/2}$–σ^*_R linear relation, which was explained by the electrostatic effect of the field.

It is interesting to note that, in an alkaline solution (pH 12), $E_{1/2}$ for the aminoalkyl esters is also satisfactorily correlated with the $\sigma^*_{R_i}$ constants of the substituents at the nitrogen atom in the alkylamino-group ($\rho^*_\pi = -0.110 \pm 0.006$; $S = \pm 0.002$; $r = 0.995$).[71] However, under these conditions ρ^*_π is negative, suggesting the dominant influence in this series of the nitrogen protonation stage, which is accelerated with increasing positive inductive effect of the alkyl substituent at the nitrogen atom.

It has been noted[57] that, on passing from acrylate esters to the corresponding methacrylate esters, $E_{1/2}$ for the esters shifts by 0.1–0.15 V towards more negative values owing to the positive inductive effect of the α-methyl group (Table 1).

III. THE KINETICS AND MECHANISM OF HYDROLYSIS

1. Kinetic Characteristics

The kinetics of the hydrolysis of the aminoalkyl esters of acids containing tertiary and certain secondary amino-groups in the alkoxy-moiety have been studied. The presence of a primary amino-group and in many cases also of a secondary amino-group leads predominantly to the O–N migration of the acyl group (see below).

Since in the acid pH range the rate of hydrolysis of aminoalkyl methacrylates is very low, data for the hydrolysis in neutral and alkaline pH ranges are mainly considered below.

The first most detailed information about the kinetics of the alkaline hydrolysis of esters of *N*-alkylaminoalcohols was reported by Agren et al.[87], Hansen[88], Zaslawsky

and Fischer[89], and Higuchi et al.[90]. Isolated and conflicting data concerning the mechanism of this reaction are quoted in other communications[91-95] and the influence of the structure of the esters on their reactivity has been examined[96,97]. Later studies[98-103], on the one hand, confirmed and greatly expanded the available information concerning the kinetics of the alkaline hydrolysis of the aminoalkyl esters and, on the other hand, made it possible to treat this reaction from the standpoint of the nature of the interaction of the functional groups (the amino- and ester groups); despite the hypotheses put forward[93,104,105], this problem remained open for a long time.

Many studies of the kinetics and mechanism of the hydrolysis of the aminoalkyl esters were made by pH-stat[88,89,92,106] and spectrophotometric[87,90,98,101,102,107] methods; in a few instances chromatography[108] and colorimetry[107] were used. However, in the case of esters capable of being reduced at a dropping mercury electrode, the polarographic method proved to be the most convenient and promising[99] (see Section I). The reaction is then followed on the basis of the time variation of the limiting current, proportional to the concentration of the aminoalkyl ester. The only complication which may arise when the polarographic method is used to investigate the kinetics of the hydrolysis of esters on the basis of the wave for the initial ester is the possible influence of the hydrolysis product on this wave: adsorption or other effects. An appropriate test is therefore necessary in each instance. The hydrolysis products derived from the aminoalkyl esters of $\alpha\beta$-unsaturated acids considered in the present review did not influence the polarographic wave of the initial ester[99,100]. It is noteworthy that the polarographic method has been used successfully also in the study of the kinetics of the hydrolysis of many other esters[109-114].

Since, depending on the pH of the solution, the aminoalkyl esters can exist both as neutral molecules (RN) and as species protonated at the nitrogen atom (RNH^+), in the general case the hydrolysis of such esters can be described by the sum of the following reactions[87,88,99]:

$$\mathrm{RN} \xrightarrow[k'_{OH^-}]{OH^-(I)} \quad ; \quad \mathrm{RN} \xrightarrow[k'_{H_2O}]{H_2O(II)} \qquad \mathrm{RNH^+} \xrightarrow[k''_{OH^-}]{OH^-(III)} \quad ; \quad \mathrm{RNH^+} \xrightarrow[k''_{H_2O}]{H_2O(IV)} \qquad (10)$$

where k' and k'' are the rate constants for the reactions of the non-protonated and protonated forms of the esters respectively.

Bearing in mind that the rate of hydrolysis of the aminoalkyl esters is very low in the acid pH range[71,88], the influence of reaction (IV) [mechanism (10)] may be neglected at pH $\geqslant$ 7.[99] Therefore the hydrolytic process to which mechanism (10) refers can be described by the following kinetic equation[87-89]:

$$-\frac{dC_{est}}{dt} = \left(k'_{OH^-}C_{OH^-}\frac{K_a^0}{K_a^0 + a_{H^+}/f_{RNH^+}} + k'_{H_2O}\frac{K_a^0}{K_a^0 + a_{H^+}/f_{RNH^+}} + k''_{OH^-}C_{OH^-}\frac{a_{H^+}/f_{RNH^+}}{K_a^0 + a_{H^+}/f_{RNH^+}}\right)C_{est} = k_{exp}C_{est}, \qquad (11)$$

where k'_{OH^-}, k'_{H_2O}, and k''_{OH^-} are the corresponding rate constants, K_a^0 is the thermodynamic acid dissociation constant of RNH^+ (since Tur'yan and coworkers[72,73] obtained K_a at a comparatively low ionic strength, in the calculations below it was assumed that $K_a^0 \simeq K_a$), f_{RNH^+} the activity coefficient of RNH^+, k_{exp} = const. at a constant pH, and C_{est} is the analytical concentration of the ester. In relation to the polarographic method, when the limiting current $\bar{i}_{lim}$ of the aminoalkyl ester is directly proportional to the sum of the concentrations of its protonated and non-protonated form, i.e. to C_{est}, Eqn. (11) becomes at a constant pH

$$\frac{d\bar{i}_{lim}}{dt} = k_{exp}\bar{i}_{lim}. \qquad (12)$$

The suitability of a pseudofirst-order equation [Eqns. (11) and (12)] for the description of the kinetics of the hydrolysis of the aminoalkyl esters has been confirmed in a number of studies[88,89,99,102]. On the other hand, the fact that the hydrolysis of the aminoalkyl esters constitutes the sum of the reactions of the protonated and non-protonated forms of the ester has not been always taken into account[97]. The experimental psuedo first-order rate constants k_{exp} can be found graphically on the basis of Eqn. (11) or (12).

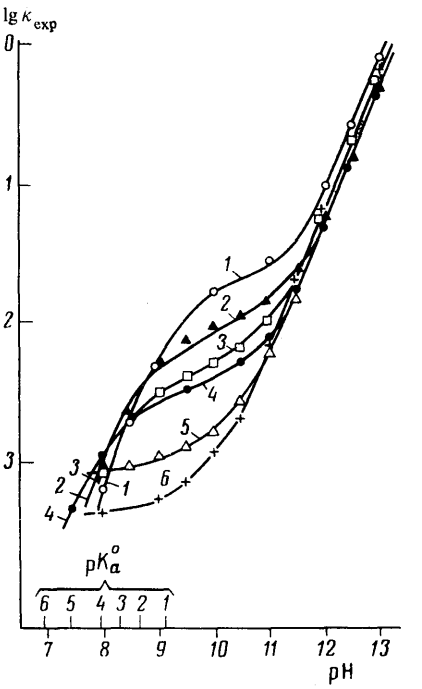


Figure 5. Variation of the experimental hydrolysis rate constant with pH.[99] Curves—experimental data; symbols—data calculated by Eqn. (13) (Table 3): 1) M–OCH_2.$CH_2NHC(CH_3)_3$; 2) M–$OCH_2CH_2N(C_2H_5)_2$; 3) M–OCH_2.$CH_2N(CH_3)C_4H_9$; 4) M–$OCH_2CH_2N(CH_3)_2$; 5) M–OCH_2.$CH_2N(CH_3)CH_2$–CH=CH_2; 6) M–$OCH_2CH_2N(CH_2$–CH=$CH_2)_2$.

The contribution of reactions (I)–(III) [mechanism (10)] depends on the pH of the medium in which the ester is hydrolysed and this determines the characteristic form of the lg k_{exp}–pH curves obtained[90,98,99] in studies of the rate of hydrolysis of the aminoalkyl esters over a wide pH range. These curves (Fig. 5) have two steep sections with an intervening low-slope section. Fig. 5 shows that, in the region where pH $\gg$ pK_a^0, reaction (I) predominates (the upper steep section represents the linear dependence of lg k_{exp} on pH with a slope close to unity): at pH values close to pK_a, the rate constant k_{exp} varies insignificantly

with pH, which suggests a dominant contribution of either stage (II) or stage (III), since in both cases there should be a low-slope section of the $\lg k_{exp}$–pH relation, i.e. these stages are kinetically indistinguishable[88,99] [Eqn. (11)]. In agreement with experimental data and the theory[99] [Eqn. (11)], the low-slope section of the $\lg k_{exp}$–pH curves is displaced more towards lower values of k_{exp} and pH the lower the value of pK_a^0. At $pH \ll pK_a^0$ the lower steep linear section is observed in the plot of $\lg k_{exp}$ against pH with a slope close to unity, which shows that stage (III) predominates in this instance [Eqn. (11)], provided that RN has been almost completely converted into RNH^+. For aminoalkyl esters with a low value of pK_a^0, it proved impossible to observe experimentally the lower steep section (Fig. 5).

Table 3. The rate constants for the alkaline hydrolysis of the aminoesters $CH_2=C(CH_3)COOCH_2CH_2R$ (H_2O; 25°C; ionic strength 0.5; polarographic method[99,100]).

R	pK_a	k'_{OH^-}, litre mole^{-1} min^{-1}	k''_{OH^-}, litre mole^{-1} min^{-1}
$NHC(CH_3)_3$	9.12	4.5±0.5	435±40
$N(C_2H_5)_2$	8.66	3.1±0.6*	550±90**
$N(CH_3)C_4H_9$	8.28	3.4±0.3	670±50
$N(CH_3)_2$	7.94	2.5±0.1	990±40
$N(CH_3)CH_2CH=CH_2$	7.39	3.4±0.2	1280±90
$N(CH_2CH=CH_2)_2$	6.93	3.9±0.2	1450±100
H		2.1±0.0	—
$\overset{+}{N}(CH_3)_3$		35.9±0.3	—

*$E'_{act}(k'_{OH^-}) = 12.1 \pm 0.4$; $\lg A' = 7.6 \pm 0.5$ (E_{act} is the activation energy in kcal mole^{-1} and A is the pre-exponential factor).

**$E''_{act}(k''_{OH^-}) = 19.9 \pm 2.3$; $\lg A'' = 16.0 \pm 1.6$.

In the solution of the problem of the separate determination of the rate constants for the kinetically indistinguishable stages (II) and (III), it has been shown[88] on the basis of a comparison with the kinetics of the hydrolysis of 2-dialkylaminoethyl bromides that the influence of stage (II) may be neglected. Comparison of the rates of hydrolysis of acetylcholine, ethyl acetate, and diethylaminoethyl acetate in neutral and alkaline solutions also led to the qualitative conclusion[39] that stage (III) predominates. A similar conclusion has been arrived at by a more rigorous procedure (by analysing the influence of the ionic strength of the solution on the kinetics of the hydrolysis).[99] Thus in the general case the hydrolysis of the aminoalkyl esters is described by reactions (I) and (III) [mechanism (10)] and Eqn. (11) can be written as follows:

$$k_{exp} = k'_{OH^-}C_{OH^-}\frac{K_a^0}{K_a^0 + a_{H^+}/f_{RNH^+}} + k''_{OH^-}C_{OH^-}\frac{a_{H^+}/f_{RNH^+}}{K_a^0 + a_{H^+}/f_{RNH^+}}. \qquad (13)$$

The applicability of Eqn. (13) has also been confirmed[99] by comparing the experimental and calculated kinetic curves (Fig. 5).

The second-order rate constants, calculated by Eqn. (13) for aminoalkyl methacrylates[99,100], and most reliable data[87–89,92,101,102,115] for other aminoalkyl esters are listed in Tables 3–5.

One should note that, in the study of the kinetics of the hydrolysis of the aminoalkyl esters in buffer systems, general alkaline catalysis is sometimes possible. The effect of acetate and phosphate ions on the kinetics of the hydrolysis of choline esters and esters with a tertiary alkylamino-group has been investigated. However, in the case of choline esters[98,107,116,117] as well as esters with a tertiary amino-group[94,107] this effect could be observed only under conditions where the influence of more effective catalysts is slight (pH 5–6) and for esters with a tertiary amino-group the contribution of the catalytic effect of the components of the buffer mixture to the overall hydrolysis rate constant was insignificant[71,90,94,118,119].

Table 4. The rate constants and activation parameters for the alkaline hydrolysis of the aminoesters $C_6H_5.COOCH(R)(CH_2)_nNR'_2$ (60°C; 30 wt.% aqueous ethanol; ionic strength 0.1; spectrophotometric method[101,102]).

n	R	R'	pK_a	k'_{OH^-}, litre mole^{-1} min^{-1}	E'_{act}, kcal mole^{-1}	$\lg A'$	k''_{OH^-}, litre mole^{-1} min^{-1}	E''_{act}, kcal mole^{-1}	$\lg A''$
1	H	CH_3	7.24	6.75±0.09	12.6±1.1	7.3	9 000±1200	11±1	9.4
1	H	C_2H_5	7.73	7.9±0.2	12.5±2.0	7.3	5 900±480	14±1	11.1
2	H	CH_3	7.67	7.6±0.5	10.7±0.3	6.1	2 100±120	11±1	8.7
2	H	C_2H_5	8.41	6.7±0.5	11.6±0.3	6.6	780±120	14±1	10.2
1	C_6H_5	CH_3	6.30	1.84±0.06	11.5±0.2	6.0	76 000±8400	17±3	14.2
1	C_6H_5	C_2H_5	7.00	1.52±0.03	9±1	4.3	26 400±1800	10±2	9.5
2	C_6H_5	CH_3	7.32	1.15±0.02	9.4±0.2	4.4	2 580±120	16±2	12.1
2	C_6H_5	C_2H_5	8.07	0.86±0.06	6.2±2.0	2.2	469±42	7±1	5.4
3	C_6H_5	CH_3	8.00	0.82±0.02	7.0±1.5	2.7	2 210±240	13±1	10.0
—	$C_6H_5COOCH_2CH_3$			3.68±0.06					

Table 5. The rate constants for the alkaline hydrolysis of the aminoesters $RCOO(CH_2)_nN(R')_2$ (25°C; H_2O; pH-stat method).

n	R	R'	k'_{OH^-} litre mole^{-1} min^{-1}	k''_{OH^-}, litre mole^{-1} min^{-1}	Ionic strength	References
2	CH_3	CH_3	6.0	2 560	0.07	88
3	CH_3	CH_3	8.4	350	0.07	88
2	C_2H_5	C_2H_5	2.5	1 580*	—	87
2	CH_3	C_2H_5	—	31 000**	0.006	89
2	C_2H_5	CH_3	—	14 400	0.1	92
—	$C_6H_5COOC{\equiv}CCH_3(C_2H_5)_2$		7.46***	167	—	115

*Spectrophotometric method.
**60°C.
***Aqueous ethanol.

2. Hydrolysis of Aminoalkyl Esters in the Non-Protonated Form. The Influence of the Structure of the Ester

The introduction of an amino-group into the ethyl methacrylate molecule leads to an acceleration of the hydrolysis of the ester (Table 3). Such acceleration relative to analogues without an NR_2 group in the alcohol residue has also been observed for esters of azobenzene carboxylic[120], glycolic[96], acetic[88,89,96], and benzoic[87,93,101] acids. However, the influence of the amino-group on the reactivity of the esters is small and cannot be explained by the postulated[93,98,105] activation of the carbonyl bond by the intramolecular interaction of the

β-nitrogen atom with the carbonyl carbon atom, i.e. N: → C=O. It was concluded[88,89,99-101,103,121] that there is no nitrogen–carbonyl interaction and that the inductive effect of the non-protonated alkylamino-group predominates. This conclusion was based on the following characteristics of the influence of the structure: (1) as regards the general relation between $\lg k_{OH^-}$ and σ^*_R obtained for methacrylates with various alkoxy-groups, the aminoalkyl ester behaves in the nonprotonated form as an ordinary alkyl ester in accordance with the value of its σ^*_R;[100] (2) a change in the basicity of the amino-group does not affect significantly the rate of hydrolysis of the non-protonated forms of the aminoalkyl esters, as shown by the absence[99,101] of an appreciable influence of the nature of the substituents at the nitrogen atom in the alkoxy-group (Tables 3 and 4); (3) the influence of the basicity of the carbonyl group on the reactivity of the non-protonated forms of aminoalkyl esters with a variable acid component and of the ethyl esters of substituted benzoic acids is approximately the same[103]; (4) studies on infrared spectra showed[121] that the frequencies and intensities of the band associated with the vibrations of the C=O bond in aminoesters and their analogues without an amino-group in the alkoxy-moiety do not differ appreciably from one another, while in the case of the postulated nitrogen–carbonyl interaction the differences should have been significant.

It is interesting to note that an appreciable variation of the activation energy with the number of methylene units and with the nature of the substituent at the nitrogen atom has been noted for esters of secondary benzyl alcohols containing a tertiary amino-group in the alkyl chain, in contrast to esters of primary aminoalkyl carbinols[101]. These data can be accounted for[101] by the nucleophilic catalysis by the amino-group, i.e. by the direct interaction of the amino- and ester groups. However, since spectroscopic evidence was not obtained for such interaction, the authors[101] suggested that the interaction is manifested mainly in the transition state and not in the initial state.

Other structural characteristics of esters in the non-protonated form which have been observed[101] include a distinct decrease of reactivity on passing from esters of primary aminoalcohols to those of secondary amino-alcohols and further to esters of tertiary aminoalcohols as well as a decrease of reaction rate with increase in the length of the hydrocarbon chain by a CH_2 group in the alcoholic component of the ester[88,96,101], which has been explained by steric hindrance[96].

3. Hydrolysis of Aminoalkyl Esters Protonated at the Nitrogen Atom. The Influence of the Structure of the Ester

It has been shown for esters of various acids[87-89,99,102,115] that the protonation of the amino-group increases the reactivity of the esters by 2–3 orders of magnitude compared with the initial non-protonated esters and their analogues without an NR_2 group in the alkoxy-moiety (Tables 3–5).

Such acceleration of the hydrolysis of the protonated ester can in general be a result of three effects: (a) the powerful inductive effect of the $+NHR'R''$ group via the chain of carbon atoms ($\sigma^* \simeq 3$);[122] (b) the electrostatic effect of the positive charge on the nitrogen atom (the interaction of N^+ with the C=O group); (c) the effect of the intramolecular hydrogen bond (IAHB) $^+NH\ldots O{=}C$.

These effects can be separated and their contributions to the overall acceleration of the hydrolysis can be estimated quantitatively with the aid of correlation analysis[123] using the principles described by Palm et al.[124] and assuming that each effect is independent of the structure of the acyl residue. In this case the inductive effect, calculated from the data of Ignat'eva et al.[100], accelerates the reaction by a factor of 4–5 and the electrostatic effect, determined for the $^+N(CH_3)_3$ group, accelerates it by a factor of 5–6. Bearing in mind that the values of σ^* and the electrostatic effects for the $^+NR_3$ and $^+NHR'R''$ groups are approximately the same, the difference by a factor of 15–40 between the values of k_{OH^-} for compounds with the $^+NR_3$ and $^+NHR'R''$ groups can be regarded as a result of the catalytic effect of the intramolecular hydrogen bond. The inductive effect and other factors have been shown by a computational procedure to exert their influence in the same order[88,100,102].

The hypothesis of the intramolecular interaction of the carbonyl and protonated amino-groups via hydrogen bonding, put forward for the first time by Shätzle et al.[93], has been used by many investigators[87,88,124-126] to explain the acceleration of the hydrolysis of the protonated forms of the aminoesters. However, convincing evidence for such interaction was obtained only in studies of the structural influences on the reactivities of the aminoesters[88,89,99,100,102,115,127].

The following characteristics of the influence of the structure confirm this hypothesis. (1) An increase of k''_{OH^-} with decrease of pK_a for the aminoester has been observed[88,99,102]. Since the energy of the hydrogen bond depends on the acidity of the dialkylammonium groups, it was natural to suppose that the decrease of pK_a should lead indirectly to an increase of the strength of the intramolecular hydrogen bond and hence to an enhancement of the catalytic effect of the $^+NHR'R''$ group, causing the increase of k''_{OH^-}. This has been confirmed by the linear variation of $\lg k''_{OH^-}$ with pK^0_a, observed by Tur'yan et al.[99]. It has been suggested[102] that, following the introduction of a phenyl residue into aminoethyl ester molecules (in contrast to aminopropyl esters, the $-I$ effect in the α-position of the alkoxy-group accelerates the reaction for the same reason, while the inductive effect of the C_6H_5 group on the carbonyl atom should be the same regardless of the length of the chain between the carboxy- and amino-groups. (2) The increase in the length of the chain between the nitrogen atom and the ester group by one CH_2 unit decreases k''_{OH^-} by a factor of 4–8, while the expected decrease due to the inductive effect is by a factor of 7–15.[102]. (3) The effect of the spatial proximity of the ammonium and ester groups, discovered by Babaeva et al.[127] on comparing the rates of hydrolysis of esters of the ethylene and acetylene series,

$$\Delta \lg k^{*}_{OH^-} = \lg k^{*}_{OH^-(\overset{+}{N}HR'R'')} - \lg k_{OH^-(\overset{+}{N}(CH_3)_3)},$$

is responsible for the increased reactivity of the protonated forms of the aminoester. When such proximity was hindered, the difference between the rate constants for the $^+NR_3$ and $^+NHR'R''$ derivatives was not greater than by a factor of 1.5–2. (4) The observed correlation[100] between $\Delta \lg k''_{OH^-}(\Delta \lg k''_{OH^-}(\overset{+}{N}HR'R'')) = \lg k''_{OH^-}(\overset{+}{N}HR'R'') - \lg k_{OH^-}[\overset{+}{N}(CH_3)_3])$ and the sum of the Taft constants $\Sigma\sigma^*_{R_i}$ of the substituents at the nitrogen atom also constitutes significant confirmation of the influence of the

$^+$NHR'R" group via intramolecular hydrogen bonding. The similarity of the values of ρ^* in the relations between $\lg k'_{OH^-}$ and σ^*_R (for esters with a variable alkoxy-group) and between $\Delta\lg k''_{OH^-}$ and $\Sigma\sigma^*_R$ led to the conclusion[100] that the efficiences of the transmission of influences via the chain of carbon atoms and via the intramolecular hydrogen bond are approximately the same.

Thus the intramolecular interaction between the carbonyl and ammonium groups, transmitted via the hydrogen bond, is dominant in the acceleration of the hydrolysis of the protonated aminoester. However, the mechanism of this interaction between the functional groups cannot be accounted for by a change in the electron density at the carbonyl carbon atom, as suggested by some investigators[88,128]. The study of the activation parameters (activation energy and the pre-exponential factor)[71,102] showed that the acceleration of the reaction of the protonated aminoester owing to intramolecular hydrogen bonding is most probably associated with the interaction of the solvent with the initial and transition states in the reaction and that the main influence of the hydrogen bond is most probably manifested in the transition state, where it facilitates proton transfer from N^+H to O^- [see the process mechanism below; stage (II) in mechanism (17)], rather than in the initial state. The latter factor leads to a decrease of the degree of solvation of the transition state and hence to a change in solvation entropy. Data obtained in a study[103] of the infrared spectra in the region corresponding to the vibrational band of the C=O bond of aminoesters, characterising the initial state of the ester group, as well as the results of a ^{1}H NMR study[129] of the $\overset{+}{N}H\ldots O{=}C$ interaction agree with the conclusion that there is no hydrogen bond in the initial state of the protonated aminoester[102]. Although the ^{1}H NMR data were obtained in chloroform and cannot be transferred mechanically to aqueous solutions in which the hydrolysis was studied, they also support the view that there is no intramolecular hydrogen bond in the initial state of the aminoester molecule (the earlier attempts at a direct determination of the strength of the hydrogen bond[130] were unsuccessful).

4. Kinetics of the Hydrolysis of the Aminoalkyl Esters in a Two-phase Water–Organic Liquid Emulsion

The study of the kinetics of chemical reactions in multiphase systems is of great theoretical and practical interest[131-133]. The theoretical and experimental principles of the application of the polarographic method in the study of the kinetics of chemical reactions in a two-phase emulsion system (water–benzene), including the study of the kinetics of the hydrolysis of aminoesters in such a system[135], were examined for the first time by Tur'yan et al.[134]. This type of system makes it possible to simulate to some extent the conditions of emulsion polymerisation[134] and this is very important from the practical point of view. On the other hand, owing to the rapid establishment of the equilibrium distribution of the components in the emulsion (large contact area), it is possible to test important theoretical relations for the kinetics of reactions in multiphase systems[134].

A polarographic study of the kinetics of the hydrolysis of aminoesters in a two-phase water–organic liquid emulsion has been made[135] and data have been obtained[135] for the equilibrium distribution of the aminoester between the aqueous and benzene phases, these being necessary for a theoretical interpretation of the kinetic measurements and for the development of a polarographic method whereby the aminoester can be determined (see below).

It has been shown[135] that in the general case the distribution of the aminoester between the aqueous and benzene phases is complicated by the dissociation of the protonated aminoester in the aqueous phase and, regardless of the pH of this phase, virtually only the non-protonated form of the aminoester is distributed in the water–benzene emulsion. These conclusions have been justified experimentally by the following findings: (1) the dependence of the partition coefficient $(K_c)_A$ on the pH of the aqueous phase; (2) the suitability for the calculation of the partition coefficient of the expression

$$(K_c)_A = \frac{(C_{RN})_B(K_a + a_{H^+}/f_{H^+})}{K_a\,(C^0_{est})_{H_2O}}, \qquad (14)$$

where $(K_C)_A$ is the ratio of the equilibrium concentrations of the non-protonated form of the aminoester in the aqueous and benzene phases. Eqn. (14) has been obtained taking into account the equilibrium between the protonated and non-protonated aminoester forms; the concentration of the latter is expressed in terms of the acid dissociation constant of the aminoester and its experimental overall concentration in the aqueous phase $(C^0_{est})_{H_2O}$. The partition coefficient calculated in this way (Table 6) was constant.

Table 6. The partition coefficient and the rate constants for the hydrolysis of diethylaminoethyl methacrylate in the water–benzene system at 25 °C (polarographic method)[135].

$(K_c)_A$	k_1^{EM}, min^{-1} (expt.)	k_1^{EM}, min^{-1} (calc.)	$k_1^{H_2O}$, min^{-1}
210±1.6	$9.9\cdot10^{-5}$	$9.3\cdot10^{-5}$	$1.1\cdot10^{-2}$

Alkaline hydrolysis of aminoesters in the emulsion at a constant pH is a pseudomonomolecular process and is described by the equation for first-order kinetics with respect to the aminoester[135].

A kinetic equation suitable for the polarographic study of the kinetics of chemical reactions in a two-phase system under the conditions of the equilibrium distribution of the components has been obtained[134] on the basis of the study of Abramzon and Kogan[133]. The equilibrium conditions are quite reliably realised in the case of an emulsion[134,135]. The above equation for the pseudomonomolecular alkaline hydrolysis of the aminoester in the emulsion (bearing in mind that the reaction proceeds virtually only in the aqueous phase and the concentration of OH^- ions in the benzene phase is insignificant) is of the following form[135]:

$$\lg i_{lim} = \text{const} - \frac{1}{2.3}\,\frac{V_1 k_1^{H_2O}}{V_1 + V_2(K_c)_A}\,t = \text{const} - k_1^{em} t, \qquad (15)$$

where t is the duration of hydrolysis, V_1 and V_2 are the volumes of the aqueous and benzene phases respectively, and $k_1^{H_2O}$ is the rate constant for alkaline hydrolysis in the aqueous buffer solution at the same pH and ionic strength as in the aqueous phase of the emulsion.

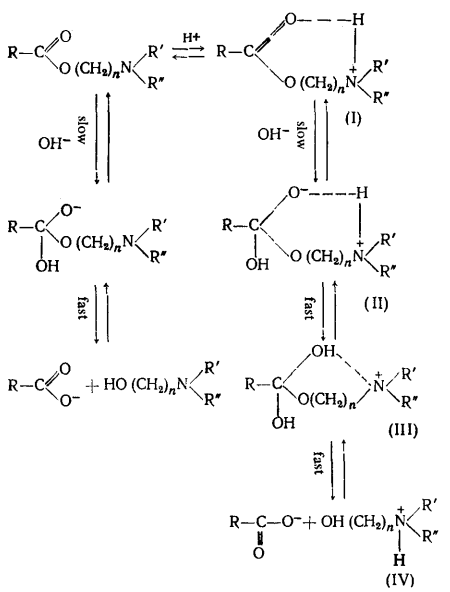
The sharp decrease of the effective rate constant in the emulsion (k_1^{em}),

$$k_1^{em} = \frac{1}{2.3} \cdot \frac{V_1 k_1^{H_2O}}{V_1 + V_2 (K_c)_A} \quad , \qquad (16)$$

compared with the aqueous medium (Table 6) has been explained by the redistribution of the reactants between the phases: the aminoester passes almost completely to the benzene phase [$(K_c)_A$ = 210], while the hydrolysis proceeds in the aqueous phase. The validity of the theoretical postulates has been confirmed by the similarity of the experimental effective rate constant for the hydrolysis of the aminoester in the water–benzene emulsion and the value calculated by Eqn. (16).

5. The Mechanism of the Hydrolysis

The alkaline hydrolysis of the aminoalkyl esters (in both protonated and non-protonated forms) by hydroxide ions proceeds via a bimolecular $B_{AC}2$ mechanism (according to Ingold's classification)[136] and, when account is taken of the nature of the interaction of the functional groups discussed above, the overall reaction can be described by the following scheme[71,99,102]:



(17)

IV. THE KINETICS AND MECHANISM OF ISOMERISATION

1. Process Kinetics

In a series of acryl derivatives of aminoalkanols, aminophenols, and other compounds containing in the molecule both the hydroxy-group and primary or certain secondary amino-groups, the O–N migration of the acyl group is a well known phenomenon[95,105,137–144], but most studies on the latter have been qualitative or semiquantitative.

The results obtained at the beginning of the 1960s led to the conclusion that esters containing a primary or secondary amino-group can as a rule exist only in the protonated form, the free bases rearranging to the corresponding amides[95,105,139–144]. It has been established that the process is intramolecular, the dependence of the rate of reaction on the pH of the medium has been demonstrated, and the hypothesis has been put forward that an intermediate compound of the type of hydroxyoxazolidine is formed in the reaction.

A number of studies have been made on the reaction kinetics[52,126,145–147]. The kinetics of the O–N isomerisation of *O*-acetylethanolamine to *N*-acetylethanolamine have been studied by the pH-stat method in the pH range from 7.0 to 9.7.[126] Using a spectrophotometric method, the same reaction was studied in a buffer system at pH 7.9, 8.2, and 8.5.[146]

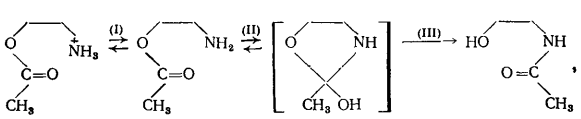
The O–N migration of the acyl group in a series of aminoalkyl methacrylates in the pH range 8.0–10.5 has been investigated in detail by the polarographic method[52,147]. This method proved to be the most promising when the aminoesters are capable of being reduced at a dropping mercury electrode (as in the study of their hydrolysis; see Sections I and III). The process in the buffer solution, where the aminoesters investigated give rise to polarographic reduction waves, was followed directly from the time variation of the limiting current, which is directly proportional to the concentration of the aminoester (the sum of the concentrations of the protonated and non-protonated forms).

The use of the polarographic method also made it possible to elucidate the influence of the simultaneous hydrolytic reaction, which was done using a different supporting electrolyte: a buffer solution at pH 4.75 containing 5% of formaldehyde[148–152]; the reduction wave of both the initial aminoester and of the hydrolysis product (the corresponding aminoalcohol) was observed in this solution[52,147]. Comparison of the results of the polarographic study in the presence and absence of formaldehyde in the solution led to the conclusion[52,147] that the hydrolysis has an extremely insignificant influence on the isomerisation kinetics. The same conclusion concerning 2-aminoethyl acetate was reached in another study[126] based on pH-stat data.

It has been noted[52,126,146,147] that the acyl group does not migrate in the protonated form of the aminoester, since nucleophilic attack by the protonated amino-group on the carbonyl carbon atom bearing a partial positive charge is unlikely. The reaction is both catalysed by hydroxide ions[52,126,146,147] and is subject to general base catalysis[146,147].

The isomerisation kinetics at constant pH are described by a first-order equation with respect to the aminoester[52,126,146,147]. Using the polarographic method, the experimental rate constants k_{exp} can be found by means of Eqn. (12) from a plot of $\lg \bar{i}_{lim}$ against t. Division by the coefficient $p = K_a/\{K_a + [H^+]\}$ (K_a is the acid dissociation constant of the aminoester), defined as the fraction of the non-protonated form of the aminoester, yields the rate constant referred to the non-protonated form.

The variation of $\lg(k_{exp}/p)$ with pH is illustrated in Fig. 6. On the basis of Hansen's experimental results[126], it has been shown[153] that the above relation has a similar form for the isomerisation of 2-aminoethyl acetate. The complexity of the dependence of the rate of rearrangement on the pH could not be accounted for by Hansen's mechanism[126]:



(18)

according to which stage (III) is catalysed by hydroxide ions and the rate-limiting stage varies with pH: stages (III) and (II) are rate-limiting at low and high pH values respectively.

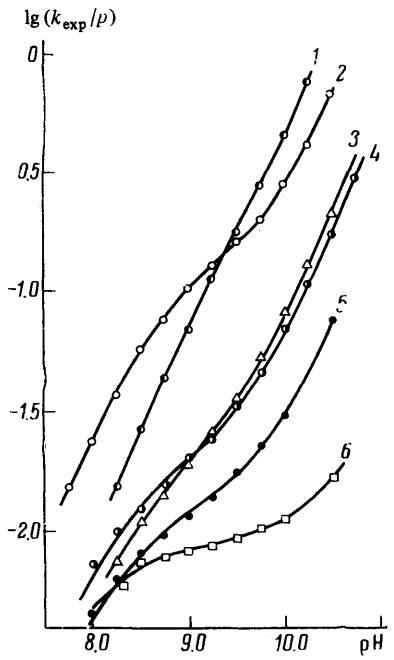
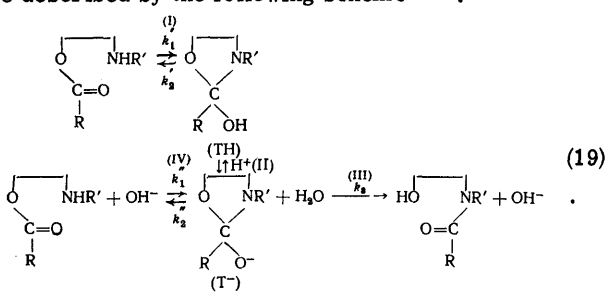


Figure 6. Variation with pH of the experimental isomerisation rate constant referred to the non-protonated form of the aminoester[52,147]. Symbols—experimental data; curves—calculated data: 1) M–$OCH_2CH_2NHCH_3$; 2) M–$OCH_2CH_2NH_2$; 3) M–$OCH_2CH_2NHC_2H_5$; 4) M–$OCH_2CH_2NHC_4H_9$-n; 5) M–$OCH_2CH_2NHC_4H_9$-iso; 6) M–$OCH_2CH_2NHC_3H_7$-iso.

The most probable mechanism, which can account for the O–N migration of the acyl group[52,147,153] is analogous to the mechanism of the aminolysis of esters[153–155] and can be described by the following scheme[52,147]:



(19)

Mechanism (19) has been adopted[153] on the basis of studies of the hydrolysis of iminoesters[156]. The hydrolysis of iminoesters and the aminolysis of esters are accompanied by the formation and cleavage of the same types of intermediates.

In contrast to the studies by Hansen[126] and Martin et al.[146], in mechanism (19) account is taken of two forms of the intermediate—the undissociated form (TH) and the anion (T^-). It has been shown[153] that the undissociated form is not converted directly into the amide. Application of the method of steady states with respect to [TH] + [T^-] in relation to the polarographic method yielded the following kinetic equation[52,147]:

$$\frac{d\bar{r}_{lim}}{dt} = \frac{(k_1' + k_1''[OH^-])\, k_3 \frac{K_1}{[H^+]}}{k_2' + (k_2'' + k_3)\frac{K_1}{[H^+]}} \frac{K_a}{K_a + [H^+]} \bar{r}_{lim}, \qquad (20)$$

where K_1 is the acid dissociation constant of TH; the rate constants k_2'' and k_3 include the concentration of water. k_1' includes not only the rate constant for the non-catalysed stage but also the kinetic terms associated with catalysis by the HPO_4^{2-} and CH_3COO^- ions of the universal buffer mixture[147]. At pH 8–10.5 these terms are almost independent of the pH, since the concentrations of the above ions change insignificantly in this range; therefore the rate constant k_1' can be referred to by convention as the rate constant of the non-catalysed stage. It has been shown[52,147] that the catalytic effect of the borate anion may be neglected.

Eqns. (12) and (20) with [H^+] replaced by [OH^-] yielded the relation describing the experimental rate constant for the migration of the acyl group in the non-protonated form of aminoalkyl methacrylates[147]:

$$\frac{k_{exp}}{p} = \frac{(k_1' + k_1''[OH^-])\,(k_3 K_1 / k_2' K_w)\,[OH^-]}{1 + \frac{(k_2'' + k_3) K_1}{k_2' K_w}[OH^-]}, \qquad (21)$$

where K_W is the ionic product of water. In conformity with both experiment[52,147] and theory, k_{exp} = const. at constant pH. Eqn. (21) can be rearranged to the linear relation

$$\frac{k_{exp}}{p[OH^-]} = a + b[OH^-] - c\frac{k_{exp}}{p}, \qquad (22)$$

where

$$a = k_1' \frac{k_3 K_1}{k_2' K_w}; \qquad (23)$$

$$b = k_1'' \frac{k_3 K_1}{k_2' K_w}; \qquad (24)$$

$$c = \frac{(k_2'' + k_3) K_1}{k_2' K_w}. \qquad (25)$$

Hence, taking into account mechanism (19), we have

$$k_1' = \frac{a^2}{ac - b}; \qquad (26)$$

$$k_2'' = \frac{ab}{ac - b}. \qquad (27)$$

The kinetic parameters of the O–N rearrangement of the acyl group in aminoalkyl methacrylates, including the rate constants k_1' and k_1'' (Table 7), have been calculated[147] on a computer from experimental data by Eqns. (22)–(27) (Fig. 6). Solution[153] of an equation of type (20) yielded k_1' = 0.13 min^{-1} and k_1'' = 1.08×10^4 litre $mole^{-1}$ min^{-1} for aminoethyl acetate.

Mikhlin et al.[147] (Fig. 6) and Schmir[153] showed that the calculated lg (k_{exp}/p)–pH curves agree satisfactorily with the experimental curves. Like the kinetic curves for the hydrolysis of aminoesters, these plots are characterised by three sections: the lower and upper sections (which are steeper and approach a straight line with a slope of

unity) and the middle section (with a lower slope). This type of kinetic relation has been explained [mechanism (19)] [52,147] taking into account the different effects on the process, as a function of the pH, of the non-catalysed stage (I) and the simultaneous stage (IV) catalysed by OH^- ions and also taking into account the changes in the rate-limiting stage as a function of the pH.

Table 7. The kinetic parameters of the O–N migration of the acyl group in aminoalkyl methacrylates[147] $M=CH_2=C(CH_3)C(=O)$.

Ester	$10^{-3}a$	$10^{-7}b$	$10^{-5}c$	$10^2k'_1$, min^{-1}	k''_1, litre $mole^{-1}$ min^{-1}	pK_a^*
M—$OCH_2CH_2NH_2$	22.5±0.5	23.6±2.10	1.74±0.09	13.8	1450	8.70
M—$OCH_2CH_2CH_2NH_2$	2.34±0.02	1,98±0.075	0.32±0.01	9.8	830	9.62
M—$OCH_2CH_2NHCH_3$	6.86±0.11	10.8±0.8	0.38±0.02	31.0	4900	8.96
M—$OCH_2CH_2NHC_2H_5$	4.51±0.19	10.1±0.9	2.27±0.17	2.2	530	9.15
M—$OCH_2CH_2NHC_4H_9$-n	7.37±0.41	1.48±0.14	3.82±0.32	2.0	410	9.09
M—$OCH_2CH_2NHCH_2CH=CH_2$	2.56±0.11	2.41±0.17	1.31±0.11	2.1	200	8.36
M—$OCH_2CH_2NHC_4H_9$-iso	4.96±0.21	6.07±0.46	4.10±0.25	1.25	150	8.91
M—$OCH_2CH_2NHC_3H_7$-iso	8.33±0.21	1.83±0.07	9.38±0.27	0.91	20	9.13

*The values of K_a were taken from Dokolina et al.[73]

2. The Rate of Isomerisation and the Influence of the Structure of the Aminoester

The influence of the structure of aminoalkyl methacrylates on k'_1 has been analysed on the basis of the results of Mikhlin et al.[147] It has been established that the nature of the alkyl substituents at the nitrogen atom has the opposite influence on the isomerisation rate constant compared with their influence on the nucleophilic reactivity of the nitrogen atom in the amino-group. This cannot be explained by hypothesis that the rate-determining stage involves the abstraction of a proton from the amino-group, based on the Taft inductive effect[157], because the compound with the allyl substituent deviates appreciably from the correlation, and, furthermore, the coefficient ρ^* is found to be unrealistically large.

This behaviour of the above compounds, as in other reactions of amines with electrophilic agents[158–160], can be explained by the influence of steric effects. It was noted previously[144] that the steric factor can have a decisive influence on the rate of the O–N migration of the acyl group and that aminoalkyl methacrylates with a t-alkyl group at the nitrogen atom of a secondary amino-group or with a primary amino-group at a tertiary carbon atom do not undergo isomerisation at all[161,162]. The ability of arylaminoalkyl methacrylates and acrylates to exist without O–N isomerisation can be accounted for by the steric effect in combination with the reduced nucleophilicity of the nitrogen atom in the secondary arylamino-group[164].

The use of Eqn. (28), which takes into account not only the Taft[157] steric effects[165,166] but also the steric effect of the "sixth" atom, revealed[52,247] a satisfactory correlation (Table 8) with respect to k''_1:

$$\lg k''_1 = \lg k_0 + \rho^*\sigma^* + \delta E_s^c + \gamma\Delta\sigma. \qquad (28)$$

Best results were obtained with E_S^C and E_S^0; the correlation with E_S was much less satisfactory.

A satisfactory correlation has also been obtained[147] using the Swain–Scott equation[165]:

$$\lg k = a + sn = (-18.4 \pm 3.9) + (4.2 \pm 0.8)n; \quad (r = 0.935;\ S = 0.252). \qquad (29)$$

The nucleophilicities in Eqn. (29) were taken from Hall's paper[166] for the corresponding primary amines. The aminoester with a primary amino-group deviates from the correlation.

The rate constant for the isomerisation of 2-aminoethyl methacrylate is higher than for 2-aminopropyl methacrylate, which can be explained by the more powerful influence in the former instance of the inductive effect of the amino-group via the chain of carbon atoms.

In conclusion one should note that the rate of migration of the acyl group in 2-aminoethyl methacrylate[147] is lower than the rate of the analogous reaction for 2-aminoethyl acetate[126,153] owing to the conjugation effect.

Table 8. The parameters of the correlation based on Eqn. (28).[147]

Steric constant	$\lg k_0$	ρ^*	δ	γ	r	S
E_s^c	3.63±0.06	−2.10±0.22	1.75±0.09	0.144±0.011	0.998	0.041
E_s^o	3.64±0.07	−1.98±0.29	1.99±0.13	0.166±0.015	0.997	0.055
E_s	3.20±0.26	−8.13±3.54	3.26±1.17	0.33±0.11	0.939	0.258

V. ANALYTICAL APPLICATIONS

The ability of aminoalkyl esters of $\alpha\beta$-unsaturated acids to be reduced at a dropping mercury electrode has been used in the development of polarographic methods for the analysis of the esters. The polarography is usually carried out with quaternary ammonium salts as the supporting electrolytes in non-aqueous solvents (methanol, ethanol, and dimethylformamide).

A polarographic method for the determination of monomeric aminoalkyl acrylates and methacrylates in the presence of their polymers and copolymers with *N*-vinylcarbazole has been proposed[68,69]; a 0.05 M solution of $(C_2H_5)_4NI$ in dimethylformamide was used as the supporting electrolyte.

The possibility of the polarographic determination of diethylaminoethyl methacrylate in a mixture with acrylonitrile using a 0.025 M solution of $(C_2H_5)_4NI$ in methanol as the supporting electrolyte has also been demonstrated[86]. A method for the determination of the residual monomeric diethylaminoethyl methacrylate in the latex has been described[65]; it is based on the extraction of the aminoester from the reaction mixture with benzene and its subsequent polarography in a solution of a tetraalkylammonium salt in a benzene–ethanol mixture. As stated above, owing to the high partition coefficient, quantitative extraction is simple and rapid[65].

In contrast to non-aqueous solutions of tetraalkylammonium salts, a more readily available electrolyte—the universal buffer solution (pH 7.5) in which NaOH has been replaced by LiOH in order to obtain a more distinct threshold of the wave—has been proposed[65] as the supporting electrolyte. The method is based on the selection of

the optimum pH, concentrations of the buffer components, and the ionic strength of the supporting buffer solutions.

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