Protolytic properties and reactivity of aminomethylated calix[4]resorcarenes in reactions with esters of phosphorus acids

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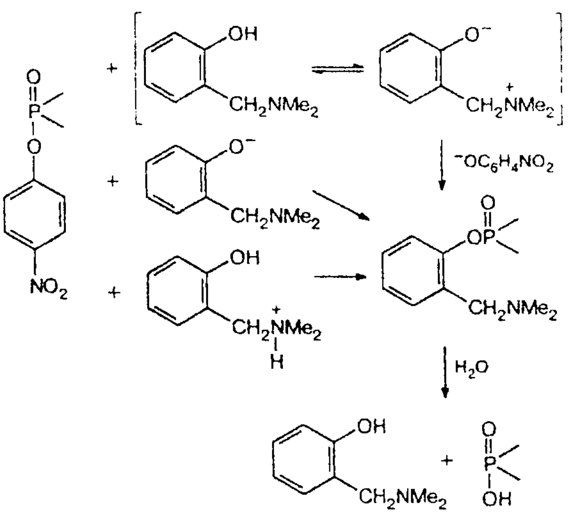
The acid-base properties and the kinetics of reactions of aminomethylated calix[4]resorcarenes (AMC) with *p*-nitrophenyl esters of phosphorus acids in aqueous solutions of propan-2-ol (80 vol.% Pr^iOH) were studied by potentiometry, UV spectrophotometry, and ^{31}P NMR spectroscopy. The effect of the length of the hydrocarbon radical and substituents at the nitrogen atom on the protolytic properties and reactivity of AMC was studied. The reactions studied occur in two stages. At the first stage, phosphorylated AMC are formed, which are hydrolyzed to the corresponding acids at the second stage.

Key words: kinetics, protolytic properties, aminomethylated calix[4]resorcarenes, esters of phosphorus acids.

Aminomethylated calix[4]resorcarenes (AMC) are widely used for synthesis of various functional derivatives of calix[4]arenes.[1–3] The presence of closely arranged hydroxy and amino groups on the upper "rim" of the hydrophobic cavity formed by the aromatic rings and fixed by the "belt" of intramolecular hydrogen bonds (IHB)[4,5] allows AMC to be potential models of active centers of hydrolytic enzymes.[6]

We have previously shown that aminomethylated phenols (AMP), which are structural units of AMC, in water-alcoholic[7,8] and micellar[9] media are bifunctional catalysts of hydrolysis of *p*-nitrophenyl esters of phosphorus acids. In particular, depending of the pH of the medium and the content of ethanol, the reactivity of 2-dimethylaminomethylphenol (AMP-1) is determined by its forms: phenoxide (pH > 9), zwitterionic, neutral (pH 7—9), and protonated (pH < 7), whose rate constants differ sharply.[7] For example, in the reaction with *p*-nitrophenyl bis(chloromethyl)phosphinate in a 40% aqueous solution of ethanol, the values of bimolecular rate constants are 449.00, 57.00, and 0.24 mol^{-1} L s^{-1} for the phenoxide, zwitterionic, and protonated forms, respectively. In these media, the reactions of AMC with esters of phosphorus acids occur in two stages: at the first stage, *p*-nitrophenolate is formed due to the ester interchange and formation of phosphorylated AMP, and the second stage is the hydrolysis of the latter due to the intramolecular catalysis by the aminomethyl group (Scheme 1).

Scheme 1



The purpose of this work is to study the reactivity of AMC (**1**—**4**, H_8L) in the reactions with esters of phosphorus acids **5** and **6** in aqueous propan-2-ol (Pr^iOH, 80 vol.%) (Scheme 2). It is known that the investigation of the reactivity of polyfunctional compounds, such as AMC, is tightly associated with the knowledge of their physicochemical parameters, for example, constants of acid-base and tautomeric equilibria. Therefore, we studied the protolytic properties of compounds **1**—**4** and the influence of the length of hydrocarbon

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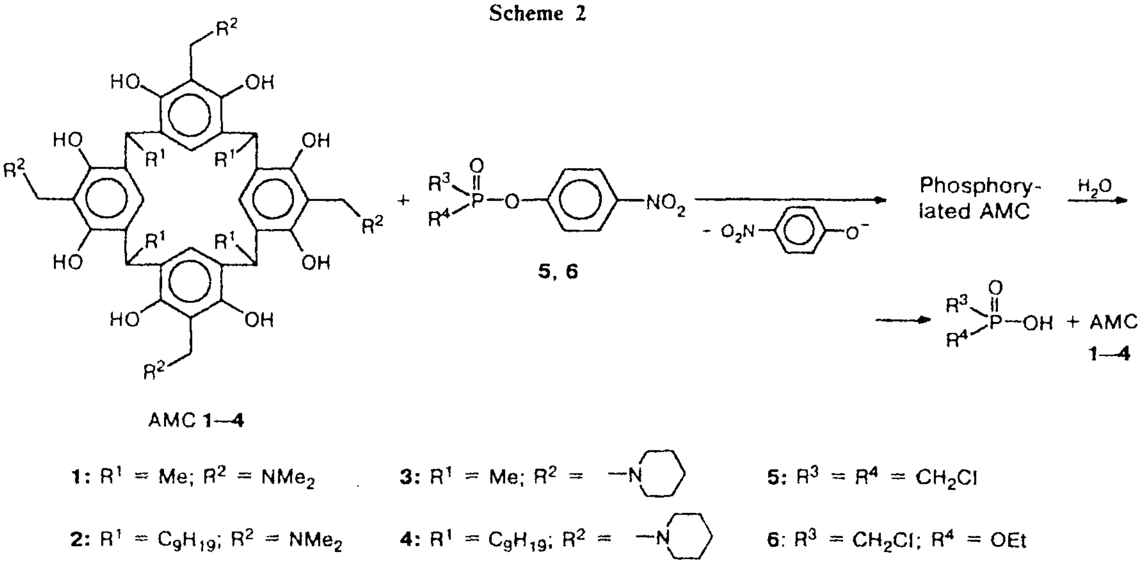
Scheme 2



radicals (R^1) and the structure of the substituent at the nitrogen atom (R^2) on these properties.

Experimental

Compounds 1—4 were synthesized by the known procedure.[10] The stereoisomeric homogeneity corresponding to the product with *cis*-orientation of all aliphatic chains R^1 at the C atoms linking aryl groups was monitored by ^{1}H NMR spectra.

Synthesis of 5,11,17,23-tetrakis(*N*,*N*-dimethylamino)methyl-4,6,10,12,16,18,22,24-octahydroxycalix[4]arene (1). A solution of bis(dimethylamino)methane (BDAM) (2.99 g) in toluene (10 mL) was added to a solution of 2,8,14,20-tetramethyl-4,6,10,12,16,18,22,24-octahydroxycalix[4]arene (4 g) in ethanol (40 mL). The reaction mixture was refluxed in an argon atmosphere for 5 h. The precipitate that formed during refluxing was filtered off, washed twice with acetone, and dried *in vacuo*. The product obtained in 62% yield (4.02 g) is decomposed above 200 °C. Found (%): C, 67.09; H, 7.78; N, 7.44. $C_{44}H_{68}O_8N_4$. Calculated (%): C, 68.40; H, 7.78; N, 7.30. IR (Nujol), ν/cm^{-1}: 3250, 2500, 1610. ^{1}H NMR (300 MHz, $C_6D_5CD_3$), δ: 1.60 (s, 24 H, $N(CH_3)_2$); 1.76 (d, 12 H, $CHC\underline{H}_3$, $^3J_{HH}$ = 7.32 Hz); 3.45 (s, 8 H, NCH_2); 4.89 (q, 4 H, $ArC\underline{H}Ar$, $^3J_{HH}$ = 7.32 Hz); 7.46 (s, 4 H, $Ar\underline{H}$); 9.00 (m, 8 H, OH).

Synthesis of 5,11,17,23-tetrakis(*N*,*N*-dimethylamino)methyl-4,6,10,12,16,18,22,24-octahydroxy-2,8,14,20-tetranonylcalix[4]arene (2). A solution of BDAM (1.65 g) in toluene (10 mL) was added to a solution of 2,8,14,20-tetranonyl-4,6,10,12,16,18,22,24-octahydroxycalix[4]arene (4 g) in ethanol (30 mL). The reaction mixture was refluxed in an argon atmosphere for 8 h. The reaction course was monitored by TLC. The solvent was distilled off, and the residue was dried *in vacuo*. The product obtained in 70% yield (3.45 g) is decomposed above 200 °C. Found (%): C, 76.51; H, 10.65; N, 4.49. $C_{76}H_{124}O_8N_4$. Calculated (%): C, 74.75; H, 10.16; N, 4.59. IR (Nujol), ν/cm^{-1}: 3250, 2500, 1900, 1610. ^{1}H NMR (250 MHz, $CDCl_3$), δ: 0.9 (t, 12 H, $(CH_2)_7C\underline{H}_3$, $^3J_{HH}$ = 6.39 Hz); 1.20 (s, 56 H, $(CH_2)_7$); 2.10 (m, 8 H, $C\underline{H}_2(CH_2)_7$); 2.27 (s, 24 H, $N(CH_3)_2$); 3.69 (s, 8 H, NCH_2); 4.25 (t, 4 H, $ArC\underline{H}Ar$, $^3J_{HH}$ = 7.45 Hz); 7.09 (s, 4 H, $Ar\underline{H}$); 9.09 (m, 8 H, OH).

Synthesis of 4,6,10,12,16,18,22,24-octahydroxy-2,8,14,20-tetramethyl-5,11,17,23-tetrakis(piperidino)methylcalix[4]arene (3). A solution of piperidine (2.99 g) in benzene (10 mL) and a 37% aqueous solution of formaldehyde (3.5 mL) were added to a solution of 2,8,14,20-tetramethyl-4,6,10,12,16,18,22,24-octahydroxycalix[4]arene (3.8 g) in ethanol (40 mL). The reaction mixture under an argon atmosphere was kept at –20 °C for 8 h. The reaction course was monitored by TLC. The solvents were partially distilled off, and the precipitate that formed was filtered off, washed twice with methanol, and dried *in vacuo*. The product obtained in 71% yield (4.32 g) is decomposed above 230 °C. Found (%): C, 70.99; H, 8.56; N, 5.37. $C_{56}H_{76}O_8N_4$. Calculated (%): C, 72.06; H, 8.21; N, 6.01. IR (Nujol), ν/cm^{-1}: 3280, 2500, 1900, 1610. ^{1}H NMR (250 MHz, $CDCl_3$) is difficult to decode.

Synthesis of 4,6,10,12,16,18,22,24-octahydroxy-2,8,14,20-tetranonyl-5,11,17,23-tetrakis(piperidino)methylcalix[4]arene (4). A solution of piperidine (0.38 g) in benzene (10 mL) and a 37% aqueous solution of formaldehyde (0.45 mL) were added to a solution of 2,8,14,20-tetranonyl-4,6,10,12,16,18,22,24-octahydroxycalix[4]arene (0.90 g) in ethanol (10 mL). The reaction mixture under an argon atmosphere was kept at –20 °C for 22.5 h. The reaction course was monitored by TLC. The solvents were distilled off, and the precipitate that formed was filtered off, washed twice with methanol, and dried *in vacuo*; 75% yield (0.94 g), m.p. 183—185 °C. Found (%): C, 75.49; H, 12.03; N, 4.12. $C_{88}H_{140}O_8N_4$. Calculated (%): C, 76.50; H, 10.51; N, 4.10. IR (Nujol), ν/cm^{-1}: 3310, 2500, 1950, 1610. ^{1}H NMR (250 MHz, $CDCl_3$) is difficult to decode.

pH Metric titration was carried out in a thermostatted cell at 20 °C on an I-130 ionometer using carbonate-free KOH. Propan-2-ol was purified by the standard procedure.[11] Glass electrodes were calibrated with standard buffer solutions followed by the estimation of the liquid potential on going from aqueous to water-propan-2-ol solutions according to the described procedure.[12] The pK_w values in water—propan-2-ol solutions were taken from Ref. 13. Because of the poor solubility of compounds 1—4 in alcoholic and water-alcoholic media, the titrated solutions were hydrochloric tetrasalts of compounds **1**—**4** (C_{1-4} = $3.5 \cdot 10^{-3}$ mol L^{-1}). Deprotonation constants were determined using mathematical processing by the CPESSP program[14] of the data of pH metric titration of freshly prepared water—propan-2-ol solutions of acidic tetrasalts of compounds **1**—**4** with a propan-2-ol solution of KOH using the titration method in a variable volume. UV spectra of compounds **1**—**4** in water—propan-2-ol solutions (C_{1-4} = 1.3—$3.5 \cdot 10^{-4}$ mol L^{-1}) were obtained on a Specord UV-VIS instrument.

The kinetics of the reactions of compounds **1**—**4** with substrates **5** and **6** was studied by spectrophotometry under pseudo-monomolecular conditions ($C_{5,6}$ = $4 \cdot 10^{-5}$ mol L^{-1}) by an increase in the optical density (λ 400 nm) due to the formation of *p*-nitrophenoxide ion, using a Specord UV-VIS spectrophotometer at 25 °C, pH 9.0 and 10.9. The observed rate constants (k_{obs}) were calculated by a first-order equation. The binding constants of substrates (K_{bind}), critical micelle formation concentrations (CMC), and rate constants of reactions of aggregates (k_m) were calculated by the equation presented previously.[16]

$$k_{obs} = \frac{k_{H_2O} + k_m K_{bond} C_{surf}}{1 + K_{bond} C_{surf}},$$

where k_{H_2O} is the rate constant of the reaction in a water—propan-2-ol phase, and C_{surf} is the concentration of AMC corrected to CMC.

^{31}P NMR spectra were obtained on a Bruker MSL 400 instrument with a working frequency of 161.97 MHz at 308 K. Chemical shifts are presented relative to 85% H_3PO_4.

Results and Discussion

According to the data of potentiometric titration at pH < 3, all four nitrogen atoms of compounds **1**—**4** (H_8L) are in the protonated form ($H_{12}L^{4+}$), which is transformed with the pH increase first into the neutral form (H_8L) and then into the mono- (H_7L^-) and dianion (H_6L^{2-}) (Table 1):

$$H_{12}L^{4+} \xrightleftharpoons{K_1} H_{11}L^{3+} + H^+, \qquad (pK_1)$$

$$H_{11}L^{3+} \xrightleftharpoons{K_2} H_{10}L^{2+} + H^+, \qquad (pK_2)$$

$$H_{10}L^{2+} \xrightleftharpoons{K_3} H_9L^{2+} + H^+, \qquad (pK_3)$$

$$H_9L^{+} \xrightleftharpoons{K_4} H_8L + H^+, \qquad (pK_4)$$

$$H_8L \xrightleftharpoons{K_5} H_7L^- + H^+, \qquad (pK_5)$$

$$H_7L^- \xrightleftharpoons{K_6} H_6L^{2-} + H^+. \qquad (pK_6)$$

The fraction distribution of the ionized forms of compound **2** at different pH values of the solutions is presented in Fig. 1.

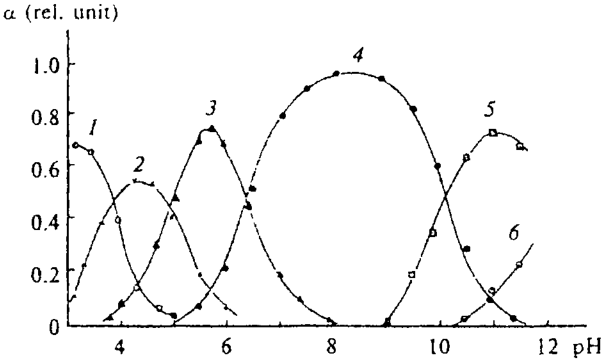


Fig. 1. Fraction distribution of ionized forms of compounds **1**—**4** *vs.* pH of solutions: *1*, $H_{11}L^{3+}$; *2*, $H_{10}L^{2+}$; *3*, H_9L^+; *4*, H_8L; *5*, H_7L^-; and *6*, H_6L^{2-}.

Table 1. Values of pK_a of different forms of AMC (**1**—**4**) and calix[4]resorcarene* (**7**) in an 80% (v/v) water—propan-2-ol solution

Compound	pK_1	pK_2	pK_3	pK_4	pK_5	pK_6
1	2.5	4.3	5.4	7.6	10.2	12.9
2	2.5	3.9	5.5	7.5	10.5	12.1
3	2.5	3.9	5.4	7.5	10.5	12.1
4	2.5	3.9	5.4	7.5	10.5	12.1
7*	—	—	—	—	9.0	10.0

* 4,6,10,12,16,18,22,24-Octahydroxy-2,8,14,20-tetramethylcalix[4]arene (**7**); pK_7 (**7**) = 10.0, pK_8 (**7**) = 11.5.

Note that the acidity of the first and second protons is high (pK_1 = 2.5, pK_2 = 3.9—4.3, Table 1), which is evidence for the mutual effect, probably by IHB of four groups protonated at the nitrogen atom and localized on the "rim" of the cavity of compounds **1**—**4**. The pK_4 values are close to pK_a of AMP-1 forms protonated at the nitrogen atoms in 80 vol.% propan-2-ol and 2-diethylaminomethylphenol (AMP-2) in 70% ethanol, being 7.0 and 7.45 pK_a units, respectively. At the same time, the acidities of the first and second hydroxyl protons (pK_5 and pK_6) of compounds **1**—**4** are lower by 1 and 2 units than the corresponding pK_a values of calix[4]resorcarene (**7**) (Table 1). The pK_5 value is close to pK_a of the phenoxide form of AMP-2 in a 70% water—ethanol solution (10.85 pK_a units).[17] A tendency for increasing by 1—2 units in pK_a of phenoxide forms and decreasing in pK_a of amino groups as compared to the corresponding phenols and benzylamines is characteristic of molecules with strong IHB, which are capable of forming zwitterionic forms in polar solutions, such as AMP.[18] An increase in the solvent polarity, for example, an increase in the water content in water-ethanol solutions, results not only in the appearance of the zwitterionic form of AMP, but also in an increase in its fraction. For example, when the content of ethanol is 70 vol.%, AMP-2 exists at the corresponding pH values in the

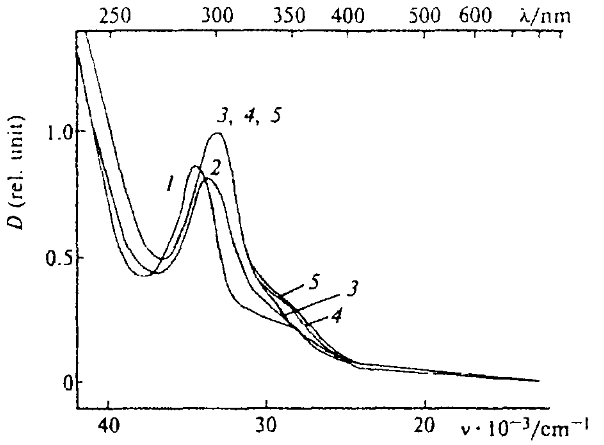


Fig. 2. Changes in the optical density (D) in UV spectra of solutions of **2** (C_2 = 1.3 · 10^{-4} mol L^{-1}) in propan-2-ol (*1*) and in an 80% (v/v) aqueous solution of propan-2-ol (*2*) in the presence of one- (*3*), five- (*4*), and tenfold (*5*) excess of KOH.

neutral form only, whereas at a 10 vol.% content of ethanol, the fraction of zwitterions is 0.8.

For AMC with different structures, the presence of the zwitterionic form was shown in such polar solvents as DMSO and acetonitrile, which is manifested as the bathochromic shift of the main absorption peak and the appearance of a shoulder due to the n→π*-transition in the UV spectra and the downfield shift of signals of the N—CH_3 protons in the ^{1}H NMR spectra.

The analysis of the UV spectra of compounds **1**—**4** also indicates the presence of zwitterions (Fig. 2). In particular, these spectra exhibit two main most intense bands of π→π*-absorption at 240 and 293 nm (Fig. 2, curve *1*) in propan-2-ol and at 240 and 300 nm in an aqueous solution of propan-2-ol (Fig. 2, curve *2*), as well as a shoulder in the region of 330—340 nm responsible for the n→π*-absorption of the phenoxide (zwitterionic) form (see Ref. 1). The intensity of this shoulder increases when the AMC : KOH ratio changes from 1 : 1 to 1 : 5 and changes insignificantly at the 1 : 10 ratio, which indicates the presence of zwitterions already at neutral pH values, where, according to the value of pK_5 10.2—10.5 (Table 1), no monoanions should be observed.

The dependences of k_{obs} of the reactions of substrate **5** on the concentrations of compounds **1**—**4** at pH 9 are presented in Fig. 3. As can be seen, the reactivity of AMC in the medium studied changes when the substituents at the nitrogen atoms R^2 are replaced and is independent of the length of the hydrocarbon radical R^1 (Fig. 3, curves *a* and *b*), *i.e.*, in an aqueous solution containing 80 vol.% propan-2-ol, the hydrophobicity factor has no effect on the reactivity of AMC, unlike anions of calix[4]resorcarenes in a medium containing 80 vol.% DMF.[16] However, all kinetic curves (Fig. 3, curves *a* and *b*) reach a plateau, which indicates that substrate **5** is most likely bound by aggregates of compounds **1**—**4**. Since the hydrophobicity of substituents has no effect on the reactivity of compounds **1**—**4**, intermolecular hydrogen bonds are evidently the driving force for the formation of these aggregates. To process the kinetic curves reaching a plateau (Fig. 3), we used Eq. (1), which takes into account the distribution of the substrate between the aqueous and micellar phases, and in our case, between the water-alcoholic medium and AMC aggregates. We obtained the parameters of the reactions studied: K_{bind}, k_m, and CMC (Table 2).

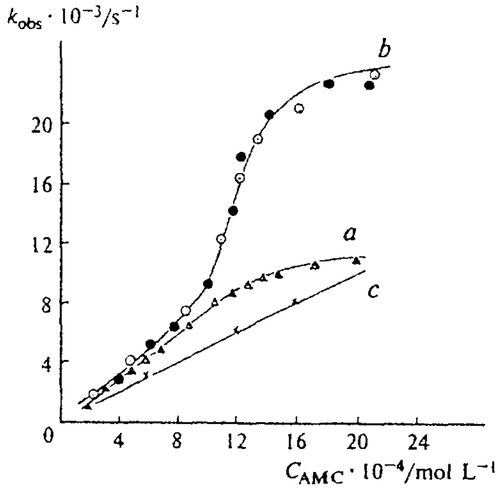


Fig. 3. Dependences of the observed rate constants of the reaction (k_{obs}) of substrate **5** with compounds **1**, **2** (*a*) and 3, 4 (*b*) on their concentrations in an 80% (v/v) aqueous solution of propan-2-ol and on the concentration of AMP-2 (*c*) in a 70% (v/v) aqueous solution of ethanol, pH 9.0, 25 °C.

In the region below 1 · 10^{-3} mol L^{-1}, k_{obs} for compounds **1**—**4** are approximately equal to k_{obs} for AMP-2 in a 70% (v/v) water-ethanol solution (Fig. 3). Note that the reactivity of AMP-2 at this pH is determined by the phenoxide form, whose fraction is 0.01, since the zwitterionic form is absent, and the neutral form is low-reactive.[8]

As in the case of AMP, the H_7L^- monoanion, whose content at pH 9.0 for 1—4 is equal to 0.05 (see Fig. 1), is the species responsible for the reactivity of AMC. In addition, we cannot rule out the contribution of the zwitterionic form, whose reactivity is higher than that of

Table 2. Parameters of the reactions of substrate **5** with **1**—**4** in an 80% (v/v) water—propan-2-ol solution at pH 9.0

AMC	CMC · 10^{-4} /mol L^{-1}	k_m · 10^{-2} /s^{-1}	K_{bond} /L mol^{-1}
1	1.7	2.3	470
2	1.6	2.3	485
2*	0.18	0.05	5370
3	1.3	3.7	235
4	1.5	3.8	250

* At pH 10.9, the reaction with substrate **6**.

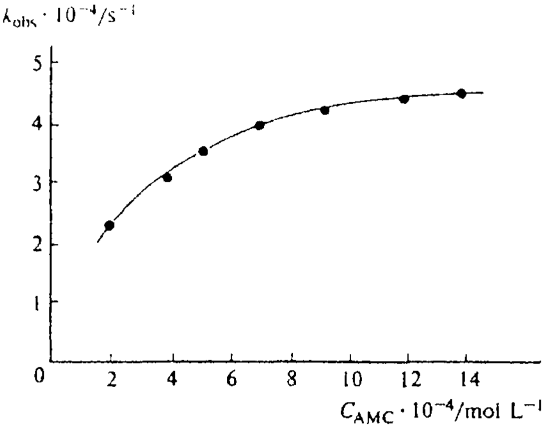


Fig. 4. Dependence of the observed rate constants of the reaction (k_{obs}) of substrate **6** with **2** on its concentration (C_2 : C_{NaOH} = 1 : 8), pH 10.9, 80 vol.% Pr^iOH, 25 °C.

the neutral form in the reactions with esters of phosphorus acids.[7,8] This probably explains the higher reactivity of compounds **3** and **4**, for which, according to the UV spectra, the fraction of zwitterions is higher than those for **1** and **2**.

The dependence of k_{obs} of the reaction of substrate **6** with **2** on its concentration at pH 10.9 (the AMC : NaOH ratio is 1 : 8) is presented in Fig. 4, and the parameters of the reactions calculated from Eq. (1) are given in Table 2. At this pH, compound **2** exists as the H_7L^- monoanion, whose fraction is ~0.8 (see Fig. 1). As can be seen from the data in Table 2, an increase in the amphiphilic character of AMC results in a sharp decrease in CMC and an increase in K_{bind} of aggregates with substrates, *i.e.*, in a change in the properties of these aggregates. The formation of aggregates by anions of calix[4]resorcarenes with similar properties has previously[16] been observed by us in 80 vol.% DMF.

We also studied the kinetics of the reaction of compound **1** with substrate **6** by the ^{31}P NMR method. The changes in the intensities of the ^{31}P NMR signals with time of the reaction of **1** (C_1 = 1.5 · 10^{-2} mol L^{-1}) with substrate **6** (C_6 = 3 · 10^{-3} mol L^{-1}) in an 80 vol.% water-propan-2-ol solution at pH 9.0 (35 °C) are presented in Fig. 5. The chemical shifts (δ ^{31}P) belong to substrate **6** (16.7 ppm), an intermediate product of ester interchange, phosphorylated AMC (16.7 ppm), and ethyl chloromethylphosphonate formed during the reaction (12.9 ppm). Signals in ^{31}P NMR spectra were identified by comparison with chemical signals of products of the reactions modeling hydrolysis[7] and ester interchange. The identity of the chemical shifts of compound **6** and phosphorylated AMC was shown by comparison of the spectra of solutions of substrate **6** and the reaction mixture containing **6** and **1** in dry propan-2-ol; both spectra contain a single signal with the chemical shift of 16.2 ppm. The formation of *p*-nitrophenoxide ion was simultaneously observed by spectrophotometry in the reaction mixture of **1** with **6** in dry propan-2-ol.

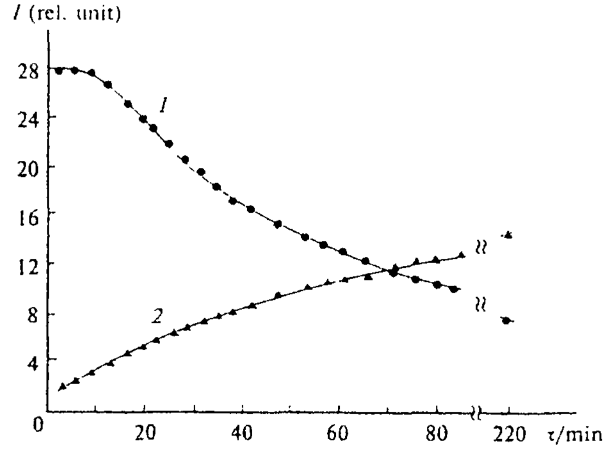


Fig. 5. Change in the intensities of the ^{31}P NMR signals in the course of the reaction of **1** (C_1 = 1.5 · 10^{-2} mol L^{-1}) with substrate **6** (C_6 = 3 · 10^{-3} mol L^{-1}) in an 80% (v/v) water-propan-2-ol solution at pH 9, 35 °C. Chemical shifts δ ^{31}P: 16.7 (*1*) and 12.9 (*2*).

The analysis of the ^{31}P NMR spectra in the course of the reaction of **1** with **6** shows that during the first 6 min the intensity of the signal with the chemical shift of 16.7 ppm remains almost unchanged; then it begins to decrease along with an increase in the intensity of the signal of the acid with the chemical shift of 12.9 ppm. This signal remains single 1 day after the beginning of the reaction. The observed rate constants of the decomposition of phosphorylated AMC and the formation of ethyl chloromethylphosphonate calculated from a first-order equation are 2.9 · 10^{-4} s^{-1} (r = 0.999) and 2.4 · 10^{-4} s^{-1} (r = 0.998), respectively. It is noteworthy that phosphorylated AMC are much less stable than phosphorylated AMP.

Thus, it is shown by the ^{31}P NMR method that the reactions of esters of phosphorus acids with AMC, as well as with AMP, occur in two stages (see Scheme 2). At the first stage, *p*-nitrophenoxide ion and phosphorylated AMC are formed, and the second, slower stage is the decomposition of the latter to form the corresponding acid.

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