## Aminolysis of O-alkyl O-4-nitrophenyl chloromethylphosphonates in reverse micellar solutions of the nonionic surfactant

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The reaction of *n*-hexylamine with O-alkyl O-4-nitrophenyl chloromethylphosphonates in toluene solutions of poly(ethylene glycol)-600 monolaurate (PM) has been studied by spectrophotometry. The reverse micelles of the nonionic surfactant increase more than tenfold the observed rate constant of aminolysis. The catalytic activity of the surfactant is practically independent of the alkyl radical length of phosphonate. An increase in the concentration of amine results in a decrease in the catalytic efficiency. The character of the dependence of the rate constant on the concentration of PM is affected by the alkyl chain length of the substrate.

Key words: phosphonates, aminolysis, micellar catalysis; nonionic surfactant; substrate specificity.

The presence of surfactants in solutions results in a noticeable change in the reactivity of organic compounds. We have previously shown<sup>1-3</sup> that the effect of reverse micelles on processes depends substantially on the structure and concentration of a surfactant and a nucleophile in the solution. However, the dependence of the catalytic effect of micelles on the structure of an organophosphorus substrate was not studied. In this work, we studied the effect of poly(ethylene glycol)-600 monolaurate (PM) micelles on the reactions of *n*-hexylamine with *O*-alkyl *O*-4-nitrophenyl chloromethyl-phosphonates in toluene.

$$C_{n}H_{2n+1}O(CICH_{2})P(O)OC_{6}H_{4}NO_{2}-p + n-C_{6}H_{13}NH_{2} ----$$
  
1--4

 $---- C_n H_{2n+1} O(CICH_2) P(O) NHC_6 H_{13} - n + HOC_6 H_4 NO_2 - p$  (1)

n = 2 (1), 4 (2), 6 (3), 8 (4)

Micelle formation of PM has been studied previously.<sup>2</sup> It has been established that in toluene at 36 °C, the critical micelle concentration (cmc) of PM ranges from  $5 \cdot 10^{-4}$  to  $2 \cdot 10^{-3}$  mol L<sup>-1</sup> (cmc-1), whereas at concentrations equal to 0.07–0.10 mol L<sup>-1</sup> (cmc-2) and 0.21–0.24 mol L<sup>-1</sup> (cmc-3), the structure of micellar aggregates is rearranged.

## Experimental

Esters 1-4 were synthesized according to the procedure described previously.<sup>4</sup> Purity of the compounds obtained was

confirmed by elemental analysis data. n-Hexylamine (highpurity grade) was kept above NaOH and distilled prior to use. The PM sample (Ferak) was used without preliminary purification. Toluene was purified by a standard method.

The kinetics of the reactions was studied using spectrophotometry on Specord UV-VIS and SF-26 spectrophotometers by the appearance of the absorption band of 4-nitrophenol at 317 nm. The concentration of the substrate in all experiments was  $1 \cdot 10^{-4}$  mol L<sup>-1</sup>. The values of observed first-order rate constants (k) were calculated by the least-squares method on an IBM PC.

## **Results and Discussion**

In the absence of surfactants, the dependence of the observed first-order rate constant of reaction (1) on the concentration of amine  $(C_A)$  is nonlinear (Fig. 1) and can be described by Eq. (2).

$$k = k_1 C_A + k_2 C_A^2$$
 (2)

The  $k_1$  and  $k_2$  values for the reactions involving compounds 1-4 are presented in Table 1. The  $k_2$  constant in Eq. (2) can be assigned to a catalytic process involving the second amine molecule.<sup>5</sup> The decrease in the rate constant of the reaction of ester 3 with *n*-hexylamine as compared to that of the aminolysis of compounds 1 and 2 may be the result of steric effects. However, as the length of the hydrocarbon radical of phosphonate increases, association of the substrate in the nonpolar medium most likely begins to play a favorable role along with the steric factor. This leads to higher rates of aminolysis of ester 4 than those of ester 3 (see Fig. 1).

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**Table 1.** Coefficients in Eqs. (2) and (3) describing the kinetics of aminolysis of esters 1-4 in toluene in the presence of PM (0.05 mol  $L^{-1}$ ) and in the absence of PM at 40 °C

Substrate	$k_1 \cdot 10^4$ /L mol <sup>-+</sup> s <sup>-1</sup>	$k_2 \cdot 10^4$ /L <sup>2</sup> mol <sup>-2</sup> s <sup>-1</sup>	$k_3 \cdot 10^3$ /L mol <sup>-1</sup> s <sup>-1</sup>
1	1.1	3.6	3.3
2	1.1	3.7	2.5
3	1.5	1.5	2.6
4	1.2	2.4	3.1



Fig. 1. Dependences of the observed rate constant (k) of aminolysis of esters 1 (1), 2 (2), 3 (3), and 4 (4) on the concentration of *n*-hexylamine  $(C_A)$  in toluene at 40 °C in the absence of the surfactant.

In the presence of PM, the rate constant of reaction (1) increases more than by an order of magnitude (Figs. 2-4, Table 2). The dependence of k on the amine concentration becomes linear (see Fig. 2) and can be described by the equation

$$k = k_3 C_{\mathsf{A}^-} \tag{3}$$

The  $k_3$  values of the aminolysis of phosphonates in the presence of PM (0.05 mol L<sup>-1</sup>) are presented in Table 1. The transfer of the reactants from the solvent bulk to the polar nucleus of a micelle results in replacement of the microenvironment of the reactants. The nucleus of the PM micelle is formed by head groups containing the carbonyl group and hydroxyethyl fragments capable of forming hydrogen bonds. The first order of the reaction with respect to amine in Eq. (3) can be due to the fact that the surfactant begins to act as the catalyst of the process instead of the second nucleophile molecule.

The dependences of the observed rate constants of aminolysis of phosphonates on the surfactant concentration are presented in Figs. 3 and 4. The character of the



Fig. 2. Dependences of the observed rate constant of aminolysis of esters 1 (1), 2 (2), 3 (3), and 4 (4) on the concentration of *n*-hexylamine in toluene in the presence of PM (0.05 mol  $L^{-1}$ ) at 40 °C.



Fig. 3. Dependences of the observed rate constant of the reaction of *n*-hexylamine with esters 1 (1), 2 (2), 3 (3), and 4 (4) on the concentration of PM in toluene at 40 °C;  $C_A = 0.05 \text{ mol } L^{-1}$ .

curves changes with an increase in the length of the hydrocarbon radical of the substrate. For compounds 1-3, the concentration dependence tends to reach a plateau, while in the case of ester 4, the curve passes through a maximum. The catalytic effect of surfactants is related to the concentration of the reactants when they are transferred from the solvent bulk to micelles and to the influence of the micellar microenvironment on the transition state of the process. The concentration curves reach a plateau, which is explained by the com-



Fig. 4. Dependences of the observed rate constant of the reaction of *n*-hexylamine with ester 1 on the concentration of PM in toluene at 40 °C (1), 50 °C (2), and 60 °C (3);  $C_A = 0.3 \text{ mol } L^{-1}$  (1) and 0.05 mol  $L^{-1}$  (2, 3).

plete bonding of the reactants by micelles of the surfactants.<sup>6</sup> However, when the reactants are strongly bound, they are transferred to the micellar pseudo-phase already at a low concentration of the surfactant. In this case, further increase in the content of the surfactant in the solution can result in a decrease in the rate constant due to dilution of the reactants and in the appearance of maxima in the kinetic curves.<sup>6</sup> Table 2 presents the parameters of micelle-catalyzed reactions in the cmc-1--cmc-2 concentration range calculated by the equation<sup>7</sup>

$$k = \frac{k_{\rm m} K_{\rm bond} (C_{\rm S} - \rm cmc) + k_0}{1 + K_{\rm bond} (C_{\rm S} - \rm cmc)}$$

where  $k_m$  and  $k_0$  are the rate constants of the reaction in the micellar phase and the solvent bulk, respectively;

Table 2. Parameters of the PM-catalyzed reaction of n-hexylamine<sup>n</sup> with esters 1-4 in toluene

Subs- trate	<i>Т</i> /°С	$\frac{k_{\max} \cdot 10^4}{/\mathrm{s}^{-1}}$	$k_{\text{max}} \cdot k_0^{-1}$	$\frac{k_{\rm m} \cdot 10^4}{/{\rm s}^{-1}}$	K <sub>bond</sub> /L mol <sup>-1</sup>	cmc-1 $\cdot$ 10 <sup>3</sup> /mol L <sup>-1</sup>
1	40	3.9	35	6.3	5.6	1
2	40	3.2	29	6.5	4.3	1
3	40	3.3	31	6.7	4.3	I
4	40	3.5	32	7.2	5.0	4.5
15	40	20	28	41	4.7	4
1	50	5.2	41	20	1.9	2.5
1	60	6.9	49	33	1.3	1_4

<sup>*a*</sup>  $C_{\rm A} = 0.05 \text{ mol } L^{-1}$ . <sup>*b*</sup>  $C_{\rm A} = 0.3 \text{ mol } L^{-1}$ .

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with surfactant micelles; and  $C_S$  is the surfactant concentration. It can be seen that the  $K_{bond}$  value for the substrate is almost independent of the alkyl chain length. In the case of micelle-bound phosphonate, an increase in the length of its hydrocarbon radical can result, on the one hand, in the replacement of the region of localization of the substrate in the micelle and, on the other hand, in a change in the parameters (cmc, size, etc.) of the micelles. The rearrangement of the structure of micellar aggregates<sup>8-10</sup> can also result in a change in the parameters of the whole system (dielectric constant, packing density of surfactant molecules in the aggregate. solubilization of the reactants). As a result, for substrates with different hydrophobicities, the dependences of the rate constant on the surfactant concentration can be different.

The experimentally observed catalytic activity of reverse micelles (the  $k_{max}/k_0$  ratio, where  $k_{max}$  are the maximum k values that are achieved in the concentration dependences) changes slightly as the alkyl chain of the substrate increases (see Table 2). The maximum catalytic effect was observed for aninolysis of phosphonate with the ethyl substituent. An increase in the concentration of *n*-hexylamine results in a decrease in the catalytic effect of the surfactant (see Table 2).

The effective values of activation parameters of the reaction of ester 1 with *n*-hexylamine are presented in Table 3. It can be seen that in the presence of PM, the activation energy increases, and the absolute value of activation entropy decreases, *i.e.*, in the case of aminolysis of 4-nitrophenyl ester of acids of tetracoordinated phosphorus in the presence of the cationic surfactant in chloroform,<sup>3</sup> the acceleration of aminolysis of compound 1 in micellar solutions of PM is caused by a favorable change in the entropy factor.

Thus, the catalytic activity of reverse micelles of the nonionic surfactant in the reactions of n-hexylamine with O-alkyl phosphonates depends weakly on the hydrophobicity of the substrate.

**Table 3.** Effective values of activation energy  $(E_{a,eff})$  and entropy  $(\Delta S_{eff}^{*})$  of the PM-catalyzed reaction of *n*-hexylamine with ester 1 in toluene

$C_{\rm PM}$ /mol L <sup>-1</sup>	E <sub>a,eff</sub> /kJ_mol <sup>-1</sup>	$-\Delta S_{eff}^{*}$ /J mol <sup>-1</sup> K <sup>-1</sup>
0	10.5	315
0.04	13.7	284
0.08	17.9	266
0.10	22.2	251
0.14	25.6	239
0.18	26.0	236
0.22	23.8	242
0.26	24.5	240
0.30	25.2	238

Note.  $C_{\rm A} = 0.05 \text{ mol } L^{-1}$ .

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