The inverted micellar catalysis of the reaction of 2-aminomethylphenols with 4-nitrophenyl bis(chloromethyl)phosphinate

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The parameters of the reaction of *para*-substituted 2-aminomethylphenols with 4-nitrophenyl bis(chloromethyl)phosphinate in toluene catalyzed by reversed micelles of polyethylene glycol-600 monolaurate depend on the nucleophile structure. The efficiency of the catalytic action increases in the series of substituents $C_9H_{19}{}^i$ < H < Cl. An increase in the catalytic activity of micelles in the region of structural rearrangement of micelle aggregates was observed.

Key words: micellar catalysis; micelle structure; nonionic surfactant; 2-aminomethylphenols.

Micelles of nonionic surfactants exhibit a catalytic effect in nonaqueous media.[1—3] The influence of reversed micelles on nucleophilic substitution in esters of phosphorus-containing acids has scarcely been studied. Previously,[6] we demonstrated a high catalytic activity of polyethylene glycol-600 monolaurate (PM) and mono-*p*-isooctylphenyl ether of polyethylene glycol-450 in the aminolysis of 4-nitrophenyl phenyl (chloromethyl)phosphonate[4,5] and a high activity of PM in the reaction of *p*-nitrophenyl bis(chloromethyl)phosphinate (PNCP) with 2-alkylaminomethylphenols having long-chain alkyl substituents at the nitrogen atom.

In the present work, we studied the effect of PM reversed micelles on the reactions of *para*-substituted 2-aminomethylphenols (AMP), namely, 2-dimethylaminomethyl-4-isononylphenol (**1**), 2-dimethylaminomethylphenol (**2**), and 2-dimethylaminomethyl-4-chlorophenol (**3**) with PNCP in toluene.

Experimental

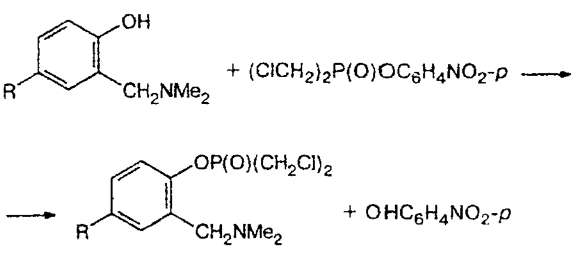
2-Aminomethylphenols were synthesized as described previously;[7,8] PNCP was prepared by a known procedure.[9] A PM sample of Ferak was used as received. Phenol and *N*,*N*-dimethylbenzylamine (DBA) were distilled prior to use. Toluene was purified by the standard procedure.

The reaction kinetics was studied by spectrophotometry on Specord UV-VIS and SF-26 instruments based on the intensity of the absorption band of 4-nitrophenol at 322.6 nm. The substrate concentration in the experiments with AMP was $5 \cdot 10^{-5}$ mol L^{-1}; that in experiments with PhOH was $2 \cdot 10^{-4}$ mol L^{-1} without a surfactant or $1 \cdot 10^{-4}$ mol L^{-1} in the presence of PM. The observed first-order rate constants (*k*) were calculated by the least-squares method using an IBM PC.

Results and Discussion

In a nonaqueous low-polarity medium, the process under consideration follows the pathway given below (Scheme 1) to yield phosphorylated AMP and 4-nitrophenol.

Scheme 1



R = $C_9H_{19}{}^i$ (**1**), H (**2**), Cl (**3**)

The aminomethyl group present in the AMP molecule facilities the phenolysis due to the formation of an intramolecular hydrogen bond[10] and to the enhancement of the nucleophilicity of the reaction site. The reaction of PNCP with unsubstituted phenol cannot be detected during 6 h even at high nucleophile concentrations (up to 5 mol L^{-1}). The introduction of DBA into the system accelerates the phenolysis due to the formation of an intermolecular hydrogen bond between phenol and amine.[11] The rate constant for

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the reaction of PhOH (0.01 mol L^{-1}) with PNCP in the presence of DBA (0.01 mol L^{-1}) in toluene at 40 °C is $6.8 \cdot 10^{-5}$ s^{-1}. Meanwhile, the rate constant for the reaction of compound **2** (0.01 mol L^{-1}) with PNCP under the same conditions is 57 times as high ($3.9 \cdot 10^{-3}$ s^{-1}).

The observed rate constants for the reactions of compounds **1**—**3** with PNCP depend linearly on the AMP concentration (C_{AMP}), and at 40 °C they obey the equation $k = k_{2,0} \cdot C_{AMP}$, where the $k_{2,0}$ values for **1**—**3** are 0.71, 0.39, and 0.054 mol^{-1} L s^{-1}, respectively.

In micellar solutions of PM, the k value increases with increasing surfactant concentration (C_{PM}) (Figs. 1, 2). According to the data published previously,[4] the critical micelle concentration of PM in toluene at 36 °C is $5 \cdot 10^{-4}$—$2 \cdot 10^{-3}$ mol L^{-1} ($C_{mc\text{-}1}$), whereas at concentrations of 0.07—0.1 mol L^{-1} ($C_{mc\text{-}2}$) and 0.21—0.24 mol L^{-1} ($C_{mc\text{-}3}$), structural rearrangement of micelle aggregates occurs. Plots of k *vs* C_{PM} for nucleophilic substitution in esters of tricoordinated phosphorus acids are characterized by a plateau[4] or by a maximum,[4,5] which can be described[12,13] by Eqs. (1) or (2), respectively.

$$(k - k_0)/(k_m - k) = K_{bond} \cdot C_{surf}, \qquad (1)$$

where k_0 and k_m are the rate constants for the reaction in the solvent bulk or in the micellar phase, K_{bond} is the normalized constant of the binding of the substrate to the surfactant micelles, and C_{surf} is the PM concentration corrected for C_{mc}

$$k = \frac{(k_m / V)K_A K_B C_{surf} + k_0}{(1 + K_A C_{surf})(1 + K_B C_{surf})}, \qquad (2)$$

where V is the molar volume of the surfactant, K_A is the constant of the binding of the substrate to the micelle, and K_B is the constant of the binding of the nucleophile to the micelle.

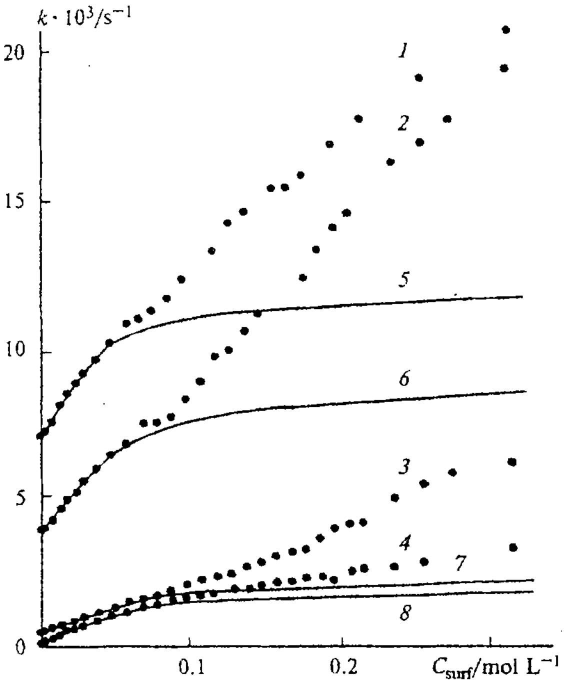

Fig. 1. Experimental (*1, 2, 3, 4*) and calculated (*5, 6, 7, 8*) observed rate constants (k) for the reaction of PNCP with **1** (*1, 5*), **2** (*2, 6*), and **3** (*3, 7*) and PhOH (0.01 mol L^{-1}) in the presence of DBA (0.01 mol L^{-1}) (*4, 8*) *vs* the concentration of PM (40 °C, C_{AMP} = 0.01 mol L^{-1}).

In the $C_{mc\text{-}1}$—$C_{mc\text{-}2}$ concentration range, the plots shown in Figs. 1 and 2 are well described by Eq. (1); therefore, below we use only the data calculated from this equation.

The k values found experimentally for surfactant concentrations of more than $C_{mc\text{-}2}$ exceed the calculated values (see Fig. 1); this can be due to structural rearrangement in micellar aggregates. A loss of symmetry by reversed micelles changes the dielectric constant, the density of packing of surfactant molecules in the micelle,[14] solubilization of the reactants,[15,16] and, apparently, their mutual orientation. Combination of these factors results in an enhanced catalytic activity of micelles in the $C_{mc\text{-}2}$ and $C_{mc\text{-}3}$ regions.

Table 1 presents the k_m and K_{bond} values calculated from the dependence of k on C_{PM} in the $C_{mc\text{-}1}$—$C_{mc\text{-}2}$ range by the least-squares method using Eq. (1). In the series of AMP **1**, **2**, and **3** the k_m value and the constant for the substrate binding to micelles decrease. The latter may be due to the increase of the competing interaction

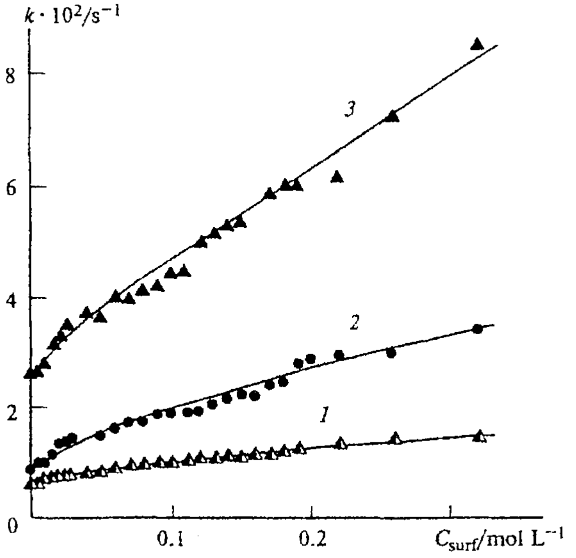

Fig. 2. The observed rate constant (k) for the reaction of PNCP with **1** as a function of the concentration of PM in toluene at T/°C = 25 (*1*), 40 (*3*), and 55 (*2*); C_{AMP}/mol L^{-1} = 0.01 (*1, 2*), 0.035 (*3*).

Table 1. Parameters of micelle-catalyzed reactions of PNCP with AMP (0.01 mol L^{-1}) and PhOH (0.01 mol L^{-1}) in toluene solutions of PM

Nucleophile	T /°C	$k_m \cdot 10^3$ /s^{-1}	K_{bond} /mol^{-1} L	$C_{mc-1} \cdot 10^3$ /mol L^{-1}
1	40	12	30	3.7
2	40	9.4	19	6.3
3	40	2.7	11	7.5
1*	40	43	65	4.8
1	25	7.5	66	4.7
1	55	19	26	3.7
PhOH**	40	2.5	13	1.6

* C_{AMP} = 0.035 mol L^{-1}. ** In the presence of 0.01 mol L^{-1} of DBA.

Table 2. Bimolecular rate constants for the reaction of AMP with PNCP in toluene solutions of PM at 40 °C

AMP	C_{PM} /mol L^{-1}	$k_{2,PM}$ /mol^{-1} L s^{-1}	K*	K_1**
1	0.04	0.92	1.3	
1	0.08	1.1	1.5	1.6
1	0.26	1.7	2.4	
2	0.08	0.85	2.2	2.0
2	0.26	1.7	4.3	
3	0.08	0.17	3.1	2.6
3	0.26	0.44	8.1	

* $K = k_{2,PM}/k_{2,0}$. ** $K_1 = K_{PM\ 0.26\ M}/K_{PM\ 0.08\ M}$.

Table 3. Effective activation energy and activation entropy of the reaction of PNCP with **1** (0.01 mol L^{-1}) in toluene as a function of the PM concentration

C_{PM} /mol L^{-1}	$E_{a,eff}$ /kJ mol^{-1}	$-\Delta S^{\neq}_{eff}$ /J K^{-1} mol^{-1}
0	12.7	254
0.015	14.6	246
0.04	18.7	232
0.1	19.8	226
0.14	18.4	230
0.2	18.4	228
0.22	19.8	227
0.26	21.8	216
0.32	22.5	213

of AMP with polar surfactant fragments upon an increase in the nucleophile dipole moment.[17]

The dependence of k on the concentration of AMP for a micellar-catalyzed reaction is linear. It is described by the equation $k = k_{2,PM} \cdot C_{AMP}$, and the slope of the curves depends on the surfactant concentration (Table 2). The transition from compound **1** to **2** and to **3** at a specified PM concentration results in lower values of $k_{2,PM}$. However, since the $k_{2,0}$ values decrease in this series more significantly than $k_{2,PM}$, the catalytic activity (K) increases (see Table 2). The parameter K_1 reflects the change in the catalytic activity upon the rearrangement of the micelle structure, because PM concentrations of 0.08 and 0.26 mol L^{-1} are associated with the ranges of surfactant concentrations preceding and following the rearrangement of aggregates. The K_1 value increases in the series **1** < **2** < **3**; therefore, the strongest influence of the structural factor on the catalytic activity of micelles is typical of the most polar chloro-substituted AMP.

The temperature has no influence on the character of dependence of k on the surfactant concentration (see Figs. 1 and 2). Over the whole range of PM concentrations studied, which corresponds to the micellar state of PM in the solution, the effective activation energy of the reaction of PNCP with **1** is higher, while the magnitudes of the activation entropy are lower than those without a surfactant (Table 3), *i.e.*, the acceleration of the process in PM solutions is due to the entropy factor.

Thus, the catalytic activity of the reversed micelles of PM toward the reaction of PNCP with AMP depends on the structure of the nucleophile (the nature of the substituent in the benzene ring of AMP) and the surfactant concentration. The catalytic activity increases with a decrease in the hydrophobicity, increase in the polarity of the nucleophilic reagent, and an increase in the PM concentration, favorable for the structural rearrangement of the micelles.

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