Reactions of esters of tetracoordinated phosphorus acids with nucleophilic reagents in highly organized media

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Characteristic features of reactions involving esters of phosphorus-containing acids in highly organized media (micelles, liquid crystals, vesicles, and emulsions) are surveyed.

Key words: highly organized media; esters of tetracoordinated phosphorus acids; nucleophilic substitution; catalysis.

Organophosphorus compounds (OPC) are widely used as pesticides, medicines, and components of various chemical processes. Therefore, it was of interest to comprehensively study their chemical reactivity and the ways to control it. Highly organized media (micelles, liquid crystals, vesicles, microemulsions) make it possible to change the rates and the mechanisms of chemical reactions. In addition, the use of highly organized media has much in common with the modeling of the enzymatic catalysis.[1,2]

Micellar systems constitute one of the most studied fields in which highly organized media have an effect on processes involving OPC. For quantitative description of the catalytic action of micelles, a number of models are used, such as the "enzyme" model, suggested by Menger and Portnoy,[3] and the pseudo-phase model developed by Berezin and coworkers.[4] Reactions involving OPC have served as a convenient base for the development of an ion-exchange model,[5] its modification,[6] and a model based on the law of mass action.[7] Quantitative processing of the kinetic data for micellar reactions makes it possible to characterize the reactivities of compounds in a micellar microenvironment and to evaluate the efficiency of binding the reactants to micelles. The reactivity of OPC in micellar solutions was studied in relation to reactions of esters derived from tetracoordinated phosphorus acids (TPA) with various nucleophiles[8–12] and also reactions involving compounds of tricoordinated phosphorus.[13] We have systematized the available data taking into account the type of nucleophile participating in a reaction and the reaction mechanism.

Micellar catalysis of reactions of esters of phosphorus-containing acids with inorganic nucleophiles

Reactions of esters of TPA with inorganic nucleophiles in micellar solutions of surfactants have been studied using completely and incompletely substituted esters of phosphoric, thiophosphoric, phosphonic, and phosphinic acids as examples.

In the case of completely substituted esters of phosphorus-containing acids, hydroxide,[14–24] fluoride,[14–18] hydroperoxide,[25–27] and perborate ions[28] were used as inorganic nucleophiles. These ions react with the substrates by an S_N2P mechanism.[29] The character of the effect of micelles on these processes and the extent to which these processes are affected depend on the nature of the micelles (the sign of their charge), the length of the hydrocarbon radical and the structure of the head group of the surfactant, the structure of the substrate, the concentrations of the reactants, and on the electrolytes or other compounds added to the system. The reactions of 4-nitrophenyl diphenyl phosphate (NPDP) with hydroxide and fluoride ions are catalyzed by cationic micelles of cetyltrimethylammonium bromide (CTAB), whereas anionic micelles of sodium dodecyl sulfate (SDS) and an nonionic surfactant, poly(ethylene glycol)-1050 dinonylphenyl ether (Igepal), inhibit the process.[16] The effect of the nature of the surfactant is explained, as a rule, by electrostatic reasons: the attraction of nucleophilic counterions to the micellar surface of the cationic surfactant leads to collection of the reactants in micelles and thus to acceleration of bimolecular processes, while in the case of a nonionic or anionic surfactant, the negatively charged nucleophiles are weakly bound to the micellar surface or are even repelled from a micellar surface having the like charge.[10]

An increase in the length of the hydrocarbon radical of a cationic surfactant results in an increase in the catalytic activity of micelles. For example, decyltrimethylammonium bromide has a slight effect on the alkaline hydrolysis of NPDP, while dodecyltrimethylammonium bromide accelerates this reaction 3.5-fold, and CTAB accelerates it 12-fold.[14,16] The reaction of NPDP with fluoride anion is accelerated 11-fold by

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dodecyltrimethylammonium bromide[14] and 35-fold by CTAB.[16] The increase in the catalytic activity of micelles with increase in the length of the hydrocarbon radical may be due to the alteration of properties of the micellar surface (decrease in the charge density, the more pronounced "roughness"). The fact that the micelle surface becomes more rough facilitates penetration of a substrate into the Stern layer and favors its efficient binding.[14]

An increase in the length of the hydrocarbon radical of an anionic surfactant results in an increase in the inhibitory effect of the micelles, which has been shown in relation to the alkaline hydrolysis of *O*-ethyl *S*-propyl *O*-2,4-dichlorophenyl thiophosphate (Ethaphos) in the presence of sodium ethyl *N*-alkylaminomethylphosphonates of general formula $C_nH_{2n+1}NHCH_2P(O)O^-OEt\ Na^+$, n = 9, 10, 12.[30]

The presence of aryl fragments or the second quaternary nitrogen atom in the head group of the cationic surfactant has an effect on the efficiency of micellar catalysis in the reactions of completely substituted esters of TPA with inorganic nucleophiles.[15,18,22] The introduction of aryl fragments increases the catalytic activity of the cationic surfactant.[15,22,28] For example, the catalytic activity of micelles of hexadecyltriphenylphosphonium bromide in the decomposition of diethyl 4-nitrophenyl phosphate (Para-oxon) in aqueous solutions containing sodium perborate is substantially higher than that of tributylhexadecylphosphonium bromide[28]. The high catalytic effect of hexadecyldimethylphenylammonium bromide compared to that of CTAB in the reaction of OH^- and F^- with NPDP can be attributed[15] to the stronger binding of the substrate to micelles resulting from dispersion interactions. The higher catalytic activities of benzylhexadecyldimethylammonium bromide and hexadecyldimethylphenylammonium bromide compared to that of CTAB in the alkaline hydrolysis of phosphates and phosphonates is explained by the fact that the interaction of hydroxide ions with substrates in the "pseudobenzene" Stern layer of micelles containing aryl groups is facilitated owing to partial dehydration of the reactants.[22]

Transition from mono- to dicationic surfactants increases in some cases the efficiency of the catalysis. The micellar aggregates formed by the surfactants with two cationic centers $RN^+Me_2(CH_2)_nN^+Me_2R\ 2Br^-$ and $RN^+Me_2(CH_2)_3NH(CH_2)_3N^+Me_2R\ 2Br^-$ (R = n-$C_{16}H_{33}$, n = 4, 6) (**1**) exert stronger catalytic effects (up to 5-fold) on the hydrolysis of NPDP[18] and ethyl bis(4-nitrophenyl) phosphate,[34] respectively, than the CTAB micelles. This is due to the stronger binding of the reactants to the micelles of a dicationic surfactant. The constants of binding between the substrate (**A**) and nucleophile (**B**) in solutions of **1** and CTAB calculated from the Berezin equation[35] using the kinetic data are (K_b/mol^{-1} L) 1720 (**A**, **1**), 1370 (**A**, CTAB), 180 (**B**, **1**), 70 (**B**, CTAB).[34]

The effect of the head group of an anionic surfactant in the reactions of esters of TPA with inorganic nucleophiles has been studied[30] in relation to the alkaline hydrolysis of Ethaphos in micellar solutions of disodium monododecyl phosphate (MDPA), sodium *O*-ethyl *N*-dodecylaminomethyl phosphate (EDAPA), and SDS. In the presence of these surfactants, the rate of the reaction decreases 40—90-fold and the inhibitory effect increases in the order MDPA < EDAPA < SDS. The K_b of the substrate with the micelles varies in the same order (3000, 4200, and 5300 mol^{-1} L, respectively, 25 °C, 0.1 mol^{-1} L of NaOH).

When a substrate, poorly soluble in water, passes from the aqueous phase to a weakly polar micellar environment, with the simultaneous electrostatic repulsion of nucleophilic OH^- ions from the micellar surface of an anionic surfactant, the reactants are separated from each other and, consequently, the rate constants of the reactions dramatically decrease. The fact that MDPA was the least active may be due to the relatively weak binding between the Ethaphos and micellar aggregates.[30]

The dependence of the observed rate constants (k_{obs}) of reactions of OPC on the concentration of the nucleophilic reagent in a micellar solution for cationic surfactants is nonlinear, unlike that for the reaction in water. As the concentration of the nucleophile increases, the rate constant initially dramatically increases, and then the increase in the k_{obs} decelerates.[14,36] The linear character of the dependence of k_{obs} on the concentration of the nucleophile, when its concentration is low, is due to ion exchange: the higher the concentration of the nucleophilic anions, the higher the extent to which they replace the indifferent counterion in the Stern layer. At higher concentrations of the nucleophile, its electrolytic effect is also manifested[14] as a decrease in the potential of the surface, which decreases binding of the nucleophilic anions.[36]

In the case of anionic or nonionic surfactants, an increase in the concentration of the reagents also affects the activity of micelles. An increase in the concentration of the alkali results in a decrease in the inhibitory effect of the EDAPA and SDS micelles on the alkaline hydrolysis of Ethaphos.[37] An increase in the concentration of the reagent acting as an electrolyte leads to a decrease in the negative charge of micelles, since it is sorbed more efficiently on the surface of counterions. This decreases the electrostatic repulsion of hydroxide anions from micelles and facilitates the hydrolysis. In the case of nonionic poly(ethylene glycol)-450 mono-4-isooctylphenyl ether (Triton X-100), an increase in the concentration of the alkali increases the inhibitory effect of micelles on the hydrolysis of dimethyl 4-nitrophenyl thiophosphate (Methaphos).[37] An increase in the alkalinity of the solution enhances the salting-out effect of the electrolyte (alkali), thus leading to a stronger binding of the substrate to micelles (K_b of the substrate increases). The binding of hydroxide ions is still slight,

Table 1. Catalytic activity of CTAB micelles in the solvolysis of 4-nitrophenyl phosphonates (0.05 *M* phosphate buffer solution, pH 6.85, 25 °C) and in the alkaline hydrolysis of phosphates

Substrate	$k_0 \cdot 10^3$ /s^{-1}	k_m /s^{-1}	k_m/k_0	K/N /mol^{-1} L
$ClCH_2P(O)(OEt)OC_6H_4NO_2$-4 (**2**)	0.04	0.007	175	200
$ClCH_2P(O)(OPh)OC_6H_4NO_2$-4 (**3**)	0.40	0.071	178	4300
$ClCH_2P(O)(OBu^n)OC_6H_4NO_2$-4 (**4**)	0.035	0.067	2000	1000
$MeP(O)(C_6H_4NO_2\text{-}4)_2$ (**5**)	0.34	0.1	295	1800
$PhP(O)(OC_6H_4NO_2\text{-}4)_2$ (**6**)	0.36	0.052	144	7500
$(EtO)_2P(O)OC_6H_4NO_2$-4[a] (**7**)	0.085[b]	—	9[b,c]	—
$(n\text{-}C_6H_{13}O)_2P(O)OC_6H_4NO_2$-4[a] (**8**)	0.075[b]	—	18[b,c]	—
$(PhO)_2P(O)OC_6H_4NO_2$-4[a] (**9**)	4.9[b]	—	12[b,c]	—

[a] See Ref. 19. [b] 0.01 mol L^{-1} NaOH, 25 °C. [c] The maximum observed increase in the rate constant.

which results in an even greater separation of the reactants in the system and, consequently, to a more substantial decrease in k_{obs}.

In a study of micellar-catalyzed reactions, it is important to take into account the effect of the components of the buffer solution. This problem is complicated by the fact that the latter can act as reagents and also exhibit the salting effect.[34,37,38] It is known that both the alkaline hydrolysis of TPA esters and the reaction involving borate anions are sensitive to the effect of micelles of a cationic surfactant. The relatively higher concentrations of components of the buffer solution suggest that in micellar solutions, along with the attack of the hydroxide ion on the substrate, a substantial contribution is made by the buffer catalyzed hydrolysis.[34,38] The salting effect caused by the buffer components is manifested in the alkaline hydrolysis of bis(4-nitrophenyl) methylphosphonate in micellar solutions of CTAB as a decrease in the efficiency of micellar catalysis at high concentrations of borate and phosphate ions.[37] This may be due to the displacement of the OH^- ions from the Stern layer and saturation of the layer with less reactive components of the buffer solution.

An example of the effect of micelles on the reactions of TPA esters with noncharged inorganic nucleophiles is provided by a study of the spontaneous hydrolysis of medicinal preparations, Nibuphin (4-nitrophenyl di-*n*-butylphosphinate) and Pyrophos (tetraethyl monothionopyrophosphate), in micellar solutions of anionic or nonionic surfactants.[39] A decrease in the rate of the process results in an increase in the hydrolytic stabilities of these preparations. For example, in a 0.05 mol L^{-1} solution of SDS, the hydrolysis of Nibuphin decelerates by a factor of 8, and the hydrolysis of Pyrophos decelerates by a factor of 4.

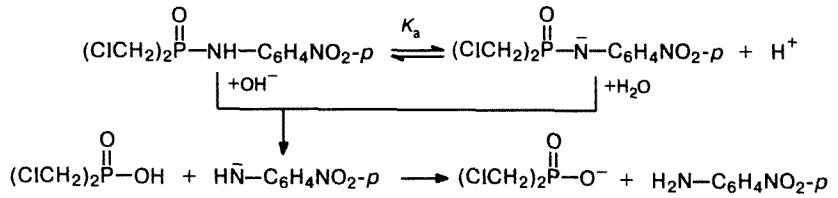
The efficiency of micellar-catalyzed reactions involving esters of TPA depends as well on the structural features of the substrate. In a study of the catalytic effect of CTAB micelles on the solvolysis of 4-nitrophenyl phosphonates and the alkaline hydrolysis of phosphates,[19,40] no correlation between the efficiency of binding of the substrate to the micelles and the catalytic activity of the latter has been found (Table 1). Replacement of the Me group in compound **5** by the Ph group (compound **6**) leads to an increase in the constant of binding of the substrate to micelles (K/N, where N is the aggregation number of surfactant molecules in the micelle).

As this takes place, the catalytic effect of the micelles (the ratio of the rate constant of the reaction in the micellar phase to the rate constant in water, k_m/k_0) decreases twofold. The increase in the binding by more than an order of magnitude on going from phosphonate **2** to **3** does not result in an increase in the catalytic activity. However, the replacement of the Et group in compound **2** by a Bu group (compound **4**) increases the K/N value and the catalytic activity of the micelles. The absence of a simple correlation between the efficiency of solubilization of the substrate by micelles and the catalytic activity of the micelles can be associated with different ways of localization and orientation of the reactants in the CTAB micelles. It is known that polar and aromatic parts of molecules are normally arranged in the surface layer of cationic micelles, whereas nonpolar aliphatic chains tend to plunge into the low-polarity core of the micelle.[14,41] The presence of phenyl substituents substantially increases the degree of binding of the substrate to the micelle, probably due to specific interactions of the π-electron system of the ring with the components of the Stern layer of the micelle.[41] However, this can restrict somewhat the mobility of the molecule and, consequently, increase the catalytic activity of micelles only slightly (compounds **2** and **3**, **7** and **9**) or even decrease it (compounds **5** and **6**). An increase in the length of the alkyl substituents is favorable for the binding of the substrate and also for deeper plunging of the latter in the boundary area of the Stern layer and of the micelle core; thus, the molecule is arranged in such a way that the alkyl substituents are directed toward the core of the micelle. For compounds **2** and **4**, **7** and **8** (see Table 1), the overall effect of these factors is positive, which leads to enhancement of the catalytic action of micelles.

Micellar catalysis of the hydrolysis of 4-nitroanilide of bis(chloromethyl)phosphinic acid (NCPA), which exists in alkaline media (pK_a 9.55)[43] both in a neutral and in an anionic form, has been studied.[42] The determination of the contributions of these forms to the overall process is hampered by the fact that the hydrolysis yields in both cases the same products (Scheme 1).

However, the study of the effect of surfactant micelles on this reaction in the 6.86—13.0 pH range made it possible to conclude[42] that both the neutral and the anionic forms of the substrate are reactive. In solution of CTAB at pH values lower than the pK_a of the anilide, micelles of the cationic surfactant catalyze the hydrolysis; with the pH lying in the region of pK_a, they exert no

Scheme 1



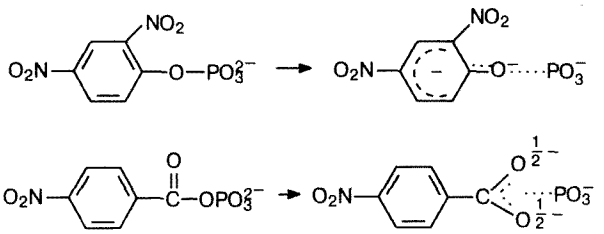
catalytic effect, and at pH > pK_a, they inhibit the process. In solutions of SDS, the reactions are inhibited by the micelles of the anionic surfactant at pH ~ pK_a, and at high pH values, no effect is observed. This approach does not solve the question of the quantitative contribution of each of the substrate forms; however, it makes it possible to give preference to one or the other of these pathways. In the pH > pK_a region, the hydrolysis of the ionic form of the anilide predominates, and at pH < pK_a, the major contribution is made by the reaction of the neutral form of NCPA.[42]

When the anionic forms of acid esters of TPA react with inorganic nucleophiles (OH^- or H_2O), the P—O bond cleaves by the S_N2P or S_N1P mechanism, which affects the way in which surfactant micelles influence these processes. For example, cationic micelles can affect the spontaneous hydrolysis of dianionic and monoanionic forms of monoesters of phosphorus-containing acids in different ways.[15,16,44–47] The constants of binding of the anions derived from acid esters of TPA to the micelles of a cationic surfactant are rather high, due to not only hydrophobic interactions, but also electrostatic interactions. However, the crucial role in the micellar catalysis of monomolecular processes is played by the effect of micellar microenvironment on the transition state of the process (solvation and electrostatic effects), rather than by the collection of the reactants. The decomposition of aryl phosphate dianion may also be favored by the variation of the angles at the phosphorus—oxygen bond, caused by the specific interactions of the anionic substrate with the quaternary ammonium ion on the micelle surface, which results in molecular strain and in an increase in the energy of the molecules, and brings the structure of the initial state of the substrate closer to the transition state structure.[45]

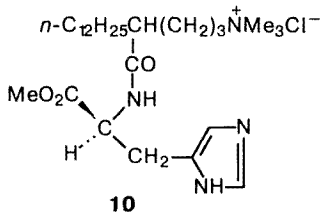
The efficiency of micellar catalysis of monomolecular processes depends on the degree of charge delocalization in the transition state of the reaction.[48] For example, in the hydrolysis of the 2,4-dinitrophenyl phosphate dianion in micellar solutions of a cationic surfactant, k_{obs} increases to a larger degree than in the case of the hydrolysis of the 4-nitrobenzoyl phosphate dianion,[44] which forms a transition state with a less delocalized charge (Scheme 2).

The presence of functional groups in the molecule of a cationic surfactant has an effect on the catalytic activity of micelles in a monomolecular process. The efficiency of the catalysis of the spontaneous hydrolysis of the 2,4-nitrophenyl phosphate dianion by the micelles of histidine surfactant (**10**) (Scheme 3) is somewhat lower than that of the catalysis by CTAB micelles.[49]

Scheme 2



Scheme 3



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The micelles of a cationic surfactant have a slight effect on the rate of the hydrolysis of the monoanion of phosphate monoesters.[31,44] For example, the monoanion of 4-nitrophenyl phosphate is not activated by CTAB micelles, although it is efficiently bound. It has been suggested that the micelles hamper the proton transfer, which is an important step of decomposition of the monoanion.[9,45] It has been found that the formation of micelles from the substrate has no effect on the rate of the hydrolysis of the monoanions derived from long-chain monoalkyl phosphates.[50] The rates of hydrolyses of *n*-decyl phosphate and methyl phosphate monoanions are similar. In the micelles of *n*-decyl phosphate monoanion, there exits a hydrogen bond between the neighboring phosphate groups, which efficiently stabilizes the micellar structure, but does not promote the hydrolysis. Elimination of the metaphosphate ion re-

quires in this case a rearrangement of hydrogen bonds, which is apparently unfavorable.[50]

The effect of micelles of anionic or nonionic surfactants on the rate of the spontaneous hydrolysis of the anions derived from TPA esters is explained from the electrostatic viewpoint. 4-Nitrophenyl phosphate monoanion and 2,4- and 2,6-dinitrophenyl phosphate dianions are not bound to the anionic micelles of SDS due to the strong electrostatic repulsion. Nonionic micelles bind these substrates weakly. This results in anionic and nonionic surfactants having no effect on the reaction rate.[45] The micelles formed by the zwitterionic surfactant n-$C_{12}H_{25}N^+$ $(Me)_2CH_2CO_2^-$, are also not very efficient.[46]

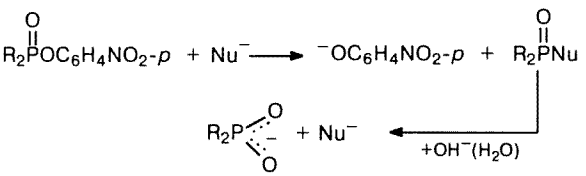
The alkaline hydrolysis of the anions derived from mono- and diesters of tetracoordinated phosphorus acids under the conditions of micellar catalysis has been studied using bis(2,4-dinitrophenyl) phosphate,[51,52] 4-nitrophenyl ethyl phosphate,[31] 2,4-dinitrophenyl phosphate,[51] and 4-nitrobenzoyl phosphate[44] as examples. The most appreciable (up to 30-fold) acceleration by CTAB micelles was observed in the hydrolysis of bis(2,4-dinitrophenyl) phosphate monoanion. SDS has no effect on this process, and nonionic surfactants (Triton X-114, Igepal) decelerate it. The unexpected substantial decrease in the reaction rate in the presence of Igepal micelles is apparently due to the fact that the substrate, poorly soluble in water, goes to the micellar phase and thus becomes far removed from the anionic nucleophile.[51,52]

Reactions with organic nucleophiles in micellar solutions of surfactants

The effect of micelles on the nucleophilic substitution reactions of esters of TPA with organic nucleophiles has been studied in relation to the reactions of OPC with phenoxide,[53,54] thiophenoxide,[54] oximate,[53,55–57] amidoximate,[58] 2-iodoso- and 2-iodoxybenzoate,[59–68] 3-chloroperoxybenzoate and butylperoxide ions,[25] 4-(*N*,*N*-dialkylamino)pyridine 1-oxides,[69] hydroxamic acids,[70,71] *ortho*-aminomethylphenols (AMP),[72–74] and amines.[44,46,75–78]

The catalytic activities of cationic micelles in the reactions of TPA esters with organic nucleophiles are usually high. For example, nucleophilic substitution reaction of NPDP with aryloxy ions (phenoxide and 4-alkylphenoxide ions) is accelerated almost 10^4 times in the presence of CTAB.[53,54] However, calculations in the context of the pseudophase model of micellar catalysis indicate that the second-order rate constants of processes involving organic nucleophiles in the micellar pseudophase ($k_{2,m}$) are close to[53,58] or lower than[56,72] those in water ($k_{2,0}$). This may be due to the fact that the nucleophile and the substrate are arranged unfavorably when they pass to the micelles,[56,72] and also to the fact that the reactants are localized in the weakly polar micelle core.[72] The fact that $k_{2,m}$ is similar to or lower than $k_{2,0}$ indicates that the catalytic effect of micelles is mostly governed by the collection of the reactants in the micellar phase[53] and by the shift of the acid-base equilibrium of a reagent toward the increase in the proportion of the nucleophilic anionic form.[56] The experiments with excess substrate with respect to the nucleophile carried out in some cases[55,59] showed that in a NPDP—nucleophile—surfactant system, the first step giving the phosphorylated nucleophile and 4-nitrophenoxide anion can be followed by either a quick step (for example, in the case of 2-iodosobenzoate),[59] or a slow step (in the case of oximes)[55] involving regeneration of the nucleophile (Scheme 4).

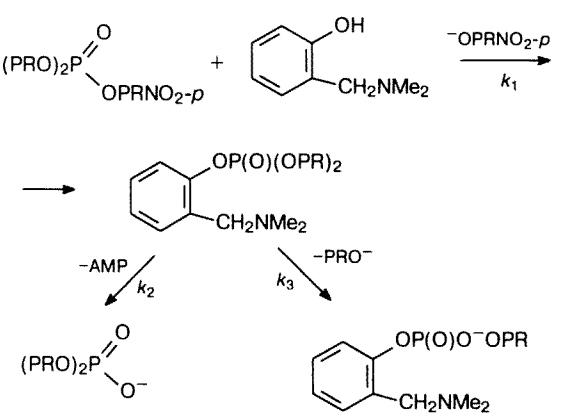
Scheme 4



R = OAr, OAlk Nu — 2-iodosobenzoate, oxime

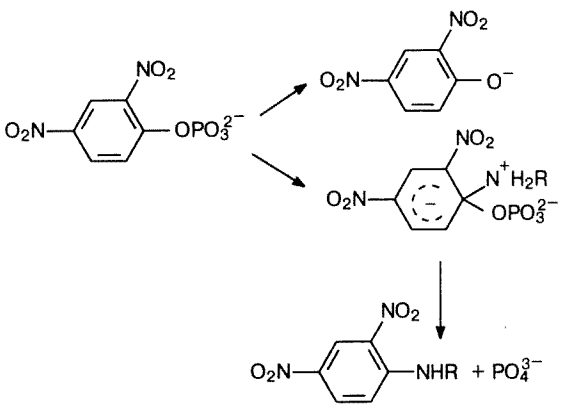
In some cases, decomposition of the intermediate can occur by several pathways. In a ^{31}P NMR study of the reaction of *o*-dimethylaminomethylphenol with NPDP (pH 9—10.5), it has been found that this reaction occurs in two steps both in the presence and in the absence of a surfactant (cetylpyridinium bromide (CPB) or SDS).[74] The first step yields the product of transesterification (phosphorylated AMP), and in the second step this product is hydrolyzed according to two pathways giving approximately equal amounts of diphenyl phosphate and *o*-dimethylaminomethylphenyl phenyl phosphate (Scheme 5).

Scheme 5



In the systems containing P—O—Ar and P—O—Alk fragments in the presence of amines, decomposition of a substrate may occur simultaneously by several pathways, due to the possibility of cleavage of the P—O, O—Ar, or O—Alk bonds.[46,78] In this case, micelles have an effect on relative rates of these pathways. In fact, the substantial increase in the rate of the CTAB-catalyzed hydrolysis of 2,4-dinitrophenyl phosphate dianion on the addition of primary amines is caused by the attack of the amine on the aryl group to give *N*-alkyl-2,4-dinitroaniline (Scheme 6). When the reaction is carried out in aqueous solutions in the presence of amines, 2,4-dinitrophenoxide ion usually predominates in its mixture with *N*-alkyl-2,4-dinitroaniline formed in the reaction.

Scheme 6



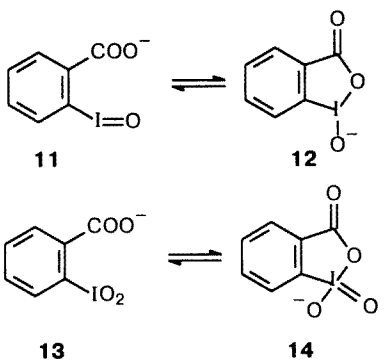
R = n-C_nH_{2n+1} (n = 6, 8, 9, 10)

In the presence of CTAB, aniline is formed predominantly in the case of any of the amines added. Secondary amines exert a smaller catalytic effect; tertiary amines are inactive.[46]

Further example is provided by the reaction of Methaphos with ethylenediamine in the presence of CTAB.[78] A specific feature of this process in an aqueous medium is that it involves alkylation of the amine and reactions at the phosphorus atom occurring in parallel (70 and 30 %, respectively); the latter include phosphorylation of the amine, general base catalysis by the amine, and the alkaline hydrolysis of the substrate (Scheme 7).

The introduction of CTAB retards the alkylation 2.5-fold and accelerates the attack on the phosphorus atom 5-fold. Consequently, only 15 % of the product of amine alkylation is produced.

In recent years, much attention has been paid to the micellar catalysis of the hydrolysis of TPA esters in the presence of 2-iodosobenzoic acid (IBA), 2-iodoxybenzoic acid (IOBA), and their analogs.[59—68] In the case of iodosobenzoate (**11**) and iodoxybenzoate (**13**) ions, species **12** and **14** are the reactive forms:[59,60]



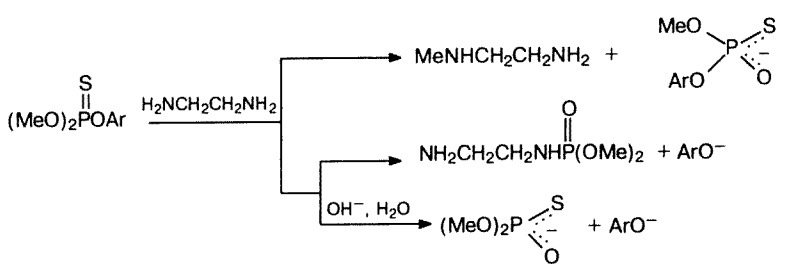
11 **12**

13 **14**

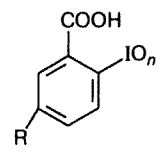
In a study of the effect of IBA and IOBA derivatives on the rate of hydrolysis of NPDP and 4-nitrophenyl isopropylphenylphosphinate in micellar solutions of cetyltrimethylammonium chloride (CTAC), the maximum increase in the reaction rate has been observed for compounds **18** and **15—17**.

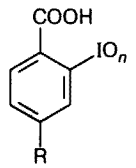
The variation of the alkyl chain of the latter has only slight effect on the catalytic activity of the acids. The activities of 2-iodoxybenzoic acids are similar to those of the analogous IBA.[63]

Scheme 7

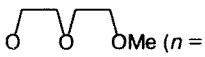


Ar = $C_6H_4NO_2$-p

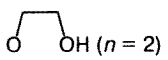




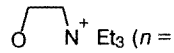
15: R = OC_8H_{17} (n = 1, 2),



16: R = OC_4H_9 (n = 1, 2),

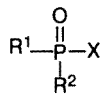


17: R = $OC_{12}H_{25}$ (n = 1, 2),

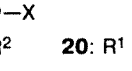


18: R = Me (n = 1,2), NO_2 (n = 1, 2)

R = $COOH_2$ (n = 1), NO_2 (n = 1, 2)

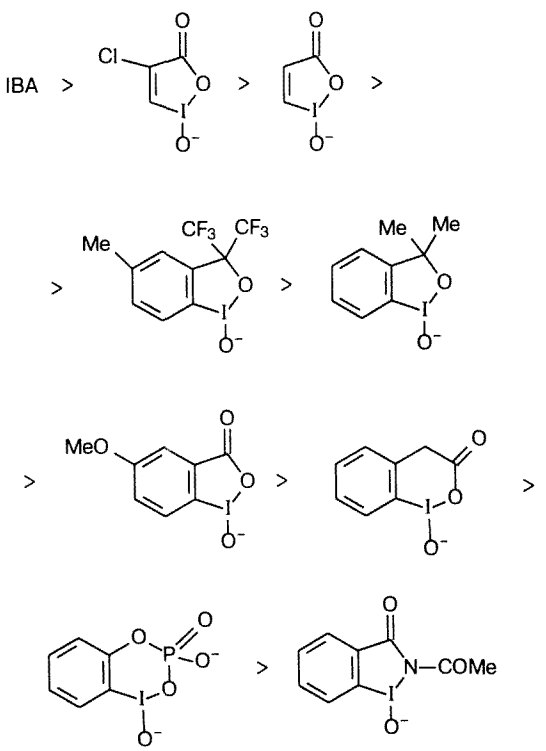


19: R^1 = Me, R^2 = Pr^iO, X = F

20: R^1 = Me, R^2 =  , X = F

21: R^1 = OEt, R^2 = NMe_2, X = CN

Decomposition of NPDP in micellar solutions of CTAC in the presence of analogs of IBA has been studied previously.[67,79] These compounds are less active than IBA, and in terms of their catalytic effect, they can be arranged in the following series:



The efficiency of IBA, IOBA, and their derivatives as catalysts in the hydrolysis of OPC also depends on the structure of the substrate.[61–65] The effect of IBA on the decomposition of NPDP and compounds **19**—**21** in micellar solutions of CTAB has been studied.[61]

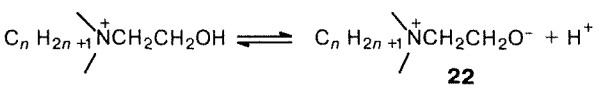
The presence of IBA leads to a 7—50-fold increase in the bimolecular rate constants of the hydrolysis of compounds **19**—**21** (1600-fold for NPDP). Such a change in the catalytic activity of IBA is attributed to unfavorable distribution of substrates **19**—**21** between the micellar and aqueous phases.[61] The constants of binding of OPC increase in the order **21**,**19** < **20** ≪ NPDP. The catalytic activity of the micelles varies in the same order.

Functional micellar catalysis and catalysis by metal complexes

Considerable interest in functional micellar catalysis is caused not only by the pronounced catalytic effects involved, but also by the fact that the structure of the catalytically active sites of micelles and the globular character of the micellar aggregates bring functional micellar catalysis closest to enzymatic catalysis.[2] Efficient micellar catalysts for reactions involving TPA esters are surfactants containing an imidazole fragment[49,80] or amino,[22,81,82] hydroxyl,[14,17,19,22,31,36,44,46,83–86] oxime,[58,83,87–91] hydroxamate,[90] aldehyde,[32,92] 2-iodosobenzoic,[33,59,62–66] or 2-iodoxybenzoic[63,65] group.

High catalytic activities of micelles of functional surfactants are caused, as a rule, by nucleophilic properties of the functional groups. For example, a surfactant with a 2-hydroxyethyl group dissociates in the pH ≈ pK_a region or at higher pH to give zwitterionic form (**22**), which is reactive toward the TPA esters (Scheme 8).

Scheme 8



22

The first step of the process may yield no products of alkaline hydrolysis.[85] The high activity of compound **22** is also indicated by other factors:

— in alkaline solutions, hydroxyethyl containing surfactants are more efficient catalysts than their analogs containing no functional groups.[17,19] The only exception is provided by the hydrolysis of the 2,4-dinitrophenyl phosphate dianion. The catalytic activity of the micelles of 2-hydroxyethylhexadecyldimethylammonium bromide (HHDAB) in this process is close to that of CTAB,[46] which may be due to the monomolecular mechanism of the decomposition of this dianion;

— the reactions with fluoride ions, which occur at lower pH values than the alkaline hydrolysis, when the

content of the zwitterionic form of the functional surfactant is low, are equally accelerated by the micelles of the hydroxyethyl-containing surfactant and the micelles of CTAB;[31]

— in the processes of nucleophilic substitution in TPA esters, the choline anion acts as a stronger nucleophile than the OH ion;[14,44]

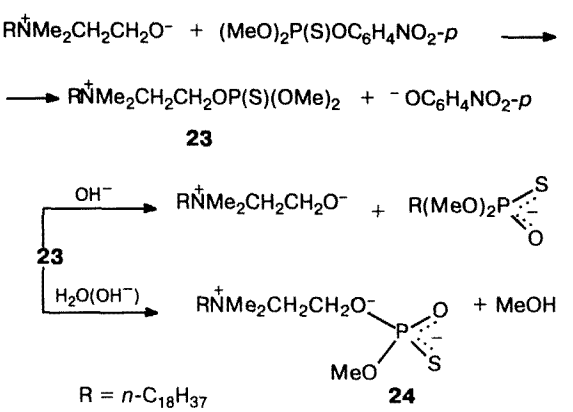
— the kinetic isotope effect of the solvent (k_{H_2O}/k_{D_2O}) in the alkaline hydrolysis of di-*n*-hexyl 4-nitrophenyl phosphate in the presence of HHDAB is 0.9;[19]

— in the alkaline hydrolysis of bis(4-nitrophenyl) ethyl phosphate in aqueous solutions and also in micellar solutions of CTAB, the fast step detected by spectrophotometry yields one mole of 4-nitrophenol per mole of substrate. In micellar solutions of 2-hydroxyethyldimethyloctadecylammonium bromide, up to 1.83—1.92 moles of 4-nitrophenol is liberated, which indicates that the reaction mechanism has changed;[86]

— in a ^{31}P NMR monitoring of the nucleophilic substitution in Methaphos in alkaline micellar solutions of 2-hydroxyethyldimethyloctadecylammonium bromide, the signal at 69.4 ppm corresponding to product **23** was found to disappear a short time after its appearance, and instead, two new peaks (57.0 and 57.5 ppm) were found to arise, which were assigned to compound **24** and dimethyl thiophosphate, respectively[85] (Scheme 9).

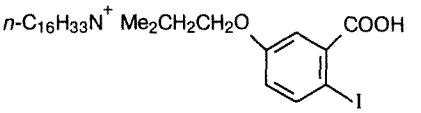
In the case of functional micellar catalysts containing amino groups or histidine fragments, general base catalysis is also possible;[22,49,80—82] for example, it was observed in the hydrolysis of 4-nitrophenyl *n*-butyl chloromethylphosphonate in the presence of higher *n*-alkylamines.[81] Micelles with neutral and protonated *n*-alkylamines are present in the solution. The absence of amides in the reaction products (according to ^{31}P NMR spectra), the value of the deuterium isotope effect of the solvent (1.6—1.7) at a degree of protonation of the

Scheme 9



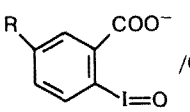
amine α of 0.3—0.4, as well as the invariability of the reaction rate constant in the micellar phase at $\alpha < 0.5$ make it possible to conclude that when the ester is hydrolyzed with mixed micelles by a mechanism of general basic catalysis, the neutral form of the amine is the active form.[81]

Among the known functional surfactants, those containing aldehyde groups[32,92] as well as derivatives of 2-iodoxybenzoic and 2-iodosobenzoic acid[33,59,62—66] proved to be the most efficient catalysts (Table 2). In the latter case, decomposition of phosphorus-containing substrates accelerates 10^2—10^4-fold[33] compared to their solvolysis in a solution of **25**/CTAC (1 : 5) at pH 8.

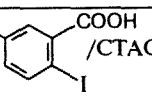


25

Table 2. Effect of functional surfactants on the rate of decomposition of NPDP in an alkaline medium (25 °C)

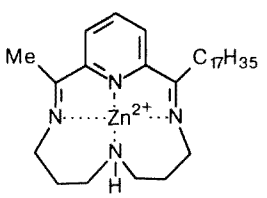
Surfactant	$k_0 \cdot 10^{-3}$ [a] /s^{-1}	k_{max} [b] /s^{-1}	k_{max}/k_0	Conditions	References
n-$C_{16}H_{33}N^+Me_3Br^-$	4.9	0.056	12	0.01 mol L^{-1} NaOH	15,16
n-$C_{16}H_{33}N^+Me_2CH_2CH_2OHBr^-$	4.9	1.5	310	0.01 mol L^{-1} NaOH	19,31
n-$C_{16}H_{33}N^+Me_2CH_2CH_2OHCl^-$	2.0	3.0	1500	0.005 mol L^{-1} NaOH	92
n-$C_{16}H_{33}N^+Me_2CH_2Im\ Cl^-$	0.0097	0.0037	380	Borate buffer solution, pH 8.0	49
n-$C_{12}H_{25}N^+Me_2CH_2CHO$	0.011	0.02	1800	Borate buffer solution, pH 9.0	32
 /CTAC (1:5)	0.077[c]	1.1	14700	Borate buffer solution, pH 9.0 μ = 0.01 (KCl)	33

R = *n*-$C_{16}H_{33}N^+Me_2CH_2CH_2O$

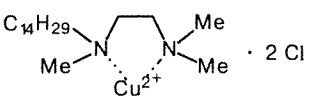
[a] Without addition of a functional surfactant. [b] In the presence of a functional surfactant. [c] In the presence of  /CTAC (1 : 5)

The high concentration of functional groups on the micelle surface where substrates are mostly localized, the high degree of their deprotonation due to a positive charge on the micelles, and the desolvation of the reactants create conditions for quick chemical reactions. Catalytic properties of the micelles of functional surfactants are more clearly manifested when they are used in mixtures with nonfunctional surfactants. The latter compounds increase the solubility of the functional surfactants or stabilize the micelles.[87,88] The high catalytic effect of the micelles of functional surfactants in reactions involving esters of TPA makes it possible to regard these compounds as being among the most promising types of catalysts ensuring decomposition of OPC under mild conditions.

A number of studies[55,77,93–97] have been devoted to the effect of metal complexes on the hydrolysis of TPA esters in micellar solutions of surfactants. Owing to the long-chain hydrocarbon radicals present in the ligand molecules, these complexes are efficiently bound to micelles or act themselves as functional micelle forming surfactants. The most active catalysts of the hydrolysis of TPA esters are complexes **26** and **27** (see Refs. 97 and 94, respectively) (Table 3).



26



27

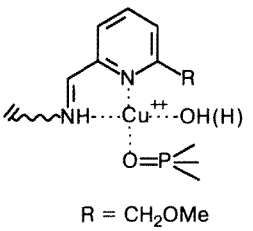
Among the known functional catalysts of the hydrolysis of TPA esters, only derivatives of iodosobenzoic acid surpass complex **27** in the catalytic effect (see Table 2). However, they are inferior to complex **27** in stability, especially in the presence of sulfur containing compounds, enols, and so on.[94]

It has been suggested[94,97] that the activity of metal-complex systems is due to the hydroxide ion formed from the deprotonated aqua ligand.

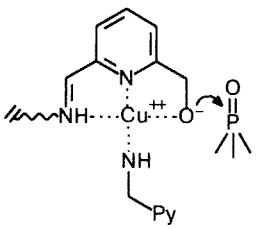
$$[(M)(L)OH_2]^{2+} \rightleftharpoons [(M)(L)OH]^{+} + H^{+}$$

Therefore, the high catalytic activity of metal containing micelles of compound **27** in the hydrolysis of NPDP is explained by the simultaneous localization of the substrate and the reactive complex Cu[L][OH]$^+$ on the micellar surface and by electrophilic catalysis arising due to the ability of copper ions to polarize the P=O bond.[94]

The variation of the L : M stoichiometric ratio may have an effect on the reactivity and the mechanism of the action of the complexes. When the hydrolysis of NPDP was carried out in solutions of CTAB in the presence of Cu^{2+} complexes **28** and **29**, the complexes with L : M = 1 : 1 for **28** and L : M = 2 : 1 for **29** exhibited the highest catalytic activities.[95]



28



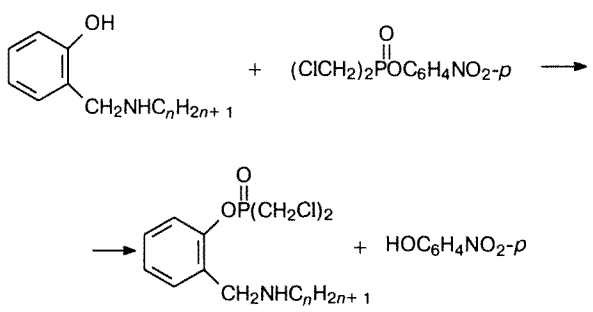
29

Investigation of the reactivity and the nature of the action of metal complexes in the presence of micelles gives an insight into the mechanism of decomposition of phosphate esters in the presence of metal containing enzymes[95] and provides conditions for a search for efficient catalytic systems for the reactions involving esters of TPA.

Catalysis of reactions in inverted micelles and other highly organized media

Only a few studies have been devoted to the effect of surfactant micelles on reactions involving OPC in nonaqueous media.[98–101] The presence of poly(ethylene glycol)-600 monolaurate in the toluene solution increases the k_{obs} of the reaction of 4-nitrophenyl bis(chloromethyl)phosphinate with 2-alkylaminomethylphenols by more than an order of magnitude. The position of the maximum on the concentration plot of k_{obs} depends on the content of AMP in the solution (Scheme 10).

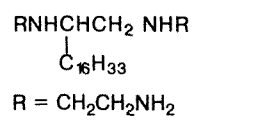
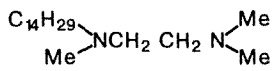
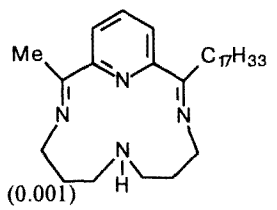
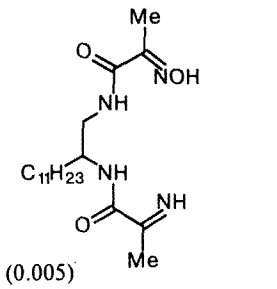
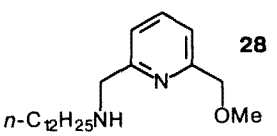
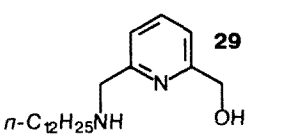
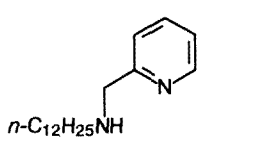
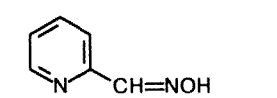
Scheme 10



n = 5, 8, 12, 16

When the concentration of the nucleophile increases, the maximum value of k_{obs} shifts toward high concentrations of the surfactant. A specific feature of the dependence of k_{obs} of the reaction on the concentration of AMP is that the surfactant micelles exert not only a

Table 3. Micellar catalysis of reactions involving esters of TPA in the presence of metal complexes ([L] : [M], 1 : 1)

Ligand ([L]/mol L^{-1})	Metal	Substrate	Surfactant	k_{cat}/k_0[a]	Conditions	References
 (0.005)	Mn^{2+}	Acetyl phosphate	—	3	pH 7.0 (collidine buffer solution), μ = 0.6, 39 °C	78
 (0.0015)	Cu^{2+}	NPDP	—	8000[b]	pH 6.0 (0.01 mol L^{-1} *N*-ethylmorpholine buffer solution), 25 °C	95
 (0.001)	Zn^{2+}	NPDP	0.02 mol L^{-1} Bridge 35[d]	770[c]	pH 8.0 (0.01 mol L^{-1} aminosulfonate buffer solution), 25 °C	98
 (0.005)	Zn^{2+}	Acetyl phosphate	0.025 mol L^{-1} CTAB	140	pH 11.0 (NaOH), 40 °C	94
	Cu^{2+}	«	«	108		«
	Ni^{2+}	«	«	60		«
 **28** (0.001)	Cu^{2+}	NPDP	—	29	pH 6.25 (0.05 mol L^{-1} 2-(*N*-morpholino)ethane-sulfonate buffer solution), 35 °C	96
	Cu^{2+}		0.004 mol L^{-1} CTAB	13[d]		«
 **29** (0.001)	—	NPDP	0.004 mol L^{-1} CTAB	1.5[d]	pH 6.25 (0.05 mol L^{-1} 2-(*N*-morpholino)ethane-sulfonate buffer solution), 35 °C	96
	Cu^{2+}	NPDP	—	29		«
	Cu^{2+}	NPDP	0.004 mol L^{-1} CTAB	4[d]		«
 (0.002)	Cu^{2+}	NPDP	0.004 mol L^{-1} CTAB	14[e]	pH 6.25 (0.05 mol L^{-1} 2-(*N*-morpholino)ethane-sulfonate buffer solution), 35 °C	98
 (0.001)	Zn^{2+}	NPDP	0.001 mol L^{-1} CTAB	0.8[f]	pH 6.0 (0.02 mol L^{-1} acetate buffer solution), 25 °C	55

[a] k_{cat} is the rate constant in the presence of a metal complex, and k_0 is the rate constant in the absence of a metal complex. [b] For k_{cat} at pH 6.0 and k_0 at pH 8.0; for k_{cat} and k_0 at pH 6.0, $k_{cat}/k_0 > 10^5$. [c] ZnL(Br)(ClO_4) complex; k_0 was measured in the presence of 0.02 mol L^{-1} of Bridge 35. [d] Oxyethylated lauryl alcohol (n = 23). [e] k_0 was measured in the presence of 0.004 mol L^{-1} of CTAB. [f] k_0 was measured in the presence of 0.001 mol L^{-1} of CTAB.

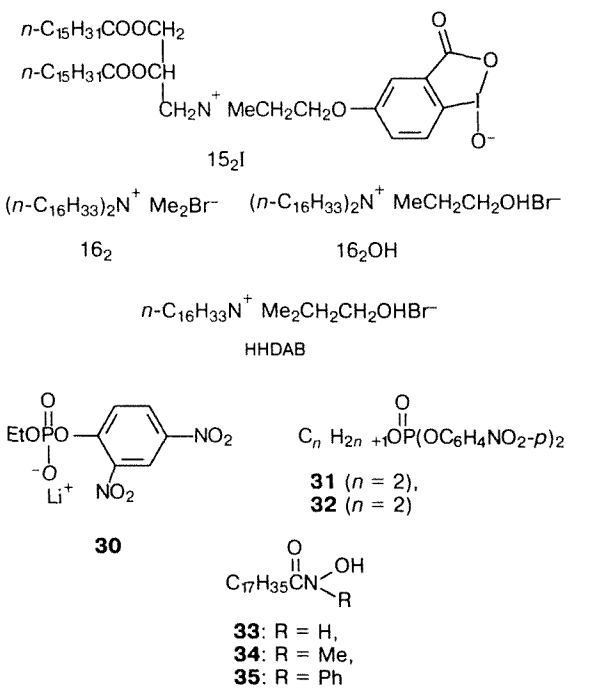
catalytic effect, but also an inhibitory effect. It has been shown previously[99] that the catalytic activity of inverted micelles depends on the structures of the nonionic surfactant and reactants and also on their concentrations. The catalytic efficiency of micelles of nonionic surfactants in the reactions of 4-nitrophenyl phenyl chloromethylphosphonate with methyl-, *n*-butyl, and *n*-hexadecylamine in toluene increases on going from poly(ethylene glycol)-600 monolaurate to Triton X-100, with an increase in the degree of oxyethylation of the surfactant and with a decrease in the concentration and the length of the hydrocarbon radical of the amine. Whereas in the case of 4-nitrophenyl phenyl chloromethylphosphonate the efficiency of micellar catalysis can be as high as four orders of magnitude,[99] CTAB and HHDAB inverted micelles in a hexanol—water system are inefficient catalysts for spontaneous hydrolysis of 2,4-dinitrophenyl phosphate.[98]

Studies in the field of micellar catalysis of the reactions involving esters of TPA are deeply intertwined with studies of the catalysis in media containing vesicles,[84,101–105] lyotropic liquid crystals,[106–111] or microemulsions.[68,112–116]

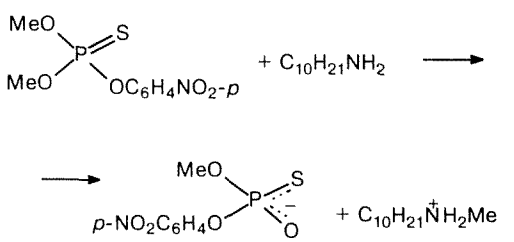
The catalytic action of vesicles has been studied in the works dealing with decomposition of OPC,[103–105] with the mechanism of reactions of 4-nitrophenyl phosphates with nucleophilic reagents (hydroxamates,[101] iodosobenzoic functional surfactants,[102] hydroxide ions,[103–105] and fluoride ions[105]), or with a search for the most efficient surfactant—cosurfactant combinations.[102] Table 4 presents the rate constants of the decomposition of TPA esters (NPDP, **30**—**32**) in vesicular (16_2, 16_2OH, $15_2I/16_2$) and micellar (CTAB, HHDAB) solutions of surfactants.

There is no essential difference between the catalytic effects exerted by these systems. The catalytic efficiency of vesicular solutions of surfactants is higher than the efficiency of micellar aggregates by a factor of no more than three (see Table 4).

The alkaline hydrolysis of *O*-*n*-alkyl 4-nitrophenyl methylphosphonates in a CTAB-hexanol—water system,[106] dealkylation of Methaphos in a *n*-decylammonium chloride—*n*-decylamine—water system,[107–109] and IBA-catalyzed hydrolysis of phosphinates in a myristyltrimethylammonium bromide—1-decanol—NH_4Br—water system[111] are examples of the catalysis in liquid crystal media. Depending on the concentration of the components of these systems, micellar and liquid crystal phases affecting noticeably the rate and the course of the processes studied are formed. The place where the substrate is localized is of great importance for these processes. The higher rate constants of the hydrolysis of 4-nitrophenyl ethylphenylphosphinate in the micellar and liquid crystal phases containing rod-shaped or spherical aggregates compared to the rate constant observed in the liquid crystal phase with disk-shaped aggregates are due to the fact that in the phases containing rod-shaped or spheric aggregates, the ester is localized predominantly at the interface with water, rather than in the hydrocarbon medium, as in the case of the liquid-crystal phase with disk-shaped aggregates.[110] The fact that dealkylation of Methaphos occurs in the lamellar phase of the *n*-decylammonium chloride—*n*-decylamine—water system is apparently also caused by the features of the substrate localization[107–109] (Scheme 11).



Scheme 11



In an FT-IR spectroscopic study, it has been found that the local environment of the substrate is inhomogeneous, its larger fraction occurring in the hydrocarbon part of the lamellar and its smaller part at the surfactant—water interface.[109] In this connection, the absence of the nucleophilic reaction with abstraction of the 4-phenoxide anion at the phosphorus atom may be due to the fact that the $OC_6H_4NO_2$-4 group of the Methaphos is drawn in the nonpolar part of the lamella, which hampers the attack of the amine on the phosphorus atom and opens up possibilities of a reaction at the carbon atom.[109] It was found that dealkylation of

Table 4. Decomposition of esters of TPA in vesicle and micellar solutions

Surfactant	Substrate	Nucleophile	$k_{obs} \cdot 10^3$ [a] /s^{-1}	k_{obs}/k_0 [b]	Conditions	References
16_2	NPDP	0.5 mol L^{-1} OH^-	365 ($4.0 \cdot 10^{-4}$ mol L^{-1})	17.4	25 °C, 0.05 mol L^{-1} KOH	106
CTAB	NPDP	0.5 mol L^{-1} OH^-	310 ($8.0 \cdot 10^{-4}$ mol L^{-1})	—	25 °C, 0.05 mol L^{-1} KOH	«
16_2	NPDP	0.5 mol L^{-1} F^-	650 ($2.0 \cdot 10^{-4}$ mol L^{-1})	360	25 °C, 0.05 mol L^{-1} KF	«
CTAB	NPDP	0.5 mol L^{-1} F^-	410 ($5.0 \cdot 10^{-4}$ mol L^{-1})	—	25 °C, 0.05 mol L^{-1} KF	«
16_2—OH	NPDP	—	0.93 ($0.6 \cdot 10^{-3}$ mol L^{-1})	32	25 °C, pH 9.0 (0.02 mol L^{-1} Tris buffer solution, μ = 0.01, KCl)	85
HHDAB	NPDP	—	2.0 ($0.8 \cdot 10^{-3}$ mol L^{-1})	69	25 °C, pH 9.0 (0.02 mol L^{-1} Tris buffer solution, μ = 0.01, KCl)	«
16_2—OH	30	—	2.21 ($0.9 \cdot 10^{-3}$ mol L^{-1})	167	25 °C, 0.1 mol L^{-1} NaOH	«
HHDAB	30	—	0.7 ($1.8 \cdot 10^{-3}$ mol L^{-1})	53	25 °C, 0.1 mol L^{-1} NaOH	«
16_2[c]	31	$5.0 \cdot 10^{-5}$ mol L^{-1} **33**	28[d]	—	30 °C, pH 8.8 (0.02 mol L^{-1} borate buffer solution, μ = 0.01, KCl)	102
CTAB[c]	31	$5.0 \cdot 10^{-5}$ mol L^{-1} **33**	9.1[d]	—	«	«
16_2[c]	31	$5.0 \cdot 10^{-5}$ mol L^{-1} **34**	74[d]	—	«	«
CTAB[c]	31	$5.0 \cdot 10^{-5}$ mol L^{-1} **34**	88[d]	—	«	«
16_2[c]	31	$5.0 \cdot 10^{-5}$ mol L^{-1} **35**	50[d]	—	«	«
CTAB[c]	32	$5.0 \cdot 10^{-5}$ mol L^{-1} **35**	8.3[d]	—	«	«
16_2[c]	32	$1.0 \cdot 10^{-5}$ mol L^{-1} **34**	8.6[d]	—	«	«
CTAB[c]	32	$1.0 \cdot 10^{-5}$ mol L^{-1} **34**	7.8[d]	—	«	«
$15_2I/16_2$[e]		NPDP	14.3		25 °C, pH 8.0 (Tris buffer solution)	103

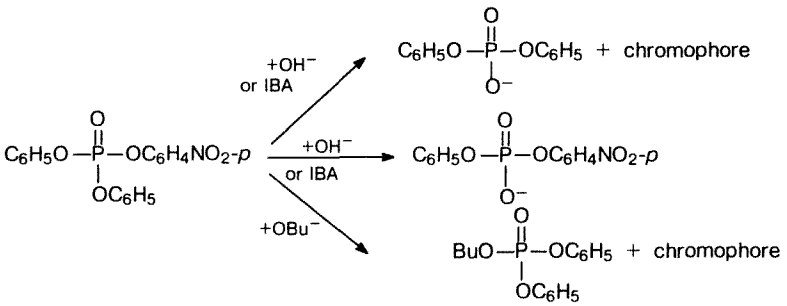
[a] The concentration of the surfactant at which k^{max}_{obs} is observed is presented in parentheses. [b] k_0 is the rate constant measured in the absence of a surfactant. [c] 0.001 mol L^{-1} of the surfactant. [d] The observed rate contstant of the first step of the process. [e] $1.9 \cdot 10^{-4}$ mol L^{-1} of 15_2I, $3.8 \cdot 10^{-4}$ mol L^{-1} of 16_2.

Methaphos is characterized by slight binding of the substrate to the liquid crystal phase, compared to its binding to micelles, and by close values of the rate constants in micellar and lamellar phases, which indirectly attests to similarity of properties of the surfaces of micelles and lyotropic liquid crystals.[107,108]

Microemulsions, *i.e.*, water and oil dispersions, are known to possess large inner interfacial surface areas. By varying the ratio between the oil and water and the proportion of surfactant in the system, one can change the interfacial surface area between the oil and water over wide limits. Microemulsions are convenient objects for the investigation of reactions between water- and oil-soluble compounds, if they are capable of reaching the interface.[117] The reactions of NPDP, Para-oxon, and di-*n*-hexyl 4-nitrophenyl phosphate with hydroxide and fluoride ions in hexadecane—water microemulsions stabilized by Bridge 96, CTAB, or 1-butanol have been studied previously.[118,119] The presence of 1-butanol in this system has an effect on the effective surface charge of the microemulsion. The effective surface potentials of the microemulsion (at a phase volume of 85—15 %) and of CTAB micelles are 28—58 and 130 mV, respectively. The lower charge of the microemulsion is due to the dilution of the surfaces of drops by the surface active alcohol.[119] It was found that in all of these cases the reaction obeyed the first order with respect to both the ester and the nucleophile. The reactivity of the substrates in the reactions with hydroxide and fluoride ions varies in the following order: NPDP >> Para-oxon > di-*n*-hexyl 4-nitrophenyl phosphate. In micellar solutions, the most water-soluble substrate (Para-oxon) is distributed between the micellar and aqueous phases, while in microemulsions, it is wholly dissolved in microdrops.[119] The hydrolysis of NPDP catalyzed by iodosobenzoate or its derivatives[68,112—116] has been studied in microemulsions based on a system containing hexadecane—water—CTAB,CTAC—1-butanol, *N*,*N*-dibutyl formamide, trialkyl(C_8—C_{10})methylammonium chloride (Adogen 464) in the presence or in the absence of toluene or *n*-hexyl benzoate[68,112—115] or in a microemulsion based on the CTAB—1-methyl-2-pyrrolidone—toluene—borate buffer solution system.[116] In microemulsion systems, iodosobenzoate is virtually unconsumed during the reaction and acts as a real catalyst.[68] It has been found by ^{31}P NMR spectroscopy that in microemulsions based on the CTAB,CTAC—*n*-butanol,Adogen 464—*n*-hexadecane—water system, both in the presence and in the absence of IBA, hydrolysis of NPDP yields mostly diphenyl phosphate anions (75—90 %) and 4-nitrophenyl phenyl phosphate (6—13 %) (Scheme 12).

In butanol-containing media, butyl diphenyl phosphate (up to 10 %) is also formed; this compound is hydrolyzed giving a variety of secondary products.[112] The maximum rate of the hydrolysis catalyzed by

Scheme 12



iodosobenzoate in this system is observed in the presence of Adogen 464, which is due to the higher surface charge of the microemulsion drops in this case, and, consequently, the higher concentration of the negatively charged nucleophile near the surface of these drops.

Conclusions

The presented data on reactions involving esters of TPA in colloidal systems based on surfactants indicate that the character and degree of the effect of highly organized media depend on a number of factors. The catalytic effect of organized associates depends on the composition of the medium and the structures and concentrations of the reactants. An important role is played by the area of localization and by the orientation of the reacting species. In surfactant-containing systems, the mechanisms of reactions may change, which is important for controlling the reactivities of the compounds and which can enable solution of problems of increasing the hydrolytic stabilities of medicinal preparations[39] and fast decomposition of wastes of pesticides[30,36] and other toxic OPC.[94] Highly organized media are of interest as regards modeling the structures and functions of biocatalytic systems. Many biochemical processes occur in microheterogeneous systems containing organic and aqueous phases. The effects of the micromedia, rigid fixation of the reactants, the specificity with respect to the sizes and configurations of the reactant molecules, the clear-cut substrate specificity, and the high catalytic effects bring the catalysis in colloidal systems close to enzymatic catalysis. Of particular importance in this field is further development of studies dealing with catalysis with participation of metal complexes,[96] as well as investigation of the kinetics of processes in nonaqueous media.[1]

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