Kinetics of reaction of sodium *p*-octylphenolate with *O*-ethyl-*O*-*p*-nitrophenyl ethylphosphonate

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In aqueous and aqueous-alkaline solutions, sodium *p*-octylphenolate forms anionic micelles that absorb *O*-ethyl-*O*-*p*-nitrophenyl ethylphosphonate before the reaction that proceeds on the micellar surface. The micelle formation is suppressed in systems containing organic solvent and water. However, for these systems, the rate of the reaction with phenolates is affected by the association of ions in the ion pairs.

Key words: phenolates, micelle formation, micellar catalysis, esters, transesterification, hydrolysis, rate constants.

Phenolate anions are strong nucleophiles, but their basicity is not high. Therefore, reactions with their participation can easily occur in aqueous solutions at ordinary temperatures and moderate pH values of the medium. The influence of the structure of the phenolates and substrates on the rates of reactions of nucleophilic substitution at phosphoryl[1—6] and carbonyl[7] groups has been studied in a number of works.

Similar reactions are known to be significantly accelerated when carried out in micellar solutions of cationic surfactants.[8,9] The use of nucleophilic reaction centers as head groups of surfactant molecules can also enhance the reactivity of anionic nucleophiles.[10—12] The data on the reactivity of phenolates that form functionalized micelles are lacking, which prompted us to study the kinetics of substitution at a phosphoryl group with the participation of *p*-octylphenolate, which is capable of micelle formation in aqueous solutions. The formation of anionic micelles by phenolates containing long-chain alkyl radicals in the benzene ring has been shown previously.[13]

Experimental

In the present work, distilled samples of phenols, dried and distilled DMF, bidistilled water, cetyltrimethylammonium bromide of reagent grade purity, and chemically pure NaOH were used. *O*-Ethyl-*O*-*p*-nitrophenyl ethylphosphonate was used as the substrate, which undergoes transesterification with phenolates to eliminate *p*-nitrophenolate.[5,6] The reaction was monitored spectrophotometrically on a Specord UV-VIS instrument by following the change in absorbance at the analytical wavelength of 400 nm that corresponds to *p*-nitrophenol anion. The reaction was carried out in quartz cells kept at constant temperatxre (±0.2 °C). The initial concentrations of the substrate (0.0001 mol L^{-1}) provided pseudomolecular conditions of the processes in all the experiments. The values of the observed rate constants, k, were calculated on the basis of the equation $\ln(D_L-D) = -kt + \ln(D_L-D_0)$, where D is the optical density of the system at the moment t from the start of measurements and D_0 and D_L are D values at $t = 0$ and $t > 7/k$, respectively (the latter condition was verified after the calculation of k). The values of the observed rate constants k and parameters of Eq. (1) (see below) were calculated with the use of the programs of regression analysis based on the least-squares method.

Results and Discussion

The rate of the transesterification of the esters of acids of tetracoordinate phosphorus by phenolates containing no long-chain alkyl radicals in a nucleus is normally described by a first-order kinetic equation with respect to phenolate.[2,3] For the reaction studied:

$$p\text{-}C_8H_{17}C_6H_4O^- + Et(EtO)P(O)OC_6H_4NO_2\text{-}p =$$
$$= p\text{-}NO_2C_6H_4O^- + Et(EtO)P(O)OC_6H_4C_8H_{17}\text{-}p$$

the kinetic order with respect to sodium *p*-octylphenolate is not constant and drops to zero with an increase in its concentration in the system. At the same time, the observed rate constant k increases and achieves a maximum value (Table 1). This behavior is due to the peculiarities of the mechanism of the process that includes pre-reaction equilibrium of the binding of the substrate with the sodium *p*-octylphenolate micelles.

The substrate distributed between the micelles and the aqueous solution participates in two parallel reactions. The above-mentioned transesterification with the participation of *p*-octylphenolate anions that form the surface of micelles occurs in the micellar pseudophase. A fraction of the substrate that is maintained in the

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 850—853, April, 1996.

Table 1. Rate constants for substrate decomposition in aqueous solution at different concentrations of sodium *p*-octylphenolate (C) at 25 °C

$C \cdot 10^2$ /mol L^{-1}	$k \cdot 10^2$ /s^{-1}	$k^* \cdot 10^2$ /s^{-1}
0	—	5.01
0.3	0.009	—
0.5	0.046	4.12
0.62	0.050	—
1.0	0.064	3.18
1.5	0.070	2.35
2.0	0.109	1.46
2.5	0.117	—
3.0	0.133	—
4.0	—	0.92
5.0	0.138	0.80
10.0	0.127	0.46

* For the system containing NaOH (0.3 mol L^{-1}).

aqueous phase reacts with water and a hydroxide ion (the latter is a result of the partial hydrolysis of sodium *p*-octylphenolate). In these processes, elimination of *p*-nitrophenolate ion from the substrate also takes place. With increase in the content of sodium *p*-octylphenolate in the system, virtually complete binding of the substrate by micelles occurs and as a result, the growth of k values stops (see Table 1). Some decrease in the rate constant after the maximum point can be caused by an increase in the radius of the micelle as the concentration of the surfactant in the aqueous solution increases. This should result in a reduction in substrate activity owing to the change in the ratio of the volume of micelles to their surface area.[14]

The dependence of the observed rate constant on the concentration of sodium *p*-octylphenolate (C) is described by the equation[15] often used for the description of the kinetics of reactions catalyzed by micelles:

$$k = [k_{aq} + k_m \cdot K_S(C - \mathrm{cmc})]/[1 + K_S(C - \mathrm{cmc})], \quad (1)$$

where k_{aq} is the rate constant of the reaction in the aqueous phase, k_m is the rate constant at the surface of micelles, K_S is the constant of the binding of the substrate by micelles, and cmc is the critical micelle concentration. From the data listed in Table 1, the values of k_m = 0.0016 s^{-1}, K_S = 144 L mol^{-1}, as well as the value of cmc = 0.0039 mol L^{-1} for the aqueous solution of sodium *p*-octylphenolate, were calculated.

To the contrary, the change in k value is opposite to the change in C, and the k value tends to a minimum value (see Table 1) when a constant excess of alkali is indroduced into the system. A similar reduction in the rate of reactions with the participation of anionic nucleophiles upon introduction of anionic surfactants into the reaction medium has been previously observed.[16] In the process under study, *p*-octylphenolate is also a nucleophilic reagent, but its reactivity is substantially lower than that of hydroxide ion. Therefore, the binding of the substrate by the negatively charged micelles hampers its reaction with hydroxide ion because of electrostatic repulsion of the latter by micelles. The values of k_m = 0.0023 s^{-1}, K_S = 185 L mol^{-1}, and cmc = 0.0056 mol L^{-1} calculated according to Eq. (1) for the alkali-containing system (see Table 1) are comparable to those mentioned above for micellar solutions of *p*-octylphenolate containing no alkali. The increase in K_S value is a result of salting out the substrate by NaOH from the aqueous phase into the micellar pseudophase. The close values of k_m for the two sets of experiments (see Table 1) allow one to suggest that in an excess of alkali, transesterification of the substrate also occurs in the micellar pseudophase.

In the system containing both the anionic (*p*-octylphenolate) and cationic (cetyltrimethylammonium bromide, CTAB) surfactants, the reaction rate increased with increase in the concentration of the cationic surfactant (Table 2). When two surfactants differing in charge and structure are both present in the system, mixed micelles are formed, whose charge depends on the ratio of their molar concentrations. If the cationic surfactant prevails, the micelles become positively charged. Anions that are present in the system, in particular hydroxide anion, which is formed upon the partial hydrolysis of sodium *p*-octylphenolate, are concentrated around micelles in the Stern layer. Under these conditions, decomposition (alkaline hydrolysis) of the substrate sorbed by micelles is possible. This is confirmed by the abrupt increase in the rate constants upon introducing NaOH to the system.

The reaction of the formation of *p*-nitrophenolate anion in the alkali-containing system (Table 3) is of the first order with respect to NaOH concentration. The rate constant of bimolecular reaction of alkaline hydrolysis of the substrate, $k_2 = k/C_{\mathrm{NaOH}}$ (0.017 L mol^{-1} s^{-1}), proved to be nearly 10 times lower than that of alkaline hydrolysis of the substrate in the

Table 2. Rate constants for substrate decomposition in aqueous systems containing sodium *p*-octylphenolate and cationic surfactant (CTAB) at 25 °C

[p-$C_8H_{17}C_6H_4ONa$] /mol L^{-1}	[CTAB] /mol L^{-1}	[NaOH] /mol L^{-1}	$k \cdot 10^2$ /s^{-1}
0.050	0	0	0.138
	0.015	0	0.149
	0.050	0	0.164
	0.100	0	0.282
	0.120	0	0.416
0.100	0	0.3	0.493
	0.022	0.3	1.24
	0.043	0.3	3.11
	0.100	0.3	3.22
	0.200	0.3	3.83

Table 3. Rate constants for substrate decomposition in aqueous-alkaline solutions of sodium *p*-octylphenolate (0.1 mol L^{-1}) at 25 °C

[NaOH] /mol L^{-1}	$k \cdot 10^2$ /s^{-1}	$k_2 \cdot 10^2$ /L mol^{-1} s^{-1}
0.1	0.104	1.04
0.2	0.256	1.28
0.3	0.388	1.29
0.45	0.515	1.15
0.90	0.967	1.07
0.95	1.04	1.10

absence of the surfactant (0.155 L mol^{-1} s^{-1}). It thus follows that the extent of substrate binding with micelles under the experimental conditions (see Table 3) was equal to ~90 %.

In order to compare the micellar effects in the processes with the participation of phenolates, we studied the influence of the cationic surfactant, CTAB, on the reaction of the substrate with PhONa. The rate constants of the reaction of the substrate with PhONa (0.05 mol L^{-1}) in aqueous solution of cationic surfactant (CTAB) at 25 °C are presented below.

$C_{CTAB} \cdot 10^2$ /mol L^{-1}	0	0.50	0.75	1.0	1.5	2.0	3.0	5.0
$k \cdot 10^3$ /s^{-1}	0.79	1.63	2.33	3.52	5.02	5.19	6.40	6.81

The values of k_m = 0.0078 s^{-1} and K_S = 176 L mol^{-1} determined by us for this system show that the nature of surfactant affects slightly the binding of the substrate by micelles. The k_m value for the system with a cationic surfactant is nearly 5 times greater than that for the process in which sodium *p*-octylphenolate participates, although the experiments with PhONa were carried out at the reduced concentration of the latter. The high k_m value for aqueous micellar solutions of CTAB cannot be explained by the difference in the reactivity of the phenolates studied, which, apparently, varies only slightly. An increase in k_m value in the system with the cationic surfactant seems to be caused by the contribution of the reaction with the hydroxide ion, which is formed in small amounts upon the hydrolysis of PhONa.[6]

It is noteworthy that already for an extent of hydrolysis of PhONa of 8 %, the k_m value in the system with the cationic surfactant was determined only by this factor, because the CTAB micelles strongly accelerate the alkaline hydrolysis of the substrate. The rate constants of hydrolysis of the substrate in aqueous-alkaline solution (0.04 *M* NaOH) of cationic surfactant (CTAB) at 25 °C are presented below.

$C_{CTAB} \cdot 10^2$ /mol L^{-1}	0	0.1	0.2	0.4	0.6	1.0
$k \cdot 10^2$ /s^{-1}	0.584	2.31	3.58	4.65	4.93	5.12

Relatively high values of k_m = 0.075 s^{-1} and K_S = 280 L mol^{-1} are obtained for the reaction of the substrate with hydroxide ion catalyzed by the CTAB micelles. The enhanced K_S value as compared to that obtained in a previous set of experiments shows that the binding of the substrate by cationic CTAB micelles also undergoes the effect of salting out by NaOH.

The activation parameters of the reactions of the substrate with hydroxide ion and phenolate differ significantly (Table 4). Therefore, their comparison for the systems studied helps to explain the mechanisms of the processes occurring. In systems containing *p*-octylphenolate anion, the activation energy E_a is close to that obtained for the reaction with phenolate ion in an aqueous solution in the absence of micelles. This is in line with the suggestion that transesterification of the substrate prevails over alkaline hydrolysis in the micelles even in an excess of alkali in the system. The enhanced value of the Arrhenius pre-exponent (*A*) for the transesterification of the substrate in the micelles of *p*-octylphenolate shows that the substrate and nucleophile are efficiently concentrated in the micellar phase. In alkaline hydrolysis of the substrate catalyzed by CTAB, the *A* value is substantially lower. This can be connected with the fact that in the bulky Stern layer hydroxide ions are concentrated to a lesser extent as compared to

Table 4. Rate constants and thermodynamic parameters of substrate decomposition in aqueous systems at different temperatures

Components of the system	$k \cdot 10^3$/s^{-1} at					*E* /kJ mol^{-1} L^{-1}	log*A*
	15 °C	25 °C	35 °C	45 °C	55 °C		
0.05 mol L^{-1} p-$C_8H_{17}C_6H_4ONa$	—	1.38	2.10	4.44	9.44	52.8	6.34
0.05 mol L^{-1} p-$C_8H_{17}C_6H_4ONa$, 0.3 mol L^{-1} NaOH	1.82	4.10	8.62	16.0	—	55.4	7.32
0.05 mol L^{-1} C_6H_5ONa	—	0.79	1.74	3.62	5.47	53.3	6.26
0.05 mol L^{-1} C_6H_5ONa, 0.05 mol L^{-1} CTMA	—	5.42	10.1	14.5	25.1	40.4	4.83
0.3 mol L^{-1} NaOH	24.6	41.8	70.7	122	—	40.6	5.74
0.04 mol L^{-1} NaOH 0.01 mol L^{-1} CTMA	20.4	42.4	66.0	117	—	43.4	6.19

Table 5. Rate constants of the reaction of the substrate with sodium *p*-octylphenolate in systems containing organic solvents at 25 °C

Rate constant	$[p\text{-}C_8H_{17}C_6H_4ONa]$/mol L^{-1}			
	0.025	0.050	0.075	0.100
	Ethylene glycol—H_2O			
$k \cdot 10^3$/s^{-1}	0.41	0.62 (0.94)*	0.88	1.22 (1.5)*
$k_2 \cdot 10^2$/L mol^{-1} s^{-1}	1.64	1.24 (1.9)*	1.17	1.22 (1.5)*
	Polyethylene glycol—H_2O			
$k \cdot 10^3$/s^{-1}	0.58	2.15	3.85	5.91
$k_2 \cdot 10^2$/L mol^{-1} s^{-1}	2.3	4.3	5.1	5.9
	DMF—H_2O			
	$[p\text{-}C_8H_{17}C_6H_4ONa]$/10^2 mol L^{-1}			
	0.25	0.50	0.75	1.00
$k \cdot 10^2$/s^{-1}	0.035	0.418	1.94	6.23
k_2/L mol^{-1} s^{-1}	0.14	0.84	2.6	6.2

* For the reaction of the substrate with C_6H_5ONa under the same conditions.

p-octylphenolate ions participating in the micelle formation. The above-mentioned assumption on the possibility of alkaline hydrolysis of the substrate in a system containing phenolate and CTAB is confirmed by the fact that the E_a value estimated for the system is close to that found for alkaline hydrolysis of the substrate and is much lower than that for transesterification (see Table 4).

When the reactions involving phenolate ions are carried out in solvents that are less polar than water, their mechanism is complicated by ion association.[17] We estimated the rate constants for the reaction of the substrate studied with sodium *p*-octylphenolate in several solvents that differ in their polarity.

The decrease in the polarity of the proton-donor solvent on passage from water to an ethylene glycol—water system (92.8 % ethylene glycol, v/v) results in *p*-octylphenolate losing the capability of micelle formation and reacting like other phenolates. For sodium *p*-octylphenolate and for PhONa, a decrease in the bimolecular rate constant $k_2 = k/C_{\mathrm{PhO^-}}$ was observed in this system with increased concentration of phenolates (Table 5), which attests to the substantial association of the latter. One can suggest that the formation of loose ion pairs separated by a solvent[17] occurs in this system, and these pairs exhibit lesser reactivity as compared to free anions.

To the contrary, the k_2 value in the system containing 92.8 % polyethylene glycol-400 in water, v/v (see Table 5) increased with increase in the concentration of *p*-octylphenolate ion, indicating the formation of ion pairs with higher reactivity than those of free anions. Apparently, in this case contact ion pairs, not separated by a solvent, are formed, and they are capable of electrophilic catalysis by a cation.

The association of sodium *p*-octylphenolate in ion aggregates with enhanced reactivity is most pronounced in the water—DMF system (99.3 % DMF, v/v). The rate constants obtained for this system (see Table 5) are many times higher as compared to other systems studied, including micellar solutions. Previously,[5] we have established that in DMF ion pairs of phenolates exhibit higher reactivity than free ions in the reactions of transesterification at the phosphorus atom.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 95-03-09277a).

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Received June 20, 1995;
in revised form November 9, 1995