The influence of the structure of tetracoordinate phosphorus acid esters on the catalytic effect of the sodium dodecyl sulfate—hexanol—water ternary reverse micellar system

L. Ya. Zakharova,* F. G. Valeeva, R. A. Shagidullina, and L. A. Kudryavtseva

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center, Russian Academy of Sciences,
8 ul. Akad. Arbuzova, 420088 Kazan, Russian Federation. Fax: +7 (843 2) 75 2253. E-mail: vos@iopc.kcn.ru

The catalytic effect of the sodium dodecyl sulfate—hexanol—water ternary reverse micellar system in the alkaline hydrolysis of O-alkyl O'-aryl chloromethylphosphonates as a function of the substrate structure was studied. The micellar effect is mainly determined by a change in the electronic properties of the substituents, while the hydrophobicity plays a secondary role. The kinetic data were examined in the framework of the pseudo-phase model of micellar catalysis. The rate constants of the reaction in the surface layer and the partition constants of the reactants were calculated.

Key words: reverse micelles, pseudo-phases, surface layer, kinetics, hydrolysis, phosphonates.

Reverse micelles are widely known as biomimetic structures that work according to the "guest-host" principle.¹ The main qualitative regularities of catalysis of chemical reactions in these systems are poorly studied and only a few quantitative studies were performed. We have previously^{2,3} shown that in the reverse micellar system sodium bis(2-ethylhexyl) sulfosuccinate (AOT)decane-water the alkaline hydrolysis of phosphonates proceeds more slowly than in water, and in the system sodium dodecyl sulfate (SDS)-hexanol-water the reaction is accelerated. To reveal the main reasons for catalysis of reactions and to solve the problem of substrate specificity in these organized media, the range of substrates under study should be enlarged. With this purpose, we studied the kinetics of the hydrolysis of O-alkyl O'-arvl chloromethylphosphonates (1-10)(Scheme 1) at different ratios Z = |hexanol|/[SDS] and $W = [H_2O]/[SDS]$ and examined the kinetic data in the framework of the pseudo-phase model of micellar catalysis.

Experimental

Compounds 1-10 were prepared by a known procedure.⁴ The synthesized esters were triply distilled. The purity of compounds 5-10 was confirmed by elemental analysis (Table 1). Phosphonates 1-4 have been synthesized by us previously.⁵

SDS (high-purity grade) was doubly recrystallized from ethanol. Reverse micellar systems were prepared by the mixing of three components according to the phase diagram^{6,7} followed by shaking to the formation of a transparent solution. The molar ratios $W = [H_2O]/[SDS]$ and Z = [hexanol]/[SDS] were varied in the intervals of 9.8–37 and 5–49, respectively. The reaction kinetics was studied spectrophotometrically on a Specord M-400

Scheme 1



 $\begin{array}{l} X = NO_2, \ R = Et \ (1), \ Bu^n \ (2), \ n\mathchar`C_6H_{13} \ (3), \ n\mathchar`C_8H_{17} \ (4); \\ R = Et, \ X = Br \ (5), \ H \ (6), \ Et \ (7), \ Bu^n \ (8), \ n\mathchar`C_8H_{17} \ (9), \\ iso\mathchar`C_{12}H_{25} \ (10) \end{array}$

instrument by the change in the optical density of the anion of the leaving group. The initial concentration of the substrate was $5 \cdot 10^{-5}$ mol L⁻¹, and the concentration of the nucleophile much exceeded that of the substrate. The observed rate constants (k_{obs}) were calculated using the weighted least-squares method from the dependence $\ln(D_{\infty} - D) = -k_{obs}t + \text{const}$, where D and D_{∞} were the optical densities of the solution at the moment t and at the end of the reaction.

The kinetic data were examined according to the pseudophase approach. For the reaction that occurs in the surface layer, where a reactant is distributed between the oil phase and the surfactant monolayer and the second reactant is distributed between the surface layer and water, the equation for the observed rate constant has the form⁸

$$k_{\rm obs} = \frac{k_{\rm i}K_{\rm S}K_{\rm OH}[\rm OH]_{\rm tot}}{(K_{\rm S}+Z)(K_{\rm OH}+W)[\rm Surf]},$$
(1)

where Surf is a surfactant; k_i/s^{-1} is the rate constant in the surface layer corresponding to the nucleophile concentration

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Substrate	B.p. /°C	n _D ²⁰		Molecular formula			
	(p/Torr)		С	н	Hal	Р	
5	165 (0.02)	1.5425	$\frac{34.38}{34.45}$	<u>3.47</u> 3.51	<u>36.70</u> 36.84	<u>9.80</u> 9.89	C ₉ H ₁₁ O ₃ PBrCl
6	120 (0.05)	1.5115	<u>45.99</u> 46.06	<u>5.15</u> 5.12	<u>15.20</u> 15.14	<u>13.27</u> 13.21	C ₉ H ₁₂ O ₃ PCI
7	125 (0.04)	1.5095	<u>50.20</u> 50.28	<u>6.13</u> 6.09	<u>13.59</u> 13.52	<u>11.90</u> 11.81	C ₁₁ H ₁₆ O ₃ PCI
8	125 (0.03)	1.5020	<u>53.62</u> 53.70	<u>6.93</u> 6.88	<u>12.31</u> 12.25	<u>10.74</u> 10.67	C ₁₃ H ₂₀ O ₃ PCl
9	145 (0.03)	1.4970	<u>58.78</u> 58.87	<u>8.12</u> 8.08	<u>10.29</u> 10.25	<u>8.98</u> 8.95	C ₁₇ H ₂₈ O ₃ PC1
10	165 (0.03)	1.4990	<u>62.58</u> 62.61	<u>8.98</u> 8.94	<u>8.89</u> 8.82	<u>7.72</u> 7.70	C ₂₁ H ₃₆ O ₃ PCl

Table 1. Physicochemical parameters of compounds 5-10

expressed as the molar ratio [OH]/[SDS]; k_i is related to the pseudo-first order rate constant k_i'/s^{-1} and the second-order rate constant $k_{2,i}/L$ mol⁻¹ s⁻¹ by the correlations

$$k_{i}' = k_{i} \frac{[OH^{-}]}{[Surf]}, \qquad k_{2,i} = k_{i} V.$$
 (2)

where V is the molar volume of the surfactant $(L \mod^{-1})$; [OH]_{tot} is the total concentration of the OH⁻ ion (mol L⁻¹); K_S is the partition constant of the substrate between the oil phase and surfactant:

$$K_{\rm S} = \frac{[\rm S]_i[\rm hexanol]}{[\rm S]_o[\rm Surf]};$$

and K_{OH} is the partition constant of the OH⁻ ion between the aqueous phase and surfactant:

$$K_{\rm OH} = \frac{[\rm OH^-]_i[\rm H_2O]}{[\rm OH^-]_w[\rm Surf]}.$$

The molar concentrations of the substrate (S), hexanol, and the surfactant are given in brackets; and indices i, o, and w refer to the surface layer and the oil and aqueous pseudo-phases, respectively. The main assumptions and approximations used in the pseudo-phase model have been discussed previously.⁹

Results and Discussion

According to the pseudo-phase approach, three microscopic regions are distinguished in the reverse micelles: the aqueous core, the surface layer formed by hydrocarbon chains of the surfactant, and the oil pseudophase.¹⁰ It is most likely that the reaction involving the hydrophobic substrate and hydrophilic nucleophile proceeds in the surface layer of the surfactant, whose amphiphilic properties provide affinity to both reactants.

We compared the reactivities of the substrates in two series: 1-4, where the hydrophobicity of the alkoxyl group changes, and 1, 5-10, where both the electronic properties and hydrophobicity of the leaving group considerably change. In the absence of surfactants, the reactivity of compounds 1-4 in water slightly decreases with an increase in R, which is related to an increase in the steric hindrances for the attack of the reaction center.⁵ The kinetic data for substrates 1-4 in SDS reverse micelles are presented in Fig. 1. It can be seen that an increase in the hydrophobicity of the alkyl group affects k_{obs} only on going from 1 to 2, whereas k_{obs} for substrates 2-4 is virtually the same. This behavior of substrates 1-4 in the reverse micellar system SDS-hexanol-water sharply differs from that observed in the direct CPB and CTAB micelles, where the catalytic effect substantially increases with an increase in the hydrophobicity of the substrates.^{5,11}

When the SDS concentration and water content in the system increase, k_{obs} decreases. This tendency has previously been observed by us and other researchers.^{2,8} It is most likely that this regularity is characteristic of reactions that occur in the surface layer of the reverse micelles. The decrease in the rate constant with increase in the SDS and water concentrations can be due to the dilution of the reactants in the micelles when the volume fraction of the dispersed phase increases.

In series 1, 5–10 (variation of the substituent in the leaving group) in water in the absence of a surfactant, the reactivity changes nonuniformly. The constant $k_{2,w}$ decreases substantially in series 1, 5, and 6 ($k_{2,w} = 4.0$, 0.55, and 0.24 L mol⁻¹ s⁻¹, respectively) due to the weakening of the electron-withdrawing properties of the substituent X in the series NO₂, Br, and H, which destabilizes the leaving group.¹² The reactivities of 6 and 7 in water are almost equal (Table 2), and an increase in the length of the alkyl substituent in compounds 7–10 gradually decreases the reactivity due to the enhancement of the positive inductive effect of the substituent.

The kinetic data for substrates 5-10 are presented in Figs. 2 and 3. In SDS reverse micelles and in water, a noticeable decrease in the hydrolysis rate of phosphonates 1, 5, and 6 is observed (see Figs. 1 and 2), which is likely related to a decrease in $k_{2,i}$ in this series (see



Fig. 1. Observed rate constants of alkaline hydrolysis (k_{obs}) of substrates 1-4 (curves 1-4, respectively) as functions of the SDS concentration (a) at W = 15.1, [NaOH] = 0.002 mol L⁻¹, and 25 °C and of the water content (b).

Table 2). In addition, the catalytic effect decreases in this series. The maximum acceleration of the reaction of substrates 1, 5, and 6 in a micellar solution as compared to water $(k_{obs}/k_w)_{max}$ is equal to 30, 14, and 3.6, respectively. The reactivity of substrates 6–10 in SDS reverse micelles noticeably differs from their behavior in water. In micellar solutions we observed a substantial difference in k_{obs} for 6 and 7 and virtually the same rate constants for phosphonates 7–10 (see Fig. 2), whereas $k_{2,w}$ smoothly decreased with an increase in the length of the alkyl group in the *para*-position of the leaving group.

Thus, in the SDS reverse micellar system, a decrease in the electron-withdrawing properties of X that destabilizes the leaving group considerably decreases k_{obs} , whereas an increase in the hydrophobicity of the sub-

Table 2. Results of kinetic data processing by Eq. (1)

Sub- strate	Ks	K _{OH}	k _i	k _{2.i} ^a	k _{2.w} ^b	$k_{2,i}/k_{2,w}$	$(k_{obs}/k_w)_{max}^{c}$	
			/s=1	L mol	L mol ⁻¹ s ⁻¹			
5	100	7	5.40	2.00	0.55	3.6	14	
6	80	2.2	1.90	0.70	0.24	2.9	3.6	
7	80	40	0.15	0.05	0.20	0.26	2.2	
8	70	9.4	0.3	0.11	0.16	0.69	2.6	
9	90	90	0.14	0.05	0.12	0.42	3.1	
10	60	40	0.14	0.05	0.08	0.62	4.9	

 $^{a} V = 0.37 \text{ L mol}^{-1}$ (see Ref. 8).

^b The second-order reaction rate constant in water is designated by $k_{2,w}$.

^c The maximum acceleration equal to the ratio of the rate constants of the pseudo-first order in a micelle to water is designated by $(k_{obs}/k_w)_{max}$.

stituent X has almost no effect on the hydrolysis rate (see Fig. 2). As a result, the catalytic effect of SDS reverse micelles changes in the series of substituents X as follows:

$$NO_2 > Br > H > Et \approx Bu^n \approx p - C_8 H_{17} \approx iso - C_{12} H_{25}$$

This order of changing the reactivity confirms our previous¹¹ assumption that in reverse micelles, unlike direct



Fig. 2. Observed rate constants of alkaline hydrolysis of substrates 6-10 as functions of the SDS concentration (curves 1-5, respectively); W = 15.1, 0.01 M NaOH, 25 °C. Similar dependence for substrate 5 is shown in insert.



Fig. 3. Observed rate constants of alkaline hydrolysis of substrates 6-10 as functions of the water content (curves l-5, respectively); 0.01 *M* NaOH, 25 °C. Similar dependence for substrate 5 is shown in insert.

micelles, the effect of concentrating directly related to the hydrophobicity of the reactants plays a secondary role. As in series 1-4, k_{obs} decreases with an increase in the SDS concentration (see Fig. 2). The dependence of k_{obs} on W for substrates 6-9 somewhat differs from that in series 1-4. A noticeable decrease in k_{obs} with an increase in W is observed only for compounds 5 and 6, whereas for substrates 7-10 k_{obs} is almost independent of W (see Fig. 3).

The plots of k_{obs} as a function of [NaOH] for substrates 5 and 6 are presented in Fig. 4. As in the earlier work,³ in SDS reverse micelles, unlike AOT, the straight line does not pass through zero, whereas in the case of substrate 5 (X = Br), two pronounced regions with different slopes are observed. It has been shown³ that this change in the slope can be related to the transposition of the reaction zone, which changes the microenvironment of the reactants and their reactivity. It is most likely that an increase in the alkali concentration creates favorable conditions for the redistribution of the OH⁻ ions between the aqueous phase and surface layer due to an increase in the electrochemical potential of the OH⁻ ion in the micelle core.

We are the first to observe an interesting specific feature of the behavior of substrates 6-10: depending on the concentrations of the surfactant and alkali and the W value, the SDS—hexanol—water reverse system exhibits either an acceleration or retardation of alkali hydrolysis as compared to the reaction rate in water (see Fig. 4).

We have previously shown that for the SDShexanol-water system at low alkali concentrations, the pseudo-phase model becomes inadequate for the kinetic data. Probably, under these conditions, processes that



Fig. 4. *a*. Observed rate constant of the alkaline hydrolysis of 5 as a function of the concentration of NaOH for water (*I*) and at [SDS]/mol L⁻¹ = 0.75 (2), 0.52 (3), 0.38 (4), 0.26 (5), and 0.15 (6); W = 15.1, 25 °C. *b*. Observed rate constant of alkaline hydrolysis of **6** as a function of the concentration of NaOH at [SDS]/mol L⁻¹ = 0.75 (*I*), 0.38(2), 0 (3), 0.26 (4), and 0.15 (5); W = 15.1, 25 °C.

occur in other pseudo-phases, rather than only those at the interface, contribute to the k_{obs} value. Similar behavior was observed for substrates 1-4, whose hydrolysis kinetics was measured, because of their high reactivity at low alkali concentrations (0.002 mol L⁻¹ NaOH). Under these conditions, Eq. (1) is not fulfilled. It is most likely that at a low alkali concentration the OH⁻ ions are concentrated in the aqueous core and do not penetrate into the surface layer due to the electrostatic repulsion from the head groups. The reaction of the substrates with the OH⁻ ions in water, probably, contributes mainly to k_{obs} . An increase in the NaOH concentration can result in the redistribution of the OH⁻ ions between the aqueous phase and interphase via the concentration gradient, which is facilitated by a partial counterbalance of the charge of the head groups by the Na⁺ cations.

For substrates 5–10, Eq. (1) is fulfilled (concentration of NaOH 0.01 mol L^{-1}) (Fig. 5), which can serve as



Fig. 5. Linearization of the kinetic data for substrates 5-10 by Eq. (1) (straight lines 1-6, respectively); W = 15.1, 0.01 M NaOH.

kinetic evidence for the occurrence of the reaction in the surface layer. It is seen from the data in Table 2 that the partition constant of the substrates $K_{\rm S}$ weakly depends on their hydrophobicity. At the same time, K_{OH} for the more hydrophobic substrates is higher than that for compound 6, whose benzene ring contains no substituent. By contrast, k_i for this substrate is much higher than those for its substituted homologs, which results in a higher value of k_{obs} . The alignment of the reactivity of substrates 2-4 and 7-10 in reverse micelles as compared to water should be mentioned. The rate of the alkaline hydrolysis of these phosphonates in micelles is almost the same (see Figs. 1-3), and substrate specificity is absent. As has been shown previously,5,11 the principle of recognition of substrates by their hydrophobicity acts in direct micelles, i.e., the differential influence of micelles on the reactivity is observed. This indicates different mechanisms of the catalytic effect of direct and reverse micelles.

It is seen from the data in Table 2 that for substrates 5 and 6 $k_{2,i}/k_{2,w} > 1$, *i.e.*, the micellar microenvironment has a favorable effect on the reactivity. As the hydrophobicity of the substrates in the series 7-10increases, $k_{2,i}/k_{2,w}$ becomes lower than unity, which indicates the destabilizing effect of the transfer of the reaction from the aqueous phase to the micellar phase. It can be assumed that the reaction series under study is sensitive to the microenvironment of the reactants. An insignificant variation of the experimental conditions resulting in a change in the localization or orientation of compounds can lead to transition from catalysis of the reaction to inhibition (see Fig. 4).

Thus, study of the kinetics of the alkaline hydrolysis of phosphonates in the SDS-hexanol-water reverse micellar system showed that the change in the electronwithdrawing properties of the substituent has the strongest influence on the micellar effect, and the hydrophobicity is insignificant.

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