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Reactivity of Inorganic α-Nucleophiles in Acyl Group Transfer Processes in Water and Surfactant Micelles:
II.[1] Alkaline Hydrolysis of Ethyl 4-Nitrophenyl Ethylphosphonate in Systems Based on Dimeric Cationic Surfactants

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Abstract—Alkaline hydrolysis of ethyl 4-nitrophenyl ethylphosphonate in organized nanosized systems based on dimeric surfactants and co-micelles [with cetyl(trimethyl)ammonium bromide as co-surfactant]. Transfer of the reaction from water to the micellar pseudophase accelerates the alkaline hydrolysis by a factor of 10 to 170. The maximum acceleration has been observed for tetraalkylammonium surfactant 16–3–16. The main factors responsible for micellar effects of surfactants are both substrate concentration and change of the reactivity of hydroxide ion in going from bulk water to surfactant micelles.

Keywords: organized nanosized systems, dimeric cationic surfactants, acyl substrates, micellar effects, reactant concentrating.

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Decomposition of highly toxic organophosphorus compounds in solution in conformity to the "green chemistry" principles requires a safe and cheap solvent [2, 3]. For this purpose, the most appropriate solvent is water despite significant limitations related to low substrate solubility. Since organophosphorus compounds, as well as other model analogs of environmental toxicants, are often almost insoluble in water, aqueous surfactant solutions are commonly used as medium for decomposition of such substrates [4, 5]. In this case, the reactants are distributed between the micellar pseudophase and bulk water via electrostatic and hydrophobic interactions, and the observed increase of the reaction rate is determined mainly by concentrating of the reactants and specific physicochemical properties of the micellar environment. Among new synthetic surfactants, of particular interest as host molecules are gemini surfactants. This unique class of surfactants features a number of unusual physicochemical characteristics such as very low critical micelle concentration (CMC), highly efficient adsorption, etc. [6–10]. Most publications on physical chemistry of dimeric surfactants are concerned just with their specific aggregation properties [6–10]. Problems related to the reactivity of various nucleophiles, including conventional ones and α-nucleophiles, and reagent structure–surfactant–micellar effects relationships have been explored to a lesser extent [11–14].

Herein, we report micellar catalysis of the alkaline hydrolysis of ethyl 4-nitrophenyl ethylphosphonate (ENPEP) in organized nanosized systems based on tetraalkylammonium surfactants **1** and **2**. The micellar effects of dimeric cationic surfactants were compared with those of their monomeric analog, cetyl(trimethyl)-ammonium bromide, in order to find our whether the use of surfactants **1** and **2** is more advantageous or not (Scheme 1).

Alkaline hydrolysis is considered a background reaction, which should make it possible to estimate variation of micellar effects when a typical α-nucleophile such as hydroperoxide ion is taken as a reagent.

Kinetics of alkaline hydrolysis of ENPEP in the presence of surfactants 1 and 2 and cetyl(trimethyl)-ammonium bromide. Alkaline hydrolysis of acyl substrates (S), including ENPEP, in the presence of surfactants proceeds concurrently in the micellar (m) and

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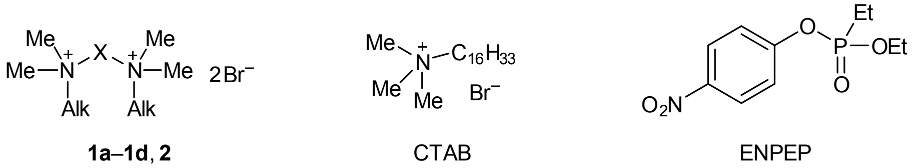
[1] For communication I, see [1].

Scheme 1.



1, X = $(CH_2)_2$, Alk = $C_{16}H_{33}$ (**a**), $C_{14}H_{29}$ (**b**), $C_{12}H_{25}$ (**c**), $C_{10}H_{21}$ (**d**); **2**, X = $(CH_2)_3$, Alk = $C_{16}H_{33}$.

aqueous (w) phases (Scheme 2). The observed rate constants k_{obs} increase with rise in pH, unambiguously indicating that the reactive species is hydroxide ion (Fig. 1). The dependence of k_{obs} on the surfactant concentration (c_0, M) is more complicated: as the substrate binding tends to be complete, the k_{obs} value approaches a certain limiting value ($k_{\text{obs,max}}$), and further increase of c_0 is accompanied by weakening of the substrate concentration effect, which could lead to decrease of k_{obs} (Fig. 1).

The effect of micelles on the reaction rate in water is usually considered in the framework of the pseudophase model (Scheme 2) [4, 5, 15, 16], according to which substrate distribution (overall concentration $[S]_0$) between water and micelles is given by Eq. (1):

$$[S]_m = K_S\,[D]_n[S]_0/(1 + K_S[D]_n) = K_S c[S]/(1 + K_S c), \quad (1)$$

where $[D]_n = [D]_0 - \text{CMC} = c_0 - \text{CMC} = c$ (M) is the concentration of micellized surfactant, CMC (M) is the critical micelle concentration; K_S (L/mol) is the substrate binding constant, and the concentrations are reduced to the overall volume of the solution [15].

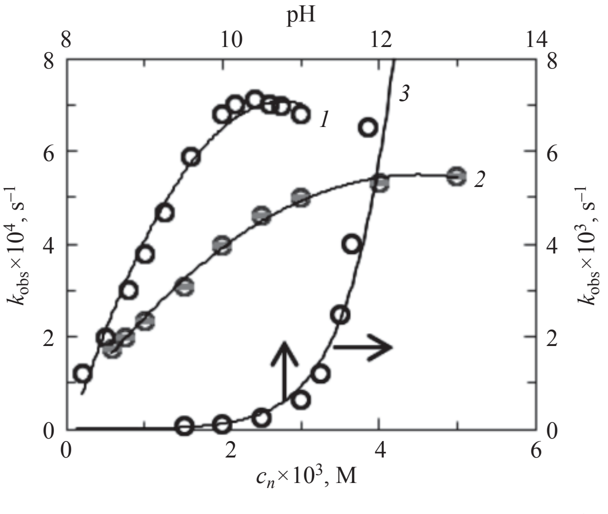


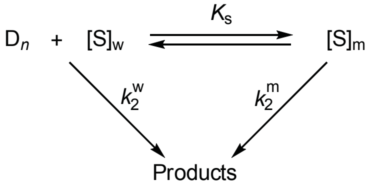
Fig. 1. Dependences of the observed rate constants (k_{obs}, s^{-1}) for the alkaline hydrolysis of ENPEP on the concentrations of surfactants (*1*) **2** and (*2*) **1a** at pH 10.0 and (*3*) on pH in the presence of surfactant **1c**; temperature 25°C.

With account taken of Scheme 2 and Eq. (1), the observed rate constant can be expressed as Eq. (2):

$$k_{\text{obs}} = (\chi k_m K_s c + k_2^w[\text{OH}^-])/(1 + K_s c). \quad (2)$$

Here, c is the mole fraction of dimeric surfactant; k_m (s^{-1}) is the reduced first-order rate constant of the reaction in surfactant micelles, $k_m = k_2^m/V_m$; V_m (L/mol) is the partial molar volume; and k_2^m and k_2^w (L mol^{-1} s^{-1}) are the second-order rate constants characterizing the nucleophilicity of hydroxide ion in water and surfactant micelles. Because of the complexity of choice, the V_m value for dimeric cationic surfactants was assumed to be 0.597 L/mol [17, 18], and V_m = 0.37 L/mol was taken for CTAB [15]. Table 1 contains some physicochemical parameters of the alkaline hydrolysis of ENPEP in the presence of surfactants **1** and **2** and CTAB.

Scheme 2.



Micellar effects of surfactants in the alkaline hydrolysis of ENPEP. Critical micelle concentration is the most important characteristic of the micelle formation process. CMC values for dimeric surfactants like **1** and **2** determined by different methods (conductometry, tensiometry, etc.) have been reported in [18–21]; these methods utilized water as a solvent. The CMC values determined under the conditions of our kinetic experiments may be different from those given in [18–21]. This may be due to several factors, including the presence of buffer additives. For example, the CMC of **1d** was estimated by us at 6×10^{-3} M on the basis of our kinetic data (Fig. 2; cf. CMC = 6.96×10^{-3} M [21]). The CMC values regularly increase as the alkyl substituent on the nitrogen becomes shorter: 2.1×10^{-5} (**1a**) [19], 8.7×10^{-4} (**1c**), 6.96×10^{-3} M (**1d**) [21]. Hydrophobicity

Table 1. Physicochemical parameters of alkaline hydrolysis of ethyl 4-nitrophenyl ethylphosphonate in the presence of surfactants **1** and **2**

Substrate	χ[a]	$k_m \times 10^4$,[b] s^{-1}	$k_2^m \times 10^4$,[c] L mol^{-1} s^{-1}	K_S,[d] L/mol	k_m/k_{obs}^w[e]
16–3–16 (**2**)	1	2.6×10^{-3}	0.15	171±39	170
16–2–16 (**1a**)	1	2.6×10^{-3}	0.15	107±21	170
16–2–16	0.5	1.2×10^{-3}	0.72	190±12	80
16–2–16	0.25	7.42×10^{-4}	4.43	202±14	50
16–2–16	0.1	4.68×10^{-4}	2.79	235±15	31
14–2–14 (**1b**)	1	4.74×10^{-4}	2.83	443±36	32
12–2–12 (**1c**)	1	5.00×10^{-4}	2.98	256±25	33
12–2–12	0.5	3.60×10^{-4}	2.15	472±27	24
12–2–12	0.25	5.22×10^{-4}	3.12	345±13	35
12–2–12	0.1	5.28×10^{-4}	3.15	473±58	35
10–2–10 (**1d**)	1	1.19×10^{-4}	0.71	420±44	8
10–2–10	0.5	3.31×10^{-4}	1.98	483±105	22
10–2–10	0.25	4.74×10^{-4}	2.83	422±36	49
10–2–10	0.1	5.60×10^{-4}	3.34	357±36	37
CTAB	1	3.42×10^{-4}	2.04	584±60	23

[a] Mole fraction of dimeric surfactant in co-micelles with CTAB.
[b] Reduced first-order rate constant.
[c] Reactivity of hydroxide ion in the micellar pseudophase.
[d] Substrate binding constant.
[e] Micellar effects of surfactants; pH 10.0, 25°C.

of the surfactants should be expected to change in the same order. Hydrophobic interactions are one of the main factors responsible for the micelle formation process. Therefore, the observed decrease of CMC with increase of the alkyl chain length reflects the efficiency of micelle formation.

Undoubtedly, the micellar effects of surfactants are related to their hydrophobic properties. In fact, elongation of the alkyl "tail" is accompanied by increase of the observed rate constants (Fig. 3) which change in the following order: **2** > **1a** = **1b** ≈ **1c** ≈ CTAB > **1d**. The micellar effect can be evaluated by the ratio k_{obs}(Surf))/k_{obs}^w or k_m/k_{obs}^w. Provided that $k_{obs}^w \approx 1.5\times10^{-5}$ s^{-1} and that pH = 10.0, the k_m/k_{obs}^w ratio changes from ~10^2 (**1a**, **2**) to ~10 (**1d**) (Table 1). It should be noted that k_{obs}(Surf)/k_{obs}^w (**2**) is higher than k_{obs}(Surf)/k_{obs}^w (**1a**) by a factor of 1.4. This difference is fairly insignificant, and primarily reflects the efficiency of substrate concentrating in mitcelles formed by **1a** and **2** (cf. K_S values in Table 1).

Shortening of the alkyl chain increases the solubility of surfactants in water. However, increase in the solubility is accompanied by increase of the critical micelle concentration. Therefore, micelles are formed at higher surfactant concentrations, and similar rates of hydrolysis of ENPEP are observed at different c_0 values. For example, $k_{obs} \approx 1.0\times10^{-4}$ s^{-1} in the hydrolysis of ENPEP in the micellar system based on surfactant **2** is achieved at $c_0 \approx 2.0\times10^{-4}$ M, whereas the corresponding concentrations of **1a**, **1b**, **1c**, **1d**, and CTAB are ~4.0×10^{-4}, ~6.0×10^{-4}, ~1.0×10^{-3}, ~1.2×10^{-2}, and ~1.0×10^{-3} M, respectively.

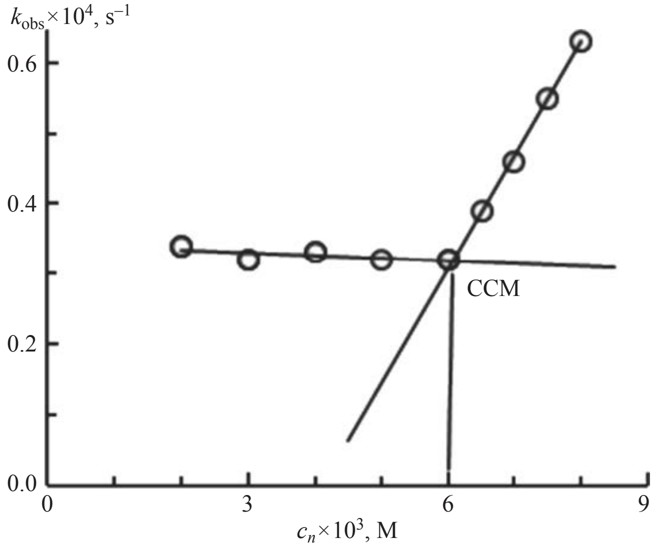


Fig. 2. Determination of the critical micelle concentration of surfactant **1d** from the kinetic data; pH 10.0, 25°C.

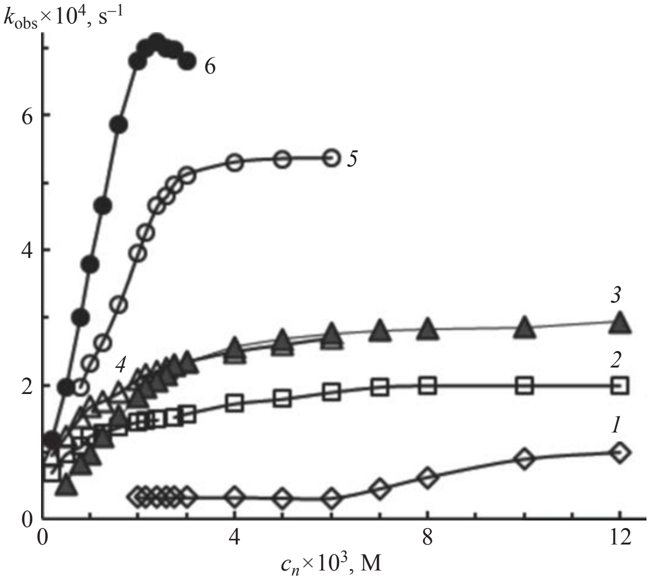


Fig. 3. Dependences of the observed rate constants (k_{obs}, s^{-1}) for the reaction of ENPEP with hydroxide ion in micelles on the overall concentration of surfactants (*1*) **1d**, (*2*), CTAB, (*3*) **1c**, (*4*) **1b**, (*5*), **1a**, and (*6*) **2**; pH 10.0, temperature 25°C.

Factors responsible for micellar effects of surfactants. Presumably, the main factors responsible for the acceleration of alkaline hydrolysis of ENPEP in the presence of surfactants are reactant concentration effect and change of the microenvironment upon transfer of the reaction from water to micellar pseudophase.

The effect of reactant concentration reflects primarily the ability of micellar pseudophase to solubilize various compounds [4, 5]. Solubilization by micelles in aqueous medium is closely related to the hydrophobicity and biphilicity of substrates. Ethyl 4-nitrophenyl ethylphoshonate is an electrically neutral substrate which binds to surfactant micelles mainly via hydrophobic interactions. The binding constants K_S characterizing the efficiency of substrate solubilization increase as the alkyl chain shortens (Table 1), which seems surprising. A different relation was observed between the binding constant and alkyl chain length for dimeric cationic and functionalized imidazolium surfactants [22–24]: both K_S values and micellar effects of surfactants increased with rise in the number of methylene units. In these cases, the effect of reactant concentrating was crucial in the micellar catalysis. Unusual variation of the substrate solubilization efficiency was also noted for functionalized tetraalkylammonium surfactants [24]. It should be emphasized that dimeric surfactants, including those containing an Alk_3N^+ head group, are characterized by easy modification of the micelle structure; in particular, arbitrarily spherical, rod-shaped, thread, etc., micelles can be formed [13]. In order to minimize contact of the spacer with water, dimeric surfactants with $n = 3$ (**1a**, **2**) form micellar aggregates 16–*n*–16 as worm-like threads. Such micelles are likely to create a more favorable reaction medium than does CTAB. Nevertheless, as shown in [13], the optimal spacer length in terms of reaction rate is $n = 4$, and the optimal micelle shape is thread-like.

The second factor that should be considered in the analysis of micellar effects is the influence of microenvironment on the rate of alkaline hydrolysis. For all the examined surfactants, the second-order rate constant in the micellar pseudophase is significantly lower than k_2^w in water ($k_2^w = 0.15$ L mol^{-1} s^{-1} [25]; Table 1). This pattern is typical of most alkaline hydrolysis reactions [15, 14, 22–24, 26, 27]. On the other hand, as we noted above, the contribution of micellar effects ranges from ~10 to 10^2 times. This is not surprising. The overall reaction rate will increase even when the second-order rate constant in micelles is lower than in water, provided that the reactants are concentrated in a small micelle volume. This mode of variation of micellar effects is primarily determined by the favorable substrate distribution between water and micellar pseudophase. First, it should also be kept in mind that decrease of the polarity of the medium reduces the reactivity of hydroxide ion. Second, unlike electrically neutral hydrophobic substrates, there are no interactions (hydrophobic, electrostatic) that would contribute to the concentration of hydroxide ions in surfactant micelles.

From the practical viewpoint, the pattern of variation of physicochemical properties of surfactants (CMC, K_S) makes the basis for proper choice of a strategy for the modification of their structure with the goal of creating supernucleophilic organized nanosized systems for the decomposition of organophosphorus compounds. For example, shortening of the alkyl chain increases the solubility of surfactants in water. Undoubtedly, this counts in favor of surfactants with shorter alkyl substituents. The solubility of dimeric surfactants in water can be partially improved by using co-micellar systems where one of the surfactants is monomeric CTAB. Moreover, as shown in [28], different micelle types at different ratios behave as aggregates with averaged properties of the constituent micelles. In this case, mixed micelles occupy an intermediate position, as evident from the similarity of the aggregation numbers of the monomers, effective fractional charge of micelles, etc. The effect of CTAB in co-micelles **1a**/CTAB and **1c**/CTAB is radically different. The observed rate constant k_{obs} increases for **1a**/CTAB ($Alk = C_{16}H_{33}$) with rise in the mole fraction of the dimeric surfactant (Fig. 4). The opposite pattern

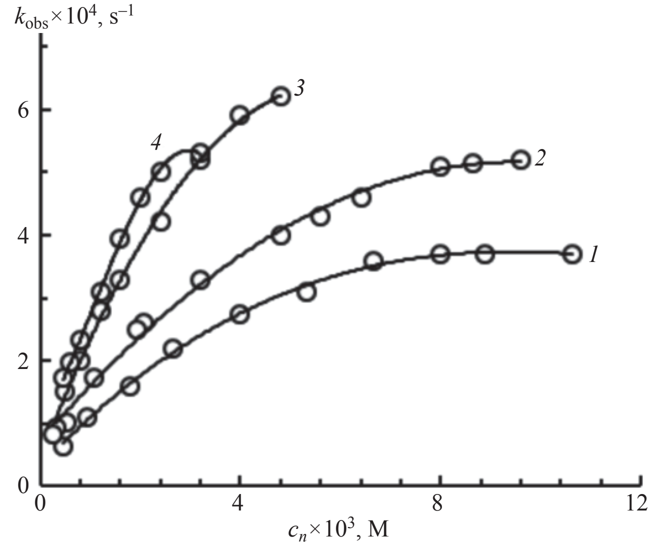


Fig. 4. Dependences of the observed rate constants (k_{obs}, s^{-1}) for the reaction of ENPEP with hydroxide ion on the overall surfactant concentration in co-micelles **1a**/CTAB with a fraction of **1a** (χ) of (*1*) 0.1, (*2*) 0.25, (*3*) 0.5, and (*4*) 1.0; pH 10.0, temperature 25°C.

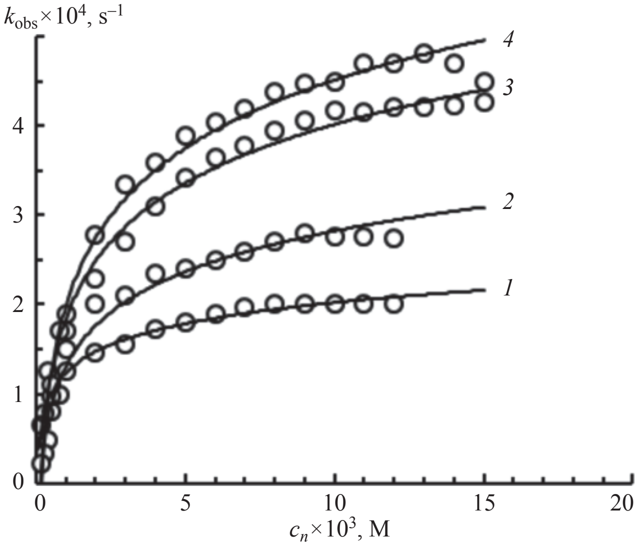


Fig. 5. Dependences of the observed rate constants (k_{obs}, s^{-1}) for the reaction of ENPEP with hydroxide ion on the overall surfactant concentration in co-micelles **1c**/CTAB with a fraction of **1c** (χ) of (*1*) 1.0, (*2*) 0.5, (*3*) 0.25, and (*4*) 0.1; pH 10.0, temperature 25°C.

is observed for co-micelles **1c**/CTAB: the k_{obs} value decreases as the fraction of dimeric surfactant increases (Fig. 5). This relation between the co-micelle composition and observed rate constants is quite expected: in the first case, k_{obs}(**1a**/CTAB) > k_{obs}(**1a**), and in the second case, k_{obs}(**1c**/CTAB) > k_{obs}(CTAB). These findings just reflect the contribution of hydrophobic interactions and concentration effects to the increase or decrease of the observed rate constant. It should also be noted that the size and properties of mixed micelles can be controlled only by variation of their composition.

In summary, dimeric surfactants **1a** and **2** with a long-chain alkyl tail group and anomalously low CMC values at a concentration lower by an order of magnitude make it possible to achieve the same rate of alkaline hydrolysis of ethyl 4-nitrophenyl ethylphosphonate as in the presence of surfactants **1b**–**1d**. Undoubtedly, the magnitude of micellar effects depends on the micelle morphology which is directly related to the number of methylene units in the spacer between the cationic head groups. Variation of the spacer structure is one of the possible ways of modification of dimeric surfactants with the goal of obtaining supernucleophilic systems based on a common nucleophile, hydroxide ion.

EXPERIMENTAL

(Ethane-1,2-diyl)bis[alkyl(dimethyl)ammonium] dibromides **1a**–**1d** and (propane-1,3-diyl)bis[hexadecyl(dimethyl)ammonium] dibromide (**2**) were synthesized as described in [29]. Commercial hexadecyl(trimethyl)ammonium bromide (Sigma–Aldrich) was recrystallized from acetonitrile. The structure of these compounds was confirmed by elemental analyses and ^{1}H NMR spectra recorded on a Bruker Avance II 400 instrument.

All solutions for kinetic measurements were prepared using doubly distilled water just before use. The acidity of the medium was maintained constant (pH 10.0) using a sodium tetraborate buffer; pH values were monitored with a Metrohm 744 pH meter. The kinetics of alkaline hydrolysis of ENPEP were studied following the accumulation of 4-nitrophenoxide ion by spectrophotometry (λ 420 nm) at 25±0.5°C using a Thermo Electron Genesys 10S UV-VIS spectrophotometer. The pseudofirst-order rate constants (k_{obs}, s^{-1}) were calculated using the equation

$$\ln(D_\infty - D_\tau) = \ln(D_\infty - D_0) - k_{obs}\tau,$$

where D_0, D_τ, and D_∞ are the optical densities at the initial moment, time τ, and after reaction completion, respectively.

The experimental data were processed in the framework of the corresponding kinetic model by the least-squares method; and the accuracy of the calculated parameters was characterized by mean-root-square deviations.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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