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Kinetic Regularities of Micellar Catalysis in the Dephosphorylation with Peroxide Anion

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Abstract—The acid-base equilibrium of hydrogen peroxide in water solutions of cetyltrimethylammonium bromideand the reactivity of hydroxide and peroxide anions with respect to 4-nitrophenyl diethyl phosphate were investigated. In the micelles the acid ionization constant of the hydrogen peroxide increased three-fold. The application of the pseudophase distribution model under the conditions of competitive sorption of HO^- and HOO^- anions with the micelles of cetyltrimethylammonium bromide to the estimation of the main kinetic parameters of the micellar process was tested.

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The nucleophilic substitution involving the peroxide anion HOO^- in the micellar solutions of cetyltrimethylammonium bromide (**I**) is one of the procedures for decomposition of organophosphorus compounds employed as pesticides, poisons, and components of war gases [1–3]. The attractive features of micellar decontamination agents underlain by hydrogen peroxide are due to several factors, among which the following should be mentioned:

– HOO^- anion is among the most efficient α-nucleophiles relative to electrophilic substrates [3, 4], and this property is completely revealed under the conditions of the micellar catalysis [1, 2, 5];

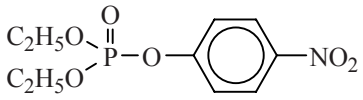
– alongside the high nucleophilic reactivity the hydrogen peroxide (especially in the presence of activators [6, 7]) is an efficient oxidant in the presence of compound **I** [8, 9] providing a possibility to perform simultaneously oxidation-nucleophilic processes in the systems containing H_2O_2;

– micellar solutions of compound **I** efficiently solubilize hydrophobic substrates [2, 10, 11] securing their solubility in water environment;

– the system H_2O_2–H_2O–(**I**) can be regarded as environmentally safe without qualifications [2, 6].

Micellar-catalyzed reactions of nucleophilic substitution in organophosphorus compounds involving inorganic anions (HO^- [10, 11, 12], F^- [13], BrO^- [14]) are the best studied among the processes occurring in the highly organized media: micelles, microemulsions, vesicles, ionic fluids. Examples are also known of reactivity investigation of HOO^- as an active agent in dephosphorylation in the presence of cationic surfactants [2] under the conditions of partial deprotonation of the hydrogen peroxide ($[H_2O_2] >> [HO^-]$, pH ≈ 8–9). For the successful involvement of ion HOO^- into nucleophilic reactions more alkaline media should be used for the ionization constant of the hydrogen peroxide $pK_a = 11.6$ [2, 4, 15], therefore in the range of pH 8–9 only 0.03–0.3% of the hydrogen peroxide is persent in the reactive HOO^- form.

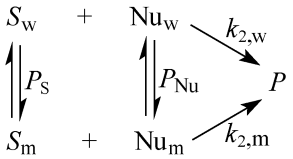
The target of the present study was the investigation of reactivity of HOO^- and HO^- anions towards 4-nitrophenyl diethyl phosphate (paraoxon) **II** in micellar solutions of compound **I** at variation of pH of the water phase from 8.5 to 12.5.



II

The paraoxon in its structure is a model analog of organophosphorus anticholinesterase ecotoxicants and neuroparalytic poisons of G-series [3, 11, 14].

A number of models is applied to the quantitative description of micelles action, the most popular among them are enzymatic [10], pseudophase [10, 16], and ion-exchange models [17, 18]. We believe that the most successful and informative approach to the study of physicochemical fundamentals of micellar catalysis in nucleophilic reactions is the kinetic, so-called pseudophase distribution model of I.V. Berezin [16]. In the framework of this model the reaction between substrate (S) and nucleophile (Nu) is thought to proceed simultaneously both in water (w) and micellar (m) pseudophases, and the distribution of reagents between the phases is characterized by the distribution coefficients P_{Nu} and P_S.



(1)

Here $k_{2,w}$ and $k_{2,m}$, l mol^{-1} s^{-1} are second order rate constants of the reaction between the substrate and the nucleophile in water and micellar phases respectively.

According to this model the expression for the apparent second order rate constant is as follows:

$$k_2 = \frac{k_{app}}{[Nu]_o} = \frac{k_{2,w} + (k_{2,m}/V)K_S K_{Nu} D_n}{(1 + K_S D_n)(1 + K_{Nu} D_n)} \quad , \qquad (2)$$

where $k_{app.}$, s^{-1} is the apparent rate constant; $[Nu]_0$, mol l^{-1} is the initial concentration of the nucleophile in the micellar system; K_S and K_{Nu}, l mol^{-1} are the constants of binding of substrate and nucleophile in the micelles that are in the following way connected to the distribution coefficients: $K_S = P_S V$, $K_{Nu} = P_{Nu} V$; V, l mol^{-1} is the molar volume of the surfactant; D_n, mol l^{-1} is the concentration of the surfactant minus the value of the critical concentration of micelle formation.

Equation (2) permits [10] quantitative estimation of the factors governing the catalytic effect of micelles, and also to give a description of the maximum acceleration:

$$\left(\frac{k_{app}}{k_w}\right)_{max} = \frac{k_{2,m}}{k_{2,w}} \cdot \frac{K_S K_{Nu}}{V(\sqrt{K_S} + \sqrt{K_{Nu}})^2} \quad , \qquad (3)$$

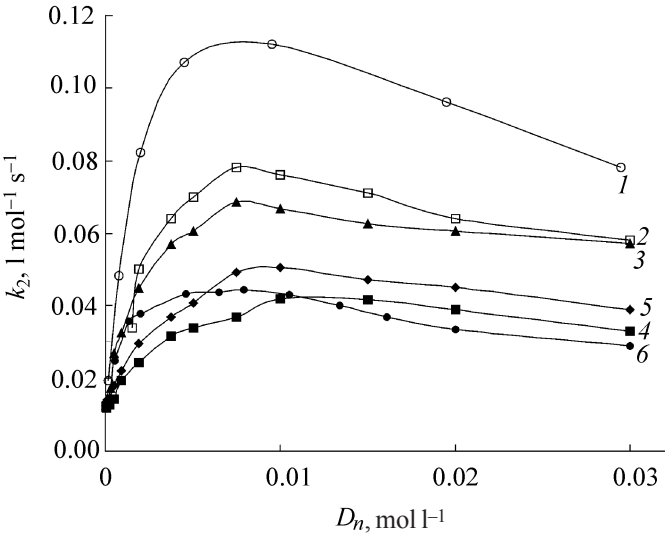


Fig. 1. Effect of the concentration (D_n) of compound **I** on the rate of alkaline hydrolysis of paraoxon at pH 11.00 (*1*), 11.60 (*2*), 12.02 (*3*), 12.40 (*4*), 12.65 (*5*), 13.20 (*6*); 25°C.

where k_w, s^{-1} is the apparent rate constant of the reaction in water at the zero concentration of compound **I**.

The first term in tha right part of equation (3) characterizes the change in the medium effect on the reaction rate in the micellar conditions (F_m), and the second term, the effect from the concentration of the substrate and the nucleophile in the micelle (F_c).

Decomposition of paraoxon in the system HO$^-$–(I)–H$_2$O. The reaction of substrate **II** with anion HO$^-$ was studied in a water solution of compound **I** in the concentration range 0–0.05 mol l^{-1} at pH of the micellar system varied from 11.0 to 13.2.

The pH stabilization of the micellar system was performed using phosphate buffer solution, and the acidity was changed by adding the concentrated KOH solution. In the range of pH < 11.0 the hydrolysis occurs with very low rate irrespective of the concentration of the cationic surfactant. The dependence of the apparent rate constants of the second order reaction $k_2^{HO^-} = k_{app}^{HO^-}/[HO^-]_0$ on D_n ($k_{app}^{HO^-}$, s^{-1} is the apparent rate constant of the alkaline hydrolysis; $[HO^-]_0$, mol l^{-1} is the concentration of HO$^-$ anion in the micellar system) is presented on Fig. 1. The processing of these data according to equation (2) where Nu = HO$^-$ made it possible to determine the kinetic parameters of the micellar-catalyzed reaction of substrate **II** with anion HO$^-$ (Table 1).

The calculated rate constant of the second order reaction of alkaline hydrolysis in the micelle [$k_{2,m}^{HO^-}$,

Table 1. Results of the quantitative treatment of kinetic data on the alkaline hydrolysis of paraoxon along equations (2) and (3)[a]

Series no.	pH	$k_{2,m}^{HO^-} \times 10^3$, l mol^{-1}s^{-1}	K_S, l mol^{-1}	K_{HO^-}, l mol^{-1}	$(k_m / k_w)_{max}$	F_m	F_c
1	11.00	1.29 ± 0.11	340 ± 40	44 ± 13	11	0.13	86
2	11.60	1.12 ± 0.06	574 ± 101	26 ± 6	6.9	0.11	59
3	12.02	1.33 ± 0.09	844 ± 85	18 ± 5	5.5	0.13	42
4	12.40	1.15 ± 0.11	1148 ± 88	15 ± 3	4.2	0.12	34
5	12.65	1.27 ± 0.12	1246 ± 200	21 ± 2	4.0	0.13	30
6	13.20	1.18 ± 0.02	1630 ± 200	18 ± 4	4.4	0.12	35

[a] For experimental conditions, see Fig. 1.

l mol^{-1} s^{-1})] is ten times smaller than the analogous value in water {$k_{2,w}^{HO^-}$ = 0.01 l mol^{-1} s^{-1}) [4]}, which is characteristic of reactions occurring in the micellar pseudophase [2, 3, 10]. The acceleration of the reaction in the case in question (4–11-fold) originates from the concentration of the reagents in the micelle (F_c) and is the result of combination of F_m and F_c factors. The decrease in the value $(k_m/k_w)_{max}$ in going to more concentrated alkali solutions (series no. *1–6*, Table 1) is due to the decrease in the difference in concentrations $[HO^-]_w$ and $[HO^-]_m$ with the growing overall concentration $[HO^-]_0$, and it is reflected in the value of the binding constant of the nucleophile with the micelle:

$$K_{HO^-} = \frac{[HO^-]_m}{[HO^-]_w D_n}, \quad (4)$$

where $[HO^-]_m$, mol l^{-1} is the molar concentration of HO^- anion in the micelle calculated relative to the volume of the micellar system. Evidently the quantity of HO^- anion bound with the micelle is limited by the volume of the micellar phase (the value of calculated anions concentration on the micelles surface amounts to 4–6 mol l^{-1} [2]), and therefore the value K_{HO^-} decreases approximately twofold at increasing the nucleophile concentration in the water phase. On the other hand, in more alkaline solutions the binding constant of substrate K_S (Table 1) considerably grows due to the salting-out effect of HO^- anion whose concentration increases ~200 times in going from pH 11.0 to 13.2.

Micellar effects of compound **I** in the systems with HO^- anion are now the best studied [3, 10, 11]. Nonetheless, the published K_{HO^-} values for analogous processes of nucleophilic substitution vary in a relatively wide range, from 30 to 365 [10]. We believe that the values of the binding constants K_{Nu} and K_S are quite individual characteristics of the given micellar system and are governed by a number of factors where the main ones are the electrolytic characteristics of the water phase.

Decomposition of paraoxon in the system H_2O_2–HO^-–(I). In contrast to the micellar system where a single anion functions as a nucleophile, in the system H_2O_2–HO^- at least six new factors are present which should be taken into account in the estimation of the physicochemical parameters of the micellar catalysis:

– existence of the acid-base equilibrium:

$$H_2O_2 + HO^- \leftrightarrows H_2O + HOO^-; \quad (5)$$

– shift of the apparent pK_a value of the hydrogen peroxide in the presence of micelles, and consequently, the dependence of the concentration of the reactive form $[HOO^-]$ on the concentration of compound **I** in the system;

– distribution of the neutral form of H_2O_2 between the water and micellar phases;

– probability of the competitive sorption of HO^- and HOO^- anions on the micelle surface;

– proceeding of two parallel routes of the substrate deomposition: the alkaline hydrolysis and the reaction with anion HOO^-;

– additional effect of HO^- as electrolyte on the processes involving HOO^-.

The ratio of the paraoxon decomposition processes involving HO^- and HOO^- anions in the presence of compound I. To make a quantitative estimate of the contribution from the route involving HO^- anion into the overall rate of substrate consumption we studied the decomposition rate of substrate **II** (k_{app}, s^{-1}) in the system H_2O_2–HO^- ($[H_2O_2]_O$ = 0.032 mol l^{-1}) at various pH of the water phase (from 11.0 to 12.5) in water and water solutions of compound **I** ([**I**] = 0.03 mol l^{-1}). In the same conditions the rate of the alkaline hydrolysis of paraoxona ($k_{app}^{HO^-}$, s^{-1}) in the absence of H_2O_2 was independently measured.

It follows from the data obtained (Table 2) that on decreasing acid properties of the medium the contribution of the hydrolysis process into the overall rate of the substrate consumption continuously grows both in water and in the micellar system. Yet even at the high values of pH > 12.0 the apparent rate in the system H_2O_2–HO^- (k_{app}, s^{-1}) is considerably larger that the analogous rate of individual alkaline hydrolysis ($k_{app}^{HO^-}$, s^{-1}), and it permits neglecting the contribution of the alkaline hydrolysis in the micellar system H_2O_2–HO^-–(**I**). The attention is also attracted by the close values of the ratio $k_{app}^{HOO^-}/k_{app}^{HO^-}$ in water and in micellar system at various pH. This means evidently that the ratio of the concentrations of the reacting anions [HOO^-] and [HO^-] in water and micellar phases is conserved. This situation may originate from the close order of magnitude of the binding constants K_{HOO^-} and K_{HO^-}. Therefore anion HO^- can affect the ionization process of H_2O_2 in solutions of compound **I** and consequently the extent of binding of anion HOO^- with the micelle.

Apparent acid ionization constant of H_2O_2 in solutions of compound I. The pK_a value for hydrogen peroxide in water equals 11.6 [2, 4, 5, 15], therefore in keeping with equation (6) at high pH should form anion HOO^- in a considerable amount.

$$\alpha = \frac{K_a}{K_a + a_{H^+}}, \qquad (6)$$

where α is the fraction of HOO^- calculated on the overall amount of H_2O_2 in solution; K_a is the acid-base ionization constant of hydrogen peroxide; a_{H^+} is the activity of hydrogen ions.

Taking into account that in the micellar catalysis the main nucleophile is HOO^- anion the expression of the apparent reaction rate constant is as follows:

$$k_{app} = k_2[HOO^-]_o = k_2\frac{K_a'}{K_a' + a_{H^+}}[H_2O_2]_o . \qquad (7)$$

Where K_a' is the apparent acid-base ionization constant of hydrogen peroxide in the presence of compound **I**; $[H_2O_2]_O$ and $[HOO^-]_O$ are the initial concentrations of hydrogen peroxide and peroxide anion calculated on the total volume of the micellar system.

The K_a' values in water solutions of compound **I** were estimated by two independent procedures: kinetic and spectrophotometric methods. The estimation of K_a' value by the kinetic method was performed by measuring the decomposition rate of substrate **II** in the system H_2O_2–HO^-–(**I**) ($[H_2O_2]_0$ = 0.05 mol l^{-1} in a phosphate buffer) at a fixed concentration of compound **I** (0–0.03 mol l^{-1}) in a wide pH range of water phase (8.5–12.5). The K_a' values were computed after the linearization of the experimental data in the coordinates $k_2' - k_2' a_{H^+}$ ($k_2' = k_{app}/[H_2O_2]_O$) (Fig. 2), (Table 3). Here are also compiled the K_a' data measured by spectrophotometry as described in EXPERIMENTAL. These data demonstrate that in the studied interval of compound **I** concentrations the value K_a' increased nearly 3 times (from 2.5×10^{-12} to 7.4×10^{-12}) indicating the prevailing solubilization by micelles of compound **I** of the anionic form of hydrogen peroxide HOO^- as compared to neutral molecules.

Table 2. Ratio of apparent decomposition rates of paraoxon in systems HO^- ($k_{app}^{HO^-}$, s^{-1}) and H_2O_2–HO^- ($k_{app}^{HOO^-}$, s^{-1}) in water and in the presence of compound **I**, 25°C[a]

Series no.	pH	$(k_{app}^{HOO^-}/k_{app}^{HO^-})_w$	$(k_{app}^{HOO^-}/k_{app}^{HO^-})_m$
1	11.0	625	455
2	11.5	372	314
3	11.7	320	328
4	12.0	193	155
5	12.5	77	93

[a] $[H_2O_2]_0$ = 0.032 mol l^{-1}, $[I]_0$ = 0.03 mol l^{-1}.

Constants of binding anion HOO^- with micelles of compound I. The dependence of constant K_a' on the

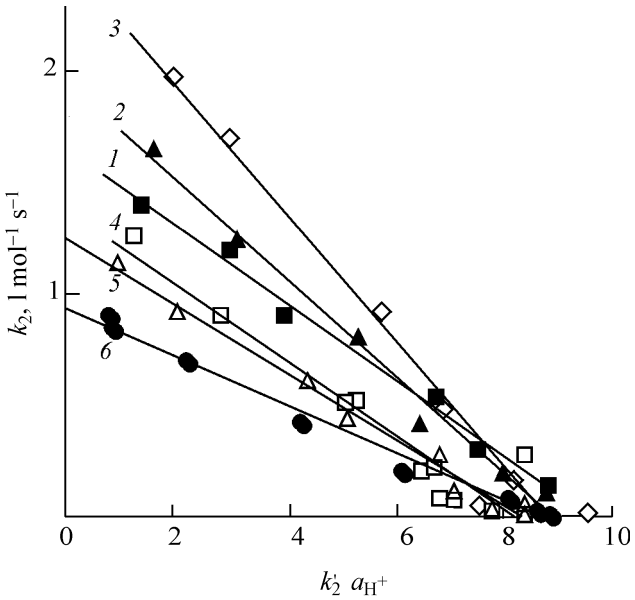


Fig. 2. Dependence $k_2' - k_2' a_{H^+}$ for reaction of paraoxon with anion HOO^-; $[H_2O_2]_O$ = 0.05 mol l^{-1}, pH = 8.5–12.5; [I] = 0.001 (*1*), 0.0033 (*2*), 0.005 (*3*), 0.01 (*4*), 0.02 (*5*), 0.03 (*6*) mol l^{-1}.

Table 3. The values of apparent constant K_a' of acid-base ionization of hydrogen peroxide at various concentrations of compound **I**, 25°C

Series no.	[I] × 10^2, mol l^{-1}	$K_a' \times 10^{12}$	
		a	b
1	0	2.46	2.58
2	0.05	–	4.04
3	0.1	3.53	–
4	0.3	4.08	4.72
5	0.33	4.32	–
6	0.5	4.38	–
7	1.0	5.67	5.92
8	1.5	–	6.09
9	2.0	6.70	6.73
10	2.5	–	6.81
11	3.0	7.16	7.40
12	K_{HOO^-}	74 ± 48	51 ± 14
13	$K_{H_2O_2}$	15 ± 12	7.9 ± 7.7

[a] Determined by equation (7), for experimental conditions, see Fig. 2.

[b] Determined spectrophotometrically by equation (15), $[H_2O_2]_0$ = 0.07 mol l^{-1}.

concentration of compound **I** is described by the following equation [19]:

$$K_a' = K_a \frac{1 + K_{HOO^-}[I]}{1 + K_{H_2O_2}[I]} . \quad (8)$$

The quantitative treatment of the K_a' dependences on [**I**] obtained in various series of experiments (Table 3) permitted the estimation of the binding constants of anion HOO⁻ (K_{HOO^-}) and of hydrogen peroxide by the micellar phase (Table 3, series nos. *12*, *13* respectively). The values are statistically insignificant and demonstrate that the micelles interact very weakly with the molecules of the hydrogen peroxide. The binding constant was estimated in [8] by micellar chromatography at about 1, namely, the hydrogen peroxide has no prevalence of residing in any of the phases, be it water or micellar.

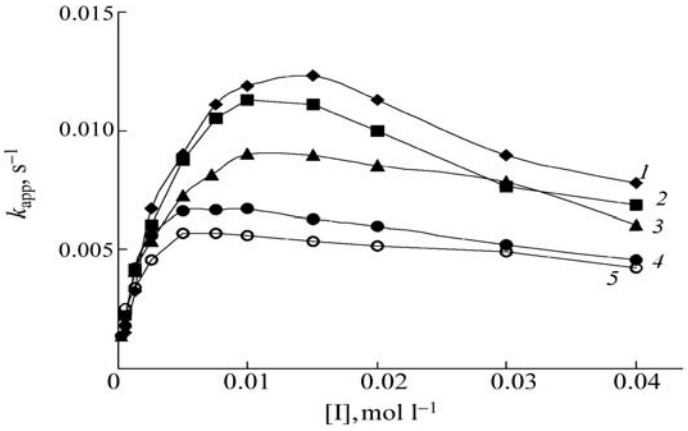


Fig. 3. Effect of the concentration of compound **I** on the rate of paraoxon reaction in the system H_2O_2–HO⁻ at pH 8.5 (*1*), 9.5 (*2*), 10.5 (*3*), 11.5 (*4*), 12.0 (*5*); [HOO⁻] = 0.002 mol l^{-1} (pK_a = 11.6); 25°C.

As expected the K_{HOO^-} values estimated by different methods (kinetic and spectrophotometric) are close to those of K_{HO^-} computed in the framework of a simple distribution model from the results of alkaline hydrolysis of substrate **II** (pH 11.0–13.2, Table 1). This fact should lead to a considerable competition between the anions HOO⁻ and HO⁻ in the process of their transfer from the water to micellar phase. Presumably just this circumstance resulted in the large error obtained in the estimation of K_{HOO^-} values by the kinetic method (Series no. *12*, Table 3) that was applied at a wide variation of water phase pH (from 8.5 to 12.0) under the conditions of increase of $[HO^-]_w$ more than 3500-fold (Fig. 3).

On Fig. 3 kinetic results are presented of paraoxon decomposition in the system H_2O_2–HO⁻–**I** in the pH range 8.5–12.5 at a variable concentration of compound **I** (0–0.04 mol l^{-1}) and constant $[HOO^-]_w$ (0.002 mol l^{-1}). These data demonstrate a clear trend in the decrease of the absolute value of observed micellar effect by over 2 times at increasing pH from 8.5 to 12.5. These changes in the value of $(k_{app.}/k_w)_{max}$ cannot be ascribed to the growth of the concentration of anions HOO⁻ and HO⁻ in the water phase, since under the experimental conditions $[HOO^-]_w$ is constant and as already shown the contribution of the alkaline hydrolysis of substrate **II** in the micellar system is negligibly small (Table 2). The only logical explanation of the decrease of the micellar acceleration of the reaction involving HOO⁻ anion at growing pH is the increasing competing sorption on the micelle surface of HO⁻ ion due to its increasing concentration in the water phase. It is also of interest that the mathematical treatment of the data obtained (Fig. 3) in the framework of the pseudophase model (2) does not provide satisfactory results: the computed kinetic parameters (K_{HOO^-}, K_S, $k_{2,m}^{HOO^-}$) are statistically insignificant, and the correlation coefficient R is small (0.7–0.8). Therefore the quantitative description of the observed acceleration effect should be more proper to perform along the alternative kinetic pseudophase model (9) [19], that takes into consideration the variation of the concentration of anion HOO⁻ depending on the

concentration of compound **I** along the total profile of the micellar process (Fig. 3).

$$k_2' = \frac{k_{app}}{[H_2O_2]_o} = \frac{k_{2,w} + (k_{2,m}/V)K_S K_{HOO^-} D_n}{(1+K_S D_n)(1+K_{HOO^-} D_n)(1+a_{H^+}/K_a')}. \quad (9)$$

The analysis of the data of Table 4 where are compiled the kinetic parameters of the decomposition of substrate **II** in the system H_2O_2–HO^-–**I** in the pH range 8.5–12.5, indicates the dependence of the micellar binding constants K_{HOO^-} and K_S, and also the values of the reaction acceleration $(k_{app}/k_w)_{max}$ on the content of HO^- anions in the water phase.

The increase in the binding constants of substrate (K_S, Table 4) was due to the salting-out effect of ion HO^- [5, 10, 12] that is independently confirmed by the data of Fig. 4. The dependence of apparent rate constants of substrate **II** decomposition in the micellar system on anion HO^- concentration is a broken line characterizing the effect of electrolytic additives on the micellar-catalytic processes [10, 12].

Yet we presume that the main reason of the decrease in the acceleration in the system under study in going from pH 8.5 to 12.5 (Fig. 3) is the weakening of the binding by micelles of the anion HOO^- caused by the partial neutralization of their surface charge by the HO^- anions. In other words, anions HOO^- are displaced from the Stern layer, and it is saturated with weakly reactive anions HO^-.

Hence although the contribution of alkaline hydrolysis into the overall rate of substrate **II** consumption in the system H_2O_2–HO^-–**I** is insignificant, the presence of anion HO^- can essentially affect the value and the character of the micellar effect in reactions involving the anion HOO^-. Therefore it is reasonable to presume that one of the factors governing the micellar effect in this system is the ratio of local concentrations of the corresponding ions on the micelle surface which, all the other conditions being equal, would depend on the ratio

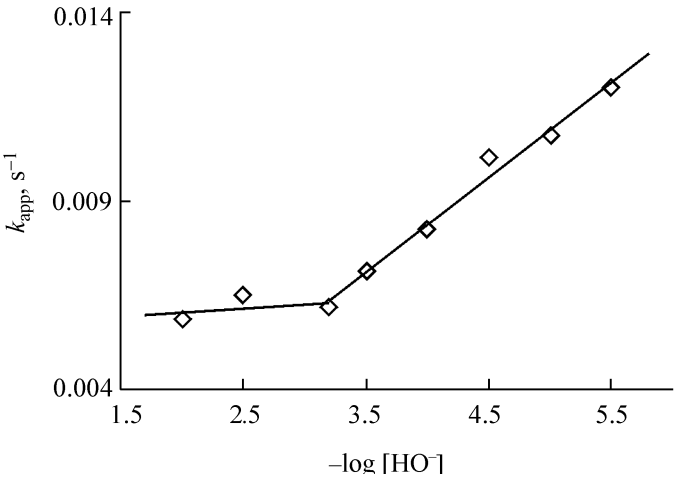


Fig. 4. Dependence of apparent rate constants of paraoxon decomposition in the presence of compound **I** (0.005 mol l^{-1}) on the log anion HO^- concentration in the system H_2O_2–HO^-–I; $[HOO^-]_w$ = 0.002 mol l^{-1}, 25°C.

of the initial concentrations of anions HOO^- and HO^- in the micellar system.

Kinetic parameters of paraoxon decomposition in the system H_2O_2–HO^-–I. In order to obtain more correct interpretation of the kinetic data (Fig. 3) we applied the distribution (10) that considers the simultaneous reaction of substrate **II** with anions HOO^- and HO^- accounting for the competitive binding of these anions by micelles of compound **I**.

$$k_{app} = \frac{k_{2,w}^{HOO}[HOO^-]_w + (k_{2,m}^{HOO}/V)K_S D_n m_{HOO}}{1+K_S D_n} + \frac{k_{2,w}^{HO}[HO^-]_w + (k_{2,m}^{HO}/V)K_S D_n m_{HO}}{1+K_S D_n}, \quad (10)$$

where m_{HOO^-} and m_{HO^-} are local concentrations of anions HOO^- and HO^- calculated with respect to the volume of the micellar pseudophase.

In the quantitative estimation of kinetic results of the substrate **II** decomposition in the system H_2O_2–HO^-–**I**

Table 4. Kinetic parameters of paraoxon decomposition in the system H_2O_2–HO^-–**I**, 25°C [a]

Series no.	pH	$k_{2,m}^{HOO^-}$, l mol^{-1} s^{-1}	K_{HOO^-}, l mol^{-1}	K_S, l mol^{-1}	$(k_{app}/k_w)_{max}$	F_m	F_c
1	8.5	0.089 ± 0.004	65 ± 8	300 ± 60	15	0.18	84
2	9.5	0.080 ± 0.004	56 ± 10	350 ± 50	23	0.16	79
3	10.5	0.078 ± 0.010	40 ± 8	470 ± 97	10	0.28	60
4	11.5	0.077 ± 0.012	36 ± 10	490 ± 150	7	0.15	52
5	12.0	0.069 ± 0.009	18 ± 3	670 ± 120	5	0.14	37

[a] For experimental data, see Fig. 3.

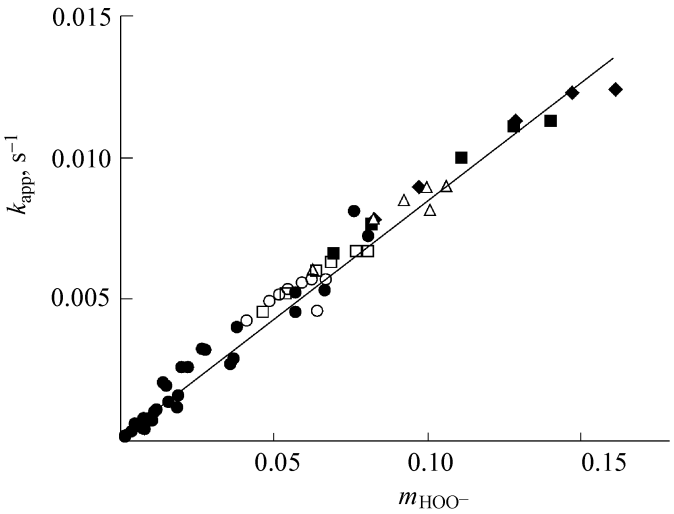


Fig. 5. Dependence of apparent rate constants of paraoxon decomposition in the system H_2O_2–HO^- on the local concentration of HOO^- anaion on micelle surface, 25°C. pH 8.5 (◆), 9.5 (■), 10.5 (Δ), 11.5 (□), 12.0 (○), 8.5–11.0 (●).

(Fig. 3) along equation (10) we used the following initial data: $k_{2,w}^{HOO^-} > 0.5$ l mol^{-1} s^{-1} [4], $k_{2,w}^{HO^-} > 0.01$ l mol^{-1} s^{-1}) [4], $k_{2,m}^{HOO^-} > 0.09$ l mol^{-1} s^{-1}) (Table 4), $k_{2,m}^{HO^-} > 0.001$ l mol^{-1} s^{-1}) (Table 1), the K_S values for definite pH were taken from Table 4. Values of $[HOO^-]_w$ were calculated by the equation:

$$[HOO^-]_w = \frac{K_a'}{K_a' + a_{H^+}} [H_2O_2]_o , \qquad (11)$$

where K_a' is the apparent constant of acid-base ionization of H_2O_2 at a given concentration of compound **I** as indicated in Table 3.

The binding constants of anions K_{HOO^-} and K_{HO^-} were calculated from the local concentrations of anions HOO^- and HO^- in the micelle:

$$K_{HOO^-} = \frac{m_{HOO^-}}{[HOO^-]_w - m_{HOO^-} D_n} , \qquad (12)$$

$$K_{HO^-} = \frac{m_{HO^-}}{[HO^-]_w - m_{HO^-} D_n} . \qquad (13)$$

The values of concentrations m_{HOO^-} and m_{HO^-}, and also the binding constants of anions HOO^- and HO^- at various ratios of $[HOO^-]_w$ and $[HO^-]_w$ are compiled in Table 5. The calculated values obviously demonstrate the decrease more than twice in the concentration of anion HOO^- on the micelle surface, and consequently, in K_{HOO^-} with the growth of anion HO^- concentration in the system under investigation in going to more alkaline media (pH variation from 8.5 to 12). The absolute value of micellar effect characterized by the ratio $(k_{app}/k_w)_{max}$ also diminished in this extent. The value $k_{2,m}^{HOO^-}$ (Table 5) is calculated for the concentrations of compound **I** > 0.0075 mol l^{-1} corresponding to the conditions of the maximum binding of the substrate as shown in the descending branch of the dependence of k_2 on D_n (Fig. 3)

Table 5. Effect of pH of the water phase on the local concentrations of anions HO^- and HO^- on micelle surface, 25°C[a]

Series no.	pH	$[HOO^-]_w / [HO^-]_w$	m_{HOO^-}	K_{HOO^-}, l mol^{-1}	$m_{HO^-} \times 10^3$	K_{HO^-}, l mol^{-1}	$k_{2,m}^{HOO^-}$, l mol^{-1} s^{-1}
1	8.5	633	0.13 ± 0.02	69 ± 11	0.08 ± 0.02	29 ± 6	0.081
2	9.5	63.3	0.12 ± 0.02	64 ± 7	0.7 ± 0.2	25 ± 5	0.084
3	10.5	6.33	0.095 ± 0.008	52 ± 4	5 ± 1	21 ± 2	0.087
4	11.5	0.633	0.07 ± 0.02	47 ± 4	50 ± 2	21 ± 5	0.090
5	12.0	0.2	0.057 ± 0.007	35 ± 6	115 ± 32	20 ± 1	0.089

[a] For experimental data, see Fig. 3, calculations by equation (10).

Table 6. Local concentration of anion HOO^- on micelle surface at variation of concentration of anion HOO^- in water phase, 25°C[a]

Series no.	pH	$[HOO^-]_o$, mol l^{-1}	$k_{app} \times 10^3$, s^{-1}	m_{HOO^-}	$k_{2,m}^{HOO^-}$, l mol^{-1} s^{-1}	N [b]
1	8.5	3.15×10^{-4}–8.09×10^{-4}	0.428–2.62	0.0077–0.020	0.100	5
2	9.0	7.07×10^{-5}–1.20×10^{-3}	0.210–3.27	0.0016–0.027	0.107	6
3	9.5	1.20×10^{-3}–9.74×10^{-3}	0.610–3.74	0.0048–0.081	0.091	5
4	10.0	6.65×10^{-5}–6.65×10^{-4}	0.150–2.05	0.0014–0.014	0.097	5
5	11.0	4.16×10^{-4}–4.16×10^{-3}	0.810–8.10	0.0076–0.076	0.088	6

[a] [I] = 0.03 mol l^{-1}. [b] Number of measurements.

$$k_2' = \frac{k_{app}}{[H_2O_2]_0} = \frac{k_{2,w} + (k_{2,m}/V)K_S K_{HOO^-} D_n}{(1+K_S D_n)(1+K_{HOO^-} D_n)(1+a_{H^+}/K_a')} \quad (14)$$

The value $k_{2,m}^{HOO^-}$ was independently estimated in the system H_2O_2–HO^-–**I** at the constant concentration of compound **I** 0.03 mol l^{-1} and at variation of $[HOO^-]_0$ in the conditions of a constant or of altering pH of the water phase (Table 6).

The unified computation of $k_{2,m}^{HOO^-}$ from the dependence of k_{app} on m_{HOO^-} using the data of various reaction series (Fig. 5) yielded the value of the rate constant of the second order reaction between substrate **II** and anion HOO^- equal 0.090 ± 0.007 l mol^{-1} s^{-1} with a high correlation coefficient $R = 0.979$.

The comparison of the rate constants of the second order reaction in water ($k_{2,w}$) and micellar ($k_{2,m}$) phases shows that the reaction of substrate **II** with anions HOO^- and HO^- in the micellar pseudophase occurs at lower rates than in the water phase. The ratio $k_{2,m}/k_{2,w} \approx 0.2$ is close in value to the corresponding ratios for dephosphorylation of 4-nitrophenyl diphenyl phosphate with anions HOO^- and HO^- [2, 18], and also to the analogous ratios for a number of similar processes involving inorganic nucleophiles [10].

The coincidence of values K_{HOO^-}, K_{HO^-}, $k_{2,m}$ obtained from independent experiments (Table 1, 3, 4) with the results of the calculations by equation (10) demonstrate that the applied model is adequate to the data of the kinetic experiments.

The estimation of micellar catalytic effects by equation (3) shows that the main factor governing the acceleration of the decomposition of substrate **II** in the system H_2O_2–HO^-–**I** is the concentration of the reagents in micelles (F_c = 40–80, Table 4). At the same time the transfer of reaction into the micellar environment leads to a considerable reduction in the reactivity both of anions HOO^- and HO^- (F_m = 0.1–0.2, Table 1, 4). The combination of these effects results in the observed acceleration from 5 to 15 times depending on the ratio of the reacting anions $[HOO^-]_w/[HO^-]_w$.

We studied in detail the micellar action of compound **I** in oxidation of methyl phenyl sulfide in the system H_2O_2–HCO_3^-–HO^- [9], and we established that the maximum oxidation rates were observed in a relatively narrow pH range of the water phase from 8 to 9.5. This fact significantly limits the simultaneous decomposition of ecotoxicants by oxidative and nucleophilic mechanisms for at pH 9.5 only 1% of hydrogen peroxide is present in the reactive form HOO^-.

Nonetheless, the shift of pK_a of the hydrogen peroxide in the presence of compound **I**, especially pronounced in weakly alkaline environment, in combination with the micellar catalytic effect (up to 15 times) makes it possible at pH 8.5 to provide the rate of substrates decomposition by the nucleophilic mechanism comparable with the rate of this process at pH ~ 10.2 under constant $[H_2O_2]_0$. This fact is practically important for designing systems for efficient cleavage of highly toxic organophosphorus compounds by the nucleophilic mechanism and for sulfides oxidation under mild environmentally safe conditions.

The results obtained demonstrated that the use of water solutions of cetyltrimethylammonium bromide consideraly improved the processing parameters of the H_2O_2–HO^- system as an active component of the multi-purpose oxidation-nucleophilic system.

EXPERIMENTAL

4-Nitrophenyl diethyl phosphate from Aldrich was used without preliminary purification. Hydrogen peroxide of "pure for analysis" grade, 33% water solution, was distilled in a vacuum (5 mm Hg), the concentration of H_2O_2 in solution was determined by titration with permanganate. Cetyltrimethylammonium bromide (**I**) from Merk was recrystallized from a mixture ethanol–diethyl ether, 1:1, till mp 207–208°C was reached. $Na_2HPO_4 \cdot 12H_2O$ of "chemically pure" grade was used without additional purification for preparation of the phosphate buffer solution (μ 0.01).

The reagents solutions were prepared directly before the kinetic runs. The acidity of solutions was checked using a pH-meter OP 211/1 Radelkis (Hungary) with an accuracy of 0.05 pH units. The required pH of the buffer solutions was adjusted with concn. KOH solution. The variation of compound **I** concentration was performed by diluting the initial solution containing components whose concentrations remained constant within the given series of runs.

We established by special experiments that within 3 h (the time sufficient for chemical measurements within one series) no decomposition of H_2O_2 under alkaline conditions occurred. We also did not find any oxidation of 4-nitrophenol liberated in the course of the target reaction.

The reaction progress was monitored by spectrophotometry at λ 405 nm under concentration restrictions

[HOO^-] >> [S]. The apparent rate constants remained constant in the course of the process.

The measurement of apparent acid-base ionization constant of H_2O_2. The apparent acid ionization constant K_a' was measured by spectrophotometric procedure by the optical density of water solutions of hydrogen peroxide in the presence and the absence of compound **I** at λ 260 nm. The concentration of [HOO^-] in water and water solutions of compound **I** ([**I**] = 0.005–0.03 mol l^{-1}) at a fixed pH value was calculated by the equation:

$$D_{260\,nm} = 17([H_2O_2]_0 - [HOO^-]) + 230[HOO^-], \quad (15)$$

where $D_{260\,nm}$ is the optical density of a hydrogen peroxide solution at a definite concentration $[H_2O_2]_0$ and a given pH; 17 and 230 are extinction coefficients of H_2O_2 and HOO^- anion at λ 260 nm [20]. From expression (16) K_a' values were determined in the presence of compound **I** at pH 10.

$$[HOO^-] = \frac{K_a'}{K_a' + a_{H^+}} [H_2O_2]_0 \quad (16)$$

To estimate the K_a' values by kinetic method we measured the rate of substrate **II** decomposition in the system H_2O_2–HO^- ($[H_2O_2]_0$ = 0.05 mol l^{-1} in a phosphate buffer) at a fixed concentration of compound **I** (0–0.03 mol l^{-1}) in a wide pH range of the water phase (8.5–12.5). The expression for the apparent rate constant (k_{app}, s^{-1}) is described by equation (7).

The K_a' values were calculated after linearization of the experimental data in the coordinates $k_2' - k_2' \cdot a_{H^+}$ ($k_2' = k_{app}/[H_2O_2]_0$) (Fig. 2) (Table 3).

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