DECONTAMINATION OF METHYL PARATHION IN ACTIVATED NUCLEOPHILIC SYSTEMS BASED ON CARBAMIDE PEROXISOLVATE

Вивчено нуклеофільне розщеплення метилпаратіона HOO^--аніоном, що генерується з пероксисольвата карбаміду у присутності бікарбонату амонію та борної кислоти. Виявлена супернуклеофільна реакційна здатність аніону дипероксобората $B(OH)_2(OOH)_2^-$. Показана можливість використання твердих джерел пероксиду водню в деконтамінаційних системах. Визначено величину α-ефекту (k_{HOO^-}/k_{HO^-}), яка вказує на аномально високу реакційну здатність HOO^--аніона в розкладанні фосфорних ефірів

Ключові слова: нуклеофільне заміщення, пероксид водню, пероксисольват карбаміду, метилпаратіон, пероксоборат, пероксокарбонат

Изучено нуклеофильное расщепление метилпаратиона HOO^--анионом, генерируемым из пероксисольвата карбамида в присутствии бикарбоната аммония и борной кислоты. Обнаружена супернуклеофильная реакционная способность аниона дипероксобората $B(OH)_2(OOH)_2^-$. Показана возможность использования твердых источников пероксида водорода в деконтамінаційних системах. Определена величина α-эффекта (k_{HOO^-}/k_{HO^-}), которая указывает на аномально высокую реакционную способность HOO^--аниона в разложении фосфорных эфиров

Ключевые слова: нуклеофильное замещение, пероксид водорода, пероксисольват карбамида, метилпаратион, пероксоборат, пероксокарбонат

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1. Introduction

Especially dangerous pesticides of organophosphorus (OP) nature represent a real threat to human health and the environment. Many active ingredients of pesticides are known or possible carcinogens; they produce acute or chronic toxic effects, suppress immunity, as well as cause disorders of the endocrine, central and peripheral nervous systems [1]. It is also known that organophosphates adversely affect the reproductive function, produce intrauterine fetal malformations and constitute an increased risk for children [2].

Nevertheless, at present, in agriculture there is a wide range of organophosphorus esters as well as phosphoric and phosphonic acid derivatives, including paraoxon, methyl parathion, diazinon, chlorophos, and glyphosate. These pesticides are characterized by a high degree of neurotoxicity due to the ability to phosphorylate and suppress cholinesterase, which can lead to lethal effects [2].

The world community has adopted a number of directives [3, 4] regulating the range of pesticides as well as the procedures for the use, treatment, utilization, and security measures. It should be noted that methyl parathion (MP), which is the subject of this study, according to the Rotterdam Convention [4], is a particularly dangerous substance and is listed in Annex III. This means that MP is subject to a prior informed consent procedure in international trade up to a ban in the countries of Europe and North America [5]. The new version of the FAO Code [3] introduced changes aimed at minimizing potential risks with the adoption of the concept of "life cycle". This document places considerable

emphasis on the destruction of all types of "outdated" and forbidden pesticides, as well as the decontamination of the premises and used containers in which they were stored. Thus, the problem of finding new technical solutions related to the disposal of banned pesticides, as well as the elimination of the consequences of turnover and storage, is an important and urgent task of ecological chemical science.

2. Literature review and problem statement

Methyl parathion (O,O-dimethyl-O-4-nitrophenyl triophosphate) is one of the most common organophosphorus pesticides that is often found in surface and ground water at concentrations of up to 0.1 mg/l. In the USA, the average concentration of MP in the groundwater of developed agricultural areas is up to 0.46 µg/l [6]. These figures are of alarming significance given that the acute oral toxicity parameter LD_{50} reaches values of 2–30 mg/kg and 3–5 mg/kg in rats and dogs, respectively. MP has been classified by the World Health Organization as a very toxic US EPA pesticide and as extremely hazardous [1]. Despite the prohibition of MP in many developed countries, its use continues, including in Ukraine.

Such a situation with the circulation of particularly dangerous compounds stimulates the scientific search for effective methods for the destruction of OP pesticides. Alkali hydrolysis, oxidative chlorination [6], alcohol monoethanolamine or potassium butoxide are used as the main technological approaches for the destruction of OP [7, 8]. The general disadvantages of the methods of chemical detoxification are toxicity of the applied technologies, a significant corrosive load on the equipment due to the aggressive degassing media, and a large amount of contaminated wastewater. It should also be noted that the above-mentioned methods are absolutely unacceptable for decontaminating infected skin of man and animals, clothing, industrial premises, and warehouses. In addition, the reagents used in industrial technologies (alkalis, alkali metal alcohols, and amines) do not differ in their high reactivity to phosphoric and phosphonic esters [6]. The rate of decomposing MP and its analogues can be increased by the use of α-nucleophiles [8, 9], the typical representative of which is the peroxide anion HOO^- [10] and its derivatives – peroxoaniones [11].

In addition to high reactivity, hydrogen peroxide (H_2O_2) as a degassing agent provides universality of action for nucleophilic and oxidative mechanisms [12] and satisfies the basic norms and requirements of eco-friendly technologies [13]. However, the use of concentrated aqueous solutions of H_2O_2 for applied purposes poses additional risks in storage and transportation.

Solid peroxisolvate of carbamide (hydroperite, $CO(NH_2)\times\times2H_2O_2$, (I)), as an alternative source of H_2O_2, opens up new perspectives for creating effective decontamination systems for long-term storage. The study of the kinetics of MP decomposition in such systems is of not only scientific but also practical interest. The applied use of the relevant tests should ensure minimization of environmental risks for humans and the environment that are associated with the "life cycle" of OP pesticides.

3. The aim and objectives of the study

The aim of this study is to investigate the effect of hydrogen peroxide activators such as ammonium bicarbonate (NH_4HCO_3) and boric acid ($B(OH)_3$)) on the kinetics of nu-

cleophilic decomposition of MP by carbamide peroxisolvate and potassium hydroxide in an aqueous medium.

The aim is implemented by solving the following tasks:
– to determine the reactivity of MP in the reactions of alkaline hydrolysis and perhydrolysis of MP in an aqueous medium;
– to study the influence of NH_4HCO_3 and $B(OH)_3$ on the kinetics and the mechanism of nucleophilic decomposition of MP.

4. Materials and methods for studying the kinetics of decomposing methyl parathion

4. 1. Materials and equipment used in the tests

In the work, methyl parathion (by Aldrich) and a KOH alkali (by Lachema) were used without preliminary purification. Bidystilled water was used to prepare the solutions.

Hydrogen peroxide (AR grade) in the form of a 33 % aqueous solution was pre-distilled in vacuo (5 mm Hg). Carbamide peroxisolvate was prepared according to the well-known method [14].

The concentration of H_2O_2 in the solutions and the content of hydrogen peroxide in the peroxysolvates were controlled by permanganametometric titration [15].

4. 2. The method of kinetic measurements

All solutions were prepared in bidistilled water directly before each series of kinetic measurements. The acidity of the solutions was monitored using the pH meter "Metrohm-827" (Switzerland) with an accuracy of down to 0.02 units of pH. The pH meter was adjusted according to standard pH-metric buffer solutions. The required pH value was set by a concentrated KOH solution. The ionic strength was recorded by the introduction of KCl.

Discrete experiments have shown that during 5 hours (time sufficient for kinetic measurements within one series) the by-product of the H_2O_2 decomposition under alkaline conditions is not observed. No oxidation reaction of 4-nitrophenol released during the course of the target reaction was detected either.

The reaction was controlled spectrophotometrically on the Specord M-40 UV VIS device at $\lambda=405$ nm and $T=25$ °C by the change in the absorption of 4-nitrophenolate ion in time under the concentration conditions of $[OH^-]=[HOO^-]>>[MP]$. The initial concentration of the substrate was $5-10^{-5}$ M^{-1}, and the degree of its transformation exceeded 80 %.

5. Results of the kinetic tests on the reactions of nucleophilic decomposition of methyl parathion

5. 1. Alkaline hydrolysis and perhydrolysis of MP in water

MP in the H_2O_2/OH^- solution was converted mainly in two directions – perhydrolysis with the contribution of the generated HOO^- anion ($H_2O_2+HO^- \rightleftharpoons H_2O+HOO^-$) and alkaline hydrolysis by the HO^- anion:

$$(1)$$
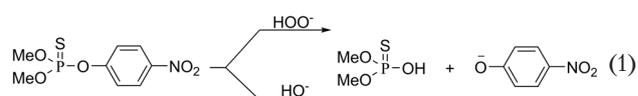
The choice of MP as a model substrate is due to the fact that it belongs to a group of especially dangerous pesticides

and is an analogue of combatant toxic substances such as phosphoric and phosphonic esters (GB and VX). Nevertheless, the reactivity of MP in nucleophilic processes with the participation of the hydroperoxide anion has been insufficiently studied and requires detailed elaboration, both in terms of kinetic parameters and in terms of establishing the interaction mechanism.

The contribution of alkaline hydrolysis was estimated by decomposing MP in aqueous KOH solutions with pH variation in the range of 9–10.5 in the presence and absence of NH_4HCO_3 and $(B(OH)_3)$. Fig. 1 shows the dependence of the observed rate constants (k'_{HO^-}) of the alkaline hydrolysis of MP on the concentration of the hydroxide ion.
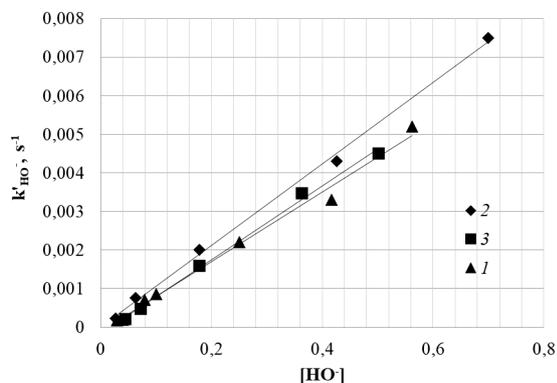

Fig. 1. The dependence of the observed rate constants (k'_{HO^-}) of the alkaline hydrolysis of MP on the concentration of hydroxide ions ([HO^-]) in aqueous solutions:
1 − HO^-; 2 − HO^-/($B(OH)_3$); 3 − HO^-/NH_4HCO_3;
[NH_4HCO_3]=[$B(OH)_3$]=0.2 M^{-1}; 25 °C

Fig. 1 shows that the presence of NH_4HCO_3 or $B(OH)_3$ in the reaction system does not change the rate of the alkaline hydrolysis of MP. The calculation of second-order rate constants k_{HO^-} ($M^{-1}s^{-1}$) was carried out according to the concentration dependence

$$k'_{HO^-} = k_{HO^-} \cdot [KOH], \qquad (2)$$

where [KOH], M^{-1} is the concentration of alkali.

The values of k_{HO^-} for conditions 1–3 (Fig. 1) are given in Table 1, and within the experimental error, they coincide for all the systems studied (Table 1, No. 1−3). The minimum values of the segment cut off along the ordinate axis indicate that the contribution of a possible process of the neutral hydrolysis of MP to the overall rate of using the substrate is insignificant. The second order constant of this process does not exceed 2 10^{-6} $M^{-1}s^{-1}$, which practically does not affect the reaction rate of the MP decomposition.

Fig. 2 shows the dependence of the observable constants of the MP decomposition rate (k'_{HO^-}) in the systems H_2O_2/HO^- (4) and (I)/HO^- (5). The kinetic method was used to determine the constant of the acid-base ionization of H_2O_2 (K_a) in the systems under study by the equation

$$k_i = k_{HOO^-} \cdot \left[HOO^- \right]_0 = k_{HOO^-} \cdot \frac{K_a}{K_a + a_{H^+}} \cdot [H_2O_2]_0, \qquad (3)$$

where $[HOO^-]_0$ is the initial concentration of the hydroperoxide anion; k_i is the difference of the constants ($k'_{HOO^-} - k'_{HO^-}$), which characterizes the contribution of the MP decomposition with the help of the HOO^- anion.

Table 1

The rate constants of the second order of the hydrolysis (k_{HO^-}) and perhydrolysis (k_{HOO^-}) of methyl parathion in water, 25 °C

No.	Nucleophile	$k_{HO^-} \cdot 10^3$, ($M^{-1}s^{-1}$)	k_{HOO^-}, ($M^{-1}s^{-1}$)	$\alpha = k_{HOO^-}/k_{HO^-}$	pK_a
	Methyl parathion				
1	HO^-	8.90±0.34	–	–	–
2	HO^-/($B(OH)_3$)	10.0±0.7	–	–	–
3	HO^-/NH_4HCO_3	9.62±0.76	–	–	–
4	H_2O_2/HO^-	–	895±45	101	11.49
5	(I)/HO^-	–	818±67	92	11.67
	Paraoxon [13]				
6	HO^-	10.0	–	–	11.60
7	H_2O_2/HO^-	–	580	58	–
8	(I)/HO^-	–	540	54	–

The values of pK_a for hydrogen peroxide (curve 4 in Fig. 2) and for hydroperite I (curve 5 in Fig. 2) were determined from the data of the kinetics of the MP decomposition to be close – 11.49 and 11.67, respectively (Table 1). These values differ little from the value of the acid-base ionization constant of H_2O_2 obtained for parahoxone perhydrolysis (pK_a=11.60) under similar conditions [13].
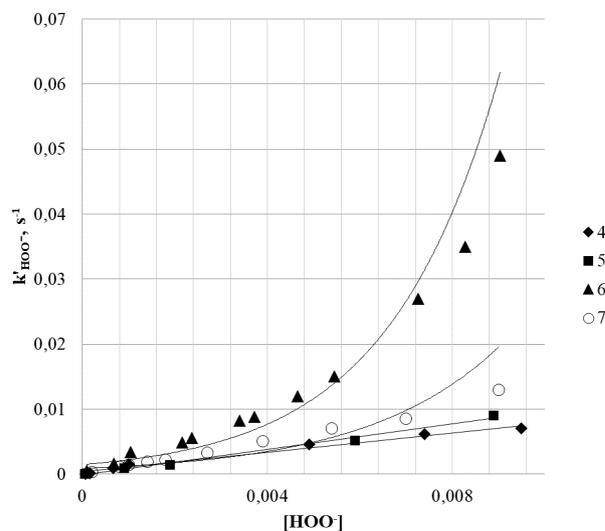

Fig. 2. The dependence of the observed rate constants (k'_{HOO^-}) on the MP perhydrolysis on the concentration of the peroxide anion ([HOO^-]) in aqueous solutions:
4 − H_2O_2/HO^-; 5 − (I)/HO^-; 6 − (I)/HO^-/($B(OH)_3$);
7 − (I)/HO^-/NH_4HCO_3; [$H_2O_2]_0$=0.02 M;
[$(B(OH)_3)_0$]=[$NH_4HCO_3]_0$=0.2 M; 25 °C

The rate constants of the second order k_{HOO^-}, ($M^{-1} s^{-1}$) of the MP perhydrolysis, calculated by equation (4) of the concentration dependences (Fig. 2), have similar values (Table 1, No. 4 and 5) and are essentially independent of the nature of the H_2O_2 source:

$$k'_{HOO^-} = k_{HOO^-} \cdot \left[HOO^- \right]_0. \qquad (4)$$

Summing up the performed kinetic tests, it can be stated that the interaction of the anions HO^- and HOO^- takes place under the S_N2 mechanism. In both cases, there is a depen-

dence in the coordinates "$k'_{HOO^-} (k'_{HO^-}) - [HOO^-]([HO^-])$" with a high degree of correlation. In addition, a significant α-effect (α=92–101, No. 4 and 5, Table 1) is observed for the reaction of MP perhydrolysis in the system (I)/HO⁻, which exceeds the analogue value for paraoxon (α=54–58, No. 7 and 8).

5. 2. Perhydrolysis of MP in the presence of NH_4HCO_3 and $(B(OH)_3$

In contrast to the systems of alkaline hydrolysis (curves 1–3, Fig. 1), in the systems containing hydrogen peroxide in the form (I), additives NH_4HCO_3 and $(B(OH)_3$ lead to an increase in the rate of perhydrolysis (cf. curves 4 and 5 and curves 6 and 7 in Fig. 2). The growth of the observed decay rate constants of MP (k'_{HOO^-}) is especially noticeable in the range of pH 10–11.

The activating effect of the HCO_3^- anion can be related to the formation of a peroxhydrocarbonate anion in the system H_2O_2/NH_4HCO_3. According to the authors of [16], the peroxhydrocarbonate anion has supernucleophilic properties and is formed under the following equation:

$$HCO_3^- + H_2O_2 \rightleftharpoons HCO_4^- + H_2O, \qquad (5)$$
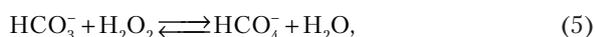
where K is the equilibrium constant for the formation of the peroxomonocarbonate anion, and it is equal to 0.33 M⁻¹ [16].

Equilibrium (5) at pH 8–9 is set relatively quickly (within ~5 to 30 min). With further increase of pH, the transformation of the HCO_4^- anion into the CO_4^{2-} anion (pK_a=9.4 [16]) occurs according to the equation

$$HCO_4^- \rightleftharpoons CO_4^{2-} + H^+. \qquad (6)$$

In the conditions of the pseudo-first order with respect to the substrate, the equation for the observed rate constant k_{obs} (s⁻¹) in the system (I)/HO⁻/NH_4HCO_3 corresponds to the equation

$$k_{obs} = k'_{HO^-} + k'_{HOO^-} + k'_{HCO_4^-} + k'_{CO_4^{2-}}, \qquad (7)$$

where $k'_{HCO_4^-}$ and $k'_{CO_4^{2-}}$ are the observed constants of the rate of nucleophilic substitution with the peroxomonocarbonate anions and peroxocarbonate.

The solution of the system of equations (5)–(8) and the corresponding calculation according to the data of Table 2 allow determining the most probable values of the rate constants of the second order $k_{HCO_4^-}$ and $k_{CO_4^{2-}}$:

$$k_i = k_{obs} - (k'_{HO^-} + k'_{HOO^-}) =$$
$$= k_{HCO_4^-} \cdot [HCO_4^-] + k_{CO_4^{2-}} \cdot [CO_4^{2-}]. \qquad (8)$$

The concentrations of $[HCO_4^-]$ and $[CO_4^{2-}]$ were calculated by using equilibriums (5) and (6) as well as the known values of K and K_a of the HCO_4^- anion (2.51 10⁻¹¹ M [16]).

With the joint presence of hydrogen peroxide and boric acid in the solution, the broad range of pH 6–14 presents the formation of peroxoanions such as monoperexoborate $B(OH)_3(OOH)^-$ (MPB) and diperoxoborate $B(OH)_2(OOH)_2^-$ (DPB) according to the equations:
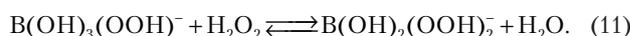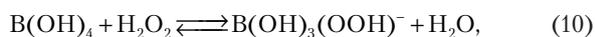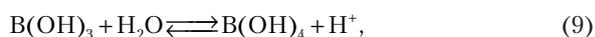
$$B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+, \qquad (9)$$

$$B(OH)_4^- + H_2O_2 \rightleftharpoons B(OH)_3(OOH)^- + H_2O, \qquad (10)$$

$$B(OH)_3(OOH)^- + H_2O_2 \rightleftharpoons B(OH)_2(OOH)_2^- + H_2O. \qquad (11)$$

Table 2

The contribution of the routes with HOO⁻ (k_{HOO^-} [HOO⁻]), HCO_4^- ($k_{HCO_4^-}$ $[HCO_4^-]$), CO_4^{2-} ($k_{CO_4^{2-}}$ $[CO_4^{2-}]$) to the total rate of MP decomposition MP ($k_н$) in water*, 25 °C

pH	$k_н$ 10³, s⁻¹	k_{HOO^-} $[HOO^-]$ 10³, s⁻¹	$k_{HCO_4^-}$ $[HCO_4^-]$ 10⁵, s⁻¹	$k_{CO_4^{2-}}$ $[CO_4^{2-}]$ 10³, s⁻¹
9.01	0.301	0.181	7.32	0.036
9.24	1.14	0.720	5.94	0.09
9.34	1.42	0.904	3.21	0.112
9.46	1.91	1.26	2.01	0.192
9.52	2.24	1.62	1.13	0.216
9.76	3.39	2.43	0.212	0.234
9.92	5.12	3.51	0.104	0.459
10.07	7.06	4.86	0.061	1.08
10.15	8.51	6.34	0.042	1.55
10.31	13.3	8.12	0.006	3.01

Note: * – means the system (I)/HO⁻/NH_4HCO_3; [HO_2O_2]₀=0.02 M; [NH_4HCO_3]₀=0.2 M; 25 °C

The constants of equilibriums (9)–(11) in water have the following values: (9) – $pK_a^{B(OH)_3} = 8.96$; (10) – K_{MPB}=20; (11) – K_{DPB}=2.0 [16].

In view of the concentration conditions for equations (9)–(11) and in accordance with the mathematical model developed for borate catalyzed oxidation of diethyl sulfide [18], the values were calculated for the concentrations of the peroxoanions [MPB], [DPB], and [HOO-], and also the equilibrium concentration of the hydrogen peroxide [H_2O_2]$_p$. The calculations were carried out according to the formulae of [18]:

$$[B(OH)_3(OOH)^-] =$$
$$= \frac{K_{MPB}K_a^{B(OH)_3}[B(OH)_3]_0[H_2O_2]_p}{K_a^{B(OH)_3} + [H^+]}, \qquad (12)$$

$$[B(OH)_2(OOH)_2^-] =$$
$$= \frac{K_{MPB}K_{DPB}K_a^{B(OH)_3}[B(OH)_3]_0[H_2O_2]_p^2}{K_a^{B(OH)_3} + [H^+]}. \qquad (13)$$

The ratios of the formed peroxoborates depend on the ratios of the initial concentrations of $B(OH)_3$, H_2O_2 and the pH medium. At relatively low concentrations of $B(OH)_3$, H_2O_2 (<1 M⁻¹) in the range of pH 6–14, the main products are anions of monoperoxoborate $B(OH)_3(OOH)^-$ and dieroxoborate $B(OH)_2(OOH)_2^-$; at higher concentrations of the reagents, the products are polyperoxoborates of the structure $B_2(O_2)_2(O_2H)_n(OH)_{4-n}$ (n=0, 2 or 4) [17]. For this reason, a clear separation of nucleophilic substitution routes with the determination of the reactivity of the peroxoborate generated in the system is often impossible.

The values of the observed rates of the methyl parathion decomposition ($k_н$, s⁻¹) in solutions of carbamide peroxysolvate (I) in the range of pH values 9–10.3 are given in Table 3. The equation for calculating the contribution of nucleophilic substitution routes to different anions has the form

$$k_i = k_{obs} - \left(k'_{HO^-} + k'_{HOO^-}\right) =$$
$$= k_{MPB} \cdot \left[B(OH)_3(OOH)^-\right] + k_{DPB} \cdot \left[B(OH)_2(OOH)_2^-\right]. \quad (14)$$

Under the conditions of the maximal accumulation of the anions $B(OH)_3(OOH)^-$ and $B(OH)_2(OOH)_2^-$ (pH 10), there is a significant acceleration of nucleophilic substitution in the presence of $(B(OH)_3)$ in comparison with the rate of substitution with the HOO^- anion: the $k_н$ of the catalytic process in about 5 times higher than the k'_{HOO^-} of the non-catalytic reaction.

This kind of dependence is consistent with the accumulation dynamics of the active peroxoanions $B(OH)_3(OOH)^-$ and $B(OH)_2(OOH)_2^-$ when the pH of the solution varies, which is presented in Fig. 3. Calculations of the concentration of the anions were made for the concentration conditions $[CO(NH_2)_2 \cdot H_2O_2]_0 = 0.02$ M^{-1}; $[B(OH)_3]_0 = 0.2$ M^{-1}.

Table 3

The contribution of the routes with HOO$^-$ (k_{HOO^-} [HOO$^-$]), MPB (k_{MPB} [MPB]), and DPB (k_{DPB} [DPB]) to the overall decomposition rate of MP ($k_н$) in water, 25 °C

pH	$k_н$ 10^2, s^{-1}	k_{HOO^-} [HOO$^-$] 10^2, s^{-1}	k_{MPB} [MPB] 10^2, s^{-1}	k_{DPB} [DPB] 10^2, s^{-1}
9.15	0.051	0.009	0.005	0.031
9.34	0.162	0.061	0.01	0.072
9.66	0.341	0.094	0.022	0.201
9.7	0.497	0.195	0.031	0.251
9.86	0.560	0.213	0.037	0.299
9.9	0.827	0.306	0.05	0.445
10.0	0.884	0.335	0.056	0.467
10.07	1.21	0.419	0.072	0.597
10.2	1.54	0.492	0.12	0.834
10.26	2.77	0.654	0.231	1.86
10.3	3.59	0.745	0.211	2.20
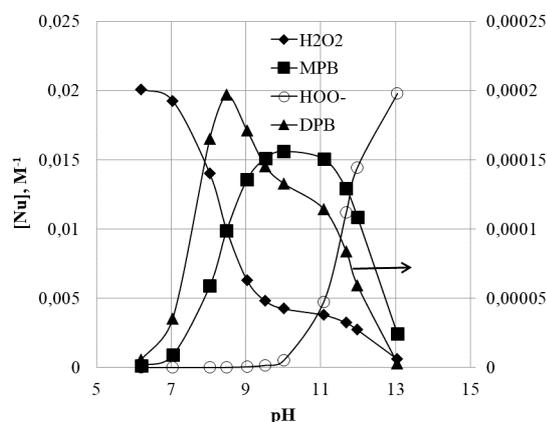
Fig. 3. The dependence of the concentrations of $[H_2O_2]_p$, [MPB], [DPB], [HOO$^-$] on the pH of the medium, 25 °C

The processing of experimental data (Table 3) using equations (6)–(10) has helped determine the rate constants of the second order of the nucleophilic substitution in MP by the monoperexoborate anions and diperoxoborate anions: k_{MPB} and k_{DPB}, respectively. The processing of the results was carried out in accordance with the mathematical model detailed in studies [17, 18].

6. Discussion of the results of the kinetic research

6. 1. The α-effect of the HOO$^-$ anion in the reaction with methyl parathion

The α-effect of the HOO$^-$ anion in the reaction of MP perhydrolysis, which is estimated as a ratio of k_{HOO^-}/k_{HO^-} is about 100 (Table 1, No. 4 and 5). This means that the HOO$^-$ anion is 100 times more reactive than the OH$^-$ anion, although the pK_a of the first of them is almost 4 units less than the pK_a of the second.

In other words, the HOO$^-$ anion exhibits abnormal reactivity with respect to electrophilic substrates. The phenomenon of supernucleophilicity (higher nucleophilic reactivity than it can be predicted in accordance with its basicity) of the HOO$^-$ anion is known and has been sufficiently studied [19]. As to the interpretation of the causes of supernucleophilicity, the main proposed ones are the following:

– intramolecular interactions with the formation of H-bonds with the stabilization of transient states of the intermediates (characteristic of the S_N2 mechanism);

– effects of solvation of intermediate products and desolvation of nucleophile.

It is likely that during the nucleophilic substitution, HOO$^-$ forms a cyclic transition state (TS), which is stabilized by H-binding according to the structure

$$(15)$$

Such a 5-member cyclic TS is impossible for the reaction with OH$^-$, and in the case of the HOO$^-$ anion, it can be considered as the main cause of the α-effect. However, if we compare the value of the α-effect for paraoxon (54–58) with the same values for methyl parathion (92–101), then the above hypothesis is untenable. Under all the same conditions, the TS with the participation of the HOO$^-$ anion for PO has greater stability due to the presence of oxygen atoms ($P=O$) rather than the TS with MP with sulfur atom ($P=S$) in the structure. Therefore, if the main reason for the α-effect is the stability of the transition state, then reciprocal values are to be expected – the α-effect for PO should exceed the α-effect for MP. This suggests that the TS stabilization with intra-molecular interactions and H-binding cannot be the only cause of the origin of the α-effect for nucleophilic substitution reactions near the electrophilic phosphorus atom.

The hypothesis of the authors of [20] seems to be the most acceptable explanation for the difference between the supernucleophilic properties of the HOO$^-$ anion in the processes under consideration: the $P=S$ bond in MP is twice more polarized than the $P=O$ bond in PO. Accordingly, it can be stated that the polarizability of unsaturated bonds near the electrophilic center is an important factor responsible for the magnitude of the α-effect.

6. 1. Reactivity of peroxoanions in the nucleophilic substitution reaction

Decomposition of MP in the system (I)/HO$^-$/NH$_4$HCO$_3$ under the concentration conditions given in Table 2 occurs along the main routes:

– alkaline hydrolysis (HO$^-$);

– perhydrolysis (HOO$^-$);

– nucleophilic interaction with the peroxomonocarbonate anion (HCO_4^-);

– nucleophilic interaction with the peroxocarbonate anion (CO_4^{2-}).

Also, the expansion of the substrate by the aminolysis of the released ammonia, along with the route of oxidation, etc., is also likely. However, due to the insignificant contributions of these routes, they were not considered in the general kinetic scheme.

The values of the second-order rate constants $k_{HCO_4^-}$ and $k_{CO_4^{2-}}$, calculated using equations (5)–(8) and the data of Table 2, make 0.12 M^{-1}s^{-1} and 1.43 M^{-1}s^{-1}, respectively. From these values it follows that the peroxocarbonate anions in the reactions of the nucleophilic substitution are less reactive, in contrast to the oxidation processes [21]: the difference is almost an order of magnitude for the HCO_4^- anion and two orders of magnitude for the CO_4^{2-} anion. Nevertheless, the results obtained have some scientific and practical significance.

On the one hand, the study has confirmed the supernucleophilicity of "atypical nucleophiles", which are the peroxoaniones anions of carbonic acid. On the other hand, there is a reason to expect that the activation of H_2O_2 by hydrocarbons will create additional routes for decomposing OP under the nucleophilic mechanism formed by the peroxoanion in the system (I)/HO$^-$/NH$_4$HCO$_3$.

The nature and probable mechanisms of the α-effect produced by the HCO_4^- and CO_4^{2-} anions are discussed in detail in [16]. It should only be added that the system (I)/HO$^-$/NH$_4$HCO$_3$ can radically solve the problem of creating soft decontamination systems of universal action (for oxidizing and nucleophilic mechanisms) that contain hydrogen peroxide and hydrocarbon and can be used in optimal systems for oxidation at pH 9–10.

The catalytic action of boric acid on the kinetics of nucleophilic substitution in MP is quantitatively described by a mechanism involving the reaction of the anions: HO$^-$, HOO$^-$, B(OH)$_3$(OOH)$^-$ and B(OH)$_2$(OOH)$_2^-$ (14).

The processing of experimental data (Table 3) in the framework of linear anamorphosis [18] has helped determine the rate constants of the second order k_{MPB}=20.6 M^{-1}s^{-1} and k_{DPB}=94.7 M^{-1}s^{-1}. The reactivity of the generated peroxoborate anions exceeds the one for the HOO$^-$ anion: ~2 times for MPB, and ~10 times for DPB. It should be noted that in the published studies there is very limited information on the nucleophilic activity of peroxoborates [21]. There are articles [22] demonstrating the absence of any influence of boric acid on the processes of perhydrolysis of 4-nitrophenyl ether of diethylphosphonic acid.

However, the formation of peroxoborates in the investigated range of pH 9–10, which is described by equations (9) and (10), is almost an undeniable fact. This approach is widely used by researchers to interpret kinetic regularities and the mechanism of oxidation in the system H_2O_2/B(OH)$_3$ near electrophilic centers [17, 18]. As a rule, peroxoborates are characterized by high reactivity, which is three to four orders of magnitude higher than the oxidizing capacity of the original hydrogen peroxide. That is why the system (I)/HO$^-$/(B(OH)$_3$ can be considered as a promising basis for decontamination formulations to decompose substrates as ecotoxicants of various chemical types (GB, VX and HD compounds).

The obtained results demonstrate that peroxoborates exhibit nucleophilic activity in the range of pH 10–11, in contrast to the peroxocarbonate anions active in the pH range of 7–9 (Table 2, 3). This fact has some practical value for the design of universal decontamination systems. In such systems, there is the possibility of oxidation of HD compounds at a shift of pH values into the alkaline region, with increasing the rate of decomposition of GB and VX compounds by the nucleophilic mechanism.

7. Conclusions

1. The conducted kinetic experiment demonstrates the prospect of using carbamide peroxysolvate as a degassing agent for the decomposition of methyl parathion and analogous organophosphorus ethers by the nucleophilic mechanism. The peroxide anion in reaction with methyl parathion exhibits a significant α-effect due to the polarizability of the unsaturated bond near the electrophilic phosphorus atom.

2. The study has determined the supernucleophilic reactivity of the peroxocarbonate and peroxoborate anions in relation to methyl parathion. Activation of hydrogen peroxide with ammonium bicarbonate and boric acid can be considered as a new approach to the creation of soft ecological systems of decontamination of nucleophilic and oxidative effects. Mixtures of carbamate peroxysolvate with certain amounts of activators may be recommended as effective long-term storage systems for decomposing highly toxic organophosphorus pesticides. Such mixtures are very promising for the development of decontamination formulations that can be used to eliminate the effects of contamination produced by chemical weapons components, toxic pesticides, and toxic active pharmaceutical ingredients.

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