Досліджено вплив активаторів на розкладання N-фосфонометилгліцину під дією пероксиду водню та гідроксиду калію. Як системи деконтамінації було вивчено суміші гідроксиду калію, пероксиду водню, борної кислоти, цетилпіридиній хлориду та борату моноетаноламіну. Показано, що борна кислота є ефективним активатором пероксиду водню як α-нуклеофілу в міцелярній системі деконтамінації N-фосфонометилгліцину.

Встановлено, що N-фосфонометилгліцин не вступає в реакції розщеплення при високих значеннях pH без участі активуючих агентів. При pH 13 очікуваний полуперіод розпаду субстрату за нуклеофільним механізмом становить біля 3 годин.

Показано, що при деконтамінації N-фосфонометилгліцину в системі луг, пероксид водню, цетилпіридиній хлорид, борна кислота створюються сприятливі умови для нуклеофільної атаки на фосфорорганічну сполуку за рахунок утворення міцел та активації механізму утворення пероксид-іонів. У вказаній системі константа швидкості реакції другого порядку у 2 рази вища ніж у неактивованій системі.

Встановлено, що борат моноетаноламіну не виявляє суттєвого активуючого впливу на міцелярний нуклеофільний каталіз при деструкції N-фосфонометилгліцину.

Визначено оптимальні умови деконтамінації N-фосфонометилгліцину в міцелярній системі знезараження: концентрації цетилпіридинію хлориду – 0,25 моль/л та борної кислоти – 0,15 моль/л. Доведено, що важливою умовою є оптимальний pH системи, який повинен знаходитись у проміжку від 10,5 до 11,5.

Зроблено висновок, що дослідження деконтамінації N-фосфонометилгліцину в умовах м'якого міцелярного каталізу має теоретичне та вагоме прикладне значення, обумовлене мінімізацію ризиків, пов'язаних з виробництвом, використанням та утилізацією фосфорорганічних сполук

Ключові слова: деконтамінаційна система, пероксид водню, N-фосфонометилгліцин, пероксоборат, дезактивація, фосфорорганічні сполуки

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DEVELOPMENT OF A DECONTAMINATION SYSTEM FOR DECOMPOSING N-(PHOSPHONOMETHYL) GLYCINE

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1. Introduction

Since the late 1990s, the world community has been paying considerable attention to the removal of pesticides from circulation if they are recognized by the FAO as outdated. Thus, the use of organochlorine pesticides has almost completely been discontinued in the EU, but the wide use of organophosphorus compounds (OPhCs) remains a problem. Ukraine widely and actively uses plant protection products based on dimethoate, glyphosate, chlorpyrifos, and pyrimifos-methyl (actelic) [1].

Pesticides based on OPhCs can enter the body in many ways, including inhalation, absorption by the skin, and ingestion. That is why an OPhC is one of the most common causes of poisoning that occurs as a consequence of use in agriculture, through accidental or directed exposure. These compounds have a significant toxic effect on plants and insects as well as on warm-blooded animals and humans [2].

The most commonly used herbicidal drug is N-(phosphonomethyl)glycine (glyphosate). Until recently, this pesticide was considered one of the safest active ingredients in the agrochemical industry, but studies of the last decade confirm the fact of its direct influence on the development of the embryo and fetus (autism spectrum disorders); moreover, they link chronic poisoning with glyphosate directly with an increased risk of morbidity lymphogemepoietic oncological diseases [3].

That is why one of the priority tasks of the chemical industry of Ukraine and the EU is, in general, to search for OPhC decontamination systems and to eliminate the consequences of their actions.

2. Literature review and problem statement

Since the introduction of N-(phosphonomethyl)glycine on the agrochemical market in 1974, the frequency of its use has increased by more than 100 times [4]. In 2015, the International Agency for Research on Cancer concluded that N-(phosphonomethyl)glycine should be considered as a possible carcinogenic agent. In its statement, the agency relied on its own studies of statistical data and data in vitro [5, 6]. However, according to the findings of the WHO and the FAO statistical report for 2016, there is no direct link between the use of N-(phosphonomethyl)glycine and the increased risk of oncological diseases [7]. Nevertheless, in March 2016, a study was published to confirm the increased risk of lymphohematopoietic cancer in people who had had direct contact with N-(phosphonomethyl)glycine and its salts. According to the ECHA classification, N-(phosphonomethyl)glycine has a toxic effect on the mucous membranes of the organism and is harmful to aquatic flora and fauna [8].

It should be noted that most of the research has been funded by organizations whose sphere of activity is directly related to the agrochemical sector of the world chemical market.

Due to the controversy of the findings of the global organizations, the European Commission has decided to start a study on the problem associated with the use of N-(phosphonomethyl)glycine. A ban on the use of this pesticide has also been initiated, which should come into force since 2020. In 2017, however, it was decided to extend the permit to use N-(phosphonomethyl)glycine for a period of 5 years. In connection with this, there is a problem with the subsequent possibility of using medications based on N-(phosphonomethyl)glycine [9].

The simplest solution to the problem of reducing the harmful impacts of OPhCs is the development of effective methods of decontamination of residues of such compounds.

An effective method for the destruction of OPhCs is alkaline hydrolysis in the presence of metals and alcohol monoethanolamine. The common disadvantages of such OPhC deactivation schemes are the high corrosion load for the decontamination technological equipment and the decomposition products toxicity. In addition, alkalis used in the industrial technology for the decontamination of toxic substances have low chemical activity with respect to phosphorus acids [10, 11]. As a consequence of this, there are relatively low values of the rate constants of the destruction of toxic OPhCs.

The rate of decomposing OPhCs can be increased by the use of α-nucleophiles [12], the typical representatives of which are peroxide anion (HOO^-) [13] and peroxoanion [14]. In addition to the high reactivity of hydrogen peroxide H_2O_2, it provides a universal effect on nucleophilic and oxidative mechanisms and also meets all requirements of environmental safety [15].

According to existing studies, hydrogen peroxide does not exhibit significant oxidizing properties. In order to activate it in a reaction medium, borates [16], carbonates, and the like are introduced, which activate hydrogen peroxide to form peroxy acids of a high reactivity [17].

Among the activating compounds, the most promising are hydrocarbons and boric acid [18]. In the case of hydrocarbonates, peroxo-monocarbonate anion (HCO_4^-) is formed, which exhibits a significant activating ability in weakly alkaline solutions. When using boric acid as an activator, several activating compounds are formed, each of which in turn increases the inactivation rate of the contaminated solution [1]. However, the effect of hydrocarbons and boric acid on the rate of decomposing N-(phosphonomethyl)glycine in an alkaline solution of hydrogen peroxide has not been studied yet.

The research into the use of borate monoethanolamine makes sense in order to reduce the negative impact on the working surfaces, decrease the toxicity of waste, and reduce the amount of washing water, especially in agrochemical industries. This compound, in theory, has a higher reactivity than monoethanolamine and boric acid and, according to patent data, has significant anti-corrosion properties [19].

Thus, the study of decontamination of N-(phosphonomethyl)glycine in soft micellar catalysis has a theoretical and significant application value, as it minimizes the risks associated with the production, use and utilization of OPhCs.

3. The aim and objectives of the study

The aim of this study is to investigate the effect of activators on the decomposition of N-(phosphonomethyl) glycine under the action of hydrogen peroxide and potassium hydroxide in conditions of micellar catalysis.

This will enable us to establish a scientifically sound theoretical basis for the development of a composition of highly effective industrial detergents and disinfectants for the destruction of N-(phosphonomethyl)glycine.

The aim is to solve the following objectives:

– to investigate the reactivity of N-(phosphonomethyl) glycine in nucleophilic cleavage and oxidation reactions involving hydrogen peroxide and boronic acid peroxoanion;

– to determine the optimal conditions for the decomposition of N-(phosphonomethyl)glycine in a decontamination system based on hydrogen peroxide.

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

4. 1. Materials and equipment used in the experiment

We used N-phosphonomethyl glycine 95.3 % (Sichuan leshan tongda agro-chemical technology CO. LTD., PRC), cetylpyridinium chloride (CPC) (Dishman Pharmaceuticals and Chemicals, India), methanol for gradient HPLC (Sigma-Aldrich, Inc., Germany), alkali KOH (Lachema, Czech Republic), ammonium hydroxide NH_4HCO_3 and potassium dihydrogenphosphate KH_2PO_4 (Khimlaborreactive LLC, Ukraine), 1,4-dioxane (Alfa Aesar, Germany), and boric acid $B(OH)_3$ (Shanghai Yixin Chemical Co., Ltd., PRC) without preliminary purification. High-purity water of grade 1 was used to prepare solutions.

Hydrogen peroxide (reagent grade) in the form of 33 % aqueous solution was pre-distilled in vacuo (5 mm Hg).

Monoethanolamine borate was synthesized according to a known method. For this, 60 g of monoethanolamine were heated to 110 °C. Then 61 g of boric acid were added. The reaction of condensation was carried out at 160 °C until the formation of a precipitate and the evaporation of water.

To prepare the mobile phase, we introduced 0.84337 g of potassium dihydrogen phosphate into a volumetric flask of 1000 cm^3 and dissolved in 500 cm^3 of deionized water. The solution was thoroughly mixed, and 40 cm^3 of gradient methanol were added. After that, the volume of the label was filled with water. The pH of the 2.1 solution was achieved by adding orthophosphoric acid.

The decomposition of H_2O_2 in alkaline medium is not observed for 5 hours, which is sufficient for conducting research within a single series [17].

At the stage of kinetic study preparation, the following equipment was used: pH meter pH-150 MI (Measuring Equipment LLC, Russia); scanning UV spectrophotometer OPTIZEN POP (Mecasys, South Korea); laboratory of water treatment RO-4 (Werner, Germany); Sartorius Stedim biotech Arium H_2O pro DI-T (Sartorius, Germany); Analytical Scales AccuLab ALC 110.4 (Sartorius, Germany); Brookfield TC-200 water cooled thermostat with Brookfield TC-350 cooling system (Brookfield, United States of America). In addition, the following ancillary materials were used:

– cuvettes made of quartz glass with a 1 cm thickness of the optical layer;

– single-channel automatic dispensers of 5–50 μl and 20–200 μl;

– disposable rubber gloves;

– water of grades 1 and 3;

– a timer.

4. 2. Decontamination systems for N-(phosphonomethyl)glycine

In the course of research on the methods of decontamination of N-(phosphonomethyl)glycine in the framework of this study, already known methods were used as the basic ones [1, 15, 16]. The decontamination of N-(phosphonomethyl)glycine was accomplished by creating conditions for alkaline perhydrolysis when supplying the system with peroxide anions as α-nucleophile and nucleophilic substitution activators, as well as by forming micellar systems when using the surfactant.

The peroxide anion was introduced into the system in the form of hydrogen peroxide (H_2O_2).

Hydrogen peroxide is a "soft" nucleophile in terms of environmental safety and corrosion activity in relation to alloyed steels used in the chemical industry.

For the formation of micellar conditions as a detergent additive, the system included cetylpyridinium chloride. In systems to decontaminate OPhCs, CPC has two significant advantages: first, the cationic surfactant creates the necessary conditions for a nucleophilic attack on the electrophilic centers of the OPhC, and secondly, CPC is one of the safest micelles forming agents, which allows it to be used in all areas of the chemical industry without exception.

In theoretical modeling of the study series, the assertion was made of two trends in the chemical degradation of the OPhC: perhydrolysis involving an HOO^- anion and alkaline hydrolysis at the expense of an OH^- anion [15].

4. 3. The methods of studying the kinetics of degradation of N-(phosphonomethyl)glycine

The control over the decomposition of N-(phosphonomethyl)glycine was performed according to the validated method CIPAC *284/TC/(M)/ on the LC-2030C 3D liquid chromatograph (Shimadzu, Japan) with a PDA detector and using the LabSolutions software.

The analytical column Zorbax® 5 μm SB-CN 80 Å, LC Column 250 * 4.6 mm was used for analysis.

The terms of conducting chromatographic analysis were the following:

– mobile phase: phosphate buffer solution:methanol= =96:4 (v/v);

– flow rate: 2 cm^3/min;

– during the analysis, no solvent was used because there was no need for additional extraction;

– thermostat temperature of the column: 40 °C;

– thermostat temperature of the injector: 20 °C;

– volume of the injection: 50 μl;

– detection wavelength: PDA, λ=195 nm;

– N-(phosphonomethyl)glycine retention time: 5.5±0.5 min;

– chromatography time: 10 min.

Preparation of standard solution (solution of comparison):

In a two-volume volumetric flask of 25.0 cm^3, 50 mg of N-(phosphonomethyl)glycine and 15 cm^3 of solvent were added. The flasks were placed in an ultrasound bath and treated with ultrasound for 2–3 minutes. The flasks were then removed from the bath, held for 5–10 minutes at ambient temperature, and the volume of the solvent was diluted to the label.

Applicability of the chromatographic system:

The RSD for 5 consecutive injections of standard solution should not exceed 1.5 %. The number of theoretical plates for the peak of N-(phosphonomethyl)glycine on the chromatogram of the standard solution is not less than 2,500.

4. 4. The method of studying the influence of the concentration of cetylpyridinium chloride on the rate of decomposing N-(phosphonomethyl)glycine

To determine the optimal concentration of CPC, an appropriate weighing material was added to the chemical glass, as well as hydrogen peroxide (at a rate of 0.2 mol/L; 0.9750±0.0010 g) and 50 cm^3 of the working solution were supplied. The pH of the solution was adjusted to 10.5 ($[OH^-]$=0.3 mmol/L).

The kinetics of decomposing N-(phosphonomethyl) glycine was investigated according to the procedure outlined in 4.3.

4. 5. The method of studying the influence of boric acid concentration on the rate of decomposing N-(phosphonomethyl)glycine

Samples of the $OH^-/H_2O_2/CPC/B(OH)_3$ system were prepared as follows: the appropriate weight of $B(OH)_3$ was introduced into a chemical glass, and then the added components were CPC (0.4575±0.0010 g), hydrogen peroxide (0.9750±0.0010 g), and 50 cm^3 of the working solution. The pH of the solution was adjusted to 10.5 ($[OH^-]$=0.3 mmol/L).

The kinetics of decomposing N-(phosphonomethyl)glycine was investigated according to the procedure outlined in 4.3.

5. Results of the study of the nucleophilic decomposition of N-(phosphonomethyl)glycine

5. 1. Alkaline hydrolysis of N-(phosphonomethyl) glycine

The study of the decomposition of N-(phosphonomethyl) glycine was carried out in the range of [OH^-] from 0.001 to 100.0 mmol/L (pH=8.0–13.0). The appropriate level of concentration of hydroxyl ions was provided by adding a concentrated solution of KOH to the working solution.

Changes in the concentration (in the peak area) of N-(phosphonomethyl)glycine were controlled by high performance liquid chromatography with triple analysis of samples at intervals of 60 minutes (Table 1).

Table 1

The dependence of the concentration of N-(phosphonomethyl)glycine on the concentration of hydroxyl ions and the reaction time

[OH^-], mmol/L	Probe analysis time, s			Standard deviation, %
	3.600	7.200	86.400	
	Peak area (S), c.u.			
0.001	660.805	660.124	660.435	0.09
0.003	662.679	662.139	662.598	0.12
0.01	660.585	661.266	661.037	0.08
0.03	671.112	671.578	671.953	0.25
0.1	666.494	661.292	665.888	0.39
0.3	660.802	661.919	661.551	0.21
1	771.730	768.523	769.197	0.35
3	767.636	767.716	767.644	0.03
10	735.898	739.943	736.890	0.31
30	768.123	768.523	768.413	0.14
100	767.603	767.716	767.711	0.01

The value of the standard deviation during the analysis does not exceed 0.39 % (Table 1), which suggests, according to this method, that the process of alkaline hydrolysis of N-(phosphonomethyl)glycine is absent in the investigated pH range of solutions 8–13.

5. 2. Perhydrolysis of N-(phosphonomethyl)glycine with the involvement of potassium hydroxide and hydrogen peroxide as α-nucleophile

A series of samples of a working solution with a concentration of 0.2 M hydrogen peroxide in the range of [OH^-]=0.001–100 mmol/L, corresponding to a pH of 8–13, was analyzed to determine the optimal concentration of hydroxyl ions in the decomposition of N-(phosphonomethyl)glycine.

The area of the peak of the control solution, that is, the peak area at the beginning of the reaction was 735,793 c.u. The minimum peak area, that is, the peak area after the completion of the reaction, was 215,722 c.u.

On the basis of the obtained data, the observed constants of the first-order reaction rates (k_i, s^{-1}) are calculated by formula (1):

$$k_i = \frac{1}{t} \times \ln \frac{S_\infty - S_0}{S_\infty - S_t}, \quad (1)$$

where t is the reaction time, s; S_∞ is the peak area of the N-(phosphonomethyl)glycine after the reaction, c.u.; S_t is peak area of N-(phosphonomethyl)glycine at a certain time, c.u.; S_0 is the peak area of N-(phosphonomethyl)glycine at the beginning of the reaction, c.u.

According to the data obtained, the dependence of the constant of the reaction rate k_i on the pH medium has an extreme nature: in the [OH^-] range of 0.001 to 0.1 mmol/L (pH 8–10), it increases, reaches the maximum values in the range of [OH^-]=0.3–3.0 mmol/L (pH 10.5–11.5), after which it rapidly decreases (Fig. 1).

In the OH^-/H_2O_2 system, the most probable mechanisms for the decomposition of N-(phosphonomethyl)glycine are nucleophilic perhydrolysis of HOO^- anion and oxidation with hydrogen peroxide H_2O_2. In this case, the equation for the observed rate constant k_i has the expression

$$k_i = k^2_{HOO^-} \times [HOO^-] + k^2_{H_2O_2} \times [H_2O_2]_e, \quad (2)$$

where $k^2_{HOO^-}$ and $k^2_{H_2O_2}$ are the rate constants of the second-order nucleophilic substitution and oxidation, respectively; $[HOO^-]$ and $[H_2O_2]_e$ are the concentrations of anion peroxide and hydrogen peroxide at a given pH value.

Table 2 shows the data for calculating $k^2_{HOO^-}$ and $k^2_{H_2O_2}$ by equation (2).

The linearization results on the kinetic data of decomposing N-(phosphonomethyl)glycine in the coordinates $k_i/[H_2O_2]_e - [HOO^-]/[H_2O_2]_e$ for the system are presented in Fig. 2. Calculation in the framework of a linear regression allows determining the values of $k^2_{HOO^-} = 2.0 \times 10^{-4}$ $M^{-1}s^{-1}$ and $k^2_{H_2O_2} = 1.25 \times 10^{-3}$ $M^{-1}s^{-1}$ with a satisfactory correlation coefficient of R=0.960.

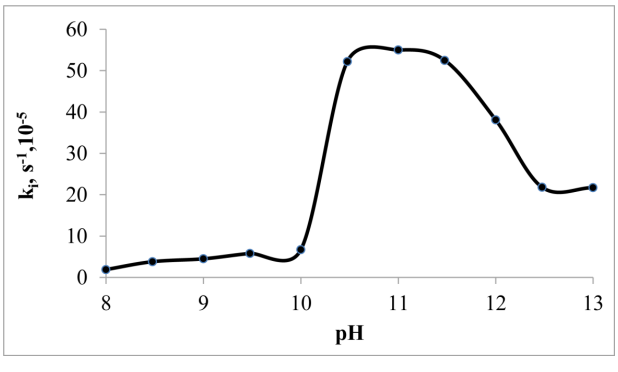

Fig. 1. The dependence of the rate constant of the first-order reaction k_i on the pH in the OH^-/H_2O_2 system

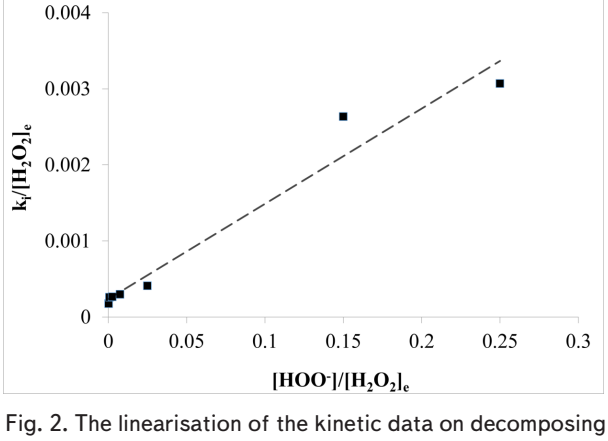

Fig. 2. The linearisation of the kinetic data on decomposing N-(phosphonomethyl)glycine in the coordinates $k_i/[H_2O_2]_e - [HOO^-]/[H_2O_2]_e$ for the OH^-/H_2O_2 system

To determine the optimal concentration of hydrogen peroxide as α-nucleophile for the system of decontaminating N-(phosphonomethyl)glycine, a study of the dependence of the rate constant of the second-order reaction $k^2_{HOO^-}$ on the concentration of $[H_2O_2]$ at pH=10.5 ($[OH^-]$=0.3 mmol/L) was performed. The results are presented in Fig. 3.

Table 2

The kinetic results of the decomposition of N-(phosphonomethyl)glycine in the OH^-/H_2O_2 system

$[OH^-]$, mmol/L	$k_i \times 10^4$, s^{-1}	$[HOO^-] \times 10^2$, mol/L	$[H_2O_2]_e$, mol/L	$k_i / [H_2O_2]_e \times 10^4$, mol/L
0.001	0.35	0.005	0.2000	1.75
0.003	0.52	0.015	0.1999	2.60
0.01	0.53	0.050	0.1995	2.65
0.03	0.59	0.149	0.1985	2.97
0.1	0.80	0.488	0.1951	4.10
0.3	4.90	1.395	0.1861	26.3
1	4.91	4.00	0.1600	30.7

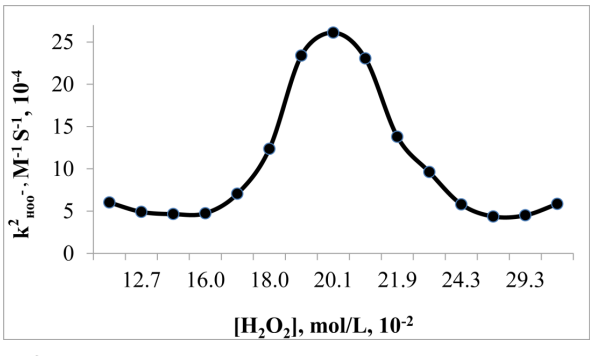

Fig. 3. The dependence of the rate constant of the second order $k^2_{HOO^-}$ on $[H_2O_2]$ in the samples of the OH^-/H_2O_2 system

Based on the data obtained, it can be argued that for $[OH^-]$=0.3 mmol/L, that is, at pH=10.5, the optimal concentration of hydrogen peroxide for the systems of decontaminating N-(phosphonomethyl)glycine is 0.2 mol/L.

5. 3. The effect of the concentration of cetylpyridinium chloride on the rate of decomposing N-(phosphonomethyl)glycine

According to the procedure outlined in 4.4, the pH of the solution was adjusted to the value of 10.5 ($[OH^-]$=0.3 mmol/L).

It is known that at pH 10.5 only 7 % of the output hydrogen peroxide is in the anionic form of HOO^- (pK_a for H_2O_2 is 11.5). Therefore, in the future calculations, the process of perhydrolysis is not taken into account. Based on the obtained kinetic data on the influence of the concentration of cetylpyridinium chloride on the rate of decomposing N-(phosphonomethyl) glycine, the constants of the second-order reaction rate $k^2_{H_2O_2}$ are calculated by formula (3):

$$k^2_{H_2O_2} = k_i / [H_2O_2]. \quad (3)$$

The dependence of the second-order reaction rate constant $k^2_{H_2O_2}$ on the concentration of [CPC] in the OH^-/H_2O_2/CPC system is shown in Fig. 4.

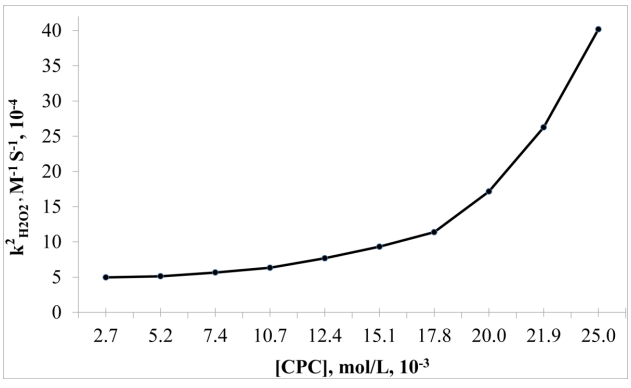

Fig. 4. The dependence of the second-order reaction rate constant $k^2_{H_2O_2}$ on the concentration of CPC in the OH^-/H_2O_2/CPC system

In contrast to the data obtained in previous studies of the kinetics of decomposing methyl parathion in the analogous system [1], the dependence of the second-order reaction rate constant $k^2_{H_2O_2}$ on the concentration of CPC in the OH^-/H_2O_2/CPC system is not extreme. This may be due to the peculiarities of the chemical structure of the organophosphorus substrates studied.

5. 4. The influence of boric acid on the rate of decomposing N-(phosphonomethyl)glycine

By preliminary analysis of the working solution, the peak area of N-(phosphonomethyl)glycine was determined prior to the reaction at 589,531 c.u. The peak area of the N-(phosphonomethyl)glycine after the reaction was 160,736 c.u.

It has been found experimentally that the decomposition reaction of N-(phosphonomethyl)glycine is activated no earlier than in 1 hour 30 minutes. In connection with this, the beginning of the samples analysis shifted to 5,400 seconds.

According to the kinetic study, using formula (3), the constants of the second-order reaction rates $k^2_{H_2O_2}$ for the OH^-/H_2O_2/CPC/$B(OH)_3$ system were determined. The dependence of the second-order rate constant on the content of boric acid in the system is shown in Fig. 5.

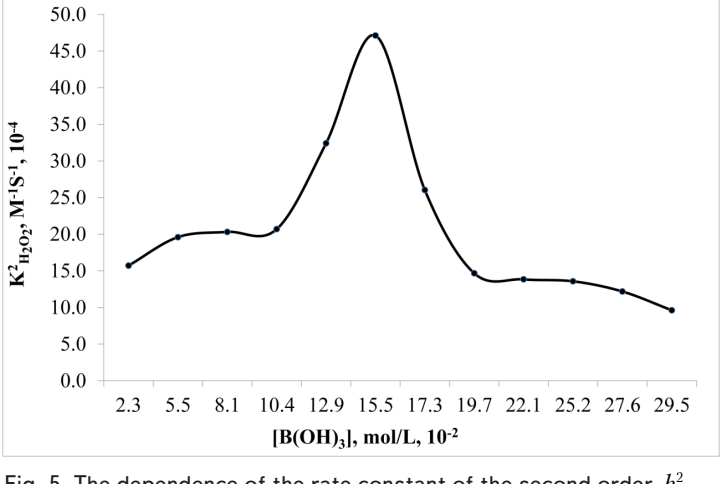

Fig. 5. The dependence of the rate constant of the second order $k^2_{H_2O_2}$ on $[B(OH)_3]$ in the OH^-/H_2O_2/CPC/$B(OH)_3$ system

This dependence has a clearly expressed extreme character (Fig. 5). The results of the study directly indicate the concentration of boric acid in the system, in which the

second-order rate constant of decomposing N-(phosphonomethyl)glycine takes a maximum value.

5. 5. The influence of borate monoethanolamine on the rate of decomposing N-(phosphonomethyl)glycine

To prepare samples of $OH^-/H_2O_2/CPC/NH_2(CH_2)_2OB(OH)_2$, the corresponding weight of borate of monoethanolamine was introduced into the chemical glass, and the added components were CPC (0.4475±0.0010 g), hydrogen peroxide (0.9750±0.0010 g), and 50 cm^3 of the working solution. The pH of the solution was adjusted to 10.5 ($[OH^-]$=0.3 mmol/L).

In the course of the analysis, the peak area of N-(phosphonomethyl)glycine was determined prior to the start of the reaction, which was 589,531 c.u. The peak area of the N-(phosphonomethyl)glycine after the reaction was 16,082 c.u.

It has been found experimentally that the decomposition reaction of N-(phosphonomethyl)glycine is activated no earlier than in 1 hour 30 minutes, as in the case of boric acid. In connection with this, the beginning of the analysis of samples shifted to 5,400 seconds.

Formulae (1) and (2) determine the constants of the reaction rates of the first and second order for a series of samples in the system $OH^-/H_2O_2/CPC/NH_2(CH_2)_2OB(OH)_3$ (Table 3).

Table 3

The constants of the reaction rate of the first and second order in the samples of the $OH^-/H_2O_2/CPC/NH_2(CH_2)_2OB(OH)_3$ system

The tested solution	k_i, s^{-1}, 10^{-4}	V (c.u.)*	RSD, %**	$k^2_{H_2O_2}$ $M^{-1}s^{-1}$, 10^{-4}	V (c.u.)*	RSD, %**
1	0.11	0.00	1.14	5.83	0.07	1.14
2	0.21	0.00	2.08	4.46	0.09	2.08
3	0.20	0.00	1.21	2.53	0.03	1.21
4	0.17	0.00	0.40	1.63	0.01	0.40
5	0.15	0.00	1.77	1.22	0.02	1.77
6	0.14	0.00	2.48	0.94	0.02	2.48
7	0.14	0.00	1.61	0.82	0.01	1.61
8	0.12	0.00	1.40	0.56	0.01	1.40
9	0.11	0.00	2.98	0.48	0.01	2.98
10	0.13	0.00	2.24	0.53	0.01	2.24
11	0.14	0.00	0.95	0.49	0.00	0.95
12	0.17	0.00	2.59	0.56	0.01	2.59

*Notes: * – V (c.u.) is the peak area in the chromatogram; ** – RSD, % is the relative standard deviation of the determined peak area in the chromatogram*

The values of the constants of the reaction rate of the second order $k^2_{H_2O_2}$ indicate a negative effect of the content of borate monoethanolamine on the rate of decontaminating N-(phosphonomethyl)glycine. Even the insignificant content of the compound at the level of 0.02 mol/L slows down the reaction almost twice (Fig. 6).

This effect can be explained by the low degree of dissociation of borate monoethanolamine in solution and, as a consequence, the absence of free boron ions, as well as the monoethanolamine ion.

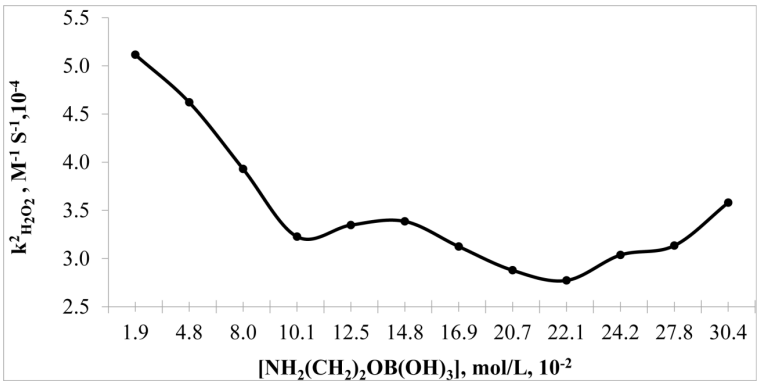

Fig. 6. The dependence of the rate constant of the second order $k^2_{H_2O_2}$ of decomposing N-(phosphonomethyl)glycine on the concentration of borate monoethanolamine

6. Discussion of the results of the kinetic studies of decomposing N-(phosphonomethyl)glycine under the influence of hydrogen peroxide and potassium hydroxide

The kinetic data on the decomposition of N-(phosphonomethyl)glycine in the coordinates of $k_i/[H_2O_2]_e$ – $[HOO^-]/[HOO^-]$ for the OH^-/H_2O_2 system after the linearization (Fig. 2) make it possible to compare the values of the constants $k^2_{HOO^-}$ and $k^2_{H_2O_2}$. Such analysis firstly testifies to the prevailing contribution of oxidation in the general rate of consumption of the substrate. Secondly, it explains the nature of the extreme dependence of the observed constant k_i on the pH of the medium, which is presented in Fig. 1. In alkaline media (pH>10.5), hydrogen peroxide is transformed into an anionic form of HOO^-, which has an extremely low reactivity with respect to N-(phosphonomethyl)glycine. At pH 13, the expected half-life of the substrate decay according to the nucleophilic mechanism is about 3 hours.

The obtained results determine the required pH level, which provides the required reaction rate for decontamination of N-(phosphonomethyl)glycine. The pH=10.5 ($[OH^-]$=0.3 mmol/L) is optimal in the establishment of the decontamination system for N-(phosphonomethyl)glycine.

At the same time, for this value of pH, the optimum value of the concentration of hydrogen peroxide is 0.2 mol/L, as evidenced by the characteristic extremum on the dependence curve of the second-order rate constant $k^2_{HOO^-}$ on $[H_2O_2]$ in the samples of the OH^-/H_2O_2 system (Fig. 3).

Considering the dependence of the second-order rate constant $k^2_{H_2O_2}$ on the concentration of CPC in the $OH^-/H_2O_2/CPC$ system (Fig. 4), it should be noted that it was previously shown [1] that the maximum rate of the degradation of OPhCs (by the example of methyl parathion) is observed at the concentration [CPC]=0.01 mol/L. However, the obtained data suggest a gradual increase in the reaction rate of decomposing N-(phosphonomethyl) glycine with an increase in the concentration of CPC in the system. It should be noted that there is a decrease in the rate constant of the second order of oxidation of N-(phosphonomethyl)glycine at the interval of the investigated CPC concentrations of 0.0027–0.0178 mol/L. In

the absence of CPC, this value is equal to $1.25 \cdot 10^{-3}$ $M^{-1}s^{-1}$ (according to the results in Fig. 1). Reducing the reactivity of H_2O_2 in the anisole oxidation reaction in the presence of cationic surfactants was described earlier [15]. The absence of the rate constant of the classical extreme dependence on the concentration of the detergent in the system under investigation also indicates the participation in the decomposition of the N-(phosphonomethyl)glycine of a neutral H_2O_2 molecule. Nevertheless, an increase in the concentration of CPC leads to an increase in the reactivity of the substrate more than 3 times. This may be due to the catalytic action of CPC by a mechanism other than the expected concentration of the reagent and the substrate in the micellar phase.

Given the technological aspects, the use of significant surfactant content is not economically and practically feasible. For this reason, the optimal level of concentration of CPC from the point of view of "content-efficiency" is the concentration of 0.025 mol/L.

The obtained results enable us to recommend the following composition of components as the base of the decontamination system: $[OH^-]$=0.3 mmol/L; $[H_2O_2]$=0.2 mol/L, and [CPC]=0.25 mol/L.

The analysis of the dependence of the second-order rate constant $k^2_{H_2O_2}$ on $[B(OH)_3]$ in the $OH^-/H_2O_2/CPC/B(OH)_3$ system (Fig. 5) has made it possible to determine the optimal concentration of boric acid as an activator in the decontamination system of N-(phosphonomethyl)glycine.

The results presented in Fig. 5 show that the rate constant of the second order reaches its maximum at $4.71 \cdot 10^{-3}$ $M^{-1}s^{-1}$ at a concentration of boric acid of 0.15 mol/L.

7. Conclusions

1. The study has specified the influence of activators on the decomposition of N-(phosphonomethyl)glycine under the effect of hydrogen peroxide and potassium hydroxide. It has been shown that boric acid is an effective activator of hydrogen peroxide as α-nucleophile in the micellar decontamination system of N-(phosphonomethyl) glycine.

2. It has been found that N-(phosphonomethyl)glycine does not enter the splitting reaction at high pH values without the involvement of activating agents. It has been shown that monoethanolamine borate does not exhibit any significant activating effect on micellar nucleophilic catalysis in the degradation of N-(phosphonomethyl) glycine.

3. The optimal conditions of decomposing N-(phosphonomethyl)glycine in the micellar decontamination system have been determined to be as follows: 0.25 mol/L of the concentration of cythylpyridinium chloride and 0.15 mol/L of the concentration of boric acid. It has been proven that an important condition is the pH of the system, which should be in the range from 10.5 to 11.5.

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