На прикладі деконтамінації параоксону (O,O-діетил-O-4-нітрофенілфосфату) та метилпаратіону (O,O-диметил-O-4-нітрофенілтіофосфату) з твердих поверхонь (металу, тканини, пластику) досліджено методи індивідуального знезараження фосфорорганічних естерів нервово-паралітичної дії. Як дегазаційні системи було вивчено суміші гідроперіту, борної кислоти, цетилпіридиній хлориду та монтморилонітової наноглини. Показано, що застосування міцелярної системи разом з наноглинами суттєво підвищує ступінь адсорбції фосфорорганічних субстратів із зараженої поверхні. При цьому присутність у системах з гідроперитом активатора (борної кислоти) сприяє збільшенню швидкості реакції у міцелярному середовищі майже у 20 разів в порівнянні з системами без активації.

Встановлено, що у досліджених міцелярних системах зберігається супернуклеофільність HOO⁻-аніону по відношенню до електрофільних субстратів – параоксону та метилпаратіону. Зроблено висновок, що присутність монтморилоніту (натрій- та органомодифікованого) збільшує величину α-ефекту, як у системах тільки с гідроперитом, так і в системах з активатором борною кислотою.

Встановлено ефект прискорення похідними монтморилоніту процесу розкладання фосфорорганічних субстратів в міцелярному середовищу. Цей факт може бути використаний при конструюванні «зелених» деконтамінаційних систем швидкої дії.

Аналіз даних щодо швидкості дезактивації параоксону та метилпаратіону на твердих поверхнях в досліджених міцелярних деконтамінаційних системах дозволив обрати як оптимальну систему на основі гідроперіту, борної кислоти, цетилпіридиній хлориду та органомодифікованого монтморилоніту.

Порівняно періоди напіврозпаду параоксону та метилпаратіону у досліджених міцелярних системах з відомими й застосованими в підрозділах НАТО деконтамінаційними системами. Зроблено висновок, що швидкості деконтамінації в запропонованих системах є вищими, або не поступаються швидкостям в відомих системах. При цьому запропоновані системи на основі твердого джерела пероксиду водню мають переваги з точки зору екологічної безпеки, технологічності, стабільності.

Параметри швидкості деконтамінації й ступеню розпаду параоксону та метилпаратіону дозволяють рекомендувати досліджені міцелярні системи як перспективні для індивідуальної дезактивації фосфорорганічних сполук.

Розробка швидкодіючих деконтамінаційних рецептур, м'яких за характером дії на організм людини та екологічно безпечних, є необхідним та актуальним завданням у низці технологічних рішень зі знешкодження токсичних фосфорорганічних субстратів, таких як пестициди, компоненти хімічної зброї та активні фармацевтичні інгредієнти

Ключові слова: деконтамінаційна система, пероксид водню, пероксисольват карбаміду, параоксон, метилпаратіон, пероксоборат, дезактивація, фосфорорганічні сполуки

DEVELOPMENT OF CHEMICAL METHODS FOR INDIVIDUAL DECONTAMINATION OF ORGANO- PHOSPHORUS COMPOUNDS

L. Vakhitova
PhD, Senior Researcher*
V. Bessarabov
PhD, Associate Professor**
E-mail: drvib500@gmail.com
N. Taran
PhD, Senior Researcher*
G. Kuzmina
PhD, Associate Professor**
V. Derypapa
Researcher**
G. Zagoriy
Doctor of Pharmaceutical Sciences,
Professor**
A. Popov
Doctor of Chemical Sciences, Professor*
*L. M. Litvinenko Institute
of Physical-Organic Chemistry and
Coal Chemistry of the National Academy
of Sciences of Ukraine
Kharkivske shosse str., 50, Kyiv, Ukraine, 02160
**Department of Industrial Pharmacy
Kyiv National University
of Technologies and Design
Nemyrovycha-Danchenka str., 2,
Kyiv, Ukraine, 01011

1. Introduction

Especially dangerous substances of organophosphorus nature (OPC) pose a real threat to human health and to the environment. Many active ingredients of pesticides are known or possible carcinogens. They have acute or chronic toxic effects, they suppress immunity and cause disturbances of the endocrine, central and peripheral nervous systems [1]. OPC also affect the reproductive function adversely, they lead to intrauterine fetal malformations and increase the risk for children [2].

The main areas of application of OPC are: pesticides in agriculture (paraoxon (PO), methyl parathion (MP), diazinon, chlorophos, glyphosate); components of chemical

weapons (sarin, soman, VX-gases); active pharmaceutical ingredients (armine, nibuphine) [3–6].

In 1993, there was an international convention signed on the prohibition of the development, production, stockpiling and use of chemical weapons and on their destruction [7]. It planned the annihilation of existing reserves by 2007. In addition, there were directives [3, 4] adopted, which regulate a range of pesticides of organophosphorus nature, and the procedure for their use, treatment, utilization, and safety measures.

However, there are large stocks of prohibited pesticides and warfare poisonous agents today [1]. This situation leads to poisoning with OPC. Poisoning with OPC poisoning is a cause of annual death of 200–300 thousand people in the world due to contamination of soil and water and unintentional use of pesticides [1, 8].

In addition, there were cases of the use of neuro-paralytic agents and other OPC in the course of military operations in Syria (2017), terrorist attacks in Matsumoto and Tokyo Metro (1994, 1995) and Salisbury (2018) registered.

Thus, the problem of effective decontamination of toxic compounds formed in terrorist acts and emergency situations in chemical and pharmaceutical industries appears in addition to the problem of large-scale industrial utilization of components of chemical weapons and forbidden pesticides.

2. Literature review and problem statement

One can divide the existing methods of decontamination of OPC into three categories [1, 8, 9]:

1) physical decontamination involves passive methods aimed at removal of a pollutant from any given surface (biotic one or abiotic one). Physical methods consist in adsorption, dissolution, evaporation or washing of an agent with preservation of its chemical structure;

2) mechanical decontamination involves procedures for isolation of poisonous substances by covering with soil or other inert material. We use mechanical decontamination for cases where other methods are not available;

3) chemical decontamination means neutralization of an agent by chemical transformations, such as hydrolysis, alcoholysis, oxidation, recovery, etc.;

4) enzymatic decontamination occurs with using of enzymes, which provide hydrolysis of OPC.

A combination of physical and chemical methods [1], that is, simultaneous purification and neutralization, is better for more effective and fast decontamination. Such an approach should minimize consequences for human health and environmental risks. Recent trends in research and development of chemical protection from OPC relate to application of nanotechnologies in the design of methods of decontamination [1, 8]. Nano-sized materials, including nanoclay, have a significant surface area for adsorption of poisonous substances and catalytic activity in nucleophilic substitution processes [9].

One should understand the term «individual decontamination» as decontamination of contaminated parts of a body, clothing materials and equipment immediately after contamination [10, 11].

Usually individual decontamination of victims consists in collection of liquid drops by adsorbents, washing with water with detergent and chemical neutralization by available means [1, 9]. The whole set of procedures takes some time,

which can have fatal consequences both for health and for lives of victims.

Considering the extraordinary toxicity of OPC (Table 1), one of the main indicators of decontamination formulation should be a rate of chemical decomposition of a substrate. The most popular technological approaches for destruction of OPC are alkaline hydrolysis with the use of sodium hydroxide, chlorine oxidation with sodium hypochlorite [13], and alcoholysis by monoethanolamine or potassium butoxide [14, 15].

Table 1

Estimated toxicity* of common nerve agents [12]

Toxic substance	LD_{50} (through skin), mg/kg of body weight	LC_{50}, ppm	LC_{t50}, mg·min/m^3	IDLH, ppm
GA (tabun)	1	2	100–400	0.03
GB (sarin)	1.7	1.2	50–100	0.03
GD (soman)	0.35	0.9	25–70	0.008
GF	0.03	–	–	–
VX	0.01	0.3	5–50	0.002

*Note: * – LD_{50} (through skin): the average lethal dose of toxic substance required to kill half of members of the tested population; LC_{50} (inhalation way): the average lethal concentration of toxic substance required to kill half of members of the tested population; LCt_{50} (inhalation way): a dose, which leads to severe residual injury faster than to death; IDLH: the concentration of toxin in the air, which is immediately dangerous to life and health*

It is possible to use sodium hypochlorite for disinfection at a concentration of 0.5 % for staff and 5 % for equipment [16]. Such low concentrations of the deactivator do not provide a required rate of decomposition of a poisonous substance, but its increase is impossible due to a strong irritating effect on eyes, skin and open wounds. Sodium hydroxide, in turn, splits organophosphorus esters into the corresponding phosphonic acids at moderate rates, but it causes significant chemical burns of skin and eyes even to irreversible consequences. The combination of hypochlorites and alkalis (93 % of calcium hypochlorite and 7 % of sodium hydroxide) gives a mixture, which is highly effective for disinfection of OPC [17]. People use also sodium phenolate or sodium cresolat, chloramines in alcoholic solution, potassium permanganate and other chemical compounds for decontamination of OPC [15]. Table 2 shows the composition of commercial decontamination agents used in the world practice at the contamination with organophosphorus poisonous agents.

Table 2

OPC decontamination systems

Commercial name	Chemical composition
DS2 [1]	diethylenetriamine 70 %, 2-methoxyethanol 28 %, sodium hydroxide 2 %
DF-200 [18]	quaternary ammonium compounds, 8 % hydrogen peroxide, glycerol diacetate
RSDL [19]	2,3-butanedione monoxime, Dekon 139, methyl ether of polyethylene glycol
M291 [17]	sodium hypochlorite 0.5 %, soap water 1 %
IPP-95 [10]	B chloramine, zinc oxide, magnesium stearate, zeolite, magnesium stearate, carbamide, silicone oil
IPP-8 [10]	ethoxyethanol, isopropanol, dimethylformamide, sulfolane metallic sodium

Literary sources [10, 17, 18] indicate that people usually use a combination of physical and chemical methods of decontamination for decontamination of OPC. As a rule, the first stage is absorption of a substrate by Fuller's Earth or other adsorbents (clays, napkins). Then, there goes treatment of the collected material with decontamination systems for neutralization of a poisonous substance [21, 22].

The general disadvantages of the above methods of chemical detoxification are: toxicity of materials used, multi-component composition (some systems have two or three components) and low reactivity of decontaminators. It is possible to increase the rate of decomposition of OPC by the use of α-nucleophiles [3, 4, 20]. The typical representative of α-nucleophiles is peroxide HOO^- anion and its derivatives – peroxo-anions.

Hydrogen peroxide (H_2O_2) has high reactivity. And it provides universality of action by nucleophilic and oxidative mechanisms and satisfies the basic standards and requirements of «green» technologies, the so-called «Decon Green» systems, as a decontaminating agent [3]. Researchers studied solid sources of hydrogen peroxide – peroxysolvates, in detail in relation to OPC [3, 23]. Their use opens up new avenues for creation of effective decontamination systems of long-term storage.

The study in the proposed direction is promising in the complex of struggle against threats to increase a level of terrorist acts with the use of organophosphorus agents. In addition, there is a need to dispose of prohibited pesticides of organophosphorus nature, to eliminate consequences of technogenic accidents and to introduce effective methods of cleaning of technological equipment of chemical and pharmaceutical enterprises.

3. The aim and objectives of the study

The aim of the study is to find the optimal «Decon Green» system for fast and effective decomposition of paraoxon (PO) and methyl parathion (MP) by physical and chemical decontamination methods using carbamide peroxysolvate and montmorillonite nanoclays.

It is necessary to solve the following tasks to achieve the objective:

– determination of the influence of boric acid and nanoclays on the rate of decomposition of PO and MP using micellar decontamination systems based on carbamide peroxysolvate;

– investigation of the effect of the micellar decontamination system on the decontamination of PO and MP on metal, plastic and fabric surfaces.

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

4. 1. Materials and equipment used in the study

We used cetylpyridinium chloride (CPCl) (Dishman Pharmaceuticals and Chemicals, India), methyl parathion and paraoxon (Sigma-Aldrich, Inc., Germany), KOH alkali (Lachema, Czech Republic), NH_4HCO_3 ammonium hydroxycarbonate (JSC Bashkir Soda Company, RF), 1,4-dioxane (Alfa Aesar, Germany), $B(OH)_3$ boric acid (Shanghai Yixin Chemical Co., Ltd., PRC) without preliminary purification. We used montmorillonite modified by cations of thal-

lium bis-hydroxyethyl methylammonium, Garamite 7303 and Cloisite Na^+ unmodified bentonite clay (BYK Additives & Instruments, UK) as nanoclays. High-purity water of 1st grade was used for preparation of solutions.

Hydrogen peroxide («chemically pure») in the form of 33 % aqueous solution was pre-distilled in a vacuum (5 mm mercury). Carbamide peroxysolvate (hydroperite, $CO(NH_2)_2 \cdot H_2O_2$, (UHP)) was obtained according to the known methodology [24].

The following equipment was used for kinetic studies: «pH-150 MI» pH meter (LLC «Measuring equipment», Russian Federation); «OPTIZEN POP» scanning UV spectrophotometer (Mecasys, South Korea).

4. 2. Preparation of decontamination compositions

The decontamination composition was prepared by peeling of the components (Table 3) in the required ratio on ML-1 ball vibration mill at a temperature of 20–25 °C for 5 to 10 minutes to particle sizes of 50–80 microns.

Table 3

Composition of decontamination compositions

Components \ No. of composition	1	2	3	4	5	6
Carbamide peroxysolvate (UHP)	+	+	+	+	+	+
Boric acid	–	+	–	–	+	+
Garamite 7303	–	–	+	–	+	–
Cloisite Na^+	–	–	–	+	–	+
Cetylpyridinium chloride	+	+	+	+	+	+
Potassium hydroxide	+	+	+	+	+	+

The finished mixture of the dose weight was stored in sealed glass or plastic container hidden from the direct sunlight. The mixture was poured into a glass or plastic container before use, it was added with an appropriate amount of water heated to 50 °C, mixed until complete dissolution of the components and used to decontaminate toxic chemicals.

4. 3. Contamination of surfaces

A comparison of the effectiveness of decontamination was performed for model substrates – PO (O, O-diethyl-O-4-nitrophenyl phosphate) and MP (O, O-dimethyl-O-4-nitrophenyl triophosphate).

The steel plates, painted with HP-799 paint, were used, as well as polystyrene plates and 3M Micropore™ surgical patch, which were used as a simulation of skin surface, as test surfaces.

The surfaces were contaminated with drops of PO and MP in the horizontal position of the plates. The substances were used in the amount of 0.02 ml, which corresponded to a concentration of 2.48 g/m² for PO and 2.72 g/m² for MP.

The samples were stored for no more than 30 minutes in a dry box.

4. 4. Decontamination

The decontamination procedures were performed horizontally on contaminated surfaces. 20 g of decontamination composition solution was prepared in 150 ml of water. The solution was placed in a contaminated sample to determine the decomposition rate of OPC. The process was controlled by the amount of 4-nitrophenolate anion in the reaction solution by UV spectroscopy at $\lambda = 405$ nm at certain intervals by

the method of sampling from the reaction mass. Teflon syringe filters were used with a pore diameter of 0.45 μm to collect samples containing clays from the decontamination system.

4. 5. Methodology of kinetic measurements

All solutions of decontamination compositions (No. 1–6, Table 3) were prepared based on high-purity water of 1st grade immediately before each series of kinetic measurements.

Separate experiments showed that there was no the by-product of H_2O_2 decomposition under alkaline conditions during 5 hours (time sufficient for kinetic measurements within a single series). There was also no reaction of oxidization of 4-nitrophenol released during the course of the target reaction. The contribution of the reaction of alkaline hydrolysis was not more than 5 % of the total consumption of the substrate.

The course of the reaction was controlled spectrophotometrically at $\lambda = 405$ nm and $T = 25$ °C by changing of the absorption of 4-nitrophenolate-ion in time under the concentration conditions $[HOO^-] \gg [S]$. The initial concentration of the substrate [S] was $5 \cdot 10^{-5}$ M^{-1}, and the degree of its transformation exceeded 80 %. The kinetic results presented below were the average of three kinetic measurements, their average error did not exceed ±10 %.

5. Results of the nucleophilic decomposition of paraoxon and methyl parathion

5. 1. Substantiation of the choice of the decontamination system

To achieve the objective set in this study, the kinetics of decomposition of PO and MP were studied by the nucleophilic mechanism in decontamination systems that met the following conditions:

– commercial availability and high reactivity of used reagents;

– universality of chemical action in relation to different classes of poisonous substances (decomposition by nucleophilic and oxidative mechanisms);

– absence of special conditions of use (temperature, pressure, etc.);

– high degree of ecological safety of chemical components of the system and of products of OPC decomposition;

– possibility of application for removal of a poisoning substance from skin surface of injured people;

– chemical stability during storage and transportation.

The system was chosen that met the above requirements as much as possible as a decontamination system: hydroperite/boric acid/cetylpyridinium chloride. We added Garamite 7303 or Cloisite Na$^+$ nanoclays to the decontamination system to enhance adsorption from contaminated surfaces and solubility of organophosphorus substrates. The choice of components of the system was not random. We based it on the results of studies [3, 25–27].

Nucleophile is hydroperite ($CO(NH_2)_2 \cdot H_2O_2$, UHP). We know that hydrogen peroxide in the form of H_2O_2, HOO^--anion and peroxo-anions provides high reactivity and universality in relation to the substrates of ecotoxicants of the two main types – analogues of yperite and compounds of pentavalent phosphorus [25]. However, the use of H_2O_2 concentrated aqueous solutions creates additional risks in storage, transportation and operation at subzero temperatures in practice. Therefore, it is advisable to use solid (anhydrous) reagents such as hydroperite, which is a non-toxic, stable at storage and commercially available crystalline material, as alternative to H_2O_2 sources.

The presence of alkali (KOH, NaOH) in the decontamination composition is a prerequisite for generation of $CO(NH_2)_2 \cdot H_2O_2/OH^-$ nucleophile – HOO^--anion) in the solution:
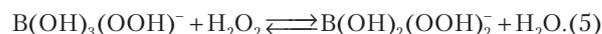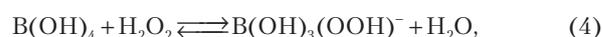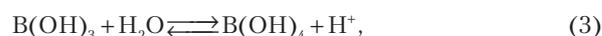
$$H_2O_2 + HO^- \rightleftharpoons H_2O + HOO^-. \tag{1}$$

HOO^--anion is responsible for the rate constant of decomposition of (k_i) substrates in the studied systems according to equation:

$$k_i = k_{HOO^-} \cdot \left[HOO^- \right]_0 = k_{HOO^-} \cdot \frac{K_a}{K_a + a_{H^+}} \cdot \left[H_2O_2 \right]_0, \tag{2}$$

where $[HOO^-]_0$ is the initial concentration of hydro peroxide-anion; k_i (s^{-1}) is the difference of ($k'_{HOO^-} - k'_{HO^-}$) constants, which characterizes the contribution of decomposition of substrates by HOO^--anion; k'_{HO^-} (s^{-1}) and k_{HOO^-}, (s^{-1}) are observed constants of the rate of alkaline hydrolysis and perhydrolysis; k_{HOO^-}, (M^{-1}s^{-1}) is a rate constant of the second order of perhydrolysis; K_a is a constant of acid-base ionization of H_2O_2.

The activator was boric acid ($B(OH)_3$). It is possible to accelerate the decomposition of poisonous substances by the oxidation mechanism by activation of hydrogen peroxide with carbonates, borates, and molybdates in order to obtain more reactive peroxo-anions. The addition of boric acid to UHP solution at pH of 6–14 contributes to formation of the following peroxo-anions: monoperoxoborate – $B(OH)_3(OOH)^-$ (MPB) and diperoxoborate $B(OH)_3(OOH)^-$ (DPB), according to equations:

$$B(OH)_3 + H_2O \rightleftharpoons B(OH)_4 + H^+, \tag{3}$$

$$B(OH)_4 + H_2O_2 \rightleftharpoons B(OH)_3(OOH)^- + H_2O, \tag{4}$$

$$B(OH)_3(OOH)^- + H_2O_2 \rightleftharpoons B(OH)_2(OOH)_2^- + H_2O. \tag{5}$$

The equation for calculation of the contribution of nucleophilic substitution with different anions takes the form:

$$k_i = k_{obs} - \left(k'_{HO^-} + k'_{HOO^-} \right) =$$
$$= k_{MPB} \cdot \left[B(OH)_3(OOH)^- \right] + k_{DPB} \cdot \left[B(OH)_2(OOH)_2^- \right], \tag{6}$$

where k_{obs} (s^{-1}) is the observed rate constant in $CO(NH_2)_2 \times \times H_2O_2/B(OH)_3$ system; k_{MPB} (M^{-1}s^{-1}) and k_{DPB} (M^{-1}s^{-1}) are the second order rate constants for $B(OH)_3(OOH)^-$ and $B(OH)_2(OOH)_2^-$ peroxo-anions, respectively.

It is known that the nucleophilic reactivity of generated peroxoborate anions exceeds the nucleophilic reactivity for HOO^--anion in relation to MP: MPB by ~2 times, and DPB by ~10 times [3]. The detergent was cetylpyridinium chloride ($C_{16}H_{33}C_5H_4NCl$). The decontamination usually goes in nano-sized polycomponent systems such as: microemulsions, micelles of various nature and water-alcohol

mixtures in presence of detergents to increase the solubility of substrates in aqueous reactive media [25]. We can use cationic surfactants as detergents to ensure the effective flow of nucleophilic processes in micellar solutions. Anionic detergents slow down nucleophilic reactions in the studied systems, and neutral ones do not affect the rate of chemical transformations significantly.

Nanoclays were montmorillonite modified by cations of tall bis-hydroxyethyl methylammonium (Garamite 7303) and Cloisite Na^+ bentonite clay. Nanoclays have a significant surface area (400–900 m^2/g according to various estimates) and they can act as sorbents for organic molecules due to their nanostructure organization and layered construction.

The choice of paraoxon and methyl parathion as a model substrate can be explained by the fact that they are pesticides of organophosphorus nature and analogues of warfare agents (GB and VX). Nevertheless, the reactivity of PO and MP is insufficient in nucleophilic processes with participation of peroxo-anions and it requires detailization for construction of effective and environmentally safe decontamination formulations.

5. 1. Micellar catalysis of perhydrolysis of paraoxon and methyl parathion

The conversion of PO and MP in $CO(NH_2)_2 \cdot H_2O_2/OH^-$ system (No. 1, 3, 4, Table 3) went by the two following mechanisms: perhydrolysis with participation of the generated HOO^--anion and alkaline hydrolysis by HO^--anion.

If there are both hydrogen peroxide and boric acid $CO(NH_2)_2 \cdot H_2O_2/B(OH)_3/OH^-$ (No. 2, 5, 6, Table 3) in the solution, there are routes with participation of MPB and DPB peroxoborates added to hydrolysis and perhydrolysis (5).

The contribution of the alkaline hydrolysis process, as shown earlier [25] in similar nucleophilic systems, is negligible, therefore, it was not taken into consideration when examining kinetic results.

The data on kinetic studies of decomposition of PO and MP in $CO(NH_2)_2 \cdot H_2O_2/OH^-$ (No. 1) and $CO(NH_2)_2 \times \times H_2O_2/B(OH)_3/OH^-$ (No. 2) systems at pH 10, variations of [CPCl] concentration and $[HOO^-]=0.01$ M constancy showed a classical micellar effect which is maximal for systems containing $B(OH)_3$ (Fig. 1).
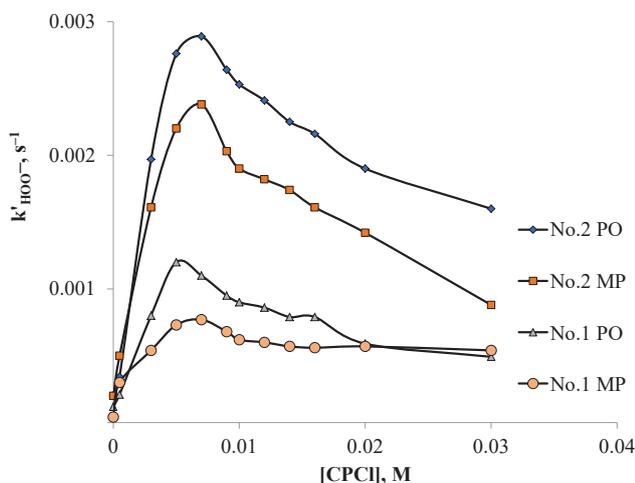

Fig. 1. Effect of the concentration of cetylpyridinium chloride ([CPCl]) on the decomposition rate of paraoxon (PO) and methyl parathion (MP) in $CO(NH_2)_2 \cdot H_2O_2/OH^-$ (No. 1) and $CO(NH_2)_2 \cdot H_2O_2/B(OH)_3/OH^-$(No. 2) systems at pH=10, $[HOO^-]=0.01$ M, 25 °C

We performed the mathematical processing of the obtained results (Fig. 1) in the framework of the kinetic pseudo-phase model:

$$k_{HOO^-} = \frac{k_{obs}}{[H_2O_2]_0} =$$
$$= \frac{k_{HOO^-,w} + (k_{HOO^-,m}/V)K_S K_{HOO^-} D_n}{(1+K_S D_n)(1+K_{HOO^-} D_n)(1+a_{H^+}/K_a')}, \quad (7)$$

where K_{HOO^-} and K_S are the constants of the micellar binding of peroxo-anion and the substrate, respectively; k_{HOO^-}, k_{HOO^-} are the rate constants of the second order of perhydrolysis of substrates in water and in the micellar phase, respectively; V is the molar volume of cetylpyridinium chloride; D_n is the [CPCl] concentration excluding the value of the critical concentration of micelles formation (CCM).

The kinetic model (7) gave us possibility to perform quantitative estimation of factors, which determined the micellar effect, and to describe a value of the maximum acceleration by the following equation:

$$\left(\frac{k_{obs}}{k_w}\right)_{max} = \frac{k_{HOO^-,m}}{k_{HOO^-,w}} \cdot \frac{K_S K_{HOO^-}}{V(\sqrt{K_S} + \sqrt{K_{HOO^-}})^2}. \quad (8)$$

The first right-side (F_m) multiplier characterizes the effect of changes in the micropropagation of reagents at transition of the reaction from the volume phase into the micellar phase, and the second (F_c) multiplier is the effect of concentration of reagents in micelles.

Processing of data in Fig. 1 in accordance with the equation (7) made it possible to determine the kinetic parameters of the micellar catalysis of the decomposition of PO and MP by individual HOO^--anion (Table 4, No. 1) and $B(OH)_3(OOH)^-$ and $B(OH)_2(OOH)_2^-$ peroxo-anions (Table 4, No. 2).

It is necessary to note that one should consider the parameters of No. 2 system as values providing a qualitative understanding of micellar catalysis, and they are not its quantitative characteristics. Because the decomposition of substrates in the system with $B(OH)_3$ activator occurs by complex mechanisms involving at least three anions – HOO^-, $B(OH)_3(OOH)$ and $B(OH)_2(OOH)_2^-$. Therefore, the use of the pseudo-phase model (7), which takes into consideration the nucleophilic substitution of only one anion, is not correct. The obtained results made it possible to establish the expected decrease in the rate constant of the second order of perhydrolysis in the micelle (k_{HOO^-}, $M^{-1}s^{-1}$, No. 1, Table 4). For nucleophilic substitution by HOO^--anion in water, these values were 0.54 $M^{-1}s^{-1}$ (for paraoxon) and 0.82 $M^{-1}s^{-1}$ (for methyl parathion). Nevertheless, the acceleration of the reaction for the investigated systems of the case made up 9–28 times and occurred due to the effect of concentration of reagents in the micelle (F_c).

The obtained kinetic results testified to the promising application of micellar solutions for deactivation of hydrophobic organophosphorus substrates. On the one hand, there was an increase in the rate of decomposition of substrates ((k_{obs}/k_w)$_{max}$, Table 4) under these conditions. On the other hand, the values of the constants of the micellar binding of PO and MP (K_S, Table 4) and F_c parameter indicated a high degree of solubility by CPCl micelles unambiguously.

Table 4

Results of quantitative analysis of the kinetic data of paraoxon and methyl parathion perhydrolysis in No. 1 and No. 2 decontamination systems using equations (7), (8)

System No.	$k_{2M} \cdot 10^3$, $M^{-1}s^{-1}$	K_S, l/mol	K_{HOO^-}, l/mol	$(k_{obs}/k_w)_{max}$	F_m	F_c
Paraoxon						
1	0.074	540	44	12	0.14	86
2	0.152	755	40	28	0.28	100
H_2O_2–CTAB*–OH^- [28]	0.071	400	37	9	0.14	65
Methyl parathion						
1	0.081	820	54	9	0.09	94
2	0.174	991	49	21	0.16	131

*Note: * – cetyltrimethyl ammonium bromide*

There are calculations of the α-effect of HOO^--anion, which are estimated as k_{HOO^-}/k_{HO^-} ratio, in Table 5. k_{HO^-} values are the rate constants of the second order of alkaline hydrolysis, they were 0.15 $M^{-1}s^{-1}$ for PO and 0.09 $M^{-1}s^{-1}$ for MP. We should estimate α-effect of HOO^--anion correctly in No. 1, No. 3, No. 4 decontamination systems, where there was no $B(OH)_3$ activator. The value of α-effect was 27–78. This means that HOO^--anion was 100 times more reactive than OH^--anion. Although pK_a of the first of them was almost 4 units less than pK_a of the other.

One should consider the value of α-effect for No. 2, No. 5, No. 6 systems as the presence of supernucleophilicity (higher nucleophilic reactivity than it can be predicted in accordance with its basicity) of $B(OH)_3(OOH)^-$ and $B(OH)_2(OOH)_2^-$ peroxo-anions. There is the study on this issue in the decomposition reaction of MP in paper [3].

5. 2. The rate of deactivation of paraoxon and methyl parathion

Table 5 shows values for the imaginary rate constants of the second order of the reactions of nucleophilic substitution of PO and MP (k_{HOO^-}, $M^{-1}s^{-1}$) in the investigated reaction media (No. 1–No. 6, Table 3). They were calculated based on the total concentration of HOO^--anion at a fixed pH of the decontamination system by equation (2). The initial concentration of hydroperite was 0.1 M, the ratio of the components was $[H_2O_2]:[B(OH)_3]:[CPCl]:[nano-clay]=1:1:0.05:0.1$ (by weight) and the amount of KOH alkaline was such that the pH of the aqueous solution was 10 ± 0.2 in the decontamination system.

The value k_{HOO^-} is a gross-value, it does not take into consideration distribution by pseudo-phases (in the micelle of a detergent or in the volume of clay), as well as contributions of routes with participation of peroxo-anions formed according to equations (4), (5). Such an approach seems more informative for us for comparison of the rates of decomposition of substrates in dynamic media prone to phase and aggregation transitions with different solubilization properties in relation to hydrophobic substrates.

Table 5 shows the kinetic parameters of the decomposition of OPC of VX type by known deactivating agents for estimation of the reactivity of the investigated decontamination system (H_2O_2/$B(OH)_3$/CPCl/nano-clay) [1, 17, 29].

Table 5

Rates of deactivation of paraoxon and methyl parathion k_{HOO^-} ($M^{-1}s^{-1}$) in No. 1-No. 6 decontamination systems

Decontamination system	k_{HOO^-}, metal	k_{HOO^-}, polystyrene	k_{HOO^-}, fabric	$\tau_{1/2}$, s*	k_{HOO^-}/k_{HO^-}
Paraoxon					
1	3.74	4.31	3.96	29	27
2	16.0	18.3	17.2	21	114
3	8.01	7.45	7.01	48	50
4	9.24	7.21	8.34	44	55
5	21.7	23.1	22.5	16	150
6	19.4	20.6	23.0	17	140
Methyl parathion					
1	2.94	3.36	2.57	39	32
2	12.2	14.4	13.9	27	150
3	6.01	5.93	5.21	63	64
4	7.34	5.81	7.96	51	78
5	16.7	17.1	19.4	20	197
6	16.1	18.6	20.5	20	204
OPC of VX type					
Decon Green [29]: 0.75 M NaHCO₃, 0.743 g UHP, 1.0 ml t-BuOH, 1 ml H₂O	–	–	–	450	–
M291 [17]	–	–	–	90	–
DS2 [1]	–	–	–	600**	–
DF-200 [18]	–	–	–	600***	–

*Note: * – calculated for [UHP]=1 M; ** – transformation>99.9 %; *** – transformation 97.8 %*

6. Discussion of results from kinetic studies

There is supernucleophilicity of HOO⁻-anion preserved in relation to electrophilic substrates of PO and MP in the investigated micellar systems. We can state that the presence of montmorillonite (sodium- or organomodified) increases the magnitude of α-effect, in systems with hydroperite only (No. 1, 3, 4, Table 5) and in systems with B(OH)$_3$ activator (No. 2, 5, 6, Table 5). The volume of the kinetic experiment does not make possible to answer the question on the reason for the acceleration of the reaction in the presence of montmorillonite. Among the main hypotheses, there may be the assumption of the influence of clays by three main mechanisms:

1) molecular interactions of the active centers of montmorillonite (centers of Bronsted-Lewis) with formation of H-bonds with stabilization of transitional states of intermediates (are characteristic for S_N2 of a mechanism);

2) increase of polarizability of unsaturated bonds P=O (P=S) near the electrophilic center;

3) catalytic effect in nucleophilic substitution reactions.

The hypotheses require further study and development.

If one considers the systems with nanoclays as a combination of physical and chemical methods of decontamination of OPC, the problem of selection of an optimal substrate sorbent for decontamination procedures can be a separate scientific research and it requires additional studies. It is also necessary to obtain more detailed information on the influence of nanoclay structure on the rate of the process of substrate decomposition.

A significant result in favor of the micellar systems is the fact that the rate of reaction in the presence of B(OH)$_3$ (No. 2 system, Table 5) is almost 5 times higher than the similar value for formulations where the activator is absent (No. 1 system, Table 5) We should note that there is very limited information on the nucleophilic activity of peroxoborates in the literary sources [30]. However, formation of peroxoborates in the investigated pH range of 9–10, which is described by equations (4) and (5), is an undeniable fact. This approach is widely used by researchers to interpret kinetic patterns and the mechanism of oxidation in H$_2$O$_2$/B(OH)$_3$ system near electrophilic centers [27]. As a rule, peroxoborates have high reactivity, which is three to four orders of value higher than the oxidizing capacity of the original hydrogen peroxide. That is why one can consider UHP-B(OH)$_3$ system as a promising basis for a universal decontamination formulation for decomposition of substrates-ecotoxicants of different chemical nature (GB, VX and HD compounds).

In addition to the reactivity problem, the decontamination system should have a high solubilization affinity with the substrate under decontamination. Analysis of the data from Table 5, which contains the kinetic parameters of paraoxon and methyl parathion decomposition in No. 1, 2 decontamination systems at pH 10, indicates the dependence of K_{HOO^-} and K_S constants of micellar binding of K_{HOO^-} and K_S on the content of borate-anions in the system. An increase in K_S value, which can serve as a measure of the solubility of substrates in the system, is predictable and understandable in terms of knowledge of the influence of electrolytic impurities on the micellar-catalytic processes. The estimation of the micellar catalytic effects by the equation (8) shows that the main factor, which is responsible for acceleration of the decomposition of PO and MP in CPCl

micelles, is the concentration of reagents in the micelle (F_c=86–131, Table 4).

The kinetic parameters of the micellar decomposition of the substrates (Table 5) do not make it possible to explain the effect of the acceleration of reactions observed with the use of a hydroperite: $(k_{obs}/k_w)_{max}$=12 for UHP (No. 1 system, PO, Table 5), $k_{obs}/k_w)_{max}$=9 for H$_2$O$_2$ solution [28]. The values of the binding constants (K_{HOO^-}, K_S), as well as k_{2M}^{HO} values (No.1, Table 4, PO), almost do not differ from the analogous values for H$_2$O$_2$–CTAB–OH system [28], (Table 2). There are known examples of the positive effects of carbamide impurities on the rate of micellar-catalytic processes in the presence of CTAB, as a consequence of introduction of carbamide molecules into the micelle structure [28]. The authors of the study suggest to consider a decrease in sizes of micelles, and, accordingly, an increase in the surface area, where a chemical interaction occurs, as the main cause of the micellar acceleration in the presence of carbamide.

Thus, the performed kinetic studies give us possibility to determine the benefits of decontamination of OPC in UHP/B(OH)$_3$/CPCl/nanoclay micellar system:

– additional (except for the expected micellar one) increase in the rate of PO and MP decomposition due to the presence of carbamide and nanoclay in the decontamination system;

– an increase in the solubility of substrates in the micellar medium due to B(OH)$_3$ in 1.5 times (according to Table 5);

– universal nature of the chosen decontamination system in relation to VX, GB, GD agents decomposed mainly by the nucleophilic mechanism, and in relation to HD agents of HD, decomposition of which requires an oxidizing mechanism of action.

Given the modern requirements for decontamination systems, one should pay special attention to the ecological characteristics of components of the system, the rate of chemical transformations, ease of use, shelf life and the absence of special storage and use conditions.

Comparison of the half-decomposition period ($\tau_{1/2}$, s) for PO and MP in No. 1–6 systems (Table 5) with known and used in NATO subdivisions decontamination systems (M291 [17], DS2 [1], DF-200 [18]) indicates that the decontamination rates in the investigated systems are higher, or not less than the rates in known systems. In this case, the proposed systems based on a solid hydrogen peroxide source have advantages in terms of environmental safety, processability, and stability.

Analysis of the data from Table 5 makes us choose the No. 5 system – UHP/B(OH)$_3$/CPCl/Garamite 7303 as the optimum system. At first glance, components of No. 5 system are not carcinogenic or mutagenic substances, they do not affect reproduction functions, they do not possess cumulative and other chronic influences. However, it is necessary to carry out additional theoretical calculations *in silico* or tests on the endo- and exotoxity of the selected decontamination system as a means of individual decontamination for the practical implementation of the results of the study. Such study with the use of the developed method of complex quantitative estimation of the effectiveness of decontamination systems of organophosphorus compounds in terms of the integrated effect of the products of decomposition of toxic substances on the human body should be a logical and promising direction for introduction of the investigated micellar systems as an effective tool for the destruction of organophosphorus toxic compounds [32].

7. Conclusions

1. The methods of individual decontamination of organophosphorus esters of nervous-paralytic action were studies using the example of decontamination of paraoxon and methyl parathion from solid surfaces (metal, fabric, and plastic). The mixtures of hydroperite, boric acid, cetylpyridinium chloride and montmorillonite nanoclay as decontamination system were examined. It has been shown that application of the micellar system together with nanoclay increases the degree of adsorption of organophosphorus substrates from the contaminated surface significantly.

2. It was established that there is supernucleophilicity of HOO$^-$-anion preserved in relation to the electrophilic substrates – paraoxon and methyl parathion, in the investigated micellar systems. It was concluded that the presence of montmorillonite (sodium- and organomodified one) increases the magnitude of α-effect, both in systems with hydropyrite only, and in systems with an activator of boric acid.

3. The effect of acceleration of the process of decomposition of organophosphorus substrates by derivatives of montmorillonite in the micellar medium was established.

4. Parameters of the decontamination rate and the degree of decomposition of paraoxon and methyl parathion give us possibility to recommend investigated micellar systems as promising for individual deactivation of organophosphorus compounds.

Acknowledgement

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