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 paraaxon, 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emphasis on the destruction of all types of “outdated” and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 elimi-
nation 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-diethyl-O-4-nitrophenyl tri-
phosphate) 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 agri-
cultural areas is up to 0.46 µg/L [6]. These figures are of alarming
significance given that the acute oral toxicity parameter LD₅₀
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 Or-
ganization as a very toxic US EPA pesticide and as extremely haz-
ardous [1]. Despite the prohibition of MP in many developed
countries, its use continues, including in Ukraine.

Such a situation with the circulation of particularly dan-
gerous compounds stimulates the scientific search for effective
methods for the destruction of OP pesticides. Alkali hydrolysis,
oxidative chlorination [6], alcohol monoethanolamine or potas-
sium butoxide are used as the main technological approaches
for the destruction of OP [7, 8]. The general disadvantages of the
methods of chemical detoxification is toxicity of the
applied technologies, a significant corrosive load on the equip-
ment 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
acid and requirements of eco-friendly technologies [13]. However,
the use of concentrated aqueous solutions of Н₂О₂
is one of the most common organophosphorus
as a degassing agent provides universality of action for nucleophil
ic and oxidative mechanisms [12] and satisfies the basic norms
of applied technologies, a significant corrosive load on the equip-
ment 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
acid and requirements of eco-friendly technologies [13]. However,
the use of concentrated aqueous solutions of Н₂О₂ for applied
purposes poses additional risks in storage and transportation.

Solid peroxisolvate of carbamide (hydroperite, СО(NH₂)₂
×2H₂O, (1)), as an alternative source of Н₂О₂, 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 hy-
drogen peroxide activators such as ammonium bicarbonate
(NH₄HCO₃) 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 alka-
line hydrolysis and perhydrolysis of MP in an aqueous medium;
– to study the influence of Н₄HCO₃ and B(OH)₃ on the
kinetics and the mechanism of nucleophilic decomposi-
tion 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 puri-
fication. Bidistilled 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 Н₂О₂ in the solutions and the
content of hydrogen peroxide in the peroxysolvates were
controlled by permanganometric 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 concen-
trated 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 Н₂О₂ decomposition under alkaline
conditions is not observed. No oxidation reaction of 4-nitro-
phenol 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 λ=405 nm and
T=25°C by the change in the absorption of 4-nitrophe-
nolate ion in time under the concentration conditions of
[OH·]=[HOO·]>>[MP]. The initial concentration of the
substrate was 5–10⁻³ M⁻¹, and the degree of its transforma-
tion 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

In the Н₂О₂/ОH⁻ solution was converted mainly in
two directions – perhydrolysis with the contribution of the
generated HOO· anion (Н₂О₂+H⁺=H₂O+HOO·) and
alkaline hydrolysis by the HO· anion:

\[
\text{MeO}_3\text{S}+\text{O}^\cdot+\text{H}^\cdot\rightarrow \text{MeO}_3\text{S}^\cdot+\text{H}_2\text{O}
\]

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 combat 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 NH₄HCO₃ and (B(OH)). Fig. 1 shows the dependence of the observed rate constants \( k'_{\text{HO}} \) of the alkaline hydrolysis of MP on the concentration of the hydroxide ion.

\[
k'_{\text{HO}} = k_{\text{HO}} \cdot [\text{KOH}], \tag{2}\]

where [KOH], M⁻¹ is the concentration of alkali.

The values of \( k_{\text{HO}} \) 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 \( 2 \times 10^{-2} \) M⁻¹s⁻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 \( (k'_{\text{HO}}) \) in the systems \( \text{H}_{2}\text{O}_{2}/\text{HO}^- \) (4) and (I)/HO⁻ (5). The kinetic method was used to determine the constant of the acid-base ionization of \( \text{H}_{2}\text{O}_{2} \) (\( K_a \)) in the systems under study by the equation

\[
k_i = k_{\text{HO}} \cdot [\text{HOO}^-]_i = k_{\text{HO}} \cdot \frac{K_a}{K_a + [\text{H}_{2}\text{O}_{2}]} [\text{H}_{2}\text{O}_{2}]_i, \tag{3}\]

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

### Table 1

<table>
<thead>
<tr>
<th>No</th>
<th>Nucleophile</th>
<th>( k'_{\text{HO}} ) ( \times 10^4 ) (M⁻¹s⁻¹)</th>
<th>( k_{\text{HO}} ) ( \times 10^4 ) (M⁻¹s⁻¹)</th>
<th>( \alpha = \frac{k_{\text{HO}}}{k'_{\text{HO}}} )</th>
<th>pK₀</th>
<th>Methyl parathion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HO⁻</td>
<td>8.90±0.34</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>HO⁻/(B(OH))</td>
<td>10.0±0.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>HO⁻/NH₄HCO₃</td>
<td>9.62±0.76</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>H₂O₂/HO⁻</td>
<td></td>
<td>895±45</td>
<td>101</td>
<td>11.49</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>(I)/HO⁻</td>
<td></td>
<td>818±67</td>
<td>92</td>
<td>11.67</td>
<td></td>
</tr>
</tbody>
</table>

The values of pK₀ for hydrogen peroxide (curve 4 in Fig. 2) and for hydroperoxide (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 \( \text{H}_{2}\text{O}_{2} \) obtained for parahoxone perhydrolysis (pK₀=11.60) under similar conditions [13].

The rate constants of the second order \( k_{\text{HO}} \) (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 \( \text{H}_{2}\text{O}_{2} \) source:

\[
k'_{\text{HO}} = k_{\text{HO}} \cdot [\text{HOO}^-]_b. \tag{4}\]

Summing up the performed kinetic tests, it can be stated that the interaction of the anions HO⁻ and HOO⁻ takes place under the \( S_{2}2 \) mechanism. In both cases, there is a depen-
dence in the coordinates “$k_{\text{HOO}}' \cdot [\text{HOO}^-] \cdot [\text{HO}^-]$” 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 paraaxon (α=54–58, No. 7 and 8).

5.2. Perhydrolysis of MP in the presence of NH₄HCO₃ and (B(OH)₄)

In contrast to the systems of alkaline hydrolysis (curves 1–3, Fig. 1), in the systems containing hydrogen peroxide in the form (I), additives NH₄HCO₃ and (B(OH)₄) 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 ($k_{\text{HOO}}'$) is especially noticeable in the range of pH 10–11.

The activating effect of the HCO₃⁻ anion can be related to the formation of a perhydroxocarbonate anion in the system H₂O₂/NH₄HCO₃. According to the authors of [16], the perhydroxocarbonate anion has supernucleophilic properties and is formed under the following equation:

$$\text{HCO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}_3\text{O}^+.$$ (5)

where K is the equilibrium constant for the formation of the peroxomonocarbonate anion, and it is equal to 0.33 М⁻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 HCO₃⁻ anion into the CO₃²⁻ anion (pKₐ=9.4 [16]) occurs according to the equation

$$\text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+.$$ (6)

In the conditions of the pseudo-first order with respect to the substrate, the equation for the observed rate constant $k_{\text{obs}}$ (s⁻¹) in the system (I)/HO⁻/NH₄HCO₃ corresponds to the equation

$$k_{\text{obs}} = k_{\text{HHO}}' + k_{\text{HOO}}' \cdot [\text{HCO}_3^-] + k_{\text{CO}_3^{2-}}',$$ (7)

where $k_{\text{HCO}_3^-}$ and $k_{\text{CO}_3^{2-}}$ 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 $k_{\text{HCO}_3^-}$ and $k_{\text{CO}_3^{2-}}$:

$$k = k_{\text{HHO}}' - (k_{\text{HCO}_3^-}' + k_{\text{HOO}}'),$$

$$ = k_{\text{HCO}_3^-}' \cdot [\text{HCO}_3^-] + k_{\text{CO}_3^{2-}}' \cdot [\text{CO}_3^{2-}]'.$$ (8)

The concentrations of [HCO₃⁻] and [CO₃²⁻] were calculated by using equilibriums (5) and (6) as well as the known values of K and Kₐ of the HCO₃⁻ anion (2.51 10^{-11} М [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 diperexoborate B(OH)₅(OOH)²⁻ (DPB) according to the equations:

$$\text{B(OH)}_3 + \text{H}_2\text{O} \rightleftharpoons \text{B(OH)}_3^- + \text{H}_3\text{O}^+.$$ (9)

$$\text{B(OH)}_5 + \text{H}_2\text{O} \rightleftharpoons \text{B(OH)}_5^- + \text{H}_2\text{O}.$$ (10)

The values of the observed rates of the methyl parathion decomposition ($k_{\text{obs}}$ 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

$$\text{B(OH)}_3(\text{OOH})^- + \text{H}_2\text{O} \rightleftharpoons \text{B(OH)}_3(\text{OOH})^- + \text{H}_2\text{O}.$$ (11)
The contribution of the routes with HOO\(^-\) \((k_{\text{HOO}}\times \text{HOO}^-)\), MPB \((k_{\text{MPB}}\times \text{MPB})\), and DPB \((k_{\text{DPB}}\times \text{DPB})\) to the overall decomposition rate of MP \((k)\) in water, 25 °C

<table>
<thead>
<tr>
<th>pH</th>
<th>(k_{\text{HOO}} \times \text{HOO}^-) s(^{-1})</th>
<th>(k_{\text{MPB}} \times \text{MPB}) 10(^2) s(^{-1})</th>
<th>(k_{\text{DPB}} \times \text{DPB}) 10(^2) s(^{-1})</th>
<th>(k) s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.15</td>
<td>0.009</td>
<td>0.002</td>
<td>0.035</td>
<td>0.05</td>
</tr>
<tr>
<td>9.34</td>
<td>0.061</td>
<td>0.010</td>
<td>0.072</td>
<td>0.09</td>
</tr>
<tr>
<td>9.66</td>
<td>0.094</td>
<td>0.022</td>
<td>0.201</td>
<td>0.25</td>
</tr>
<tr>
<td>9.7</td>
<td>0.195</td>
<td>0.031</td>
<td>0.251</td>
<td>0.28</td>
</tr>
<tr>
<td>9.86</td>
<td>0.213</td>
<td>0.037</td>
<td>0.299</td>
<td>0.32</td>
</tr>
<tr>
<td>9.9</td>
<td>0.306</td>
<td>0.050</td>
<td>0.445</td>
<td>0.47</td>
</tr>
<tr>
<td>10.0</td>
<td>0.335</td>
<td>0.056</td>
<td>0.467</td>
<td>0.49</td>
</tr>
<tr>
<td>10.07</td>
<td>0.419</td>
<td>0.072</td>
<td>0.597</td>
<td>0.60</td>
</tr>
<tr>
<td>10.2</td>
<td>0.492</td>
<td>0.12</td>
<td>0.834</td>
<td>0.85</td>
</tr>
<tr>
<td>10.26</td>
<td>0.654</td>
<td>0.231</td>
<td>1.86</td>
<td>1.87</td>
</tr>
<tr>
<td>10.3</td>
<td>0.745</td>
<td>0.211</td>
<td>2.20</td>
<td>2.25</td>
</tr>
</tbody>
</table>

Fig. 3. The dependence of the concentrations of [H\(_2\)O\(_4\)]\(^-\), [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: \(k_{\text{MPB}}\) and \(k_{\text{DPB}}\), 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 \(\alpha\)-effect of the HOO\(^-\) anion in the reaction with methyl parathion

The \(\alpha\)-effect of the HOO\(^-\) anion in the reaction of MP perhydrolysis, which is estimated as a ratio of \(k_{\text{HOO}}/k_{\text{HO}}\), 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 \(pK\alpha\) of the first of them is almost 4 units less than the \(pK\alpha\) 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\(_2\)2 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

\[
\begin{align*}
\text{O} & \quad \text{S} \\
\text{P} & \quad \text{O} \\
\text{R} & \quad \text{H} \\
\end{align*}
\]

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 \(\alpha\)-effect. However, if we compare the value of the \(\alpha\)-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 \(\alpha\)-effect is the stability of the transition state, then reciprocal values are to be expected – the \(\alpha\)-effect for PO should exceed the \(\alpha\)-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 \(\alpha\)-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 \(\alpha\)-effect.

6.1. Reactivity of peroxoanions in the nucleophilic substitution reaction

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

- alkaline hydrolysis (HO\(^-\));
- perhydrolysis (HOO\(^-\));
– нуклеофильное взаимодействие с пероксомонокарбонатным аннионом (HCO₃⁻);
– нуклеофильное взаимодействие с пероксокарбонатным аннионом (CO₃²⁻).

Также, обсуждается влияние подобных анионов на окислительные процессы, а также используемые в таком качестве анионы, которые не были рассмотрены в общем кинетическом схеме.

В таблице 2 приведены значения констант скорости второго порядка, рассчитанные по уравнениям (5)–(8) и данные по процессам пергидролиза 4-нитрофенилэфир 2,5-диизопропилфенола.

Таблица 2. Значения констант скорости второго порядка для пергидролиза 4-нитрофенилэфир 2,5-диизопропилфенола.

Константы скорости второго порядка, рассчитанные в этой работе, существенно отличаются от значений для пероксокарбонатных анионов. Это говорит о больших различиях в активности анионов в зависимости от pH.

Нуклеофильная активность ряда нитрозоточной базы (MPB) в 7–9 раз выше, чем в DPB. В то время как пероксокарбонатные анионы активны в pH 10–11, это не происходит для пероксокарбонатных анионов, уточняют исследователи. Так что система (1)/NO₂⁻/B(OH)₃ может быть использована в качестве предиктивного подхода для определения компонентов в кислотных реактивных системах.

Следует отметить, что в нуклеофильных системах (GB, VX и HD соединения), на которые существует возможность окисления, может быть использована более сложная система, включающая дополнительные пути распада OP под воздействием фосфорной кислоты.

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 nucleeofilic mechanism. The peroxo anion in reaction with methyl parathion exhibits a significant α-effect due to the polarizability of the unsaturated bond near the electrophilic center.

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 boracic acid can be considered as a new approach to the creation of soft ecological systems of decontamination of nucleophilic and oxidative effects. Mixtures of carbamide peroxysolvate with certain amounts of activators may be recommended as effective long-term storage systems for decomposing highly toxic organophosphorus pesticides.

References


