

UDC 662.164.2

O. E. Shumeiko^{1,2}, M. I. Korotkikh^{1,2}

¹L. M. Litvinenko Institute of Physical-Organic Chemistry and Coal Chemistry of the National Academy of Sciences of Ukraine, 50, Kharkiv highway str., 02155 Kyiv, Ukraine

²Institute of Organic Chemistry of the National Academy of Sciences of Ukraine, 5, Academician Kukhar str., 02660 Kyiv, Ukraine

Chemical Warfare Agents: Structure, Properties, Decontamination (Part 2)

Abstract

The review is aimed at summarizing and systematizing information about various methods of deactivation of chemical warfare agents that are necessary on the battlefield, as well as in laboratories, research institutions, and facilities of production, storage, and destruction of poisonous substances. The review presents the main directions of neutralizing warfare poisonous substances, which are the most effective in the conditions of their real use. In the second part of this work, the methods of deactivating warfare poisons using nucleophilic reagents, primarily α -nucleophiles, which have high efficiency and can react as nucleophiles and as oxidants, are considered in detail. A promising area of degradation of such products is the use of supernucleophilic systems based on functionalized detergents, as well as adsorption and photocatalytic deactivation methods. The material presented above shows the importance of general knowledge about the physical and chemical properties of chemical warfare agents, the rate of their decomposition, the advantages and disadvantages of certain available technologies for their application. This review can be useful for finding new and improving known methods for decontamination of chemical warfare agents and other ecotoxicants, and protecting the environment.

Keywords: chemical warfare agents; nerve agents; vesicants; decontamination; detection; protection

О. Є. Шумейко^{1,2}, М. І. Короткіх^{1,2}

¹Інститут фізико-органічної хімії і вуглехімії ім. Л. М. Литвиненка Національної академії наук України, вул. Харківське шосе, 50, м. Київ, 02155, Україна

²Інститут органічної хімії Національної академії наук України, вул. Академіка Кухаря, 5, Київ, 02660, Україна

Бойові отруйні речовини: структура, властивості, дезактивація (частина 2)

Анотація

Огляд спрямовано на узагальнення та систематизацію інформації про різні методи дезактивації бойових отруйних речовин, необхідних на полі бою, а також у лабораторіях, дослідних установах, на об'єктах виробництва, зберігання та знищення отруйних речовин. В огляді наведено основні напрями знешкодження бойових отруйних речовин, які є найбільш ефективними в умовах їх реального застосування. У другій частині цієї роботи докладно розглянуто методи дезактивації бойових отруйних речовин за допомогою використання нуклеофільних реагентів, насамперед α -нуклеофілів, які мають високу ефективність і можуть реагувати і як нуклеофіли, і як окислювачі. Перспективним напрямом деградації таких продуктів є застосування супернуклеофільних систем на основі функціоналізованих детергентів, а також методів адсорбції та фотокаталітичної дегазації. Викладений матеріал доводить важливість загальних знань про фізичні та хімічні властивості бойових отруйних речовин, швидкість їх розкладання, про переваги та недоліки тих чи інших доступних технологій їх застосування. Цей огляд може бути корисний для пошуку нових й удосконалення відомих методів дезактивації бойових отруйних речовин та інших екотоксикантів, захисту довкілля.

Ключові слова: бойові отруйні речовини; нервово-паралітичні речовини; шкірно-наривні речовини; дезактивація; виявлення; захист

Citation: Shumeiko, O. E.; Korotkikh, M. I. Chemical warfare agents: Structure, properties, decontamination (Part 2).

Journal of Organic and Pharmaceutical Chemistry 2024, 22 (3), 10–23.

<https://doi.org/10.24959/ophcj.24.313307>

Received: 3 August 2024; **Revised:** 27 October 2024; **Accepted:** 30 October 2024

Copyright © 2024, A. E. Shumeiko, N. I. Korotkikh. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0>).

Funding: Grant of the Ukrainian National Academy of Sciences 6.2/2-2023.

Conflict of interests: The authors have no conflict of interests to declare.

■ Introduction

Deactivation on the battlefield is the rapid removal of chemical warfare agents (CWAs) from military equipment, other equipment, personnel, and various objects by both chemical and physical methods. Therefore, a solid surface that is contaminated with poisonous substances is the main object of decontamination. Actually, the surface's nature and its interaction with applied chemical agents are the main problems in the development of a CWAs decontamination system. In addition, one should keep in mind that deactivating agents are not supposed to cause corrosion or damage to surfaces after deactivation. This review describes the chemical reactions mainly for the four main warfare poisons. These are sarin, soman, mustard gas, and VX. This is due to their extremely strong toxicity and stability, as well as their large reserves in a number of countries around the world [1]. The main attention here is given to such methods of CWAs deactivation as oxidative/nucleophilic reactions, photocatalytic reactions, and adsorption methods of deactivation.

Thus, to neutralize CWAs, nucleophilic reagents can be used, primarily α -nucleophiles, which are highly effective and can act both as a nucleophile and as an oxidizing agent [2]. The methods of decontamination of CWAs with hydrogen peroxide solutions turned out to be very effective. However, it has a low reaction rate and requires activation with reagents, such as carbonates, molybdates, phthalates, etc. Studies of the reactivity of hydrogen peroxide and its activators have led to the creation of universal formulations of the nucleophilic-oxidizing mechanism of action, which are quite effective in relation to the main types of CWAs [3].

The way to increase the efficiency of systems for splitting CWAs should be sought not only in the structural modification of the corresponding agent, but also in the use of alternative methods of influencing the reaction rate, for example, by changing the properties of the medium. In this sense, the use of a microorganized medium (micellar solutions, microemulsions, ionic liquids,

concentrated aqueous solutions of quaternary ammonium salts, etc.) is already widely used to solve a number of applied and fundamental problems [3, 4].

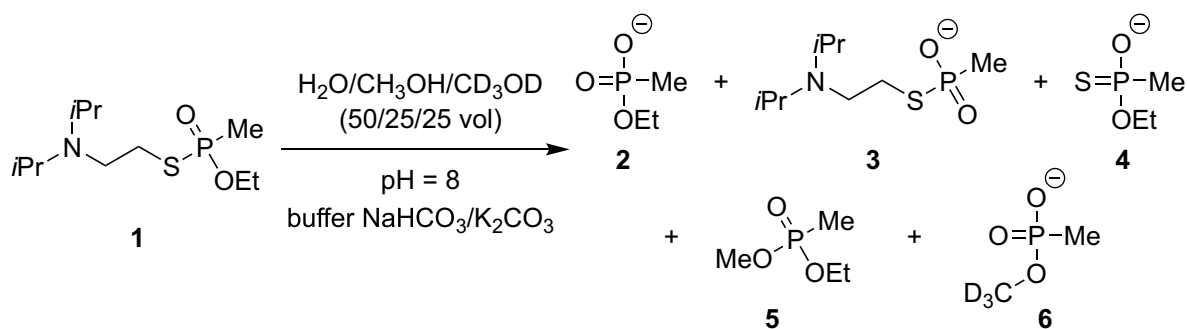
Works on the application of photocatalytic deactivation of CWAs using composites obtained on the basis of zirconium and terephthalic acid, which are made from plastic waste, seem very interesting [5]. This is important, taking into account the problems of ecology and the application of "green" chemistry methods.

Further, the most interesting works in this direction will be considered in detail, primarily those related to the practical use of the proposed methods of decomposition of warfare poisonous substances.

■ Nucleophilic/oxidative decontamination of warfare poisons

Nucleophilic reagents, primarily α -nucleophiles, which have high efficiency, can be used to decontaminate CWAs [1]. For example, work [2] provides data on deactivation of the nerve agent VX – an inhibitor of acetylcholinesterase **1**. Its deactivation by simple hydrolysis in an aqueous-alkaline medium does not give a satisfactory result due to the formation of a stable toxic product of hydrolysis **3** (**Scheme 1**) [3]. The formation of compounds **5** and **6** indicates the participation of alcohols in the process (as parallel transesterification to hydrolysis).

However, the combination of hydrolysis with an oxidation reaction is highly effective in achieving the complete destruction of the VX agent [4]. In this work, the authors studied the behavior of VX in relation to five α -nucleophiles: magnesium monoperoxyphthalate, metachloroperbenzoic acid, potassium monopersulfate, hydrogen peroxide, and hydrogen peroxide with boric acid. All reactions studied were carried out at pH 8. This pH value was chosen since it minimized the risk of corrosion when the metal surface was degassed. It was shown that during the VX hydrolysis in a water-methanol solution, the hydrolytic compound formation occurred due to nucleophilic attack of both water and methanol, mainly



Scheme 1. Hydrolysis of VX (1) in solution $\text{H}_2\text{O}/\text{CH}_3\text{OH}/\text{CD}_3\text{OD}$

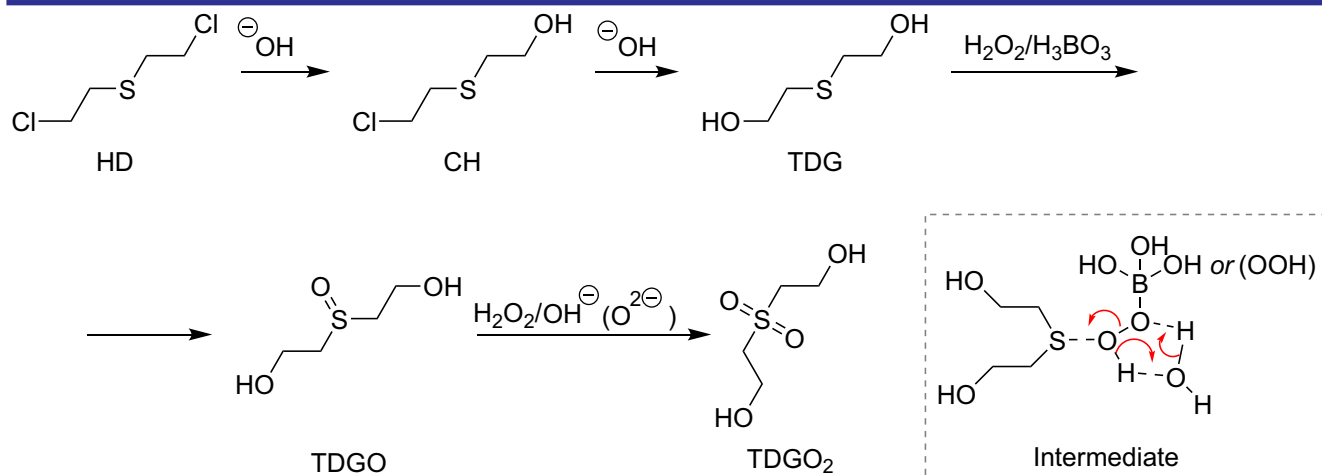
at the phosphorus atom. The oxidative-nucleophilic reaction involving α -nucleophiles increased from 200 to 2000 times compared to simple hydrolysis in a water-methanol solution at pH 8. Using 20 equivalents of magnesium monoperoxyphthalate, it was possible to achieve complete destruction of VX, which turned into non-toxic phosphonate **2** (Scheme 1). It should be noted that decontamination using magnesium monoperoxyphthalate was successfully extended to soman [5].

The methods of decontamination of CWAs with hydrogen peroxide solutions turned out to be very effective. However, H_2O_2 shows a low reaction rate and requires its activation by other reagents, such as HCO_3^- [6–8], MoO_4^{2-} [9–11], etc. Moreover, the rate of the activation reaction between H_2O_2 and HCO_3^- is not as high as expected [6, 12]. The activation of H_2O_2 using MoO_4^{2-} is much more effective, however, at the same time, there is a loss of active oxygen [13], which leads to a decrease in the rate of CWAs destruction within a fairly short time [9, 14].

Another disadvantage of MoO_4^{2-} as an activator of hydrogen peroxide is, for example, that mustard gas can be easily re-oxidized to the corresponding sulfone [9], which exhibits rather high

toxicity. In work [15], the authors investigated boric acid as an activator of hydrogen peroxide reacting with H_2O_2 to form peroxoborates, which could quickly oxidize sulfur to sulfoxide [16]. The decomposition of peroxoborate itself occurs rather slowly, which gives a good perspective for using such solutions for the purpose of CWAs decontamination [17, 18]. In the work mentioned above [15], the nucleophilic/oxidative reactivity of the $\text{B}(\text{OH})_3\text{-H}_2\text{O}_2$ system was studied, while special attention was paid to the influence of the pH of the medium and temperature on the reaction rate. Thioanisole and paraoxon were used as CWAs imitators. The ^{11}B NMR analysis showed that $\text{B}(\text{OH})_3$ quickly reacted with H_2O_2 to form peroxoborates ($[\text{B}(\text{OH})_{(4-x)}(\text{OOH})_x]^-$). Their content depended on pH and solution temperature. It was shown that peroxoborates acted as oxidants for the primary oxidation of sulfide in the pH range of 8–12, and that O_2^- was responsible for further oxidation of sulfoxide.

Paraoxon decomposes due to OOH^- ions, and the rate of decomposition increases exponentially with pH increasing. The data provided suggest that mustard gas, soman, and VX are effectively decomposed into non-toxic products in a solution of $\text{B}(\text{OH})_3\text{-H}_2\text{O}_2$ at pH 9–11. **Scheme 2**

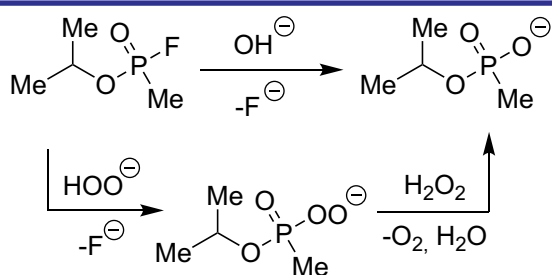


Scheme 2. Destruction of mustard gas in the system $\text{B}(\text{OH})_3\text{-H}_2\text{O}_2$ (HD – mustard gas, CH – 2-chloroethyl-2'-hydroxyethyl sulfide, TDG – thiodiglycol, TDGO – thiodiglycol sulfoxide, TDGO₂ – thiodiglycol sulfone)

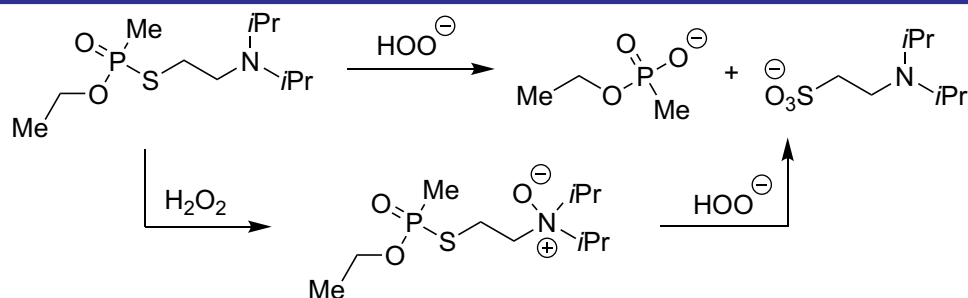
shows the diagram of the mustard gas decomposition.

It should be noted that in the presence of activators, such as carbonates, bicarbonates, and molybdates, hydrogen peroxide, in organic solvents provides rapid decontamination of a wide range of warfare poisons, and it is important at low temperatures ($-30\text{ }^{\circ}\text{C}$). Such solutions are non-toxic, do not cause corrosion, and are environmentally safe [14]. Concern for the environment became the reason to abandon the use of chlorine-containing products (for example, in bleaching processes) and replace them with systems based on hydrogen peroxide. These “green” peroxide products allow for avoiding the use of toxic and carcinogenic organochlorine compounds. Another advantage of peroxides is that they can be used for the CWAs deactivation in the cold season. For example, the freezing point of 50% H_2O_2 is $-40\text{ }^{\circ}\text{C}$. Previously, *Menger and Rourk* [19] demonstrated effectiveness of microemulsion formulations using 30% H_2O_2 . These microemulsions did not freeze or delaminate at $-18\text{ }^{\circ}\text{C}$ and were effective against various CWAs mimics. The scheme of the sarin deactivation reaction in the presence of activated $\text{B}(\text{OH})_3$ is shown in **Scheme 3**.

Inorganic α -nucleophiles – HOO^- and ClO^- ions exhibiting anomalously high reactivity are of particular interest as the basis of compositions for the breakdown of ecotoxicants and hazardous substances [20–23]. In the alkaline medium, VX-type CWAs are quickly destroyed due to the nucleophilic attack of the hydrogen peroxide



Scheme 3. The sarin deactivation reaction in the presence of activated $\text{B}(\text{OH})_3$

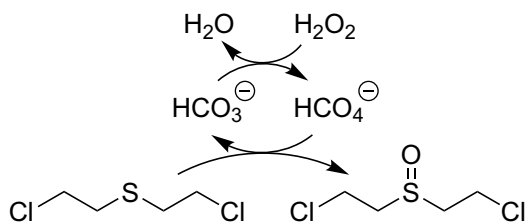


Scheme 4. The VX deactivation with a peroxyhydroxide ion

ion on the phosphorus atom. Peroxyhydrolysis of VX takes place, according to the scheme given below (**Scheme 4**), with the formation of ethylmethylphosphonic acid. VX *N*-oxide is another reaction product, which further, at a slower stage, undergoes nucleophilic attack to form an acid. At the same time, the released thiol is oxidized to sulfonate [24].

The reaction of VX with the HOO^- anion proceeds approximately 40 times faster than with the more basic HO^- ion ($\tau_{1/2} = 45\text{ s}$, $23\text{ }^{\circ}\text{C}$, $[\text{HOO}^-] = 0.1\text{ M}$), which allows for efficient splitting of VX in the alkaline medium by nucleophilic mechanism. Concentrated solutions of hydrogen peroxide, which exhibit oxidizing properties under these conditions, oxidize mustard gas and various ecotoxicants in neutral and acidic medium. To ensure the decomposition of ecotoxicants by both nucleophilic and oxidative mechanisms, the pH of the medium is of great importance [24, 25]. Since the optimal conditions for carrying out these reactions are different, and $\text{pK}_a(\text{H}_2\text{O}_2) = 11.5\text{--}11.6$, hydrogen peroxide can hardly be considered a universal deactivation agent [22]. Nevertheless, numerous studies of the reactivity of hydrogen peroxide and its activators (carbonates, molybdates, phthalates, etc.) led to the creation of universal formulations of the nucleophilic-oxidizing mechanism of action, which are quite effective in relation to the main types of CWAs [25]. Thus, the activation of H_2O_2 with sodium hydrogen carbonate leads to the appearance of a HCO_4^- anion in the reaction mixture in slightly alkaline media. It is a more powerful oxidant than H_2O_2 , and this makes it possible to destroy not only sarin and VX, but mustard gas as well (**Scheme 5**).

The use of potassium molybdate as an activator of hydrogen peroxide in microemulsions of the oil/water type makes it possible to design universal systems for destructing CWAs of various nature [26]. The advantage of this system is that the oxidation of mustard gas mainly leads to the formation of sulfoxide, and not to highly toxic sulfone [26].

Scheme 5. The mustard gas deactivation using a HCO_4^- ion

Salts of hypochlorous acid have been widely used in the decomposition of CWAs and ecotoxins [24]. Hypochlorites are deactivation substances of universal action and are used for detoxification of the human skin, equipment, and terrain [24]. In nucleophilic substitution reactions at the tetracoordinated phosphorus atom, the ClO^- ion acts as a true nucleophilic catalyst and decomposes sarin-type CWAs to phosphonic acids (Scheme 6).

The high oxidizing activity of hypochlorous acid plays an important role in deactivation of mustard gas, which undergoes destruction in alkaline media with the formation of a number of oxidation and elimination products (Scheme 7). It should be emphasized that sulfoxide is formed at the first stage of this rather complex process, which is further transformed into other products.

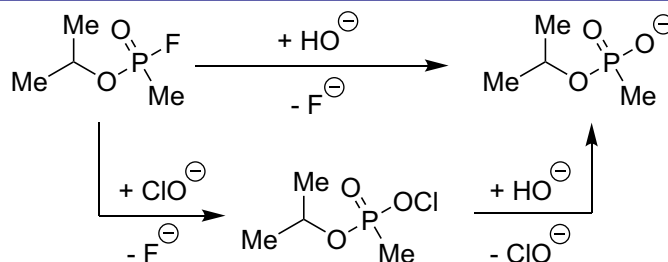
Hypochlorite solutions can be used for the VX deactivation, especially at low pH values (Scheme 8). At the same time, only 3 moles of “active” chlorine are used to destroy 1 mole of VX.

More than 10 moles of “active” chlorine are needed to oxidize 1 mole of VX in alkaline media.

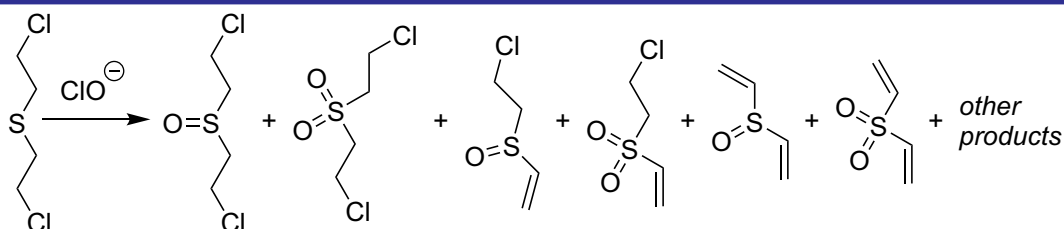
Thus, it can be concluded that the use of systems based on hydrogen peroxide for deactivation of CWAs is effective from the point of view of both the reaction rate and environmental protection.

Convenient for practical use, oxidizing systems consisting of one reagent have also been developed, both against combat poisonous substances and various ecotoxins [27]. The reagent L-Gel proposed consists of an aqueous solution of a mild oxidizer Oxone™ (potassium peroxydisulfate) together with a gel-forming agent based on silica gel Cab-O-Sil EH-5. L-Gel is non-toxic, environmentally friendly, does not cause corrosion, maximizes contact time due to its thixotropic nature, and sticks to any surface. Table 1 shows comparative data on the effectiveness of decontamination of a mustard imitator – chlorodiethyl sulfide for various oxidizing systems compared to the “L-Gel” proposed.

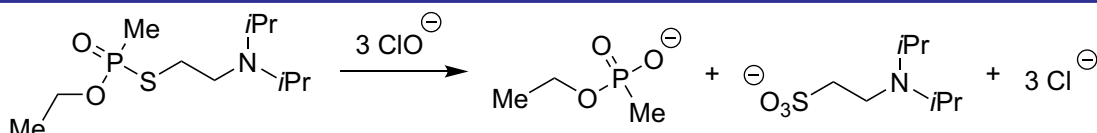
The reactions were carried out at pH = 3, except for sodium hypochlorite (pH = 12). The ratio of the oxidizing agent to chlorodiethyl sulfide was 2. In general, in many cases, chlorine-containing oxidizing reagents, such as NaOCl, $\text{Ca}(\text{OCl})_2$ or dichloroisocyanurate salts, are used for deactivation of CWAs [24]. However, such processes strongly affect the environment and are



Scheme 6. The sarin deactivation using a hypochlorite anion



Scheme 7. The mustard gas deactivation using a hypochlorite anion



Scheme 8. The VX deactivation scheme using a hypochlorite anion

Table 1. Oxidation of chlorodiethyl sulfide

Oxidant	Reaction time (min)	Percentage of oxidation
Sodium hypochlorite	30	91
Hydrogen peroxide	30	100
Ammonium peroxydisulfate	10	40
L-Gel	10	100

associated with high costs of disposal. With these shortcomings, a heterogeneous catalyst based on saponite clay containing Nb^V was proposed. It selectively converts toxic sulfur-containing chemical warfare agents into non-toxic products with a reduced negative impact on the environment under extremely mild conditions [28]. Due to the introduction of Nb^V centers into the saponite framework, a bifunctional catalyst with strong oxidizing and acidic properties was obtained. When it is used, high activity and selectivity for the oxidative deactivation of the mustard imitator – 2-chloroethyl ethyl sulfide in the presence of an aqueous solution of hydrogen peroxide at room temperature is observed. **Scheme 9** shows the specified reaction.

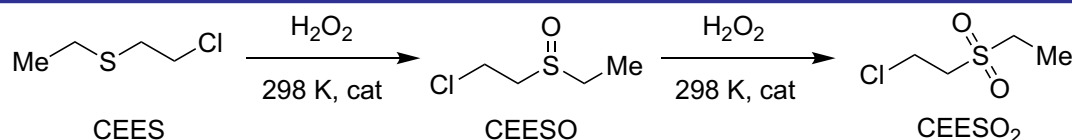
Porous oxides are also promising materials as they demonstrate remarkable chemical, physical and mechanical stability, as well as good dispersion of the catalytically active metal. Thus, nanostructured inorganic metal oxides, such as Al₂O₃, ZnO, and TiO₂, have been widely studied in relation to the CWAs oxidation or other methods of their destruction [29]. The process of deactivation of soman, mustard gas, and VX with such a combined reagent as a solution of sodium peroxycarbonate and tetraacetylenediamine was studied. It was shown that the optimal pH value for the degradation of mustard and VX was about 7.5–9.0 and 8.5–9.5, respectively, and the effectiveness of soman decontamination reached its maximum at pH 9.5–10.5 and a temperature from 0 °C to 45 °C [30]. To obtain a decontamination percentage of > 99%, the molar ratio between active oxygen and CWA should be at least 3, 2, and 10 for soman, mustard gas, and VX, respectively. The analysis of products using gas chromatography/mass spectrometry, liquid chromatography/mass spectrometry, and ion chromatography showed that the decomposition of soman

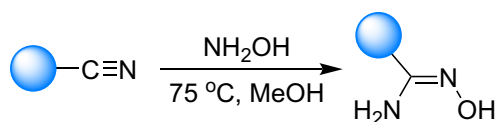
was a process of perhydrolysis. It was indicated that the decomposition of mustard gas occurred by oxidation of atoms C and S and release of HCl. At the same time, the process of the VX decomposition was *via* the oxidation of atoms C, S, and N and the breaking of C-C, C-N, C-S, and P-S bonds.

Attention was drawn to the work [31] where the authors found that palladium-on-carbon catalyzed the deep oxidation of organophosphorus and organosulfur compounds with oxygen in water at 90 °C in the presence of carbon monoxide. This system is the first example of catalytic cleavage of phosphorus-carbon bonds. Starting with trimethylphosphine oxide, the phosphorus-containing products formed during the sequential breaking of the P-C bond were dimethylphosphinic, methylphosphonic, and phosphoric acids. A similar sequence of reactions was observed for triethylphosphine oxide, except that intermediate products formed by partial oxidation of ethyl groups, such as phosphonoacetic acid, were also observed. Deep oxidation of dimethyl and diethyl sulfides occurs through the mediation of the corresponding sulfoxides. For methyl derivatives, the ease of oxidation decreases in the series: (CH₃)₂S > (CH₃)₂SO > (CH₃)₂SO₂ and corresponds to a system acting as an electrophilic oxidant. These results are important in the creation of systems for the deactivation of CWAs and various ecotoxicants.

Using polymer materials containing active nucleophilic centers capable of destructing phosphorus and sulfur esters seems promising. For example, in work [32], the processes of degradation of CWAs by polyacrylamideoxime and poly(*N*-hydroxyacrylamide) were studied. Those polymers are capable of generating nucleophilic oximate groups *via* dissociation of amidoxime or hydroxamic groups, respectively. They are environmentally friendly, economical, and non-toxic polymers, which are essentially products of one-stage addition of available polyacrylonitrile and polyacrylamide (**Scheme 10**).

The polymers were converted into their corresponding oximate salts at pH values higher than the pK_a of oximate or amidoximate groups – 7.5 and 10.8, respectively. The authors focused

**Scheme 9.** Deactivation of 2-chloroethyl ethyl sulfide (CEES) in the presence of a catalyst based on saponite-Nb^V and hydrogen peroxide. Oxidation products – CEESO (sulfoxide), CEESO₂ (sulfone)



Scheme 10. The reaction of the interaction of polyacrylonitrile with hydroxylamine with the formation of polyacrylamidoxime

on the characteristics of functional polymers as deactivating agents for such CWAs as VX, sarin, and soman. The considered polymeric amidoximes in the form of cross-linked polyamidoximate salts can act as effective dephosphorylating agents due to the formation of amidoximate ions on the surface of polymer salt particles without an excess of hydroxyl ions present. Such reactive polymers can be promising materials for the modification of surfaces, such as textiles, coatings, and sorbents. The half-life of VX during heterogeneous hydrolysis was 6 min in the presence of polyacrylamidoxime. Under the same conditions, the half-life for sarin was less than 3 minutes.

In the same aspect, the work [33] is of interest, in which water-soluble polymeric materials based on polyalkylamines modified with nucleophilic groups were introduced as catalysts for the hydrolysis of warfare poisons. The choice of polymer materials was based on the criteria of simplicity of their synthesis, solubility in water, and the rate of hydrolysis of CWAs imitators. The study involving diisopropyl fluorophosphate showed that at a constant pH value, 4-aminopyridine-substituted polyallylamines and polyvinylamines were the most effective for this process.

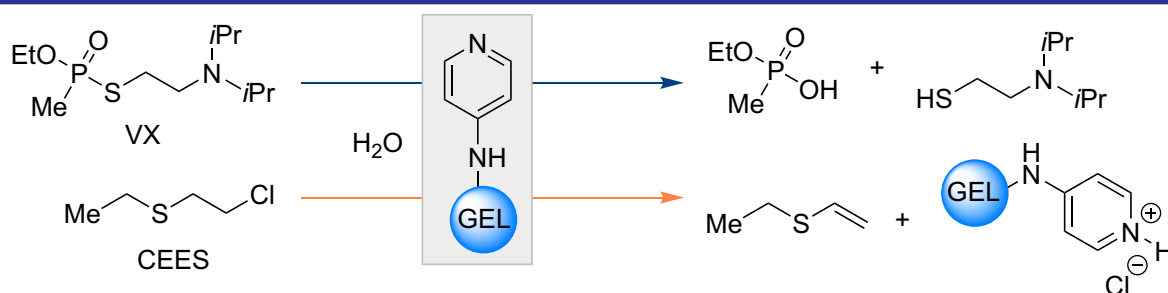
Hydrogel particles of 4-aminopyridine-substituted polyallylamines and polyvinylamines cross-linked with epichlorohydrin revealed pH-dependent swelling and ionization systems that affected the rate constants of the nucleophilic hydrolysis of diisopropylfluorophosphate [32]. The study was conducted on the deactivation of VX and soman in suspensions or gels of both polymers with a concentration of 2.5–3.7 wt.%, which swelled in water or in a mixture of DMSO/water. The half-life of soman was 12 and 770 min at pH 8.5 and 5, respectively. Adding VX to 3.5–3.7 wt.% suspensions

in DMSO- d_6 and D_2O , with an initial VX concentration of 0.2 vol.%, led to 100% degradation of VX in less than 20 min. In addition, the gels of both polymers facilitated the reaction of dehydrochlorination of mustard gas and its analog – 2-chloroethylethyl sulfide (**Scheme 11**).

The ability of such aminopyridine-modified polyalkylamine materials to decompose the most stable CWAs in combination with water solubility and the presence of numerous amino groups, which provide convenient “handles” for covalent attachment to polymeric and inorganic carriers, opens prospects for their wide application, for example, in fabrics and other materials that contribute to quick and effective decontamination of CWAs.

■ Supernucleophilic systems based on functional detergents for the neutralization of chemical warfare agents

It is quite difficult to create a compound that would surpass the hydroxylamine anion in an aqueous solution in terms of its nucleophilic reactivity. Therefore, the way to increase the efficiency of systems for splitting CWAs should be sought not so much in the structural modification of the splitting agent, but in the use of alternative methods of influencing the reaction rate, for example, by changing the properties of the medium, in which it occurs [2, 33–35]. In this sense, the use of microorganized media (micellar solutions, microemulsions, ionic liquids, concentrated aqueous solutions of quaternary ammonium salts, etc. [36–42]) is already widely used to solve a number of applied and fundamental problems. The indisputable advantage of micellar systems compared to other organized microheterogeneous media is that a radical change in the properties of the medium is achieved by the introduction of rather small amounts of micelle-forming substances (in amounts above the critical concentration of micelle formation, which varies



Scheme 11. Deactivation reactions of VX and mustard imitator (CEES)

within 10^{-6} – 10^{-2} mol L⁻¹) [38, 39]. At the same time, the main component of such systems in most cases is water, which makes them extremely attractive for practical use from the point of view of “green” chemistry [43].

The use of solutions of cationic surfactants as a medium for the destruction of CWAs with nucleophilic reagents allows for their effective solubilizing (most of CWAs are difficult to dissolve in water in the absence of detergents), and also ensures wetting of hydrophobic and highly developed surfaces [2, 35, 38, 44]. At the same time, achieving the effects of micellar catalysis leads to an additional increase in the rate of the process of splitting CWAs by nucleophilic reagents (hydroxide ion, oximate ion, etc.) by 10 – 10^3 times [45–57].

One of the most promising ways to increase the efficiency of the binding of nucleophilic reagents by micelles is the creation of functional detergents – surfactants, which have reactive fragments in their structure. When implementing this approach, the concentration of nucleophilic groups on the surface of micelles will always be equal to the concentration of a surfactant [58]. The most promising here is the use of an α -nucleophile fragment as a functional group, which ensures a sharp increase in the rate due to the implementation of the α -effect. Currently, the main types of functional surfactants containing a supernucleophilic fragment are detergents based on hydroxylamine derivatives and detergents containing peroxy- and iodoxocarboxylate groups. Oxime derivatives are of particular interest among this group of reagents. This is due to the ease of structural modification, which makes it possible to obtain oximes that split CWAs in a wide

range of the medium acidity (neutral, slightly alkaline, alkaline) [59]. **Figure 1** shows some typical detergents based on alkylated imidazole and pyridine containing an oxime group.

CWAs imitators – 4-nitrophenyl esters of diethylphosphonic (1), diethylphosphoric (2) and toluenesulfonic (3) acids were most often used to study the reactivity of functional surfactants (**Figure 2**).

Below is the reaction scheme characterizing the reactivity of the oximate group of functionalized surfactants, which consists of a nucleophilic attack of the oximate fragment (Ox⁻) of the functionalized surfactants on the electron-deficient phosphorus and sulfur atoms of the nitrophenolate ion (**Scheme 12**).

Table 2 shows data on half-life periods for decomposition reactions of CWAs imitators – paraxone and armine [33]. The half-life periods of organophosphorus compounds indicate that these functionalized surfactants have high reactivity and can be successfully used to destroy CWAs as part of personal protective equipment and mixtures for treating various surfaces.

■ Adsorption methods and photocatalytic deactivation of chemical warfare agents

Works on the application of photocatalytic deactivation of CWAs using composites obtained on the basis of zirconium and terephthalic acid, which are made from plastic waste, seem very interesting. This is important, based on the problems of ecology and the use of “green” chemistry methods. For example, the work [60] shows the synthesis of such composites and evaluates their photocatalytic activity in the degradation

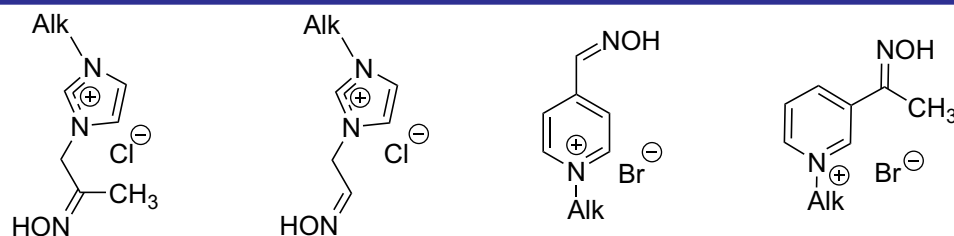


Figure 1. Structural formulas of some typical functionalized surfactants

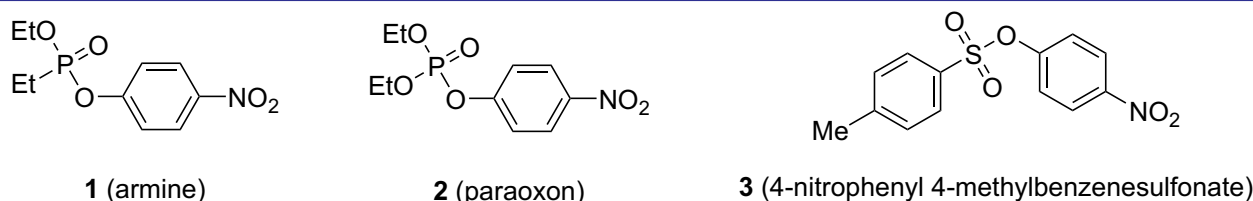
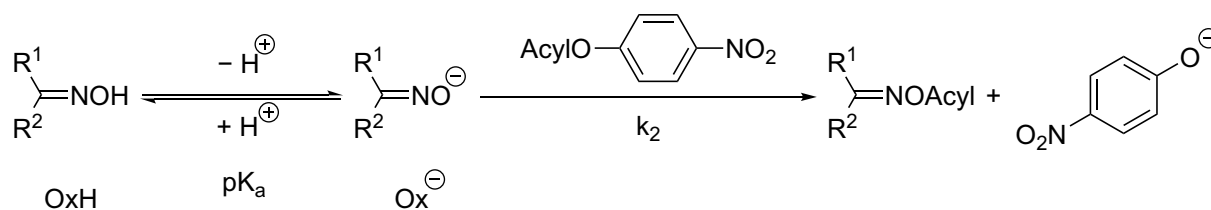


Figure 2. Structural formulas of substrates based on phosphorus and sulfur esters



Note: $R^1(R^2)C=NO^-$ – the corresponding anionic surfactant fragment (Ox^-)

Scheme 12. The reaction scheme of functional detergents with acyl-containing substrates

Table 2. Half-life periods ($\tau_{1/2}$) in the destruction of paraxone and armine (water, 25 °C) with the participation of functionalized detergents

Functional detergent	Paraxone $\tau_{1/2}$ (s)	Armine $\tau_{1/2}$ (s)
	14	2
	43	2
	45	3
	37	3
	180	20

of an imitator of a chemical warfare agent – dimethyl 4-nitrophenyl phosphate. The composite synthesized had a large surface area ($1440 \text{ m}^2 \text{ g}^{-1}$) and a large pore volume ($1.49 \text{ cm}^3 \text{ g}^{-1}$). Composite samples absorbed visible light with a band gap of 2.13–2.88 eV. They showed a high efficiency for the degradation of an imitator of sarin with a short half-life ($t_{1/2} = 2.17 \text{ min}$) at pH 7 by exposure to visible light. Capture experiments have confirmed that H^+ and O_2^- radicals play an important role in photocatalytic degradation. The composite performs two processes at the same time: hydrolysis and photocatalytic oxidation in water.

Noteworthy is the work [61], in which the authors found that barium titanate nanoparticles with sizes of 8–12 nm obtained by the gel collection method were effective photocatalytic

detoxifiers of CWAs vapors, in particular, a mustard imitator (2-chlorodiethyl sulfide). Relatively monodisperse, homogeneously spherical nanoparticles of barium titanate, initially dispersed in alcohol solvents, form a stable and porous aggregated structure that resembles a nanostructured material with pores of an average diameter 4.6 nm and a relatively narrow distribution of their sizes (2.5–8 nm). Due to its porosity and polar chemically active surface, a large amount of CWAs imitator and its decomposition products are adsorbed on barium titanate. The reported absorption by weight of the CWAs simulant was the highest among a number of materials and nanocomposites known for their detoxification activity and tested under the same conditions (169 mg g^{-1} compared to 117 mg g^{-1} for zinc oxide and $< 100 \text{ mg g}^{-1}$ for other oxides transition metals). In addition to adsorption, barium titanate nanomaterial acts simultaneously as an effective heterogeneous catalyst, decomposing toxic vapors into alcohols, sulfides, and thiols – molecules with much lower toxicity than CWAs [62]. Hydrolysis and dehydrohalogenation were the predominant ways of detoxification through the formation of a cyclic sulfonium intermediate both in the light and in the dark. Irradiation with ambient light promoted photooxidation and photodegradation by radical intermediate products formed. It should be concluded that barium titanate nanoparticles with an oxygen-rich surface are being investigated as a potentially useful medium for photoreactive detoxification of chemical warfare agents.

It is worth paying attention to the study of photolytic and photocatalytic reactions of deactivating sarin, soman, mustard gas, and chlorocyanide in the air [63]. It has been shown that the vapors of these CWAs (except for chlorocyanide) can be effectively removed by UV light of a bactericidal lamp by photolysis or photocatalysis. Such a photocatalytic reaction leads to photoinduced polymerization directly under the action of UV irradiation, as well as the splitting of CWAs into small inorganic compounds on the surface of a TiO_2 catalyst. It has been confirmed

that the static photolysis approach can be used to decontaminate sarin vapors indoors. At the same time, it has been demonstrated that the dynamic photocatalytic approach to the destruction of sarin and soman vapors is much more effective than photolysis, and its use is considered appropriate for the disinfection of nerve-paralytic CWAs in the air. **Table 3** shows data on the rate constants of the corresponding CWAs cleavage reactions.

Interesting results were obtained by the authors [64], who used photocatalytic and sonophotocatalytic methods of processing reaction mixtures in aqueous TiO_2 suspensions. CWAs imitators were used as reagents – dimethyl methylphosphonate, diethyl phosphoramidate, pinacolyl methylphosphonate and butylaminoethanethiol. The complete conversion of imitators into inorganic products was achieved in 600 min, and only for butylaminoethanethiol it took more time. Sonolysis accelerated the photodegradation of dimethyl methylphosphonate. No degradation of imitators was observed without ultraviolet irradiation. The final decomposition products were PO_4^{3-} , CO_2 , NO_3^- , NH_4^+ , SO_4^{2-} .

Degradation of dimethyl methylphosphonate proceeds by sequential oxidation of methoxy groups and then methyl groups. Destruction of diethyl phosphoramidate begins with the breaking of the P-NH_2 bond with the formation of diethyl phosphate, which is further transformed into ethyl phosphate [65]. Destruction is also facilitated by the oxidation of α - and β -carbons of ethoxy groups with the formation of ethylphosphonoamidate, hydroxyethylethylphosphonoamidate, and other products. Photocatalytic degradation of pinacolyl methylphosphonate begins with the oxidation of the pinacol fragment, which products are methylphosphonic acid and acetone. The results demonstrate the possibility of photocatalysis for the destruction of CWAs in the aqueous phase. The optimization of degradation conditions is necessary to achieve practical high efficiency.

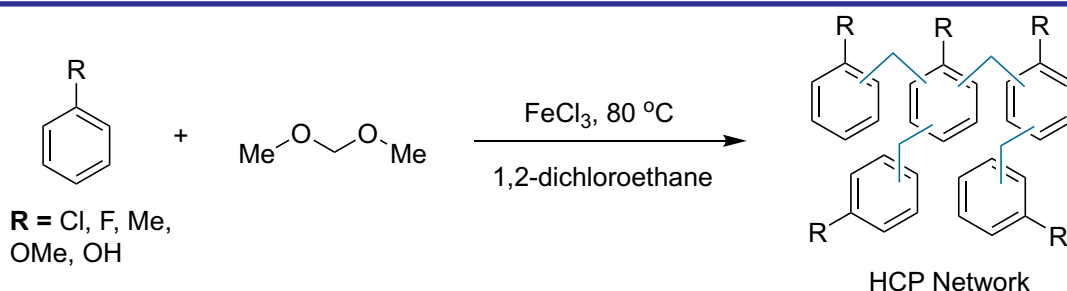
Table 3. Rate constants of the first-order reactions of photolysis and photocatalysis of CWAs vapors

CWAs	Initial concentration (mg L^{-1})	$k \times 10^2 (\text{min}^{-1})$	
		Photolysis	Photocatalysis
Sarin	1.7	2.32	5.97
Soman	0.94	4.09	7.25
Mustard	0.42	2.54	1.19

The question of using polymer sorbents for CWAs deactivation is reflected in many recent publications. They provide the effective adsorption of CWAs and the possibility of their deactivation in large volumes and in a short period of time. Hyper-crosslinked polymers are a class of sorbents that are produced using a simple and controlled method called “linking” [66]. Several hyper-crosslinked polymers and their properties, including the absorption capacity in relation to CWAs imitators, were reported. A hyper-crosslinked polymer derived from fluorobenzene showed the greatest potential when used for CWAs neutralization and was tested against real agents, including sarin and mustard gas, showing absorption close to 20 mL g^{-1} [66]. **Scheme 13** shows a simplified scheme for the synthesis of such a polymer based on halobenzenes.

The ability of hyper-crosslinked polymers to absorb large volumes of liquid due to the swelling of porous networks is a property that can be used in many other areas, for example, in medical purposes for treating wounds. The maximum swelling of hyper-crosslinked polymers, along with the inclusion of catalytic groups in the network to ensure chemical deactivation of agents, will contribute to the development of a universal polymer material capable of absorbing and destroying stocks of all known CWAs.

It is known that sorbent materials are usually used for the physical removal of chemical warfare agents from contaminated surfaces. They remove CWAs in liquid form by their physical adsorption. After adsorption, the sorbent is removed by wiping until clean surfaces are



Scheme 13. The synthesis of hyper-crosslinked polymer meshes

obtained. One such work [67] presents data on the decontamination composition based on nanomaterials containing TiO_2 , MgO , and ZnO nanoparticles for use against chemical warfare agents. This decontamination composition was prepared by mixing 90% of TiO_2 nanoparticles with a size of 5–15 nm, 8% of MgO nanoparticles with a size of 5–15 nm and 2% of ZnO nanoparticles with a size of 20–30 nm. As the authors showed, the composition prepared proved its effectiveness in physically removing 98–99% of contaminated glass, rubber, and metal surfaces [68]. It effectively removed chemical warfare agents from the contaminated skin. Examples of the chemical decomposition of 97% of mustard gas in 24 hours and 99.9% of sarin in 2 hours are given in contrast to Fuller's earth, which chemically decomposes only 63% of mustard gas and 59% of sarin in 24 hours.

■ Conclusions

The material presented in the review relates to the analysis of various methods of decontamination of chemical warfare agents, ecotoxicants, and various pollutants that are widely used to clean surfaces and air. The main degradation processes of CWAs that have been described above include hydrolysis, oxidation, photolysis. The use of these reactions, both individually and in various combinations, allows for creating unique formulations and technologies capable of a quick and efficient destruction of both chemical warfare agents and other ecotoxicants. An important method of CWAs deactivation is the use of nucleophilic/oxidizing systems, primarily α -nucleophiles, which are highly efficient and can react as nucleophiles and oxidants. It has been shown that the use of systems based on hydrogen peroxide for deactivation of CWAs is effective both from the point of view of the reaction rate and environmental protection. Being convenient for practical use, oxidizing systems consisting of one reagent have also been developed, both against chemical warfare agents and various pollutants.

An equally important method of decontamination of CWAs is the use of supernucleophilic systems based on functional detergents, which makes it possible to increase efficiency not only due to structural modification of the agent that

breaks down ecotoxicants, but also by using alternative methods of influencing the reaction rate, for example, by changing properties of the solvent in which it occurs.

In this sense, microorganized systems (micellar solutions, microemulsions, ionic liquids, concentrated aqueous solutions of quaternary ammonium salts, etc.) are widely used to solve a number of applied and fundamental problems. The indisputable advantage of micellar systems compared to other organized microheterogeneous media, is that a significant change in the properties of the medium is achieved by the introduction of rather small amounts of micelle-forming substances, above the critical concentration of micelle formation, which varies within 10^{-6} – 10^{-2} mol l^{-1} . At the same time, the main component of such systems, in most cases, is water, which makes them extremely attractive for practical use from the point of view of "green" chemistry.

Works on the application of photocatalytic deactivation of CWAs using composites obtained on the basis of zirconium and terephthalic acid, which are made from plastic waste, seem very interesting (this is important, based on environmental issues). It is worth paying attention to the research of photolytic and photocatalytic reactions of deactivation of sarin, soman, mustard gas and chlorocyanide in the air. Thus, vapors of these CWAs (except chlorocyanide) can be effectively removed by UV light from a germicidal lamp. Such a photocatalytic reaction leads to photoinduced polymerization directly under the action of UV irradiation, as well as the splitting of CWAs into small inorganic compounds on the surface of the TiO_2 catalyst. Photocatalytic and sonophotocatalytic methods of processing reaction mixtures in aqueous TiO_2 suspensions have also been developed. The question of using polymer sorbents for deactivating CWAs is reflected in many recent publications. They provide effective adsorption of CWAs and the possibility of their deactivation in large volumes and in a short period of time.

Thus, ensuring high reaction rates and forming decomposition products that are safe for nature and humans and their subsequent complete disposal should be the basis of methods and technologies for decontaminating chemical warfare agents.

References

- Popov, A.; Kapitanov, I.; Serdyuk, A.; Shumeiko, A. Reactivity of nucleophiles and α -effect in substitution processes at electron – deficiency centers (Part 1). *Ukr. Khim. Zh.* **2020**, *86* (7). <https://doi.org/10.33609/2708-129X.86.7.2020.3-31>.
- Popov, A. F. Design of green microorganized systems for decontamination of ecotoxicants. *Pure Appl. Chem.* **2008**, *80* (7), 1381–1397. <https://doi.org/10.1351/pac200880071381>.
- Yang, Y. C.; Szafraniec, L. L.; Beaudry, W. T.; Rohrbach, D. K. Oxidative detoxification of phosphonothiolates. *J. Am. Chem. Soc.* **1990**, *112* (18), 6621–6627. <https://doi.org/10.1021/ja00174a025>.
- Popov, A.; Kapitanov, I.; Serdyuk, A.; Shumeiko, A. Reactivity of nucleophiles and α -effect in substitution processes at electron – deficiency centers (Part 2). *Ukr. Khim. Zh.* **2020**, *86* (8). <https://doi.org/10.33609/2708-129X.86.8.2020.77-100>.
- Bromberg, L.; Hatton, T. A. Nerve Agent Destruction by Recyclable Catalytic Magnetic Nanoparticles. *Ind. Eng. Chem. Res.* **2005**, *44* (21), 7991–7998. <https://doi.org/10.1021/ie0506926>.
- Richardson, D. E.; Yao, H.; Frank, K. M.; Bennett, D. A. Equilibria, Kinetics, and Mechanism in the Bicarbonate Activation of Hydrogen Peroxide: Oxidation of Sulfides by Peroxymonocarbonate. *J. Am. Chem. Soc.* **2000**, *122* (8), 1729–1739. <https://doi.org/10.1021/ja9927467>.
- Bakhmutova-Albert, E. V.; Yao, H.; Denevan, D. E.; Richardson, D. E. Kinetics and Mechanism of Peroxymonocarbonate Formation. *Inorg. Chem.* **2010**, *49* (24), 11287–11296. <https://doi.org/10.1021/ic1007389>.
- Wagner, G. W. Studies on Residue-Free Decontaminants for Chemical Warfare Agents. *Environ. Sci. Technol.* **2015**, *49* (6), 3755–3760. <https://doi.org/10.1021/es506045a>.
- Wagner, G. W.; Procell, L. R.; Yang, Y.-C.; Bunton, C. A. Molybdate/Peroxide Oxidation of Mustard in Microemulsions. *Langmuir* **2001**, *17* (16), 4809–4811. <https://doi.org/10.1021/la010334h>.
- Chiarini, M.; Bunton, C. A. Oxidation of Thioanisole by Peroxomolybdate in Alcohol-Modified Micelles of Cetylpyridinium Chloride. *Langmuir* **2002**, *18* (23), 8806–8812. <https://doi.org/10.1021/la026156p>.
- Taube, F.; Hashimoto, M.; Andersson, I.; Pettersson, L. Characterisation of aqueous peroxomolybdate catalysts applicable to pulp bleaching. *J. Chem. Soc., Dalton Trans.* **2002**, (6), 1002–1008, 10.1039/B107936K. <https://doi.org/10.1039/B107936K>.
- Zhao, S.; Xi, H.; Zuo, Y.; Wang, Q.; Wang, Z.; Yan, Z. Bicarbonate-activated hydrogen peroxide and efficient decontamination of toxic sulfur mustard and nerve gas simulants. *J. Hazard. Mater.* **2018**, *344*, 136–145. <https://doi.org/10.1016/j.jhazmat.2017.09.055>.
- Nardello, V.; Marko, J.; Vermeersch, G.; Aubry, J. M. 90Mo NMR and kinetic studies of peroxomolybdate intermediates involved in the catalytic disproportionation of hydrogen peroxide by molybdate ions. *Inorg. Chem.* **1995**, *34* (20), 4950–4957. <https://doi.org/10.1021/ic00124a007>.
- Singh, B.; Prasad, G.; Pandey, K.; Danikhel, R.; Vijayaraghavan, R. Decontamination of Chemical Warfare Agents (Review Article). *Def. Sci. J* **2010**, *60*, 428–441. <https://doi.org/10.14429/dsj.60.487>.
- Zhao, S.; Xi, H.; Zuo, Y.; Han, S.; Zhu, Y.; Li, Z.; Yuan, L.; Wang, Z.; Liu, C. Rapid activation of basic hydrogen peroxide by borate and efficient destruction of toxic industrial chemicals (TICs) and chemical warfare agents (CWAs). *J. Hazard. Mater.* **2019**, *367*, 91–98. <https://doi.org/10.1016/j.jhazmat.2018.12.075>.
- Davies, D. M.; Deary, M. E.; Quill, K.; Smith, R. A. Borate-catalyzed reactions of hydrogen peroxide: kinetics and mechanism of the oxidation of organic sulfides by peroxoborates. *Chem. Eur. J.* **2005**, *11* (12), 3552–3558. <https://doi.org/10.1002/chem.200401209>.
- Deary, M. E.; Durrant, M. C.; Davies, D. M. A kinetic and theoretical study of the borate catalysed reactions of hydrogen peroxide: the role of dioxaborirane as the catalytic intermediate for a wide range of substrates. *Org. Biomol. Chem.* **2013**, *11* (2), 309–317. <https://doi.org/10.1039/C2OB26842F>.
- Lobachev, V. L.; Zimtseva, G. P.; Matvienko, Y. V.; Rudakov, E. S. Kinetics of the oxidation of diethyl sulfide in the B(OH)₃-H₂O₂/H₂O system. *Theor. Exp. Chem.* **2007**, *43* (1), 44–49. <https://doi.org/10.1007/s11237-007-0004-4>.
- Menger, F. M.; Rourk, M. J. Deactivation of mustard and nerve agent models via low-temperature microemulsions. *Langmuir* **1999**, *15*, 309–313. <https://doi.org/10.1021/la980910i>.
- Picard, B.; Chataigner, I.; Maddaluno, J.; Legros, J. Introduction to chemical warfare agents, relevant simulants and modern neutralisation methods. *Org. Biomol. Chem.* **2019**, *17* (27), 6528–6537. <https://doi.org/10.1039/C9OB00802K>.
- Wagner, G. W.; Sorrick, D. C.; Procell, L. R.; Brickhouse, M. D.; McVey, I. F.; Schwartz, L. I. Decontamination of VX, GD, and HD on a Surface Using Modified Vaporized Hydrogen Peroxide. *Langmuir* **2007**, *23* (3), 1178–1186. <https://doi.org/10.1021/la062708i>.
- Mikutta, R.; Kleber, M.; Kaiser, K.; Jahn, R. Organic matter removal from soils using hydrogen peroxide, sodium hypochlorite, and disodium peroxodisulfate. *Soil Sci. Soc. Am. J.* **2005**, *69*, 120–135. <https://doi.org/10.2136/sssaj2005.0120>.
- Wagner, G. W.; Yang, Y.-C. Rapid Nucleophilic/Oxidative Decontamination of Chemical Warfare Agents. *Ind. Eng. Chem. Res.* **2002**, *41* (8), 1925–1928. <https://doi.org/10.1021/ie010732f>.
- Yang, Y. C.; Baker, J. A.; Ward, J. R. Decontamination of chemical warfare agents. *Chem. Rev.* **1992**, *92* (8), 1729–1743. <https://doi.org/10.1021/cr00016a003>.
- Wagner, G.; Yang Y.-C. (US Department of Army). Universal Decontaminating Solution for Chemical Warfare Agents. US Patent US6245957B1, June 12, 2001.
- Wagner, G.; Procell, L.; Yang Y.-C.; Bunton C. (US Department of Army). Molybdate/peroxide microemulsions useful for decontamination of chemical warfare agents. US Patent US6723891B1, April 20, 2004.
- Raber, E.; McGuire, R. Oxidative decontamination of chemical and biological warfare agents using L-Gel. *J. Hazard. Mater.* **2002**, *93* (3), 339–352. [https://doi.org/10.1016/S0304-3894\(02\)00051-1](https://doi.org/10.1016/S0304-3894(02)00051-1).
- Carniato, F.; Bisio, C.; Psaro, R.; Marchese, L.; Guidotti, M. Niobium(V) Saponite Clay for the Catalytic Oxidative Abatement of Chemical Warfare Agents. *Angew. Chem., Int. Ed.* **2014**, *53* (38), 10095–10098. <https://doi.org/10.1002/anie.201405134>.
- Shen, Z.; Zhong, J.-Y.; Yang, J.-C.; Cui, Y.; Zheng, H.; Wang, L.-Y.; Wang, J.-L. Decontamination of Chemical Warfare Agents by Zn²⁺ and Ge⁴⁺ co-doped TiO₂ nanocrystals at sub-zero temperatures: A solid-state NMR and GC study. *Chem. Phys. Lett.* **2018**, *707*, 31–39. <https://doi.org/10.1016/j.cplett.2018.07.033>.
- Qi, L.; Zuo, G.; Cheng, Z.; Wang, L.; Zhou, C. Treatment of chemical warfare agents by combined sodium percarbonate with tetraacetylenediamine solution. *Chem. Eng. J.* **2013**, *229*, 197–205. <https://doi.org/10.1016/j.cej.2013.05.108>.
- Hogan, T.; Simpson, R.; Lin, M.; Sen, A. The deep oxidation of chemical warfare agent models: facile catalytic oxidative cleavage of phosphorus-carbon and sulfur-carbon bonds using dioxygen. *Catal. Lett.* **1997**, *49* (1), 59–63. <https://doi.org/10.1023/A:1019088818029>.

32. Bromberg, L.; Schreuder-Gibson, H.; Creasy, W. R.; McGarvey, D. J.; Fry, R. A.; Hatton, T. A. Degradation of Chemical Warfare Agents by Reactive Polymers. *Ind. Eng. Chem. Res.* **2009**, *48* (3), 1650–1659. <https://doi.org/10.1021/ie801150y>.
33. Popov, A. F.; Savelova, V. A. Modern approaches to the construction of highly efficient nucleophilic systems. *Theor. Exp. Chem.* **1999**, *35* (1), 1–17. <https://doi.org/10.1007/BF02511123>.
34. Gonzaga, F.; Segues, B.; Perez, É.; Rico-Lattes, I.; Lattes, A. Decontamination chimique. II. Oxydation de composés soufrés en milieu micellaire: rôle de la lipophilie des substrats. *C. R. Acad. Sci., Ser. IIc: Chim.* **1998**, *1* (3), 209–216. [https://doi.org/10.1016/S1387-1609\(99\)80082-6](https://doi.org/10.1016/S1387-1609(99)80082-6).
35. Delfino, R. T.; Ribeiro, T. S.; Figueroa-Villar, J. D. Organophosphorus compounds as chemical warfare agents: a review. *J. Braz. Chem. Soc.* **2009**, *20*, 407–428. <https://doi.org/10.1590/S0103-50532009000300003>.
36. Ariga K.; Kunitake, T. *Supramolecular Chemistry—Fundamentals and Applications*; Springer: Heidelberg, 2006.
37. Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*; Wiley, 2008.
38. Holmberg, K. *Handbook of Applied Surface and Colloid Chemistry*; Wiley: Chichester, England; New York, 2002.
39. Lion, C.; Despagne, B.; Delmas, G.; Fosset, L. Destruction Du Paraoxon Par Une Nouvelle Série de Sels de N-Alkyl Hydroximinomethylpyridinium. *Bull. Soc. Chim. Belg.* **1991**, *100* (7), 549–554. <https://doi.org/10.1002/bscb.19911000710>.
40. Menger, F. M.; Elrington, A. R. Rapid Deactivation of Mustard via Microemulsion Technology. *J. Am. Chem. Soc.* **1990**, *112* (22), 8201–8203. <https://doi.org/10.1021/ja00178a074>.
41. Toullec, J.; Moukawim, M. Cetyltrimethylammonium Hydroperoxide: An Efficient Reagent for Promoting Phosphate Ester Hydrolysis. *Chem. Commun.* **1996**, No. 2, 221. <https://doi.org/10.1039/cc9960000221>.
42. Gonzaga, F.; Perez, E.; Rico-Lattes, I.; Lattes, A. New Microemulsions for Oxidative Decontamination of Mustard Gas Analogues and Polymer-Thickened Half-Mustard. *New J. Chem.* **2001**, *25* (1), 151–155. <https://doi.org/10.1039/b003671o>.
43. Zimmerman, J. B.; Anastas, P. T.; Erythropel, H. C.; Leitner, W. Designing for a Green Chemistry Future. *Science* **2020**, *367* (6476), 397–400. <https://doi.org/10.1126/science.aay3060>.
44. Marrs, T. C.; Maynard, R. L.; Sidell, F. R. *Chemical Warfare Agents: Toxicology and Treatment*; Wiley: Chichester, West Sussex, England; Hoboken, NJ, 2007.
45. Han, X.; Balakrishnan, V. K.; vanLoon, G. W.; Buncel, E. Degradation of the Pesticide Fenitrothion as Mediated by Cationic Surfactants and α -Nucleophilic Reagents. *Langmuir* **2006**, *22* (21), 9009–9017. <https://doi.org/10.1021/la060641t>.
46. Han, X.; Balakrishnan, V. K.; Buncel, E. Alkaline Degradation of the Organophosphorus Pesticide Fenitrothion as Mediated by Cationic C_{12} , C_{14} , C_{16} , and C_{18} Surfactants. *Langmuir* **2007**, *23* (12), 6519–6525. <https://doi.org/10.1021/la063521u>.
47. Balakrishnan, V. K.; Han, X.; vanLoon, G. W.; Dust, J. M.; Toullec, J.; Buncel, E. Acceleration of Nucleophilic Attack on an Organophosphorothioate Neurotoxin, Fenitrothion, by Reactive Counterion Cationic Micelles. Regioselectivity as a Probe of Substrate Orientation within the Micelle. *Langmuir* **2004**, *20* (16), 6586–6593. <https://doi.org/10.1021/la049572d>.
48. Omakor, J. E.; Ikenna Onyido; vanLoon, G. W.; Buncel, E. Mechanisms of Abiotic Degradation and Soil–Water Interactions of Pesticides and Other Hydrophobic Organic Compounds. Part 3. Nucleophilic Displacement at the Phosphorus Centre of the Pesticide Fenitrothion [O,O-Dimethyl O-(3-Methyl-4-Nitrophenyl) Phosphorothioate] by Oxygen Nucleophiles in Aqueous Solution: α -Effect and Mechanism†. *J. Chem. Soc., Perkin Trans. 2* **2001**, No. 3, 324–330. <https://doi.org/10.1039/b008615k>.
49. Martinek, K.; A.K. Yatsimirski; Osipov, A. P.; Berezin, I. V. Micellar Effects on Kinetics and Equilibrium of Synthesis and Hydrolysis of Benzylideneaniline. *Tetrahedron* **1973**, *29* (7), 963–969. [https://doi.org/10.1016/0040-4020\(73\)80046-8](https://doi.org/10.1016/0040-4020(73)80046-8).
50. A Comparative Analysis of Pseudophase Ion-Exchange (PIE) Model and Berezin Pseudophase (BPP) Model: Analysis of Kinetic Data for Ionic Micellar-Mediated Semi-Ionic Bimolecular Reaction. *Bull. Korean Chem. Soc.* **2007**, *28* (7), 1135–1140. <https://doi.org/10.5012/bkcs.2007.28.7.1135>.
51. Kapitanov, I. V.; Mirgorodskaya, A. B.; Valeeva, F. G.; Gathergood, N.; Kuca, K.; L. Ya. Zakharova; Yevgen Karpichev. Physicochemical Properties and Esterolytic Reactivity of Oxime Functionalized Surfactants in PH-Responsive Mixed Micellar System. *Colloids Surf., A* **2017**, *524*, 143–159. <https://doi.org/10.1016/j.colsurfa.2017.04.039>.
52. Quina, F. H.; Chaimovich, Hernan. Ion Exchange in Micellar Solutions. 1. Conceptual Framework for Ion Exchange in Micellar Solutions. *J. Phys. Chem.* **1979**, *83* (14), 1844–1850. <https://doi.org/10.1021/j100477a010>.
53. Menger, F. M.; Portnoy, C. E. Chemistry of Reactions Proceeding inside Molecular Aggregates. *J. Am. Chem. Soc.* **1967**, *89* (18), 4698–4703. <https://doi.org/10.1021/ja00994a023>.
54. Al-Lohedan, H.; Buntun, C. A. Ion Binding and Micellar Effects upon Reactions of Carboxylic Anhydrides and Carbonate Esters. *J. Org. Chem.* **1982**, *47* (7), 1160–1166. <https://doi.org/10.1021/jo00346a003>.
55. Buntun, C. A.; Lawrence Baylor Robinson. Micellar Effects upon the Reaction of P-Nitrophenyl Diphenyl Phosphate with Hydroxide and Fluoride Ions. *J. Org. Chem.* **1969**, *34* (4), 773–780. <https://doi.org/10.1021/jo01256a002>.
56. Buntun, C. A.; Ihara, Y. Micellar Effects upon Dephosphorylation and Deacylation by Oximate Ions. *J. Org. Chem.* **1977**, *42* (17), 2865–2869. <https://doi.org/10.1021/jo00437a018>.
57. Kapitanov, I.; Serdyuk, A.; Shumeiko, A.; Prokop'eva, T.; Popov, A. Acid-base properties of functionalized surfactants in micellar systems. *Ukr. Khim. Zh.* **2017**, *83* (8), 94–102 [in Russian].
58. Singh, N.; Karpichev, Y.; Tiwari, A. K.; Kuca, K.; Ghosh, K. K. Oxime Functionality in Surfactant Self-Assembly: An Overview on Combating Toxicity of Organophosphates. *J. Mol. Liq.* **2015**, *208*, 237–252. <https://doi.org/10.1016/j.molliq.2015.04.010>.
59. Le, D. V.; Nguyen, M. B.; Dang, P. T.; Lee, T.; Nguyen, T. D. Synthesis of a UiO-66/G-C3N4 Composite Using Terephthalic Acid Obtained from Waste Plastic for the Photocatalytic Degradation of the Chemical Warfare Agent Simulant, Methyl Paraoxon. *RSC Advances* **2022**, *12* (35), 22367–22376. <https://doi.org/10.1039/D2RA03483B>.
60. Giannakoudakis, D. A.; Pearsall, F.; Florent, M.; Lombardi, J.; O'Brien, S.; Bandosz, T. J. Barium Titanate Perovskite Nanoparticles as a Photoreactive Medium for Chemical Warfare Agent Detoxification. *J. Colloid Interface Sci.* **2018**, *531*, 233–244. <https://doi.org/10.1016/j.jcis.2018.07.053>.
61. Liu, Y.; Moon, S.-Y.; Hupp, J. T.; Farha, O. K. Dual-Function Metal–Organic Framework as a Versatile Catalyst for Detoxifying Chemical Warfare Agent Simulants. *ACS Nano* **2015**, *9* (12), 12358–12364. <https://doi.org/10.1021/acs.nano.5b05660>.
62. Zuo, G.-M.; Cheng, Z.-X.; Li, G.-W.; Shi, W.-P.; Miao, T. Study on Photolytic and Photocatalytic Decontamination of Air Polluted by Chemical Warfare Agents (CWAs). *Chem. Eng. J.* **2007**, *128* (2-3), 135–140. <https://doi.org/10.1016/j.cej.2006.10.006>.
63. Vorontsov, A. V.; Davydov, L.; Reddy, E. P.; Lion, C.; Savinov, E. N.; Smirniotis, P. G. Routes of Photocatalytic Destruction of Chemical Warfare Agent Simulants. *New J. Chem.* **2002**, *26* (6), 732–744. <https://doi.org/10.1039/b109837c>.

64. Horikoshi, S.; Watanabe, N.; Mukae, M.; Hidaka, H.; Serpone, N. Mechanistic Examination of the Titania Photocatalyzed Oxidation of Ethanolamines. *New J. Chem.* **2001**, *25* (8), 999–1005. <https://doi.org/10.1039/b102186i>.
65. Wilson, C.; Main, M.; N. John Cooper; Briggs, M. E.; Cooper, A. I.; Adams, D. J. Swellable Functional Hypercrosslinked Polymer Networks for the Uptake of Chemical Warfare Agents. *Polym. Chem.* **2017**, *8* (12), 1914–1922. <https://doi.org/10.1039/c7py00040e>.
66. DeCoste, J. B.; Peterson, G. W. Metal–Organic Frameworks for Air Purification of Toxic Chemicals. *Chem. Rev.* **2014**, *114* (11), 5695–5727. <https://doi.org/10.1021/cr4006473>.
67. Prasad, G. K.; Gautam, A.; Kannan, G. M.; Acharya, J.; Gupta, A. K.; Thakare, V. B.; Singh, B. Nanomaterials Based Decontamination Formulation for Use in Personal Decontamination Kit against Chemical Warfare Agents. *Defense Life Science Journal* **2017**, *3* (1), 5. <https://doi.org/10.14429/dlsj.3.12056>.
68. Szinicz, L. History of Chemical and Biological Warfare Agents. *Toxicology* **2005**, *214* (3), 167–181. <https://doi.org/10.1016/j.tox.2005.06.011>.

Information about the authors:

Olexander E. Shumeiko (*corresponding author*), graduated from the Faculty of Chemistry of the Donetsk National University, Ph.D. in Chemistry, Senior Researcher of the Department of Chemistry of Heterocyclic Compounds, L. M. Litvinenko Institute of Physical Organic Chemistry and Coal Chemistry of the National Academy of Sciences of Ukraine. The area of scientific interests of O. E. Shumeiko is the study of the reactivity and mechanism of nucleophilic substitution and addition reactions under the transphase catalysis conditions, the study of systems of nucleophilic and nucleophilic / oxidizing action for splitting ecotoxicants, the development of methods of synthesis of dimeric functional surfactants, organized microheterogeneous systems, the study of their physicochemical properties. <https://orcid.org/0000-0001-5856-9871>; e-mail for correspondence: ashumeiko@ukr.net.

Mykola I. Korotkikh, Dr.Sci. in Chemistry, Professor, Head of the Laboratory of Chemistry of Stable Carbenes, Institute of Organic Chemistry and Chief Researcher of the L. M. Litvinenko Institute of Physical Organic Chemistry and Coal Chemistry of the National Academy of Sciences of Ukraine. The current research is connected with the synthesis, structures, reactivities, and catalytical properties of heteroaromatic carbenes, carbenoids, and their analogs. Earlier works were devoted to the synthesis of heterocyclic derivatives of small rings, ring transformations of heterocycles, and materials relevant to the pharmaceutical and polymer industries. <https://orcid.org/0000-0003-0774-6588>; e-mail for correspondence: nkorotkikh@ua.fm.