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Chemical Warfare Agents: Structure, Properties, Decontamination (Part 1)

Abstract

The review is aimed at summarizing and systematizing information on various methods of deactivation of chemical warfare agents required on the battlefield, in laboratories, research institutions, production facilities, as well as information on storage and destruction of poisonous substances. The review provides data on warfare poisons with different tactical and physiological characteristics and outlines the main directions of their neutralization, which are the most effective under the conditions of their real use. In the first part of this review, the methods of deactivation of warfare poisonous substances using functionalized metal-organic framework materials, on which reactions of their transformation into low-toxic products take place, are considered in detail. In addition, metal-organic frameworks are porous crystalline structures that have many areas of application and can be used as adsorbents and catalysts. The above material 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 of decontamination of chemical warfare agents and other ecotoxicants, for environmental protection.

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

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Бойові отруйні речовини: структура, властивості, дезактивація (частина 1)

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, про зберігання та знищення отруйних речовин. В огляді наведено відомості про різні за тактико-фізіологічними характеристиками бойові отруйні речовини й окреслено основні напрями їх знешкодження, які є найбільш ефективними в умовах їх реального застосування. У першій частині цього огляду докладно описано методи дезактивації отруйних речовин за допомогою металоорганічних каркасних функціоналізованих матеріалів, на яких відбуваються реакції їх перетворення на малотоксичні продукти. Крім того, металоорганічні каркаси є пористими кристалічними структурами, які мають безліч сфер застосування і можуть бути використані як адсорбенти та каталізатори. Викладений матеріал засвідчує важливість загальних знань про фізичні й хімічні властивості бойових отруйних речовин, швидкість їх розкладання, переваги й недоліки тих чи інших доступних технологій їх застосування. Цей огляд може бути корисний для пошуку нових та удосконалення відомих методів дезактивації бойових отруйних речовин та інших екотоксикантів, для захисту довкілля.

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

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■ Introduction

This review is prepared for the generalization and analysis of the known and newest methods of decontamination of combat poisonous substances, and various ecotoxicants, which are aimed at protecting the environment, life, and health of people.

Among the types of weapons of mass destruction, chemical weapons are probably one of the most dangerous, spreading over large areas and affecting huge numbers of people and animals. Such compounds are extremely toxic synthetic chemicals that can be dispersed as gas, liquid, aerosol, or products adsorbed on any surface and turned into a powdery state. These poisonous substances have either a lethal effect or render a person incapacitated [1]. Thousands of toxic substances are known, but only a few of them are classified as chemical warfare agents (CWAs) by their characteristics, namely, those that are highly toxic, imperceptible to the senses, act quickly after distribution, and are persistent in the environment. All of them are listed as chemicals in the Chemical Weapons Convention. According to the Convention, chemical weapons are defined as toxic chemical substances and their precursors, munitions, and devices, as well as any equipment that is specifically intended for use directly in connection with such weapons [2]. If one looks into history, the first use of chemical weapons occurred during the chlorine gas attack that Germany carried out on April 22, 1915, in Ypres (Belgium).

The first part of this review considers in detail the methods of deactivation of poisonous substances using metal-organic functionalized framework materials (MOFs), on which reactions of their transformation into low-toxic products take place. Metal-organic frameworks are porous crystalline structures that have many applications and can be used as adsorbents and catalysts.

MOFs contain metal or metal-oxide nodes connected by organic linkers and form a crystalline structure. They can be 1-, 2- or 3-dimensional, and the latter are of particular interest since they have the property of forming highly porous networks.

The MOFs structure can be easily varied by changing the metal node or organic linker to achieve the desired chemical and physical properties. The most effective are zirconium-based MOFs, which differ in the pore size and show a significant thermal and chemical stability [3].

Most of the research conducted in this area is focused, first of all, on the possibilities of effective application of the results obtained in combat conditions where the rate and ease of application of decontamination are important [4].

■ Tactical indicators of warfare poisonous substances

Tactical indicators of CWAs are divided by the pressure of saturated vapor (volatility) into unstable (phosgene, hydrocyanic acid), stable (mustard gas, lewisite, VX) and poisonous smoke (adamsite). According to the nature of the action on a living organism, they are divided into lethal (sarin, mustard gas) and those that temporarily disable life force (chloracetophenone, quinuclidyl-3-benzylate). They are also divided into irritating (adamsite) and educational (chlorpicrin). CWAs can still be divided depending on the rate of the striking effect into fast-acting ones that do not have a latent period of action (sarin, soman, VX) and those that act slowly and have a latent period of action (mustard gas, phosgene, lewisite, adamsite) [2].

■ Physiological characteristics of warfare poisonous substances

According to the physiological characteristics, CWAs are divided according to their impact on humans. The following types are distinguished: nerve agents (sarin, soman, tabun, VX), vesicants (mustard gas, lewisite), general poison (hydrocyanic acid, chlorocyanine), suffocating (phosgene, diphosgene), irritant (adamsite, chlorpicrin), psychochemical action (quinuclidyl-3-benzylate). Let us take a closer look at some physicochemical characteristics of warfare poisons and the features of their use [1].

■ Nerve agents

They include a group of organophosphorus compounds (POCs) used as a striking element of chemical weapons that affect the nervous system. This is due to the fact that they are cholinesterase inhibitors. The main mechanism of their action is their selective suppression of the enzyme acetylcholinesterase, which catalyzes the hydrolysis of acetylcholine, a mediator of nervous excitation. The hydrolysis of acetylcholine in a healthy body occurs constantly and is necessary to stop the transmission of a nerve impulse, which allows the muscle to return to the state of rest. Unlike acetylated cholinesterase, phosphorylated cholinesterase formed during POCs poisoning is a very stable compound and does not undergo spontaneous hydrolysis. The process of cholinesterase inhibition is two-step. The first stage is reversible, i.e., a weak blocking occurs, and in the second stage, an irreversible blocking of the enzyme takes place. The most critical consequences of the action of such CWAs are paralysis of the respiratory muscles and suppression of the respiratory center. Ultimately, death occurs through respiratory paralysis. If the concentration of nerve-paralytic CWAs is high, death occurs instantly. Nerve-paralytic poisons can be delivered by means of artillery, aviation and missiles [2].

Sarin (isopropylmethylfluorophosphonate) is a nerve-paralytic poison and belongs to fluoroesters of phosphonic acid (**Figure 1**).

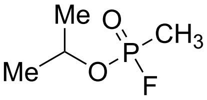


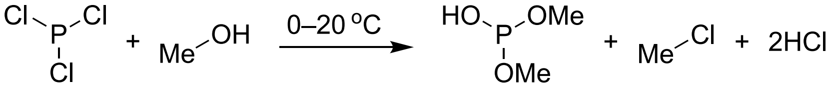
Figure 1. The structure of sarin

The methods for the sarin synthesis differ depending on the phosphorus-containing raw materials used. Usually, methylphosphonic acid dichloride and difluoride, and their mixture, as well as methylphosphonic acid diisopropyl ether, are used [5]. All these compounds can be obtained from phosphorus (III) chloride. Phosphites (phosphonates) are obtained as intermediates for the synthesis of dichloroanhydride of methylphosphonic acid. Thus, to obtain dimethyl phosphite, it is enough to mix phosphorus(III) chloride with anhydrous methanol at a temperature of 0–20 °C.

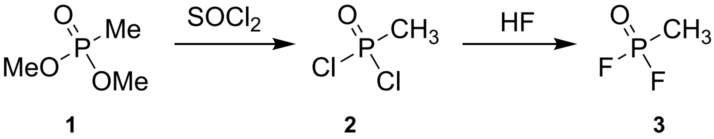
Further, to obtain the target product, the authors [5] used dimethyl methylphosphonate (**1**), which under the action of chlorinating agents ($SOCl_2$, $COCl_2$, PCl_5), turns into methylphosphonic acid dichloride (**2**), and then, after treatment with anhydrous hydrogen fluoride, into difluoride **3**. At the same time, an equimolar mixture of chloro- and fluoroderivatives is formed (**Scheme 2**).

The synthesis of dichloride without the stage of formation of phosphonates is also known – by the interaction of phosphorus trichloride with chloromethane and aluminum chloride in an organic solvent. The complex compound decomposes under the action of cold water, and preferably concentrated hydrochloric acid at -30 °C; as a result, dichloride is released from the solution. This method became the basis of the Kinner-Perrin reaction [6] and is used for the synthesis of many organophosphorus compounds. To obtain sarin, the reaction of the difluoride with isopropanol is carried out. Dichloride present in the reaction mixture also reacts with the formation of sarin. The yield of the final product is about 85% (**Scheme 3**).

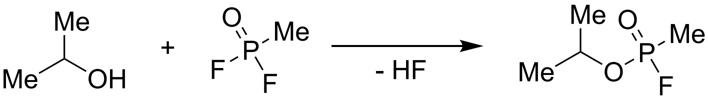
Sarin is hydrolyzed with the formation of methylphosphonic acid isopropyl ester and hydrogen fluoride. The rate of hydrolysis depends on the



Scheme 1. The scheme for the synthesis of dimethyl phosphite



Scheme 2. The scheme of forming methylphosphonic acid difluoroanhydride



Scheme 3. The sarin synthesis

pH of the environment. Thus, at pH 1.8, the half-hydrolysis period is 7.5 hours and 5 hours at pH 9. At a solution concentration of less than 14 mg L^{-1}, the half-hydrolysis period is 54 hours. At temperatures above 25 °C, the hydrolysis of sarin is capable of self-acceleration due to the catalytic effect of the products that are formed as a result of its decomposition. This is explained by the dissociation of the isopropyl ester obtained during the hydrolysis with the formation of H^+ ions. These ions can form hydrogen bonds with fluorine atoms, weakening their interaction with the phosphorus atom, thus contributing to the breaking of the F-P bond with the subsequent hydrolysis. The addition of any acids to the sarin solution leads to an increase in the rate of hydrolysis [7].

Soman is pinacolyl methylfluorophosphonate, an analog of sarin, but it is over 2.5 times more toxic than sarin. In addition, the stability of soman is somewhat higher than that of sarin. It is used as a mixture of four stereoisomers without separation (**Figure 2**).

The chemical properties of soman are similar to those of sarin, but its reactivity towards nucleophiles is somewhat reduced due to steric difficulties created by the larger pinacolyl-containing molecule [8]. The synthesis of soman is analogous to the synthesis of sarin and is carried out by the esterification of pinacoline alcohol with a mixture of methylphosphonic acid dichloride and difluoride (**Scheme 4**).

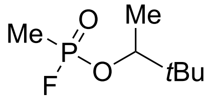


Figure 2. The structure of soman

VX is ethyl (ß-diisopropylaminoethylsulfanyl)methylphosphonate (**Figure 3**). Its toxicity is several times higher than sarin and soman. It poisons open water bodies for a very long period – up to 6 months. Its main warfare state is a coarse aerosol that poisons the ground layers of air and spreads in the direction of the wind to a depth of 5 to 20 km, affecting manpower through the respiratory system, exposed skin, and ordinary army uniforms. It also poisons the terrain, weapons, military equipment, and open reservoirs. VX is used by artillery, aviation (cassettes and pouring aviation devices), and as chemical explosives [2].

There are several variants of the VX synthesis, such as exploiting thione-thiol isomerization [3] (**Scheme 5**).

As can be seen from the given Scheme, the reaction includes the production of *O*-diethyl methylphosphonite from dichloro(methyl)phosphine, then the formation of a mixed ester (compound **QL**) from *O*-diethyl methylphosphonite and diisopropylaminoethanol, which reacts with sulfur followed by the thione-thiol rearrangement. Another version of the synthesis developed in Great Britain involves the synthesis of VX in one stage – by the reaction of sulfur, *O,O*-diethyl methylphosphonite, and diisopropylaminoethyl chloride in a benzene solution [9].

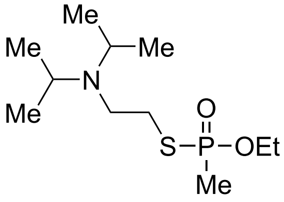
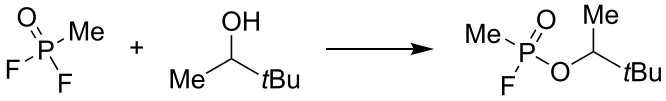
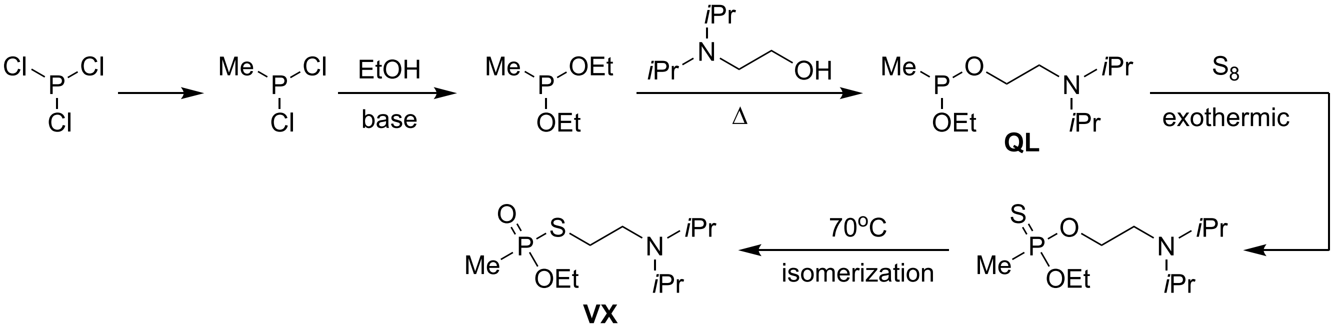


Figure 3. The structure of VX



Scheme 4. The synthetic scheme of soman



Scheme 5. The VX synthesis using the thione-thiol isomerization

■ Vesicants (blistering agents)

These include groups of sulfur- and arsenic-containing organic compounds used as a striking element of chemical weapons. In the human body, these compounds enter into the alkylation reaction with NH-groups of DNA nucleotides. This contributes to the formation of crosslinks between DNA chains leading to its inactivation. Mustard gas affects the human body in several ways: destruction of cell membranes, disruption of the carbohydrate metabolism, “tearing out” of nitrogenous bases from DNA and RNA [2].

Mustard gas (HD, iprit) is 2,2’-dichlorodiethyl thioether or 2,2’-dichlorodiethyl-sulfide (**Figure 4**). It is a chemical warfare poisonous substance with a vesicant effect, acting as cytotoxic poison, an alkylating agent.

Mustard gas can be obtained in different ways:

- from ethylene and sulfur chlorides, for example, S_2Cl_2 or SCl_2 (**Scheme 6**, *A*);
- from thiodiglycol and phosphorus trichloride (**Scheme 6**, *B*);
- from thiodiglycol and hydrochloric acid (**Scheme 6**, *C*);
- from vinyl chloride and hydrogen sulfide (**Scheme 6**, *A*).

The latter method is the most suitable due to the ease of its implementation. The reaction proceeds at room temperature (15–25 °C). Organic peroxides and ultraviolet radiation are used as reaction initiators. The reaction takes place within 10 minutes with a product yield of about 75%. When using 1-mercapto-2-chloroethane $HSCH_2CH_2Cl$ instead of hydrogen sulfide, the yield of the reaction approaches 100% [10].

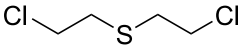


Figure 4. The structure of mustard gas

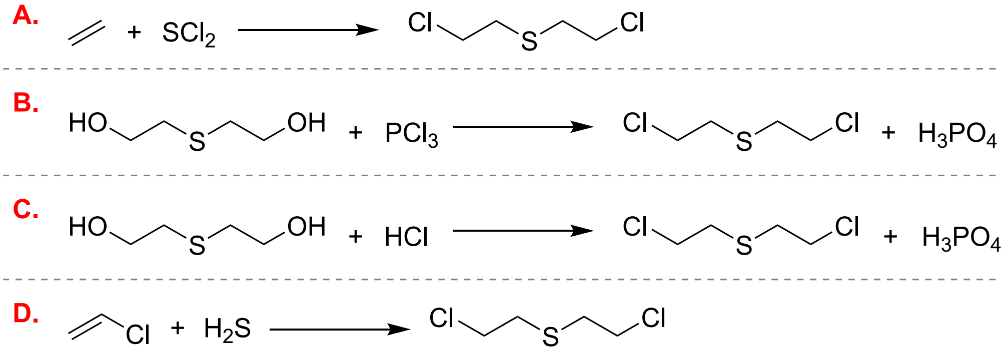
Mustard gas is a colorless liquid with the smell of garlic. Crude mustard is a dark brown, almost black liquid with an unpleasant odor. The melting point is 14.5 °C, the boiling point is 217 °C (with a partial decomposition), and the density is 1.280 g cm^{-3} (at 15 °C). Mustard gas easily dissolves in organic solvents – haloalkanes, benzene, chlorobenzene, as well as in vegetable and animal fats. Mustard reduces the surface tension of water, as a result of which it spreads over it in a thin layer like a film of oil [3].

Mustard gas reacts vigorously with chlorinating and oxidizing agents. At the same time, non-toxic products are formed, which allows such reactions to be used for its deactivation. With heavy metal salts, mustard gas forms complex colored compounds. This reaction underlies one of the methods of its detection. At normal temperature, mustard gas is a stable compound, but when heated above 170 °C, it decomposes with the formation of poisonous products of various compositions and an unpleasant odor [1].

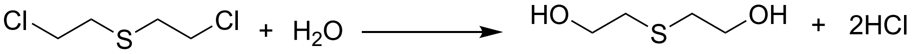
Mustard gas slowly hydrolyzes with the formation of hydrogen chloride and thiodiglycol (**Scheme 7**).

It is poorly soluble in water; therefore, it may not undergo hydrolysis for a long time. The hydrolysis process is accelerated by an increase in temperature and the presence of alkalis. It should be noted the important reaction of the mustard hydrolysis in the presence of urotropine since, in this case, one of the products is formaldehyde, which promotes wound healing [10] (**Scheme 8**).

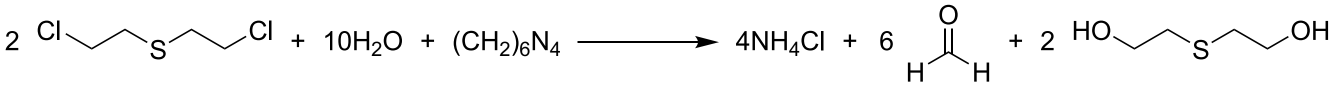
Further, as a result of the action of strong oxidizing agents (potassium permanganate, chromic and nitric, acids, hypochlorites) the sulfide



Scheme 6. Approaches to mustard gas



Scheme 7. The hydrolysis of mustard gas



Scheme 8. The urotropine-promoted hydrolysis of mustard gas

formed is oxidized to sulfoxide, and later to sulfone (**Scheme 9**).

Despite the fact that the oxidation products are also poisonous substances, this method is used for iprit deactivation because the products are crystalline low volatile substances and do not affect the skin [11].

Similar to other thioethers, mustard gas can form sulfonium compounds with metal salts. The resulting complexes have a characteristic color, so they are sometimes used in analytical chemistry [12]. Most often, reactions are carried out with halides of heavy metals: iodides and chlorides of copper, zinc, titanium, platinum and gold (**Scheme 10**).

Mustard gas has a devastating effect upon any way of penetration into the body. Damage to the mucous membranes of the eyes, nasopharynx, and upper respiratory tract can be seen even with small concentrations of mustard gas. There is a general poisoning of the organism at higher concentrations, along with local effects.

Lewisite (**Figure 5**) is a mixture of different isomers of chlorovinyldichloroarsine. It is a dark brown liquid with a sharp irritating odor. It is a warfare poisonous substance with a vesicant effect.

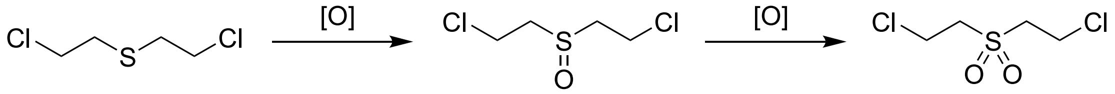
Lewisite is formed by adding acetylene to arsenic(III) chloride in the presence of catalysts – mercury dichloride or Lewis acids [12] (**Scheme 11**).

Lewisite, like other arsenic chlorides, hydrolyzes in water (**Scheme 12**, *A*). The reaction is accelerated in alkaline solutions. Lewisite also readily reacts with thiols to form the corresponding low-toxic substitution products. This underlies the use of 2,3-dimercaptopropanol in the treatment of lewisite lesions [2]. The interaction of lewisite with gaseous ammonia does not lead to a chlorine substitution reaction at the arsenic atom. In this case, a volatile adduct is formed, which decomposes when heated to 500–800 °C in an ammonia atmosphere with the formation of acetylene and elemental arsenic (**Scheme 12**, *B*). This reaction is proposed as an industrial method for the destruction of lewisite. When lewisite interacts with aqueous solutions of hypochlorites of alkali and alkaline earth metals, as well as with *N*-chloramine, lewisite undergoes the oxidative hydrolysis to chlorovinylarsenic acid (**Scheme 12**, *C*). The oxidation of lewisite with aqueous solutions of hypochlorite is one of the methods of its deactivation [3].

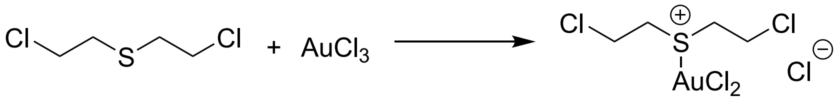
Lewisite is classified as a persistent poisonous substance. It is toxic to humans under any form of exposure, capable of penetrating through the materials of protective suits and gas masks. Lewisite also has an irritating effect on mucous membranes and respiratory organs.

■ Decontamination of warfare poison substances

Decontamination is the transformation of toxic chemicals into non-harmful products or their destruction or detoxification [13, 14]. Decontamination is a complex process that involves the participation of highly toxic chemicals with various



Scheme 9. The stepwise oxidation of mustard gas



Scheme 10. The interaction of mustard gas with metal salts

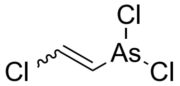
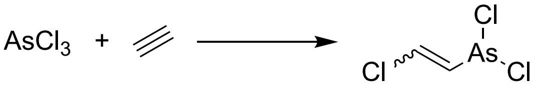
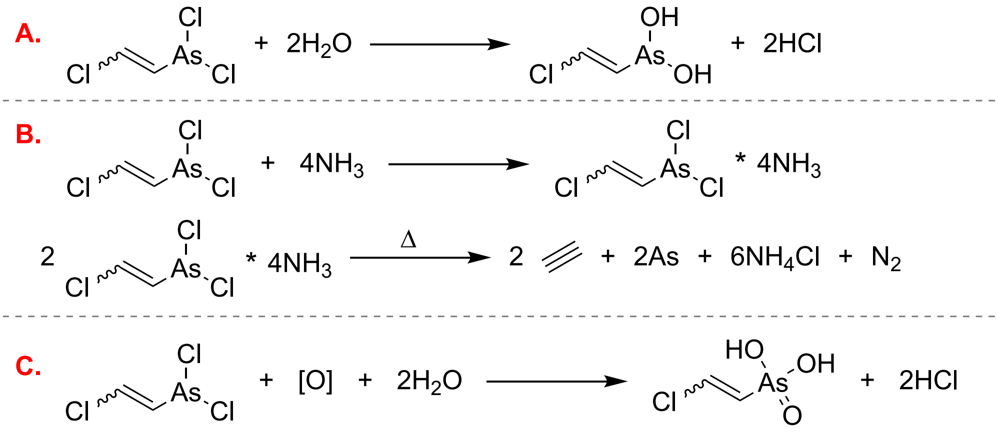


Figure 5. The structure of lewisite



Scheme 11. The synthesis of lewisite



Scheme 12. Reactions of lewisite

properties in difficult weather and other adverse conditions and a wide range of processed objects. For example, it can be the human skin and eyes, equipment with a metal / wooden / plastic surface, fields, etc. This result can be achieved by physical removal of agents or their chemical neutralization. Deactivation has the highest effect if it is carried out within 1 min after exposure to CWAs, but this is rarely possible [7].

Physical decontamination is simple and works universally, but is not as effective as chemical deactivation. It mainly involves the adsorption of a toxic chemical substance on adsorbents, such as fuller's earth, kaolin, talc, activated carbon, in extreme cases, it can be flour, sawdust or simply earth. It is possible to remove CWAs by spraying ordinary water or with soapy foam under pressure. The main disadvantage of the physical method is that the adsorbent or water used for decontamination must be subsequently neutralized and carefully disposed of.

Chemical decontamination transforms toxic poisons into harmless products that can be handled safely. Chemical reactions that are usually used in chemical decontamination methods are either nucleophilic substitution or oxidation processes [15, 16]. Usually, skin disinfectants are 0.5% sodium hypochlorite solution or household bleach, as well as chloramines. Ready-made compositions have been developed for the decontamination of equipment and various surfaces in the field, such as the DS2 preparation. It is a composition of sodium hydroxide (2%), monomethyl ethylene glycol ether (28%), and diethylenetriamine (70%). The active ingredient in this preparation is diethylenetriamine, which acts as a nucleophile and hydrolyzes CWAs into non-toxic products. Factors that determine the effectiveness of decontamination are the time of contamination, temperature, the density of contamination and the decontamination environment, the nature of CWAs and the nature of decontaminating substances. The requirements for an ideal decontamination are the speed of action, efficiency, harmlessness to humans, lack of corrosion, stability during long-term storage and the ability to rinse with water. Recently, many studies have appeared on the ways of creating decontamination systems and specific drugs, strategies for decontamination of CWAs. Therefore, it is important to consider specific works in this area.

Metal-organic framework functionalized materials for the disposal of warfare poisonous substances

One of the methods of decontamination of warfare poisons is the use of metal-organic framework compounds, on which reactions of the CWAs transformation into low-toxic products take place. MOFs are porous crystalline structures that have many areas of application and can be used as adsorbents, catalysts, and a gas storage [3, 16–25]. MOFs contain metal or metal-oxide nodes connected by organic linkers, and thus form a crystalline structure. They can be 1-, 2-, or 3-dimensional, it is the latter that are of particular interest as they have the property of forming highly porous networks.

The MOFs structure can be easily varied by changing the metal node or organic linker to achieve the desired chemical and physical properties. The most effective are zirconium-based MOFs, which differ in the pore size and which show a significant thermal and chemical stability.

Figure 6 shows organic compounds used as linkers for the formation of metal-organic frameworks of various structures. In the work mentioned above [3], the rate of hydrolysis for various CWAs imitators and four zirconium-based

MOFs was studied under conditions of the heterogeneous catalysis, and the hydrolysis rates of these imitators were compared with the rates of CWAs under the same conditions [25, 26]. As imitators, organophosphorus compounds were used, their structure was similar to real CWAs. These are dimethyl *p*-nitrophenyl phosphate (DMNP, paraxon), dimethyl chlorophosphate (DMCP), diisopropyl fluorophosphate (DFP). **Table 1** presents data on the CWAs hydrolysis rate and their imitators in *N*-ethylmorpholine.

The data in **Table 1** indicate that the hydrolysis of sarin and imitators – DMCP and DMNP – takes place most efficiently. It follows from these data that an ideal imitator should have physical and chemical properties that are similar to the CWAs being modeled (DMCP is closer to sarin, DMNP and DFP is closer to soman by their activities). Only then it is possible to more accurately predict the behavior of CWAs during their deactivation in the field.

The development of nanostructured Zr-organic framework compounds with 140 nm in size and a surface modified with oleic acid, as well as high dispersity in solution is interesting [27]. The characteristics of the catalytic degradation of both nerve agents (soman and VX) and vesicants (mustard gas) CWAs were studied. The hydrolysis rate of somane was found to be more than 3 times higher than under non-catalytic conditions, and the conversion for somane and VX reached 98 and 96%, respectively, in 3 h. These experimental data were supplemented by the density functional theory calculations, which clarified the degradation mechanism for the first time and estimated the associated energy barriers.

Fiber mats were produced by integrating a large number of metal-organic framework nanoparticles (71% by weight) into a polyacrylonitrile polymer using the electrospinning method. The corresponding composite has been shown to have a high dispersion of the polymer matrix, which leads to a thin and uniform thickness of the fibers [28, 29]. Notably, these fiber mats demonstrated excellent reusability and resistance to the VX degradation after five rinses with water. It has been shown that these materials can be produced on a large scale, which is of paramount importance for future commercialization. They can be considered as detoxification membranes and protective clothing and can be incorporated into masks to filter toxic gases for both military and civilian protective purposes.

Also noteworthy is the highly efficient self-cleaning filter presented in [30], which consists of zirconium hydroxide $[Zr(OH)_4]$ immobilized *in situ* on the surface of an activated carbon fabric $[Zr(OH)_4$-W-ACF$]$ applied to destroy CWA. Here, there is a synergistic effect of the large surface area of W-ACF, the high dispersion of CWAs, and the significant reactivity of $[Zr(OH)_4]$. The kinetics of CWAs degradation *in situ* over $Zr(OH)_4$-W-ACF was studied, and a first-order reaction was observed. The rate constant was equal to 0.244 min^{-1} and 2.31×10^{-2} min^{-1} for sarin and soman, respectively [31]. To demonstrate the practical application of this work, a suitable material for a protective suit was produced that met the criteria of breathability and strength. This opens up

Table 1. The rates of hydrolysis of CWAs and imitators in different MOFs in *N*-ethylmorpholine solutions (pH 10)

CWAs/ imitator	The hydrolysis half-life (min)			
	MOF-1	MOF-2	MOF-3	MOF-4
Soman	31	41	42	31
Sarin	2	6	7	7
DMNP (paraxon)	17	19	17	17
DFP	41	37	85	30
DMCP	< 1	< 1	< 1	< 1

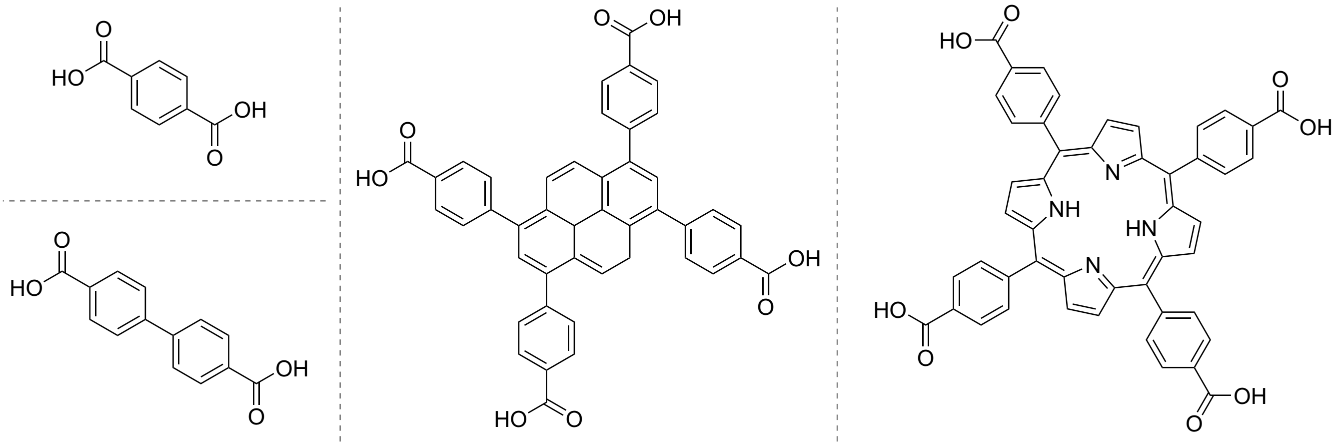


Figure 6. Organic compounds used as linkers for the formation of metal-organic frameworks of various structures

opportunities in the field of protective clothing against CWAs and, thus, can find a variety of applications in the defense and environmental sectors [32].

Attention was also drawn to the work on the use of amorphous zirconium hydroxide, which revealed its high reactivity in the processes of decomposition of CWAs [33]. Amorphous $Zr(OH)_4$ films with a thickness of 50 nm were obtained on metal substrates of arbitrary shape by the method of the cathode electrodeposition of $ZrOCl_2$ in an aqueous solution with the nanoscale control of the film thickness. The films have the rms roughness ~6-8 nm, nano-sized pores ~2.4 nm, and a high specific surface area of 132 $m^2\ g^{-1}$. They are easily scalable and may be more useful for on-site decontamination of CWAs [34]. The reactivity of these films was tested for the organophosphorus series of CWAs imitators. They showed a high rate of hydrolysis of toxic adsorbates on $Zr(OH)_4$. This is explained by a defective amorphous structure with a large surface area and a high density of uncoordinated Zr atoms (Lewis acid) and hydroxyl groups (Lewis base).

An important problem in the decontamination of CWAs is the use of deactivation agents at low temperatures. Under these conditions, CWAs change their physical properties, such as viscosity and the evaporation rate, but, at the same time, retain their toxic effect. This leads to a change in the kinetics and reaction mechanism of the CWAs degradation. For example, in work [35], the authors studied the effectiveness of the deactivation of mustard gas, soman, VX, as well as imitators, such as 2-chlorodiethyl sulfide and trimethylphosphonate, using a material made of titanium dioxide nanoparticles doped with Zn^{2+} and Ge^{4+} (Zn-Ge-TiO_2). With the aim of practical use of the powdered material and increasing the efficiency of low-temperature deactivation of CWAs, a new product was prepared by suspending Zn-Ge-TiO_2 in a hydrofluoroether. The data obtained show that the Zn (5.28 wt.%)-Ge (1.48 wt.%)-TiO_2 suspension exhibits the best photocatalytic characteristics. Compared to undoped TiO_2, the sample prepared has an unchanged crystal structure and a reduced average pore diameter (2.86 nm), which is accompanied by an increase in the specific surface area (424.9 $m^2\ g^{-1}$), crystallite size (5.8 nm) and pore volume (0.29 $cm^3\ g^{-1}$). Under artificial solar irradiation and at a temperature of -30 °C for 120 minutes, the efficiency of decomposition of mustard gas, soman and VX in suspension exceeded 99.95% [36]. This indicates the prospects of using such material for decontamination of CWAs in conditions of subzero temperatures.

Work [37] is close to the above-mentioned studies where the data on the reaction of the decomposition of the imitator of a warfare poison – dimethyl methyl phosphonate (DMMP) on Au/TiO_2 nanoparticles and pure TiO_2 are given. It has been found that small (< 5 nm) Au particles on the surface of TiO_2 activate this material in the direction of the oxidative decomposition of DMMP, in contrast to pure TiO_2, which is an effective sorbent of this imitator. At the same time, the decomposition of the imitator molecule is still observed, albeit insignificant. A direct comparison of the chemical composition of the samples showed that two mechanisms could be responsible for the catalytic activity of Au nanoparticles deposited on TiO_2 [38]. One mechanism is implemented in anaerobic conditions when DMMP in the vapor phase reacts during adsorption with the formation of various organic products and adsorbed CO. The second mechanism involves the charge transfer from Au particles to oxygen in the gas phase, which subsequently reacts with DMMP physically adsorbed on the TiO_2 material sites. This chemical process leads to the complete oxidation of DMMP with the release of CO_2 from the surface of the particles.

It should be noted that, despite the rather successful studies on the use of metal-organic framework functionalized materials (MOFs) mentioned above, they demonstrated relatively slow kinetics of capture and destruction of nerve agent and their imitators. The key issue with using MOFs for the hydrolysis of chemical substances and warfare poisons is that their framework pores are too small to let the corresponding chemical compounds into their internal space where the majority of potential active centers are located [39]. In other words, almost all the sorption capacity and the resulting hydrolysis activity were limited to the areas on the outside of the MOF crystallites (probably on defective centers with a missing linker). A related problem with known MOFs is that the most active centers for the reaction to proceed are already occupied by linkers. In order to overcome these difficulties, the authors in research [40] showed the effectiveness of using zirconium-based MOFs consisting of eight (and not twelve, as in most cases) connected nodes Zr_6 and 1,3,6,8(*p*-benzoate) pyrene linkers. The resulting structure has very wide (31 Å) pores and smaller pores (10 Å). Such wide pores allow bulky phosphoric acid ester molecules to penetrate into the MOFs structure, including a large internal space. The authors demonstrated that such MOFs were highly active for the destruction of imitators of the nerve agents of sarin and soman.

Potential applications of MOFs-based catalysts include both detoxication of CWAs stocks and other toxic substances, as well as equipment and people protection systems [41]. Although some MOFs have shown impressive results in laboratory studies, there are still several challenges that need to be addressed before they can be scaled up and used in practice. For example, when studying the hydrolysis of nerve agents using MOFs, a buffer solution of *N*-ethylmorpholine is usually added to ensure their rapid decomposition. However, for practical use in the real conditions of liquidation of CWAs stocks, such a system is not suitable from the point of view of both its technical use and safety. One of the possible solutions to this problem is the use of heterogeneous buffers. It was reported [42] about the use of polyethyleneimine as a heterogeneous (solid) buffer in a system for the hydrolysis of nerve agents and their imitators. Thus, for the hydrolysis reaction in the system consisting of a solid mixture of polyethyleneimine with zirconium MOFs, the decomposition of sarin, soman, and dimethyl-*p*-nitrophenyl phosphate occurs more efficiently than when using a buffer solution of *N*-ethylmorpholine. Finally, an important practical task is the effective integration of these or similar solid catalytic systems with clothing and filters to protect the human body.

■ Conclusions

The material presented in this review shows the importance of general knowledge about the physical and chemical properties of warfare poisons, the rate of their decomposition, and the advantages and disadvantages of certain available technologies for their application. Although many different methods and products have been developed to date, it is unlikely that only one technology will be applicable to all situations. Many factors must be taken into account here, such as the aggregate state of CWAs, climatic conditions (temperature, humidity), and characteristics of the surface being treated (non-porous and porous materials, electronics, or human skin). This should also include such factors as the size and complexity of the contaminated territory or structures under consideration, their possible further use, the expected impact on people, and the availability of resources. The main processes of CWAs decomposition outlined above include hydrolysis, oxidation, photolysis, and microbiological methods. The use of these reactions, both individually and in various combinations, makes it possible to create unique formulations and technologies that allow for quick and effective splitting of both warfare poisons and various other ecotoxicants. It should be noted that when developing CWA decontamination systems, the corresponding chemical compounds, and technologies, it is important to adhere to the principles of “green chemistry”, which are an integral part of modern chemical science, from the point of view of a responsible approach and sustainable development. Ensuring high reaction rates, bringing the process to the formation of decomposition products that are safe for nature and humans, and their subsequent complete disposal should form the basis of methods and technologies for the decontamination of chemical warfare agents.

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