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The Cu- and Zn-complex-catalyzed methanolysis of the chemical warfare nerve agents soman, sarin, and VX

Les complexes de Cu et Zn catalysent la méthanolyse des agents neurotoxiques de guerre chimique soman, sarin et VX

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ABSTRACT

The catalytic methanolysis of the chemical warfare nerve agents soman, sarin, and VX was investigated by using Cu or Zn complexes. Although VX withstood decontamination, the decomposition yield being around 96%, the soman and sarin deposited on different surfaces were almost fully destroyed under ambient conditions. The catalytic tests performed on a wide range of contaminated surfaces confirm the activity of the investigated catalytic systems, these complexes being suitable, from an economical point of view, for use in the formulation of a possible decomposition kit with military or civilian applicability.

Mots-clés:
Agents de guerre chimique
Décontamination catalytique
Méthanolyse
Complexe du cuivre
Complexe du zinc

RÉSUMÉ

La méthanolyse catalytique des agents neurotoxiques de guerre chimique soman, sarin et VX a été étudiée en utilisant des complexes du Cu ou du Zn. Bien que VX résiste à la décontamination, le rendement de décomposition étant d'environ 96%, le soman et le sarin déposés sur différentes surfaces ont été presque entièrement détruits dans les conditions ambiantes. Les essais catalytiques effectués sur une large gamme de surfaces contaminées confirment l'activité des systèmes catalytiques étudiés, ces complexes étant appropriés d'un point de vue économique pour être utilisés dans la formulation d'un éventuel kit de décomposition militaire ou civil.

1. Introduction

The chemical warfare agents (CWAs) appear to be the most toxic and deadly chemical compounds that mankind

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has ever created, their main purpose being to temporarily or permanently incapacitate one of the warring parties involved in an armed conflict [1]. On the basis of their chemical structure, CWAs are currently divided into three major groups as G-series (soman, sarin, and tabun), V-series (VX and Russian-VX), and H-series (sulfur/nitrogen mustard) agents. Among them, the most toxic CWAs are in the first two series, known as chemical warfare nerve agents, as their main role is to inactivate the enzyme acetylcholinesterase from the central nervous system [2]. Their decontamination is desirable both in storage sites and on the battlefield.

Although most of the worldwide stocks of CWAs are currently destroyed, the deteriorating conditions in Syria and the corresponding political uncertainty are raising concerns with regard to the security of chemical weapon stocks present on its territory, but also to the possibility that the parties of the civil war might use CWAs against each other. What is extremely worrying is the fact that these suspicions have already been confirmed [3]. As long as the conflict is still present, it could easily be argued that the process of bringing the respective region to "chemical quiet" and peace is, unfortunately, undefined in terms of time. Besides this, the recent terroristic attacks in Europe show just how fragile our security against such coordinated events is, and how exposed we are in the case of a deliberate release of real CWAs or their precursors and simulants [4]. Such events would require the use of a decontamination system able to extract and destroy the toxic chemicals from building materials, vehicles, or valuable sensitive equipment.

Eliminating the hazard of these toxic chemical agents requires fast and easily applicable decontamination systems, which should ideally be noncorrosive and produce minimal environmental contamination issues [5]. The literature in the field consists of several reviews and studies comprising the methods currently used nowadays in the decontamination of CWAs [6–11]. Of these, the most widely used methods in the decontamination of chemical warfare nerve agents are hydrolysis and oxidation [8]. G-series agents are commonly decontaminated through aqueous hydrolysis. However, in terms of decontamination efficiency, hydrolysis is not suitable for other chemical warfare nerve agents, such as VX or the Russian-VX, both toxic agents producing hydrolytically stable thioic acid byproducts during this process [6]. Moreover, as the CWAs are commonly combined with a polymer to better adhere to surfaces, they become minimally soluble in water. Another disadvantage of the aqueous hydrolysis is that this reaction is not catalytic, thus stoichiometric amounts of reactants are required [9]. To prevent these problems, base-catalyzed hydrolysis at an increased temperature is nowadays used on a large scale to obtain high degrees of decontamination [12,13].

Although, from a practical point of view, the hydrolysis of chemical warfare nerve agents is seen as an appropriate way for their decomposition, the hydrolyzate compounds need to be further exposed to a secondary step, until they become environmentally benign. Besides this, all the steps involve the use of increased temperatures and high amounts of water and chemicals, whereas the decomposition products should be disposed of and treated as hazardous waste. Such treatment procedures reduce the number of possible on-field applications, whereas the decontamination of sensitive equipment or even human skin is fundamentally impractical.

An alternative method for the destruction of chemical warfare nerve agents, which would eliminate the aforementioned drawbacks, has already been developed and its efficiency was proved in the case of several chemical warfare nerve agent simulants [14–17]. This method uses a catalytic system containing La^{3+} ions capable of accelerating the methanolysis of paraoxon by a factor of up to 10^9 [18,19]. Methanolysis possesses several fundamental advantages over hydrolysis. For instance, chemical warfare nerve agents react much faster in methanol than in water, as they are more soluble in lower polarity solvents such as methanol, which are presumed to facilitate a medium effect that involves better pre-equilibrium binding of the CWA molecule and the metal ion [13,20–23]. More than that, the hydrolysis of G-series agents leads to the formation of phosphoric acids, which strongly inhibit the catalysis through the anionic products that have appeared alongside their dissociation process. At the same time, during alcoholysis, this inhibition process does not occur as only neutral phosphorus esters are produced [24]. It is well documented that part of the reaction products (around 10%–25%) obtained through the hydrolysis of various V-agent simulants under basic conditions are induced by the undesired cleavage of the P–OEt bonds of the simulant molecules. As these products are anionic, they will resist to further base-promoted hydrolysis [15]. Fortunately, the methanolysis of the same toxic compounds proceeds with the formation of large amount of desired cleavage P–SR products (>90%), which, as they are neutral compounds, could be further methanolyzed [25].

Recently, our group has reported the use of such a catalytic system in the methanolysis of real CWAs, which, in liaison with heterogeneous photocatalysis, lead to the complete destruction of chemical warfare nerve agents in just 1 min of exposure to visible light [26]. Continuing this research line, herein we are reporting the use of Cu or Zn complexes in the methanolysis of the chemical warfare nerve agents soman, sarin, and VX.

2. Experimental section

2.1. Materials

Several organic and inorganic materials were used in this study: sodium methoxide (25 wt % in methanol), 1,5,9-triazacyclododecane (97%), tetrabutylammonium hydroxide (56% in water), $Zn(OTf)_2$ (98%), $Cu(OTf)_2$ (98%), anhydrous methanol (99.9%), and *N*-ethylmorpholine (99%), all obtained from Sigma–Aldrich and used as received. The chemical warfare nerve agents soman (3,3-dimethylbutan-2-yl methylphosphonofluoridate), sarin ((*RS*)-propan-2-yl methylphosphonofluoridate), and VX (ethyl ({2-[bis(propan-2-yl)amino]ethyl}sulfanyl)(methyl)phosphinate) were freshly prepared, stored, and used by trained chemical, biological, radiological, and nuclear defense (CBRN) personnel, following several synthetic procedures typically used in these cases [27].

2.2. Catalysts preparation

The catalysts have been prepared according to a synthetic procedure previously reported in Ref. [20]. Thus, stock solutions of $Zn(OTf)_2$, $Cu(OTf)_2$, tetrabutylammonium hydroxide, 1,5,9-triazacyclododecane, and sodium methoxide have been prepared to a concentration of 50 mM in anhydrous methanol. The catalysts were generated in situ by adding measured amounts of the metal triflate, 1,5,9-triazacyclododecane, and tetrabutylammonium hydroxide (for the case of Zn catalyst) stock solutions to anhydrous methanol to form a final volume of 5 mL, which will contain 50×10^{-6} mol of catalyst. For instance, during the preparation of Cu catalyst stock solution, 18.10 mg of $Cu(OTf)_2$ and 8.55 mg of 1,5,9-triazacyclododecane were used. For the preparation of Zn catalyst stock solution, besides the use of 18.17 mg $Zn(OTf)_2$ and 8.55 mg of 1,5,9-triazacyclododecane, tetrabutylammonium hydroxide was added and the resulted solution was dried over anhydrous $MgSO_4$ to remove any amounts of water the solution might contain. Later on, the pH of the final solutions is adjusted by dropping a non-inhibitory buffering agent, *N*-ethylmorpholine, to different pH values of 9.10 for Zn and 8.75 for Cu catalyst. The pH measurements were performed under nonaqueous conditions.

2.3. Catalytic tests

In this study, the chemical warfare nerve agent decomposition reactions were evaluated using two separate catalytic tests. In the first approach, the decompositions have been performed in 1.8 mL closed vials, in which 50 μL of toxic compound is added to 1 mL of anhydrous methanol. To perform the decomposition reaction 20 μL of decontamination stock solution is added in the vial, so that the final reaction mixture contains 2×10^{-7} mol of catalyst.

The reaction's evolution was followed by taking samples after 2, 5, 30, 60, and 120 min of exposure to the decontamination solution, concentrating the samples, and analyzing them using a Trace GC Ultra DSQ II gas chromatograph coupled with a mass spectrometer from Thermo Scientific, working with helium as a carrier gas and equipped with TR-5MS column and MS Quadrupole detector. For all reactions, the carbon mass balance was found to be higher than 98%.

In another approach, the decomposition reaction of the chosen CWA was realized by putting in contact, for a short period of time (5 min), 5 μL of toxic compound with 200 μL of decontamination solution onto different surfaces, such as borosilicate glass, poly(methyl methacrylate) (PMMA), unpainted and painted wood, unpainted and painted steel plates, nitrile rubber, and bromobutyl rubber.

The typical procedure comprises the spiking of the toxic compound onto 1×1 cm^2 of the aforementioned surfaces, which were previously cleaned and well dried. In all cases, the contaminated surfaces are then covered with glass Petri dishes. Under these conditions, the evaporation of both methanol and toxic compounds (especially in the case of sarin, which is the most volatile CWA from our series) is minimized. The toxic compound is left to act for 30 min and then the contaminated surfaces are decontaminated by using solutions (200 μL 10 mM) of freshly prepared metal (Cu or Zn) complex catalyst. The reaction's evolution was followed by extracting the toxic compound with dichloromethane after 5 min of exposure, concentrating the resulting extracts, and analyzing them by using a gas chromatograph. The gas chromatograph used in this study was a Clarus 600GC from Perkin–Elmer coupled with a thermal desorber Turbo matrix 300 and equipped with TR-5MS column and flame ionization detector (FID) with a sensitivity >0.015 C/°C. Helium was used as carrier gas.

In both cases, the chromatographic analysis of the samples has been done only after silylation with BSTFA (*N*,*O*-bis(trimethylsilyl)trifluoroacetamide) and TMCS (trimethylchlorosilane) at 60 °C for 30 min. We must highlight that, under our experimental conditions, the nerve agents were not degraded in the control samples without the presence of the catalysts, in both cases.

For a better evaluation of the catalytic performance, in all cases, the decomposition yields and selectivities were calculated and expressed in percentages. The decomposition yield (or conversion) was calculated as the percentage of toxic compound consumed from the initial quantity after performing the reaction, whereas the selectivity was expressed as the conversion of the CWA to the desirable reaction product divided by the overall conversion of the toxic compound.

Caution: *The manipulation of any type of CWA might cause severe injuries and/or death and is strictly regulated under Chemical Weapons Conventions agreements and its production, storage, and use require special authorization. In light of this, all reactions were performed by trained personal using safety procedures in a closed system or in a hood under good ventilation.*

3. Results and discussion

As already specified in Section 2, the catalytic tests comprise the performance of the decontamination procedure in two different ways: the first approach delivering valuable information regarding the possible mechanism of decon action, and the second one is much more applicable, proving the effectiveness of the transition metal-ion–catalyzed methanolysis process in the decontamination of different surfaces.

The CWA decomposition results obtained through the first approach are presented in Table 1. As can be observed, the degradation of the studied nerve agents through methanolysis in the presence of Cu or Zn complex catalysts led to good results (Table 1, entries 1 and 2). It is clearly seen that VX, with lower solubility in the reaction media, is the most difficult CWA to destroy from the series of toxic compounds tested in this study, whereas the resistance to catalyzed methanolysis of the others is smaller.

The experimental data obtained in solution were plotted versus time and presented in Fig. 1. It can be observed that the decomposition reaction proceeded rapidly and efficiently and only 5 min were required, through Cu-ion–catalyzed methanolysis, to destroy 50% of VX and more than 80% of the total amount of soman and sarin, whereas the Zn complex catalyst shows less activity, being able to reach a decomposition yield of almost 40% for VX and just 65% in

Table 1
The catalytic performance of the investigated catalytic systems.

Entry	Substrates	Skin contact LD_{50} (mg kg^{-1})[a]	Decomposition yield (%)[b]		TOF (h^{-1})[c]	
			Cu complex	Zn complex	Cu complex	Zn complex
1	Sarin	2.40	99	96	970	930
2	Soman	0.70	98	95	690	670
3	VX	0.14	61	58	290	270

[a] The median lethal dose (LD_{50}) for humans during skin contact with the toxic compound was estimated according to Ref. [28].
[b] The decontamination rate was calculated as the percentage of toxic compound consumed from the initial quantity after performing the reaction. An estimated GC/MS analysis error of ±1% was taken into account. The reaction time was 120 min in all cases.
[c] The turnover frequency numbers (TOF) were calculated as a ratio between moles of converted substrate and moles of used catalyst per hour.

the case of soman and sarin. The reaction rates after this interval start to decrease progressively, the obtained decomposition yields after 60 min of reaction being slightly lower than that obtained after 120 min, indicating that an inactivation effect of the catalysts appears.

The kinetics of the chemical warfare nerve agents' catalytic decomposition reactions were evaluated by plotting the experimental data versus the reaction time presuming that the methanolysis follows first-order kinetics (Fig. 2). The observed rate constants of soman methanolysis over Cu- and Zn-based catalysts obtained from the graph slopes (see Fig. 2a) were found to be 1.06×10^{-3} and 4.02×10^{-3} s^{-1}, respectively. Sarin methanolysis is characterized by slower reaction rates, the rate constants being in this case 4.62×10^{-4} and 3.64×10^{-4} s^{-1}, when Cu- and Zn-based catalysts were used, respectively (see Fig. 2b). From all studied CWAs, VX is the most difficult substrate to destroy, the rate constants of its methanolysis being determined only for the first 5 min of reaction, after this interval the reaction is too slow and the reaction mechanism too complicated

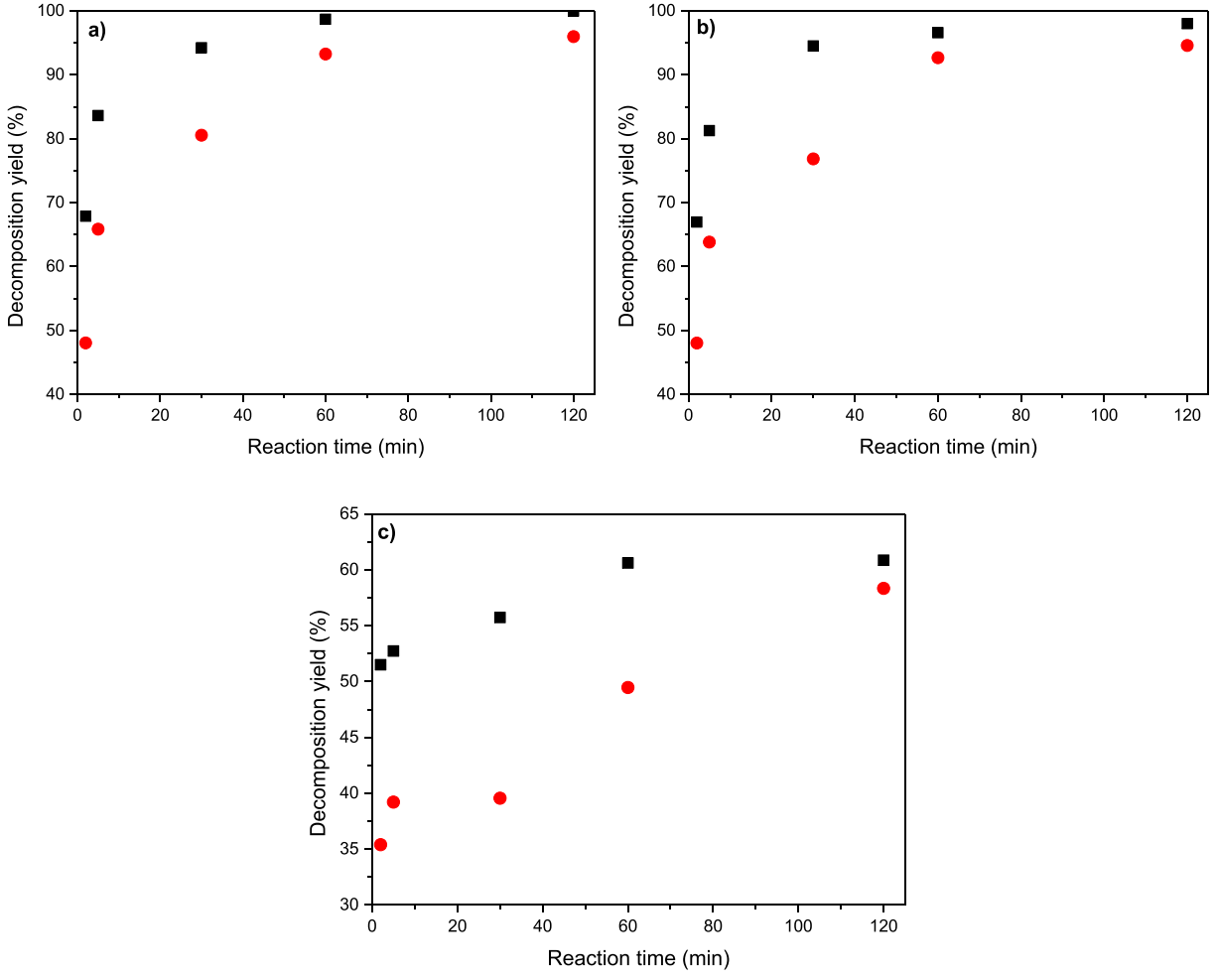


Fig. 1. Efficiency of decontamination of (a) soman, (b) sarin, and (c) VX through methanolysis reaction catalyzed by Cu (■) and Zn (●) complexes.

to estimate the reaction kinetics. However, in this situation, the reaction rate constants observed in the case of Cu- and Zn-based catalysts were found to be 6.03×10^{-3} and 3.64×10^{-3} s^{-1}, respectively (see Fig. 2c).

To explain this behavior, the mechanistic aspects of the decomposition process were evaluated based on the main reaction products derived from the catalyzed methanolysis, which were identified through GC/MS analysis. The reaction mechanism was proposed and drawn in Scheme 1.

As can be observed, the decomposition process proceeded with the elimination of hydrofluoric acid and the formation of methyl pinacolyl methylphosphonate (**2**) and isopropyl methyl methylphosphonate (**4**) as solely reaction products derived from soman and sarin, respectively. For the case of both toxic compounds, no other byproducts were identified, even after 120 min of reaction time, independently of the type of catalyst we were using in this study. As the carbon mass balance of these reactions is nearly 99%, we could conclude that the reactants are almost fully converted into products, and the selectivities for the formation of reaction products (**2**) and (**4**) were 100%.

On the basis of the byproducts detected through GC/MS analysis, the VX decomposition process occurs only through P–SR (R represents 2(diisopropylamino)ethyl) bond cleavage, first with the formation of ethyl methyl methylphosphonate (**6**) and 2-(*N*,*N*-diisopropylamino) ethanethiol (**7**), which later conducts to the formation of bis(diisopropylaminoethyl)disulfide (**8**), bis(2-*N*,*N*-diisopropylaminoethyl)sulfide (**9**), and even more complex byproducts, such as 1-[(2-diisopropylamino)ethylthio]-2-[(2-diisopropylamino)ethyldithioethane (**10**). The formation of a large amount of such byproducts changes the solution composition and thus affects the catalytic activity of Cu or Zn complexes, probably because of the blocking of the metal centers by means of weak reversible metal–S links. The carbon mass balance of VX-catalyzed methanolysis was found to be almost 98%. Depending on the type of the catalyst we used, only around 60% of VX was decomposed

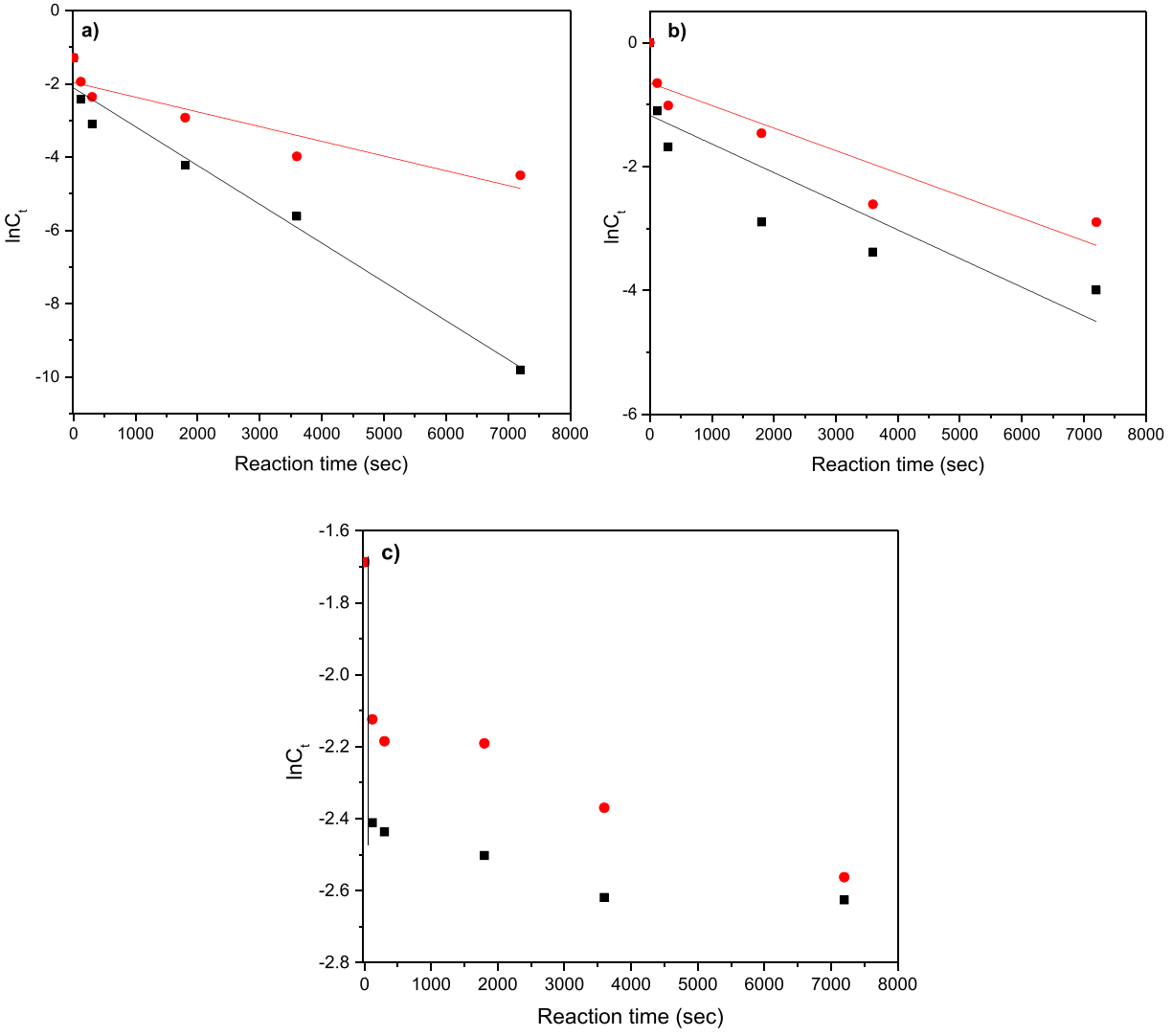
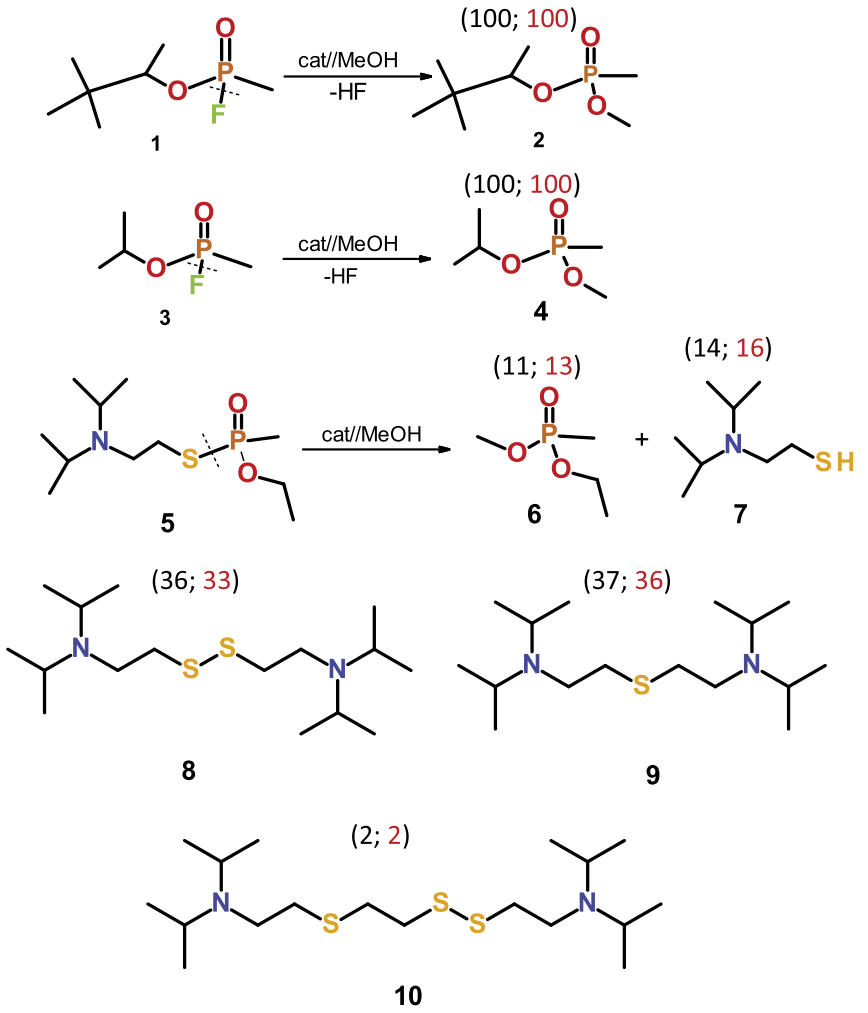


Fig. 2. Kinetics of decontamination of (a) soman, (b) sarin, and (c) VX through methanolysis reaction catalyzed by Cu (■) and Zn (●) complexes.



Scheme 1. The proposed mechanism of the Cu- and Zn-ion–catalyzed methanolysis of sarin, soman, and VX. The number from the bracket represents the selectivities for each reaction product calculated after 120 min of methanolysis in the presence of Cu- (black) and Zn-based (red) catalysts.

in 2 h of reaction (see Table 1, entry 3) and a large distribution of selectivities for the formation of the reaction products (**6**)–(**10**) was found. These values are depicted in Scheme 1.

Table 2
The catalytic performance of the Cu- or Zn-based systems over different surfaces.

Surface	Decomposition yield (%)[a]					
	Cu complex			Zn complex		
	Sarin	Soman	VX	Sarin	Soman	VX
Borosilicate glass	100	100	99	100	100	99
PMMA	100	100	99	100	100	99
Unpainted wood	100	100	99	100	100	99
Painted wood	96	96	95	96	96	96
Unpainted steel	100	100	99	100	100	99
Painted steel	95	96	94	95	97	94
Nitrile rubber	100	100	99	100	100	99
Bromobutyl rubber	100	100	99	100	100	99

[a] The decontamination rate was calculated as the percentage of toxic compound consumed from the initial quantity after performing the reaction. An estimated GC/MS analysis error of ±1% was taken into account. The reaction time was 5 min in all cases.

Although, in the case of VX, the PeOEt bond cleavage typically taking place in small proportions (around 13%) during alkaline hydrolysis under basic conditions leads to the formation of an extremely toxic product, like *S*-2-(diisopropylaminoethyl) methylphosphonothioic acid (EA2192) [9], in this case no such compound was identified under our reaction conditions. As already specified, this is among the most important advantages of methanolysis over the more known and used aqueous hydrolysis process, the toxicity of the VX decomposition products obtained in this study being far lower than that of EA2192.

On the basis of the results presented above, the second step was to prove the effectiveness of the transition metal-ion–catalyzed methanolysis process in the decontamination of different surfaces, such as borosilicate glass, Plexiglas, unpainted and painted wood, unpainted and painted steel plates, nitrile rubber, and bromobutyl rubber. These surfaces were chosen to simulate real situations that may arise during terroristic/accidental spills of CWA (see Table 2).

After the contamination procedure presented in Section 2, the exposed surfaces were attended for at least 30 min to the CWA action and then decontaminated with Cu or Zn

complex catalysts. Independently of the catalyst used in this study, in almost all cases, the decomposition yields were more than 99%, whereas over the painted surfaces only around 96% was reached. Although the reached decontamination yield in the case of painted surfaces was still high, it is clear that the thickening effect affects the rate of decontamination because of the fact that the interacted CWAs are less soluble in methanol.

4. Conclusions

This study completes the current knowledge regarding the application of an easy-to-use chemical method in the destruction of CWA, proving that extremely toxic chemical warfare nerve agents can be efficiently destroyed by catalytic methanolysis. Although at high concentration VX withstood decontamination, the decomposition yield being around 60%, soman and sarin were almost fully destroyed in almost 30 min. The catalytic tests performed on a wide range of contaminated surfaces confirmed the activity of the investigated catalytic systems, these complexes being suitable, from an economical point of view, for use in the formulation of a possible decomposition kit with military or civilian applicability.

As far as we are aware, this is the first use of Cu or Zn complex–catalyzed alcoholysis of real chemical warfare nerve agents, the data obtained in this study proving that the methanolysis of these deadly compounds is an effective strategy for CWA decontamination, which could be applied at a large scale, as it does not suffer from the known disadvantages of base-catalyzed hydrolysis under highly basic conditions.

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