Efficient heterogeneous and environmentally friendly degradation of nerve agents on a tungsten-based POM

Dana M. Mizrahi*, Sigal Saphier, Ishay Columbus

Department of Organic Chemistry, Israel Institute for Biological Research, P.O. Box 19, Ness Ziona 74100, Israel

ABSTRACT

Common (chemical warfare agent) CWA decontaminants exhibit harsh and corrosive characteristics, and are harmful to the environment. In the course of our quest for active sorbents as efficient decontaminants, Keggin-type polyoxometalate (POM) $(NH_4)_3PW_{12}O_{40}$ was tested for oxidative degradation of CWAs. Although oxidation did not take place, sarin (GB) and VX were smoothly decontaminated to non-toxic products within 1 and 10 days, respectively. Degradation was carried out directly on the powder, eliminating the need for solvents. Mustard gas (HD), whose degradation is highly dependent on oxidation, was not decontaminated by this POM. Solid state MAS NMR (^{31}P and ^{13}C) was utilized both for POM characterization and for decontamination studies monitoring.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Efficient decontamination of chemical warfare agents (CWAs) has been a major concern for several years. In view of recent unconventional attacks (Tokyo subway sarin attack [1], 2001 US anthrax envelopes [2] and London osmium tetroxide and polonium incidents) and numerous threats by terrorists to use toxic chemicals, the quest for an efficient, universal and environmentally friendly decontaminant, is more important than ever.

Decontamination of CWAs is usually carried out either by oxidation or by basic hydrolysis, as described in detail by Yang et al. [3]. Main decontamination mechanisms and products, relevant for this work, are portrayed in Schemes 1 and 2. Commonly used decontaminants include hypochlorite bleach, STB (super tropical bleach, calcium hypochlorite) and DS2 (an organic mixture, containing 2-methoxy ethoxide as the active ingredient). STB and hypochlorite bleach are typically used to decontaminate terrain and roads, while DS2 is used to decontaminate the exterior of vehicles. These decontaminants, which have been used since the early years of the 20th century, are harsh and corrosive chemicals, harmful to skin and equipment. At present, production of STB and DS2 has been largely reduced, due to their corrosive nature.

Over the last two decades, novel decontaminants have been sought, which afford efficient universal decontamination, and exhibit reduced adverse effects to equipment and the environment.

The need to avoid production of CWAs toxic degradation products [4] contributes to the complexity of the development process. Some of the proposed decontaminants are aqueous mixtures (Sandia Foam, Decon Green), organic solutions (GD5, GD6F, GDS2000) or sorbent powders (M100). Some of these novel decontaminants are dispersed in the form of fog or aerosol, intended for interior decontamination. In spite of this effort, decontamination of vehicle interior and of sensitive equipment (electronics, optical lenses, etc.) remains an open question.

Lately we have been interested in developing an active sorbent powder. Inert sorbents such as Fuller's earth, vermiculite, sand and soil are used extensively to absorb spills of toxic industrial chemicals (TICs), as a routine procedure of handling accidents. Fuller's earth is also used in the military and is capable of initially decreasing hazard by physically removing CWAs from human skin and personal equipment. However, the sorbent itself remains contaminated and requires further decontamination. An *active* sorbent is designed to retain large amounts of organic substance, while, at a slower rate, actively degrade TICs and CWAs. We envision that such a powder will assist in the removal and decontamination of CWAs from the interior of contaminated vehicles, aircraft and rooms, and from sensitive equipment. The active properties of such a powder eliminate the need for its consequent decontamination, using harsh chemicals.

Recently we have published the production and testing of several active powders, which have exhibited active degradation of VX, G agents and mustard gas (HD) to non-toxic products [5,6]. Briefly, several aspects, such as mode of active powder preparation, solvents added during preparation or decontamination and
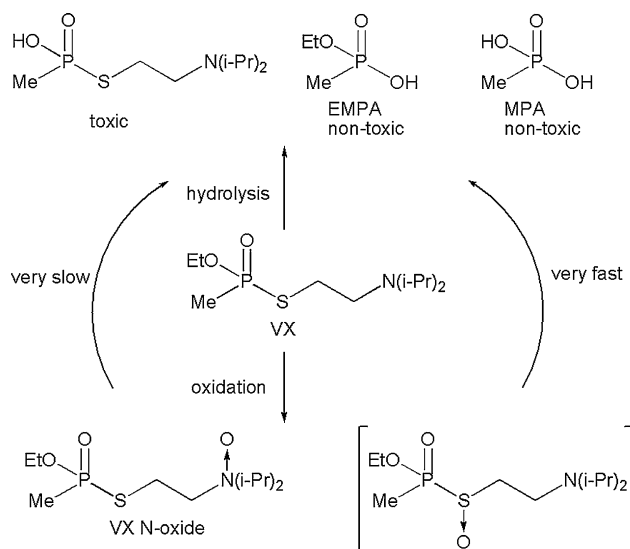
Scheme 1. VX decontamination mechanisms (phosphorus-containing products).
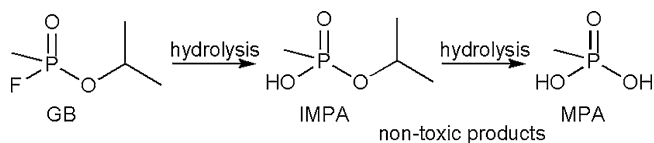
Scheme 2. Sarin decontamination mechanism (phosphorus-containing products).

availability of various ions, were investigated for influence on decontamination efficacy and products. We have established that VX quickly hydrolyzed ($t_{1/2}$ between 0.1 and 6.3 h) to non-toxic EMPA as a major product (>90%). Similarly, GB hydrolyzed immediately ($t_{1/2}$ < 10 min) to form non-toxic IMPA exclusively. HD formed a multitude of products as a result of numerous substitution and elimination processes. In this case, $t_{1/2}$ was found to be in the range of 3.5–355 h.

In the course of the present work we have tested some tungsten-based polyoxometalates (POMs). POMs are well documented for their versatile catalytic uses in synthetic chemistry. POM applications result from their redox potential, photochemical response, conductivity and ionic charge [7]. Among the POMs, Keggin-type heteroployacids (general formula $H_nXM_{12}O_{40}$, X = P,Si; M = Mo, W) and their salts have been used extensively in organic catalysis [8]. In view to their physical properties and oxidative activity, we have tested certain Keggin-type POMs as active sorbents and hereby report some unexpected reactions with CWAs.

2. Materials and methods

2.1. Materials

$(NH_4)_3PW_{12}O_{40}$ was prepared according to a literature procedure [9], by dropwise addition of an aqueous solution of $(NH_4)HCO_3$ to an aqueous solution of $H_3PW_{12}O_{40}$ at 20 °C, to form the spherical salt and at 95 °C, to form the dodecahedral salt. The colloidal mixtures were evaporated to dryness.

Oxidation experiments were carried out by adding a specified amount of 35% H_2O_2 to aqueous colloidal suspensions of either ammonium salt at ambient temperature. H_2O_2 amounts were calculated as equivalents of tungsten atoms, so that 1 equivalent H_2O_2 consisted of 12 mmol H_2O_2 per 1 mmol ammonium salt.

[13]C-labeled HD was prepared according to a literature procedure [10].

2.2. Sample preparation

Caution: These experiments should only be performed by trained personnel using applicable safety procedures. Samples of the salts were used to fill a 4-mm ZrO_2 rotor. Neat agent (VX, sarin (GB) or ^{13}C-labeled HD) at 5% (v/w) was applied via syringe to the center of the sample. The rotor was sealed with a fitted Kel-F cap. ^{31}P and ^{13}C NMR spectra were measured periodically to determine remaining CWA and identify degradation products.

2.3. Solid state NMR

^{31}P and ^{13}C MAS NMR experiments were carried out on a 500 MHz Avance (Bruker) spectrometer equipped with a 4-mm standard CP-MAS probe using direct excitation (no CP). The observation Frequency for ^{31}P was 202 MHz. The observation Frequency for ^{13}C was 125 MHz. Typical spinning rate was 5 kHz. Chemical shifts were referenced to external TMP (trimethyl phosphate) as 0 ppm for ^{31}P, and to TMS (tetramethylsilane) as 0 ppm for [13]C.

2.4. SEM

The images of scanning electron microscopy (SEM) were taken with an ESEM (Quanta 200 FEG from FEI, Netherlands). All samples were attached on aluminum specimen mount stubs by a double-sided tape made of electricity-conductive carbon.

2.5. POMs as CWAs decontaminants

Some attempts to use POMs for CWAs decontamination were published. All reported results dealt with the oxidation of mustard gas (HD) and simulants, based on POMs' capability to catalyze the oxidation of thiols to disulfides [11] and sulfides to sulfoxides and sulfones [12]. The most extensive work has been carried out by Hill et al., who investigated POM catalytic destruction of HD simulants and set to prepare a topical composition for removing and degrading contaminants [13]. In some cases, POMs were actively oxidized prior to being submerged in the topical foundation/cream, while other formulations utilized ambient air or added O_2 to oxidize the HD simulant. Decontamination efficacy was tested on HD simulants such as 2-chloroethyl ethyl sulfide (CEES), tetrahydrothiophene, diethyl- and dimethyl sulfide.

Another group reported the reactions of Keggin-type POM $H_5PV_2Mo_{10}O_{40}$ with HD and CEES in aqueous media, monitored by NMR and EPR. In this work, both oxidation and hydroxyl-chlorine substitution occurred [14].

In order to develop a POM-based active sorbent, we were interested in POMs that readily absorb organic compounds, and are able to degrade VX and GB, as well as HD, omitting the need for a solvent.

3. Results and discussion

3.1. "Sponge crystal"

During our quest for extremely porous POMs, we have been introduced to a new concept of "sponge crystals", which are porous aggregates of self-assembled nanocrystallites of $(NH_4)_3PW_{12}O_{40}$. The dodecahedral form of this POM was previously categorized as a *mesocrystal*, namely, an oriented superstructure of nanocrystals with common outer faces, formed from nonspherical, crystalline building units, and different from ion-by-ion addition, leading to a classical single crystal [15].

A recent publication [16], dealing specifically with $(NH_4)_3PW_{12}O_{40}$, described two forms of this POM, highly different in crystal structure, due to different formation temperature. When an aqueous solution of the parent acid $H_3PW_{12}O_{40}$ is
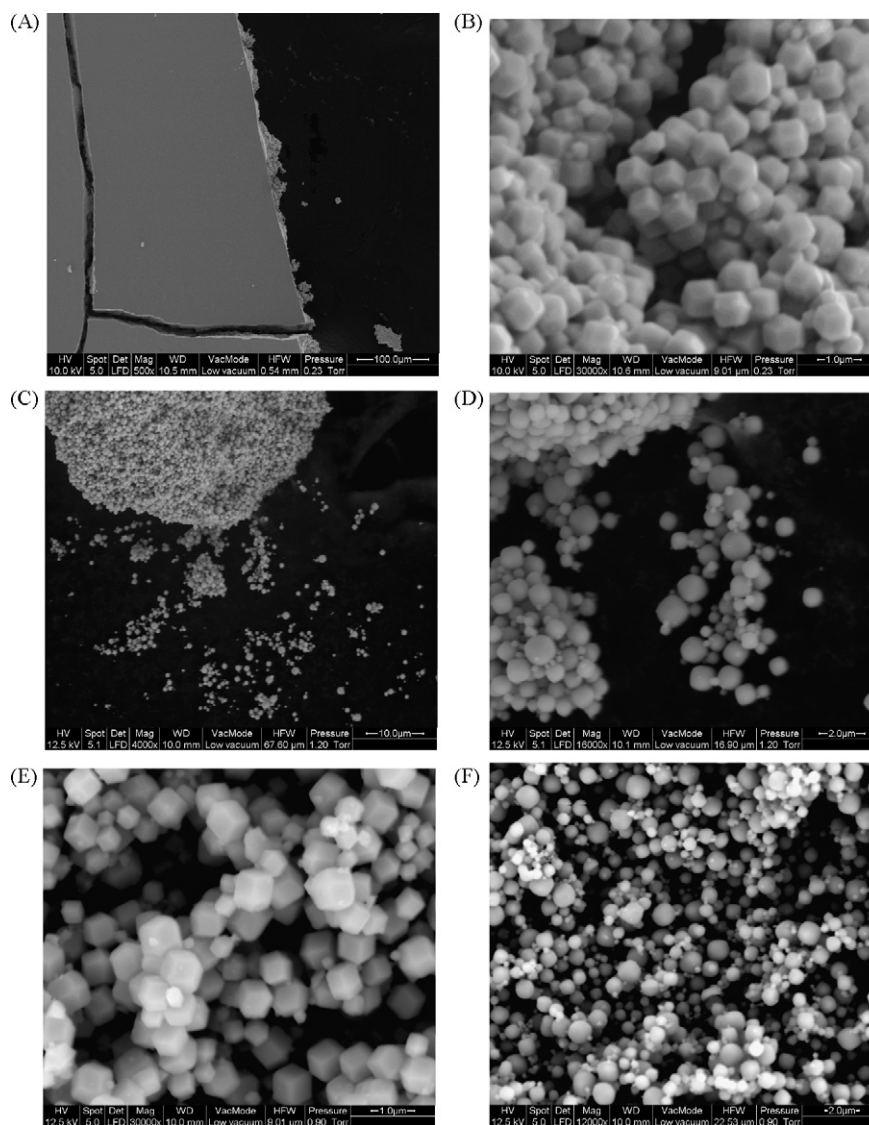
Fig. 1. SEM images showing: Dodecahedral $(NH_4)_3PW_{12}O_{40}$ (A: plate and B: particles); spherical $(NH_4)_3PW_{12}O_{40}$ (C: plate and D: particles); and "oxidized" dodecahedral $(NH_4)_3PW_{12}O_{40}$ (E) and spherical $(NH_4)_3PW_{12}O_{40}$ (F).

treated dropwise with an aqueous solution of NH_4HCO_3 at 25 °C, a spherical form of $(NH_4)_3PW_{12}O_{40}$ is produced. When the reaction is carried out at 95 °C, dodecahedral $(NH_4)_3PW_{12}O_{40}$ is formed. Characterization of the dodecahedral form by means of X-ray diffraction and volume measurements led to the observation that it resembles a single crystal more than a mesocrystal. However, unlike classic single crystals, dodecahedral $(NH_4)_3PW_{12}O_{40}$ is highly porous, due to intrinsic continuous voids within the crystals. Unlike zeolites, the intrinsic pores in $(NH_4)_3PW_{12}O_{40}$ are not structurally defined, hence, this phenomenon was termed "sponge crystal".

3.2. Preparation of POMs and oxidation procedures

$(NH_4)_3PW_{12}O_{40}$ has been previously reported to catalyze esterification [17], formation and deprotection of acylals [18], cracking of long-chain hydrocarbons [19] and of alkenes [20]. This catalytic activity, along with the porous nature of this environmentally friendly POM encouraged us to test both crystal forms for CWAs degradation.

Spherical and dodecahedral $(NH_4)_3PW_{12}O_{40}$ were prepared according to the literature [9] from 12-tungstophosphoric acid and

were examined by SEM. Both ammonium salts appeared as plates, which were constructed by sub-micron dodecahedral or spherical particles. Dodecahedral and spherical nanocrystals constructed plates of the ammonium salts (Fig. 1A–D).

Since $(NH_4)_3PW_{12}O_{40}$ produces, upon mixing with water, a dense colloidal mixture, unsuitable for solution NMR measurement, we employed solid-state ^{31}P NMR as a part of POMs characterization. Both spherical and dodecahedral salts gave single peaks at -15.7 ppm, suggesting that the phosphorus atom is located in similar environments in both crystal forms.

Although little is known about oxidation of 12-tungstophosphoric acid ammonium salt, there is vast information about oxidation of the parent acid and uses of the oxidized form $[(PO_4)\{WO(O_2)_2\}_4]^{3-}$ in catalyzing epoxidation [21,22].

Encouraged by the oxidative potential of 12-tungstophosphoric acid and by the special crystal structures of its ammonium salt, we decided to oxidize $(NH_4)_3PW_{12}O_{40}$ and to test the oxidized form's ability to oxidatively degrade CWAs. Focusing on the development of active sorbents, we planned to carry out the reactions without solvent and use solid-state NMR for monitoring.

Oxidation attempts of $(NH_4)_3PW_{12}O_{40}$ were carried out according to the optimized procedure reported by Aubry et al. [21]. The
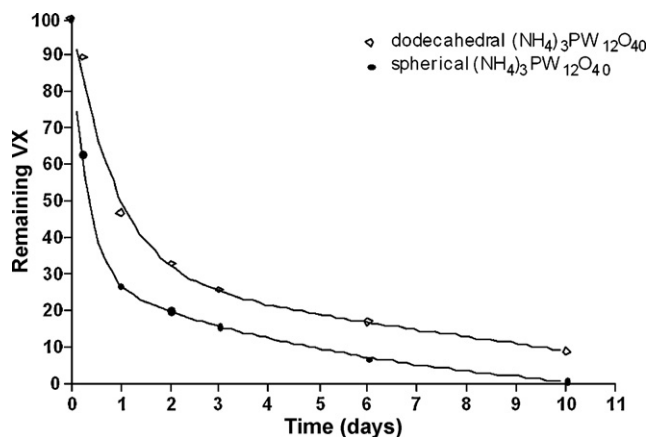
Graph 1. Degradation of VX on $(NH_4)_3PW_{12}O_{40}$.

Fig. 2. Degradation of VX by spherical $(NH_4)_3PW_{12}O_{40}$.

ammonium salt was immersed in distilled water and 35% hydrogen peroxide was added at specified amounts to afford 1, 2, 8 and 100 equivalents of H_2O_2, as compared to tungsten atoms. SEM images of oxidation products (100 eq. H_2O_2) are shown in Fig. 1(E and F). Evidently, no structural change has occurred due to oxidation. This is in contrast to previous reports dealing with the oxidation of the parent acid, leading to complete loss of the polyanionic structure and formation of new oxidized anions.

Solid-state ^{31}P NMR confirmed that all "oxidized" powders contained phosphorus atoms similar to those in the parent ammonium salts (*ca.* −15.7 ppm). In comparison, oxidation products of 12-tungstophosphoric acid were reported to display vast changes in ^{31}P NMR spectra from −14.9 to +4.2 ppm. In view of SEM and NMR data, we deduced that oxidation of the ammonium salt has not taken place.

3.3. The employment of $(NH_4)_3PW_{12}O_{40}$ to CWA decontamination

Samples of dodecahedral and spherical $(NH_4)_3PW_{12}O_{40}$ were contaminated with 5% neat VX, GB or ^{13}C-labeled mustard gas. Monitoring of CWAs fate was carried out by ^{31}P or ^{13}C solid-state NMR [23]. The experiments were carried out at ambient temperature with almost complete elimination of desorption. Graph 1 describes the reaction of VX with the ammonium salts.

VX was fully degraded by tested POMs to non-toxic phosphonic acids by 10–15 days, with $t_{1/2}$ of less than 1 day. The degradation process consisted of initial absorbing/complexing of VX into the POM, characterized by a downfield shift in the ^{31}P NMR spectra (from 52 to 57 ppm), followed by degradation of the complexed form. Highest degradation rate was achieved with spherical $(NH_4)_3PW_{12}O_{40}$. This could be explained by the fact that it displays larger BET surface area ($104\,m^2\,g^{-1}$) and micropore volume ($0.041\,cm^3\,g^{-1}$) when compared to the dodecahedral salt ($65\,m^2\,g^{-1}$ BET surface area and $0.027\,cm^3\,g^{-1}$ micropore volume) [9]. Thus, VX absorption and complexation in the micropores of the spherical salts occurs more rapidly and facilitates the chemical reaction. Fig. 2 shows the progress of VX degradation as monitored by ^{31}P solid-state NMR.

GB was fully degraded into non-toxic products within 1 day of being placed on $(NH_4)_3PW_{12}O_{40}$, with notable amounts of a product present as soon as 1 h into the experiment. Acidic degradation products were absorbed into the powder, as evident by broad and multiple peaks (Fig. 3).

As mentioned before, oxidation of thiols and sulfides occurs readily with various POMs in an oxidative media [11–13]. In our studies, we used ^{13}C-labeled mustard gas (HD). Whether placed on

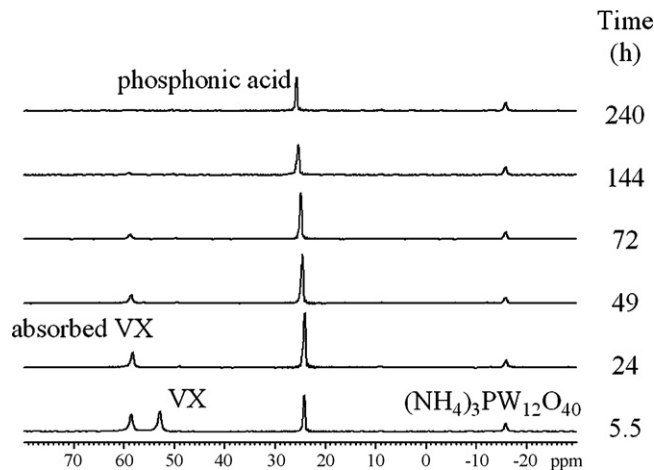spherical or dodecahedral $(NH_4)_3PW_{12}O_{40}$, no degradation of the HD was observed for as long as 4 days. Broadening of the peaks was indicative of HD being absorbed into the POM, but no chemical reaction took place, as shown by the NMR spectra in Fig. 4.

Decontamination of mustard gas (HD) favors the oxidative pathway, from thiol to sulfoxide and sulfone, which undergo facile hydrolysis. When HD was placed on $(NH_4)_3PW_{12}O_{40}$, no oxidation to the sulfoxide was achieved, hence no apparent decontamination took place.
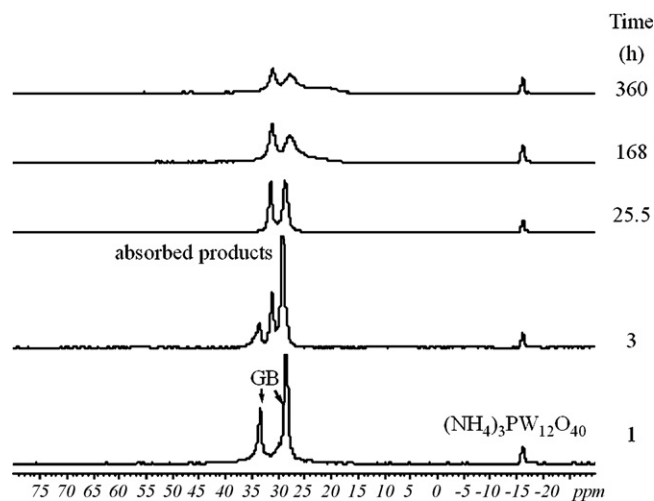

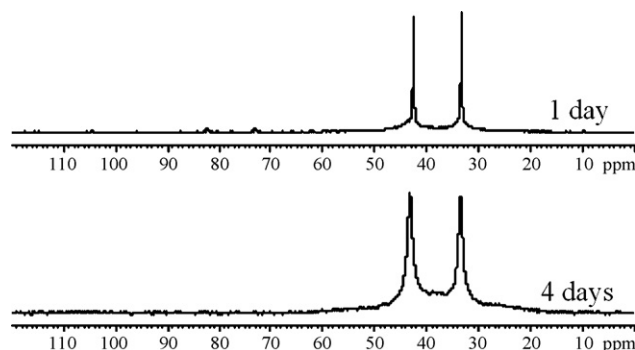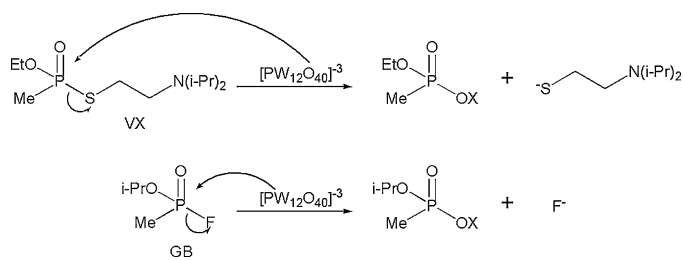**Fig. 3.** Degradation of GB by spherical $(NH_4)_3PW_{12}O_{40}$.

Fig. 4. ^{13}C solid state NMR spectra of HD placed on spherical $(NH_4)_3PW_{12}O_{40}$.

Scheme 3. Proposed mechanism for VX and GB degradation.

3.4. Proposed mechanism of CWA decontamination on $(NH_4)_3PW_{12}O_{40}$

To date, all relevant literature addressed the oxidative decontamination of sulfur-containing CWAs and simulants catalyzed or performed by POMs [11–14]. During our studies, we have established a new route for the decontamination of nerve agents by a pseudo-hydrolytic/nucleophillic mechanism. As a result, in our system, HD decontamination was not accomplished successfully.

On the other hand, VX and GB reacted smoothly with $(NH_4)_3PW_{12}O_{40}$ in a heterogeneous system, to exclusively form non-toxic MPA derivatives. It is most likely that VX and GB degradation took place following complexation to the POM, via nucleophillic attack of the $[PW_{12}O_{40}]^{3-}$ anion on the phosphorus atom, which released the leaving groups, as shown in Scheme 3. Possible MPA derivatives are the free acid ($x = H$), if the salt contains water, an ammonium salt ($x = NH_4$) or a tungstate derivative ($x = WO_n$).

4. Conclusions

The oxidation of 12-tungstophosphate ammonium salt did not take place in a facile manner, in contrast to the parent acid. Nevertheless, this POM exhibited remarkable reactivity towards VX and GB in a heterogeneous system. As most of the decontamination experiments to date were carried out with HD and HD simulants via an oxidative route, to the best of our knowledge, this is the first degradation of VX and GB by a Keggin-type POM. This work showed the possibility of efficiently decontaminating VX and GB on environmentally friendly catalysts, capable of absorbing and reacting without the addition of solvent or oxidizing agent. Short $t_{1/2}$ estimated for VX and GB decontamination on $(NH_4)_3PW_{12}O_{40}$ (less than 1 day) are encouraging for further use in clean-up procedures for a non-conventional terrorist attack. In future research, we plan to test the efficacy of POM mixtures combining the nucleophillic capability of $(NH_4)_3PW_{12}O_{40}$ with the proven oxidative characteristics of similar POMs.

We feel that these results open a whole new family of active materials with potential to catalyze facile nerve agent degradation.

References

[1] T. Okumura, N. Takasu, S. Ishimatsu, S. Miyanoki, A. Mitsuhashi, K. Kumada, K. Tanaka, S. Hinohara, Report on 640 victims of the Tokyo subway sarin attack, Ann. Emerg. Med. 28 (2) (1996) 129–135.

[2] D.B. Jernigan, P.L. Raghunathan, B.P. Bell, R. Brechner, E.A. Bresnitz, J.C. Butler, M. Cetron, M. Cohen, T. Doyle, M. Fischer, C. Greene, K.S. Griffith, J. Guarner, J.L. Hadler, J.A. Hayslett, R. Meyer, L.R. Petersen, M. Phillips, R. Pinner, T. Popovic, C.P. Quinn, J. Reefhuis, D. Reissman, N. Rosenstein, A. Schuchat, W.-J. Shieh, L. Siegal, D.L. Swerdlow, F.C. Tenover, M. Traeger, J.W. Ward, I. Weisfuse, S. Wiersma, K. Yeskey, S. Zaki, D.A. Ashford, B.A. Perkins, S. Ostroff, J. Hughes, D. Fleming, J.P. Koplan, J.L. Gerberding, The National Anthrax Epidemiologic Inves-

[3] Y.-C. Yang, J.A. Baker, J.R. Ward, Decontamination of chemical warfare agents, Chem. Rev. 92 (1992) 1729–1743.

[4] N.B. Munro, S.S. Talmage, G.D. Griffin, L.C. Waters, A.P. Watson, J.F. King, V. Hauschild, The Sources, Fate, and toxicity of chemical warfare agent degradation products, Environ. Health Perspect. 107 (12) (1999) 933–973.

[5] E. Gershonov, I. Columbus, Y. Zafrani, Facile hydrolysis-based chemical destruction of the warfare agents VX, GB, and HD by alumina-supported fluoride reagents, J. Org. Chem. 74 (2009) 329–338.

[6] Y. Zafrani, M. Goldvaser, S. Dagan, L. Feldberg, D. Mizrahi, D. Waysbort, E. Gershonov, I. Columbus, Degradation of sulfur mustard on KF/Al_2O_3 supports: insights into the products and the reactions mechanisms, J. Org. Chem. 74 (2009) 8464–8467.

[7] D.E. Katsoulis, A Survey of applications of polyoxometalates, Chem. Rev. 98 (1998) 359–387.

[8] C.L. Hill, et al., Complex catalysts from self-repairing ensembles to highly reactive air-based oxidation systems, C.R. Chim. 10 (2007) 305–312.

[9] T. Ito, K. Inumaru, M. Misono, Structure of porous aggregates of the ammonium salt of dodecatungstophosphoric acid, $(NH_4)_3PW_{12}O_{40}$: unidirectionally oriented self-assembly of nanocrystallites, J. Phys. Chem. B 101 (1997) 9958–9963.

[10] L.P. Reiff, D.F. Taber, L. Yet, Proceeding of the 1996 ERDEC scientific conference on chemical and biological defense research, 19–22 November, 1996.

[11] R. Hekmatshoar, S. Sajadi, M.M. Heravi, F.F. Bamoharram, $H_{14}[NaP_5W_{30}O_{110}]$ as a heterogeneous recyclable catalyst for the air oxidation of thiols under solvent free conditions, Molecules 12 (2007) 2223–2228.

[12] A.M. Al-Ajlouni, T.M. Daiafla, M. Al-Khateeb, New nitrophenyl-substituted polyperoxotungstate catalyst: a more active and selective for the oxidation of sulfides by hydrogen peroxide, J. Mol. Catal. A. 275 (2007) 139–147.

[13] (a) R.D. Gall, Destruction of thioether of mustard analogs by divanado decamolybdophosphonic acid, Chem. Abstr. 126 (1997) 224933;
(b) R.P. Johnson, C.L. Hill, Polyoxometalate oxidation of chemical warfare agent simulants in fluorinated media, J. Appl. Toxicol. 19 (1999) S71–S75;
(c) N.M. Okun, T.M. Anderson, C.L. Hill, Polyoxometalates on cationic silica, Highly selective and efficient O2/air-based oxidation of 2-chloroethyl ethyl sulfide at ambient temperature, J. Mol. Catalysis A. 197 (2003) 283–290;
(d) C.L. Hill, L. Xu, J.T. Rhule, E.A. Boring, Polyoxometalate materials, metal-containing materials, and methods of use thereof, US Patent 6,723,349 (2004).;
(e) C.L. Hill, L. Xu, J.T. Rhule, E.A. Boring, Polyoxometalate materials, metal-containing materials, and methods of use thereof. US Patent 7,097,858 (2006).

[14] C.M. Arroyo, J.M. Sankovich, D.L. Burman, D.W. Kahler, S.-D. Soni, B.E. Hackley Jr., Application of NMR and EPR spectroscopy to the analysis of the reaction of phosphovanadomolybdate polyoxometalate ($H_5PV_2Mo_{10}O_{40}$) with chloroethyl sulfides (half-sulfur mustard and sulfur mustard), J. Med. CBR Def. 3 (2005) 1–17.

[15] H. Cölfen, M. Antonietti, Mesocrystals: inorganic superstructures made by highly parallel crystallization and controlled alignment, Angew. Chem. Int. Ed. 44 (2005) 5576–5591.

[16] K. Inumaru, Sponge crystal: a novel class of microporous single crystals formed by self-assembly of polyoxometalate $(NH_4)_3PW_{12}O_{40}$ nanocrystallites, Catal. Surveys from Asia 10 (3/4) (2006) 151–160.

[17] B.Y. Giri, K.N. Narasimha Rao, B.L.A. Prabhavathi Devi, N. Lingaiah, I. Suryanarayana, R.B.N. Prasad, P.S. Sai Prasad, Esterification of palmitic acid on the ammonium salt of 12-tungstophosphoric acid: the influence of partial proton exchange on the activity of the catalyst, Catal. Comun. 6 (2005) 788–792.

[18] R.J. Satam, R.V. Jayaram, $(NH_4)_3PW_{12}O_{40}$ as an efficient and reusable catalyst for the synthesis and deprotection of 1,1-diacetates, Synth. Commun. 38 (2008) 595–602.

[19] H. Hayashi, J.B. Moffat, Conversion of methanol into hydrocarbons over ammonium 12-tungstophosphate, J. Catal. 83 (1983) 192–204.

[20] S.V. Nayak, J.B. Moffat, Catalytic activity and product distribution in the cracking of C6–C8 alkenes on the ammonium salt of 12-tungstophosphoric acid, Appl. Catal. 77 (1991) 251–268.

[21] C. Aubry, G. Chottard, N. Platzer, J.-M. Brégeault, R. Thouvenot, F. Chauveau, C. Huet, H. Ledon, Reinvestigation of epoxidation using tungsten-based precursors and hydrogen peroxide in a biphase medium, Inorg. Chem. 30 (1991) 4409–4415.

[22] N. Mizuno, K. Yamaguchi, K. Kamata, Epoxidation of olefins with hydrogen peroxide catalyzed by polyoxometalates, Coord. Chem. Rev. 249 (2005) 1944–1956.

[23] (a) D. Mizrahi, I. Columbus, ^{31}P MAS NMR: a useful tool for the evaluation of VX natural weathering in various urban matrixes, Environ. Sci. Technol. 39 (2005) 8931–8935;
(b) G.W. Wagner, et al., Effect of drop size on the degradation of VX in concrete, Langmuir 20 (2004) 7146–7150;
(c) G.W. Wagner, et al., Preliminary study on the fate of VX in concrete, Langmuir 17 (2001) 4336–4341;
(d) G.W. Wagner, et al., Reactions of VX, GB, GD, and HD with nanosize Al_2O_3. Formation of aluminophosphonates, JACS 123 (2001) 1636–1644.