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Aluminium sulfate and sodium aluminate buffer solutions for the destruction of phosphorus based chemical warfare agents

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Nerve agents VX and GB (sarin) are sequestered and removed by aluminium sulfate and sodium aluminate mixtures adjusted to pH 4 in solution. The products of hydrolysis are removed with the alum floc below NMR detection limits over time depending and the amount of aluminium molar excess relative to agent. Half-lives for GB decomposition are 3.1 h and 1.1 h, respectively, for a 120 and a 1200 molar excess. For VX, the half-lives are 8.5 d and 2.9 d for a 240 and a 5000 molar aluminium excess. In the case of GB, fluorine is sequestered as the hexafluoroaluminate ion. In the case of VX, no phosphorus containing hydrolysis products including the very toxic *S*-[2-(diisopropyl-amino)-ethyl]methylphosphonothiolate (EA-2192) are detected in the hydrolysate.

Introduction

Detoxifying and destroying chemical warfare agents (CWA's) have been a global concern given the vast stockpiles still in existence and the difficulties encountered in the technology as well as the social aspects of eliminating them in a safe and environmentally friendly way which has yet to be developed.[1–3] The standard method of nerve agent destruction of substances like *O*-ethyl-*S*-[2-(diisopropylamino)ethyl]methylphosphonothiolate (VX) or *O*-isopropyl methylphosphonofluoridate (GB or sarin) (Fig. 1) is high temperature basic hydrolysis.[1–3] While the method is effective in destroying these and other CWA's, there are points of concern regarding the process. One issue of concern, for example, voiced by the Delaware Riverkeeper organization was the transportation of what is perceived to be potentially harmful VX hydrolysate (VXH) from the disposal facility in Newport, Indiana, to an industrial facility in New Jersey where it would have been released into the Delaware River after final treatment.[4] The most recent solution to the VXH disposal problem is to ship it to Port Arthur, Texas, for incineration.[5] Incineration of other CWA's has had its own set of difficulties as demonstrated with challenges involving local citizen concern and frequent shutdowns at the site in Anniston, Alabama (USA), in the destruction of sarin (GB).[2] VXH is still considered a chemical weapon and the transportation through populated areas like Memphis, Tennessee, and Baton Rouge, Louisiana, could be problematic.[5] What makes VXH potentially dangerous is the presence of *S*-[2-(diisopropylamino)ethyl]methylphosphonothiolate, otherwise known as EA-2192 (Fig. 2). EA-2192 forms as a minor product in basic hydrolysis by cleaving the P–O bond instead of the P–S bond, and is about half as toxic as VX with an LD_{50} in rabbits of 17 μL kg^{-1}.[6] Furthermore, its fate in the natural environment is unknown, and an accidental spill could be extremely problematic.

An approach we are investigating is the use of aluminium sulfate (alum) and alum mixtures buffered with sodium aluminate as an alternative means of hydrolyzing and sequestering organophosphate species such as pesticides and nerve agents like VX and sarin.

Our line of inquiry seemed promising since alum and alum mixtures have a long history of usage by municipal water treatment facilities as coagulants in the purification and finishing of drinking water, and have been used by lake managers for phosphate removal from lakes and reservoirs that were impacted by excess phosphorus nutrient input giving rise to unwanted algal blooms.[7] It was these large scale applications that led us to look further into the possibility of using alum and alum mixtures as alternatives for the decontamination of CWA's, particularly the V- and G-class nerve agents. The G- and V-type nerve agents hydrolyze under a variety of conditions, and hydrolysis kinetics have been studied extensively.[8–10] The pH of alum and alum mixtures can be widely varied from strongly acidic to strongly basic depending on concentrations and proportions of components which should allow for some control over hydrolysis reaction rates. Thus it was thought that they would have great potential not only for hydrolyzing the agents, but also for rendering the

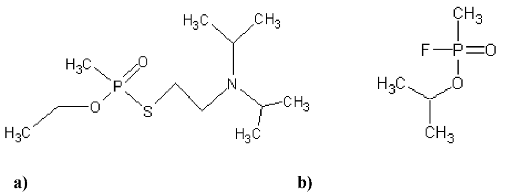

Fig. 1 Structures of VX (a) and sarin, or GB (b).

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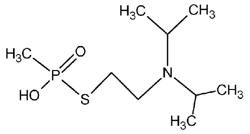

Fig. 2 *S*-[2-(Diisopropylamino)ethyl]methylphosphonothiolate EA-2192.

phosphate by-products inactive in the resultant coagulant floc that forms. The alum approach has several potential applications. For example, it represents an option for ensuring the safety of municipal drinking water supplies. In the event that a water supply is contaminated by CWA's (*e.g.* in a terrorist incident), a method will be needed to rapidly decontaminate the water to prevent a risk to public safety. Because alum is already used for water purification, it provides a possibility for decontamination that does not require materials in addition to those already in use. However, optimization of the treatment and filtering conditions may be necessary to purify water, which will require further study. The approach may also be useful for remediation of contaminated manufacturing sites or storage facilities in a way that can immobilize residual CWA and breakdown products in a nontoxic material.

In preliminary feasibility studies, we demonstrated that buffered aqueous aluminium sulfate solutions were effective for destroying GB, GD (2,2-dimethyl-1-methylpropyl methylphosphonofluoridate or soman), and VX as well as a variety of simulants such as triethyl phosphate (TEP) and tri-*n*-butyl phosphate (TBP).[11,12] In these preliminary studies, the aluminium molar concentration was at least 100 times that of the agent being treated, but the reactions were not monitored with respect to buffer-controlled experiments, so we were unable to determine if the alum buffers were kinetically superior to simple pH buffers. For those studies, alum buffers were prepared by varying the ratios of sodium aluminate and alum solutions as mentioned earlier and two major regimes were monitored—one at pH 4 and the other at pH 12. The results were encouraging in that VX, GD, and GB were hydrolyzed at ambient temperature in either regime, and in the acidic buffers, the hydrolysis products were precipitated from solution.[11,12] Evidence for hydrolysis was observed very clearly under basic conditions in ^{31}P nuclear magnetic resonance (NMR) spectra showing the formation of dealkylated and defluorinated products in the case of G agents, and ethyl methyl phosphonic acid (EMPA) and other products, notably the very toxic *S*-[2-(diisopropyl-amino)-ethyl]methylphosphonothiolate (EA-2192), in the case of VX. The evidence under acidic conditions was not as clear since, as mentioned above, hydrolysis products never appeared in the spectra, thus leading to the speculation that they were precipitated with the alum floc which ensued upon treatment.

The purpose of this paper is to report the results of recent alum treatment studies on GB and VX treated under ambient temperature conditions at pH 4 and using greater than 100 fold and 1000 fold molar excesses of aluminium. Unlike the preliminary studies, these experiments are compared to control studies using pH 4 acetate buffer. Additionally, in the case of GB, the supernatant liquid and alum floc are investigated with ^{19}F NMR and high resolution magic angle spinning ^{31}P NMR (HRMAS), respectively, to look for evidence of hydrolysis products.

Experimental

VX and GB were obtained from Aberdeen Proving Ground (APG), MD. Reactions with chemical warfare agents were done on site at Edgewood Chemical Biological Center at APG by trained personnel using applicable safety precautions. Studies on nerve agents must be conducted in government approved laboratories. All other chemicals were used as obtained commercially without further purification. For the >100 fold studies, neat agent (5 μL GB or 10 μL VX) was placed directly on 1.0 g of a solid $Al_2(SO_4)_3$–$NaAlO_2$ admixture composed of 84% (w/w) $Al_2(SO_4)_3\cdot 16H_2O$ (Aldrich) and 16% (w/w) $NaAlO_2$ (Fluka) designed to result in pH 4 solutions upon addition of 5.0 mL of water. An internal standard of 10 μL of hexamethylphosphoramide (HMPA) (Aldrich) was added to each mixture. Control mixtures composed of the same volumes of GB, VX and HMPA were prepared in a similar fashion using 5.0 mL of acetate buffer pH 4 instead of water. Vortex mixing followed by centrifugation hastened precipitation of the aluminium hydroxide floc. The supernatant solutions were monitored by ^{31}P and ^{19}F NMR (GB only) using a Bruker AVANCE 300 MHz NMR spectrometer fitted with a 5 mm broadband probe. ^{31}P HRMAS NMR spectra for GB were obtained on floc samples placed in zirconia rotors using a Bruker AVANCE 500 MHz NMR spectrometer.

In the >1000 fold studies, 1000 ppm agent solutions in isopropyl alcohol were treated with equal volumes of 1.0 M $Al_2(SO_4)_3$ and 1.0 M $NaAlO_2$ to give a total volume of 6.0 mL. Control experiments were done on agents treated with acetate buffer pH 4 instead of alum buffer as described above. These solutions were also vortex mixed and centrifuged. In the case of the >1000 fold studies chloroform extracts of supernatant solutions were analyzed using a flame ionization detector capillary gas chromatograph (Agilent Model 8690) over a period of several days.

Results and discussion

Table 1 shows the half-lives for the agents treated with acidic alum buffer compared to agent treated with pH 4 acetate buffer. In all cases, acidic alum buffer was more effective than acetate buffer at pH 4 in removing agent from solution. As expected, much larger molar excesses of aluminium tended to speed up the reaction. VX is far more refractory to acid hydrolysis even in the presence of a very large excess of aluminium ion. Pseudo first order plots of these reactions can be seen in Fig. 3–6.

Table 1 Agent hydrolysis half lives at pH 4

Agent	Alum buffer	Acetate buffer	Al : agent (mol ratio)
GB	3.1 h	77 h	120 : 1
GB	1.1 h	2.5 h	1200 : 1
VX	8.5 d	95 d	240 : 1
VX	2.9 d	12 d	5000 : 1

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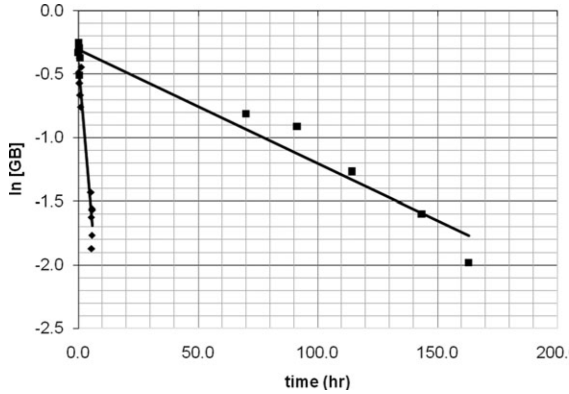

Fig. 3 Pseudo first order plot of GB treated with alum buffer (◆) and acetate buffer (■) at the mole ratio of 120 : 1. GB concentration is expressed in fraction of original amount lost.

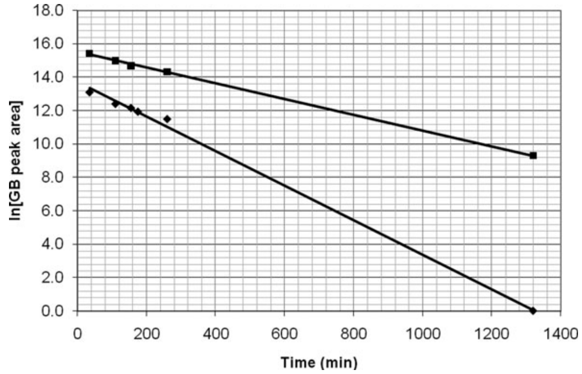

Fig. 4 Pseudo first order plot of GB treated with alum buffer (◆) and acetate buffer (■) at the mole ratio of 1200 : 1. GB concentration is expressed in GC peak area.

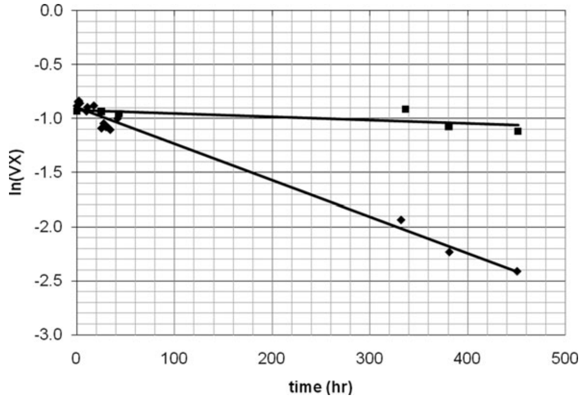

Fig. 5 Pseudo first order plot of VX treated with alum buffer (◆) and acetate buffer (■) at the mole ratio of 240 : 1. VX concentration is expressed in fraction of original amount lost.

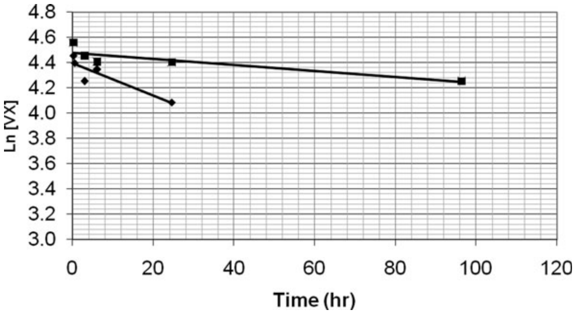

Fig. 6 Pseudo first order plot of VX treated with alum buffer (◆) and acetate buffer (■) at the mole ratio of 5000 : 1. VX concentration expressed in GC peak area.

In all cases, agent concentration eventually dropped below the detection limit of the monitoring instrumentation whether it be NMR for the >100 fold molar excesses or FID-GC for the >1000 fold. Furthermore, as was observed in the preliminary trials described above, no hydrolysis products for either GB or VX were observed in the NMR spectra, nor were they detected in the GC/MS samples. The question of whether agents were actually hydrolyzed or simply entrained in the alum floc was addressed by investigating a sample of the aluminium precipitate *via* ^{31}P HRMAS NMR. Fig. 7 and 8 show two spectra, one taken immediately after mixing and the other three days later. The peak centered around 34 ppm is the GB signal split by ^{19}F.[13] Three days later, the peak is absent, indicating hydrolysis completion. The peak near 20 ppm is most likely the aluminium complex of isopropyl methylphosphonic acid (IMPA) based on observations made by Wagner *et al.*[10] Furthermore, a ^{19}F NMR spectrum of the supernatant liquid showed a strong peak at -156 ppm which corresponds to the AlF_6^{3-} anion.[14] Thus it is clear that GB is being sequestered and hydrolyzed by the alum floc.

Evidence for VX hydrolysis has already been documented *via* NMR under the basic regime at pH 12, but the presence of EA-2192 was observed as were other basic hydrolysis products such as EMPA all in the form of their sodium salts[2,12] Wagner *et al.* previously demonstrated that nano-sized Al_2O_3 was effective in catalytically cleaving the P–S bond in VX, and that the cleavage of the O–Et bond which yields the toxic EA-2192 was not observed.[10] As mentioned earlier, no hydrolysis products could be observed in the NMR spectra for the >100 fold studies nor were they extractable in $CHCl_3$ for the >1000 fold studies. Thus, we cannot determine if EA-2192 is formed in the acidic hydrolysis regime, but what we have documented and what is perhaps most significant is the absence of it in the hydrolysate. Wagner *et al.*'s work showed the formation of

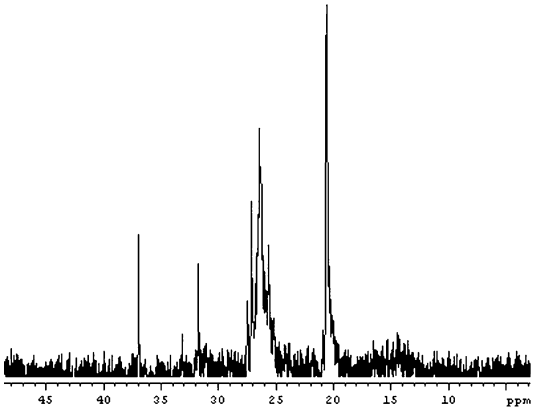

Fig. 7 Initial ^{31}P HRMAS NMR spectrum of the alum precipitate from the GB reaction mixture immediately after mixing.

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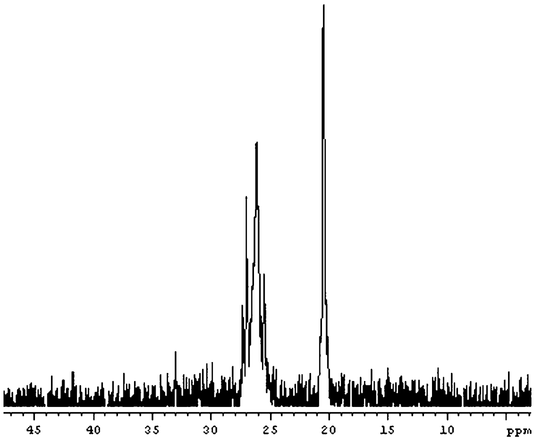

Fig. 8 Final ^{31}P HRMAS NMR spectrum of the alum precipitate from the GB reaction mixture (time = 3 d).

VX surface complexes with Al–O–P bonds which we are speculating to be present in our reactions as well. Based on Wagner *et al.*'s work and the G agent work described above, we are speculating that VX aluminium complexes are formed in the acidic alum regime, and that these complexes are hydrolyzed with the phosphorus bearing products being retained by the alum floc. Whether or not the hydrolysis leads to the formation of EA-2192 is unknown, but at least this toxic substance is absent in the hydrolysate.

Preliminary studies also showed that there was no advantage to elevating the temperatures for these reactions,[12] adding an additional attractive benefit to alum hydrolysis. Furthermore, with the products sequestered in the alum floc, landfill burial would be possible since over time this material mineralizes to gibbsite,[7] thus making it inaccessible for recovery and reconstitution into CWA's, another one of the major concerns.[2] The downside of this method, however, is the enormous aluminium molar excess required for complete destruction. A coupled technology with aluminium based dealkylating agents[15] reported by Atwood *et al.* is currently being investigated to circumvent this challenge.

Conclusions

Our studies demonstrate that chemical nerve agents such as sarin or VX can be treated effectively and relatively quickly with alum and sodium aluminate, substances which are relatively inexpensive and widely available. The most significant aspect of this research is that the phosphorus containing hydrolysis products which may include very toxic EA-2192 in the case of VX are removed from the waste stream. Further studies are needed to determine the route of alum hydrolysis and if the phosphorus bearing hydrolysis products associated with the alum floc are permanently sequestered and rendered inactive.

References

1 L. R. Ember, *Chem. Eng. News*, 2004, **82**(15), 28–30.
2 L. R. Ember, *Chem. Eng. News*, 2003, **81**(35), 26–27.
3 L. R. Ember, *Chem. Eng. News*, 2005, **83**(21), 36–37.
4 http://www.delawareriverkeeper.org/factsheets/vx_nerve_agent.htm.
5 L. R. Ember, *Chem. Eng. News*, 2008, **86**(12), 29–33.
6 Y. C. Yang, L. L. Szafraniec, W. T. Beaudry and D. K. Rohrbaugh, *J. Am. Chem. Soc.*, 1990, **112**(18), 6621–6627.
7 E. B. Welch and G. D. Cooke, *J. Lake Reservoir Manage.*, 1999, **15**, 5–27.
8 Y. C. Yang, J. A. Baker and J. R. Ward, *Chem. Rev.*, 1992, **92**, 1729–43.
9 Y.-C. Yang, *Acc. Chem. Res.*, 1999, **32**, 109–115.
10 G. W. Wagner, L. R. Procell, R. J. O'Connor, S. Munavalli, C. L. Carnes, P. N. Kapoor and K. J. Klabunde, *J. Am. Chem. Soc.*, 2001, **123**, 1636–1644.
11 D. J. Williams, V. L. H. Bevilacqua, W. R. Creasy, D. J. McGarvey, K. J. Maguire, J. S. Rice, C. A. S. Brevett, C. L. De Leon, M. J. Sanders and H. D. Durst, *"Potential Usage of Aqueous Alum for Decomposition of Chemical Warfare Agents. Part 1: Reactions with V- and G-Type Agents." ECBC-TR-431*, Edgewood Chemical Biological Center, Aberdeen Proving Ground, MD, 2005. Unclassified Report. http://www.ntis.gov/search/product.aspx?ABBR = ADA435764.
12 D. J. Williams, V. L H. Bevilacqua, W. R. Creasy, D. J. McGarvey, J. S. Rice, C. L. De Leon, M. S. Sanders and H. D. Durst, *"Potential Usage Of Aqueous Alum for Decomposition of Chemical Warfare Agents Part 2: Reactions with VX and QL." ECBC-TR-431*, Edgewood Chemical Biological Center, Aberdeen Proving Ground, MD, 2006. Unclassified Report. http://www.ntis.gov/search/product.aspx?ABBR = ADA454991.
13 W. T. Beaudry and L. L. Szafraniec, *"Nuclear Magnetic Resonance Procedure for the Characterization of GB, GD, VX, HD and L for the Chemical Agent Standard Analytical Reference Material (CASARM) Program (1984–1999)." ECBC-TR-259*, Edgewood Chemical Biological Center, Aberdeen Proving Ground, MD, 2002. Unclassified Report.
14 H. M. Kao and Y. C. Chen, *J. Phys. Chem. B*, 2003, **107**, 3367–3375.
15 A. Mitra, D. A. Atwood, J. Struss, D. J. Williams, B. J. McKinney, W. R. Creasy, D. J. McGarvey, H. D. Durst and R. Fry, *New J. Chem.*, 2008, **32**, 783–785.