

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188		
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA, 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</p>					
1. REPORT DATE (DD-MM-YYYY) 16-03-2009		2. REPORT TYPE New Reprint		3. DATES COVERED (From - To) 16-Mar-2009 -	
4. TITLE AND SUBTITLE Reactions of VX, GD, and HD with Nanotubular Titania			5a. CONTRACT NUMBER DAAD19-03-1-0326		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER 611102		
6. AUTHORS George W. Wagner, Qiang Chen, and Yue Wu			5d. PROJECT NUMBER 106013		
			5e. WORK UNIT NUMBER 622622		
			5f. WORK UNIT NUMBER 622622		
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES University of North Carolina - Chapel Hill Office of Sponsored Research 104 Airport Drive, Suite 2200, CB 1350 Chapel Hill, NC 27599 -1350			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSOR/MONITOR'S ACRONYM(S) ARO		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S) 45510-CH.2		
12. DISTRIBUTION AVAILABILITY STATEMENT Approved for public release; federal purpose rights					
13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
14. ABSTRACT Reactions of VX [O-ethyl-S-(2-diisopropylethylamino)ethyl methylphosphonothioate], GD (pinacolyl methylphosphonofluoridate), and HD [bis(2-chloroethyl) sulfide] have been examined with nanotubular titania (NTT) using 31P and 13C MAS NMR. All three agents hydrolyze on NTT with the reaction of VX being notably fast (t1/2 < 30 min), approaching the rate achievable with liquid decontaminants. 31P MAS NMR reveals that VX is adsorbed within the NTT tubules and/or its titania layers, perhaps providing optimum conditions for its					
15. SUBJECT TERMS reprint					
16. SECURITY CLASSIFICATION OF:		17. LIMITATION OF ABSTRACT		15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT U	b. ABSTRACT U	c. THIS PAGE U	SAR		Yue Wu
					19b. TELEPHONE NUMBER 919-962-0307

Report Title

Reactions of VX, GD, and HD with Nanotubular Titania

ABSTRACT

Reactions of VX [O-ethyl-S-(2-diisopropylethylamino)ethyl methylphosphonothioate], GD (pinacolyl methylphosphonofluoridate), and HD [bis(2-chloroethyl) sulfide] have been examined with nanotubular titania (NTT) using ^{31}P and ^{13}C MAS NMR. All three agents hydrolyze on NTT with the reaction of VX being notably fast ($t_{1/2} < 30$ min), approaching the rate achievable with liquid decontaminants. ^{31}P MAS NMR reveals that VX is adsorbed within the NTT tubules and/or its titania layers, perhaps providing optimum conditions for its hydrolysis by water sandwiched between the layers. Consistent with the availability of copious water on NTT, HD is hydrolyzed to its CH-TG sulfonium ion. GD hydrolysis is similarly efficient, with its products-PMPA and HF-attacking the titania structure to form a titanophosphonate species.

REPORT DOCUMENTATION PAGE (SF298)
(Continuation Sheet)

Continuation for Block 13

ARO Report Number 45510.2-CH
Reactions of VX, GD, and HD with Nanotubular ...

Block 13: Supplementary Note

© 2008 American Chemical Society. Published in Journal of Physical Chemistry C, Vol. 112,11901 (2008), (1190). DoD Components reserve a royalty-free, nonexclusive and irrevocable right to reproduce, publish, or otherwise use the work for Federal purposes, and to authorize others to do so (DODGARS §32.36). The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

Approved for public release; federal purpose rights

Reactions of VX, GD, and HD with Nanotubular Titania

George W. Wagner,^{*,†} Qiang Chen,[‡] and Yue Wu[‡]

U.S. Army Edgewood Chemical Biological Center, Aberdeen Proving Ground, Maryland 21010-5424, and Department of Physics and Astronomy and Curriculum in Applied and Material Sciences, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3255

Received: April 7, 2008; Revised Manuscript Received: May 15, 2008

Reactions of VX [*O*-ethyl-*S*-(2-diisopropylethylamino)ethyl methylphosphonothioate], GD (pinacolyl methylphosphonofluoridate), and HD [bis(2-chloroethyl) sulfide] have been examined with nanotubular titania (NTT) using ³¹P and ¹³C MAS NMR. All three agents hydrolyze on NTT with the reaction of VX being notably fast ($t_{1/2} < 30$ min), approaching the rate achievable with liquid decontaminants. ³¹P MAS NMR reveals that VX is adsorbed within the NTT tubules and/or its titania layers, perhaps providing optimum conditions for its hydrolysis by water sandwiched between the layers. Consistent with the availability of copious water on NTT, HD is hydrolyzed to its CH-TG sulfonium ion. GD hydrolysis is similarly efficient, with its products—PMPA and HF—attacking the titania structure to form a titanophosphonate species.

Introduction

Reactive sorbents have been developed for the decontamination of chemical warfare agents¹ (CWAs). Typically dry powders, the sorbents absorb, react with, and then detoxify the agents. Previous reactive sorbents fielded by the U.S. Army include “XE-555”, a mixture of polymeric/carbonaceous resins used in the M291 Skin Decontamination Kit, and “A-200”, an alumina-based material used in the M100 Sorbent Decontamination System.² Although both of these solid-phase decontaminants are able to quickly remove CWAs from surfaces, their reactions with agents such as VX [*O*-ethyl-*S*-(2-diisopropylethylamino)-ethyl methylphosphonothioate], GD (pinacolyl methylphosphonofluoridate), and HD [bis(2-chloroethyl) sulfide] are quite slow compared to typical liquid-phase decontaminants.¹ Thus, unlike spent liquid decontaminants, solid sorbent decontaminants remain contaminated for extended periods, presenting a hazard following their use.

In contrast to their conventional counterparts, nanoscale materials possess significantly different properties. Small particles yield not only higher surface areas but also greater proportions of highly reactive edge and corner defect sites.³ Additionally, unusual lattice faces may form and be stabilized in nanoparticles. Generally, metal oxides show broad-spectrum reactivity for CWAs,^{4–7} and although many such as MgO,⁴ CaO,⁵ and alumina⁶ have been fashioned into nanoparticles, they have proven unstable in the presence of air and/or moisture. Titania, on the other hand, is extremely stable, allowing it to even pass through human digestion unscathed; thus, its approval for inclusion in food items such as cookie icing (evidently, low-toxicity is an additional benefit of titania).

A relatively new form of titania is nanotubular titania (NTT)⁸ which exhibits nanoscale open-ended tubular structures formed from coaxial pairs of cylindrical titania sheets.^{9–11} The open end of the tubule is about 5 nm in diameter, whereas the *d*-spacing between the layer pairs is about 8.7 Å. This structure is depicted in Figure 1 along with the relative sizes of VX and

water molecules (see Results and Discussion). NTT possesses high surface area (250 m²/g) and has proven novel surface chemistry. Moreover, its unique structure provides for a much greater surface area than even “normal” nanocrystalline titania (50 m²/g). Additionally, its tubular structure prevents tight packing in macroscopic aggregates, thus preserving its high surface area and porosity. Further, the nanotubular form is also air-stable, suggesting that it may be as equally robust and biocompatible/nontoxic as its conventional, edible titania cousin.

On metal oxides, VX, GD, and HD typically undergo simple hydrolysis reactions, with elimination products also being observed for HD on basic materials such as MgO,⁴ CaO,⁵ and alumina.⁶ Indeed, preliminary work⁸ examining the reaction of the HD—simulant 2-chloroethyl ethyl sulfide (CEES) with NTT found a facile reaction between CEES and adventitious water to form typical hydrolysis products. Thus, reactions of VX, GD, and HD with metal oxides tend to mimic those observed in aqueous solution, with one notable exception: the formation of stable metal phosphonates^{6,12} from the hydrolysis products of VX and GD. All of these reactions, previously observed on metal oxides (MOs), are summarized in Scheme 1.

Also depicted in Scheme 1 are the simple structures of the aluminophosphonates formed from the reactions of VX, GB (isopropyl methylphosphonofluoridate), and GD with alumina⁶ and/or aluminum metal,¹² all of which possess single Al and P sites as denoted by ²⁷Al and ³¹P NMR. However, the structure of the titanophosphonate generated from the reactions of GD with titania and titanium metal is considerably more complex, exhibiting at least three different P sites as detected by ³¹P NMR with the postulated empirical formula Ti(O)[O₂P(CH₃)OPin]₂¹² (**1**).

In the present study, reactions of VX, GD, and HD with NTT are examined to determine reaction rates, to identify products, and to elucidate any unusual reaction mechanisms afforded by this unique material for the decontamination of these agents.

Experimental Section

Materials. Anatase was obtained from Aldrich. ¹³C-labeled HD (HD*), obtained locally, was employed to enhance sensitivity for ¹³C NMR experiments. Nanotubular titania was produced

* To whom correspondence should be addressed. E-mail: george.wagner@rdcom.agpea.army.mil.

† U.S. Army Edgewood Chemical Biological Center.

‡ University of North Carolina at Chapel Hill.

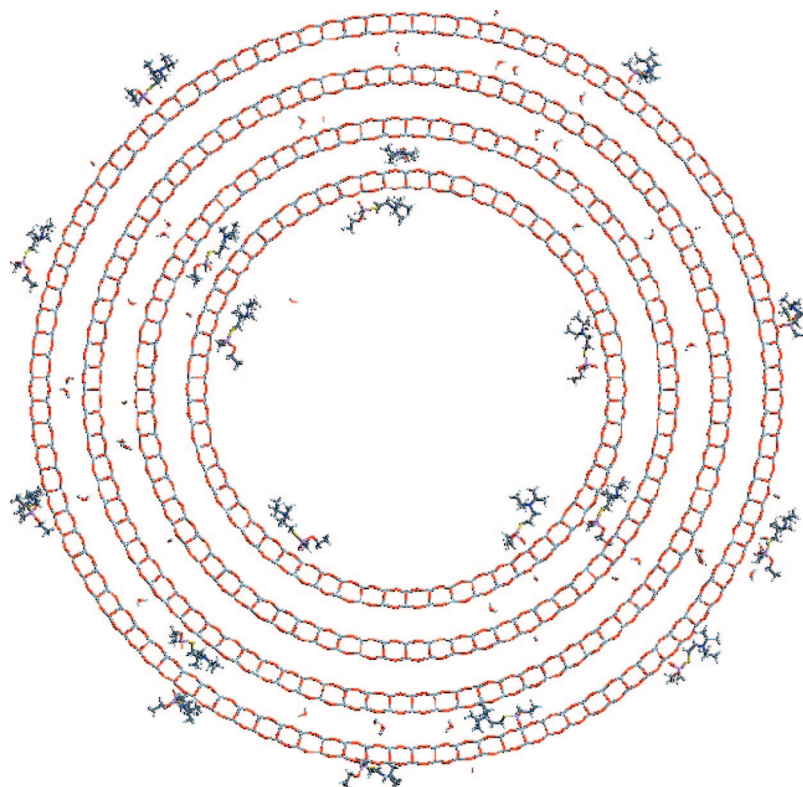


Figure 1. Structure of nanotubular titania as viewed down the open end showing paired-titanate layers and relative sizes of VX and water molecules (see Results and Discussion).

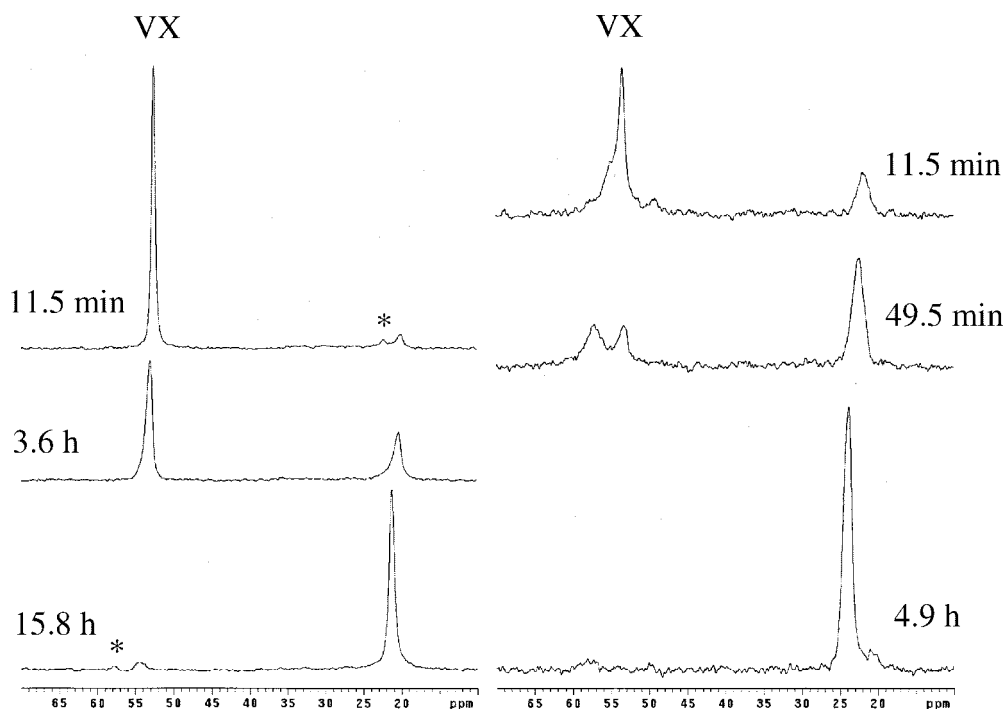


Figure 2. Selected ^{31}P MAS NMR spectra obtained for VX added to anatase (left) and nanotubular titania (right) at the indicated times. Spinning sidebands are marked by asterisks (*).

by hydrothermal synthesis from anatase nanocrystals (Aldrich) as previously described.^{8,9,13}

NMR. ^{31}P and ^{13}C MAS NMR spectra were obtained using a Varian Unityplus 300 NMR spectrometer equipped with a Doty Scientific 7 mm high-speed VT-MAS probe. Double O-ring caps were used to seal the 7 mm rotors (Doty Scientific) containing agent-contaminated samples. Spinning speeds of ca.

3000 Hz were employed. Direct polarization (DP) was used to obtain the spectra [i.e., no cross-polarization (CP) was used]. External shift references were 85% H_3PO_4 (0 ppm, ^{31}P) and tetramethylsilane (TMS; 0 ppm, ^{13}C).

Reaction Procedure. *Caution!* These experiments should only be performed by trained personnel using applicable safety procedures. Measured amounts of VX, GD, and HD were

SCHEME 1

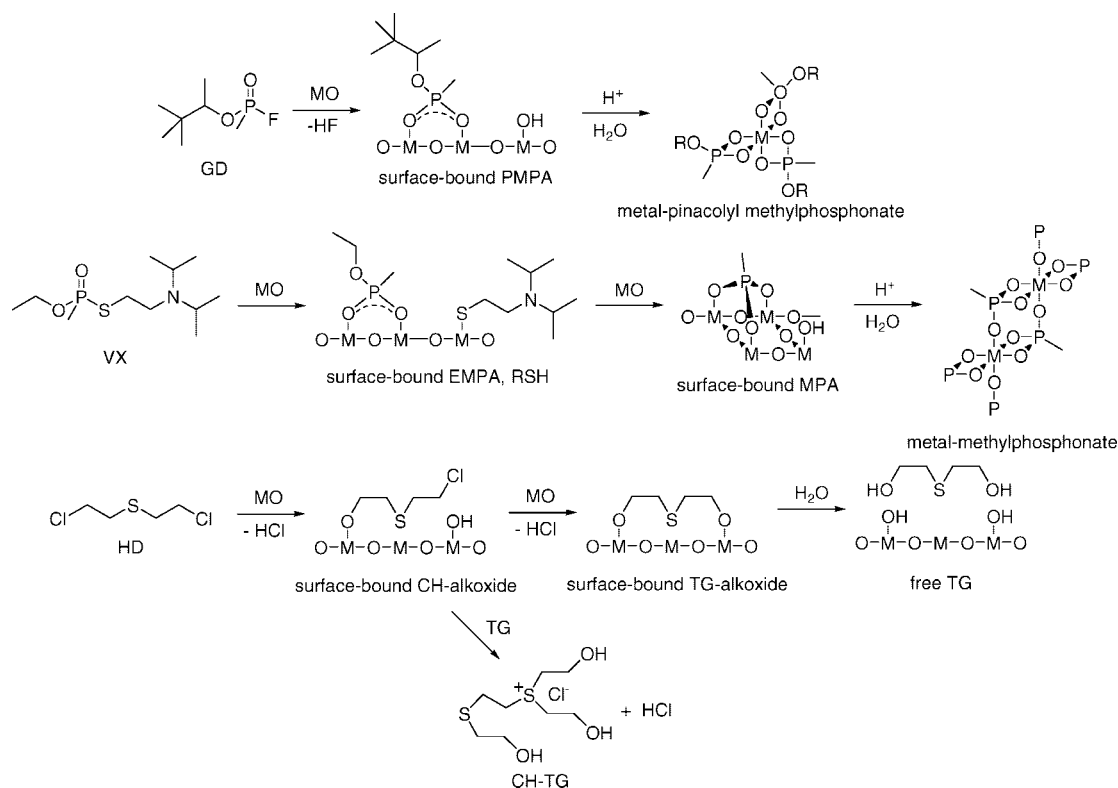


TABLE 1: Observed Half-Lives for HD, GD, and VX Deposited on Nanotubular Titania,^a Conventional Titania (Anatase),^b and Alumina^c

agent	alumina	nano-tubular titania	nanotubular titania + 20 wt % water ^d	anatase	anatase + 17 wt % water ^e
HD	18.2 h	1.8 days	3.7 h		
GD	2.7 h	1.8 h	3.3 h		
VX	15.0 days	58 min	24.7 min	4.3 h	10.5 days

^a A volume of 8 μL of VX or GD, or 7 μL of HD, added to ca. 0.15 g of nanotubular titania. ^b A volume of 5 μL of VX added to ca. 0.32 g of anatase. ^c A volume of 5 μL of VX, GD, or HD, added to ca. 0.27 g of alumina. ^d A volume of 40 μL of water (20 wt %) added prior to the agent. ^e A volume of 64 μL of water (16.5 wt %) added prior to the VX.

injected via syringe into the center of a column of NTT or anatase contained within a 7 mm NMR rotor. The rotor was sealed with the O-ring cap, and MAS NMR spectra were obtained periodically to monitor the reaction in situ.

Results and Discussion

Table 1 shows the various observed half-lives of HD, GD, and VX on alumina and NTT. Also shown are data for VX on conventional titania (anatase). Selected NMR spectra for these reactions are shown in the figures that follow.

As shown in Figure 2 for VX on anatase, both its peak (52.5 ppm) and that of the single product EMPA (20.2 ppm) remain quite sharp, which, in the absence of spinning sidebands (normally indicative of the expected large chemical shift anisotropy (CSA)¹⁴ of these compounds in the absence of motional narrowing), indicates that neither species is strongly bound to the TiO₂ surface. No toxic EA-2192 is observed, which would yield a peak near 43 ppm.¹⁵ Moreover, the rather facile reaction exhibits a half-life of only 4.3 h, which is considerably faster than the VX half-lives observed on alumina (several

days),⁶ MgO (68 h),⁴ CaO (93 h),⁵ Na–Y Zeolite (5 days),⁷ and concrete (several days to months, depending on age).¹⁶ It is only on silver-impregnated zeolite (Ag–Y)⁷ that a half-life on the order of hours is observed.

Still faster is the reaction for VX on NTT, exhibiting a half-life of just under an hour (58 min). The ³¹P MAS NMR spectra (right side of Figure 2) require additional comments. First, the VX (53.5 ppm) and EMPA (22 ppm) peaks are noticeably broader compared to those on anatase, perhaps reflecting stronger interaction with the higher surface area NTT. However, the absence of spinning side bands still indicates substantial motional narrowing of the CSAs.¹⁴ Second, an even broader, downfield-shifted VX peak emerges at 57.2 ppm. Finally, in the 4.9 h spectrum a small peak near 22 ppm (just upfield from EMPA) is assigned to VX-pyro.¹⁵

The presence of a broadened, second peak for VX was previously observed on Na–Y zeolite⁷ and attributed to adsorption within the supercage which possesses a 7.5 Å aperture at room temperature.¹⁷ As mentioned in the Introduction, the open end of the NTT tubule is about 5 nm in diameter, which is clearly large enough to accommodate the VX molecule (Figure 1). However, the possibility that VX can be accommodated between the titania sheets, with their much smaller *d*-spacing of ca. 0.87 nm, requires some scrutiny. Shown in Figure 3 are depictions of the VX molecule inserted between the titania sheet-pairs. Referring to the left side of Figure 3, subtracting the titania layer thickness of 3.2 Å results in a gap of only about 5.5 Å. Moreover, as shown on the right side of Figure 3, addition of the covalent radius of the exterior oxygens (0.73 Å) of the titania layers further reduces the gap to only about 4.0 Å. Now VX, with calculated dimensions of 11.4 × 5.2 × 5.6 Å³–12.2 × 6.0 × 6.35 Å³ with inclusion of the covalent radii of the hydrogen atoms (0.37 Å)—is clearly small enough to enter the 7.5 Å pores of Na–Y zeolite without any need for distortion. However, by relaxing its structure, it may be possible for VX

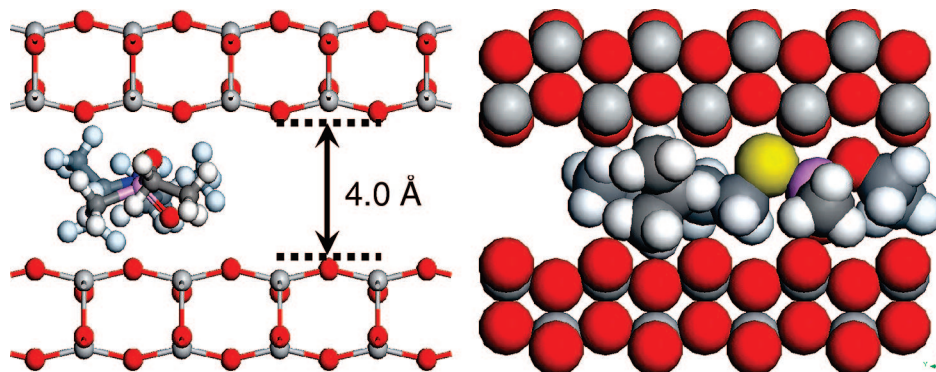
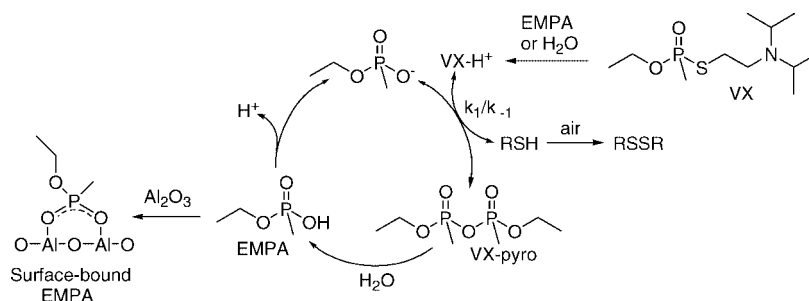


Figure 3. Depictions of VX molecule inserted between titanate sheet-pairs of NTT: left, ball-and-stick model; right, inclusion of covalent radii.

SCHEME 2



to squeeze between the much more constricting, albeit one-dimensional, 3.8 Å gap of the titania sheets as shown in the right side of Figure 3. In support of this contention, we note that for zeolites well-known cases exist where molecules seemingly larger than the pore aperture are still able to enter.¹⁷ Furthermore, during the adsorption of polar molecules (such as VX) the shape of the aperture is thought to flex slightly to enable passage.¹⁷ Thus, similar events may be occurring in the case of NTT to allow adsorption of VX between the titania sheet pairs—and effect its profoundly fast hydrolysis (see below).

Observance of VX-pyro, which is observed to build-up during the course of VX hydrolysis on NTT, is significant with regard to the mechanism. As shown by Yang et al.,¹⁸ EMPA, the common degradation product of VX, functions as a hydrolysis catalyst for VX in the so-called “water reaction”. This process, shown in Scheme 2, has also been observed for the hydrolysis of neat VX droplets in the presence of vaporized hydrogen peroxide (VHP).¹⁹ EMPA attack on (protonated) VX (k_1) results in the formation of VX-pyro, which is itself hydrolyzed back to EMPA (providing water is present). The reaction is reversible with the cleaved thiol RSH to re-form VX (k_{-1}); but in air this would be hampered by the facile air-oxidation of RSH to the disulfide RSSR. As further noted in Scheme 2, strong adsorption of EMPA occurs on oxides such as alumina, MgO, and CaO, etc., which would obviate its ability to react with VX; thus, the potentially extreme persistence of VX on these materials. However, the lack of binding or other interaction of EMPA with anatase or NTT keeps it free to catalytically react with VX on these surfaces.

Consistent with this mechanism, the addition of 21 wt % water results in further enhancement of the hydrolysis of VX on NTT, reducing the half-life to only 24.7 min. However, addition of 17 wt % water to anatase only succeeds in dramatically slowing the VX half-life on this material from 4.3 h to 10.5 days.

Strictly speaking, the VX water reaction requires only a stoichiometric amount of water. However, Yang et al.¹⁸ further

examined reactions with nonstoichiometric amounts of water, finding that initial reaction rates were faster for less amounts of water yet slower when excess water is present. It is also important to note that the half-lives observed by Yang et al.¹⁸ in their studies were on the order 13–16 h at room temperature—quite a bit slower than the half-lives exhibited by VX on (as-received) anatase and NTT (and even in the presence of VHP¹⁹). Thus, it would appear that fine-tuning the amount of water—or perhaps even metering its addition—could dramatically impact the overall achievable reaction rate.

Such processes are easily envisioned for VX adsorbed on anatase and NTT. For example, a lack of substantial microporosity on anatase would simply allow VX deposits to remain in contact with bulk surface water; thus, merely supplying excess water would slow the EMPA-catalyzed hydrolysis rate, not enhance it.

On the other hand, NTT, which ³¹P MAS NMR indicates adsorbs VX within the interior of its tubes—and possibly between the titania sheet-pairs (see above)—would tend to seclude VX from excess, bulk water. This would be especially true for VX inserted between the titania sheets. Thus, it is suspected that such fortuitous optimized metering of water to the EMPA-catalyzed reaction enables the facile hydrolysis of VX on NTT. In future work, it is hoped that by careful control of water content within the tubules and/or between the titania sheet layers,⁸ it will be possible to further hasten the hydrolysis of VX on NTT.

Of course, the ultimate goal is to destroy VX on a reactive sorbent just as fast as it can be done in a (homogeneous) decontamination solution. This would prevent any hazard associated with the spent sorbent following the actual decontamination process. This situation is strictly analogous to the concern of complete agent destruction once dissolved, adsorbed, or contacted by any decontaminant—liquid, solid, or gas—and the faster that ultimate destruction can occur, the better. Typically, complete destruction is desired within 15 or 30 min—a time frame easily achievable with liquid decontami-

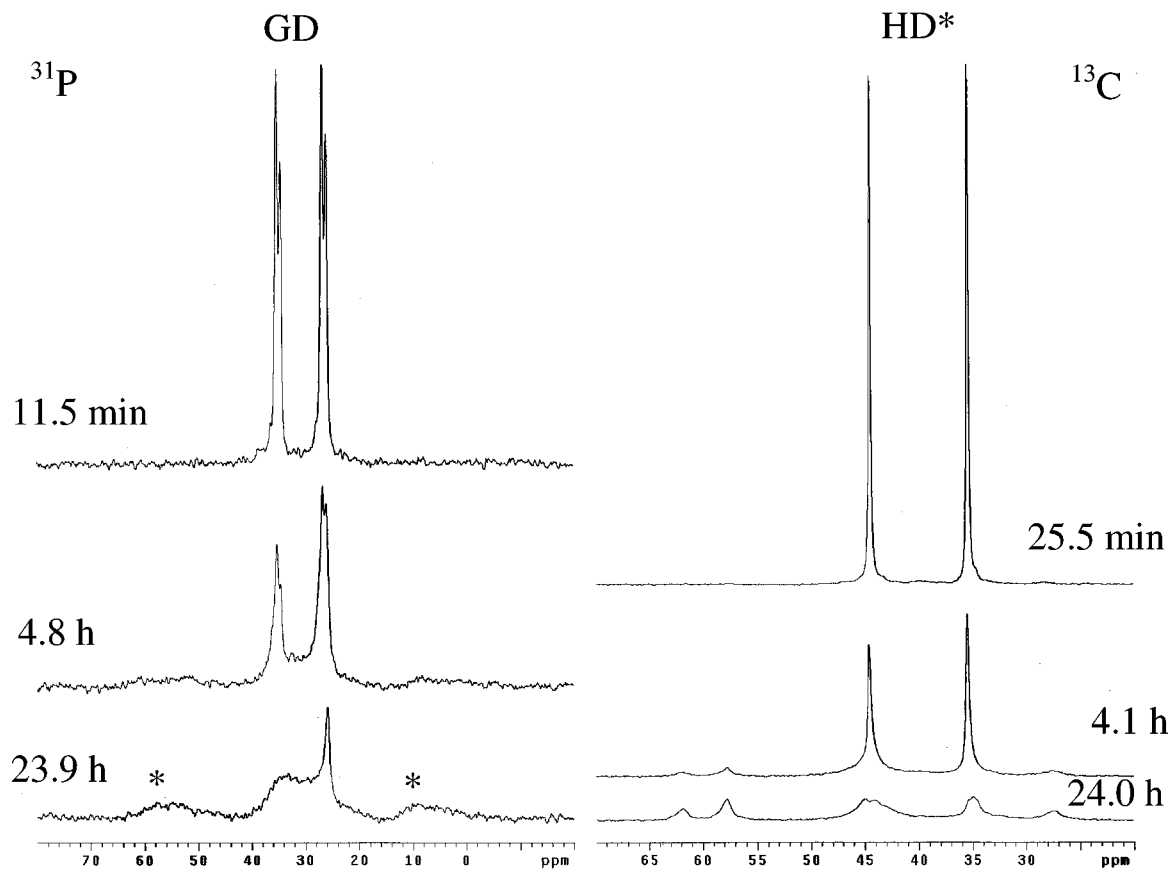


Figure 4. Selected MAS NMR spectra obtained for GD (left, ^{31}P) and HD* (right, ^{13}C) added to nanotubular titania with 20 wt % added water at the indicated times. Spinning sidebands are marked by asterisks (*).

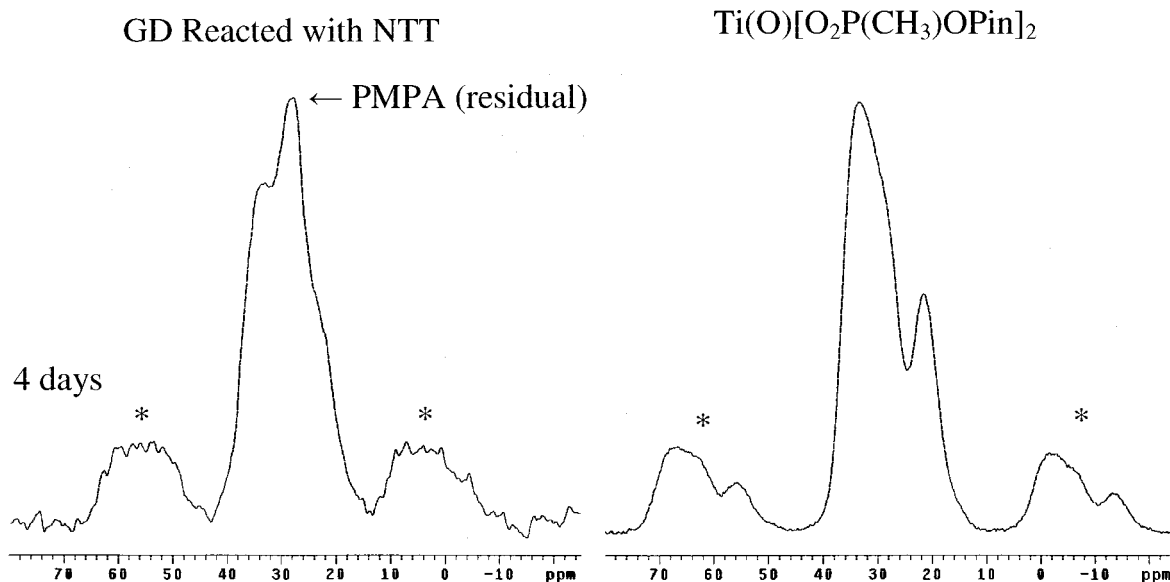


Figure 5. ^{31}P selected MAS NMR spectra obtained for GD reacted with as-received NTT (after 4 days, left) and authentic $\text{Ti}(\text{O})[\text{O}_2\text{P}(\text{CH}_3)\text{OPin}]_2$. Spinning sidebands are marked by asterisks (*).

nants.¹ The current, unoptimized half-life for VX on NTT (24.7 min) is at least in this ballpark. It will be interesting to see if the decontamination of VX on this material can be further fine-tuned and pushed to within the desired realm of liquid decontaminants.

For HD*, as shown by the ^{13}C MAS NMR spectra on the right side of Figure 4, the reaction on NTT with 20 wt % added water proceeds directly to the CH-TG sulfonium ion²⁰ (Scheme 1) as evidenced by the broad product peaks at 61.9, 57.8, 45.0,

43.0, 34.9, and 27.5 ppm. This occurred even on the as-received material consistent with the known presence of substantial water on NTT (about 3.5 H_2O per TiO_2 unit).⁸ The rate of HD hydrolysis on NTT is quite comparable to that observed on alumina and similarly varies widely with water content.

The same is true for GD where the half-life on NTT in the presence of 20 wt % water (3.3 h) is virtually identical to that observed on alumina. However, unlike the situation for HD, adding additional water to the as-received NTT material slowed

the GD hydrolysis rate from 1.8 to 3.3 h. Regarding the ^{31}P MAS NMR spectra on the left side of Figure 4 for GD, some hydrolysis to unbound pinacolyl methylphosphonate (PMPA, sharp peak at 25.8 ppm in bottom, 23.9 h spectrum) occurs as anticipated from the non-surface-binding behavior of EMPA. However, unlike VX-derived EMPA, additional broad peaks form with associated spinning sidebands indicative of a less mobile species.

Better resolution of the peaks associated with the immobile product is afforded by the ^{31}P MAS spectrum taken after 4 days for the reaction carried out on the as-received NTT (no water added), as shown in the left side of Figure 5. Following the disappearance of the GD peaks after about 10 h, the initially sharp PMPA peak continued to diminish and broaden as the other, even broader peaks emerged. Residual PMPA yields the peak at 27.4 ppm, whereas shifts for the immobile species are seen at 33.9 and ca. 23 ppm (shoulder). The peaks detected for the immobile GD-derived species is consistent with the titanophosphonate **1** species¹² mentioned in the Introduction. The ^{31}P MAS NMR spectrum¹² for authentic **1** is shown on the right side of Figure 3, which yields three characteristic peaks at 33.2, ca. 29, and 21.5 ppm. For GD-derived **1** on NTT, the ca. 29 ppm peak is evidently obscured by the residual PMPA peak at 27.4 ppm. Thus, the HF product formed in the hydrolysis of GD is able to erode NTT to allow its reaction with PMPA in the same manner previously observed for both anatase and titanium metal.¹²

Conclusions

VX, GD, and HD hydrolyze on NTT. As a reactive sorbent, NTT hydrolyzes VX extremely quickly with a half-life under 30 min. Compared to other metal oxides, anatase also hydrolyzes VX faster, but still about an order of magnitude slower than NTT. VX is observed to adsorb within the open-tube ends, or possibly even between the titania sheet-pairs, of NTT, processes suspected of enhancing its hydrolysis by effectively metering water (either exterior or intersheet bound) to optimize its autocatalyzed hydrolysis. Water is also evidently available and abundant enough to hydrolyze HD to its CH-TG sulfonium ion and GD to PMPA. The degradation products of GD—HF and PMPA—further react with NTT to form a species consistent with the previously characterized titanophosphonate $\text{Ti}(\text{O})[\text{O}_2\text{P}(\text{CH}_3)\text{OPin}]_2$. It is anticipated that by fine-tuning the water

content of NTT that hydrolysis reaction rates of all of these agents will approach those provided by typical liquid decontaminants.

Acknowledgment. We thank Messrs. Lawrence Procell and David Sorrick for assistance with the agent operations. Support for this work under U.S. Department of Defense Contract DAAD1902-1-0369 and Army Research Office Contract DAAD1903-1-0326 is gratefully acknowledged.

References and Notes

- (1) Yang, Y.-C.; Baker, J. A.; Ward, J. R. *Chem. Rev.* **1992**, *92*, 1729–1743.
- (2) Olson, C. T.; Hayes, T.; Babin, M. A.; LeClaire, R. D. *Government Testing of the Sorbent Decontamination System (SDS) in Accordance With the Decision Tree Network*, AD-B307 502; U.S. Army MRMC: Fort Detrick, MD, 2005 (unclassified).
- (3) (a) Klabunde, K. J.; Stark, J.; Koper, O.; Mohs, C.; Park, D. G.; Decker, S.; Jiang, Y.; Lagadic, I.; Zhang, D. *J. Phys. Chem.* **1996**, *100*, 12142–12153. (b) Stark, J. V.; Park, D. G.; Lagadic, I.; Klabunde, K. J. *Chem. Mater.* **1996**, *8*, 6182–6188.
- (4) Wagner, G. W.; Bartram, P. W.; Koper, O.; Klabunde, K. J. *J. Phys. Chem. B* **1999**, *103*, 3225–3228.
- (5) Wagner, G. W.; Koper, O. B.; Lucas, E.; Decker, S.; Klabunde, K. J. *J. Phys. Chem. B* **2000**, *104*, 5118–5123.
- (6) Wagner, G. W.; Procell, L. R.; O'Connor, R. J.; Munavalli, S.; Carnes, C. L.; Kapoor, P. N.; Klabunde, K. J. *J. Am. Chem. Soc.* **2001**, *123*, 1636–1644.
- (7) Wagner, G. W.; Bartram, P. W. *Langmuir* **1999**, *15*, 8113–8118.
- (8) Kleinhammes, A.; Wagner, G. W.; Kulkarni, H.; Jia, Y.; Zhang, Q.; Qin, L.-C.; Wu, Y. *Chem. Phys. Lett.* **2005**, *411*, 81–85.
- (9) Jia, Y.-Y.; Kleinhammes, A.; Kulkarni, H.; McGuire, K.; McNeil, L. E.; Wu, Y. *J. Nanosci. Nanotechnol.* **2007**, *7*, 458–462.
- (10) Mogilevsky, G.; Chen, Q.; Kleinhammes, A.; Wu, Y. Submitted for publication.
- (11) Mogilevsky, G.; Chen, Q.; Kulkarni, H.; Kleinhammes, A.; Mullins, W. M.; Wu, Y. *J. Phys. Chem. C* **2008**, *112*, 3239–3246.
- (12) Wagner, G. W.; Procell, L. R.; Munavalli, S. *J. Phys. Chem. C* **2007**, *111*, 17564–17569.
- (13) Yuan, Z.-Y.; Su, B.-L. *Colloids Surf., A* **2004**, *241*, 173–183.
- (14) Vila, A. J.; Lagier, C. M.; Wagner, G.; Olivieri, A. C. *J. Chem. Soc., Chem. Commun.* **1991**, 683–685.
- (15) Yang, Y.-C.; Szafraniec, L. L.; Beaudry, W. T.; Rohrbaugh, D. K. *J. Am. Chem. Soc.* **1990**, *112*, 6621–6627.
- (16) (a) Wagner, G. W.; O'Connor, R. J.; Procell, L. R. *Langmuir* **2001**, *17*, 4336–4341. (b) Wagner, G. W.; O'Connor, R. J.; Edwards, J. L.; Brevett, C. A. S. *Langmuir* **2004**, *20*, 7146–7150.
- (17) Breck, D. W. *Zeolite Molecular Sieves*; Krieger: Malabar, FL, 1984.
- (18) Yang, Y.-C.; Szafraniec, L. L.; Beaudry, W. T.; Rohrbaugh, D. K.; Procell, L. R.; Samuel, J. B. *J. Org. Chem.* **1996**, *61*, 8407–8413.
- (19) Wagner, G. W.; Sorrick, D. C.; Procell, L. R.; Brickhouse, M. D.; Mcvey, I. F.; Schwartz, L. I. *Langmuir* **2007**, *23*, 1178–1186.
- (20) Yang, Y.-C.; Szafraniec, L. L.; Beaudry, W. T.; Ward, J. R. *J. Org. Chem.* **1988**, *53*, 3293–3297.

JP803003K