Montmorillonite Functionalized with Pralidoxime As a Material for Chemical Protection against Organophosphorous Compounds

Abstract

Montmorillonite K-10 functionalized with 2-pralidoxime (PAM) and its zwitterionic oximate form (PAMNa) is introduced as a versatile material for chemical protection against organophosphorous (OP) compounds such as pesticides and chemical warfare agents (CWA). Upon inclusion into the montmorillonite interlayer structure, the pyridinium group of PAMNa is strongly physisorbed onto acidic sites of the clay, leading to shrinking of the interplanar distance. Degradation of diethyl parathion by PAMNa-functionalized montmorillonite in

Subject Terms

montmorillonite K-10; pyridine-2-aldoxime methiodide; functionalization; organophosphate hydrolysis; protective barrier
ABSTRACT
Montmorillonite K-10 functionalized with $\beta$-nucleophilic 2-pralidoxime (PAM) and its zwitterionic oximate form (PAMNa) is introduced as a versatile material for chemical protection against organophosphorous (OP) compounds such as pesticides and chemical warfare agents (CWA). Upon inclusion into the montmorillonite interlayer structure, the pyridinium group of PAMNa is strongly physisorbed onto acidic sites of the clay, leading to shrinking of the interplanar distance. Degradation of diethyl parathion by PAMNa-functionalized montmorillonite in aqueous-acetonitrile solutions occurred primarily via hydrolytic conversion of parathion into diethylthio phosphoric acid, with the initial stages of hydrolysis observed to be pseudo-first-order reactions. Hydrolysis catalyzed by the clay intercalated by PAMNa was 10- and 17-fold more rapid than corresponding spontaneous processes measured at 25 and 70 °C, respectively. Hydrolytic degradation of diisopropyl fluorophosphate (DFP), a CWA simulant, was studied on montmorillonite clay functionalized by PAMNa and equilibrated with water vapor at 100% relative humidity by 31P high-resolution magic angle spinning NMR and was observed to be rather facile compared with the untreated montmorillonite, which did not show any DFP hydrolysis within 24 h. The incorporation of the functionalized clay particles into elastomeric film of polyisobutylene was shown to be a means to impart DFP-degrading capability to the film, with clay particle content exceeding 18 wt %.
 Approximately 51972.19-CH
Montmorillonite Functionalized with Pralidoxime...

Block 13: Supplementary Note
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; distribution is unlimited.
Montmorillonite Functionalized with Pralidoxime As a Material for Chemical Protection against Organophosphorous Compounds

Lev Bromberg,‡ Christine M. Straut,§ Andrea Centrone,† Eugene Wilusz,§ and T. Alan Hatton*†

†Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States
‡Battelle Natick Operations, Natick, Massachusetts 01760, United States
§U.S. Army Natick Soldier Research, Development & Engineering Center, Materials and Defense Sciences Division, Natick, Massachusetts 01760, United States

ABSTRACT: Montmorillonite K-10 functionalized with α-nucleophilic 2-pralidoxime (PAM) and its zwitterionic oximate form (PAMNa) is introduced as a versatile material for chemical protection against organophosphorous (OP) compounds such as pesticides and chemical warfare agents (CWA). Upon inclusion into the montmorillonite interlayer structure, the pyridinium group of PAMNa is strongly physisorbed onto acidic sites of the clay, leading to shrinking of the interplanar distance. Degradation of diethyl parathion by PAMNa-functionalized montmorillonite in aqueous-acetonitrile solutions occurred primarily via hydrolytic conversion of parathion into diethylthio phosphoric acid, with the initial stages of hydrolysis observed to be pseudo-first-order reactions. Hydrolysis catalyzed by the clay intercalated by PAMNa was 10- and 17-fold more rapid than corresponding spontaneous processes measured at 25 and 70 °C, respectively. Hydrolytic degradation of diisopropyl fluorophosphate (DFP), a CWA simulant, was studied on montmorillonite clay functionalized by PAMNa and equilibrated with water vapor at 100% relative humidity by 31P high-resolution magic angle spinning NMR and was observed to be rather facile compared with the untreated montmorillonite, which did not show any DFP hydrolysis within 24 h. The incorporation of the functionalized clay particles into elastomeric film of polyisobutylene was shown to be a means to impart DFP-degrading capability to the film, with clay particle content exceeding 18 wt %.

KEYWORDS: montmorillonite K-10, pyridine-2-aldoxime methiodide, functionalization, organophosphate hydrolysis, protective barrier

INTRODUCTION

Large specific surface area, chemical and mechanical stability, layered structure, and high cation exchange capacity have made clays excellent adsorbent materials as well as useful components of barrier protective materials because of the existence of several types of active sites on their surface, including Bronsted and Lewis acids, and ion exchange sites. Montmorillonite clay is composed of units made up of two silica tetrahedral sheets with a central alumina octahedral sheet. The formula for montmorillonite is (Si7.8Al0.2)IV(Al3.4Mg 0.6)VIO 20(OH) 4 and the theoretical composition without the interlayer material is SiO2, 66.7%; Al2O 3, 28.3%; H2O, 5%. Montmorillonite typically consists of layered structures with strong intralayer bonds and relatively weak interlayer interactions and possesses a net negative charge of 0.8 per unit cell, and this has been responsible for giving superior activity to montmorillonite as an adsorbent. The structure of montmorillonite is affected by its exposure to water and aqueous solutions of small organic compounds. Hence, many organic molecules with polar functional groups, ions, and water molecules hydrating the ions can be intercalated in the interlayer space of montmorillonite, producing swelling (expansion of the distances between basal planes). It is well-known that clays such as montmorillonite and kaolinite accelerate the degradation of insecticides such as chlorpyrifos, paraoxon and methyl and ethyl parathions. Such degradation can be primarily attributed to the dissociative or destructive chemisorption processes occurring on clays containing interlayer metal (M) cations that display significant acidity due to the hydroxoo species formed through deprotonation of coordinated water molecules.

\[
[M(OH_2)_n]^m+ \rightarrow [M(OH_2)_{n-m}OH^{(m-1)+} + H^+]
\]

The metal hydroxoo species can serve as nucleophiles that are stronger than H2O. Like other nucleophiles containing an atom with an unshared pair of electrons adjacent to the reaction site, oximate bases are known to exhibit a much higher reactivity than common oxyanionic nucleophiles of similar basicities in many substitution processes, a phenomenon known as the alpha-effect. It is interesting to note that the literature on activity of clays modified by α-nucleophiles such as oximates is lacking.

Supporting Information
The intuitively expected synergistic effect of the α-nucleophile "added" to the already nucleophilic clay.

The present work, aimed at highly reactive, nucleophilic clay particles as components of reactive barrier materials, and thus pralidoxime (pyridine aldoxime methiodide, or PAM) was our cationic compound of choice. PAM was originally designed as a highly efficient antidote that binds to organophosphate-inactivated acetylcholinesterase. It is used by the military to combat poisoning by acetylcholinesterase inhibitors (nerve agents). We have previously observed a high activity of PAM in hydrolysis of diisopropyl fluorophosphate (DFP). Molecules like PAM and PAMNa can be introduced into the interlayer space of montmorillonite, affecting its structure depending on the density of the layer charge, the degree of exchange, and the host—guest and guest—guest interaction energy. This motivated the use of PAM as the choice for the clay particle modification. A cartoon illustrating PAM inclusion into montmorillonite is shown in Figure 1.

The PAM-modified montmorillonite appears to be reactive toward toxic organophosphates, as described below.

**Experimental Section**

**Materials.** Montmorillonite K-10, diethyl paraxon (99%), pyridine-2-aldoxime methiodide (98%), sodium methoxide (≥97%) and diisopropyl fluorophosphate (DFP, 99%) were received from Sigma-Aldrich Chemical Co. and polyisobutylene (PIB, viscosity average molecular weight 850,000) was obtained from Scientific Polymer Products, Inc. Montmorillonite K-10, an acidic clay purchased from Aldrich possesses BET surface area of 220 m²/g and the following chemical composition (average value): SiO₂ (73.0%), Al₂O₃ (14.0%), Fe₂O₃ (2.7%), CaO (0.2%), MgO (1.1%), Na₂O (0.6%), K₂O (1.9%).

Prior to the use, a fraction of PAM was converted to pralidoximate (PAMNa) by dissolving PAM in deionized water at 10 mg/mL while adjusting the pH to 8.6 by adding minute quantities of sodium methoxide, followed by lyophilization of the resulting solution. All other chemicals and solvents were obtained from commercial sources and were of the highest purity available.

**Syntheses.** The montmorillonite K-10 (MMNK-10) was functionalized by pralidoxime methiodide (PAM) at room temperature as follows. PAM was dissolved in deionized water at 10 wt % concentration after pH adjustment to 8.6 using sodium methoxide. One gram of sodium montmorillonite was added to the solution and the suspension was shaken at 250 rpm overnight. The montmorillonite particles were removed from the suspension by centrifugation (6,000 × g, 15 min), snap-frozen in liquid nitrogen and lyophilized to dryness. The pH of the solution equilibrated with the montmorillonite was 8.6.

Elastomeric films were made by casting 10 wt % solution of PIB in toluene over a Teflon surface followed by brief drying at 70 °C and then at 25 °C under vacuum until constant weight. Prior to casting, a weighed amount of montmorillonite or functionalized montmorillonite particles was added to a 1.0 g of PIB/toluene solution. The resulting paste was vigorously stirred using a spatula for 1–2 min and then spread over a Teflon sheet surface (∼10 × 5 cm) and dried.

**Methods.** XRD measurements were recorded with a PANalytical X’Pert PRO diffractometer (PANalytical B.V., Almelo, The Netherlands) equipped with an X’celerator linear detector using a CuKα radiation source. Samples were prepared as thin powder layers over zero-background plates, and progressive slits were used to illuminate a constant length of the samples (5 mm). XRD patterns were acquired over 18 h in the range of 2 to 65° 2θ using a nickel filter or a monochromator. Unit cell parameters were determined using Jade software (Jade Software Co., San Pedro, CA) with empirical peak profile fitting.

FTIR spectroscopy was performed on a NEXUS 870 FTIR spectro-meter (Thermo Nicolet Inc.). Spectra were recorded over the wave-number range between 4000 and 400 cm⁻¹ at a resolution of 2 cm⁻¹ and are reported as the average of 64 spectral scans. All samples were dried under vacuum to constant weight, ground and blended with KBr, and pressed to form the pellets used in the measurements. Thermogravimetric analysis (TGA) was conducted using a Q5000IR thermogravi metric analyzer (TA Instruments, Inc.). Samples were subjected to heating scans (20 °C/min) in a temperature ramp mode.

The kinetics of diethyl parathion degradation were studied in 4 mg/mL suspensions of the montmorillonite species suspended in monophasic solutions of parathion (6.5 mM) in acetonitrile and 50 mM solution of N-cyclohexyl-2-aminoethanesulfonic acid (CHES) in deuterium oxide (pD 8.6). The concentration of the aqueous (D₂O) buffer in acetonitrile was 27 wt % and was optimized to 1) enable monophasic solutions of water-insoluble parathion, 2) maintain pH throughout the reaction, and 3) enable proper locking of the NMR signals. The montmorillonite samples were suspended in the acetonitrile/buffer solutions and kept at 25 or 70 °C with periodic vortexing and brief sonication for proper mixing. Kinetics of parathion degradation in suspensions were assessed by liquid state 31P NMR spectrometry using a Bruker Avance 400 spectrometer operating at 161.98 MHz. At t = 0, an aliquot of parathion solution in acetonitrile was added to the clay suspension nas above and the experiment commenced. At given time intervals, the top clear solution (0.7 mL) was carefully withdrawn from the suspension by a pipet and placed into an NMR tube. The spectra were recorded by accumulation of 200 scans. The solution was placed back into the suspension immediately after each NMR measurement. The degree of parathion conversion was expressed as Fₚ = ΣF/ΣF₀, where ΣF and ΣF₀ are the sums of the integrations of the signals corresponding to the reactant (parathion, 62.4 ppm) and the products.

The observed rate constant, kₜ⁰, is found from the slope of the ln(1 − Fₚ) vs t plot

\[ \ln(1 - F) = -k_{\text{obs}}t \]
RESULTS AND DISCUSSION

Material Characterization. In the present work, we explored a concept of utilizing α-nucleophilic properties of 2-pyridine aldoxime methyl iodide (PAM) to create protective materials capable of degradation of organophosphorous compounds mimicking CWA. PAM and other oximes act as strong nucleophiles capable of deacylation and dephosphorylation of esters, and their efficiency in dephosphorylation can be enhanced by conversion into corresponding oximate anions, which in the case of PAM should be termed zwitterions (Figure 2).16,20,21

Reactivity of the oximates can suffer a saturation effect and decay with increasing basicity in aqueous solution above a pH of 9,23 and thus we performed the conversion of PAM to PAMNa at pH 8.6, i.e., just above the pKa value of 8.23 reported for PAM.22 As reported below, PAM converted to the PAMNa form by hydration water content of 4.9 wt % in pristine MMNK-10;26 this value is slightly smaller than the water content of 6.7 wt % for the band at 1595 cm⁻¹, which may be an indication of the presence of hydrates and PAM crystal polymorphs. As-received and dried under a vacuum at 25 °C MMNK-10 still contained approximately 5% of water removed by thermal dehydration at 105 °C, which is in excellent agreement with the reported hydration water content of 4.9 wt % in pristine MMNK-10,26 this value is slightly smaller than the water content of 6.7 wt % that can be deduced from the reported total cation-exchange capacity of MMNK-10 of 0.963 mol/kg,27 with the assumption of four hydration water molecules per ion.28 MMNK-10 functionalized with PAM contained approximately 3 and 6 wt % of hydrate water in the case of ClayPAM and ClayPAMNa, respectively. In the 180–220 °C temperature range, functionalized MMNK-10 samples showed a sharp degradation process, followed by broad weight loss up to 1000 °C, at which point the residual weight of the samples was 76 and 66 wt % in the case of ClayPAM and ClayPAMNa, respectively. These measurements enabled estimation of the oxime/oximate species content in the functionalized samples to be 21 wt % (0.80 mol/kg) and 28 wt % (0.98 mol/kg) for the MMNK-10 clay loaded with PAM and PAMNa, respectively. In the calculations, we assumed the molecular mass of the loaded species to be 264.06 Da (2-[(hydroxyimino)methyl]-1-methylpyridinium iodide) and 286.05 Da (sodium salt of PAM oximate, see Figure 2). The estimate obtained for PAMNa (0.98 mol/kg) corresponded well

Figure 2. Synthesis of pralidoxime from PAM.

Figure 3. FTIR spectra of PAMNa and untreated (Clay) and functionalized (ClayPAM, ClayPAMNa) montmorillonite K-10.
D2O u

presence or absence of functionalized clays or PAMNa (not shown for 0, identical spectra without the hydrolysis products were observed in the PAM solution with pH adjusted to 8.6 by sodium methoxide). At 8.6), PAMNa (pralidoxime methiodide obtained by freeze-drying (montmorillonite K-10 functionalized by sodium pralidoxime, pH 8.6), PAMNa (pralidoxime methiodide obtained by freeze-drying pralidoxime methiodide solution with pH adjusted to 8.6 by sodium methoxide).

Typical 31P NMR spectra of parathion degradation at pD 8.6, Figure 6. Typical 31P NMR spectra of parathion degradation at pD 8.6, 70 °C and time points taken at t = 0 or 2 days. Solvent: 50 mM CHES/D2O buffer (27 wt %, pD 8.6) in acetonitrile. Initial concentration of parathion, 6.5 mM. Hydrolytic species designations: Clay (montmorillonite K-10), ClayPAMNa (montmorillonite K-10 functionalized by sodium pralidoxime methiodide, pH 3.2), ClayPAMNa (montmorillonite K-10 functionalized with pralidoxime methiodide, pH 8.6), PAMNa (pralidoxime methiodide obtained by drying pralidoxime methiodide solution with pH adjusted to 8.6 by sodium methoxide).

Figure 7. Typical kinetics of parathion hydrolysis at pD 8.6 and T = 25 or 70 °C. Solvent: 50 mM CHES/D2O buffer (27 wt %) in acetonitrile. Initial concentration of parathion, 6.5 mM. Hydrolytic species designations: Clay (montmorillonite K-10), ClayPAM (montmorillonite K-10 functionalized by sodium pralidoxime, pH 7.8), PAMNa (pralidoxime methiodide obtained by drying pralidoxime methiodide solution with pH adjusted to 8.6 by sodium methoxide).

Figure 8. Predominant pathway of the nucleophilic hydrolysis of parathion in the presence of PAMNa nucleophile.

with the modified clay as a material for chemical protection. Parathion is quite stable in aqueous media at ambient temperatures. For instance, the half-life of parathion in estuarine water at room temperature and pH 7.8 is over 218 days.31 Our experiments at 70 °C were designed to accelerate the degradation, which was observed to be very slow at 25 °C. Typical 31P NMR spectra of the samples taken at the onset of the experiment and after 2 days at 70 °C are shown in Figure 6.

Signals of parathion and O,O-diethyl O-hydrogen phosphorothioate (diethylthio phosphoric acid, or DeTPA; major hydrolysis product) are seen at 62.4 and 52.0 ppm, respectively, in all samples taken after 2 days of reaction. In the case of the most reactive species, PAMNa, significant presence of tautomeric degradation products such as phosphorothioic O,S,S-acid, phosphorothioic O,S-O-acid, O,S-diethyl O-(4-nitrophenyl) phosphorothioate and O,O-diethyl S-(4-nitrophenyl) phosphorothioate (in the range 15–32 ppm) as well as phosphine oxide (0.8 ppm) was observed already after 1–2 days at 70 °C, whereas other tested degrading agents based on functionalized clay (ClayPAMNa) and the original montmorillonite K-10 (Clay) exhibited a very minor (<2 mol %) presence of the degradation products other
The obtained half-lives are collected in Table 1. Thermogravimetric analysis (Figure 4) enabled estimation of the PAM content in the functionalized clays, and thus the effective initial concentration of the PAM nucleophile (C_{cat}) in the samples of our kinetic experiments was obtained, yielding the apparent second-order hydrolysis rate constant, k^{''} = k_{obs}/C_{cat}^{''} (Table 1).

### Table 1. Kinetic Parameters of Parathion Hydrolysis by Untreated Montmorillonite K-10 (Clay), Pralidoxime in Zwitterionic Form (PAMNa) and Montmorillonite Functionalized by PAM (ClayPAM) and PAMNa (ClayPAMNa)

<table>
<thead>
<tr>
<th>Sample</th>
<th>k_{obs} (h^{-1})</th>
<th>t_{1/2} (days)</th>
<th>k''</th>
<th>Acceleration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Buffer control, 25 °C</td>
<td>8 × 10^{-5}</td>
<td>361</td>
<td>1</td>
<td>na</td>
</tr>
<tr>
<td>Clay untreated, 25 °C</td>
<td>1.4 × 10^{-4}</td>
<td>214</td>
<td>2</td>
<td>na</td>
</tr>
<tr>
<td>ClayPAMNa, 25 °C</td>
<td>8.2 × 10^{-4}</td>
<td>35</td>
<td>10</td>
<td>0.26</td>
</tr>
<tr>
<td>Buffer control, 70 °C</td>
<td>1.9 × 10^{-3}</td>
<td>15</td>
<td>1</td>
<td>na</td>
</tr>
<tr>
<td>Clay untreated, 70 °C</td>
<td>7.6 × 10^{-3}</td>
<td>3.8</td>
<td>4</td>
<td>na</td>
</tr>
<tr>
<td>ClayPAM, 70 °C</td>
<td>9.0 × 10^{-3}</td>
<td>3.2</td>
<td>5</td>
<td>2.8</td>
</tr>
<tr>
<td>ClayPAMNa, 70 °C</td>
<td>3.2 × 10^{-2}</td>
<td>0.91</td>
<td>17</td>
<td>8.1</td>
</tr>
<tr>
<td>PAMNa, 70 °C</td>
<td>6.2 × 10^{-2}</td>
<td>0.47</td>
<td>33</td>
<td>4.4</td>
</tr>
</tbody>
</table>

* Observed pseudo-first-order rate constant. *a* Half-life. *c* Apparent second-order hydrolysis rate constant. *d* Not applicable.

As is seen in Table 1, the pralidoximate indeed accelerated the parathion hydrolysis considerably. The rate enhancement was about 3-fold higher with oximate (PAMNa) compared to the oxime form of PAM, in agreement with our hypothesis of the higher nucleophilicity of the zwitterionic form of PAM. Furthermore, the untreated clay accelerated the hydrolysis, in accord with previous reports, but pralidoximate together with clay showed a synergistic effect leading to 3–5-fold higher hydrolysis acceleration than with the untreated clay alone. Of note, the rates of spontaneous hydrolysis measured herein were significantly slower at either 25 or 70 °C than the reported rates in estuarine water at comparable pH, but such a difference can be readily explained by the lower content of water (only 27 wt %) in our experiments.

**Diisopropyl Fluorophosphate Degradation.** DFP is a close analog of 2-(fluoromethylphosphoryl)oxypropane (sarin) and is widely used in protective material testing to simulate CWA. In our experiments, degradation of DFP was tested via deposition of DFP liquid directly onto materials pre-equilibrated with 100% humidity such as functionalized clay as well as elastomeric films modified with functionalized clay. Typical results of the DFP hydrolysis on MMNK-10 intercalated with PAMNa are shown in Figure 9. Notably, the functionalized clay was quite hygroscopic and visibly absorbed water at 100% humidity. The kinetics of the degradation were biphasic in all cases and accelerated with the higher amount of clay loaded into the NMR rotor, as expected. The biphasic nature of the degradation kinetics is probably due to the adsorptive nature of the clay and heterogeneity of the tested DFP-clay system. The DFP droplet deposited onto the clay layer started rapid degradation with the PAMNa molecules available in the immediate proximity, but then the kinetics became transport-limited and slowed down several-fold, due to the DFP permeation through the clay toward unreacted PAMNa sites. The observed rate constants of the initial DFP degradation on MMNK-10 functionalized with PAMNa (oxime loading, 39 wt %) varied in the range 0.14–0.81 h^{-1}, whereas the k_{obs} values estimated from the slope of the curves at t > 5 h were in the 0.02–0.03 h^{-1} range. Approximately, 75% of the initial DFP was hydrolyzed on MMNK-10 clay functionalized with PAMNa within a 24 h period, whereas no measurable DFP degradation was observed in identical experiments with untreated MMNK-10 not functionalized by the oximate.

The extent of the DFP hydrolysis by elastomeric films filled by PAMNa-intercalated MMNK-10 particles dramatically depended on the overall content of the particles in the film (Figure 10). PAMNa loadings over 12 wt % of film were...
necessary to observe any reactivity. Untreated clay devoid of PAMNa did not show any degradation of DFP within 24 h. All of the functionalized MMNK-10 particles were surrounded by PIB layers, which created a barrier for the reaction at the particle surface, at contents lower than 12. wt %. These data are consistent with the notion of the nonmonotonous dependence of the film reactivity on the content of the reactive component, which needs to be present on the surface for DFP and water accessibility to PAMNa. Once a concentration that leaves PAMNa exposed to the film surface is reached, there is proportionality between the reaction rate and the ClayPAMNa content.

**CONCLUDING REMARKS**

This work demonstrated that the clay functionalized with an oximate compound is effective in degradation of the OP toxins, including a pesticide and CWA analogue. The clay and the 2-PAM act synergistically, enhancing each other’s ability to chemisorb and degrade the OP compounds. It is believed that the functionalized clay is a simple means of creating materials for protective barriers and reactive coatings. Moreover, incorporation of ClayPAMNa (which binds to OP compounds with high efficiency) in an elastomeric film, the main component of the gloves furnished for soldiers and first responders, may address a secondary contamination issue well-known in the chemical agent and CWA threat in a benign species suitable for applications such as reactive skin decontamination lotions and other decontamination compositions.

**ASSOCIATED CONTENT**

Supporting Information. HRMAS $^{31}$P NMR spectra showing DFP degradation kinetics and $^{1}$HNMR spectra of PAM and PAMNA solutions (PDF). This material is available free of charge via the Internet at http://pubs.acs.org/.

**AUTHOR INFORMATION**

*Corresponding Author*

* tahatton@mit.edu.

**Present Addresses**

$^a$Current address: Center for Nanoscale Science and Technology, National Institute of Standards and Technology, Gaithersburg, MD 20899-6203.

**ACKNOWLEDGMENT**

The authors were supported by the Defense Threat Reduction Agency, in part by Grant HDTRA1-09-1-0012.

**REFERENCES**