U.S. ARMY COMBAT CAPABILITIES DEVELOPMENT COMMAND
CHEMICAL BIOLOGICAL CENTER

ABERDEEN PROVING GROUND, MD 21010-5424

DEVCOM CBC-TR-1774

Reaction of GD with Li_3N+H_2O for the Tactical Disablement Project

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November 2021

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)* XX-11-2021	**2. REPORT TYPE** Final	**3. DATES COVERED** *(From - To)* Feb 2019–Dec 2019

4. TITLE AND SUBTITLE
Reaction of GD with Li_3N+H_2O for the Tactical Disablement Project

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
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5d. PROJECT NUMBER
CB10412

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Director, DEVCOM CBC, ATTN: FCDD-CBR-TT, Aberdeen Proving Ground, MD 21010
Leidos Corporation; 3465 Box Hill Corporate Center Dr., Abingdon, MD 21009
Sandia National Laboratories; Albuquerque, NM 87185

8. PERFORMING ORGANIZATION REPORT NUMBER
DEVCOM CBC-TR-1774

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Defense Threat Reduction Agency, 8725 John J. Kingman Road, MSC 6201, Fort Belvoir, VA 22060

10. SPONSOR/MONITOR'S ACRONYM(S)
DTRA

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release: distribution unlimited.

13. SUPPLEMENTARY NOTES
U.S. Army Combat Capabilities Development Command Chemical Biological Center (DEVCOM CBC) was previously known as Edgewood Chemical Biological Center (ECBC).

14. ABSTRACT: (Limit 200 words)

As part of the Tactical Disablement Project, neat weapons-grade GD was reacted with lithium nitride (Li_3N) and water in glass reaction containers. Products were analyzed, and reaction schemes are provided to explain the products. Solid product was formed under some reaction conditions.

15. SUBJECT TERMS

Soman (GD)
Tactical Disablement
Decontamination
Nuclear magnetic resonance (NMR)
Liquid chromatography–mass spectrometry (LC/MS)
Lithium nitride and water (Li_3N+H_2O)

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON** Renu B. Rastogi
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			**19b. TELEPHONE NUMBER** *(include area code)*
U	U	U	UU	20	(410) 436-7545

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

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PREFACE

The work described in this report was authorized under project number CB10412. The work was started in February 2019 and completed in December 2019. At the time this work was performed, the U.S. Army Combat Capabilities Development Command Chemical Biological Center (DEVCOM CBC; Aberdeen Proving Ground, MD) was known as the Edgewood Chemical Biological Center (ECBC).

The text of this report is published as received and was not edited by the Technical Releases Office, DEVCOM CBC.

This report has been approved for public release.

Acknowledgments

The authors acknowledge the following individuals for their hard work and assistance with the execution of this technical program:

- Mr. Kevin Morrissey (DEVCOM CBC) for his contract support of this program; and
- Dr. Glenn Lawson (Defense Threat Reduction Agency; Fort Belvoir, VA) for program support and discussions.

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REACTION OF GD WITH Li_3N+H_2O FOR THE TACTICAL DISABLEMENT PROJECT

ABSTRACT

As part of the Tactical Disablement Project, neat weapons-grade GD was reacted with lithium nitride (Li_3N) and water in glass reaction containers. Products were analyzed, and reaction schemes are provided to explain the products. Solid product was formed under some reaction conditions.

1. INTRODUCTION

The objective of the tactical disablement project is to use a minimal amount of reagents to make bulk chemical agent (CA) unusable as a threat through the neutralization and/or solidification of the bulk agent. This can be done by performing reactions in the CA storage container via wet chemical approaches in order to avoid transporting the storage container.

It is anticipated that the container will have at least 10% of the volume as empty headspace to allow for expansion of the agent fill, so 10% was the target amount of additive reagents. By utilizing the CA storage container as the batch reactor, the logistical resources that are needed for decontamination can be significantly reduced. Employing the CA storage container as the reaction vessel enables the capability to add reagents to multiple containers in a short period of time, as opposed to processing one container at a time for typical flowing reactor approaches. In scenarios where a quick response is required, the material can be added to all the CA containers and left to react on their own without intervention.

Neutralization of a CA was required to greatly reduce the toxicity as a CA. This study didn't require a detailed kinetic study to determine how long it would take to reach a target amount of decontamination of the CA. Formation of solid product can interfere with dispersal or nebulization of the CA, preventing its use as a weapon. Previous studies have been done on the characterization of solid products from reactions of VX,[1] GB,[2] QL, and DF.[3]

This study demonstrates a method to perform the neutralization and solidification of bulk soman (GD) CA in a glass jar that simulates a storage container. The minimal quantities of chemical reagents are typically found to be ≈15% by weight of the amount of CA. The amount of reagent is determined by the stoichiometry of the reaction and by the addition of enough reagent for complete conversion of the CA. It is anticipated most CA containers will have empty volume in the headspace in the container to allow for thermal expansion, although it isn't known how much volume, so there is a possibility that removal of some agent to make enough volume for the addition of reagent might be necessary in some cases.

The most effective reagent for the purposes of the project was found to be lithium nitride and water ($Li_3N + H_2O$). A 100-mL scale reaction run was done and the products were analyzed. Solidification of this run wasn't complete after the first addition of reagents, so further studies were done of the solidification process in an attempt to make it more reproducible.

2. PRELIMINARY STUDIES

2.1 Reactions with $Li_3N + H_2O$

Li_3N was selected as a reagent due to its strong basicity (after reacting with water to form LiOH) and low molecular weight, even though it is not widely used as an aggressive synthesis reagent.[4,5] The reaction of $Li_3N + H_2O$ forms lithium hydroxide and ammonia (or ammonium hydroxide),[6] according to the reaction:[7]

$$Li_3N + 3\ H_2O \rightarrow 3\ LiOH + NH_3\ (\text{aq or gas})$$

These products react by caustic hydrolysis with the agent. The major product that is expected is pinacolyl methylphosphonic acid (commonly called GD acid) for hydrolysis reactions. It is possible that the GD reacts with some water first, and then the product HF reacts with the Li_3N, although we were not able to detect LiF as a solid. There was minimal bubbling of the mixture (possibly forming ammonia gas or HF) for small-scale reactions, but it was minimal compared to the amounts of reagents. It is important to note that the reactions can get very hot during the early stages of reaction, depending on the conditions of addition of water and Li_3N, so microbubbling could be due to boiling or outgassing of the water or CA. (Much more boiling has been observed in larger reaction volumes.[2,3])

Several small-scale studies were done on the reaction of GD with Li_3N. Small scale studies of GD that was used for this study were CASARM grade from U.S. Army Combat Capabilities Development Command Chemical Biological Center (CCDC CBC) Chemical Transfer Facility lot number GD-U-4238-CTF-N. The large-volume reaction runs were done with technical grade, stabilized GD (CTF lot no. GD-S-0274-CTF-N). Lithium nitride was purchased from Sigma-Aldrich (MilliporeSigma, St. Louis, MO), P/N 399558-25G. Water was from an in-house distillation system.

Test reactions were done in Nuclear Magnetic Resonance (NMR) glass sample tubes that could be analyzed directly by NMR. The solid product appears to be an ionic solid, and it dissolves in acidic water. This can account for the increase in viscosity of the liquid and formation of solid material as ionic solid precipitates out of solution. Analysis indicates that the viscous liquid is GD acid. The solid may be a lithium salt of GD acid, although it also may be LiOH that crystallizes to encapsulate liquid products. Determination of the proportions of the products in the solid material is difficult due to limitation of the analysis methods for solids or slurry. Reaction products were not mixed or homogenized due to the expectation that reactions would be in unstirred containers, so solids were allowed to settle out but retain liquid that was absorbed into the solid material. In some cases, unreacted Li_3N reagent appeared to settle to the bottom without completely reacting. Li_3N solid has a distinct brownish color, compared to white LiOH.

It was concluded that reacting Li_3N and H_2O *in situ* with the neat agent is preferable for the performance in destruction of the agent. Using the Li_3N solid directly and adding minimal amounts of water gives control on the amount of water. The use of $Li_3N + H_2O$ can also generate some heat and agitation, depending how the reagents are added in a very sensitive way. The heat promotes faster reaction.

Two similar samples were run with GD. After a week of reaction time, the residual amount of GD fell to 0.2% and 4% after 8 days of reaction in the two runs. The samples became cloudy and more viscous. Figure 1 shows one of the NMR tubes, with liquid remaining above cloudy semisolid and unreacted brown Li_3N solid powder that has settled to the bottom.

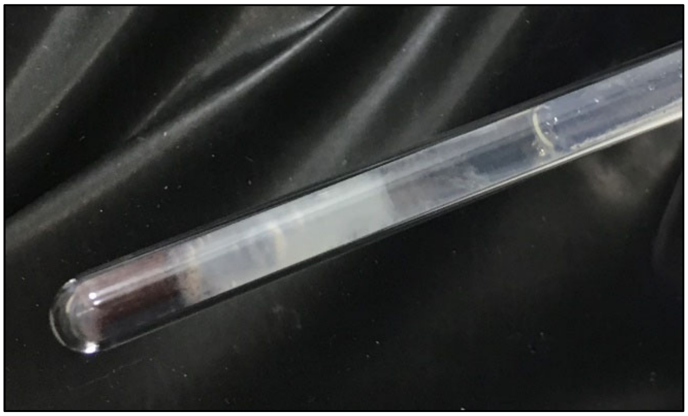

Figure 1. Reaction mixture of GD + Li_3N + H_2O in an NMR tube, sample nb097P149A. Brown solid is unreacted Li_3N. Cloudy region is gelled, viscous material, and the clear region is liquid.

3. LARGER SCALE REACTION STUDIES

3.1 10 mL reaction study of $Li_3N + H_2O$

Reactions were scaled up to 1-10 mL in glass vials. All the vials were sampled to determine residual GD using the method discussed in Section 4. Reaction times varied, and a series of kinetic time points were not measured for the samples.

A reaction with 10 mL of GD is shown in Figure 2. An amount of 0.9 g of Li_3N powder was added to the GD. Water was added in 0.1 mL increments, and after 0.4 mL was added, the mixture heated up to 60C from the reaction of water with Li_3N. The reaction was accelerated by the heat. The sample was solidified after 3 h, and the amount of residual GD was not detectable after 1 day of reaction (<1%). Reactions with GD are generally similar to GB in that fast addition of water to the Li_3N can cause heating and faster reaction.[2] On the other hand, slower reaction with pellets of Li_3N can cause slower reaction and less solidification.

3.2 100 mL reaction study of $Li_3N + H_2O$

Reactions were done using 100 mL GD under conditions with 10% water and 5% Li_3N, which were used as the standard methods for GB and VX. Some experimentation was

Figure 2: Reaction mixture of 10 mL GD + Li_3N + H_2O, using 10 mL GD, 9% Li_3N and 4% H_2O after 1 day of reaction time (sample NB0018P89B). The residual GD was below detection limits (<1%).

done using GB and the simulant dimethyl methylphosphonate (DMMP) to determine the best method for adding the reagents.[2] For this sample, Li_3N was added first to the GD in the form of pellets that were pressed at Sandia National Laboratory using a commercial pellet press, followed by water that was added rapidly. This method gave a slow reaction for this agent. Pellets without powdered reagent tend to react slowly, since most of them settle to the bottom of the liquid. The water appeared to be fully miscible in GD, so that a layer of water wasn't formed. It was found in other experiments that a layer of water can come into contact with a pellet to cause local fast reaction. The same procedure gave problems with DMMP reactions that were too fast and generated excess heat, and further work may be needed with simulant or agent studies to develop the optimized method for adding the reagents to larger container sizes. Faster addition can be an advantage, however, since heating the reagents causes the reaction to proceed faster. It can cause a hazard to the operator if safety precautions aren't taken.

After one day of reaction time, the amount of GD remaining in the liquid phase was 30%, after 1 week the amount was 11%, and after 2 weeks there was 2% GD remaining. We conclude that the approach is effective in decontaminating GD due to the alkaline hydrolysis to GD acid.

After 3 weeks of reaction time, there was approximately 50% liquid in the reaction product mixture. There appeared to be residual pellets of Li_3N reagent. An experiment was performed to determine the effect of additional water in the mixture. From the stoichiometry of the reaction, it can be calculated that the 10% water that was originally added is sufficient to either react to completion with the Li_3N reagent to form LiOH and ammonia, or to react with the GD to form GD acid, but the amount of water was not sufficient for both reactions. It appeared from the decontamination of GD that the reaction with GD was the most effective for consuming the reagent water. It was possible that the lack of water was the reason that solidification was not taking place since some Li_3N might be unreacted. As a result, additional water was added over several weeks to determine the effect. The amounts of added water are shown in Table 1.

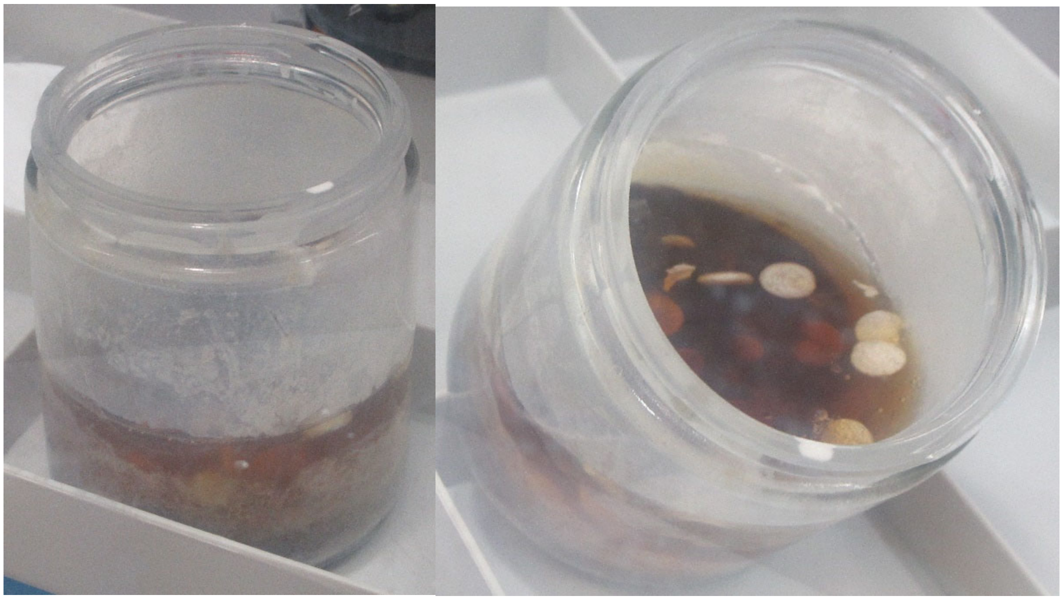

Figure 3: Reaction container of 100 mL GD with 5% Li_3N and 10% water. After 1 week of reaction, about half the product remains liquid. In the right photo, white pellets from the original Li_3N are present in the liquid.

Table 1: Addition of water to 100 mL GD reaction. The reaction contained 0.56 moles of GD and 0.14 moles Li_3N (requiring 0.57 moles of water to completely react).

Time after reaction start (days)	**Amt. added water (as vol.% GD)**	**Total Moles Water**	**Percent of water needed to completely react with Li_3N and GD**
0	10	0.56	49%
14	3	0.72	64%
21	3	0.89	78%
28	3	1.05	93%

By the final addition of water, enough water was added to reaction with 93% of both GD and the Li_3N reagent. However, the reaction product was still about half liquid. The product continued to slowly solidify for several months, but it didn't completely solidify in 4 months, and part of it was still a viscous liquid.

There are several possible reasons for the varying rates of solidification:

- First, the solidification is not necessarily due to a lack of water, since adding water did not cause more solidification. From comparison to the reaction in Figure 2, which had less water, it appears that solidification could be facilitated by less water relative to Li_3N. The stoichiometry of the reaction implies enough water has to be added to completely react with the GD for complete decontamination.
- Second, it is possible that over a long period time the water can have double duty, so that it reacts with both Li_3N to form LiOH, and then the LiOH forms the ionic solid.
- Third, it is possible that the reverse order also happens, so that GD acid can react with Li_3N, although we have not observed any noticeable reaction between GD acid and Li_3N. Instead, it appeared that excess water rapidly reacts with residual Li_3N. This observation is not consistent with the measurements that show that GD reacts within a few days even when there is residual Li_3N that remains in the reaction mixture.
- Fourth, it is possible that the reagent was passivated by being coated with an unreactive material so that it takes longer to be consumed.
- Fifth, it is also possible that the salt of GD acid is not formed as easily, or is not as insoluble, as the salts for GB or VX, so the ionic solid is not formed as fast if there is any excess water.
- Sixth, it is possible that the temperature of the initial stage of the reaction plays a key role in perhaps more completely consuming the Li_3N to conversion to LiOH and NH_3.

Clearly, the reaction involves many competing processes, and some processes can be slow due to rates that are limited by viscosity or by solids. It is necessary to measure each process in isolation in order to completely characterize the overall reaction.

4. PRODUCT ANALYSIS

4.1 ^{31}P NMR Results on Residual GD

The best quantitative method for determining the purity of nerve agents and for determining residual agent is phosphorus (^{31}P) NMR due to the simplicity of distinguishing between the agent and reaction products. [8]

However, for the reaction runs using technical grade GD, there were some difficulties using NMR due to iron impurities in the starting material that caused line broadening. It has been reported that a few hundred parts per million of paramagnetic metal ions like Fe^{3+} can broaden NMR peaks.[9] The large-volume reaction runs were done with technical grade, stabilized GD (CTF lot no. GD-S-0274-CTF-N, Aberdeen Proving Ground, MD). Paramagnetic metals that are dissolved or suspended in the liquid interfered with NMR analysis by producing broadened peaks. As a practical result, the detection limit wasn't as low for ^{31}P NMR as it would have been for GD without metal content.

All the vials or jars from reaction runs were sampled to determine residual GD. This was done by using the following preparation procedure: 1) remove a quantity (10-100 mg) of the solid and/or liquid reaction product and transferring to a sample vial, 2) weigh it, 3) add and weigh an amount of internal standard triethyl phosphate (TEP), 4) dissolve or extract with chloroform ($CDCl_3$) for 0.5-1 min. with vortexing, and 5) transfer the solution to double contained NMR tubes using an inner Teflon insert and outer glass 5 mm NMR tube. Samples were analyzed by standard ^{31}P NMR parameters on a JEOL ECS-400 Spectrometer with a relaxation delay time of 90 sec. Quantitation was calculated based on the signal of GD quartet peaks compared to triethyl phosphate internal standard (Sigma-Aldrich P/N 538728-100ML). Double containment of solutions is required for safety reasons for CA solutions. Using doubly contained tubes decreased the sensitivity to some extent, but for these samples the paramagnetic impurities were a larger source of error.

In some cases, some of the solid was not dissolved in this solvent. In those cases, the extraction efficiency of GD from the solid wasn't measured. Sampling times after the beginning of the reaction varied, and kinetic time points were not systematically measured for the samples.

5. CONCLUSION

As part of the Tactical Disablement Project, neat weapons-grade GD was reacted with lithium nitride (Li_3N) and water. Reactions were done up to 100 mL in volume of GD in glass reaction containers. Photos and video of the reaction were taken as the reaction proceeded for documentation of the solidification process of the products. Residual GD was determined as a weight percentage of the liquid reaction product.

This study demonstrates a method to perform the neutralization and solidification of bulk soman (GD) CA that should also be effective in a storage container or munition. The minimal quantities of chemical reagents are typically 15% by weight of the amount of CA, using 5% Li_3N and 10% water. This indicates that the Tactical Disablement goal of using a small amount of decontamination reagent can be used to detoxify and render useless a container or munition of GD.

Several technical issues were addressed. GD was decontaminated by a commonly-used caustic hydrolysis reaction, but the reaction was relatively slow due to the lack of mechanical stirring or heating, and due to the lack of a large excess of water and alkali. Regardless, the GD was destroyed in a week or less. Detection limits of the NMR method were relatively high, though. Determination of whether trace amounts of GD remain in the product will require development and validation of a more sensitive analytical chemistry method, possibly using gas chromatography/mass spectrometry.

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ACRONYMS AND ABBREVIATIONS

APG	Aberdeen Proving Ground
ACN	Acetonitrile
CA	chemical agent
CASARM	U. S. Army Chemical Agent Standard Analytical Reference Materiel
CCDC CBC	U. S. Army Combat Capabilities Development Command Chemical Biological Center
CTF	U. S. Army Chemical Transfer Facility
CW	chemical warfare
CWA	chemical warfare agent
DMMP	Dimethyl methylphosphonate
EIC	Extracted ion chromatogram
GD	Soman, pinacolyl methylphosphonofluoridate
GD acid	Pinacolyl methylphosphonic acid
LC/MS	Liquid chromatography/mass spectrometry
LC/MS/MS	Liquid chromagraph/tandem mass spectrometer
NMR	Nuclear magnetic resonance
TEP	Triethyl phosphate
TIC	Total ion chromatogram

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