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

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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 U.S. Army Edgewood Chemical Biological Center.

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

ABSTRACT

As part of the Tactical Disablement Project, neat weapons-grade GB 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. To find the best conditions for solid formation, further studies were done using dimethyl methylphosphonate (DMMP) as a simulant.

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 or transferring the chemical out of the container into a reactor. The reaction should take place completely without any mechanical mixing, excessive agitation, or external heating.

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. Fewer personnel are required since no sophisticated equipment needs to be set up, configured, or operated. 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. However, it was not anticipated that the toxicity will be completely eliminated by an environmentally approved decontamination such as the kind that was required for the destruction of the U.S. CA stockpile. As a result, this study didn't require a method for trace detection of residual GB in the reaction products. It also 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. Early concepts of the project involved efforts to form a solid polymer product. For example, incorporation of the CA into a reagent such as an epoxy could produce a solid polymerized matrix. However, it was found that simpler reagents could be used to form solid products, and the solids were characterized by several analytical chemistry methods. A previous study of the characterization of solid products from VX reaction has been published.[1]

This study demonstrates a method to perform the neutralization and solidification of bulk sarin (GB) CA in a glass jar that simulates a storage container. The minimal quantities of chemical reagents are typically 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 to form a solid product. It is anticipated that 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.

This approach does not require sophisticated equipment, fuel, electricity to power equipment, or large quantities of decontaminating materials. It does not generate a large amount of waste that must be treated.

Reaction of GB with several reagents were studied for the Tactical Disablement project in preliminary surveys. The most effective reagent for the purposes of the project was found to be lithium nitride and water ($Li_3N + H_2O$). A more detailed study was done on the reagent $Li_3N + H_2O$ to narrow down the range of reagent ratios.

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. Some reaction runs were done using a simulant dimethyl methylphosphonate (DMMP), which is less reactive than GB. Solidification was observed with DMMP, so it was found that a reactive CA was not needed to obtain solidification. These simulant studies provided valuable information about the limiting conditions that are required to make the products solidify.

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.[2,3] The reaction of $Li_3N + H_2O$ forms lithium hydroxide and ammonia (or ammonium hydroxide),[4] according to the reaction:[5]

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

These products react by caustic hydrolysis with the agent. The major product that is expected is isopropyl methylphosphonic acid (commonly called GB acid) for hydrolysis reactions. It is possible that the GB reacts with some water first, and then the product HF reacts with the Li_3N, although we were not able to detect LiF. 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 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 was observed in larger reaction volumes, as discussed later.)

Several small-scale studies were done on the reaction of GB with Li_3N. The GB was from U.S. Army Combat Capabilities Development Command Chemical Biological Center (CCDC CBC) Chemical Agent Standard Analytical Research Material (CASARM) program lot number GB-U-7044-CTF-N or GB-U-1244-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 first sample was without added water, and there was no sign of reaction between GB and Li_3N when no water is present. The specific quantities for the reactions for $Li_3N + H_2O$ are outlined in Table 1. Table 2 shows the calculated mole ratios and observed product consistency. GB was 50% neutralized in 10 minutes and 90% in one day using 21% additives ($Li_3N + H_2O$) to the reaction. The maximum of 99% of the GB was destroyed in two days. Complete gelling of the solution occurred in six hours.

The increase of viscosity contributed to the decrease in reaction rate with time. The reaction had some unreacted Li_3N at the bottom of the NMR sample tube, as shown in **Error! Reference source not found.** as brown solid. The other product is a colorless material with semisolid or viscous gel consistency. NMR analysis indicates that this material is mostly isopropyl methylphosphonic acid (GB acid), which could be a combination of the acid (a liquid) or the Li salt (solid) with residual water. There could also be products that can’t be detected with this kind of NMR method. A slight excess amount of water (more than 3:1 H_2O:Li_3N) with agitation would have likely resulted in complete reaction of the Li_3N to form LiOH.

NMR spectra showing the conversion of GB to product are shown in Figure 2 and Figure 3. The NMR spectra were taken of the reaction mixture in the sample tube without any sample preparation. Figure 2 shows narrower lines that are simpler for identifying the product, but Figure 3 has more complete reaction.

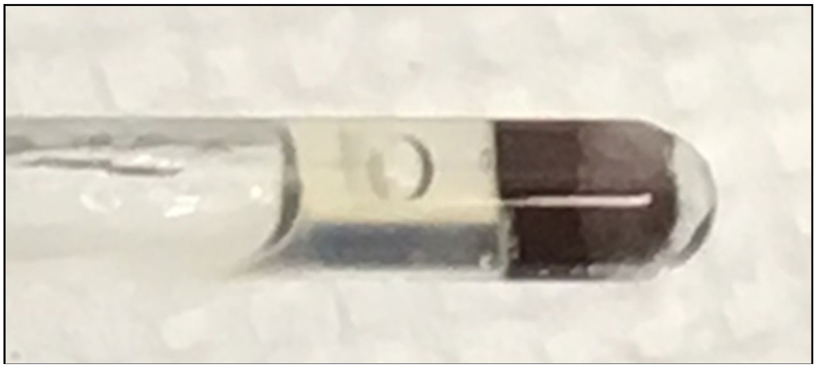

Figure 1. Photo of the NMR tube containing the reaction of GB + Li_3N + H_2O (P69C), showing the brown residue of unreacted Li_3N at the right, and the gelled translucent semisolid to the left of it. Some residual fluid remained on top of the clear solid, but it has drained to the left.

For the mole ratio of H_2O to Li_3N of 0.73 (Reaction P69C), only 31% of GB is destroyed in six days. For this reaction, complete gelling wasn't observed, although the sample was partially gelled. Reaction P87B had approximately 1.5 mole ratio of H_2O: Li_3N and exhibited 15% destruction in 10 minutes and 50% over six days. In comparison, sample P85B has a mole ratio of 3:1 of water to Li_3N, and it reacts nearly to completion to eliminate the GB. This reaction was also completely gelled. These reactions emphasis the importance of the mole ratio of H_2O:Li_3N in the reaction and that three times as many moles of water to Li_3N is about the optimum ratio.

Table 1. List of GB + Li_3N + H_2O reagent ratios in NMR tubes, from Notebook 16-0097.

Reaction ID	GB (mL)	Li_3N (mg)	H_2O (µL)	H_2O:Li_3N (mole ratio)
P69C	0.400	42.2	16	0.73
P85B	0.382	34.4	54	3.0
P87A	0.467	10.57	16.4	3.0
P87B	0.245	16.3	12.6	1.5
P121D	0.150	10[a)]	49[a)]	9.5

a) Added as LiOH and NH_4OH (aq.); corresponds to a ratio of about 0.1 LiOH:GB. Reaction performed by adding LiOH and NH_3 (aq) rather than Li_3N + H_2O. Ratio includes water consumed from making LiOH and NH_4OH from Li_3N and from ammonia solution.

Table 2. Reagent ratios and products for Li_3N reactions with GB from Table 1, from Notebook 16-0097.

Reaction ID	Li_3N:GB (w/w)	Li_3N:H_2O (w/w)	Product consistency	GB remaining after >1 week
P69C	0.083	2.64	Partly viscous plug	64% GB
P85B	0.083	0.64	Viscous, doesn't flow	1% GB
P87A	0.021	0.66	Partly solidified	63% GB
P87B	0.061	1.29	Not solidified	50% GB
P121D	0.027[a)]	0.079[a)]	Viscous liquid	25% GB

a) Added as LiOH and NH_4OH (aq.); corresponds to a ratio of 0.1 solid LiOH(H_2O):GB. Reaction performed by adding LiOH and NH_3 (aq) rather than Li_3N + H_2O. Ratios include water consumed from making LiOH and NH_4OH from Li_3N and from ammonia solution.

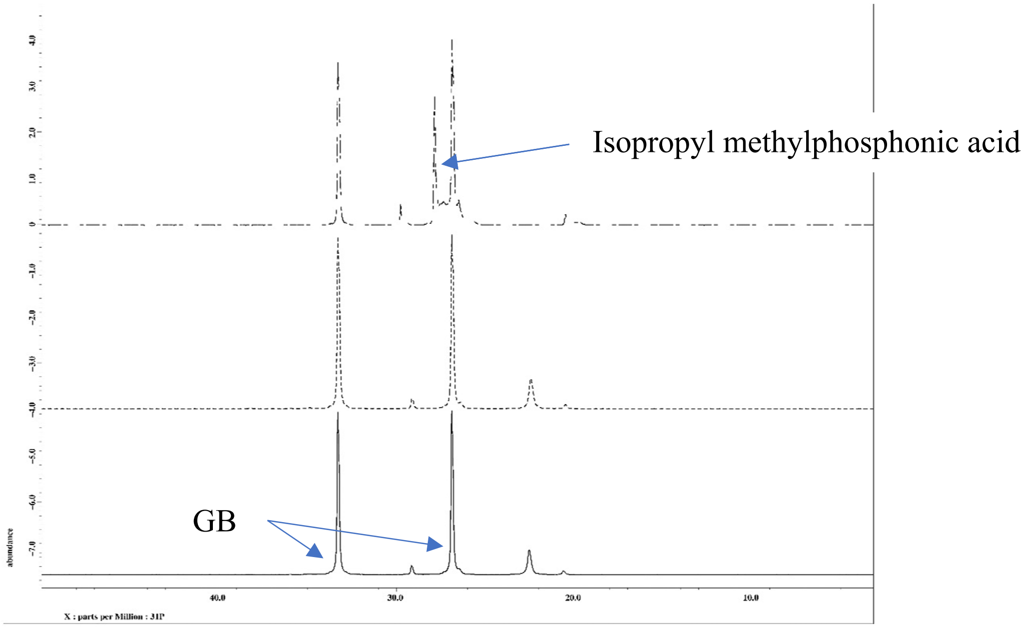

Figure 2. Solution ^{31}P NMR spectrum of GB and Li_3N (run P87B). Bottom panel: Spectrum from 4 min. after mixing; Middle panel: spectrum after 18 h reaction time; Top panel: spectrum after 13 days of reaction time.

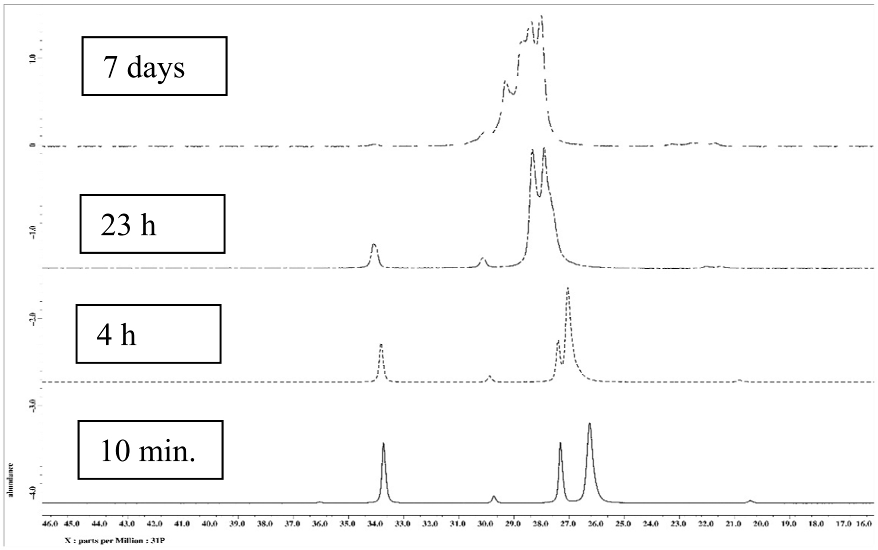

Figure 3. Solution ^{31}P NMR spectra of reaction run P85B, GB + Li_3N + H_2O. The solution gelled in about 4 h. The top panel shows a broad, low resolution peak for isopropyl methylphosphonic acid due to the high viscosity of the sample.

Reactions (e.g., P69C and P87B) with small mole ratio quantities of water have a substantial amount of unreacted Li_3N in the bottom of the NMR tube, see **Error! Reference source not found.**. The tubes were inverted to mix the reagents when they were added, but they were otherwise not agitated to mix them, so some of the solid settled to the bottom. The partially gelled, clear solid part of the solution is also shown. Since there is poor mixing in narrow NMR tubes, it is hard to say for certain that less water was the main reason for slower reaction kinetics, but it is likely a contributing factor.

Experiments revealed GB does not react directly with Li_3N. Water is needed to react with Li_3N to form the ammonia or ammonium hydroxide and lithium hydroxide (that react with the GB). Li_3N was added before the agent, and the container was inverted several times to mix the powder with the agent. It was found that no observable reaction occurred without water, indicating that Li_3N can't extract fluorine or fluoride from the GB molecule. The solid Li_3N is in the form of a red/purple powder that is easily visible, while product solid is gray colored. NMR analysis also revealed no reaction between Li_3N and GB.

The proposed reaction mechanism of GB + Li_3N + H_2O is shown in Figure 4.

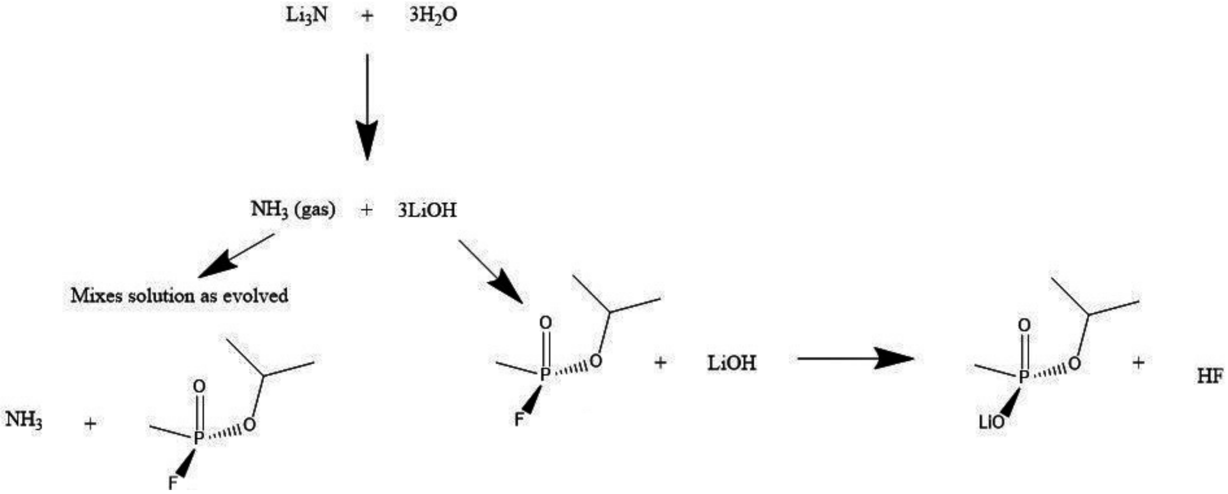

Figure 4. Proposed reaction mechanism of GB + Li_3N + H_2O. The products could form an ionic solid, which could account for the increase in viscosity and formation of solid material.

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 solid precipitates. Analysis indicates that the viscous liquid is GB acid. The solid may be a lithium salt of GB 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.

Questions that remained from these studies are how to optimize the reaction of water with GB as opposed to consumption of water by the Li_3N to make excess caustic, and how to optimize the formation of solids.

Additional reactions were performed to determine if Li_3N + H_2O is a requirement, compared to adding lithium hydroxide or ammonium hydroxide solutions directly. To test the hypothesis, separate reaction runs were performed using LiOH (Lithium hydroxide monohydrate from Sigma-Aldrich, P/N L4533-100G), NH_4OH (28-30% aqueous ammonium hydroxide, Sigma-Aldrich P/N 221228-25ML-A) solution, and a mixture of LiOH and NH_4OH aqueous solution. The reaction proportions are shown in Table 3. LiOH was added as a solid and didn't show any effect, probably due to low solubility in GB. The mixture of LiOH and NH_4OH reacted with GB to form hydrolysis products. There was a noticeable increase in viscosity, but the mixture still flowed because there was more water present for these samples compared to the $Li_3N + H_2O$ samples. There appeared to be more product peaks present in the ^{31}P NMR spectrum, but we were not able to identify every species in the reaction products. Even though the LiOH and NH_4OH solution reactions yielded significant GB destruction, the amount of volume added was higher than $Li_3N + H_2O$. As a result, in order to minimize the amount of reagents that are added to the CA, it appears that $Li_3N + H_2O$ is the preferable reagent combination.

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 more control on the amount of water than concentrated solutions of the NH_4OH reagent or solid LiOH.. The use of $Li_3N + H_2O$ may also generate some heat and agitation when added to GB that promotes reaction.

Table 3. LiOH and NH_4OH reactions with GB, from Notebook 16-0097.

RXN ID	**GB (mL)**	**$LiOH \cdot H_2O$**	**NH_4OH (30% aqueous)**	**Comments**
P121C	0.400	n/a	0.120 mL	Minimal destruction in 24 h
P121B	0.400	41 mg	n/a	Minimal destruction in 24 h
P121D	0.150	14.7 mg	0.045 mL	75% destruction in 1 week

The sample with the least residual GB was P85B, and this sample had the most Li_3N and water. The sample became viscous. The reaction mixtures sat for 2 weeks at room temperature to determine the final amount of GB remaining. It was observed there was slow reaction continuing for the second week. The continual decreasing rate of reaction over time is due to (1) consumption of the alkali reagent and (2) increase in viscosity of solution.

2.2 Reactions with $LiAlH_4$

Preliminary studies were done using lithium aluminum hydride ($LiAlH_4$) as a reagent. $LiAlH_4$ pellets were obtained from Sigma-Aldrich, P/N 323403-100G. This reagent was chosen for study because it is a strong, reactive reducing agent that is commonly used in chemical synthesis, so it is readily commercially available. It has the capability of reducing by contributing 4 electrons, which could potentially decrease the ratio of reagent to CA.

Combining 0.445 mL GB and 0.0328 g $LiAlH_4$ (sample P69B) results in significant amounts of bubbling, formation of precipitates, and smoking. Gelling was not observed, although the solution may have become more viscous. Solution ^{31}P NMR analysis shown in Figure 55 revealed 27% destruction of the GB by the time (20 minutes) the first NMR spectrum was collected. There was no additional change in the amount of GB consumed over five days, shown in Figure 6. The observation that there is no further pressure building and the lack of change of the product distribution over five days suggests the reaction is a quick-and-done type reaction, probably limited by the consumption of reagent.

The ^{31}P NMR analyses revealed the formation of two reaction products from the reaction of $LiAlH_4$ and GB: methyl phosphine (CH_3PH_2) and GB acid (isopropyl methylphosphonic acid). The presence of the fully reduced methyl phosphine at a chemical shift of -163 ppm[6,7] indicates the strength of the reducing potential of the $LiAlH_4$. The isopropyl methylphosphonic acid is the primary hydrolysis product of GB, and may indicate a reaction with lithium hydroxide or aluminum hydroxide that is formed when $LiAlH_4$ comes in contact with residual water.

Observation of the methyl phosphine product indicates that the GB lost all its P-O bonds and reduced from P(V) to P(III). No compounds with intermediate amounts of reduction were identified. CH_3PH_2 is very volatile and rapidly evaporates from the sample. The volatility of the compound makes quantitative methods difficult for determining the amount of the compound that is formed, but the amount of residual GB can be measured by ^{31}P NMR.

The compound CH_3PH_2 auto-ignites when exposed to oxygen in the air. A reaction in an autosampler vial had a visible flame above a container. The flame was small but this compound is classified as pyrophoric, so there is an explosion hazard if it accumulates in a low oxygen enclosed container.[8] After reaction, there was a gray-white solid residue. This solid residue was not collected and analyzed but it is likely a combination of Li and Al oxides and fluorides, and residual GB.

Since GB is fully reduced to CH_3PH_2, a GB molecule consumes 3 of the 4 hydrogens on each $LiAlH_4$ molecule according to the reaction stoichiometry, rather than reacting in a 1:4 molar ratio that might be anticipated if a less reduced intermediate product was formed. To fully reduce GB to CH_3PH_2 requires a theoretically calculated 24% by volume amount of $LiAlH_4$. This amount is larger than the project goals. It is possible that this amount could be added if enough of the methylphosphine evaporates as $LiAlH_4$ is added. As methylphosphine leaves the solution, more $LiAlH_4$ can be added to eventually reach 24% by volume of $LiAlH_4$. However, the escape of methylphosphine might form a flame over the container, which would complicate the addition procedure.

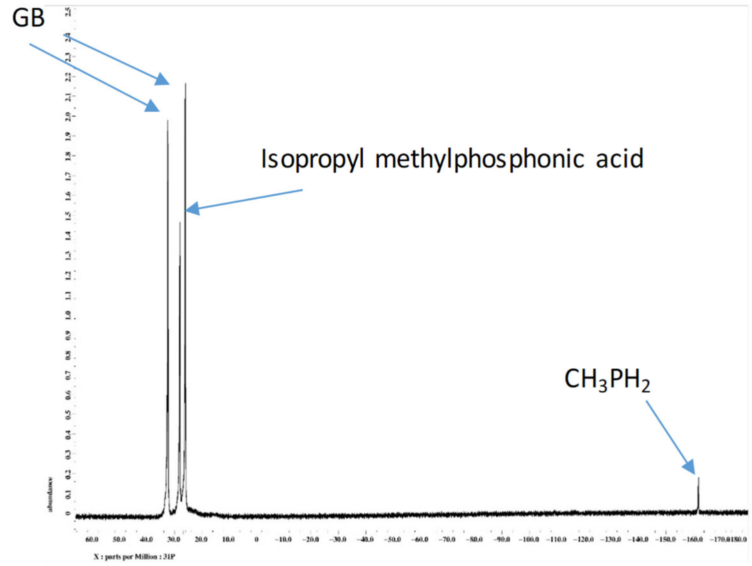

Figure 5. Reaction products of GB + LiAlH4 using ^{31}P NMR.

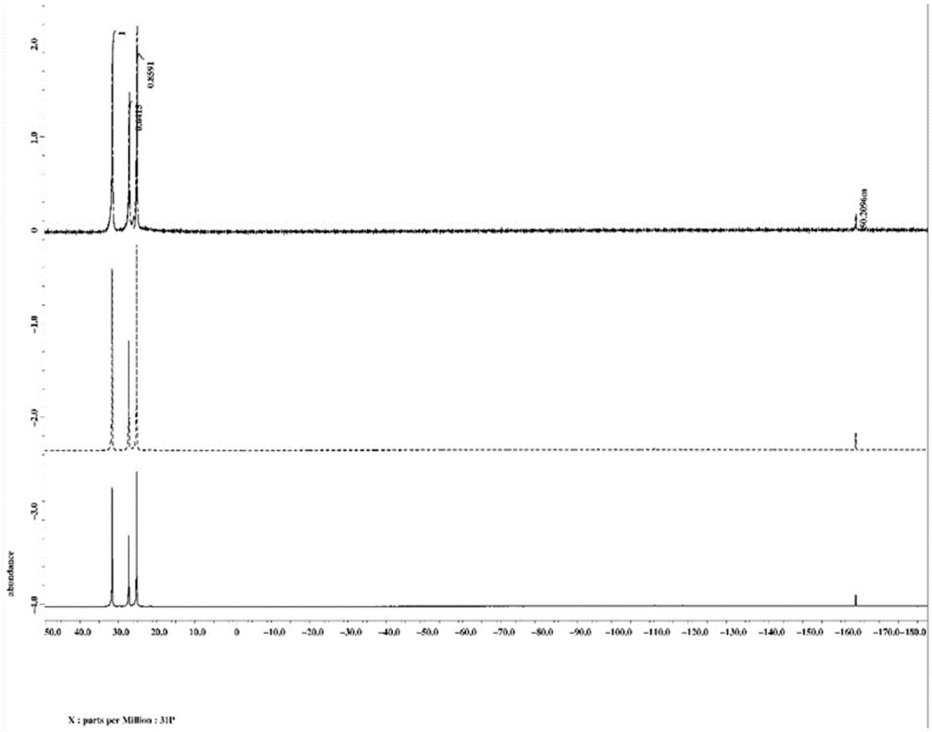

Figure 6. Reaction of GB and LiAlH4 determined by solution ^{31}P NMR. There is little reaction after the first burst of bubbling. Bottom panel: first spectrum 15 min after mixing; Middle panel: 4 hr after mixing; Top panel: 6 days after mixing, showing peak integrals.

The reagent was added as chunks of material in the NMR tube reactions, and some chunks remained that appeared to be unreacted. This may have be due to insufficient agitation in the tube or some passivation of the surface of the reagent.

A reaction was performed using a mixture of $LiAlH_4$ and Li_3N, and product vials are shown in Figure 7. No water was used, since water would react with the $LiAlH_4$. Quantitation of a sample of the final solid material after a week of reaction time indicated that there was 25% of the original GB remaining.

Because the reagent $LiAlH_4$ had undesirable effects from requiring a large percentage of reagent and production of a pyrophoric product that could lead to possibility of explosion hazard, no further work was done at a larger scale for this reagent.

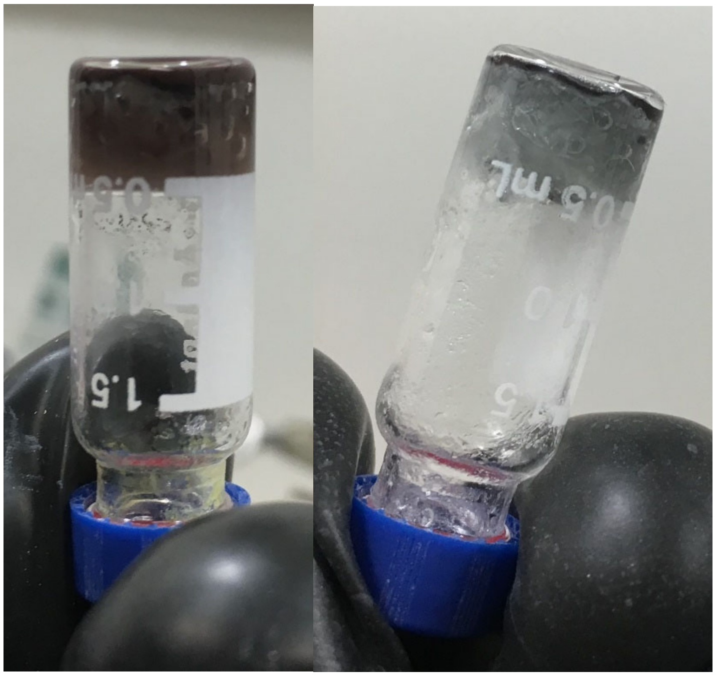

Figure 7. Reaction mixture of GB + $LiAlH_4$ + Li_3N, sample P27B. Left photo: One-week reaction time. Right photo: Two-week reaction time. Both samples have 25% residual GB.

3. LARGER SCALE REACTION STUDIES

3.1 Multiple 1-10 mL reaction studies of $Li_3N + H_2O$

More reactions were done that were scaled up to 1-10 mL in glass vials, and they are listed in Table 4. The reaction runs were done with technical grade, stabilized GB (from U.S. Army Chemical Transfer Facility [CTF] lot no. GB-S-2152-CFT-N, Aberdeen Proving Ground, MD). All the vials were sampled to determine residual GB. The method is discussed in Section 4. The amount of residual GB that was detected by ^{31}P NMR was <5% except one case, discussed below. Reaction times before sampling varied, and kinetic time points were not measured for the samples.

One of the project requirements for Tactical Disablement was to solidify the CA to prevent its intentional use or dispersal. As shown in Table 4, the first studies using the reagent

Li_3N + water indicated that the reaction formed a solidified product. However, later reactions were found to remain partly or mostly liquid (blue columns). Further study was done to determine what caused the difference between reactions that formed solid products and reactions that remained liquid. A number of reactions were run in the course of a year to test ratios of reagents. The parameters that varied for the reactions are in the table.

Table 4: List of reactions of GB with Li_3N + H_2O from Notebook 18-0018. Volumes of 1-10 mL GB were used with varying amounts of reagents. Reaction runs in blue columns remained partly or mostly liquid, and white columns solidified.

Reaction	**P67A**	**P67B**	**P89A**	**P103A**	**P103B**	**P105B**	**P121A**	**P137A**	**P143B**	**P147A**
Date	9/13/ 2018	9/13/ 2018	10/24 2018	12/10/ 2018	12/10/ 2018	12/11/ 2018	1/31/ 2019	4/23/ 2019	7/1/ 2019	7/11/ 2019
Vol GB (mL)	5.0	5.0	10.0	3.0	6.0	3.5	5.0	1.0	1.0	6.04
Form	Li_3N powder	Li_3N powder	Li_3N powder	Li_3N pellet	Li_3N pellet	Li_3N pellet	Li_3N pellet	Li_3N powder	Li_3N powder	Li_3N pellet
Li_3N Mass (g)	0.4555	0.4495	0.9149	0.1524	0.2954	0.3441	0.4388	0.0422	0.0546	0.2830
H_2O Mass (g)	0.70	0.70	0.40	0.15	0.30	0.60	0.50	0.10	0.10	0.60
ratio (GB: Li_3N)	*10.9769*	*11.1235*	*10.9302*	*19.6850*	*20.3114*	*10.1715*	*11.3947*	*23.7192*	*18.3050*	*21.3428*
ratio (Li_3N: H_2O)	0.65	0.64	2.29	1.02	0.98	0.57	0.88	0.42	0.55	0.47
Product State (Solid/Liq.)	S	S	S	S	L	S	L	S	L on top	L
Time for react. (days)	<5 min.	4 d	1 d	8 d	24 d	7 d	15 d	1 d	13 d	14 d
rate of water addition (fast/slow)	fast w/boil	fast	fast	slow	slow	slow	slow	slow	fast	slow

Particular parameters in the table are notable. The ratio of GB to Li_3N is < 12 for most of the solid products and > 18 for most of the liquid products, with a few exceptions. Sample P103A had a small amount of both Li_3N and water, giving it a high ratio of GB to Li_3N, and it is shown in Figure 8 as solidified or semisolid with some liquid absorbed in a solid matrix. The sample was stirred or swirled more than most samples, as opposed to being allowed to sit during the reaction, so most of the dark-colored Li_3N solid has reacted. The sample indicates that mixing of the samples might be advantageous for consuming all the Li_3N reagent.

Photos of typical reactions are shown in Figure 9, with Sample P89A solidified and P103B that remained liquid. Sample P121A had a low ratio but remained liquid.

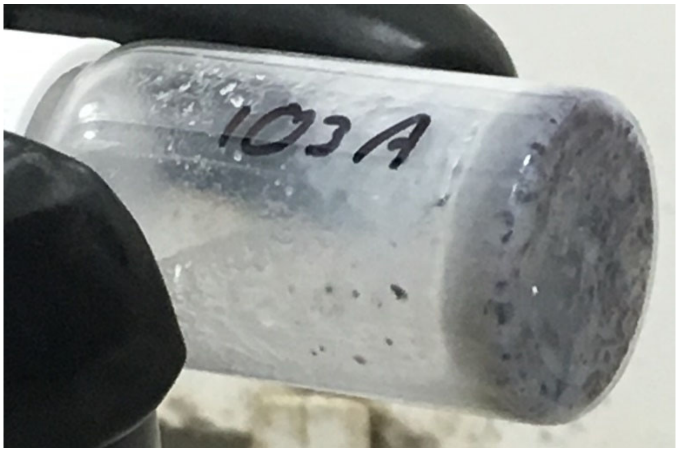

Figure 8: Photo of Sample P103A, which solidified.

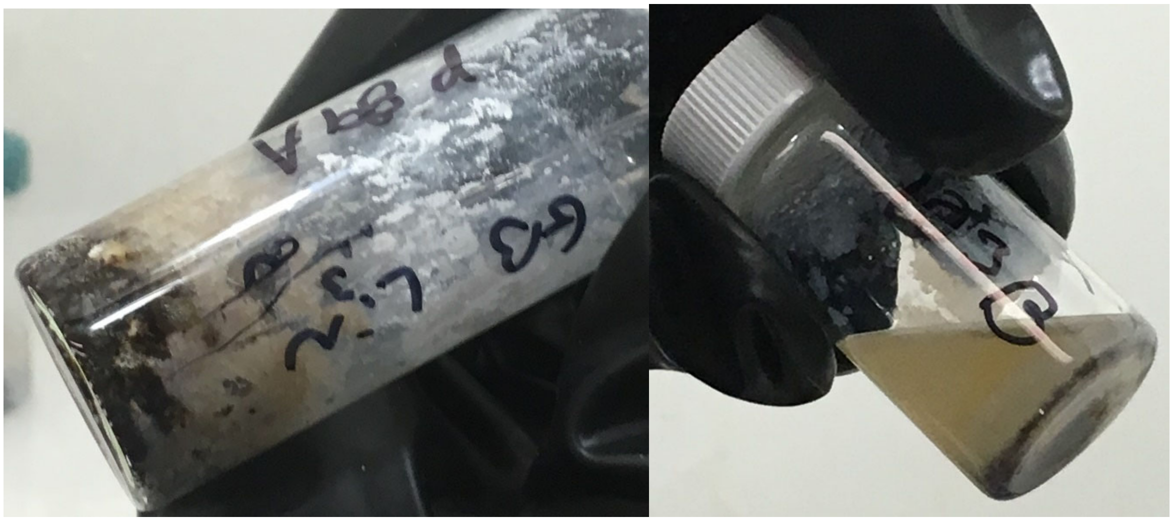

Figure 9: Photos of sample P89A, which solidified, and P103B, which remained liquid.

Sample 137A had a high ratio of GB to Li_3N but became solid, shown in Figure 10. The pair of samples P137A and P143B, shown in Figure 10, were done as a direct comparison. They were made under similar reaction conditions, and it was surprising that one of them solidified and one didn't. In both cases, the solid Li_3N powder appears to be consumed. However, P143B was one of the few samples that was done with unstabilized CASARM-grade GB (CASARM Lot No. GB-U-4065-CTF-N), as opposed to P137A that used stabilized technical grade GB. The P143B sample was made to allow higher resolution ^{31}P NMR of the products, since the unstabilized, CASARM-grade agent sample spectra had narrower NMR peaks. The last sample analysis of this sample had 26% residual GB, so the GB wasn't completely consumed. It is possible that the difference in agent source could account for the observation that the sample wasn't solid, but further study is needed to determine what effect any differences in the GB had on the reaction.

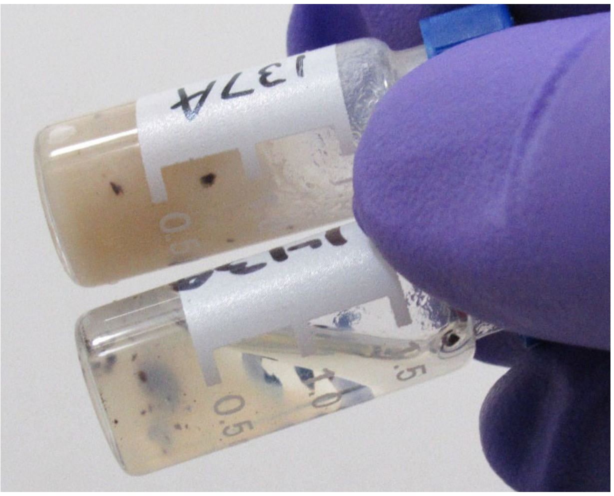

Figure 10: Photos of samples P137A (Top), which solidified, and P143B (Bottom), which is partly liquid. These samples were done as similarly as possible, except P143B was done with CASARM-grade unstabilized GB.

It is notable that some of the samples solidified quite fast, within a few minutes, while some solidified in 7-8 days, and others never solidified. The amount of solidification could be related to the speed at which water was added to the GB, but not in a simple way. The last line in Table 4 indicates how fast the water was added to the mixture of agent and solid Li_3N. When the entire amount of water was added quickly with the Li_3N suspended in the liquid agent, the reaction between Li_3N and water tended to go rapidly and there was a significant temperature increase of the liquid, even boiling the water. In these cases, the reaction product solidified within minutes.

When the water was added slowly, the reaction went slowly and little or no temperature increase occurred, and solidification took days to happen. Slow reaction between Li_3N and water happened when the solid wasn't suspended in the liquid but was in a layer on the bottom, or when the water was added slowly to form a layer on the surface that took time to mix. When the Li_3N was in the form of a pellet, reaction was slow because the surface area was more limited than for powder, as this was the reason for using the pellet form. There were cases of solidification for slow reactions with a pellet, such as P105B, shown in Figure 11, although some manual mixing was done on the sample. Mixing was important to keep the solid reagent in contact with water to keep the reaction going. For samples that weren't mixed, a layer of hydroxide or semisolid could cover the unreacted Li_3N to prevent further reaction, which was clearly shown as excess dark Li_3N on the bottom of the vial.

Slow reaction could happen when the water was added to the GB first and thoroughly mixed before the solid Li_3N was added. Dilution of water in the GB, which was unreactive with the Li_3N solid, lowered the rate of reaction. However, we found cases in which this kind of reaction was fast and unpredictable. The problem may be caused by adding small powder particles of Li_3N to the liquid. The small particles come into contact with the surface of liquid and quickly decompose to generate heat and flammable gas. This should be treated with caution since it can cause sparks and local heating.

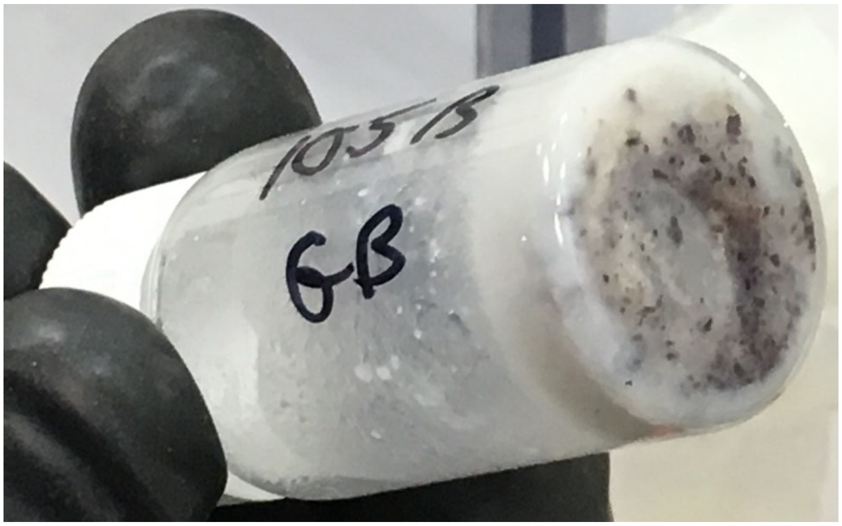

Figure 11: Photo of sample P105B, which solidified.

3.2 10-100 mL reaction studies of $Li_3N + H_2O$

Reactions were done using a quantity of 10 mL of GB and a quantity of 100 mL GB under similar conditions with 10% water and 5% Li_3N. The reaction runs were done with technical grade, stabilized GB (from U.S. Army Chemical Transfer Facility [CTF] lot no. GB-S-2152-CFT-N, Aberdeen Proving Ground, MD). For these samples, the water was added first to the GB, followed by the Li_3N. This method gave a slow reaction. No problems were observed with these GB reactions, but the procedure gave problems with DMMP reactions, discussed later.

This procedure of adding water first was done following studies on DF (difluoromethylphophonate). For that agent precursor, it appeared that it would be preferable to add water first to allow the DF to react to completion with water, so that there would be less consumption of water with Li_3N when it was added later.[9] A reaction was done in the same way with GB to see if it would be effective.

A table of these GB test reactions of Sample P23A is given in

Table 5. For sample P23A, the initial reaction product was mostly liquid, and it remained liquid for 37 days. A photo is shown in Figure 12. In order to attempt to make it solidify, additional Li_3N was added, decreasing the ratio of GB to Li_3N from 22.2 to 13.9. This was not effective in solidifying the product, and there was clearly excess Li_3N in the mixture. Additional water was added, and this was effective in solidifying the product. Photos of the initial and final mixtures are shown in Figure 12. A thin layer of liquid remains on top of the sample in the final product, but the rest is solidified.

Table 5: Table of reactions of GB with H_2O + Li_3N for sample P23A from Notebook 19-0049. Additional Li_3N and water were added to make the product solidify, and the adjusted ratios are shown.

Date	12/3/2019	1/6/2020	1/22/2020	1/28/2020
Reaction	P23A	P23A	P23A	P23A
Container	vial	vial	vial	vial
Vol. GB (mL)	10.00	10.00	10.00	10.00
Form	Li_3N pellet	Li_3N pellet /powder	Li_3N pellet /powder	Li_3N pellet /powder
Mass Li_3N (g)	0.450	0.593	0.719	0.719
Mass H_2O (g)	1.00	1.00	1.00	1.50
ratio (GB: Li_3N)	*22.22*	*16.86*	*13.90*	*13.90*
ratio (Li_3N: H_2O)	0.45	0.59	0.72	0.48
Product State (Solid/Liquid)	L	L	L	S
Time for react. (days)	37 d	16 d	6 d	6 d
rate of water addition (fast/slow)	slow, water before Li_3N	slow	slow	slow

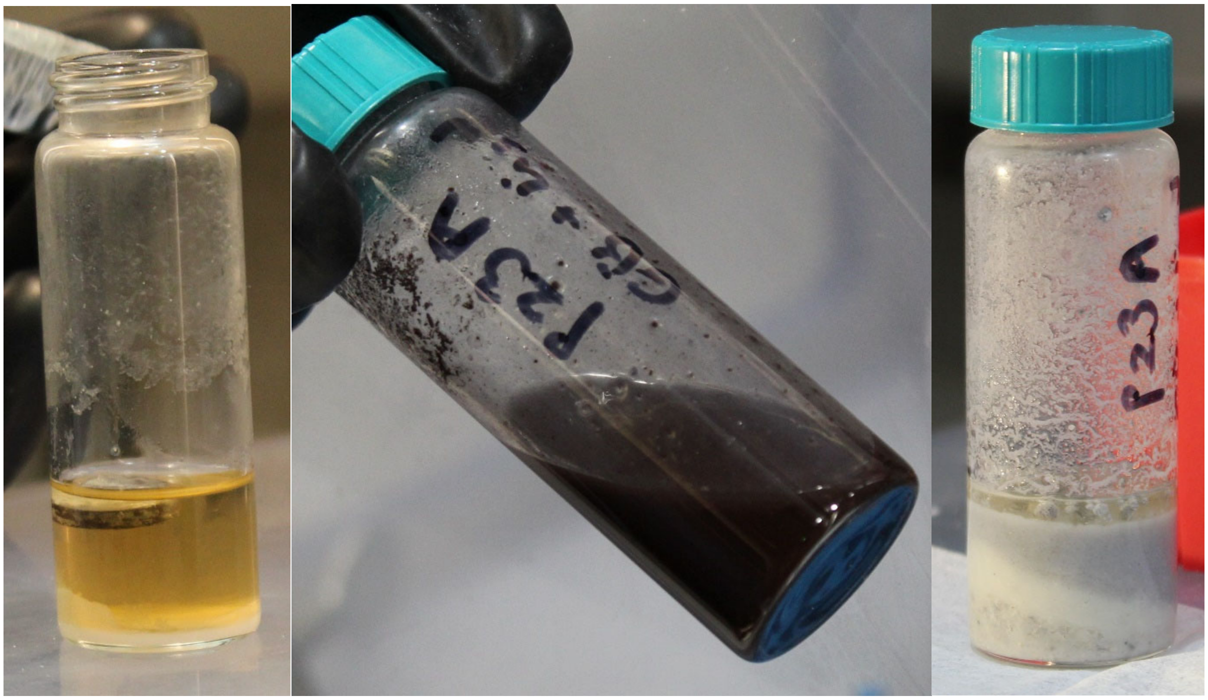

Figure 12: Photos of sample P23A. Left: first addition of water and Li_3N, with the pellet floating near the surface nearly intact; Middle: addition of excess Li_3N powder; Right: after addition of extra water.

The reaction with 100 mL of GB had similar behavior. After 1 d of reaction, the amount of GB decreased to 15%, measured by sampling and adding internal standard. After 6 d of reaction, the amount of GB was 2%, and after 14 d, it was 0.9%. The reaction product appeared to have about half the volume as wet solid, and half was liquid.

In order to attempt to solidify the entire product, additional Li_3N and water were added, as shown in Table 6. Additions of reagents were slow and didn't cause excessive heat or boiling. Photos of the reaction progress are shown in Figure 13.

Table 6: Reactions of GB with H_2O + Li_3N for sample P23B from Notebook 19-0049. Additional Li_3N and water were added to make the product completely solidify.

Date	12/3/2019	1/6/2020	2/5/2020
Reaction	P23B	P23B	P23B
Container	jar	jar	jar
Vol. GB (mL)	**100.000**	**100.000**	**100.000**
Form	**Li_3N pellet**	**Li_3N pellet /powder**	**Li_3N pellet /powder**
Mass Li_3N (g)	**5.02**	**6.02**	**6.02**
Mass H_2O (g)	**10.00**	**10.00**	**15.00**
ratio (GB: Li_3N)	*19.92*	*16.61*	*16.61*
ratio (Li_3N: H_2O)	0.50	0.60	0.40
Product State (Solid/Semisolid/Liquid)	L	L	S
Time for react. (days)	34 d	30 d	5 d
rate of water addition (fast/slow)	slow, water before Li_3N	slow	slow

Figure 13: Photos of Sample P23B, using 100 mL of GB. Left: reaction after 6 days, in which about half the product is solidified; Right: after additional Li_3N powder and water is added to solidify the product.

3.3 Further study of the solidification process using DMMP

Because of the surprising variability of solidification of the products for the GB reaction, additional studies were done using dimethyl methylphosphonate (DMMP) as a simulant for GB. DMMP is easily obtained commercially (Sigma-Aldrich, P/N 169102-500G), and it is much less toxic, so it was easier to perform multiple tests compared to GB and generate less hazardous waste. Also, energetic reactions of the Li_3N and water generated less vapor hazard from boiling of the test compound. However, DMMP is different from GB in that it is reported to have a flashpoint of 156 °F, but GB doesn't have a flashpoint.

DMMP is much less reactive to hydrolysis compared to GB. Initial small-scale studies formed solidified products with this simulant. Measurements of the products showed that DMMP hydrolyzed to a small extent (25-50%) but most of the ^{31}P-containing extractable product remained DMMP, a liquid. This result indicates that it isn't necessary to use a CA to form the solid, and for GB the acid product GB acid (or a salt of it) isn't a necessary component of the solid. From these tests, it appears that the solid is mostly LiOH and possibly an ammonium salt that has expanded in volume to absorb or encapsulate the liquid.

Several different reaction conditions were studied: 1) The method to add Li_3N powder or pellets to CA first, followed by slow addition of water using a pipet or syringe. 2) Add Li_3N first, followed by fast addition of water by quickly adding in the measured amount without mixing, which could form a local high concentration of water at the surface. 3) Add water to CA first, mix so the liquid is homogeneous, followed by addition of Li_3N powder.

Method 2 was the best method for causing rapid and complete solidification, but the water was added rapidly enough that it caused boiling at a temperature of 90-100 C because of reaction with the Li_3N solid. Stages in the reaction are shown in Figure 14 and Figure 15.

From a test on a 10 mL volume of DMMP, method 3 was slow, as it was with a GB reaction. However, unexpectedly, method 3 generated flames using a test volume of 100 mL DMMP. The fast reaction may have been due to clumps of fine powder adding to the liquid quickly. A video of the reaction was recorded. The difference between GB and DMMP could be due to the properties of the compounds. DMMP has a flashpoint of 156 °F, but GB doesn't have a flashpoint, so the spark from a reaction of a small particle of the powder might have caused an ignition to produce a flame. Also unexpectedly, the solid didn't completely and rapidly solidify, which was also observed with GB until extra reagents were added. As a result of this study, it was concluded that this kind of addition order was unpredictable and it could produce excessive heat but also incomplete solidification.

For Method 1, or for addition of Li_3N as tablets, slower reactions are produced. But often the reaction was incomplete since the tablets either don't break up or else the tablets or powder settle to bottom and don't react effectively with the added water. It appears that a layer of hydroxide product can cover the unreacted Li_3N to prevent the solidification reaction, even when there is enough hydroxide to decontaminate a CA like GB. There appears to be a competition between reaction and settling out of the Li_3N reagent onto the bottom of the reaction container. If the reagent settles, it forms a dark layer at the bottom. It becomes covered with a solid white or gelatinous product that protects it from further reaction. Liquid can remain on top of the white layer, separated from the Li_3N so that it doesn't react and solidify further. Since the unreacted Li_3N may be protected by the reacted layer on top, the remaining Li_3N may not react with remaining water to form a solid product, causing the appearance of having excess Li_3N. This can lead to incomplete solidification. Mechanical mixing can help to disperse the solid reagent.

Adding water rapidly to CA after Li_3N was suspended in it can lead to very fast reaction and vigorous boiling. Determining the optimal addition rate for larger volumes of CA may require a metering pump to control the engineering problem of addition of solid to water in a controlled, nonhazardous way.

Figure 14: Photos from sample P55B. Left: Add Li_3N to 100 mL of DMMP; Middle: Add 10 mL water with a pipet; Right: mixture is boiling for more than 20 min. of reaction time.

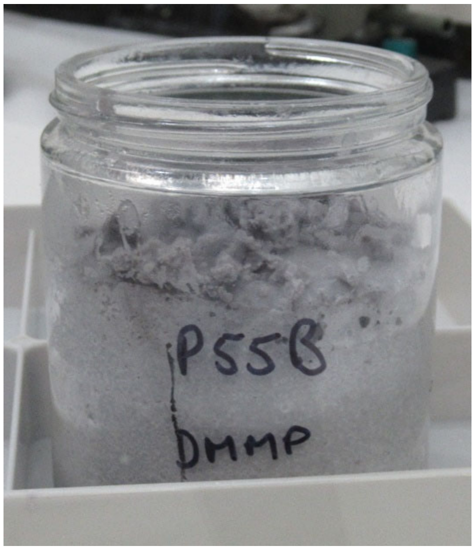

Figure 15. Final product for sample P55B. This order of addition caused rapid reaction, and the sample completely solidified in a few hours after the boiling stopped.

Another alternative that was considered was to use capsules to contain the Li_3N powder. Two types of empty capsules were commercially available. “Vegetarian” capsules (made of cellulose) were found to dissolve in 5 mL DMMP/water and had a reaction to solidify the product, shown in Figure 16 left. A capsule made of gelatin didn’t dissolve under the same conditions and no reaction was observed, shown in Figure 16 center.

Caustic solution (10% NaOH) can be used instead of water to form a solidification reaction, shown in Figure 16 right, which may slow down the reaction of water with Li_3N and help to decontaminate the CA, although reaction kinetics wasn’t measured.

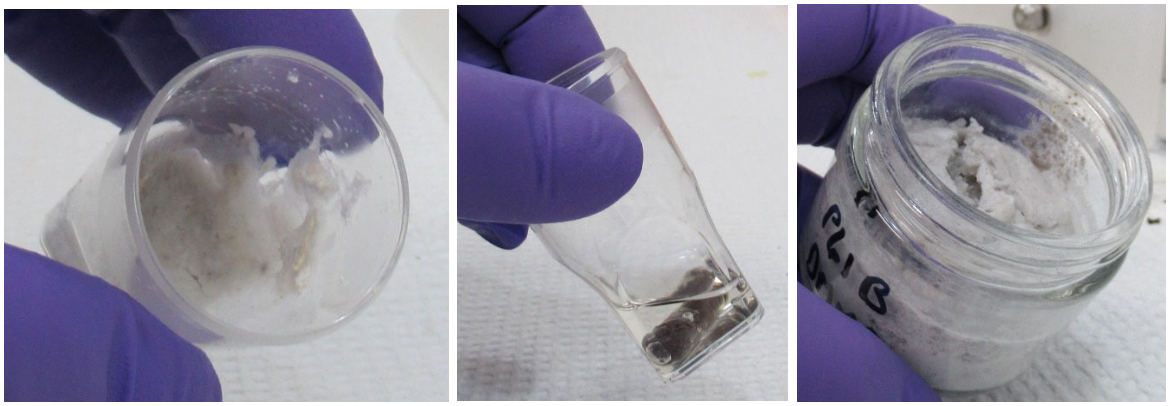

Figure 16. Reaction samples of DMMP with Li_3N + H_2O with different conditions. Left: Vegetarian capsules (made of cellulose) dissolved in DMMP/water and had reaction to solidify the product. Center: Gelatin capsule didn’t dissolve under the same conditions and no reaction was observed. Right: Caustic solution (10% NaOH) can be used instead of water to form solid product.

Because of these competing processes, it is complex to determine the simple, optimal method for adding reagents that also optimizes the reaction of the CA. This is particularly an issue if the liquid isn’t stirred. According to the project goals, the method may need to be done under difficult, time-sensitive conditions, but the method should minimize hazard to the operator. Adding the reagent fast can lead to rapid boiling, which could disperse CA agent into the air, spread it over the outside surfaces, and cause a hazard to the operators. On the other hand, adding reagents slowly makes the decontamination reaction cooler and slower, but it allows time for the solid Li_3N reagent to settle out. Slow reaction limits the complete solidification of the product, since Li_3N has less opportunity to react to completion with the liquid. Slow reaction still allows the GB to react, though, as long as there is excess water, and the caustic promotes the hydrolysis of the GB even if solidification isn’t complete.

One way to control the rate of reaction is with addition of the water. However, this is difficult because only a small change in rate of addition can cause an unexpectedly large change in rate of reaction. This could be difficult to control in the field using actual large containers of agent, without potentially causing a hazardous situation. An automated pumping system with a temperature feedback may be necessary to control the liquid addition with good precision if the goal is to minimize hazards to the operator. The reaction could also be controlled by mixing the liquid to keep the solids uniformly suspended until they react. However, these methods could require equipment.

Another way to control the rate of reaction is by changing the size of the Li_3N particles. Powdered reagent Li_3N, which consists of very fine particle size, has a high surface area and can potentially react rapidly. We pressed the powder into pellets that are about 0.5-1 cm in diameter and a few millimeters thick, although that is a labor intensive process. These pellets react slowly, and they often settle to the bottom of the reaction container without completely reacting.

Another alternative is to decrease the amount of reagent that is used. This will decrease the heating and boiling of the sample, but it will be more likely that the entire product volume will not solidify, leaving some liquid. This is particularly likely if some of the solid settles. Increasing the amount of reagent, on the other hand, will make the reaction more energetic and increase the solidification.

4. PRODUCT ANALYSIS

4.1 ^{31}P NMR Results on Residual GB

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.[1,10] However, for the reaction runs using technical grade GB, 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.[11]

The large-volume reaction runs were done with technical grade, stabilized GB (CTF lot no. GB-S-2152-CFT-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 low for ^{31}P NMR. A photo that show the color of the starting GB liquid is shown in Figure 17, compared to the same liquid after 3 days of reaction with Li_3N + water.

NMR spectra of reaction products that are typical of the reaction product extract using technical grade GB (Sample P23B, see Table 6) compared to a spectrum using unstabilized, CASARM grade GB (Sample P143B, see Table 4) are shown in Figure 18. In addition to less sensitive and less accurate quantitation for technical grade GB, the peak broadening also made it more difficult to identify impurities that are present at low percentage amounts. This problem was due to uncertain measurement of the chemical shift values and overlapping broad peaks. The chemical shift of the GB acid peak changes with pH of the solution compared to the GB peaks, so GB acid shifts relative to the GB peaks.

All the vials or jars from reaction runs were sampled to determine residual GB. This was done by using the following preparation procedure: 1) removing a quantity (10-100 mg) of the solid and/or liquid reaction product and transferring to a sample vial, 2) weighing it, 3) adding and weighing an amount of internal standard triethyl phosphate (TEP), 4) dissolving or extracting with chloroform ($CDCl_3$) for 0.5-1 min. with vortexing, and 5) transferring 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 GB compared to triethyl phosphate internal standard (Sigma-Aldrich P/N 538728-100ML).[12] 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 GB 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. It typically took several days to a week for the amount of GB to be reduced to <10% of the sample weight. In some cases, solid final reaction product was also dissolved in deuterated water (D_2O) to look for other major reaction products in addition to the main product, isopropyl methylphosphonic acid (GB acid), which was always by far the largest fraction of phosphorus-containing product.

The amount of residual GB that was detected by ^{31}P NMR was <5% except one case. Sample P143B was the only sample that was done with unstabilized GB, as opposed to the stabilized technical grade GB. The sample allowed higher resolution ^{31}P NMR of the products. The last sample analysis of this reaction had 26% residual GB, so the GB wasn't completely consumed.

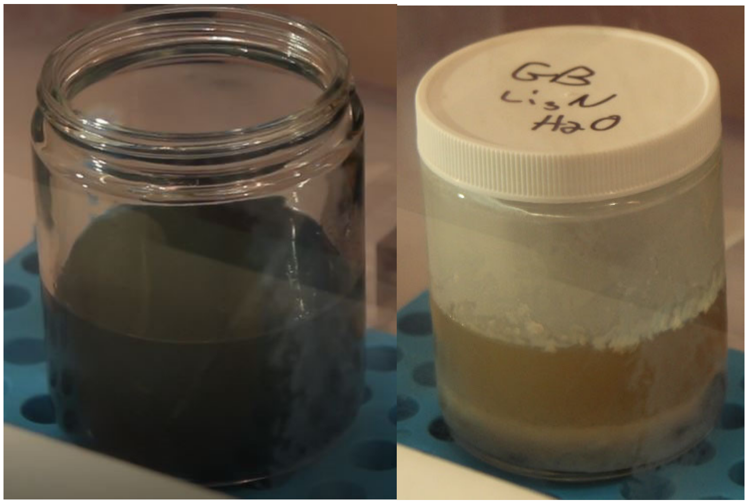

Figure 17: Technical Grade GB starting material for the 100 mL reaction run, sample P23B. Left, starting GB before addition of Li_3N (from video screen capture); Right, after 3 days, the liquid changed from black to light brown colored as solid forms (see also Figure 13). Black color is probably due to impurities containing iron.

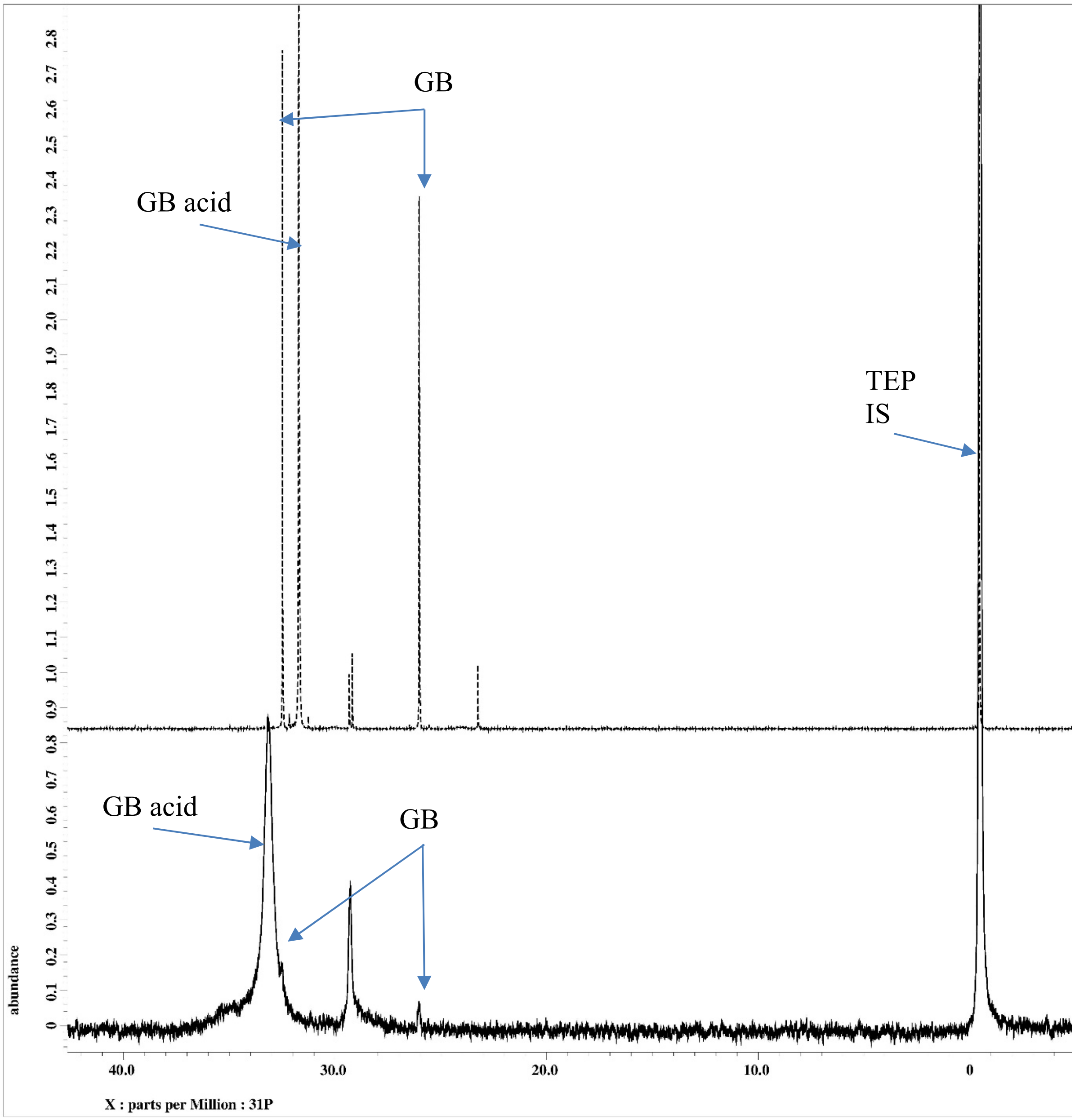

Figure 18: ^{31}P NMR spectra of reaction products at different times but that are typical of the reaction products extract using technical grade GB (bottom) compared to a spectrum using unstabilized, CASARM grade GB (top). The internal standard (IS) is triethyl phosphate (TEP).

Although it is possible to do NMR on solid material,[12] there are complications from peak broadening that make it difficult to obtain a narrow line width and assign the spectrum. As a result, the NMR studies were performed using liquid solutions of extracts.

Residual GB that was determined by using extracts vs. reaction time with the solvent $CDCl_3$ extraction for multiple samples is plotted in Figure 19. The amount of GB at time

0 h was calculated to account for the amount of decontaminant that was added and assuming 95 wt.% purity of the initial GB. Since the product mixture wasn't homogenized, the uniform amount of GB in the liquid or solid material may not have been sampled.

The rate of decrease of GB in the samples varied a large amount. Some of these samples didn't have the same amount of decontaminant, and most had different amounts of agitation and heating due to reaction of the Li_3N with water. Reaction could also slow down after solid is formed due to increased viscosity and decreased mixing. These effects could account for the rate differences. At the fastest, the GB was eliminated in a matter of a few minutes. Since the project goals didn't specify how fast the GB should be eliminated, the rate wasn't targeted as a specific criterion.

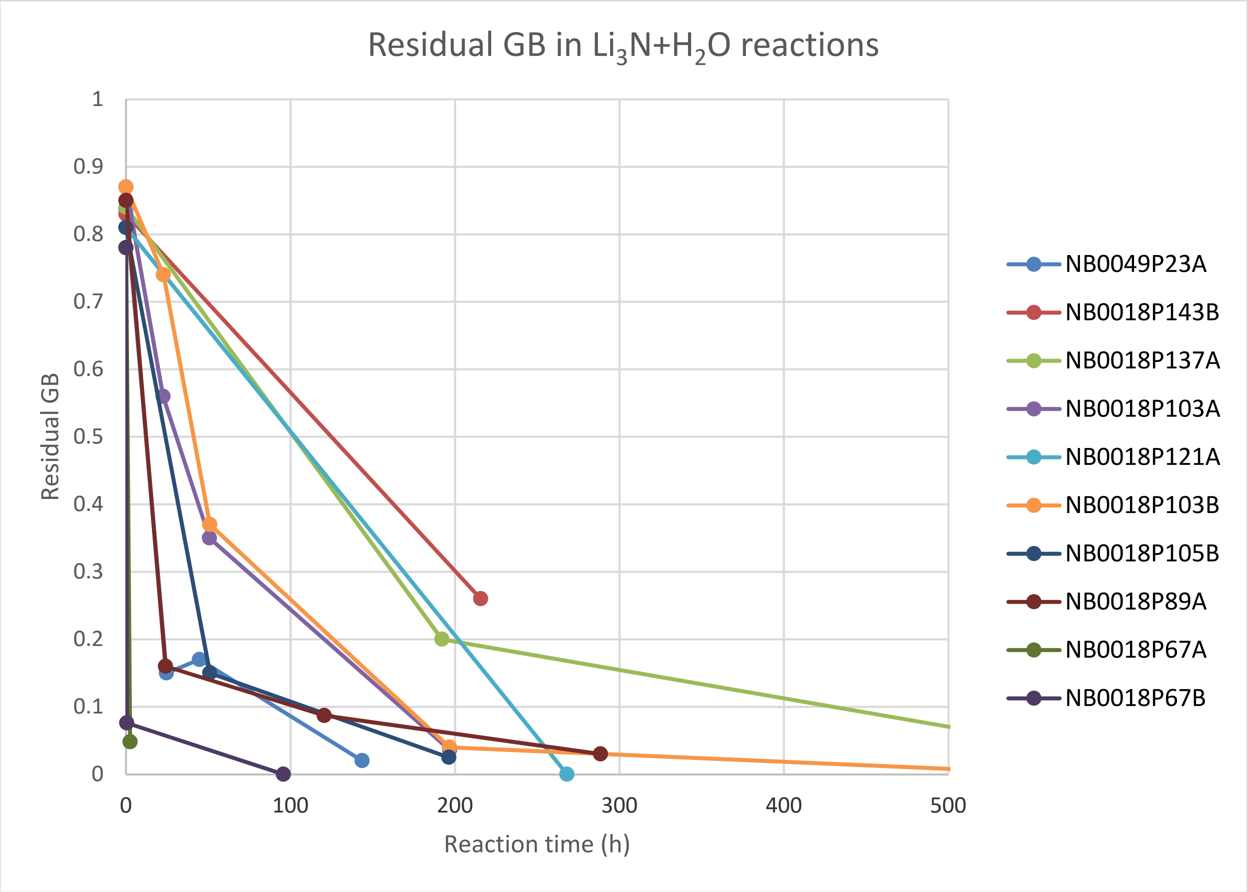

Figure 19: Plot of the residual GB in the sample numbers shown, using quantitation based on extracts in $CDCl_3$. See Tables 4 and 5 for sample descriptions.

4.2 ^{31}P, ^{13}C, and ^{1}H NMR results of product analysis

^{31}P NMR can be used to identify products of the reaction to a limited extent. The regions for the expected product peaks like GB acid are generally known, but the peaks can shift based on pH and other sample matrix effects. Peaks can be broadened as shown in Figure 3 and

Figure 18 from high sample concentrations and from paramagnetic impurities. The broadening limits the usefulness of chemical shifts for identifying peaks. It is possible to dilute the sample in solvent to improve the peak shape. Figure 20 shows a comparison of a spectra of products for a fairly high concentration and after dilution. The need for dilution to obtain spectra with good resolution indicates that it is common that detection of residual agent must be done in a separate sample from analysis of products.

The dilute spectrum shows that there are three distinct product peaks that are close to the GB acid chemical shift. From the one-dimensional ^{31}P spectrum alone, it is difficult to determine the difference between the peaks. It is possible to obtain more information with detection of other nuclei.

^{1}H NMR spectra can also be useful in some cases for determining information about phosphorus and non-phosphorus products. A spectrum for the same sample is shown in Figure 21**Error! Reference source not found.**. However, due to paramagnetic impurities, the resolution of the ^{1}H spectrum is relatively low.

By using a two dimensional (2D) NMR technique, it is possible to combine information from the ^{31}P and ^{1}H spectra. Using a data collection method called HMBC, a 2D spectrum is obtained that gives information about the peaks that are observed in the ^{31}P spectrum. Common NMR probe equipment and longer acquisition time can limit the types of 2D spectra that can be acquired, but even low resolution ^{1}H spectra provide helpful information. Figure 22 shows this type of spectrum. The projection spectra, the sum spectra in one dimension, are shown on the top and right side. The 2D plot shows that for the peaks at 33.07 and 31.61 ppm, the ^{1}H spectra are very similar. In particular, both ^{31}P peaks have ^{1}H peaks that correspond to the isopropyl group. This result implies that both peaks are from GB acid, and one of them may be due to complexing of the acid with a metal ion or another species without an NMR signal. The peak at 30.89 ppm, in comparison, does not have the peaks from the isopropyl group but only the strong doublet from the P-CH_3 group, indicating that it is from methylphosphonic acid (MPA), the secondary reaction product. No peaks are observed that would correspond to phosphonamidate (P-N) bonds from reaction of GB to ammonia (see also Section 4.3).

Although ^{31}P NMR is useful for determining residual GB and phosphorus products, ^{13}C NMR is more helpful for major products that do not have phosphorus. A typical ^{13}C NMR spectrum of the reaction products is shown in **Error! Reference source not found.**. The ^{13}C spectra are not sensitive to trace amounts of products, since ^{13}C has a natural isotopic abundance of only 1.1%, so this method isn't appropriate for trace detection. Some low abundance peaks in the ^{31}P NMR spectra can't be identified in the ^{13}C spectra. On the other hand, ^{13}C spectra have high resolution. This spectrum shows that there are several related products, and it is consistent with GB acid and MPA as the products. It can be a problem to identify what the products are without spiking by known standards of the possible compounds.

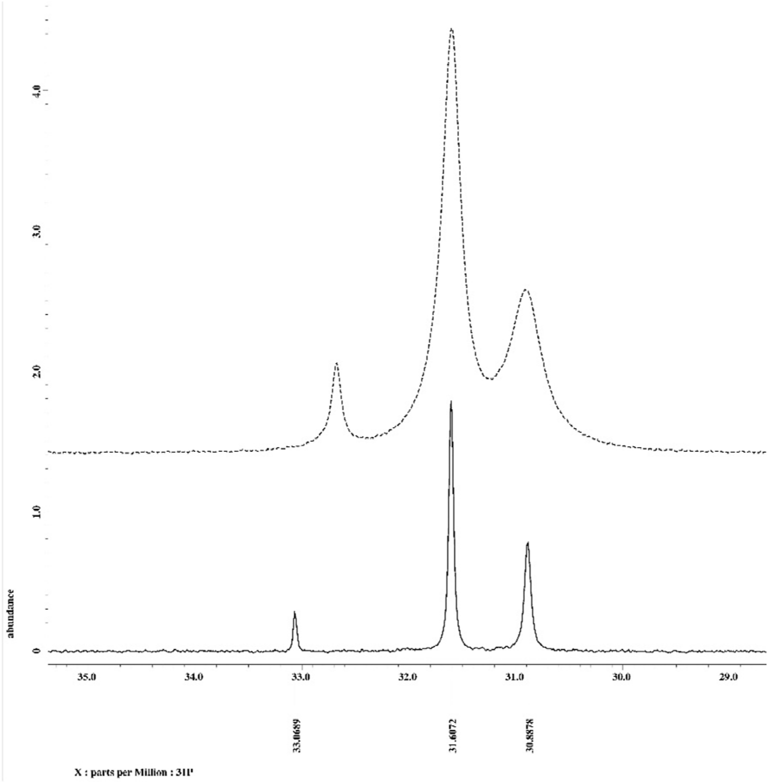

Figure 20: ^{31}P NMR spectra of sample P23B6, reaction product of the 100 mL reaction of GB + Li_3N + H_2O dissolved in D_2O water. Top spectrum: using 20 mg/mL product, and bottom spectrum: dilution by 1:10.

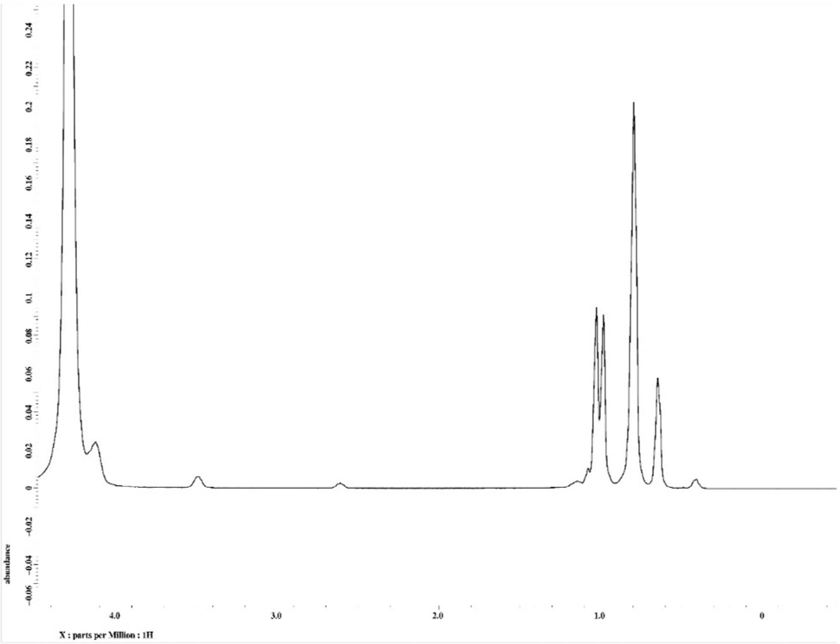

Figure 21: ^{1}H NMR spectrum of sample P23B6 dissolved in D_2O.

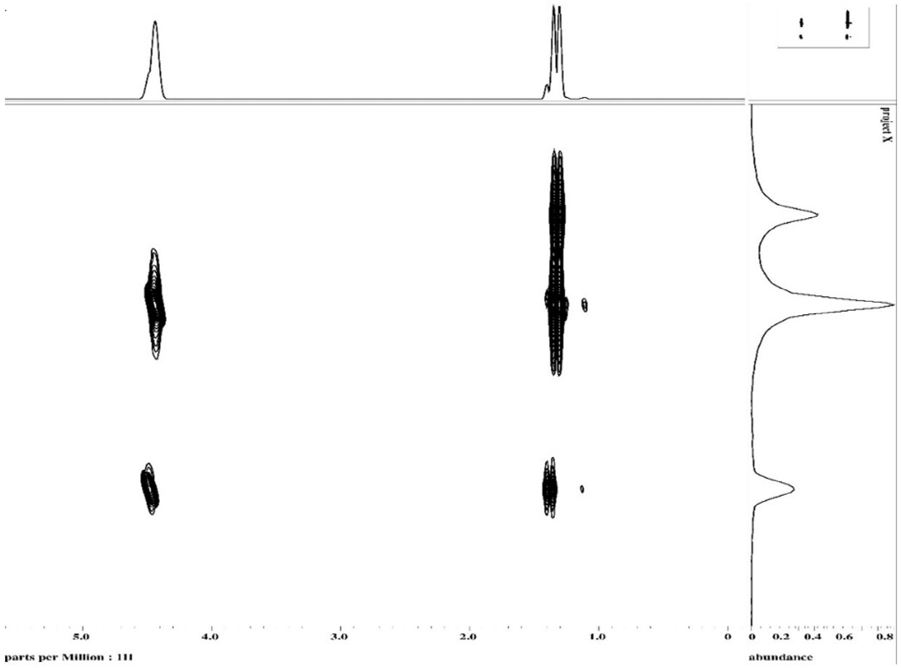

Figure 22: 2D ^{31}P-^{1}H HMBC NMR spectrum of sample P23B6 dissolved in D_2O.

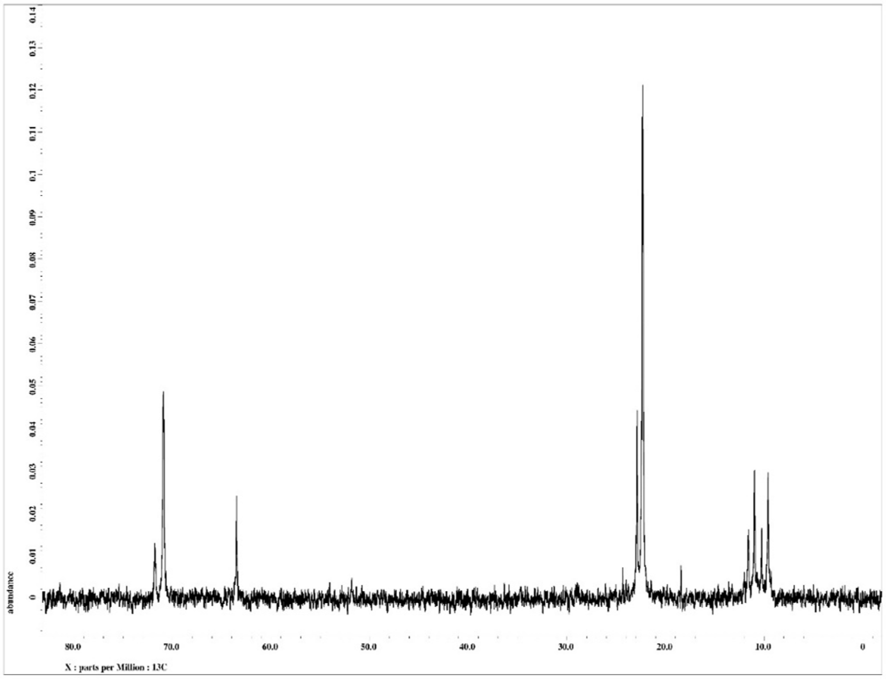

Figure 23: ^{13}C NMR spectrum of sample P23B6 dissolved in D_2O.

4.3 LC/MS Results

A method using gas chromatography/mass spectrometry (GC/MS) can been developed to detect a low amount of residual GB in the samples with good sensitivity.[13] However, this method was not validated in this product matrix since it wasn't in the project requirements.

Another analytical technique, liquid chromatograph/mass spectrometry (LC/MS) was used as a screening method for identifying major and trace components in the product. The reaction solid was dissolved in aqueous dilute hydrochloric acid (HCl), diluted by approximately 1:100, and analyzed using LC/MS using an Agilent 6410 Triple Quadrupole LC/MS/MS. Sample preparation methods and LC/MS instrument conditions were not optimized for sensitivity, but were used to obtain qualitative mass spectra to identify compounds. The mass spectra can't be used to quantify the various products to determine a mass balance without calibration standards of each compound, since the instrument signal response is different for different compounds. For example, instrument response for 2-propanol, a potential secondary reaction product, is low.

A major product of the reaction is isopropyl methylphosphonic acid (GB acid), in agreement with ^{31}P NMR results. A positive ion mass spectrum of this compound is shown in Figure 24. Main product ions are at 139 Da for $[M+H]^+$, 97 Da for a fragment $[M+H-C_3H_6]^+$, and 277 Da for $[2M + H]^+$. Ratios of these peaks can vary depending on instrument conditions and sample concentration. A corresponding peak was observed for this compound in the negative ion mass spectrum.

Another chromatographic peak was observed for 186 Da, shown in
. This is assigned to tributylamine, $(C_4H_9)_3N$, molecular weight 185 Da. The peaks at 407 and 409 Da correspond to $H^{35}Cl$ and $H^{37}Cl$ dimer adducts, $[(C_4H_9)_3N]_2H^+ \cdot HCl$. The identity of the ion was confirmed by MS/MS fragmentation.

Another compound was identified as diisopropyl methylphosphonate (DIMP), a common impurity in GB. The mass spectrum is shown in Figure 26. The $[M+H]^+$ peak is 181 Da, and 139 Da and 97 Da peaks are fragment ions. A peak at 361 Da corresponds to $[2M+H]^+$, and a 383 Da peak is $[2M+Na]^+$. Even though there is a large amount of Li^+ in the samples due to the added Li_3N, it is unusual to observe Li^+ adduct peaks compared to Na^+ adducts. Small peaks at 185 and 407 Da are from peak overlap with the tributylamine peak.

Some information was obtained from mass spectrometry about the paramagnetic impurity in the GB that caused the NMR peak broadening and made the GB black-colored. A negative ion mass spectrum is shown in Figure 27. Peak groups at 161 and 198 Da can be assigned to isotope patterns for $FeCl_3^-$ and $FeCl_4^-$. Since the samples are in HCl solution, the Fe may not be in the form of chlorides in the original GB, but it may have been digested by the HCl. Some small peaks may be attributed to Ni or Cr anion species. These ions indicate that the impurity is due to iron or steel. It isn't clear whether the Fe is present as a solute or as small particles.

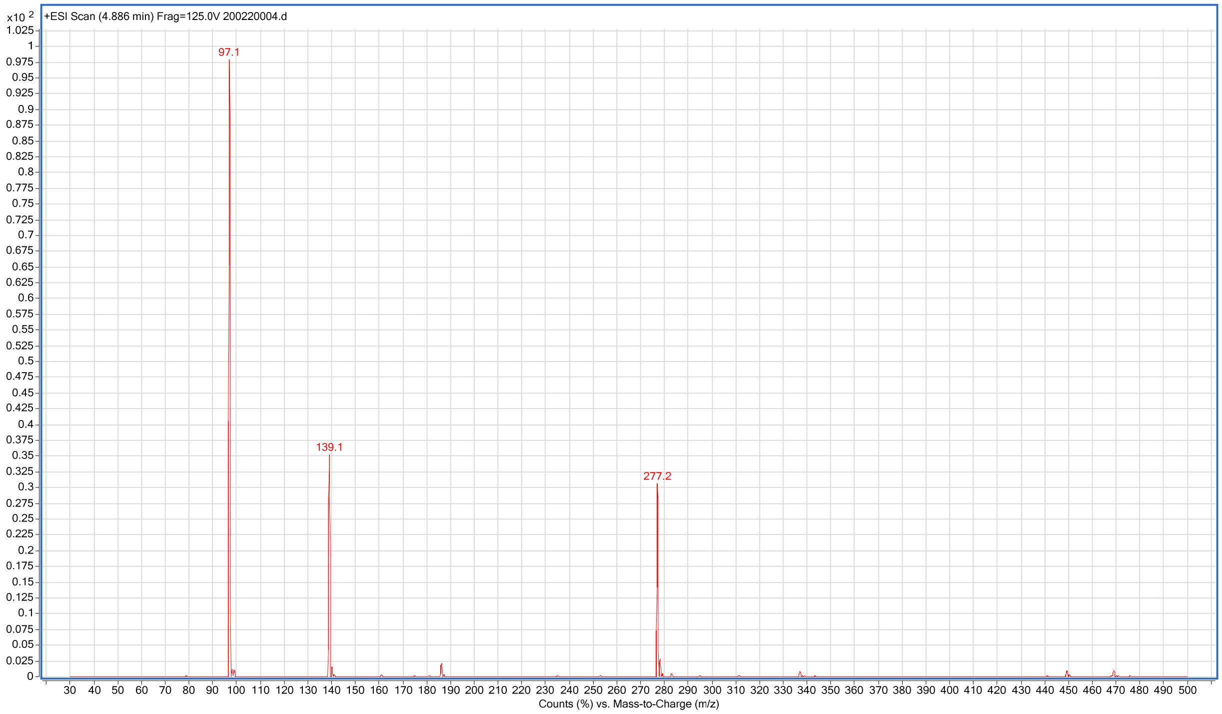

Figure 24: Mass spectrum of isopropyl methylphosphonic acid (GB acid) product from sample P23B.

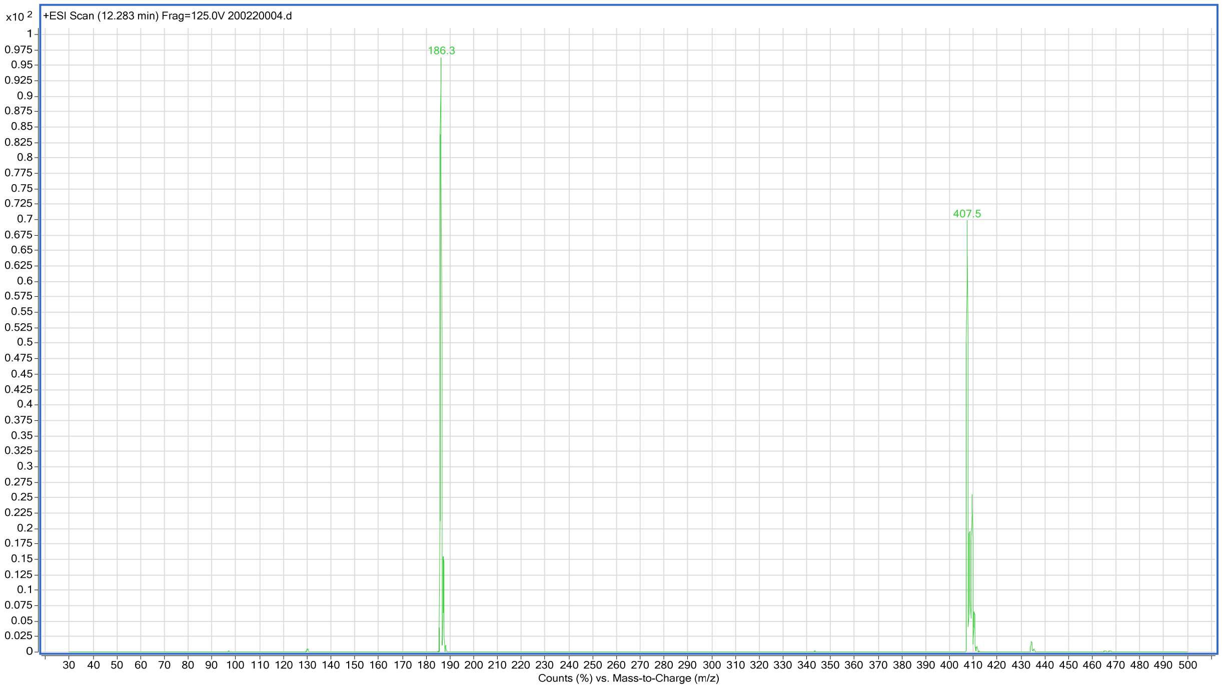

Figure 25: Mass spectrum of tributylamine, a stabilizer in the GB from sample P23B.

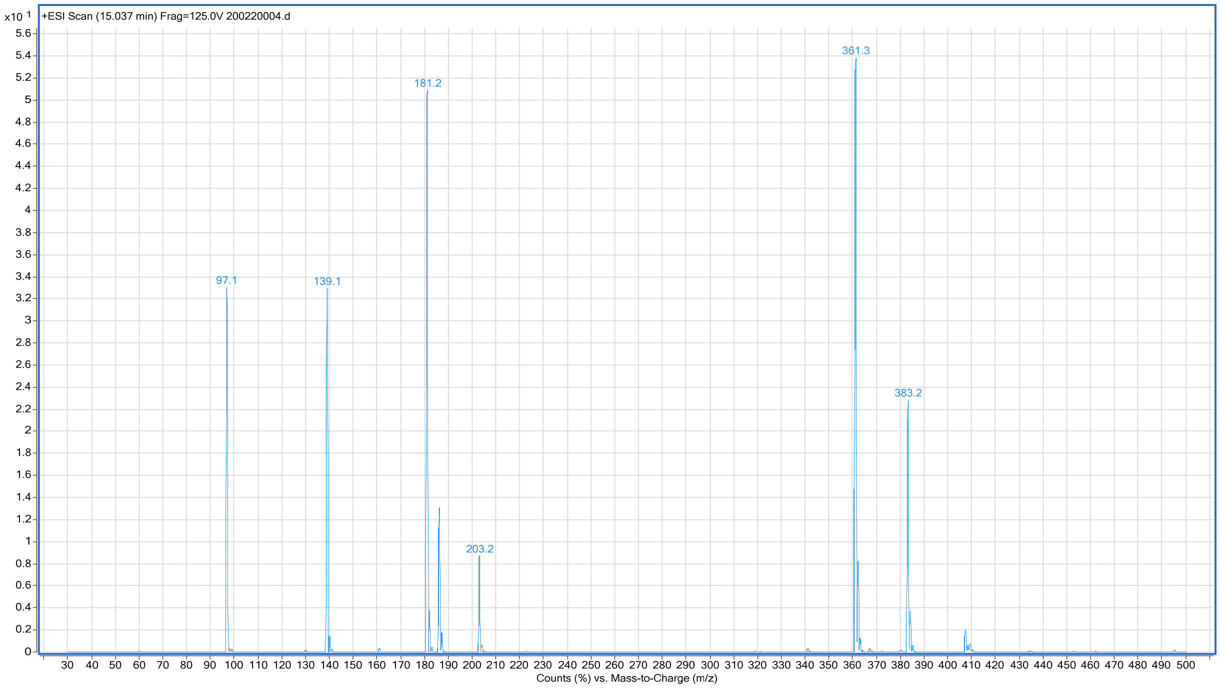

Figure 26: Mass spectrum of diisopropyl methylphosphonate, an unreactive impurity in GB from sample P23B.

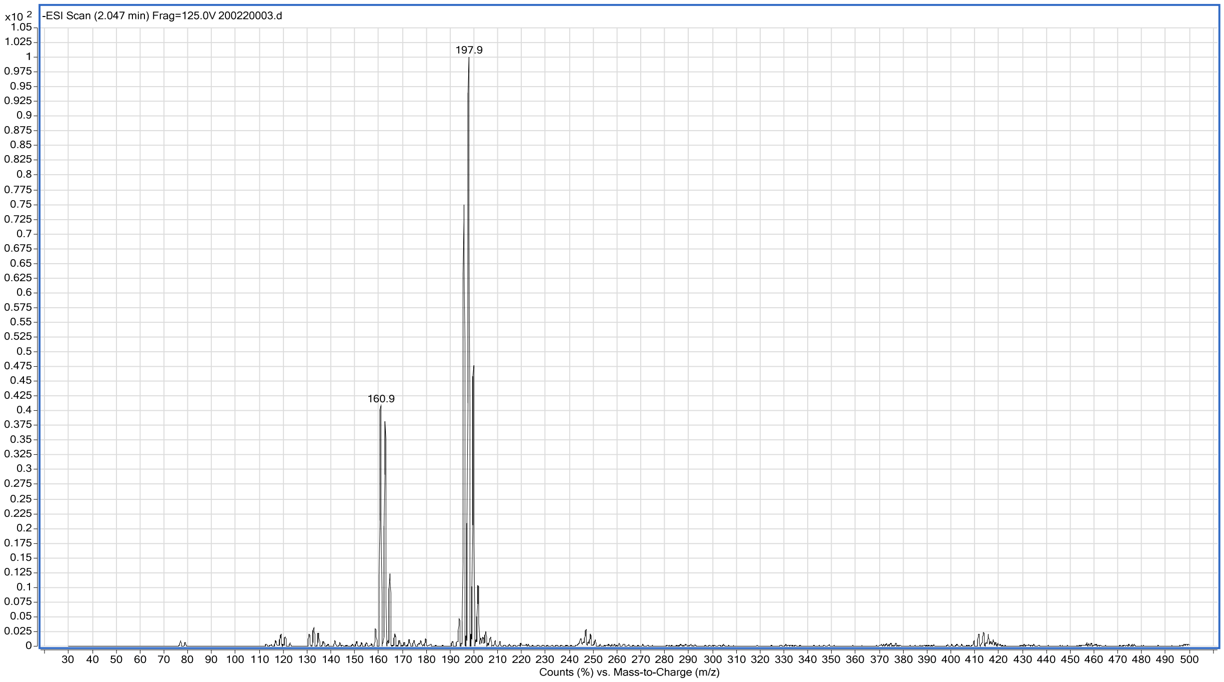

Figure 27: Mass spectrum showing iron chloride complexes using negative ion mass spectrometry from sample P23B.

Since the reagent Li_3N decomposes to form NH_3(aq) after reaction with water, it was hypothesized that reaction products between GB and NH_3 might be observed. The reaction mechanism that might be expected is shown in Figure 28. The mass spectra were examined for the possible reaction products by LC/MS, but they were not found. No other LC/MS peaks that might be consistent with this mechanism could be identified. This is consistent with the NMR results. As a result, it appears that this reaction mechanism is not a major contributor. Understanding the product compounds that contain nitrogen and the composition of the solid material will require further study.

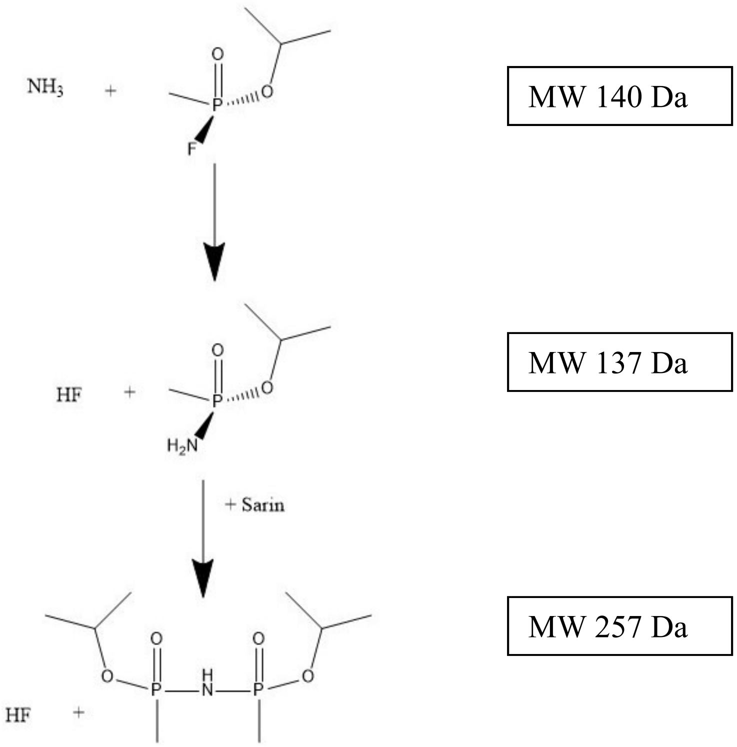

Figure 28: Hypothetical further reaction of GB and reaction products with ammonia to form larger molecules. The nitrogen substituted compounds were not detected by LC/MS.

5. CONCLUSION

As part of the Tactical Disablement Project, neat weapons-grade GB was reacted with lithium nitride (Li_3N) and water. Reactions were done up to 100 mL in volume of GB 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. Products were analyzed using ^{31}P NMR, ^{13}C NMR, and LC/MS, and reaction schemes are provided to explain the products.

This study demonstrates a method to perform the neutralization and solidification of bulk sarin (GB) 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 GB.

Several technical issues were addressed. GB 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 GB was usually destroyed in a week or less. Detection limits of the NMR method were relatively high, though. Determination of whether trace amounts of GB remain in the product will require development and validation of a more sensitive analytical chemistry method, possibly using gas chromatography/mass spectrometry.

Experiments with different amounts of CA from 1 mL to 100 mL showed similar reactivity, with some differences for larger volumes. Solid product was formed in a way that was not consistent in all reaction conditions, so further studies were done using dimethyl methylphosphonate (DMMP) as a simulant to study the conditions that were needed for formation of solid products.

The method for adding the two reagents, Li_3N powder or compressed pellets and liquid water, caused a wide variation of the reaction rate. Addition of Li_3N powder so it was evenly suspended in liquid GB followed by rapid addition of water can cause very rapid reaction, boiling of the liquid, and solidification in minutes. Slower addition of water can give the Li_3N time to settle out of suspension so that it is less likely to react, and the entire amount of agent may not be solidified. Experiments with DMMP showed that decontamination products are not necessary to produce a solid, and it is likely that the solid is formed from LiOH that expands to encapsulate the liquid.

The technical grade GB had an unusual black color. The black color arose from paramagnetic impurities that interfered with the NMR determinations to decrease sensitivity and resolution. However, it was possible to determine residual GB in the reaction product to less than 1%.

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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
GB	Sarin, isopropyl methylphosphonofluoridate
GB acid	Isopropyl 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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