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

ABERDEEN PROVING GROUND, MD 21010-5424

CCDC CBC-TR-1721

DF Reaction with Li_3N+H_2O for the Tactical Disablement Project

David J. McGarvey

RESEARCH AND TECHNOLOGY DIRECTORATE

William R. Creasy

Leidos Corporation
Gunpowder, MD 21010-0068

Mark K. Kinnan

Sandia National Laboratories
Albuquerque, NM 87185-0100

December 2020

Disclaimer

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorizing documents.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
XX-12-2020	Final	Feb 2019–Dec 2019

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

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
McGarvey, David J. (DEVCOM CBC); Creasy, William R. (Leidos Corporation); and Kinnan, Mark K. (Sandia National Laboratories)

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, APG, MD 21010-5424
Leidos Corporation, P.O. Box 68, Gunpowder, MD 21010-0068
Sandia National Laboratories, P.O Box 5800, Albuquerque, NM 87185-0100

8. PERFORMING ORGANIZATION REPORT NUMBER
CCDC CBC-TR-1721

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

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 U.S. Army Edgewood Chemical Biological Center.

14. ABSTRACT: (Limit 200 words)
As part of the Tactical Disablement Project, neat weapons-grade DF was reacted with lithium nitride (Li_3N) and water in a glass or Teflon® reaction vessels. Products were analyzed, and reaction schemes are provided to explain the products.

15. SUBJECT TERMS
methylphosphonodifluoridate or difluor (DF)
Liquid chromatography/mass spectrometry (LC/MS)
Nuclear magnetic resonance (NMR)
Tactical Disablement

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Renu B. Rastogi
U	U	U	UU	38	19b. TELEPHONE NUMBER *(include area code)* (410) 436-7545

Blank

PREFACE

The work described in this report was authorized under project number CB10412. The work was started in February 2019 and completed in September 2020. 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.

The use of either trade or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

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;
- Dr. Glenn E. Lawson (Defense Threat Reduction Agency; Fort Belvoir, VA) for program support and discussions.

Blank

CONTENTS

PREFACE iii

1. INTRODUCTION 1

2. PRELIMINARY STUDIES 3

2.1 Reactions with $Li_3N + H_2O$ 3
2.2 Reactions with $LiAlH_4$ 5
2.3 Reaction with H_2O 5
2.4 Reaction with glass 6

3. 100 ML SCALE REACTION STUDY 7

4. ^{31}P NMR RESULTS 9

5. ^{19}F, ^{1}H, and ^{13}C NMR RESULTS 11

6. GC/MS AND LC/MS RESULTS 12

6.1 DF screening method by GC/MS 12
6.2 Analysis of solid reaction product by Headspace Sampling 14
6.3 Analysis of reaction products using LC/MS 14

7. REPORT ON SUPPORT FOR THE PILOT PLANT REACTOR RUNS FOR DF DECONTAMINATION: UNPUBLISHED STUDY (2006) 15

7.1 Background 15
7.2 Experimental Method 16
7.3 Results for analysis of reactor samples 17
7.4 Results for feedstock purity analysis 17
7.5 Results for DF kinetics studies 17
7.6 Conclusions about DF kinetics 24

8. CONCLUSIONS 24

REFERENCES 25

ACRONYMS AND ABBREVIATIONS 28

FIGURES

1. Reaction Mixture from DF + Li_3N + H_2O, sample P59B..... 4
2. Reaction product of 9 mL DF with H_2O+Li_3N, after 7 days, sample P19A..... 5
3. Sample P65C made from reaction of DF with silica gel in a glass vial, after 14 days of reaction time..... 7
4. Setup of 100 mL DF reaction, Sample P21A.. 8
5. Reaction of 100 mL DF.. 8
6. Reaction of 100 mL DF with water and Li3N, after 10 days of reaction time (Sample P21A)..... 9
7. ^{31}P NMR spectrum of DF in $CDCl_3$ with proton decoupling, with triethyl phosphate (TEP) internal standard..... 10
8. ^{31}P NMR spectra of a mixture of methylphosphonofluoridate (MF) and methylphosphonic acid (MPA).. 10
9. Total ion chromatogram (top panel) and extracted ion chromatogram of m/z 99 (bottom panel) for DF spiked into 10%IPA/DCM extraction solution..... 14
10. DF reaction produces G-type nerve agents..... 15
11. DF hydrolysis..... 16
14. Spectra of MF and MPA in Chamber reactor samples.. 18
15. Spectrum of DF feedstock sample, which has a purity of 88.1 wt.% and 5 wt.% MF in $CDCl_3$ solution.. 19
16. Kinetics of MF after addition of DF to 0.3 wt% aqueous NaOH at 21 °C. 20
17. Plot of MF Concentration vs Time for DF Hydrolysis at 38 ºC in tap water. 21
18. Plot of MF Concentration vs Time for DF Hydrolysis at 49 ºC in tap water. 21
19. NMR spectra of reaction at 38 ºC with tap water as solvent. 22
20. Kinetic data for reaction of MF in a solution buffered to pH 4 at 21 °C. 23

TABLES

1. Amount of DF that remains after addition of water for Sample P53A from Notebook 18-0018 with a reaction volume of 0.4 mL DF in an NMR tube..... 6
2. MF Half-Lives for DF Reactions..... 20
3. Hydrolysis rates of MF in aqueous solutions..... 21

DF REACTION WITH Li_3N+H_2O FOR THE TACTICAL DISABLEMENT PROJECT

ABSTRACT

As part of the Tactical Disablement Project, neat weapons-grade DF was reacted with lithium nitride (Li_3N) and water in a glass or Teflon® reaction vessels. Products were analyzed, and reaction schemes are provided to explain the products.

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 neutralization and/or solidification of the bulk agent. This can be done by performing the reactions in the CA storage container with wet chemical approaches in order to avoid transporting the storage container or transferring the CA out of the container into a reactor. The reaction should take place 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 a 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 for which a short time window is required, the material can be added to all the CA containers and left to react on their own without intervention.

Neutralization of the CA was required to greatly reduce the toxicity as a CA. However, it was not anticipated that the toxicity will be completely eliminated as it is 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 CA 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. 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 study of the characterization of solid products from VX reaction has been published.[1] A study of the reaction and solidification of GB is under review.[2]

This study demonstrates a method to perform the neutralization and solidification of bulk DF (methylphosphonodifluoridate, also known as difluor). DF is a precursor for the synthesis of G agents including Sarin (GB) and Soman (GD) that was used in binary weapons. It has been an important precursor chemical in terms of international relations, since DF was 581 tons (over 96%) of the stockpile that was removed from Syria in 2013-2014 in bulk containers. It was destroyed by the U.S. Army by hydrolysis on the MV Cape Ray.[3] This was an unprecedented, complex operation.[4,5] There is suspicion that Syria has retained some amount of their stockpile.[6]

The approach in this study 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. The test reactions were done in jars that simulate storage containers. Since DF or hydrogen fluoride (HF) that may be a reaction product can react with glass, some trial runs were done in Teflon® (polytetrafluoroethylene, PTFE) containers that are unreactive, as well as glass jars.

An effective reagent for the purposes of the project was found to be lithium nitride and water ($Li_3N + H_2O$). The reagent was tested for this project on other CA including VX, GB, GD, and QL. However, DF is the most reactive chemical that was tested. DF reacts energetically with water alone, so this reaction was also examined. Preliminary surveys were done to study a few reagents, and then a more detailed study was done $Li_3N + H_2O$, the most effective reagent for several agents.

Studies were done on the reagent $Li_3N + H_2O$ to optimize the range of reagent ratios. DF is the lowest molecular weight CA compound that was tested, having a molecular weight of 100 Da. DF has two fluorine atoms that are both reactive, although the reaction of the first P-F bond is much faster. Assuming only one F atom reacts, the minimum stoichiometry of water to DF is 18/100 = 18% by weight, or 13% by volume (since the literature density of DF is 1.36 g/mL). This amount already exceeds the target amount of 10% reagent to CA ratio. If there is sufficient time for both F atoms to react, the ratio rises to 26% by volume. Since the Li_3N is known to consume some water to generate a solid material, additional water is needed that is consumed by the Li_3N. As a result, approaching the project goal of 10% reagent will not be possible.

DF is a precursor to GB, but it is in a more reactive compound than GB. This chemical difference affects the best strategy to use for destroying the compound or making it unsuitable for use as a binary munition. A goal of the overall tactical disablement project was to develop one method that could be used for all nerve agents or binary precursors, but DF is an exception due to the chemical and stoichiometry difference.

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. Further studies were done of the solidification process using DMMP in an attempt to make it more reproducible that are reported in another publication.[2] The 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.[7,8] The reaction of $Li_3N + H_2O$ forms lithium hydroxide and ammonia (or ammonium hydroxide),[9] according to the reaction:[10]

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

These products react by caustic hydrolysis with the agent. It is possible for DF to react with water first and then the product HF evaporates or reacts with the Li_3N, although LiF couldn't be detected as a reaction product. The reaction got hot during the early stages depending on the conditions of addition of water and Li_3N, and it wasn't always clear whether heat was generate from the $Li_3N + H_2O$ reaction or the $DF + H_2O$ reaction. More boiling was observed in larger reaction volumes, as discussed later.

Several small-scale studies were done for the reaction of DF with Li_3N. The DF was obtained from U.S. Army Chemical Transfer Facility (CTF) from lot number DF9003. Lithium nitride was purchased from Sigma-Aldrich (MilliporeSigma, St. Louis, MO), P/N 399558-25G. Water was from an in-house distillation system.

The first reaction sample was $DF + Li_3N$ solid powder without added water, and there was no sign of reaction. Both DF and Li_3N react vigorously with water by themselves, but they don't react with each other at ambient temperature.

DF reacted with $Li_3N + H_2O$ after water was added. In the case of sample P59B, water was added rapidly and the reaction was violent, causing splattering of the liquid outside the container (but it was inside a secondary container of acrylic plastic), shown in Figure 1.

The reaction may have been a combination of reaction of water with the Li_3N and with DF. Other reactions were not as violent, possibly due to different mixing or to the Li_3N being on the bottom of the container, so the water didn't contact it as fast. Using pellets of Li_3N instead of powder helps control the rate of reaction. Water can also be introduced in a slow manner to prevent splattering.

A reaction with 10 mL of DF was done using 6.7 wt% Li_3N and incrementally increasing the amount of water to prevent violent reaction. After addition of 0.3 mL, bubbling, heating, and evaporation of the DF was observed. After 1.0 mL of water was added (7.3 wt%), there was 16% residual DF in the sample. The Li_3N competes with DF for reaction with water, so using less Li_3N or even no Li_3N may reduce the amount of water that is needed for reaction, but without solidification. But the Li_3N is caustic, so it may also promote the reaction. Some DF may evaporate in the heat since it has a low boiling point, and the amount of evaporation wasn't measured, so it isn't clear how much DF was lost to this mechanism. Reaction with water alone was enough to degrade the DF (see Section 2.3).

Because of the vigorous reaction, alternative procedures were studied to mitigate possible hazards of the reaction. Reactions in capped containers were studied with novel methods for mixing water. For sample P19A, a 9-mL DF reaction, an amount of 1.8 mL of water was placed in a small glass vial, and the vial was stood upright in liquid DF that was placed in a larger PTFE reaction jar. The large jar was capped with a lid to contain the vapor from the DF reaction. After capping, the small vial was tipped over to let the water mix with the DF while the container was closed. The temperature of the liquid mixture rose to 55-60 C (measured on the outside of the jar with an infrared thermometer). After 5 min., the jar was opened and two tablets (0.53 g) of Li_3N were added. No further vigorous reaction was observed. In 24 h, DF was not detected, and the material solidified after a week. The solid material is shown in Figure 2.

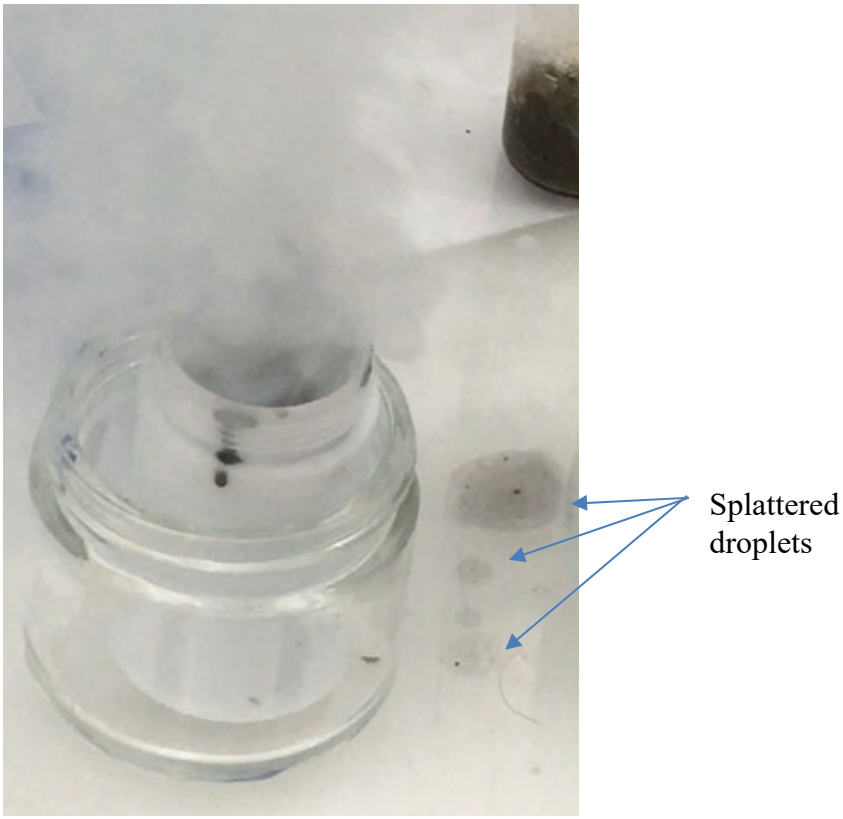

Figure 1. Reaction Mixture from DF + Li_3N + H_2O, sample P59B. As the water was added, the mixture reacted violently, smoked, and splattered out of the container. Photo is a still taken from a video.

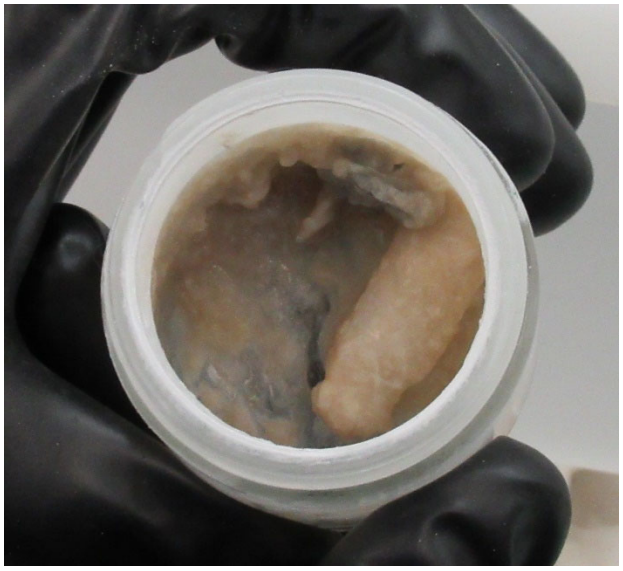

Figure 2. Reaction product of 9 mL DF with H_2O+Li_3N, after 7 days, sample P19A. The outline of the vial that was used to add water is visible on the right.

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.

When DF was added to $LiAlH_4$ (samples P55A and P61C), no reaction was observed. The reaction was attempted several times for confirmation. Reactions with both a solid pellet, smaller chunks, and powder were done.

The only time a reaction was observed for $LiAlH_4$ was when NaOH solution in water was added followed by a $LiAlH_4$ tablet. This type of reaction wasn't done for any of the other agents, and it isn't a practical approach. The NaOH solution was used to accelerate the reaction. Addition of the NaOH solution caused a flash of flame from the container when it reacted with the $LiAlH_4$. This effect was due to reaction of the $LiAlH_4$ with water, and might not have involved the DF. It didn't completely eliminate the DF, since after one day, there was still 24% DF remaining in the liquid.

No further reactions were done using $LiAlH_4$, since it didn't seem effective or useful for reducing DF.

2.3 Reaction with H_2O

It is likely that Li_3N competes with DF for reaction with water, so eliminating the Li_3N may reduce the amount of water that is needed for reaction to go to completion with DF. But the Li_3N is caustic, so it may also promote the reaction by generating base.

Reaction with water alone has been used in previous projects to decontaminate DF (see Section 7). The rate and amount of reaction depends on the ratio of excess water compared to amount of DF. An excess of water was used in the previous study, with a ratio of 1:5 DF:H_2O vol./vol. A 1:1 molar ratio of DF:H_2O is the minimum needed to remove one F from the DF molecule to leave methylphosphonofluoridic acid (MF). The weight ratio of the compounds is 18% H_2O to DF. The volume ratio is slightly smaller, 13% H_2O to DF, due to the higher density of DF. The second F from DF also can be replaced by water to form methylphosphonic acid (MPA) as the final product, but the second reaction is slower and also depends on the amount of excess water that is present. With only a small amount of excess water, MF can persist indefinitely.

Sample P53A was done with only water added. Water was added in 40 µL increments to a volume of 0.4 mL DF in an NMR tube. After 30% of water relative to DF, 11% of the DF still remained in the reaction mixture, using NMR detection. More water than the 1:1 molar ratio is needed because some of the DF is reacting to form MPA, consuming two H_2O molecules.

Table 1: Amount of DF that remains after addition of water for Sample P53A from Notebook 18-0018 with a reaction volume of 0.4 mL DF in an NMR tube.

Amt. water added (%)	Amt. DF	Amt. MF
10	72	28
20	44	56
30	11	89

2.4 Reaction with glass

A small scale reaction was done with DF and Li_3N without water (sample P47A). The reaction was done in a small glass vial. No reaction was visible, but in 24 h, the reaction mixture was solidified. However, no reaction was observed with DF and Li_3N (without water) in Teflon containers. It was hypothesized that the reaction was between DF and the glass vial. Due to the active fluorine in DF and the potential for forming HF, it is not surprising that glass can be attacked.

Another reaction was performed between a larger amount of 5 mL DF and Li_3N + water in a larger glass vial, using 0.25 g Li_3N and 0.25 g H_2O (5 wt% relative to DF), sample P61D. The reaction mixture didn't solidify, and 50% of the DF remained in the vial. The amount of water wouldn't be expected to consume all of the DF, but reaction with the glass also wasn't effective. It is possible that the larger vial didn't have enough surface area relative to the volume of DF to be as reactive. A reaction between 5.0 mL DF and 0.56 g silica gel (about 10 wt.%) was done. The DF was completely consumed in less than 5 days (Sample P65C), but it took about 18 days to completely solidify, shown in Figure 3.

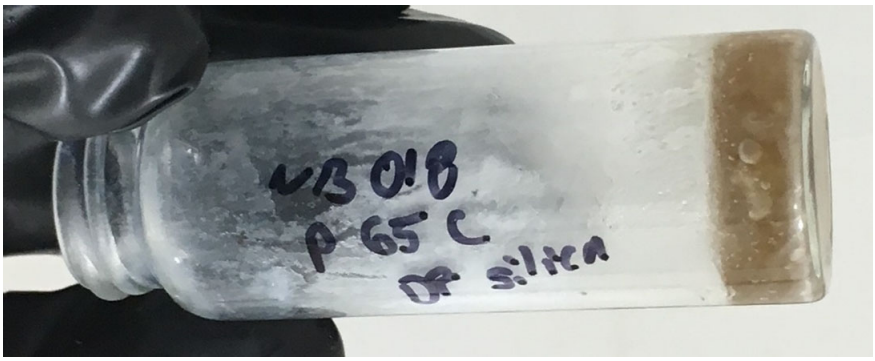

Figure 3: Sample P65C made from reaction of DF with silica gel in a glass vial, after 14 days of reaction time.

Since these chemicals are readily available, it may be a logistical advantage to be able to use them to decontaminate DF. The advantage is that water or silica gel are less reactive, less expensive, and easier to transport than Li_3N. In addition, the reaction probably releases less HF into the atmosphere, since the reaction generates less heat, evaporates less DF, and the product HF reacts with silica.

3. 100 ML SCALE REACTION STUDY

Using a $Li_3N + H_2O$ procedure similar to that for smaller volumes, a 100-mL reaction volume of DF was done. An amount of 100 mL of DF was measured by volume. Then 20 mL of water was placed in a 25 mL vial and the vial sat in the DF liquid. The outer reaction jar was capped, and then the inner vial was tipped over so water mixed with DF and the reaction proceeded. These steps are shown in Figure 4. A temperature of 50-60 C was obtained on the outer surface of the jar before any Li_3N was added.

After 3 min., the cap was removed and 5.0 g of Li_3N pellets were added and the jar was recapped. The reaction produced vigorous boiling and fog formed in the containment enclosure. Boiling continued for about 15 min. before slowing down. The temperature measured on the outside of the jar was 100 C. After 40 min., the temperature dropped to 56 C. These steps are shown in Figure 5.

For this volume of DF, it may take longer than 3 min. for the $DF + H_2O$ reaction to conclude, so more time should have been allowed before adding the Li_3N in order to prevent boiling. Since both DF and water boil at 100 C,[11] it isn't clear whether one or both were boiling. Videos and still photos were taken over the course of the reaction. DF was not detectable by NMR after one day.

Although some solid formed, the reaction product didn't completely solidify after 10 days. The mixed product is shown in Figure 6. The lid of the jar couldn't be removed, so a hole was cut in the plastic lid for sampling. The DF starting material was consumed, so no further studies were done to optimize the ratio of reagents to improve solidification, but studies on solidification of GB and the simulant dimethyl methylphosphonate are published in another report.[2] By 2 months of reaction time, the product was completely solidified, as shown in the right panel.

The pH of the solid product was determined by dissolving some solid in water and testing with a pH test strip. The pH was found to be 0-1 units, indicating that even the solid material was very acidic, at least near the surface. As discussed in Section 7, the low pH implies that the MF primary product should rapidly react to the secondary product, methylphosphonic acid (MPA).

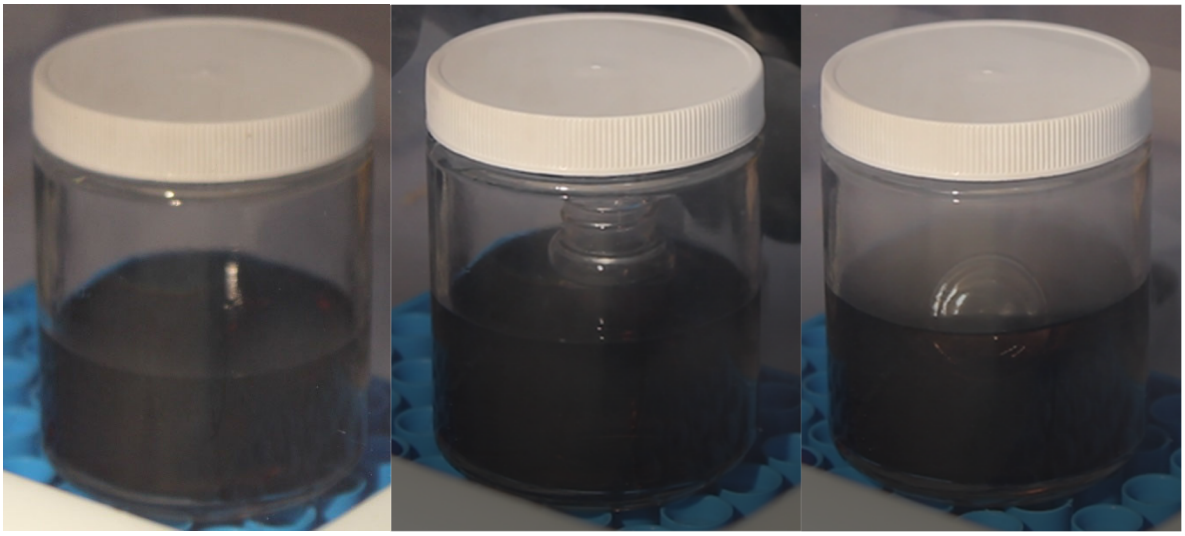

Figure 4: Setup of 100 mL DF reaction, Sample P21A. Left, original DF; Middle, DF with vial containing water; Right, small vial tipped over and reaction started between DF and water with heat and haze formation.

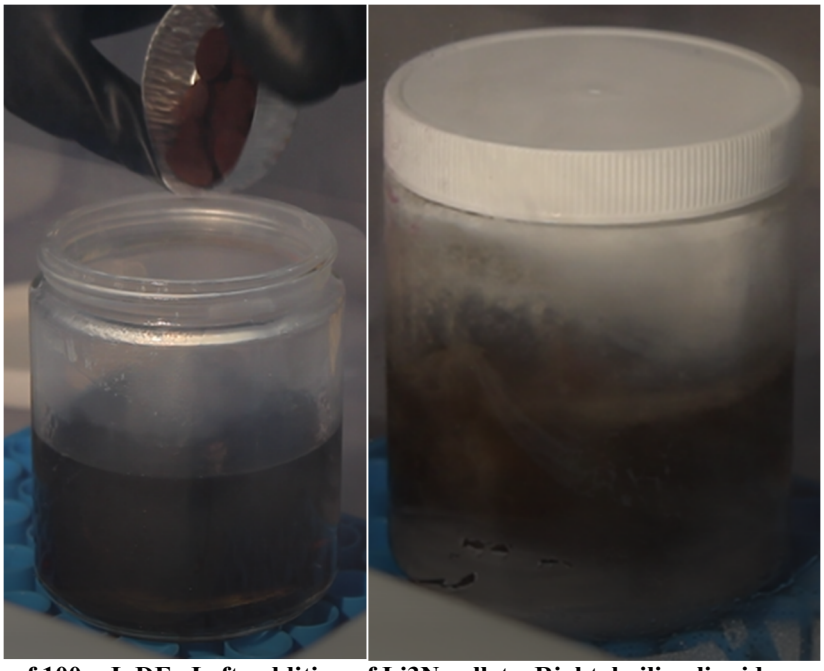

Figure 5: Reaction of 100 mL DF. Left, addition of Li3N pellets; Right, boiling liquid.

Figure 6. Reaction of 100 mL DF with water and Li3N. Left: after 10 days of reaction time (Sample P21A), right: after 2 months. The reaction product is initially a mixed liquid (brownish color) and solid (light brown). DF is not detectable by NMR after <1 day. The lid of the jar couldn't be removed, so a hole was cut in the lid to sample the product. After 2 months, the product is completely solidified.

4. ^{31}P NMR RESULTS

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. An NMR method has been reported previously.[12] For DF, since there are two ^{19}F atoms bound to ^{31}P, the ^{31}P NMR spectrum is a broadly spaced triplet. Proton decoupling can be used to make the lines narrow. An example spectrum is shown in Figure 7. Alternately, ^{19}F decoupling can be used to eliminate the triplet to narrowly spaced multiplet cause by proton splitting. (Most NMR instruments are not capable of decoupling both protons and ^{19}F atoms at the same time.)

Similarly, the first reaction product methylphosphonofluoridate (MF) is a doublet when observed by ^{31}P NMR, since one ^{19}F is bound to ^{31}P. The secondary reaction product methylphosphonic acid (MPA) is a singlet when proton decoupling is used. However, the combination of MF and MPA can have the approximate appearance of a triplet, since the MPA peak can be positioned between the two MF peaks, although it is often not centered between them and the peak ratios are not usually 1:2:1. The use of ^{19}F decoupling can definitively distinguish between a doublet and a triplet. Sample spectra are shown in Figure 8.

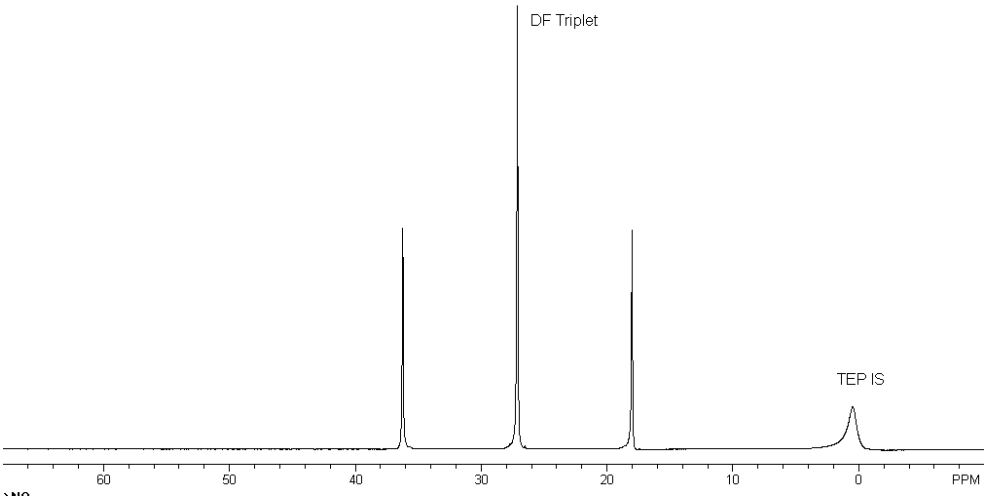

Figure 7: ^{31}P NMR spectrum of DF in $CDCl_3$ with proton decoupling, with triethyl phosphate (TEP) internal standard.

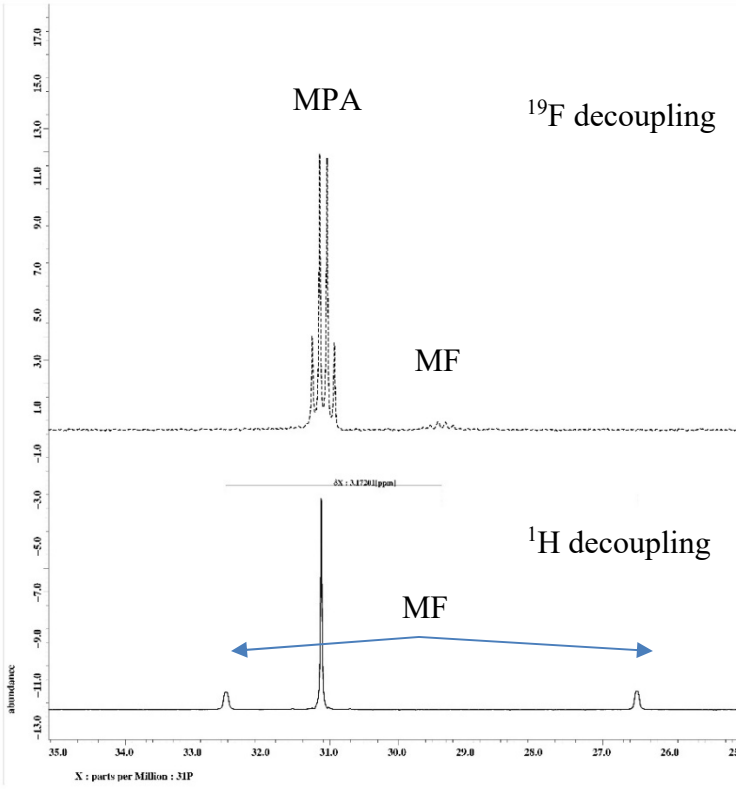

Figure 8: ^{31}P NMR spectra of a mixture of methylphosphonofluoridate (MF) and methylphosphonic acid (MPA). Top spectrum: ^{19}F decoupling showing narrow quartet from proton splitting; Bottom spectrum: proton decoupling showing central MPA singlet and small MF doublet.

All the vials or jars from reaction runs were sampled to determine residual DF. 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 DF 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 DF 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. 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. DF was never observed in aqueous solution. In this solution, the MF reacted to form MPA over time, with the rate depending on pH.

Peaks can be broadened from high sample concentrations and from paramagnetic impurities. This problem was reported previously.[13] 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. 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.

5. ^{19}F, ^{1}H, AND ^{13}C NMR RESULTS

Although ^{31}P NMR is useful for determining residual phosphorus products, it is not helpful for products that have lost phosphorus. Since DF is an unusual small molecule that has multiple different NMR active nuclei, NMR spectra with other nuclei can be acquired, but they provide limited additional information. ^{19}F spectra are very sensitive, and like ^{31}P spectra they also show multiplets for DF and MF, but there is not a peak for MPA to show that reaction product. The product HF can typically not be detected because the F atom is present in a wide range of chemical shift environments and it produces a broad peak. As a result, there is little information about how much of the HF is retained in solution, incorporated into solid, or evaporated as a gas.

^{1}H and ^{13}C spectra give information about the methyl group that shows splitting from the F and P atoms, but some interpretation is needed to identify the combination of products.

6. GC/MS AND LC/MS RESULTS

6.1 DF screening method by GC/MS

Neutralization of DF was required for this project to reduce its toxicity as a CA and its reactivity as a precursor to nerve agents. However, it was not required that the toxicity will be completely eliminated as it would be for 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 CA 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.

In a previous study in 2004-2006, the chemicals DF and QL that were stockpiled for the binary munitions program were neutralized by reaction with water in the Binary Destruction Facility (BDF) at Pine Bluff, AK, as part of the effort to destroy the U.S. chemical weapons stockpile under the Chemical Weapons Convention (CWC). In order to meet the requirements for the Organization for the Prohibition of Chemical Weapons (OPCW) Treaty Inspection of the destruction process, it was necessary to screen the neutralent solution for DF to a concentration of less than 0.1 wt% to demonstrate that the chemical was destroyed.

The method that was developed for this work was unpublished, so it is included in this report for future reference. The analysis of DF in low concentrations is significantly complex to do in a quantitative method. The method that is described uses mass spectrometry to identify compounds of interest. The analytical method was developed for the neutralent solution made from a mixture of 1 part DF to 4 parts water in a liquid matrix.

This analysis method was not validated on the reaction products in this study since it was not required by the project.

To validate an analytical method, the typical procedure involved spiking the sample matrix with a low concentration of the analyte and processing it through the sample preparation procedure, in order to demonstrate that the method is effective in detecting the analyte. This is not feasible in this case since trace amounts of DF react almost instantly with any residual water.

Analysis of DF by mass spectrometry is difficult due to its reactivity. It can be detected by direct introduction into a mass spectrometer, but it commonly doesn't survive passage through a gas chromatography column. It is generally unstable in polar protic solvents that are commonly used for liquid chromatography and can react with silica particles that are used in columns.

One approach for trace detection is to intentionally react DF with an alcohol to form a nerve agent, which can be detected by GC/MS. This method shouldn't be done with large quantities of DF due to toxicity concerns from forming the nerve agent. For this method, isopropanol is added to form GB from the DF. It is also possible to use another alcohol or an

isotopically labeled alcohol to produce a different compound with a unique mass spectral signature.

The general procedure is as follows:

a) Transfer 10 mL of aqueous sample to a 25 mL vial.
b) Measure the pH of the sample and neutralize with 0.1 M ammonium hydroxide or 0.1 M hydrochloric acid if necessary
c) Add 5 mL of dichloromethane/10% isopropanol (IPA/DCM) and tightly cap the vial.
d) Shake the vial for approximately 3 minutes and then allow the phases to separate. If needed, centrifuge for 5 minutes in a 15 mL centrifuge.
e) Transfer the dichloromethane phase (bottom layer) to another 25 mL vial with a transfer pipet. Add anhydrous sodium sulphate as necessary, cap, shake, let dry for 30 minutes. (This is an optional step to keep water out of sample and mass spectrometer.)
f) Filter 1 mL of the dried extract into an autosampler vial using a filter pipet or syringe filter and submit for GC/MS analysis.

Five sample preparations were used for validation:

1) Sample of unspiked DF neutralent (extracted in IPA/DCM)
2) Spiked sample of DF neutralent with GB, then extracted in IPA/DCM
3) Solvent blank (IPA/DCM) (may be substituted for an equipment or glassware blank during actual sample and analysis)
4) GB or DF standard in IPA/DCM.
5) Unspiked neutralent sample extracted in DCM, to check for GB in original sample.

For the DF neutralent, the following procedure was used for a sample of unspiked DF neutralent with IPA/dichloromethane extraction. This sample is prepared to react the residual DF with IPA to form GB:

a) Transfer 1.0 mL of the aqueous sample to a vial.
b) Add 0.5 mL of 10% IPA in DCM (by volume) and tightly cap the vial.
c) Shake the vial for approximately 0.5 min. and then allow the phases to separate for 2 min.
d) Transfer bottom phase to another vial, with a vial insert if necessary, for GC/MS autosampler. Submit for GC/MS analysis.

The experiments showed that DF was converted to GB from reaction with IPA under these conditions, as expected, as long as the IPA was present during the spike. In the first experiment, DF was spiked into the 10% IPA/DCM solution that was used for extractions of the neutralent solution. GB was observed in the GC/MS chromatogram of this solution. The extracted ion chromatogram of the solution is shown in Figure 9, with the GB peak at 4.26 min. The mass spectrum gave a good match to the library.

Another experiment was done to determine whether DF could be spiked into the neutralent solution, without IPA being present, and be extracted under the normal preparation

conditions. DF was spiked to an approximate concentration of 0.1% in the neutralent with the stock solution of 2% DF. The solution was then immediately (<2 min.) extracted with 10% IPA/DCM. The sample was done in triplicate. No GB was observed from this experiment. This experiment confirms that DF cannot be spiked and recovered from the blank alkaline neutralent on the time scale of this sample preparation, because it reacts too fast.

The spike and recovery measurements showed that DF or GB spiked into neutralent solution with preadded DCM/IPA solution could be successfully recovered, detected by GC/MS, and matched to a MS library spectrum.

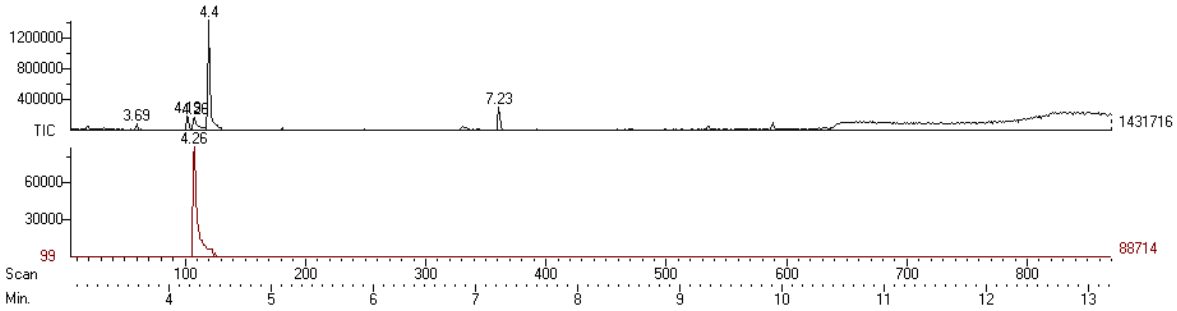

Figure 9: **Total ion chromatogram (top panel) and extracted ion chromatogram of m/z 99 (bottom panel) for DF spiked into 10%IPA/DCM extraction solution.**

6.2 Analysis of solid reaction product by Headspace Sampling

After reaction with $Li_3N + H_2O$, headspace sampling at room temperature for GC/MS analysis was done on the solid product material. No significant amounts of volatile compounds were observed in the headspace above the solid material. It is not likely that DF can be detected using this method, but only volatile products. Since products are acidic, they aren't volatile. A method for this general type of analysis has been reported.[13] The method is used to screen for volatile products that could cause a vapor hazard.

The reactivity of DF indicates that there probably isn't a long-term hazard from DF in the solid material, although some hydrogen fluoride (HF) is likely to be generated during the DF reaction, which is toxic.

6.3 Analysis of reaction products using LC/MS

The reaction solid, after dissolution in aqueous HCl, can be diluted and analyzed using Liquid Chromatography/Mass Spectrometry using an Agilent 6410 Triple Quadrupole LC/MS/MS. A method for detecting methylphosphonofluoridic acid (MF) in reaction samples has been reported.[14] Trace detection of reactants or intermediates wasn't required for this project so the method wasn't developed for trace detection of MF in these reaction samples.

7. REPORT ON SUPPORT FOR THE PILOT PLANT REACTOR RUNS FOR DF DECONTAMINATION: UNPUBLISHED STUDY (2006)

A Pilot Plant Reactor was tested with reaction runs that were used to develop decontamination reactions of methylphosphonodifluoridate (DF) and O-ethyl-O'-(2-diisopropylaminoethyl) methylphosphonite (QL), two precursors to binary chemical warfare agent systems of GB and VX, respectively. As part of the binary munition decontamination program, containers of DF and QL were destroyed at Pine Bluff Arsenal, AR.[15] The report on this analytical support for the project was unpublished, and it is the basis for this section because it includes information about the reaction kinetics of DF that is not readily available.

In support of the program to destroy the containers of binary chemicals, NMR was used for 1) sample analysis of the reactor runs that were carried out in the pilot reactor at the Toxic Test Chamber in Aberdeen Proving Ground-Edgewood Area, 2) purity determinations of the initial starting materials, and 3) bench scale studies of the kinetics of the QL and DF decontamination.

For the DF reactor runs, MF (monofluoromethylphosphonic acid) was observed as an intermediate degradation product in samples at short reaction times, in addition to MPA (methylphosphonic acid), the final degradation product. No MF was observed in the final samples after the full reaction time. For all the DF kinetic studies, it was found that DF reacts too fast to detect when it is added to water. MF is a weak cholinesterase inhibitor, so it has some toxicity. MF reacts rapidly with water at pH < 2, but it reacts several orders of magnitude slower at pH > 2.

7.1 Background

Nuclear magnetic resonance spectroscopy (NMR) was used to test the decontamination reactions of DF. In support of the program, NMR was used for sample analysis when samples were periodically pulled from the reactor for analysis. Standard NMR spectra of the starting materials were obtained for determining the purity of the starting materials that were used in the reactor. NMR was also used for bench- and instrument-scale studies of the kinetics of the DF decontamination.

DF, also known as difluoro,[7] is the precursor to G-type nerve agent (except GA) based on the general mechanism shown in Figure 10. In the actual binary munition, the isopropyl alcohol was mixed with 28% isopropylamine in a mixture called OPA, but this binary component wasn't tested in reactors.[7] DF undergoes hydrolysis in water as shown in Figure 11.

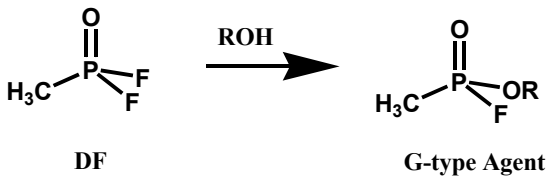

Figure 10: DF reaction produces G-type nerve agents.

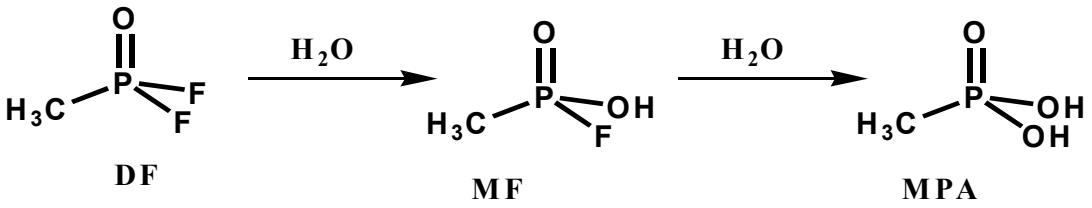

Figure 11: **DF hydrolysis.**

7.2 Experimental Method

For the sample analysis, a Bruker Avance 300 NMR instrument was used. Samples were removed from the reactor according to the test plan and transported to the NMR. Samples were run on the NMR within an hour of sampling from the reactor. Sample preparation was minimal, since the sample was transferred to a 5 mm NMR tube and added to a deuterated lock solvent. The instrumental analysis was done using ^{31}P with ^{1}H decoupling.

For the purity determinations, samples were prepared for analysis described in a Technical Report.[16] Samples were handled according to safety procedures as toxic CA samples. In brief, 100 µL of the material was transferred to a vial and weighed. An internal standard of 100 µL of triethyl phosphate (TEP) was added and weighed. TEP was unreactive with DF. Deuterated lock solvent $CDCl_3$ was added. The solution was mixed and transferred to a 4 mm diameter PTFE tube insert and capped with a PTFE cap, since DF was unreactive with PTFE but can react with glass tubes. The insert was placed in a glass 5 mm NMR tube for secondary containment of a CA sample, and the glass tube was flame sealed using an oxyacetylene torch. The doubly-contained sample was placed in the NMR and analyzed using the Bruker Avance 300 NMR with ^{31}P with ^{1}H decoupling.

For the laboratory kinetic determinations, a variety of instruments and sample preparation conditions were used. ^{31}P NMR experiments were carried out on a Varian Unity Inova 600 MHz spectrometer (tuned to 243 MHz for ^{31}P), a Varian Unity 400 MHz spectrometer (tuned to 162 MHz for ^{31}P) or a Bruker Avance 300 MHz NMR (tuned to 121 MHz). Choice of spectrometer depended primarily on instrument availability.

Reaction conditions were studied that were provided by the Pilot Plant process chemists. NMR tube reactions at various temperatures were performed for the binary component by mixing the component with aqueous solvent in a 1:5 ratio. Preliminary reactions were carried out with tap water (from the process site) as the solvent. An aliquot from the reaction was placed in an NMR tube, with ~50 uL D_2O added as a lock solvent. NMR experiments were completed on each sample at periodic time intervals.

A second set of reactions for DF was carried out in 0.3% aqueous NaOH. For DF, experiments were done in NMR tubes at 21, 38, and 50 °C (70 °F, 100 °F, and 122 °F,

respectively). An experiment was also performed at pH 4 under buffered conditions ([acetate] = 10 vol.%) with 2 vol.% DF at 21 °C to insure buffering throughout the reaction.

A conservative detection limit of approximately 0.1% (with a signal to noise ratio of 10:1) is estimated from past experience for the instrument conditions, although a specific detection limit for these samples was not measured and a minimum detection limit was not determined.

7.3 Results for analysis of reactor samples

No residual DF was observed in any reactor samples after reaction with water. For the DF reactor runs, MF was observed as an intermediate degradation product. MPA was the final degradation product. MF and MPA were both observed in the initial samples taken from the reactor. No MF was observed in the final samples. Sample spectra are shown in Figure 8 and Figure 12.

There was some difficulty in resolving the MF peaks from the MPA peak well enough to integrate for reactor samples. This problem restricted the quantitation limit. In particular, the MPA peak appeared to broaden somewhat as the reaction proceeded. This broadening may have been due to some dissolving of iron from the reactor chamber in the strongly acidic reaction solution. Dissolution of only 10-20 ppm of Fe^{3+} may have been sufficient to cause the observed broadening.

7.4 Results for feedstock purity analysis

The sample of DF that was received, designated as DF-1025-CTF, was determined to have a purity of 88.07 wt% and it had 5.08 wt% of MF as an impurity. The spectrum is shown in Figure 13. The reactor feedstock, a different lot, gave a purity of 99.6 wt% and no MF was observed. The reason for the apparent increase in purity is not known, although DF can be very sensitive to moisture or contact with glass surfaces, which can affect the purity determination. The DF triplet has the expected 1107 Hz coupling for a difluoride species, since there is a triplet caused by coupling between the ^{31}P and two ^{19}F nuclei.

7.5 Results for DF kinetics studies

DF was miscible with the initial reaction solutions of tap water and with 0.3 wt% aqueous NaOH. The reactions could be studied in the specified formulation of 1:5 by mixing 50 μL of feedstock DF with 230 μL of 0.33 wt% of aqueous NaOH and 20 μL of D_2O. Since DF and the reaction product HF react with glass, the solution was placed in a 4 mm PTFE tube insert, and the insert was capped with a PTFE cap. The insert was placed in a 5 mm glass tube.

It was found that the DF reacts too fast to measure under all conditions. No DF was detected after addition to the aqueous solution. MF was the primary decontamination product that was detected. MF reaction rates are slow enough to be determined by NMR. (MF is cholinesterase inhibitor and probably causes all physiological effects attributed to DF.[17])

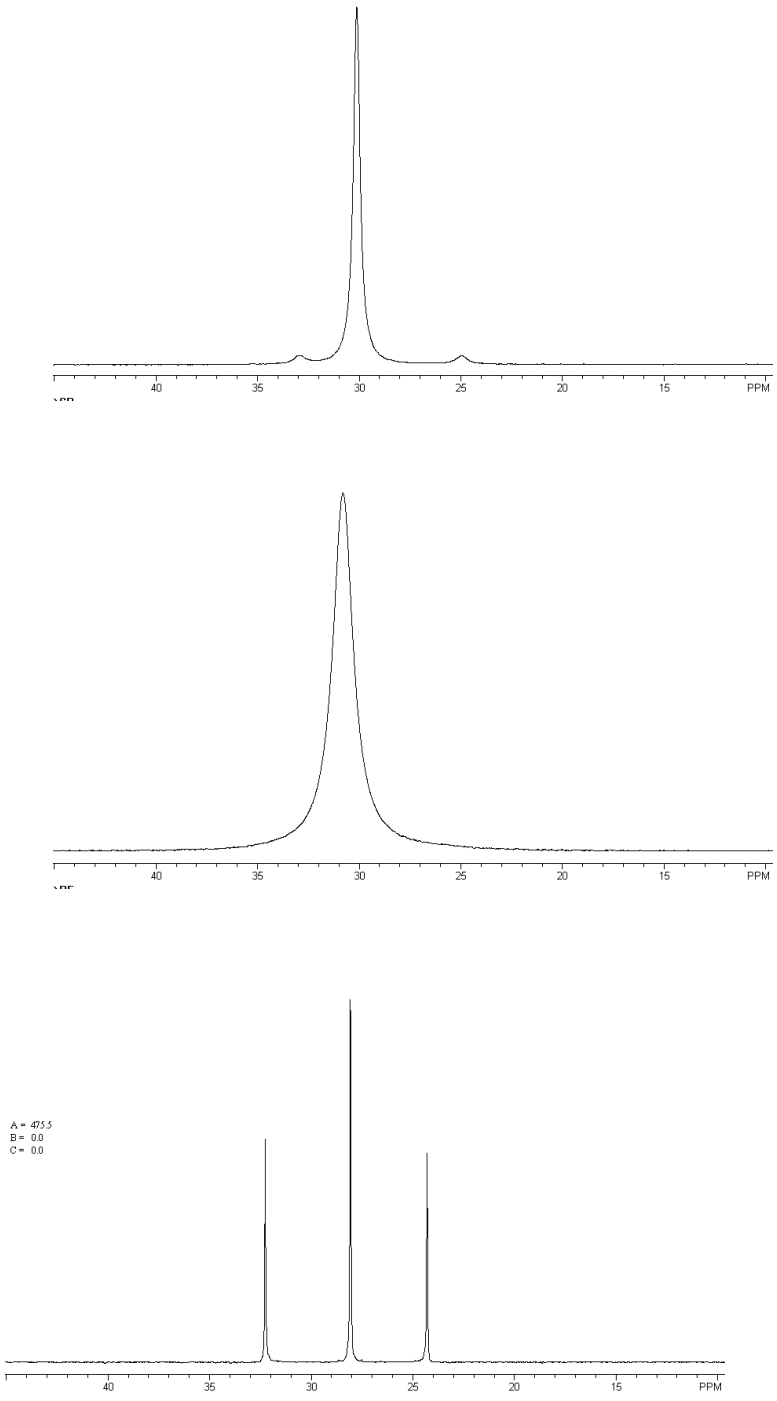

Figure 12: Spectra of MF and MPA in Chamber reactor samples. Top Panel: spectrum from sample with two small MF peaks, but the major peak is MPA. Middle Panel: spectrum from sample with broadened MPA, and MF peaks are not observed. Bottom panel: spectrum of MF and MPA in a PTFE NMR tube insert from a kinetics experiment, with typical, much narrower peaks. The center peak is the MPA peak, and the two peaks on either side are split MF peaks. Some peak broadening may be due to solution of trace amounts of iron in the acidic reactor solution.

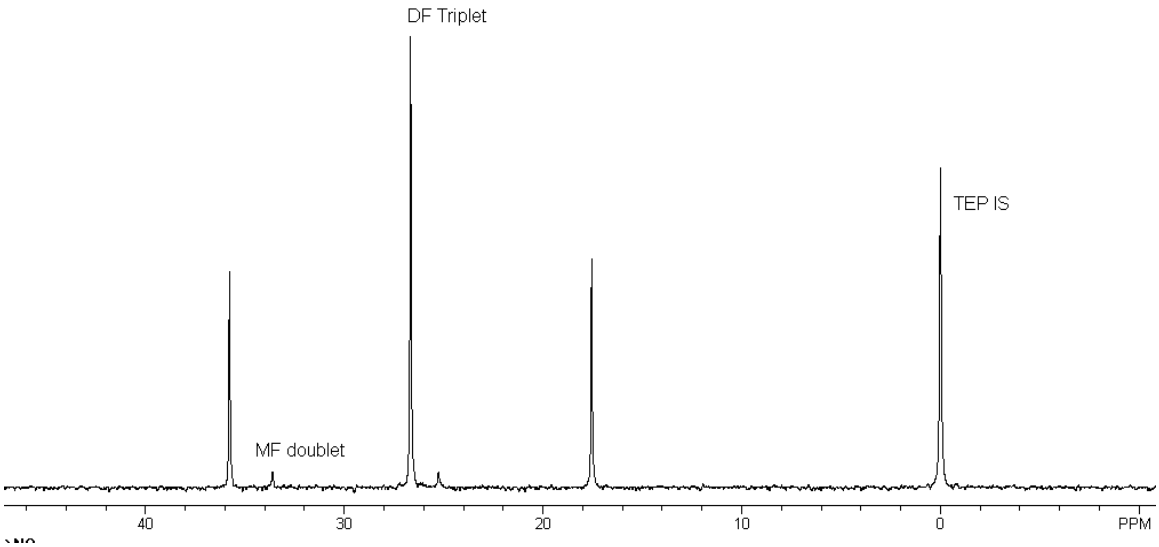

Figure 13: **Spectrum of DF feedstock sample, which has a purity of 88.1 wt.% and 5 wt.% MF in $CDCl_3$ solution. The internal standard (IS) is triethyl phosphate (TEP), used for quantitation.**

Under the conditions that were specified for use in the reactor, the aqueous reaction matrix began with 0.3% NaOH in water that was used to rinse empty containers. This solution was strongly basic with a pH of 12-13, but it had a limited buffering capacity. DF was added at 20% relative to the amount of water by volume. Each mole of DF added generated 4 moles of strong acid, so the aqueous solution quickly became strongly acidic (pH<2) as the acid generated by DF neutralized the original caustic. As the DF was added, the pH rapidly changed over a wide pH range from 13 to about 1. The samples were already acidic by the time the first NMR spectrum was taken.

A kinetic run was measured in the NMR tube using a 1:5 volume to volume DF to water at room temperature (21 °C or 70 °F) that showed the change in the amount of MF, since DF was not observed. The data is shown in Figure 14. The total run time was 45 min. The data show a kinetic behavior with the semilog plot having a linear decrease in MF concentration. This functional dependence is expected for pseudo-first order rate kinetics. The half-life is 10.0 min. at this temperature. The intercept of the plot is not zero.

The half-life is calculated by:

$$T_{1/2} = 0.693/k$$

where k is the slope of the natural log plot in units of $time^{-1}$.

Reaction studies were carried out with tap water (from the process site) as the solvent. An aliquot from the reaction was placed in an NMR tube, with 50 µL D_2O added as a lock solvent. The mixture was prepared in a fume hood at room temperature and transferred to the NMR bore, where it rapidly equilibrated in a temperature-controlled, calibrated NMR tube

heater. NMR experiments were completed on each sample at periodic time intervals. The first data point was acquired in <4 min. The data collected at 38 °C is shown in Figure 15 and gives a half-life of 5.7 min. The data for 49 °C is shown in Figure 16 and gives a half-life of 2.8 min. The results are summarized in . The rate increases with increasing temperature, regardless of the initial alkali in the reaction mixture, confirming that the reaction pH is determined by the acid generated by the DF rather than the aqueous solution. Figure 17 shows two NMR spectra from the run at 38 °C.

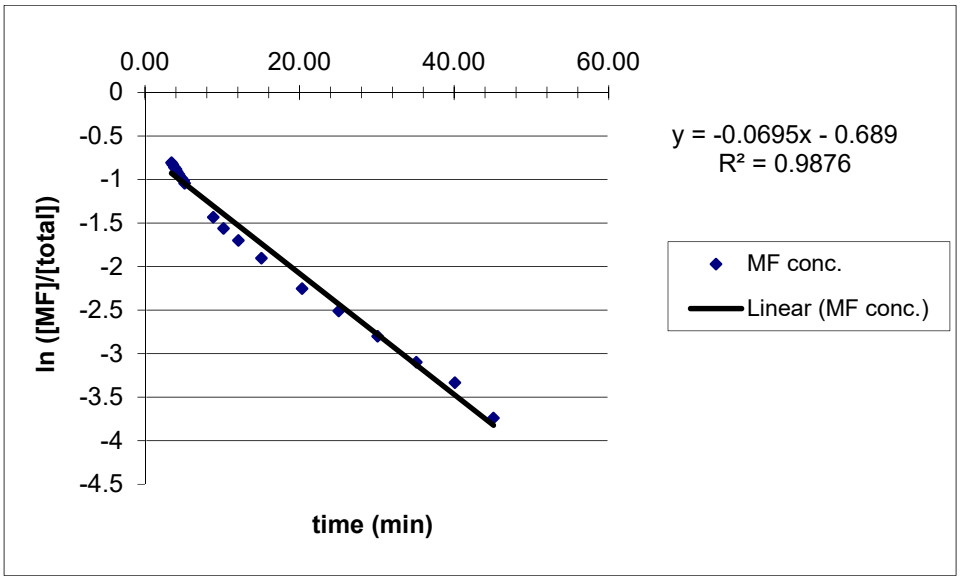

Figure 14: **Kinetics of MF after addition of DF to 0.3 wt% aqueous NaOH at 21 °C.**

Interestingly, it has been reported that MF reacts 2 to 3 orders of magnitude slower above pH 1.8 than at lower pH. Dahl and co-workers[19] measured the hydrolysis rates of MF in aqueous solutions using a fluoride sensitive electrode, and they determine the results shown in **Error! Reference source not found.**. Dahl and co-workers also reported that MF is slowly hydrolyzed at physiological pH with a half-life of about 1000 hours.[19]

Table 2: **MF Half-Lives for DF Reactions**

Solvent	Temperature (°C)	MF $T_{1/2}$ (h)
water	38 °C	0.097
water	49 °C	0.047
0.3% NaOH	21 °C	0.17
buffer at pH 4	21 °C	
Fast Segment		11.9
Slow Segment		277

Table 3: **Hydrolysis rates of MF in aqueous solutions, taken from Dahl and co-workers.[18]**

pH	0.12	0.41	1.87	2.93	4	7
$T_{1/2}$ (h)	0.017	0.067	300	1140	2160	3900

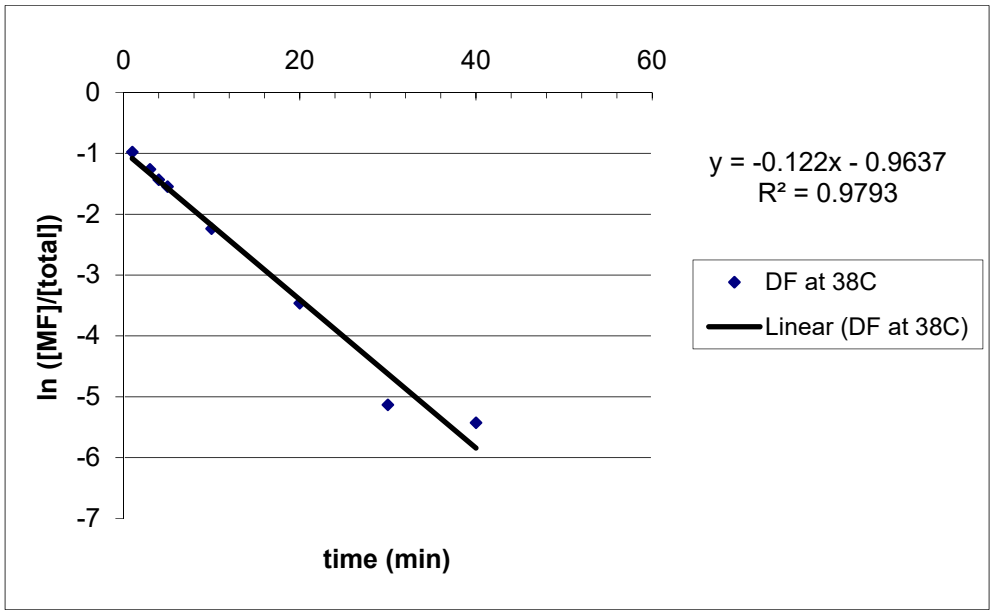

Figure 15: **Plot of MF Concentration vs Time for DF Hydrolysis at 38 ºC in tap water.**

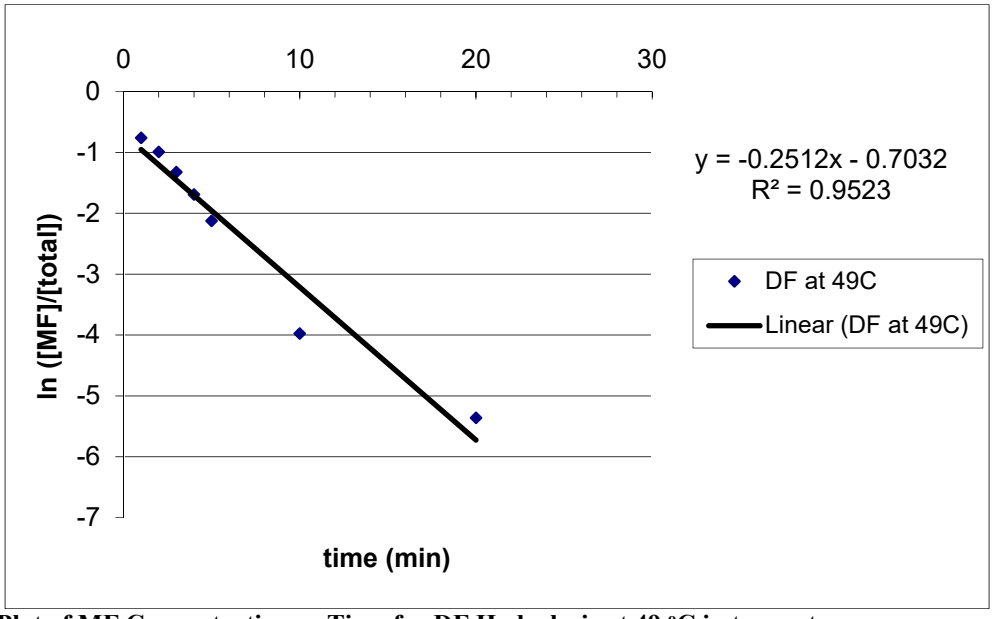

Figure 16: **Plot of MF Concentration vs Time for DF Hydrolysis at 49 ºC in tap water.**

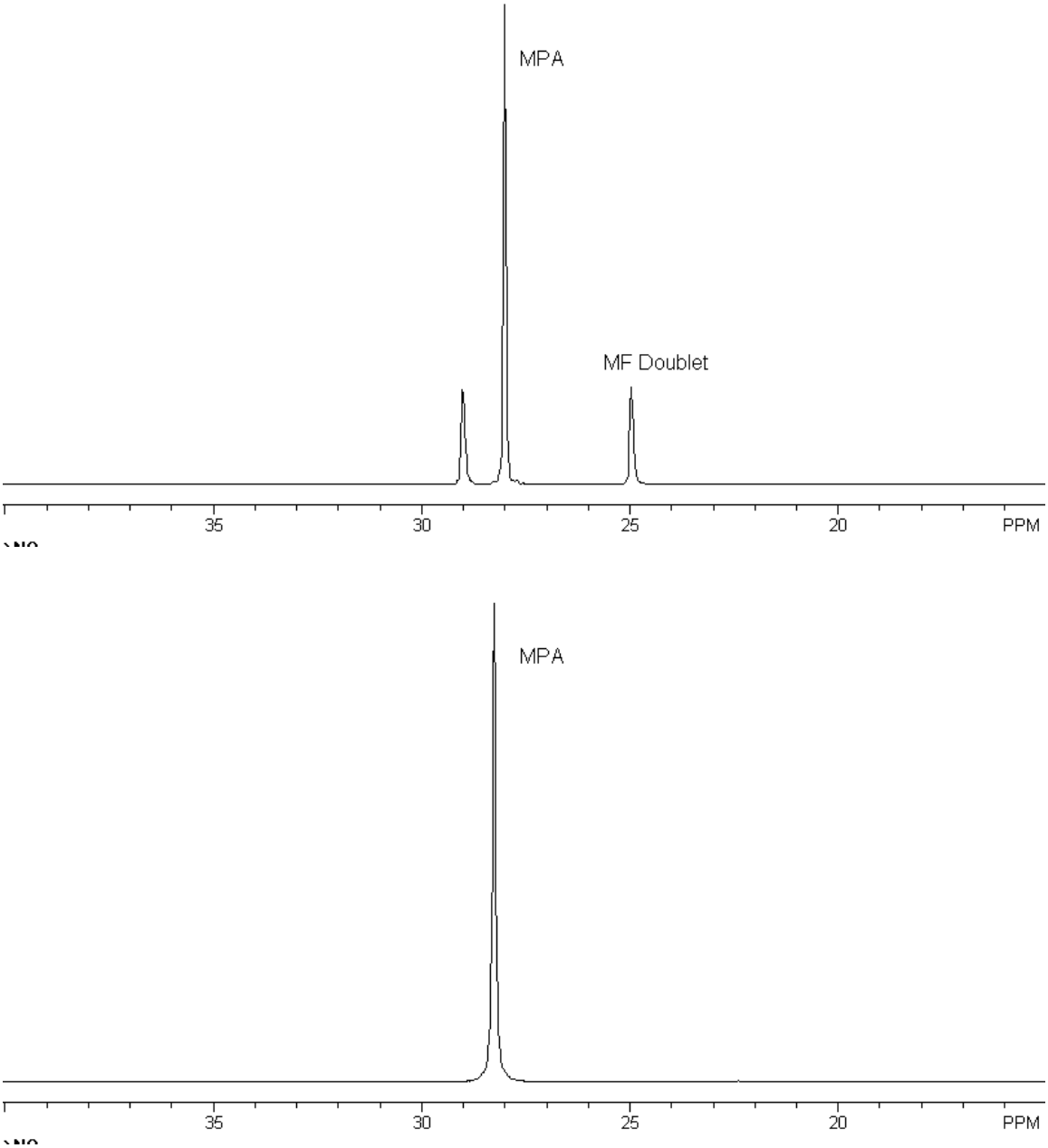

Figure 17: **NMR spectra of reaction at 38 °C with tap water as solvent. Top spectrum: after mixing. DF converts to the initial hydrolysis product, MF, which then undergoes further hydrolysis to produce MPA. Bottom spectrum: same mixture at time = 1 h when only MPA remains.**

To confirm the large change in the rate as a function of pH, a kinetic run was done with DF and water buffered to pH 4, using 10 vol.% acetic acid and NaOH added to adjust the solution to pH 4. The run was done at a temperature of 21 °C (70 °F). The amount of DF added was less than the previous run, with a ratio of only 2% by volume, in order to insure that the

buffer concentration was sufficient to keep the pH at a constant value. Kinetic results are shown in Figure 18.

The plot is bi-exponential. The half-life of MF for the first "fast" segment was found to be 11.9 h, over 70 times slower than the run with decreasing pH that goes to pH < 2. The slow segment has a half-life of 277 h. The results agree that the rate is much slower at higher pH. Even the slow rate is much faster than the rate reported by Dahl and coworkers at pH 4, which was a half-life of 2160 h.[19]

The dramatic change in rate over a narrow pH range suggests that the reaction of MF is very sensitive to protonation. It is possible that MF is protonated, and the reaction is acid catalyzed, at low pH, but that MF is not protonated at pH > 2. Studies by Saraba and co-workers indicate that the pK_a for MF is 2.6, which is consistent with the transition.[20] Their studies also indicate that the rate of MF reaction is faster at high pH (pH from 12 to 14), suggesting that the reaction may be base catalyzed as well.[20] If so, the rate in 0.3% NaOH could be a combination of fast rates at high pH and low pH with slow rates in between.

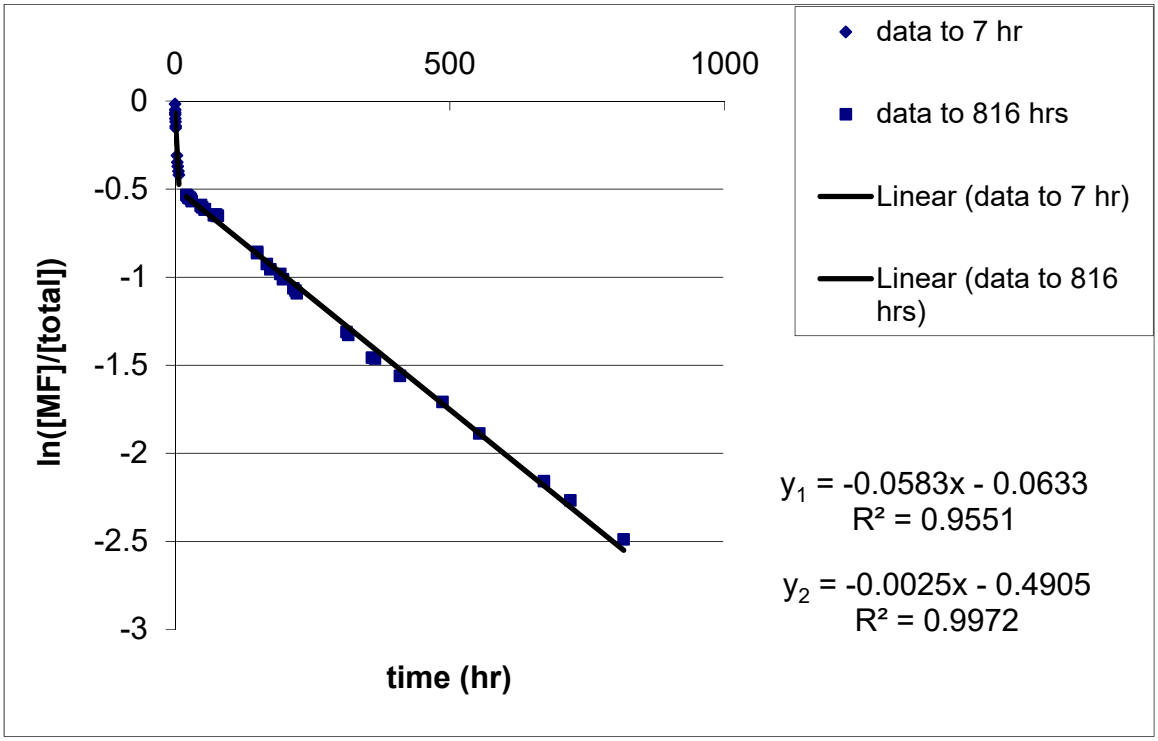

Figure 18: **Kinetic data for reaction of MF in a solution buffered to pH 4 at 21 °C.**

It is not clear why the data in Figure 18 has a biexponential rate. It is interesting that the intercept for the slow segment (0.49) is similar to the intercept for the data in Figure 14 (0.69), and the intercepts in Figure 15 and Figure 16 are slightly higher. This similarity suggests that there is a fast segment associated with these sets of data that was too fast to measure.

The reason for this fast reaction segment is unknown. Dahl and co-workers suggest that the presence of trace amounts of divalent metal ions could catalyze the reaction.[19] The divalent ions could be present in the water or as contamination in the DF. If the metal ions eventually become inert, for example by forming insoluble fluorides, the fast, catalyzed reaction would cease and the observed rate would slow down. This is one possible explanation for the kinetic behavior of the data.

The pH dependence of the reaction has implications for the reactor runs that were used to decontaminate DF. The reactor solution pH changed over a wide range. As long as sufficient DF is added to the reaction mixture to produce a pH of less than 2, the MF will react rapidly. If, for some reason, there is not enough DF to generate low pH, and the solution pH remains above 2, then the MF could be persistent.

7.6 Conclusions about DF kinetics

In each case, DF was undetected by NMR at ~60 s into the reaction. MF was the major component in the initial spectrum and it gradually reacted to MPA. The half-life of DF under these conditions is expected to be on the order of seconds. The half-life of MF was on the order of minutes for reactions that were allowed to drop to pH < 2 and on the order of hours to hundreds of hours for a buffered pH 4 reaction at 21 ºC. Comparison to other work was consistent with the strong pH dependence.

The results indicate that in order to provide a sufficient reaction rate for destruction of both DF and its toxic MF product under temperature conditions ranging from 21 ºC to 49 ºC, the solution pH should be below pH 2. It is also possible that the rate is faster above pH 12, although these conditions weren't tested in this study.

8. CONCLUSIONS

As part of the Tactical Disablement Project, neat weapons-grade DF was reacted with lithium nitride (Li_3N) and water in a glass or Teflon® reaction vessels. Products were analyzed, and reaction schemes are provided to explain the products. DF reacted rapidly both with water and with Li_3N + water, but not with Li_3N alone.

At 100-mL reaction volume, the heat that was generated by reactions of DF + Li_3N + water caused boiling at 100 C that lasted at least 20 min.

The amount of water that is required for complete reaction is at least 13 vol.% determined by the reaction stoichiometry. This amount is needed for reaction of DF to MF. Reaction continues more slowly for MF to MPA, which requires additional water.

The reaction of MF is strongly pH dependent, occurring fastest at pH<2, even when there is a large excess of water. For the reactions with Li3N, the pH will drop low enough for a fast MF reaction. The formation of solid could slow down the reaction. As a result, the MF reaction could be strongly dependent on the reaction conditions, and the rate of reaction can't be predicted without close control of the reaction.

REFERENCES

[1] McGarvey, D., W. Creasy, and M. Kinnan, "Characterization of Solid Reaction Products from the Reaction of VX with Li_3N+H_2O for the Tactical Disablement Project," CCDC CBC Technical Report CCDC CBC-TR-1635, Aberdeen Proving Ground, MD, Feb. 2020.

[2] McGarvey, D., W. Creasy, and M. Kinnan, "Reaction of GB with Li_3N+H_2O for the Tactical Disablement Project," CCDC CBC Technical Report, Apr. 2020, Aberdeen Proving Ground, MD, in preparation.

[3] OPCW, "U.S. Completes Destruction of Sarin Precursors from Syria on the Cape Ray," OPCW News, 13 Aug. 2014. https://www.opcw.org/media-centre/news/2014/08/us-completes-destruction-sarin-precursors-syria-cape-ray

[4] Blades, T. "Field Deployable Hydrolysis System Design and Deployment," Edgewood Chemical Biological Center Directorate for Program Integration.
https://ndiastorage.blob.core.usgovcloudapi.net/ndia/2015/CBRN/Blades_CBRN.pdf

[5] Trapp, R. "Lessons Learned from the OPCW Mission in Syria," Report submitted to the Director-General of the Technical Secretariat of the OPCW, 16 Dec. 2015.
https://www.opcw.org/sites/default/files/documents/PDF/Lessons_learned_from_the_OPCW_Mission_in_Syria.pdf

[6] Wintour, P. "Why does Syria still have chemical weapons?" *The Guardian*, 18 Apr 2018.
https://www.theguardian.com/world/2018/apr/18/why-does-syria-still-have-chemical-weapons

[7] Mason, Perry S., Jr. "Reactions of Lithium Nitride with some Unsaturated Organic Compounds," Louisiana State University, Ph.D. Thesis, 1963.
https://digitalcommons.lsu.edu/cgi/viewcontent.cgi?article=1897&context=gradschool_disstheses

[8] Baldwin, F. P., E. J. Blanchard, and P. E. Koenig, "Metal Nitrides in Organic Reactions. I. Reactions of Lithium Nitride with Acid Chlorides. Preparation of N,N-Diacylamides," *J. Org. Chem.*, **1965**, *30* (3), 671.

[9] Chemical Datasheet Lithium Nitride. https://cameochemicals.noaa.gov/chemical/1001.

[10] Mason, P. S. J. *Reactions of Lithium Nitride With Some Unsaturated Organic Compounds*; LSU Historical Dissertations and Theses, 1963.

[11] U. S. Army, *Potential Military Chemical/Biological Agents and Compounds*, Army Field Manual No. 3-9, Washington, D.C., Dec. 1990.

[12] Klapper, H., E. L. Stunkard, L. L. Szafraniec, D. Fielder, and J. J. Savage, The Qualitative and Quantitative Analysis of Methylphosphonic Difluoride by 1H NMR Spectroscopy, Chemical Systems Laboratory Technical Report ARCSL-TR-80035, Aberdeen Proving Ground, MD, Aug. 1980.

[13] D. J. McGarvey and W. R. Creasy, *Headspace Gas Chromatography Method for Studies of Reaction and Permeation of Volatile Agents with Solid Materials*, ECBC Technical Report ECBC-TR-1280, Edgewood Chemical Biological Center, Aberdeen Proving Ground, MD, January 2015.

[14] Wagner, G. W.; Xega, R., Creasy, W. R. "EA 6030 Hydrolysis in Decontaminants and Neutral, Mildly Acidic, and Mildly Basic Water," Edgewood Chemical Biological Center Technical Report ECBC-TR-951, Edgewood Chemical Biological Center, Aberdeen Proving Ground, MD, Jul. 2011.

[15] U. S. Army Chemical Materiel Activity, "DF (Methylphosphonic Difluoride)." https://www.cma.army.mil/df-methylphosphonic-difluoride/

[16] R. J. O'Connor, M. D. Brickhouse, D. J. McGarvey, H. D. Durst, W. R. Creasy, J. L. Ruth, *NMR METHOD FOR THE QUANTITATIVE PURITY ANALYSIS OF NEAT FEED STOCK SAMPLES,* ECBC-TR-253, Edgewood Chemical Biological Center, Aberdeen Proving Ground, MD, August 2002.

[17] A. R. Dahl, C. H. Hobbs, and T. C. Marshall, *Toxicology and Applied Pharmacology* **1986**, *84,* 561-66.

[18] A. R. Dahl, W. E. Bechtold, Y. S. Cheng, F. F. Hahn, T. C. Marshall, C. H. Hobbs, and E. J. Olajos, *Acute Toxicity of Methylphosphonic Difluoride (DF), Methylphosphonic Dichloride (DC), and their Hydrolysis Products by Inhalation and other Routes in Mice, Rats, and Guinea Pigs,* CRDEC-CR-86049, Aberdeen Proving Ground, MD, 1986.

[20] D. N. Šaraba and D. S. Veselinović, *J. Seb. Chem. Soc.* **1992**, *57*(10), 671-78.

ACRONYMS AND ABBREVIATIONS

APG	Aberdeen Proving Ground
CA	chemical agent
CTF	chemical transfer facility
CW	chemical warfare
CWA	chemical warfare agent
DF	Methylphosphonodifluoridate
EIC	Extracted ion chromatogram
GC/MS	Gas Chromatograph/mass spectrometry
LC/MS	Liquid chromatography/mass spectrometry
LC/MS/MS	Liquid chromagraph/tandem mass spectrometer
MF	Methylphosphonofluoridic acid
MPA	Methylphosphonic acid
NMR	Nuclear magnetic resonance
TIC	Total ion chromatogram

DISTRIBUTION LIST

The following individuals and organizations were provided with one Adobe portable document format (pdf) electronic version of this report:

U.S. Combat Capabilities Development
Command Chemical Biological Center
(DEVCOM CBC)
FCDD-CBR-TT
ATTN: McGarvey, D.
Evan, R.

DEVCOM CBC
Technical Library
FCDD-CBR-L
ATTN: Foppiano, S.
Stein, J.

Defense Threat Reduction Agency
DTRA-RD-IAR
ATTN: Pate, B.

Defense Technical Information Center
ATTN: DTIC OA

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