

# METHYLPHOSPHONOFUORIDIC ACID A THERMAL DEGRADATION PRODUCT OF SOME NERVE AGENTS

Michael D. Crenshaw  
Battelle Memorial Institute  
Columbus, Ohio

## ABSTRACT

The nerve agent sarin (isopropyl methylphosphonofluoridate) thermally breaks down to form methylphosphonofluoridic acid and propylene. The thermal breakdown of soman (pinacolyl methylphosphonofluoridate) probably forms methylphosphonofluoridic acid as well. Continued high temperature treatment such as that of an incinerator would continue the breakdown process. In order to prove that no methylphosphonofluoridic acid is produced, an analytical standard is required. Methylphosphonofluoridic acid was produced by disproportionation of methylphosphonic difluoride with methylphosphonic acid. However, to obtain methylphosphonofluoridic acid in high purity, modifications to its preparation were required. First, a suitable laboratory preparation of methylphosphonic difluoride containing as little methylphosphonic dichloride or methylphosphonic chloride fluoride as possible was required. Several modifications to the reaction of methylphosphonic dichloride with sodium fluoride to yield methylphosphonic difluoride were pursued with good results. Ultimately, the reaction of methylphosphonic dichloride with sodium hexafluorosilicate proved to be the most convenient. Using the methylphosphonic difluoride produced in this way, its reaction with methylphosphonic acid required prolonged heating in a sealed tube to produce methylphosphonofluoridic acid.

## INTRODUCTION

The US stockpile of chemical weapons includes the nerve agents sarin (isopropyl methylphosphonofluoridate, GB), *S*-(2-(diisopropylamino)ethyl) ethyl methylphosphonothioate (VX) and mustard gas (HD). The US Army must destroy its stockpile of chemical weapons to be in compliance with the Chemical Weapons Convention. Currently, incineration is being used to destroy the chemical weapons at Johnston Atoll and Tooele, UT. Liquid agent is treated first at 1400 °C, and the gases generated are then treated at 1200 °C in an afterburner.<sup>1</sup>

Sarin is known to thermally decompose to yield methylphosphonofluoridic acid and propylene at temperatures greater than 160 °C (Equation 1).<sup>2-4</sup> Continued high temperature incineration will further decompose the methylphosphonofluoridic acid. Complete combustion would yield carbon dioxide, phosphate (P<sub>2</sub>O<sub>5</sub>), water, and hydrogen fluoride. In order to support analysis of the incineration process, a chemical standard of methylphosphonofluoridic acid is required. Methylphosphonofluoridic acid has been prepared by the controlled thermal degradation of sarin or the disproportionation reaction between methylphosphonic difluoride and methylphosphonic acid (see Equation 2).<sup>2,5</sup> The disproportionation reaction was selected as the method for preparing methylphosphonofluoridic acid. In order to have methylphosphonofluoridic acid of suitable quality as an analytical standard, it was thought that high

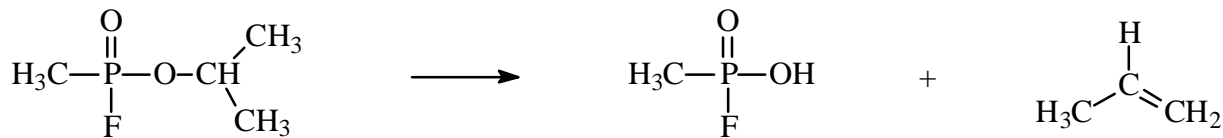
# Report Documentation Page

*Form Approved  
OMB No. 0704-0188*

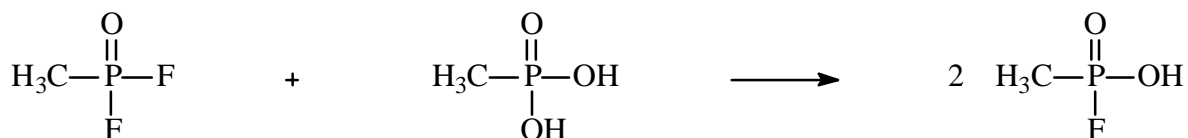
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

1. REPORT DATE <b>00 JAN 2002</b>	2. REPORT TYPE <b>N/A</b>	3. DATES COVERED <b>-</b>	
4. TITLE AND SUBTITLE <b>Methylphosphonofluoridic Acid A Thermal Degradation Product Of Some Nerve Agents</b>		5a. CONTRACT NUMBER	
		5b. GRANT NUMBER	
		5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)		5d. PROJECT NUMBER	
		5e. TASK NUMBER	
		5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <b>Battelle Memorial Institute Columbus, Ohio</b>		8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S)	
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT <b>Approved for public release, distribution unlimited</b>			
13. SUPPLEMENTARY NOTES <b>This article is from ADA409494 Proceedings of the 2001 ECBC Scientific Conference on Chemical and Biological Defense Research, 6-8 March , Marriott's Hunt Valley Inn, Hunt Valley, MD.</b>			
14. ABSTRACT			
15. SUBJECT TERMS			
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT
a. REPORT <b>unclassified</b>	b. ABSTRACT <b>unclassified</b>	c. THIS PAGE <b>unclassified</b>	<b>UU</b>
			18. NUMBER OF PAGES <b>5</b>
			19a. NAME OF RESPONSIBLE PERSON

quality precursors would be required. The purity of the commercial grade methylphosphonic acid was thought to be sufficient; however, methylphosphonic difluoride would require synthesis and purification. Also discussed here is the author's experience over the past decade with the solvent-less laboratory-scale (5-15 g) preparation of methylphosphonic difluoride and methylphosphonofluoridic acid.



Equation 1. Thermal decomposition of sarin to yield methylphosphonofluoridic acid and propylene.



Equation 2. Disproportionation reaction of methylphosphonic difluoride with methylphosphonic acid to yield methylphosphonofluoridic acid.

## RESULTS AND DISCUSSION

Previous syntheses of methylphosphonic difluoride from methylphosphonic dichloride and sodium fluoride without solvent were met with varying degrees of success. Methylphosphonic dichloride and methylphosphonic chloride fluoride were the usual impurities and sometimes were the major products. The published method calls for further treatment of the unreacted methylphosphonic dichloride and intermediate methylphosphonic chloride fluoride with sodium fluoride.<sup>6</sup> The presence of methylphosphonic dichloride in the methylphosphonic difluoride can lead to methylphosphonic chloride fluoride.<sup>7</sup> At the time this work was performed, it seemed that older sodium fluoride worked better than more recently purchased sodium fluoride. Though insufficient work was done to verify this explanation, it is possible that the older NaF powder contained enough moisture to hydrolyze a very small portion of the methylphosphonic dichloride to produce HCl which in turn produced HF and that this HF catalyzed the reaction. It is known that HF will convert methylphosphonic dichloride to methylphosphonic difluoride.<sup>8</sup> Variations of the reaction with sodium fluoride were also pursued. The addition of zinc(II) fluoride, cobalt(III) fluoride, or mercury(II) fluoride to the sodium fluoride in the method described above at a rate of 15-35% (wt/wt) did improve the yield of methylphosphonic difluoride. However, the addition of these heavy metal fluorides, especially mercury, can compound the waste disposal problem. When ZnF<sub>2</sub> was added to the sodium fluoride at 5% (wt/wt), no difference was observed compared to those reactions with no ZnF<sub>2</sub>. An alternative was sought. Zinc(II) fluoride, antimony(III) fluoride, and arsenic(III) fluoride have each been used to convert phosphorus dichlorides to phosphorus difluorides.<sup>9-12</sup> A potential problem with the use of SbF<sub>3</sub> is the contamination of the product with SbCl<sub>3</sub>.

In 1961, the use of sodium hexafluorosilicate to prepare phenylphosphonic difluoride from phenylphosphonic dichloride was published.<sup>13</sup> The by-products of the reaction with sodium hexafluorosilicate are sodium chloride and gaseous silicon tetrafluoride. Because of the extreme volatility or non-volatility of these by-products, this method seemed promising. Using this reagent, a yield of 88% and a purity of >98% were obtained. Since this work began, Farooq has published the use of sodium hexafluorosilicate, sodium tetrafluoroborate, and sodium hexafluorophosphate to prepare a variety of

phosphorus fluorides from the corresponding chlorides.<sup>14-16</sup> The disproportionation reaction of methylphosphonic difluoride with methylphosphonic acid was performed as described.<sup>5</sup> However, it was found that a much longer duration was required. During distillation, some decomposition occurred. One reference states the boiling point of methylphosphonofluoridic acid to be 69-72 °C at 2 mm. A significantly higher boiling point was observed in this work (90 °C/2.0 mm and 60 °C/0.2 mm).

## EXPERIMENTAL

Reaction of methylphosphonic dichloride with sodium fluoride and zinc, cobalt, or mercury fluoride. Fifteen grams of methylphosphonic dichloride was added in portions to a mixture of 3 to 3.5 molar equivalents of sodium fluoride containing 15-35 wt/wt percent of ZnF<sub>2</sub>, CoF<sub>3</sub>, or HgF<sub>2</sub> at room temperature under an inert atmosphere. Some fumes were generated during the addition. The mixture was heated slowly, requiring about 2 hours to reach 110 °C. The reaction was maintained at 110 °C for an additional hour and then the temperature was raised to 120 °C and the distillate of methylphosphonic difluoride collected. Yields ranged from 86 to 91%.

Reaction of methylphosphonic dichloride with sodium hexafluorosilicate. Ten grams of methylphosphonic dichloride was mixed with 1.3 molar equivalents of sodium hexafluorosilicate. The reaction mixture was slowly heated to 110 °C under an inert atmosphere over 3 hours. A gas began forming when the reaction temperature was 85 °C. Distillation gave 6.62 grams (88%) of methylphosphonic difluoride (bp 98 °C)[lit.<sup>6</sup> bp 97-100 °C]. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) 1.90 ppm (dt,  $J_{H-P} = 19.2$  Hz,  $J_{H-F} = 5.80$  Hz) (see Figure 1).

Preparation of methylphosphonofluoridic acid. Methylphosphonic difluoride (3.5 grams) and methylphosphonic acid (3.3 grams) were heated to 120 °C in a sealed tube for 64 hours. Distillation gave 3.9 grams (58% yield) of methylphosphonofluoridic acid (bp 60 °C/0.2 mm)[lit.<sup>5</sup> bp 48 °C/0.15 mm]. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) 12.975 ppm (s, 1H), 1.670 ppm (dd, 3H,  $J_{H-P} = 18.9$  Hz,  $J_{H-F} = 6.10$  Hz) (see Figure 2). When the reaction time was 48 hours, the yield was 49%.

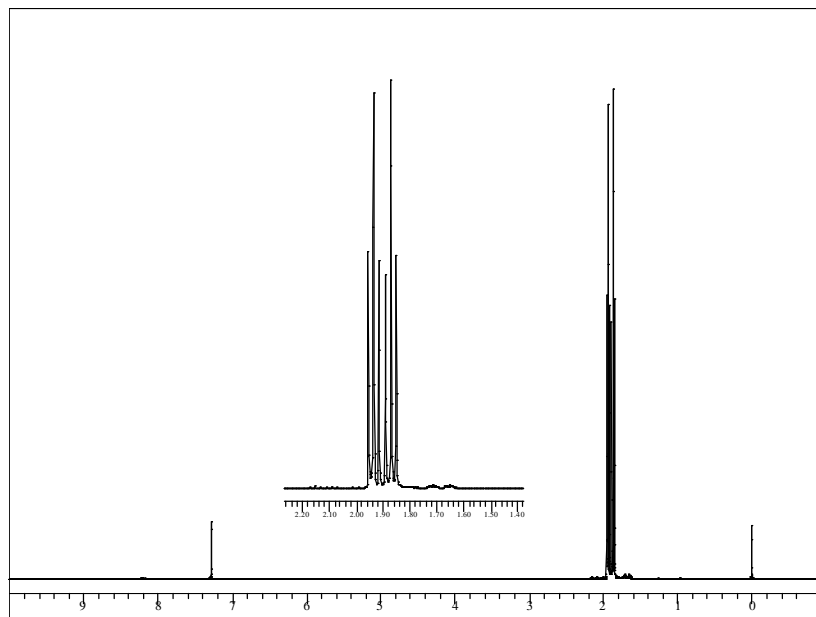


Figure 1. <sup>1</sup>H-NMR Spectrum of Methylphosphonic Difluoride.

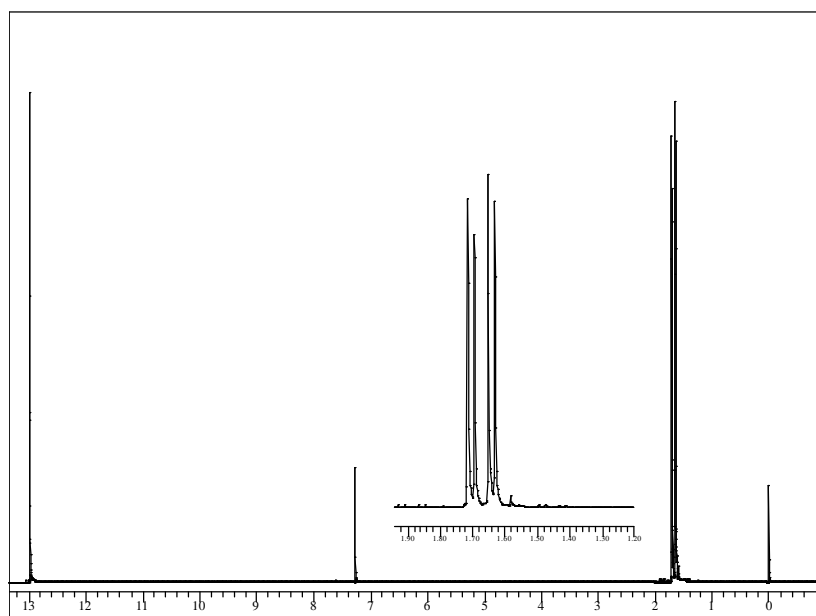


Figure 2.  $^1\text{H}$ -NMR Spectrum of Methylphosphonofluoridic Acid.

## CONCLUSIONS

A convenient synthesis of methylphosphonofluoridic acid was performed without using a toxic chemical warfare agent as the starting material. Methylphosphonofluoridic acid was prepared by the prolonged reaction of methylphosphonic difluoride with methylphosphonic acid. Distillation of the methylphosphonofluoridic acid provided a material suitable for use as an analytical standard. Variations of the reaction of methylphosphonic dichloride with sodium fluoride improved the yield and purity of methylphosphonic difluoride but sodium hexafluorosilicate was found to be the more convenient reagent for this conversion. None of these reactions required a solvent which could complicate the purification of these chemicals and possibly contaminate the product.

## REFERENCES

1. F. C. Gouldin and E. M. Fisher, "Incineration and Thermal Treatment of Chemical Agents and Chemical Weapons," *Emerging Technologies in Hazardous Waste Management 7* [Proc. I&EC Div. ACS Sympos.] 1996 (Pub. 1997), 33-47.
2. F. W. Hoffman and A. M. Reeves, "Organic Phosphorus Compounds. VII. The Preparation of Methylphosphonic Chlorofluoride," *J. Org. Chem.* 1961, 26, 3040-3041.
3. R. W. Baier and S. W. Weller, "Catalytic and Thermal Decomposition of Isopropyl Methyl Fluorophosphonate," *I&EC, Proc. Des. Develop.* 1967, 6, 380-385.
4. G. D. Sides, R. B. Spafford, and M. D. Howard, "Literature Review of Thermal Decomposition Studies of the Agents GB, VX, and HD," *Proc. of the US Army CRDEC 1984 Sci. Conf. on Chemical Defense Research.*
5. R. Bender, C. Demay, J.-C. Elkaim, and J. G. Riess, "Synthesis of Fluorophosphonic Acids by Redistribution of Fluorine Atoms and Hydroxy Groups on Phosphonic Moieties," *Phosphorus* 1974, 4, 183-186.

6. C. Monard and Jean Quinchon, "Préparation et Caractéristiques Physiques du Methylfluorophosphonate d'Isopropyle. I. Préparation et Caractéristiques Physiques de deux Echantillons de Produit pur Etalon," *Bull. Soc. Chim. Fr.* 1961, 1084-1086.
7. J. G. Riess and R. Bender, "Les Reactions de Redistribution dans les Composés Fluorophosphores. I. Redistribution du Substituant Fluor avec les Substituants Chlore, Brome, Thiocyanate, Méthoxy et Diméthylamino dans les Dérivés Phosphorylés," *Bull. Soc. Chim. France* 1972, 3700-3708.
8. P. J. R. Bryant, A. H. Ford-Moore, B. J. Perry, A. W. H. Wardrop, and T. F. Watkins, "The Preparation and Physical Properties of Isopropyl Methylphosphonofluoridate Sarin," *J. Chem. Soc.* 1960, 1553-1555.
9. L. M. Yagupol'skii and Zh. M. Ivanova, "p-Trifluorométhylphényltetrafluorophosphore et ses Dérivés," *Zh. Obshchei Khim.* 1960, 30, 4026-30 (*Chem. Abstr.* 55: 22196c).
10. R. Schmutzler, "Phosphore-Fluorine Chimie. Part VIII. Quelques Commentaires sur la "Théorie du Déplacement de Groupe," appliquée à la Résonance Magnétique Nucléaire de  $^{31}\text{P}$  de Certains Fluorures de Phosphore," *J. Chem. Soc.* 4551 (1964).
11. E. Fluck and N. Seng, "Anisotropie-Effekt in Acetylenyl-Phosphor-Verbindungen Darstellung von Acetylenylphosphonsäure-difluoriden," *Z. Anorg. Allg. Chem.* 1972, 393, 126-130.
12. M. Fild and H.-P. Rieck, "Reaktion von (Dichlorophosphinyl)méthansulfonylchlorid," *Chem. Ber.* 113, 142 (1980).
13. V. Gutmann, P. Heilmayer, and K. Utvary, "Phénylphosphoxydifluorid," *Monatsh. Chem.* 1961, 92, 196-198.
14. O. Farooq, "Fluorination of Organodichlorophosphorus Compounds with Sodium Hexafluorosilicate, Part 1," *J. Chem. Soc. Perkin Trans. 1*, 1998, 839-840.
15. O. Farooq, "Fluorination of Organochlorophosphorus Compounds with Alkali Metal Salts of Perfluorinated Complex Anions. Part 2," *New J. Chem.* 2000, 24, 81-84.
16. O. Farooq, "Fluorination of Organo-dichlorophosphorus Compounds with Alkali Metal Salts of Perfluorinated Complex Anions – Part 3," *Inorganica Chimica Acta* 2000, 303, 124-127.