METHYLPHOSPHONOFLUORIDIC ACID
A THERMAL DEGRADATION PRODUCT OF SOME NERVE AGENTS

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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 ºC, and the gases generated are then treated at 1200 ºC in an afterburner.[1]

Sarin is known to thermally decompose to yield methylphosphonofluoridic acid and propylene at temperatures greater than 160 ºC (Equation 1).[2-4] Continued high temperature incineration will further decompose the methylphosphonofluoridic acid. Complete combustion would yield carbon dioxide, phosphate (P_2O_5), 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).[2,5] 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

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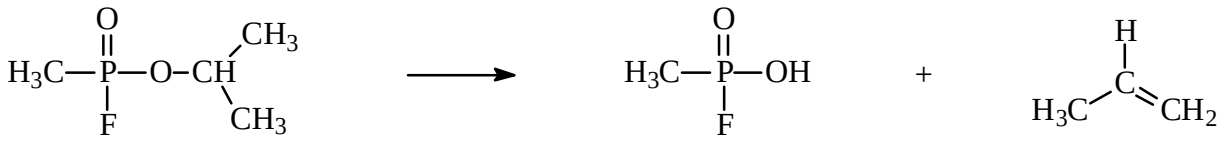
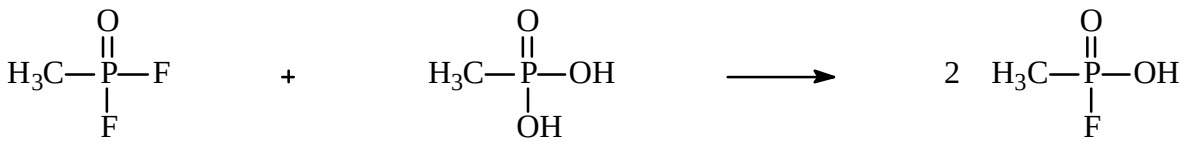
quality precursors would be required. The purity of the commercial grade methylphosphonic acid was thought to be sufficient; however, methylphosphonic difluoride would require synthesis and purification. Also discussed here is the author's experience over the past decade with the solvent-less laboratory-scale (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.[6] The presence of methylphosphonic dichloride in the methylphosphonic difluoride can lead to methylphosphonic chloride fluoride.[7] 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.[8] 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_2 was added to the sodium fluoride at 5% (wt/wt), no difference was observed compared to those reactions with no ZnF_2. 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.[9-12] A potential problem with the use of SbF_3 is the contamination of the product with $SbCl_3$.

In 1961, the use of sodium hexafluorosilicate to prepare phenylphosphonic difluoride from phenylphosphonic dichloride was published.[13] 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.[14-16] The disproportionation reaction of methylphosphonic difluoride with methylphosphonic acid was performed as described.[5] 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 ºC at 2 mm. A significantly higher boiling point was observed in this work (90 ºC/2.0 mm and 60 ºC/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_2, CoF_3, or HgF_2 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 ºC. The reaction was maintained at 110 ºC for an additional hour and then the temperature was raised to 120 ºC 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 ºC under an inert atmosphere over 3 hours. A gas began forming when the reaction temperature was 85 ºC. Distillation gave 6.62 grams (88%) of methylphosphonic difluoride (bp 98 ºC)[lit.[6] bp 97-100 ºC]. ^{1}H-NMR (300 MHz, $CDCl_3$) 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 ºC in a sealed tube for 64 hours. Distillation gave 3.9 grams (58% yield) of methylphosphonofluoridic acid (bp 60 ºC/0.2 mm)[lit.[5] bp 48 ºC/0.15 mm]. ^{1}H-NMR (300 MHz, $CDCl_3$) 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%.

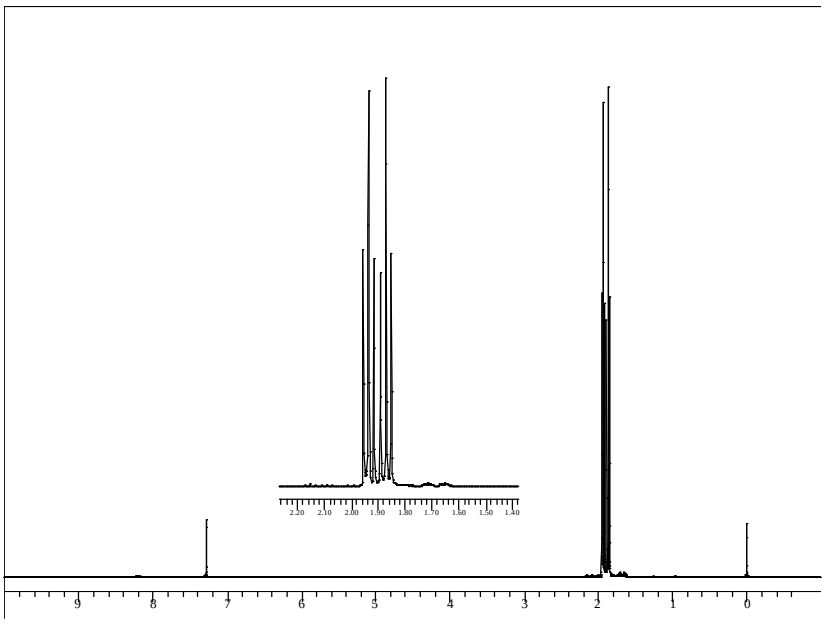


Figure 1. ^{1}H-NMR Spectrum of Methylphosphonic Difluoride.

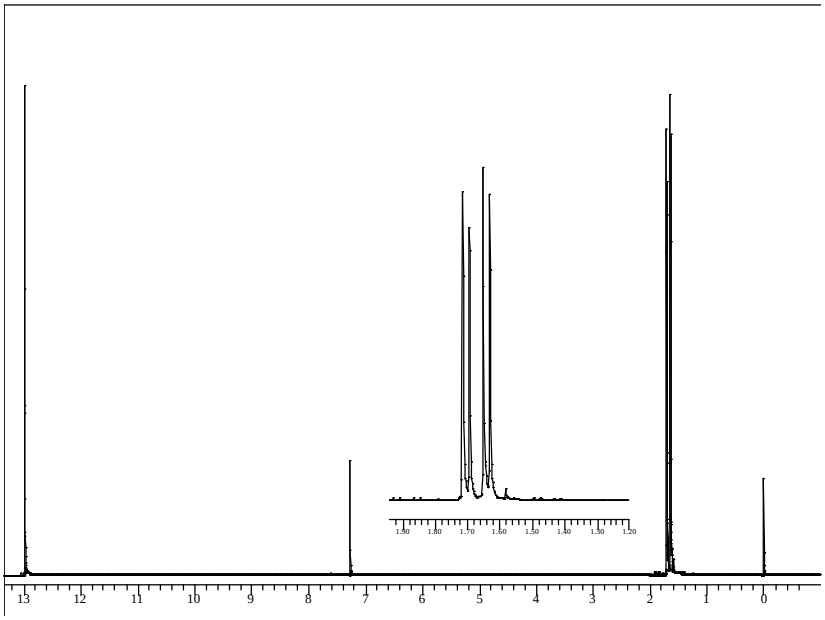


Figure 2. ^{1}H-NMR Spectrum of Methylphosphonofluoridic Acid.

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.

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