Mass Spectrometric Identification of Methylphosphonic Acid: The Hydrolysis Product of Isopropyl Methylphosphonofluoridate and Pinacolyl Methylphosphonofluoridate

Sir: For verification purposes, detection and identification of degradation products of nerve agents such as isopropyl methylphosphonofluoridate (sarin), pinacolyl methylphosphonofluoridate (soman), etc. are important, as the agent itself may be present at below the detection limit some time after their alleged use in war depending upon the prevailing weather conditions. To this end several efforts have been made by various groups of workers. The nerve agents (sarin, soman, and VX) are hydrolyzed ultimately to methylphosphonic acid (MPA),[1] as per Scheme I for sarin and soman.

Methylphosphonic acid being polar and nonvolatile, efforts had been made to analyze it by high-performance liquid chromatography (HPLC) or by gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS) after derivatization.[1-3]. Derivatization has been carried out by various means such as methylation with diazomethane,[4,5] formation of trimethylsilyl ethers or *tert*-butyldimethylsilyl ethers,[6,7] methylation with trimethylphenylammonium hydroxide, or benzylation with 1-benzyl-3-(4-chlorophenyl)triazene.[8] However, the derivatization process has some inherent limitations because of lengthy, cumbersome procedures and in some cases poor yields, instability of derivatizing reagents, or their sensitivity to moisture. All these limitations make the identification of methylphosphonic acid difficult even under ideal conditions.

We report here direct identification of the hydrolysis products of sarin and soman. The fragmentation patterns of sarin and soman lead to a peak at m/z 99[9,10] whereas MPA and other intermediates like isopropyl methylphosphonate (IMPA) and 1,2,2-trimethylpropyl methylphosphonate (TMPA), if present, give a peak at m/z 97 in aqueous solution. Identifying the m/z 97 peak by direct inlet electron impact/chemical ionization (EI/CI) and fast atom bombardment (FAB) mass spectrometry using graphite fluoride as adsorbent can lead to definite confirmation for the possible presence of nerve agents in the sample since the use of graphite fluoride as an adsorbent for concentrating solute from large volumes of air and water has been shown to have promise in environmental monitoring.[11]

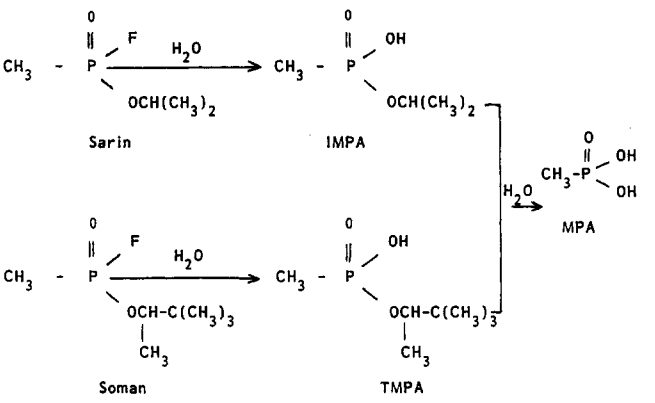
Mass spectral analysis was carried out using JEOL JMS DX-300 mass spectrometer coupled with a JMA-2000 data analysis system. The direct inlet probe temperature in EI/CI was regulated from 25 to 250 °C with a heating rate of 64 °C/min. The chamber temperature was maintained at 80 °C. EI mass spectra were recorded at 70 eV. In CI mode, isobutane (Matheson purity) was used as reagent gas. Argon (Matheson purity) was used as the bombarding atom in FAB mode.

Sarin, soman, IMPA, and MPA were synthesized in our laboratory, and the identity and the purity (>95%) were checked by analytical methods like GC (IMPA and MPA upon derivatization with diazomethane while sarin and soman directly), GC–MS (sarin and soman), and IR and ^1H and ^{31}P NMR spectrometry (all compounds).

Adequate safety measures were observed during the synthesis of sarin and soman. Synthesis and solution preparation were carried out in a fume cupboard wearing protective clothing, gloves, and a face mask. No special safety measure was adopted for handling other compounds.

Graphite fluoride $(C_2F)_n$ was obtained from Central Glass Co. Ltd., Tokyo, Japan. It is a dark gray powder which has

Scheme I



a specific surface area of 90 m^2/g (determined by a Quantasorb Jr. BET surface area analyzer) and an average particle size of 12 μm. It is thermally stable up to 400 °C and is insoluble in all solvents.

The hydrolysis of sarin and soman was done using tap water, and MPA in this hydrolyzed mixture was easily detected after 4 weeks (MPA was present up to 12 weeks beyond which we did not analyze the mixture) whereas the parent compounds could not be detected after 2 weeks when analyzed by direct sampling with EI and CI mass spectrometry. MPA was further diluted with water (10 μg in 100 mL), which was less than the detection limit of the mass spectrometer (approx 1 ng in EI/CI), and adsorbed onto graphite fluoride adsorbent. A 1-μg amount of the adsorbent was then sampled on the FAB probe tip by making a paste with 1 μL of glycerol, and mass spectra were recorded.

The EI and CI mass spectra of the hydrolysis product of sarin and soman gave the protonated molecular ion peak at m/z 97. This molecular ion peak was confirmed by high-resolution/accurate mass measurement and the molecular formula was obtained as (CH_6O_3P).

In contrast to the peak at m/z 97 for MPA in aqueous solution (the peak at m/z 96 is negligible under these conditions), neat MPA gives a major peak at m/z 96 and a very minor peak at m/z 97.

The molecular ion peak and major fragments at m/z 81 (H_2PO_3), 79 (PO_3), and 47 (PO) were further confirmed by recording EI/CI mass spectra of synthesized MPA. The FAB mass spectrum of an aqueous solution of MPA also gives a major peak at m/z 97 and a similar fragmentation pattern.

The results from the above experiments show that this direct method of detection and identification of breakdown products of nerve agents by mass spectral techniques can be very useful when such toxicants have to be verified in below nanogram levels.

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Registry No. MPA, 993-13-5; sarin, 107-44-8; soman, 96-64-0.

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TECHNICAL NOTES

Recovery of Submilligram Quantities of Carbon Dioxide from Gas Streams by Molecular Sieve for Subsequent Determination of Isotopic (^{13}C and ^{14}C) Natural Abundances

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INTRODUCTION

Quantitative recovery and isotopic analysis of CO_2 generated from organic and inorganic carbon is important for a variety of natural sample types. For example, the two most commonly used techniques for the oxidation of organic carbon to CO_2 are the sealed-tube method[1] and various modifications of the flow-through combustion method.[2] While both methods ultimately depend upon the presence of O_2 for the oxidation process, the sealed-tube method has been the method of choice for the subsequent recovery and isotopic analysis of CO_2. This is due to the relative ease with which CO_2 (sublimation point = −78.5 °C at 760 mmHg pressure) can be cryogenically removed from an otherwise noncondensible, static (i.e., nonflowing) gas mixture under vacuum. This concept has been improved upon through the use of variable-temperature cryogenic traps (VTTs)[3,4] which allow gas components having different melting points to be sequentially frozen out and distilled off for collection of essentially pure product. In contrast, CO_2 contained in carrier gas streams is generally difficult to collect at atmospheric pressure following organic carbon combustion since this usually entails using O_2 as both the oxidant and the carrier gas. Cryogenic collection of CO_2 at liquid nitrogen temperature (bp −195.8 °C) from an O_2 stream results in the condensation of liquid O_2 (bp −183.0°C), a potentially hazardous situation, and possibly in incomplete CO_2 recovery. Pumping the liquified O_2 away under vacuum, or trapping the CO_2 from the O_2 stream at temperatures below the boiling point of O_2 using VTTs, can also result in incomplete recovery and isotopic fractionation of CO_2. In fact, even when N_2 is used as the carrier gas at atmospheric pressure and liquid nitrogen temperature, intermittent condensation of the N_2 stream may occur,[5] though this is much less severe than for O_2. Finally, systems which are designed to collect CO_2 from gas streams (especially O_2) cryogenically or using partial vacuums can attain considerable complexity.

A method is therefore needed which allows CO_2 to be quantitatively recovered from O_2 and N_2 gas streams at atmospheric pressure. For isotope studies, a further requirement is that no fractionation of the carbon isotopes in the CO_2 occurs. This led us to develop a simple, convenient method which is based on the highly selective absorptive properties of aluminosilicate molecular sieves for different gases. While molecular sieves have been employed to a limited extent in some commercial organic carbon analyzers, in some cases for $\delta^{13}C$ determinations (e.g., see ref 6), a thorough assessment of the analytical capabilities of sieves has, to our knowledge, not been made. The method presented here has a low associated blank (<0.02 μmol of C), is robust over a wide range of O_2 and N_2 carrier gas flows (at least 100–2000 $cm^3 \cdot min^{-1}$) and quantities of CO_2 (at least 0.3–50 μmol of C), and is nonfractionating with respect to carbon isotopic (^{13}C and ^{14}C) natural abundances. Molecular sieves should have a variety of applications for CO_2 quantification and isotopic analysis.

EXPERIMENTAL SECTION

The specific molecular sieve used in these studies was a synthetic sodium aluminosilicate zeolite having the molecular formula

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