Nuclear Magnetic Resonance Study of the Hydrolysis of Diethyl Methylphosphonite[*]

Kenneth E. Daugherty,[†] William A. Eychaner, and John I. Stevens

Chemical Process Laboratory, Edgewood Arsenal, Maryland 21010

The products of the hydrolysis reactions of diethyl methylphosphonite at room temperature have been elucidated by means of proton nuclear magnetic resonance. The reaction was followed by observing the methyl-hydrogen resonance, phosphorus-hydrogen resonance, methylene-hydrogen resonance, and hydroxyl-hydrogen resonance. Upon addition of up to one mole of water per mole of diethyl methylphosphonite, ethyl hydrogen methylphosphinate was produced in a very rapid and complete reaction. Upon addition of greater than one mole of water—up to two moles of water per mole of diethyl methylphosphonite—the ethyl hydrogen methylphosphinate that was produced was further hydrolyzed to dihydrogen methylphosphinate in a very slow reaction. At ratios of two or more moles of water per mole of diethyl methylphosphonite, only dihydrogen methylphosphinate and ethanol were observed in solution after the reactions had come to completion. Trivalent phosphorus hydrolysis products were not observed in this reaction sequence. The chemical shifts, spin-spin coupling constants, and analytical data are described.

INTRODUCTION

Procedures have been developed for the analysis of trivalent phosphorus and pentavalent phosphorus compounds.[1] However, these procedures have had limitations, i.e., the sample was destroyed, all of the products could not be determined at the same time, and interferences were prevalent. One of the purposes of this paper is to develop a method in which the products of hydrolysis reactions of trivalent phosphorus and pentavalent phosphorus compounds can be analyzed simply and completely without altering the sample composition. One phosphorus compound of interest to the author is diethyl methylphosphonite. This compound is believed to hydrolyze in the presence of water to form ethyl hydrogen methylphosphonite (half ester) and alcohol. It is thought possible that this half ester could hydrolyze under nonoxidative conditions to form dihydrogen methylphosphonite (methylphosphonous acid).[1] The authors decided to study this system because little work has been done on investigating the hydrolysis products. Interest was generated in examining hydrolysis products of other phosphorus compounds and diethyl methylphosphonite was selected as a model compound. Proton nuclear magnetic resonance appeared to be ideally suited for this study.

The reaction sequence postulated in Fig. 1 has been followed by means of a Varian model A-60 proton nuclear magnetic resonance spectrometer with varying quantities of water and diethyl methylphosphonite (I) at room temperature. The reaction was followed by observing the methyl-hydrogen resonance (0.7 to 1.6 ppm), the phosphorus-hydrogen resonance (2.3 to 2.5 ppm and 11.3 and 11.6 ppm), the methylene-hydrogen resonance of the ethyl alcohol (3.1 to 3.6 ppm), the methylene-hydrogen resonance of the phosphorus compounds (3.3 to 4.1 ppm), and the hydroxyl-hydrogen resonance (variable ppm). All of the hydrogen resonances were measured downfield from the tetramethylsilane-external references [Fig. 2(a) and 2(b)].

Upon addition of up to one mole of water per mole (I), ethyl hydrogen methylphosphinate (IV) was produced in a very rapid reaction (Fig. 1). No evidence for the presence of ethyl hydrogen methylphosphonite (II), dihydrogen methylphosphinate (V), or dihydrogen methylphosphonite (III) was discovered. At the ratio of one mole of water per mole of (I), only (IV) and ethanol were observed in solution as (I) had been completely hydrolyzed. Upon addition of greater than one mole of water up to two moles of water per mole of (I), the initial reactant (I) was completely hydrolyzed to (IV) which was then hydrolyzed to (V) in a very slow reaction. No evidence of (I), (II), or (III) was found. At the ratio of two moles of water added per mole of (I), only product (V) and ethanol were observed in solution as (I) was completely hydrolyzed

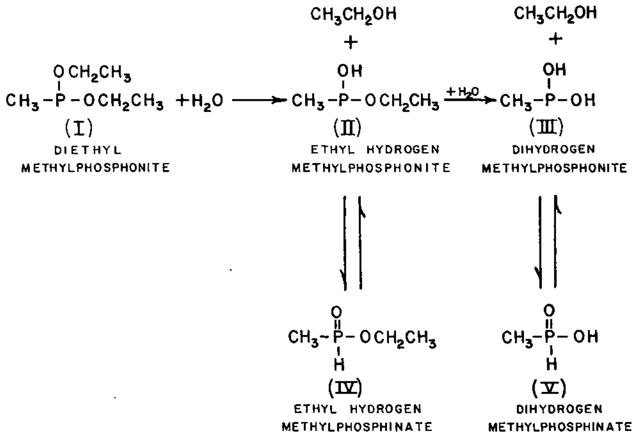

Fig. 1. Reaction sequence postulated for the hydrolysis of diethyl methylphosphonite.

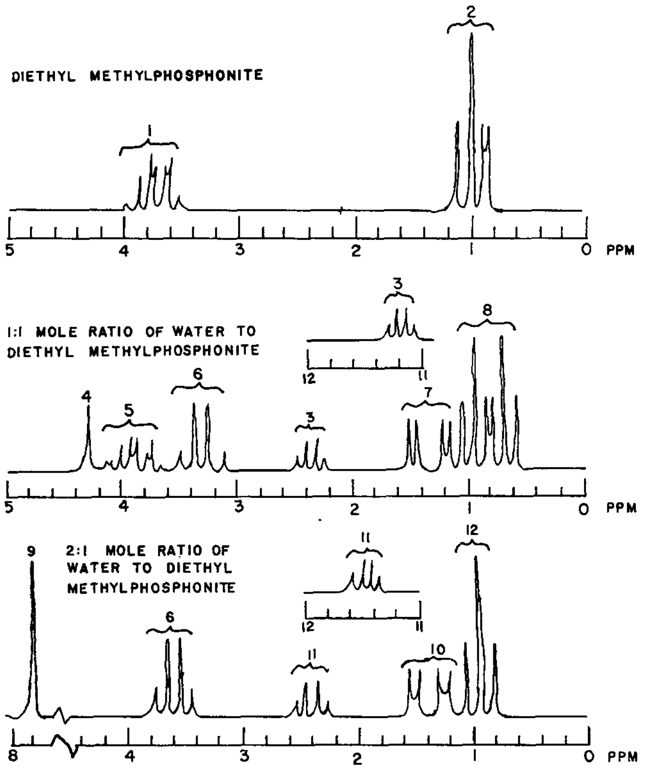

FIG. 2a. NMR spectra of diethyl methylphosphonite, a 1:1 mole ratio of water to diethyl methylphosphonite and a 2:1 mole ratio of water to diethyl methylphosphonite.

to (IV) which was then completely hydrolyzed to (V). Trivalent phosphorus hydrolysis products were not observed in this reaction sequence.

The ratios of the area of the ethanolic-hydrogen resonance to the area of the phosphorus-hydrogen resonance with varying quantities of water added to (I) were determined in order to clarify the stoichiometry of the hydrolysis reactions (Fig. 3). If any of the second hydrolysis product (V) was produced before (I) was completely hydrolyzed to (IV), up to one mole of water added to one mole of (I), this ratio would be greater than two to one. All of (I) was completely hydrolyzed to (IV) before (IV) was hydrolyzed to (V) because this ratio was two to one. The first hydrolysis reaction was much faster than the second, and thereby established this stoichiometry. The second hydrolysis reaction was found to be acid catalyzed. When more than one mole of water up to two moles of water was added per mole of (I), this ratio increased linearly up to four to one. This was due to the increasing quantity of ethanol that was produced in the reaction while the phosphorus hydrogen content remained constant. After two or more moles of water had been added per mole of (I), the ratio remained constant at a value of four to one; no further reactions occurred in this system.

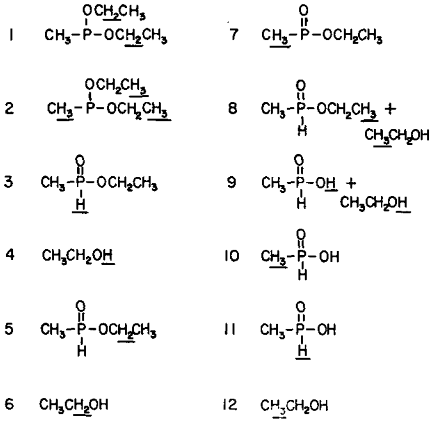

FIG. 2b. Identification of resonance peaks of NMR spectra in Fig. 2(a).

Figure 4 demonstrates the chemical shift of the hydroxyl-hydrogen resonance with respect to the mole ratio of water to (I). The hydroxyl-hydrogen shift is related to the acidity of the solution.[2] The hydroxyl-hydrogen of ethanol becomes less shielded with increasing acidity and moves downfield relative to the tetramethylsilane reference. The first hydrolysis product was a weak acid producing a chemical shift of only 8 cps. The second hydrolysis product (V) was a very strong acid producing a 200 cps hydroxyl-hydrogen chemical shift relative to the tetramethylsilane reference. The hydroxyl-hydrogen of ethanol and the hydroxyl-hydrogen of the hydrolysis product (V) interchanged and produced a single peak in the NMR spectra. When a greater than two to one mole ratio of water to (I) was obtained, the system was diluted with the excess water. Thus, the acid strength decreased and the hydroxyl-hydrogen resonance moved upfield relative to the tetramethylsilane reference.

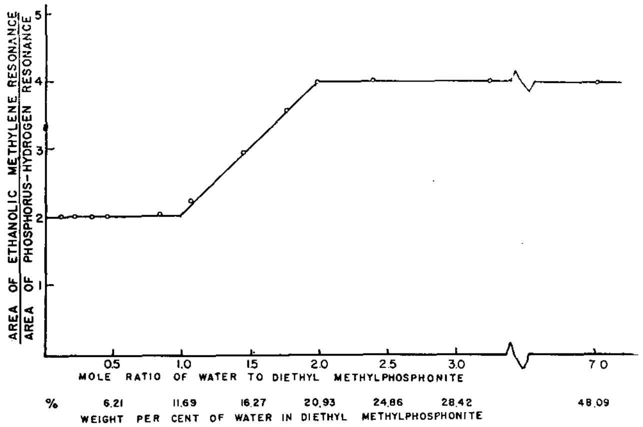

FIG. 3. Stoichiometry of the hydrolysis reactions.

From an analytical point of view, all of the products of the hydrolysis reactions can be quantitatively determined from the NMR spectra. This was important to us from the process-chemical standpoint, as we wished to know the relative quantity of water that has reacted with (I). The quantity of water that

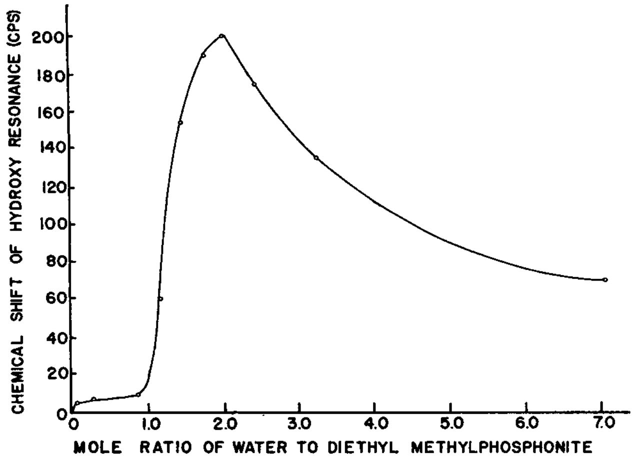

FIG. 4. Chemical shift of the hydroxyl-hydrogen resonance with respect to the mole ratio of water to diethyl methylphosphonite.

had been added to the system could be determined with an accuracy of ± 0.2%, with additions of up to 10% water (Fig. 5).

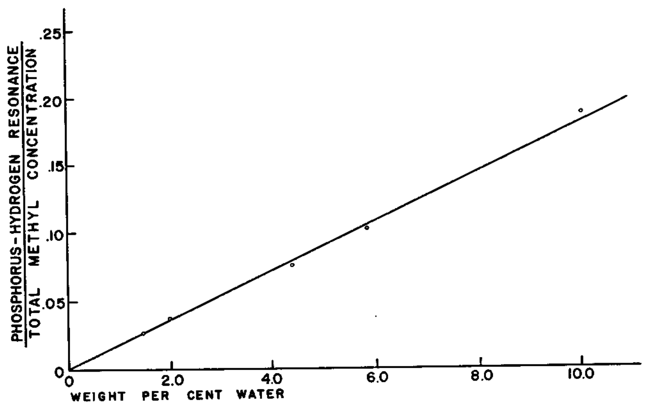

FIG. 5. Determination of the quantity of water that has reacted with diethyl methylphosphonite.

I. EXPERIMENTAL

A. Reagents

Preparation of Ethyl Hydrogen Methylphosphinate—Diethyl methylphosphonite was obtained from FMC Corp., freshly distilled and stored in a sealed bottle at 8°C. A one to one mole ratio mixture of freshly distilled water to diethyl methylphosphonite was prepared. After the solvents became miscible (one day) the reaction was complete. The ethanol produced by the reaction was evaporated under vacuum leaving the viscous oil (ethyl hydrogen methylphosphinate) which was better than 99% pure as measured by NMR.

Preparation of Dihydrogen Methylphosphinate—A two to one mole ratio mixture of freshly distilled water to diethyl methylphosphonite was prepared and the reaction was complete in three weeks at room temperature. The ethanol produced by the reaction was evaporated under vacuum leaving the viscous oil (dihydrogen methylphosphinate) which was better than 99% pure as measured by NMR.

Preparation of Various Ratios of Water to Diethyl Methylphosphonite—A series of eleven solutions was prepared ranging from 0% water to 100% diethyl methylphosphonite to 48.73% water and 51.27% diethyl methylphosphonite. These solutions ranged from a 0/1, 1/1, 2/1, up to a 7/1 mole ratio of water to diethyl methylphosphonite. The various mole ratios are shown in Fig. 4. The various weights of the water to diethyl methylphosphonite were calculated and then weighed out on a five-place Mettler balance. The solutions were stored in sealed NMR tubes and sealed volumetric flasks at room temperature.

B. Apparatus

The proton nuclear magnetic resonance spectra of the hydrolysis reactions were recorded using a Varian model A-60 high-resolution NMR spectrometer. The reported values of the chemical shifts and the spin–spin coupling constants are relative to Columbia Organic Chemicals' tetramethylsilane (TMS) (Table I). Most of the spectra were run using TMS as an ex-

Table I. NMR spectral parameters for the hydrolysis study.

	$C\underline{H}_3$-P		P-$\underline{H}$		P-OH		P-OC$\underline{H}_2$CH$_3$		P-OCH$_2$C$\underline{H}_3$	
	δ ppm (average)	J cps	δ ppm (average)	J cps	δ ppm (average)	J cps	δ ppm (average)	J cps	δ ppm (average)	J cps
Diethyl methylphosphonite[a]	1.12	8	...	...	...	...	3.81	31	1.19	15
Ethyl hydrogen methylphosphinate[a]	1.51	16	2.67 and 11.07	504	...	...	4.08	31	1.25	14
Dihydrogen methylphosphinate[a]	1.45	16	2.42 and 11.67	555	13.13	...	...	...	...	...

[a] NMR Spectral parameters relative to TMS as an internal reference.

ternal reference. The values reported for the pure diethyl methylphosphonite, ethyl hydrogen methylphosphinate and dihydrogen methylphosphinate are relative to TMS as an internal reference.

C. Procedure

Neat samples were used throughout the investigation. Integrals were recorded while the samples were spinning. The spectra were recorded with a filter bandwidth of 4.0 cps and a rf field of 0.035 mG.

II. RESULTS AND DISCUSSIONS

The oxidative state of the products of the hydrolysis reactions was checked with ^{31}P NMR. The results of this analysis confirmed the results of the proton NMR; no trivalent phosphorus compounds were observed. The hydrolysis products appear to undergo a Michaelis–Arbusov rearrangement.[3]

The phosphorus–hydrogen spin–spin interaction for ethyl hydrogen methylphosphinate has been reported by Finegold.[4] Our value of 504 cps compares favorably with his value of 5.8 cps (Table I).

The phosphorus–hydrogen spin–spin interaction for dihydrogen methylphosphinate, synthesized by a different route, has been reported by Fiat.[5] Our value of 555 cps compares quite well with his value of 561 cps (Table I). Our value of 16 cps for the phosphorus–methyl–hydrogen spin–spin interaction compares favorably with Fiat's value of 15.7 cps.

This system was somewhat unique in that the first hydrolysis reaction was very rapid (sec) and the second hydrolysis reaction was very slow (days). Thus, the system was convenient for this study.

When process-chemical studies of similar phosphorus compounds are conducted, the time required to study these compounds can be greatly reduced. Also, for this particular system, all of the compounds in the reaction mixture may be studied on one spectrum.

Proton NMR is a convenient instrument for studying reactions of this type. The methods utilized in this paper can be readily adapted for studying hydrolysis and acid or base catalyzed decompositions of a number of other types of phosphorus compounds.

ACKNOWLEDGMENT

Grateful acknowledgment is given to Harold Klapper for permitting us to confirm our results with his ^{31}P NMR.

Received 30 August 1966

---

*This paper was presented at the Fifth National Meeting of the Society for Applied Spectroscopy, 13–17 June 1966, Chicago, Illinois.

†Present address: American Cement Corporation, Technical Center, Riverside, California 92507.

1. S. Sass *et al.*, ''Control Analysis for Diethyl Methylphosphonite,'' USA Technical Memorandum 13–1 (1957).
2. J. A. Pople, W. G. Schneider, and H. J. Bernstein, *High-Resolution Nuclear Magnetic Resonance* (McGraw-Hill Book Company, New York, 1959), pp. 175–176.
3. J. R. Van Wazer, *Phosphorus and Its Compounds* (Interscience Publishers, Inc., New York, 1958), Vol. I, p. 383.
4. H. Finegold, Ann. N. Y. Acad. Sci. **70**, 885 (1958).
5. D. Fiat *et al.*, J. Chem. Soc. 3837 (1962).