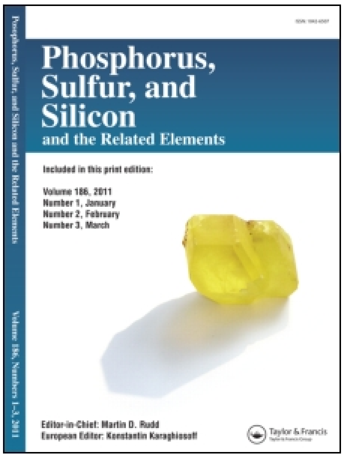

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HYDROLYSIS OF *CYCLO*-TETRA-μ-IMIDO-TETRAPHOSPHATE

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Cyclo-tetraphosphazen was made from phosphorus pentoxide and ammonium chloride. *Cyclo*-tetra-μ-imido-tetraphosphate was prepared by hydrolyzing *cyclo*-tetraphosphazene. The hydrolytic reaction of *cyclo*-tetra-μ-imido-tetraphosphate was carried out in aqueous solutions of acetic acid, citric acid, hydrochloric acid, and polyacrylic acid.

Keywords: *cyclo*-tetra-μ-imido-tetraphosphate; hydrolysis
phosphorus nitrogen compound;

INTRODUCTION

Phosphazenes are well known phosphorus-nitrogen compounds, Imidophosphates are very interesting compounds as a precursor of phosphate glass containing nitrogen, biochemical materials, and flame retardants, but few studies on the compounds have been carried out. They are also interesting compounds from a point of view of complexation. This paper describes hydrolysis of *cyclo*-tetra-μ-imido-tetraphosphate.(1)

EXPERIMENTAL PROCEDURE

High-performance Liquid Chromatography (HPLC)

A phosphate or imidophosphate sample (0.01g) was dissolved in water (10cm^3) and the solution (100mm^3) was injected into a column. The HPLC technique developed by Baba and co-workers was employed for the separation and determination of phosphate species[2-3]. The elute of 0.45 mol/dm^3 potassium chloride solution containing 0.1wt% of disodium ethylenediaminetetraacetate dihydrate and a gradient elution method were employed using a Shimadzu LC-10A apparatus. Some impovements were necessary to adopt the method for phosphorus-nitrogen compounds.

^{31}P NMR Measurement

A ^{31}P NMR spectrum of an aqueous imidophosphate solution was recorded on a JNM-α-400 spectrograph.

Preparation of *Cyclo*-tetra-μ-imido-tetraphosphate

Cyclo-tetraphosphazen was dissolved in 1,4 dioxane. Sodium acetate trihydrate was dissolved in water. Each solution was warmed at 45 ~ 50 ℃ and then mixed. The mixed solution was reacted for 3 hours at the same temperature. The white precipitate formed was quickly filtered off and washed with 70 and 90 vol% aqueous ethanol solutions and then acetone. The product was sodium *cyclo*-tetra-μ-imido-tetraphosphate.

Hydrolysis of *Cyclo*-tetra-μ-imido-tetraphosphate

After the imidophosphate was dissolved in water, acetic acid, citric acid, hydrochroric acid, or polyacrylic acid was added to the solution, and the hydrolytic reaction of *cyclo*-tetra-μ-imido-tetraphosphate was carried out. The hydrolysis process was measured by HPLC analysis and ^{31}P NMR measurement.

RESULTS AND DISCUSSION

Improvement of HPLC apparatus

When phosphorus-nitrogen compounds were analyzed by the previously described HPLC method, all of the imidophosphate were not completely decomposed ,to orthophosphate. Therefore, the determination of phosphate species was impopssible, to improve the analysis method, reaction temperature of air bath and length of reaction coil were tested at 140 ~ 160 ℃ and 2 ~ 35m, respectively. The result is shown in FIGURE 1. It was found that the complete hydrolysis of the imidophosphate to orthophosphate was achieved by the reaction temperature of 160 ℃ and the coil length of more than 30m.

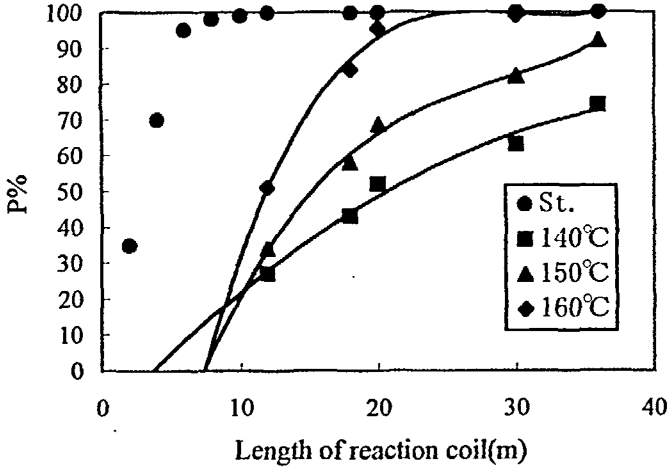

FIGURE 1 Hydrolysis of imidophosphate to orthophosphate

Hydrolysis of *Cyclo*-tetra-μ-imido-tetraphosphate

When hydrochloric acid was used, *cyclo*-tetra-μ-imido -tetraphosphoric acid[4)] was produced and it was impossible to run hydrolysis of the imidophosphate. In the case of acetic acid, the same phenomenon was observed. As for the hydrolysis of the imidophosphate in a citric acid solution, very rapid hydrolysis of the imidophosphate to orthophosphate occured. Citric acid was not a good substance to occur a stepwise hydrolysis of the *cyclo*-imidophosphate. The ^{31}P NMR spectrum of the hydrolysis products of the imidophosphate in a polyacrylic acid solution is shown in FIGURE 2. The peaks at about −7 and −12ppm correspond to the N-P-N and O-P-N linkages, respectively. The area ratio of the peaks was about 1:1. Accordingly, it was found that one of the four imino groups of the *cyclo*-imidophosphate was substituted to bridging oxygen in an acidic solution of polyacrylic acid at 70 ℃ and the content of *cyclo*-tri-μ-imido-tetraphosphate was about 40P%.

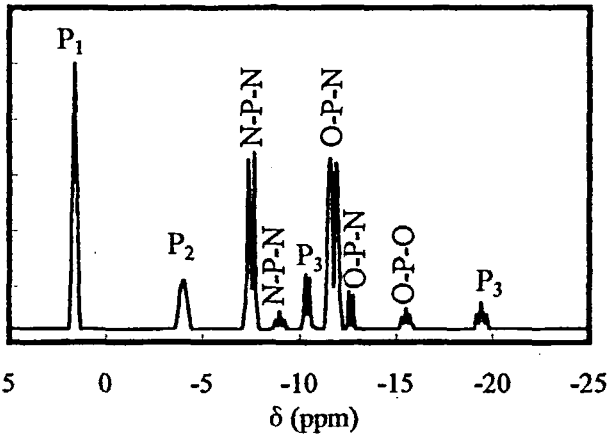

FIGURE 2 ^{31}P NMR spectrum of the hydrolyzed product at 70℃

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