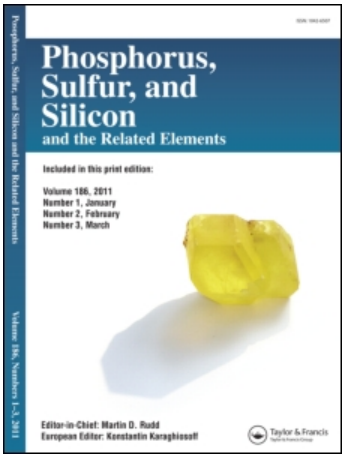

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Preparation of Ring and Chain Condensed Oligophosphates

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Online publication date: 27 October 2010

To cite this Article Watanabe, Makoto , Morita, Masanori , Sakurai, Makoto and Maeda, Mioko(2002) 'Preparation of Ring and Chain Condensed Oligophosphates', Phosphorus, Sulfur, and Silicon and the Related Elements, 177: 6, 1823 — 1826
To link to this Article: DOI: 10.1080/10426500212256
URL: http://dx.doi.org/10.1080/10426500212256

Phosphorus, Sulfur and Silicon, 2002, Vol. 177:1823–1826

1042-6507/02 $12.00 + .00
DOI: 10.1080/10426500290093306

PREPARATION OF RING AND CHAIN CONDENSED OLIGOPHOSPHATES

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(Received July 29, 2001; accepted December 25, 2001)

Preparations of small-ring and short-chain condensed phosphates were made by dry and wet processes, respectively. The crystallization of tetra-hexa-, and octaphosphates from the phosphate solution was not easy, and metal salts of these oligophosphates were amorphous and unstable at normal temperature. Guanidine tetraphosphate and ammonium hexaphosphate were crystalline and stable at normal temperature.

Keywords: Oligophosphates; preparation

INTRODUCTION

Although there are many kinds of condensed phosphates, only a few are prepared and isolated. Small-ring condensed phosphates of cyclo-tri-,[1] cyclo-hexa-,[2] cyclo-octa-,[3] and cyclo-decaphosphates[4] are prepared by a heating process, and cyclo-tetraphosphate is produced by wet chemical technique.[5] The preparation of short-chain oligophosphates is difficult, and only di- and triphosphates are made by heating process.[6] This paper describes the process of modifying the preparation of (1) cyclo-hexa-, cyclo-octa-, and cyclo-decaphosphates to find a technique that gives a higher yield, and (2) some chain oligophosphates by hydrolysis of ring oligophosphates.

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EXPERIMENTAL PROCEDURE

Preparation of Ring Oligophosphates

In every preparation of cyclo-oligophosphates, the same reaction system as that of the original one was used. The modification of the preparation of cyclo-hexa-, cyclo-octa-, and cyclo-decaphosphates was made by examining reaction temperature, reaction time, and separation process to obtain pure cyclo-oligophosphates from thermal products.

Preparation of Chain Oligophosphates

Cyclo-oligophosphates were hydrolyzed in a strongly basic solution, and the most suitable reaction conditions for selective ring opening reaction to give short-chain oligophosphates having the same chain lengths as those of the small-ring condensed phosphates were examined. The resulting solution was neutralized, and the solution was passed through a column filled with anion-exchange resin (DOWEX 1-X8) to obtain an aliquot only containing the aimed chain oligophosphate. Oligophosphate was isolated by adding a cation and/or precipitant into the oligophosphate solution. Chemical analysis, HPLC, X-ray diffractometry (XRD), and ^{31}P NMR measurement were used to analyze products.

RESULTS AND DISCUSSION

Cyclo-Oligophosphates

The modification of preparation of cyclo-hexa-, cyclo-octa-, and cyclo-decaphosphates was achieved to give a better result.

Tetraphosphate

Selective ring-opening hydrolysis of cyclo-tetraphosphate was achieved in a 5M-NaOH aqueous solution at 20°C for a few days, with guanidine hydrochloride added into the resulting solution. The precipitate was filtered off, and the filtrate was cooled at −15°C for a few days. The precipitated product was filtered off and washed with ethanol. HPLC analysis and ^{31}P NMR spectrum (see Figure 1) showed that the product is tetraphosphate. The chemical analysis of the product gave the contents: P, 16.9; N, 34.9; H_2O, 2.6%. The contents of

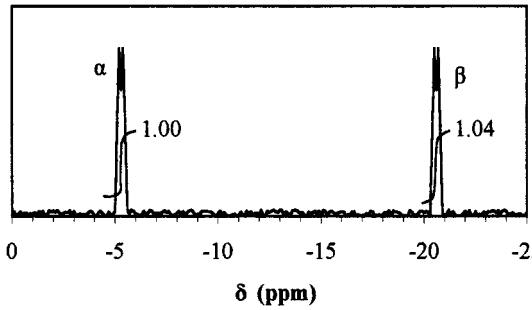

FIGURE 1 ^{31}P NMR spectrum of the product.

phosphorus, nitrogen, and water of guanidine tetraphosphate monohydrate, $(CH_5N_3)_6H_6P_4O_{13}\cdot H_2O$, are 17.4, 35.5, and 2.5%, respectively. Accordingly, the product is guanidine tetraphosphate monohydrate. The tetraphosphate was crystalline and stable at normal temperature.

Hexaphosphate

About 70 P% of hexaphosphate content was obtained by the hydrolysis of cyclo-hexaphosphate in a 10M-NaOH aqueous solution at $-7^{\circ}C$ for about 20 h. The resulting solution was neutralized with hydrochloric acid, and methanol was added into the solution. The precipitate was dissolved in water, and the solution was passed through a column filled with anion-exchange resin to do a column separation. Methanol was added into an aliquot containing only hexaphosphate and the product (Product 1) was obtained. Product 1 was dissolved in water, and the solution was passed through a column filled with cation-exchange resin to remove cations in the solution. Ammonia water and then ethanol were added into the solution, and the precipitate (Product 2) was filtered off. HPLC profiles and ^{31}P NMR spectrum of Products 1 and 2 in Figure 2 showed that the products are hexaphosphate. The Na/P molar ratio of Product 1 was 1.36, while that of octasodium hexaphosphate is 1.33. Product 1 was X-ray diffractometrically amorphous and contained 2–3% bound water. Therefore, Product 1 can be expressed by the chemical formula, $Na_8P_6O_{19}\cdot nH_2O$. Product 2 was X-ray diffractometrically crystalline and had the following chemical composition: P, 27.3; N, 16.7; H_2O, 5.5%. The contents of phosphorus, nitrogen, and water of octaammonium hexaphosphate dihydrate, $(NH_4)_8P_6O_{19}\cdot 2H_2O$, are 27.7, 16.7, and 5.4%, respectively. Product 1 was unstable and decomposed to phosphates with shorter chain-lengths at normal temperature. Product 2 was crystalline and stable at normal temperature.

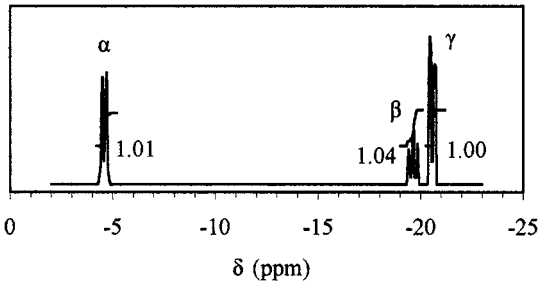

FIGURE 2 ^{31}P NMR spectrum of the product.

Octaphosphate

Selective ring-opening hydrolysis of cyclo-octaphosphate was favorably achieved in a 10M-KOH aqueous solution at 0 to -7°C, and about 70 P% of octaphosphate content was obtained. Isolation of octaphosphate was examined according to the similar manner to those of tetra- and hexaphosphates. Every metal salt of octaphosphate was amorphous and unstable at normal temperature. Several processes to obtain crystalline and stable octaphosphate were examined, but no favorable result has been obtained.

ACKNOWLEDGMENTS

This work was partly supported by a grant from the High-Tech Research Center Establishment Project of Ministry of Education, Culture, Sports, Science and Technology.

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