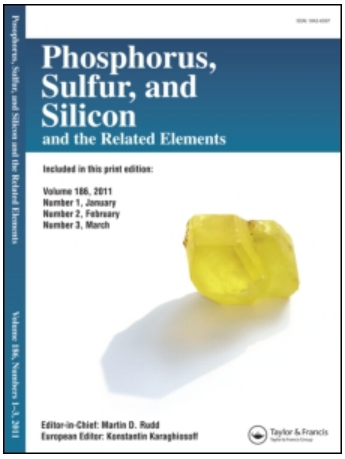

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SYNTHESIS OF HEXAPHOSPHATE BY HYDROLYSIS OF *CYCLO*-HEXAPHOSPHATE

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Sodium and ammonium hexaphosphates were prepared by hydrolyzing *cyclo*-hexaphosphate in a 10M sodium hydroxide solution at -7 ℃ for 20h. Sodium hexaphosphate was amorphous and unstable at room temperature. Ammonium hexaphosphate was crystalline and stable at room temperature.

Keywords: hexaphosphate; short-chain polyphosphate; oligophosphate

INTRODUCTION

Condensed Phosphates are well known materials. They have been used for chemical fertilizers, detergents, food additives, biomaterials, electroceramics, optoceramics, etc [1-3]. Among the many kinds of condensed phosphates, di-, tri-, tetra-, *cyclo*-tri-, *cyclo*-tetra-, *cyclo*-hexa-, *cyclo*-octa-, *cyclo*-deca-, and long-chain polyphosphates including phosphate glasses have been prepared and isolated. There are several papers on the synthesis and thermal property of *cyclo*-hexaphosphate [4-7]. This paper describes syntheses of sodium and ammonium hexaphosphates by hydrolysis of *cyclo*-hexaphosphate and their stability.

EXPERIMENTAL PROCEDURE

Chemical Analysis

The determination of phosphorus and nitrogen was achieved by the Molybdenum Blue method and the Kjeldahl technique, respectively. Sodium was determined by the atomic absorption analysis using a Shimadzu atomic absorption spectrophotometer (AA-680).

High-performance Liquid Chromatography (HPLC)

A phosphate 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 [8-9]. 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.

X-ray Diffractometry (XRD)

An XRD diagram of a powder sample was taken with nickel filtered CuK α radiation using a Rigaku RAD-1X diffractometer.

^{31}PNMR Measurement

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

Hydrolysis of *Cyclo*-hexaphosphate

Lithium *cyclo*-hexaphosphate hexahydrate was made by the method described previously [5]. The hydrolysis of short-chain polyphosphates is an acid catalyzed reaction and that of small-ring condensed phosphates is an acid and base catalyzed reaction. Accordingly, when *cyclo*-hexaphosphate is hydrolyzed in a basic solution, rapid ring-opening hydrolysis of *cyclo*-hexaphosphate to hexaphosphate occurs and the hydrolytic decomposition of the produced hexaphosphate is considered to be slow in a basic

medium. The solution with high content of hexaphosphate can be expected. Hydrolysis of lithium hexaphosphate was examined in basic solutions of alkaline metal hydroxide (LiOH, NaOH, and KOH) and ammonia water with various concentrations at 5 to -10 ℃. According to the results, it was found that the hydrolysis with a 10M sodium hydroxide solution at -7 ℃ was the most preferable condition for the ring-opening reaction of *cyclo*-hexaphosphate to hexaphosphate. The hydrolysis of lithium *cyclo*-hexaphosphate dihydrate (4.0g) was run in a 10M sodium hydroxide solution ($100cm^3$) at -7 ℃. The result was shown in Table I.

TABLE I Hydrolysis of *cyclo*-hexaphosphate in a 10M sodium hydroxide solution at -7 ℃

Reaction time (h)	Phosphates (P%)		
	Cyclo-hexa	Hexa	Others
0	100	---	---
3.5	73.5	23.2	3.3
6.5	59.0	37.2	3.8
10.0	49.5	46.9	3.6
13.5	36.2	58.0	5.8
16.0	25.1	65.9	9.0
18.0	22.2	66.7	11.1
20.0	19.4	68.6	12.0
24.0	14.3	69.0	16.7
28.0	10.7	69.7	19.6
32.0	8.1	67.4	24.5
42.0	4.6	63.4	32.0

Preparation of Sodium Hexaphosphate

According to the result in Table I, the highest content of hexaphosphate as a hydrolysis product of *cyclo*-hexaphosphate was about 70P% at the reaction time of 20 ~ 30h. Cooling with ice, the solution was slowly neutralized with 35% hydrochloric acid and

then methanol (110 ~ 120cm^3) was added in the solution. The precipitate was recrystallized with cooled water and methanol to remove sodium chloride and phosphates other than hexaphosphate. The content of hexaphosphate in the product was about 80P% and the yield was 2.5 to 3.5g. The product (10.5g) was dissolved in water (100cm^3) and the solution was passed through a column (2 × 35cm) filled with anion-exchange resin (DOWEX 1-X8). Elutes of sodium chloride solutions with concentrations of 0.15, 0.175, 0.2, and 0.225 mol/dm^3 were used continuously, and 500cm^3 of the each elute was sampled. Phosphate composition of the sampled solution was examined by HPLC. In the sampled solution containing only hexaphosphate, enough methanol to precipitate hexaphosphate was added. The precipitate was centrifuged. The total yield was about 6g.

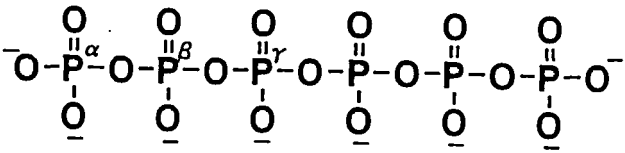
Preparation of Ammonium Hexaphosphate

The sodium hexaphosphate (3g) obtained above was dissolved in cooled water (20cm^3) and the solution was passed through a column filled with cation-exchange resin to remove sodium ions. The resulting solution was put into 29% ammonia water (65cm^3). Enough ethanol to produce precipitate was added into the solution. The precipitate was centrifuged, put into ethanol to remove excess water with cooling in a refrigerator at 5 ℃, and then filtered off. The yield was about 2.0g.

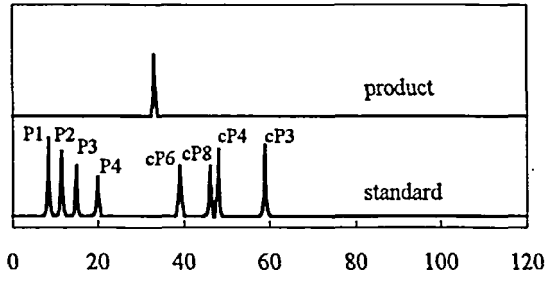
RESULTS AND DISCUSSION

Sodium Hexaphosphate

An HPLC profile of the product showed a single peak. As shown in Fig.1, the peak did not assigned to those of known condensed phosphates and the retention time of the peak was reasonably assigned to that of hexaphosphate. The Na/P molar ratio of the product was 1.36 and the calculated Na/P molar ratio of octasodium hexaphosphate is 1.33. The ^{31}P NMR spectrum of the product is shown in Fig.2. The following chemical structure is given for a hexaphosphate ion:



Hexaphosphate ion



P1: orthophosphate, P2: pyrophosphate, P3: triphosphate
P4: tetraphosphate, cP6: *cyclo*-hexaphosphate, cP8:*cyclo*-octaphosphate, cP4: *cyclo*-tetraphosphate, cP3: *cyclo*-triphosphate

FIGURE 1 HPLC profiles of the product and known oligophosphates

According to the structure, the NMR peaks in Fig.2 can reasonably be assigned as follows: doublet at around -4.6ppm, P^{α}; triplet at around -19.6ppm, P^{β}; doublet at around -20.5ppm, P^{γ}. The measured peak area ratio of P^{α}: P^{β}: P^{γ} = 1.0: 1.0: 1.0. The ratio correspond to the molar ratio of P^{α}: P^{β}: P^{γ} of hexaphosphate. All these results show that the product is octasodium hexaphosphate. The thermogravimetric measurement indicated that the product contained 2 ~ 3% of bound water. The product was amorphous according to XRD measurement. Therefore, the product is concluded to be $Na_8P_6O_{19}\cdot nH_2O$. The product was not stable at room temperature and decomposed to produce phosphates with shorter chain lengths. The decomposition of the hexaphosphate at 25°C is shown in Table II.

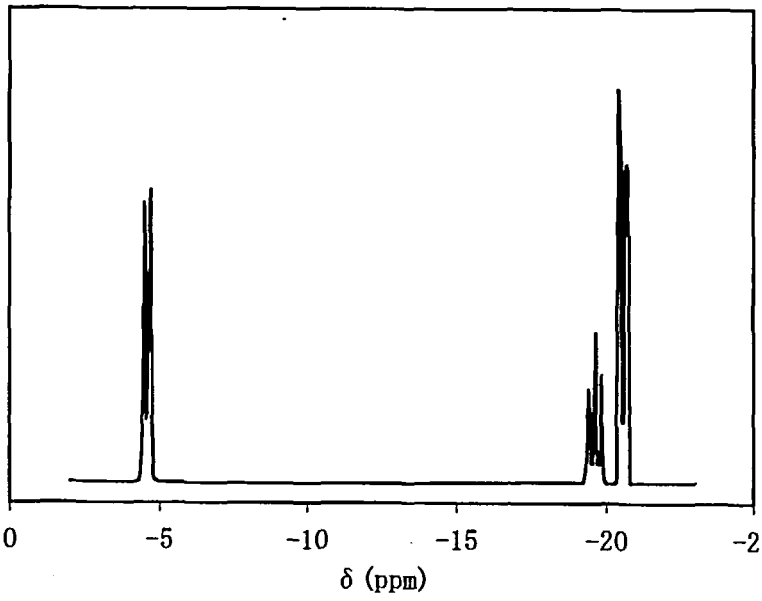


FIGURE 2 ^{31}P NMR spectrum of the product

TABLE II Decomposition of $Na_8P_6O_{19}\cdot nH_2O$ at 25 ℃

Reaction time (h)	Phosphates (P%)					
	Ortho	Pyro	Tri	Tetra	Penta	Hexa
0						100
24	5.8	0.9	0.7	3.2	23.6	65.8
192	6.0	2.0	2.2	6.8	22.0	61.0
288	6.2	3.4	3.7	7.9	21.7	57.1
456	16.1	5.4	4.9	9.4	23.3	40.9

Ammonium Hexaphosphate

The product gave the same HPLC profile and ^{31}P NMR spectrum

as those of sodium hexaphosphate. The measured contents of phosphorus and nitrogen of the product were 27.3 and 16.7%, respectively. The calculated contents of phosphorus and nitrogen of octaammonium hexaphosphate dihydrate, $[(NH_4)_8P_6O_{19}\cdot 2H_2O]$ were 27.7 and 16.7%, respectively. Accordingly, the product is concluded to be $[(NH_4)_8P_6O_{19}\cdot 2H_2O]$. The Ammonium hexaphosphate was crystalline according to XRD measurement and the data are given in Table III. The ammonium hexaphosphate was stable at room temperature.

TABLE III XRD data of $[(NH_4)_8P_6O_{19}\cdot 2H_2O]$

d(nm)	I/I$_0$	d(nm)	I/I$_0$
1.3261	15	0.4070	9
1.2582	18	0.3924	15
0.9861	21	0.3857	19
0.7190	7	0.3666	15
0.6804	13	0.3504	14
0.6267	23	0.3319	20
0.6005	30	0.3255	19
0.5878	100	0.3142	22
0.5669	79	0.3029	15
0.5590	33	0.2944	24
0.5514	59	0.2795	16
0.5175	8	0.2727	12
0.4935	20	0.2653	11
0.4624	16	0.2567	11
0.4300	9	0.2336	11
0.4176	13		

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