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Studies of Nitrogen–Phosphorus Compound. XXVII.[1] Synthesis of $N_4P_4(NH_2)_8$ and Its Hydrolysis

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The method for synthesis of $N_4P_4(NH_2)_8$ by the reaction between $(NPCl_2)_4$ and ammonia and its hydrolysis behavior were investigated. The reaction of $(NPCl_2)_4$ with liquid ammonia took place violently at first, and the resulting product contained more than several percents of an insoluble material. The extract from this product had a rather low yield, about 20—25%. However, such a drastic reaction could be avoided by the addition of a small amount of dioxane to the reaction system; then the insoluble material did not form, and the yield increased to 55—66%. The final product contained P 37—38% and N 50—51%; thus the mole ratio of N to P was exactly 3 : 1 and the composition agreed with that of $N_4P_4(NH_2)_8 \cdot H_2O$. When an aqueous solution of $N_4P_4(NH_2)_8$ was refluxed at 100 °C, the compound was initially hydrolyzed to $PO(NH_2)_3$ and $P_2O_2NH(NH_3)_4$, these being converted into $PO(ONa)(NH_2)_2$. At room temperature, the rate of hydrolysis was quite slow, but the composition of the hydrolysis products was similar to that at 100 °C. In a sodium hydroxide solution, $N_4P_4(NH_2)_8$ was converted directly into $PO(ONa)(NH_2)_2$ at an elevated temperature. The rate of the alkali hydrolysis obeyed a first-order equation, with the rate constants of 1.0×10^{-3}, 2.5×10^{-3}, 1.9×10^{-2}, and 4.2×10^{-2} at 50, 60, 80, and 90 °C, respectively. These values were about 2.7 times that of $N_3P_3(NH_2)_6$. The activation energy of the reaction was 20.8 kcal/mol. The acid hydrolysis behavior resembled that in the neutral hydrolysis, but the reaction was accelerated with acid strength. The formation of tetrametaphosphimate by the hydrolysis of $N_4P_4(NH_2)_8$, that had previously been claimed, could not be reproduced in this study.

The amidated derivatives of the lower polymers of phosphorus dichloride nitride are of interest as fireproof materials[2,3] and fertilizers.[4,5] The completely ammonated products, $N_3P_3(NH_2)_6$ and $N_4P_4(NH_2)_8$, were synthesized by the reactions between $(NPCl_2)_3$ or $(NPCl_2)_4$ and liquid ammonia.[6] The present author previously reported the synthesis of $N_3P_3(NH_2)_6$[7] and the formation of $PO(ONa)(NH_2)_2$ by the alkali hydrolysis of the trimeric variety.[8] In this work, the hydrolysis of $N_4P_4(NH_2)_8$ in neutral, alkali, and acid solutions was investigated. The experimental results partially differ from the previous explanations.[9,10] Thus an improvement in the synthesis of $N_4P_4(NH_2)_8$ and its hydrolysis behaviors will be described.

Experimental

Preparation of $N_4P_4(NH_2)_8$. $(NPCl_2)_4$ (mp 123.0—123.7 °C) used as the raw material was obtained by fractional sublimation under a vacuum from $(NPCl_2)_n$ (n=3—7), which was synthesized by the reaction between phosphorus pentachloride and ammonium chloride. $(NPCl_2)_4$ was treated with liquid ammonia in the presence of a small amount of dioxane. The resulting product was dissolved in water, and the addition of ethanol into the solution gave rise to the precipitate of $N_4P_4(NH_2)_8 \cdot H_2O$, which was separated by filtration from the mother liquor and finally vacuum-dried over over phosphorus pentoxide.

Preparation of Alkali-hydrolysis Product. A 1.00 g portion of $N_4P_4(NH_2)_8 \cdot H_2O$ was refluxed with 100 ml of 0.65 M NaOH in a stainless steel flask for 3 h. The product was precipitated by the addition of excess ethanol into the solution, purified by recrystallization using ethanol, and finally vacuum dried over phosphorus pentoxide for 24 h.

Hydrolysis. For the neutral hydrolysis, a solution of 0.05 M $N_4P_4(NH_2)_8$ (or 0.05 M $N_3P_3(NH_2)_6$) was refluxed at 100 °C. Parts of the solution were taken out at proper time intervals, and these were supplied as the samples for the analysis. Hydrolysis was also carried out at room temperature for 3 weeks. For the alkali hydrolysis, a solution containing 0.05 M $N_4P_4(NH_2)_8$ in 1 M NaOH was prepared, and divided into several test tubes. The tubes were immersed in a bath regulated to a certain temperature. They were then successively withdrawn from the bath at proper time intervals. Both $N_4P_4(NH_2)_8$ and the $PO(ONa)(NH_2)_2$ formed were determined by means of ion-exchange chromatography. The rate of alkali hydrolysis and its activation energy were calculated. For the acid hydrolysis, a solution containing 0.05 M $N_4P_4(NH_2)_8$ in 0.25 M HCl was used. The acid hydrolysis was carried out in the same way as that for the neutral hydrolysis.

Analysis. The phosphorus content was determined gravimetrically as magnesium pyrophosphate. The total nitrogen content was determined by Kjeldahl's method. The sodium content was determined by using a flame photometer. The species of phosphorus amide-compounds were analyzed by ion-exchange chromatography,[8] and distinguished by paper chromatography using an alkalisolvent.[11]

Results and Discussion

Synthesis of $N_4P_4(NH_2)_8$. The synthesizing conditions of tetrameric phosphours diamide nitride and its analytical results are summarized in Table 1.

Formation of Insoluble Material: Generally, the reaction between a low polymer of phosphorus dichloride nitride and liquid ammonia is vigorously carried out, and some partially substituted products represented by $N_nP_nCl_{2n-x}(NH_2)_x$ (n=3,4) form; these are then gradually converted into the completely substituted products. The reactions are as follows:

$$(NPCl_2)_3 + 12NH_3 \rightarrow N_3P_3(NH_2)_6 + 6NH_4Cl \quad (1)$$

$$(NPCl_2)_4 + 16\,NH_3 \rightarrow N_4P_4(NH_2)_8 + 8NH_4Cl \quad (2)$$

The composition of the reaction product in (1) agreed fairly well with the calculated values as the sum of $N_3P_3(NH_2)_6$ and 6 NH_4Cl.[7] However, in the product of Eq. 2, the nitrogen content was less than that of its calculated value, the phosphorus and chlorine contents were conversely greater, and there was a considerable amount of an insoluble material as a by-product. The relations of the content of the insoluble material to the reaction time are shown in Fig. 1.

TABLE 1. SYNTHESIS AND ANALYSIS OF TETRAMERIC PHOSPHORUS NITRIDE DIAMIDE

No.	Reaction conditions					Reaction products (g)	Reaction products			
	$(NPCl_2)_4$ (g)	NH_3 (ml)	Solvent (ml)	Temp (°C)	Time (h)		$N_4P_4(NH_2)_8$ (g)	P (%)	N (%)	Atomic ratio (P : N)
1	10.0	100	—	16—20	24	14.90	1.35	38.1	49.4	4.0 : 11.5
2	10.0	100	—	5—10	20	15.00	1.97	37.6	50.1	4.0 : 11.8
3	2.5	25	—	20—25	1	3.60	0.38	38.7	51.7	4.0 : 11.8
4	2.5	25	—	20—25	3	3.70	0.71	37.3	50.9	4.0 : 12.1
5	2.5	25	—	20—25	5	3.80	0.80	37.4	51.1	4.0 : 12.1
6	2.5	25	—	20—20	24	3.70	0.66	37.8	52.4	4.0 : 12.3
7	2.5	25	0.8	20—25	1	3.54	0.87	37.7	50.2	4.9 : 11.8
8	2.5	25	1.2	20—25	1	3.55	1.01	37.5	50.3	4.0 : 11.9
9	2.5	25	5.0	20—25	1	3.57	0.92	36.8	50.6	4.0 : 12.2
10	2.5	25	10.0	20—25	1	3.62	0.97	37.2	49.8	4.0 : 11.9
11	9.6	100	50.0	18—23	24	14.50	3.47	37.9	49.9	4.0 : 11.6
Composition of $N_4P_4(NH_2)_7.H_2O$ (Calcd values)								P : 37.99%	N : 51.54%	
Composition of $N_4P_4(NH_2)_8$ (Calcd values)								P : 40.22%	N : 54.55%	

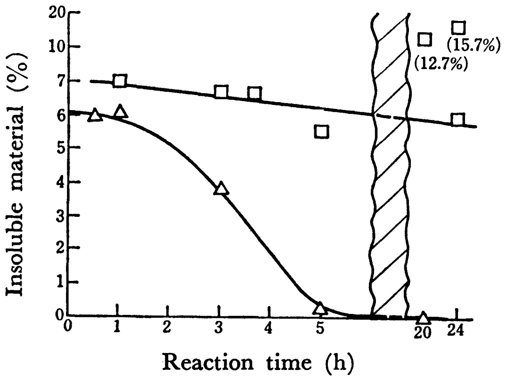

Fig. 1. Weight percent of insoluble material to reaction time.

△ : In the synthesis of N_3P_3 $(NH_2)_6$.

□ : In the synthesis of N_4P_4 $(NH_2)_8$.

In the formation of $N_3P_3(NH_2)_6$, the insoluble material disappeared in the reaction which lasted for about 5 h. Consequently, all the chloride atoms in $(NPCl_2)_3$ could be completely substituted by the amido groups. In the formation of N_4P_4 $(NH_2)_8$, the insoluble material formed did not decrease so much in the course of time. For Nos. 3—6, which use a small amount of chloride, the insoluble material content was 5—6%, while for Nos. 1 and 2, which use a great amount of chloride, it was about 15%. In these cases, no homogeneous reaction between the liquid and solid phases evidently took place. Thus the insoluble material had not disappeared even in a reaction over a long period of time such as 24 h. It was therefore not the partially substituted product designated by $N_4P_4Cl_{8-x}(NH_2)_x$, but possibly a condensed product formed by the deammonation between the amide-phosphorus compounds as the intermediates. In order for the reaction to take place smoothly, the addition of dioxane in the reaction system of $(NPCl_2)_3$ with liquid ammonia has been proposed.[7] Thus in the reaction system of $(NPCl_2)_4$ with liquid ammonia, dioxane was added which resulted in no diastic reaction and very little insoluble material being formed. When no dioxane was added, the reaction product contained more than several% of the insoluble material, and the tetrameric variety extracted from the product showed a lower yield. The yields were remarkably increased by the addition of dioxane as shown in Table 1. The yields of the tetrameric variety were also calculated as 23 (non-addition), 53, 61, 55, and 59% in Nos. 3, 7, 9, and 10, respectively. The effect of dioxane as a medium in this reaction was evident.

Composition of The Product: The tetrameric phosphorus diamide nitride, which separates ammonium chloride as the by product from the reaction product by using liquid ammonia, is an anhydrous product. However, the composition of the material crystallized from an aqueous solution of the reaction product is not yet known. For the products obtained in this work, P content was 37—38%, N content was 50—51%, and the mole ratio of P to N was exactly 1 : 3. From these results, the expected composition was given by the formula N_4P_4 $(NH_2)_8 \cdot H_2O$. The X-ray diffraction values of tetrameric phosphorus diamide nitride have not yet been registered on the ASTM X-ray data cards. An X-ray diffraction data of $N_4P_4(NH_2)_8 \cdot H_2O$ is shown in Table 2.

Hydrolysis of N_4P_4 $(NH_2)_8$. *Neutral Hydrolysis*: After refluxing of an aqueous solution of N_4P_4 $(NH_2)_8$ at 100 °C, the hydrolysis products were determined by means of ion-exchange chromatography. The results are given in Fig. 2.

Chromatogram I shows the elution for a mixture of various standard materials, while II, III, IV, V, and VI show elutions for some hydrolysis products over the course of time. The hydrolysis of N_4P_4 $(NH_2)_8$ (A) was recognized by refluxing for 30 min. A considerable amount of $P_2O_2NH(NH_2)_4$ (C) and $PO(OH)(NH_2)_2$ (D) were formed after 60 min. Form the expected hydrolysis mode shown in Fig. 7, it can be considered that $PO(NH_2)_3$ and $P_2O_2NH(NH_2)_4$ are simultaneously formed. Both $N_4P_4(NH_2)_8$ and $PO(NH_2)_3$ are typical non-electrolytes. They were therefore eluted

Table 2. X-ray diffraction data for $N_4P_4(NH_2)_8 \cdot H_2O$, its alkali hydrolysis product and $PO(ONa) \cdot (NH_2)_2$

$N_4P_4(NH_2)_8 \cdot H_2O$ α, Å I	Alkali-hydrolysis product α, Å I	$PO(ONa) \cdot (NH_2)_2$ α, Å I
8.40 M		
7.69 W		
7.19 W		
6.68 W		
6.65 W		
6.06 S	5.21 S	5.21 S
5.06 S	5.01 W	5.01 W
	4.67 M	4.67 W
		4.57 W
	4.48 M	4.48 W
	3.90 S	3.90 M
3.81 W		
	3.75 W	3.75 S
3.67 S		
3.59 M		
3.50 W		3.53 M
3.45 W		
3.34 S		
3.26 W		
	3.13 M	3.13 M
	3.00 M	3.00 S
2.92 W	2.91 W	
2.65 W	2.67 S	2.67 M
	2.60 M	2.59 M
	2.50 W	2.50 W

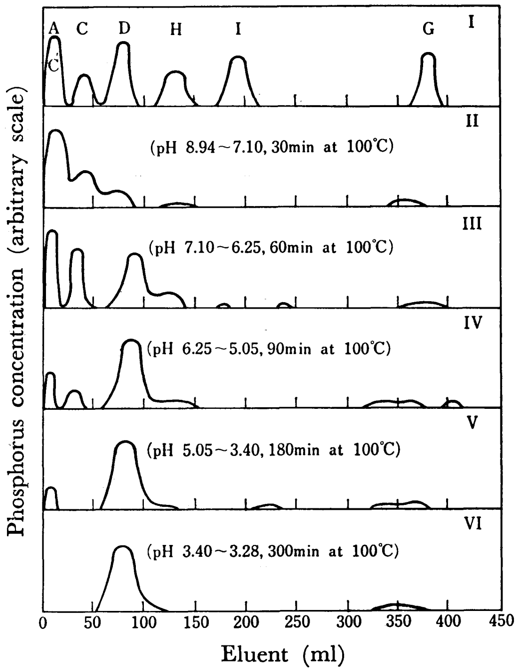

Fig. 2. Gradient elution analysis of various phosphorus compounds and hydrolysis products of $N_4P_4(NH_2)_8$. Eluent: 1 l H_2O in mixing bottle, 400 ml 0.8 mol/l KCl in stock bottle.
I: Mixture of amide phosphorus compounds and phosphates [A: $N_4P_4(NH_2)_8$, C: $P_2O_2(NH)(NH_2)_4$, C': $PO(NH_2)_3$, D: $PO(ONa)(NH_2)_2$, H: $PO(ONa)_2NH_2$, I: Na_2HPO_4, G: $Na_4P_2O_7$].
II—VI: Hydrolysis products of $N_4P_4(NH_2)_8$.

at the same position on the ion-exchange chromatogram, as is shown in Fig. 3. However, in paper chromatography, R_f 0.27 $N_4P_4(NH_2)_8$ can be clearly distinguished from R_f 0.67 $PO(NH_2)_3$. In fact, it was seen that both components exist in the solution refluxed for 60 min. The pH of the solution was gradually lowered in the course of the refluxing time. $N_4P_4(NH_2)_8$, $PO(NH_2)_3$, and $P_2O_2NH(NH_2)_4$ then decreased, and $PO(OH)(NH_2)_2$ increased as the main hydrolysis product. A part of the formed diamidophosphate gradually decomposed to monoamidophosphate (H) and some orthophosphate (I). The hydrolysis behavior of $N_3P_3(NH_2)_6$ at 100 °C had also been recognized as analogous to that of $N_4P_4(NH_2)_8$.

Hydrolysis of $N_4P_4(NH_2)_8$ and $(NPCl_2)_8$ at Room Temperature: The elution chromatograms of a mixture of standard materials and hydrolysis products of $N_4P_4(NH_2)_8$ and $(NPCl_2)_4$ are shown in Fig. 3.

In an aqueous solution, $N_4P_4(NH_2)_8$ was stable for about 3 days at room temperature, after which it graudually hydrolyzed. Chromatogram II shows an elution curve for the hydrolysis product of N_4P_4 $(NH_2)_8$ after 20 days. The rate of hydrolysis was remarkably slow, the composition of the hydrolysis products being similar to that at 100 °C. Chromatogram III shows the elution for the hydrolysis product of $(NPCl_2)_4$ (0.5 g) in an ether (7.5 ml)–aqueous ammonia (3 M, 8 ml) solution. $(NPCl_2)_4$ was partly converted into N_4P_4 $(NH_2)_8$ in spite of the presence of water. The other products were some phosphoryl triamide, tetramidoimdodiphosphate, orthophosphate, and imidodiphosphate. $(NPCl_2)_4$ (0.5 g) was also hydrolyzed in an ether (15 ml)–water (5 ml) solution. The product was neutralized by employing aqueous ammonia, and analyzed by means of ion-exchange chromatography. The result is shown as chromatogram IV. In this hydrolysis, $(NPCl_2)_4$ was converted simultaneously into a cyclic tetrametaphosphimate which gradually hydrolyzed into imidotetraphosphate, imidotriphosphate, imidodiphosphate, and some amidophosphate.

Moureu and Rocquet$^{9)}$ observed by microscopic examination that the hydrolysis product of $N_4P_4(NH_2)_8$ closely resembles $P_4N_4O_4H_4(ONH_4)_4 \cdot 4H_2O$ which$^{12)}$ was obtained by the hydrolysis of $(NPCl_2)_4$. It was concluded that the hydrolysis product of N_4P_4 $(NH_2)_8$ is the same compound as $P_4N_4O_6H_6$ $(ONH_4)_2$. However, the components were not examined by other analytical techniques. Their result was referred to in a science text.$^{13)}$ To confirm the validity of their result, the present author has investigated the hydrolysis behavior of $(NPCl_2)_4$ and $N_4P_4(NH_2)_8$. The cyclic tetrametaphosphimate was obviously formed by the hydrolysis of $(NPCl_2)_4$, but the formation of tetrametaphosphimate by the hydrolysis of $N_4P_4(NH_2)_8$ could not be recognized.

Alkali Hydrolysis: The results of alkali and ammoniacal hydrolysis are shown in Fig. 4.

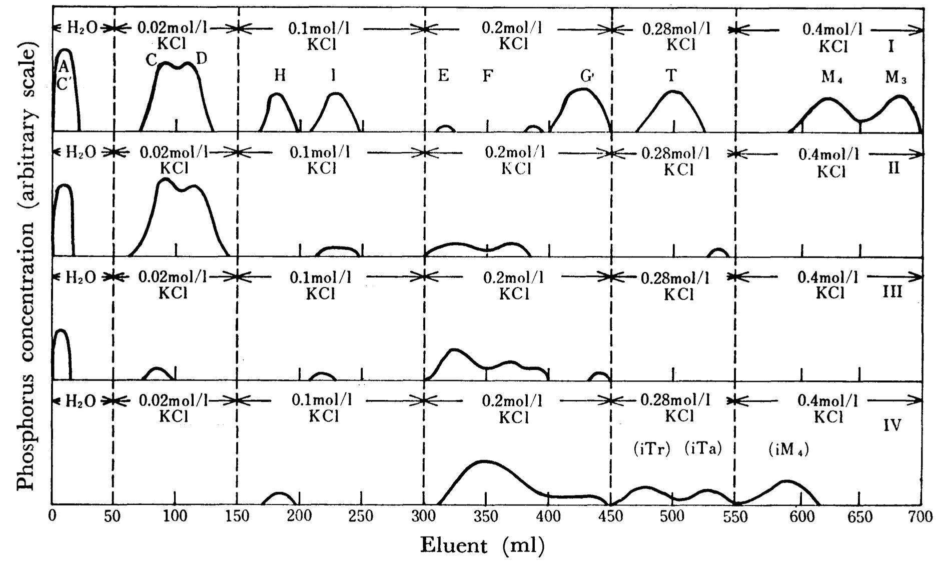

Fig. 3. Chromatographic analysis of hydrolysis products of $N_4P_4(NH_2)_8$ and $(NPCl_2)_4$ at room temperature.
I: Mixture of standard materials [A: $N_4P_4(NH_2)_8$, C: P_2O_2 $(NH)(NH_2)_4$, C′: $PO(NH_2)_3$, D: $PO(ONa)(NH_2)_2$, G: $Na_4P_2O_7$, H: $PO(ONa)_2NH_2$, I: Na_2HPO_4, T: $Na_5P_3O_{10}$, M_3: $(NaPO_3)_3$, M_4: $(NaPO_3)_4$]
II: Hydrolysis product of $N_4P_4(NH_2)_8$ for 20 day.
III: Hydrolysis product of $(NPCl_2)_4$ in ether-aqueous ammonia solution for 1 h.
IV: Hydrolysis product of $(NPCl_2)_4$ in ether-water solution for 2 h.
Estimated compounds: [E: $P_2O_2(NH)(NH_2)_2$, F: $P_2O_2(NH)(OH)_4$, iTr: $P_3O_3(NH)_2(OH)_5$, iTa: $P_4O_4(NH)_3(OH)_6$, iM_4: $P_4N_4O_4H_4(OH)_4$].

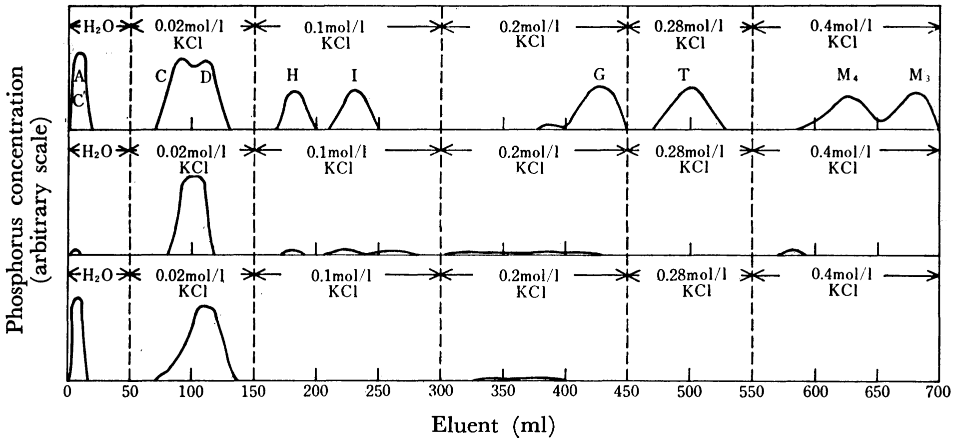

Fig. 4. Chromatographic analysis of various phosphorus compounds and hydrolysis products of N_4P_4 $(NH_2)_8$ in alkali solution.
I: Mixture of standard materials [A: N_4P_4 $(NH_2)_8$, C: $P_2O_2(NH)(NH_2)_4$, C′: $PO(NH_2)_3$, D: $PO(ONa)(NH_2)_2$, G: $Na_4P_2O_7$, H: $PO(ONa)_2NH_2$, I: Na_2HPO_4, T: $Na_5P_3O_{10}$, M_3: $(NaPO_3)_3$, M_4: $(NaPO_3)_4$].
II: Hydrolysis product of $N_4P_4(NH_2)_8$ in 0.65 M NaOH for 3 h at 100 °C.
III: Hydrolysis product of $N_4P_4(NH_2)_8$ in 3 M NH_4OH for 3 h at 100 °C.

Chromatogram I shows the elution for a mixture of the standard materials. Chromatogram II, shows that N_4P_4 $(NH_2)_8$ was converted directly into diamidophosphate. On the paper chromatogram for a certain sample of the alkali hydrolysis, only the spots of R_f 0.27 N_4P_4 $(NH_2)_8$ and R_f 0.52 $PO(ONa)(NH_2)_2$ appeared. Thus the alkali hydrolysis behavior of N_4P_4 $(NH_2)_8$ is much the same as that of N_3P_3 $(NH_2)_6$[8]. Chromatogram III shows the elution for an ammoniacal hydrolysis product. The rate of ammoniacal hydrolysis was slower than that of alkali hydrolysis even using the highly concentrated aqueous ammonia; even then N_4P_4 $(NH_2)_8$ could not be completely converted into diamidophosphate.

Composition of the Alkali Hydrolysis Product: The formation of the alkali hydrolysis products and diamidophosphate and their analyses are summarized in Table 3.

The phosphorus and nitrogen contents of the hydrolysis products were less than that of $PO(ONa)$ $(NH_2)_2$ obtained by Stokes' method,[14] but the mole ratio of N to P was close to 2 : 1, while the sodium content was greater than the expected value. The previous report[8] gave details of this reasoning. Its

Table 3. Formation and analysis of diamidophosphates

No.	Reaction conditions						Reaction products				
	Method	Sample (g)	NaOH (g)	Time (min)	Recrystallization	Dry agent	Yield (g)	P (%)	N (%)	Na (%)	P : N : Na (Atomic ratio)
1	Hydrolysis of $N_3P_3(NH_2)_6$ with NaOH solution	2.00	3.2	120	3	Phosphorus pentoxide	2.27	16.4	14.2	23.4	1 : 1.92 : 1.92
2	Hydrolysis of $N_4P_4(NH_2)_8$ with NaOH solution	1.00	2.5	150	3	Phosphorus pentoxide	1.30	15.7	13.6	24.9	1 : 1.92 : 2.14
3	Saponification of $PO(OC_6H_5)(NH_2)_2$ with NaOH solution (Stokes' method)	3.40	0.85	5	4	Phosphorus pentoxide	1.02	25.6	23.3	19.6	1 : 2.01 : 1.03

outline is explained as follows. When an oily diamidophosphate is deposited from its aqueous solution by the addition of ethanol, the salt has a character including an excess of sodium hydroxide. However, the X-ray diffraction of the alkali hydrolysis product of N_4P_4 $(NH_2)_8$ roughly agreed with that of $PO(ONa)(NH_2)_2$ as shown in Table 2, and these values also agreed with those of ASTM X-ray powder data cards. Thus the alkali hydrolysis product is obviously identical with diamidophphsate.

Rate Constants and Activation Energy of the Reaction: Both $N_4P_4(NH_2)_8$ and $PO(ONa)(NH_2)_2$ contained in an aqueous solution of the alkali hydrolysis were studied by means of ion-exchange chromatography. The percentages of $N_4P_4(NH_2)_8$ which remained in the hydrolysis are shown in Fig. 5.

The rate of the hydrolysis increased with the increase of the reaction temperature, obeying a first-order equation, with the rate constants (k) 1.0×10^{-3}, 2.5×10^{-3}, 1.9×10^{-2}, and 4.2×10^{-2} at 50, 60, 80, and 90 °C, respectively. These values are about 2.7 times the value of the alkali hydrolysis of $N_3P_3(NH_2)_6$. The activation energy, obtained from the relation of log k with the reciprocal of the reaction temperature, was 20.8 kcal/mol. This value agrees nearly with 20 kcal/mol for $N_3P_2(NH_2)_6$.[8)]

Acid Hydrolysis: The results of the acid hydrolysis are shown in Fig. 6.

The acid hydrolysis behavior resembles that of neutral hydrolysis. However, when the reaction was accelerated with an acid strength such as pH 1.0, the existence of $PO(NH_2)_3$ and $P_2O_2NH(NH_2)_4$ which are unstable in an acid solution could not be recognized. In this case, $N_4P_4(NH_2)_8$ was hydrolyzed up to the formation of orthophosphates and diphosphates.

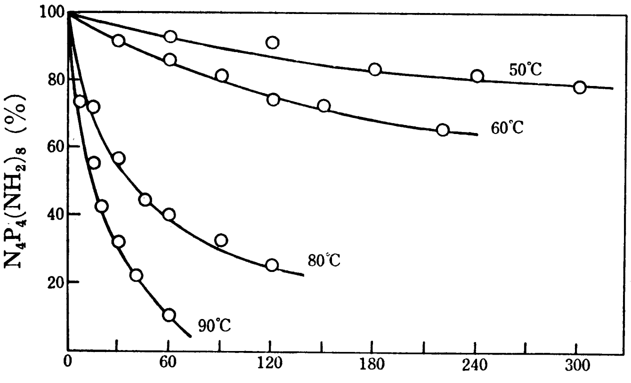

Fig. 5. Hydrolysis of tetrameric phosphorus diamide nitride in 1 M sodium hydroxide solution.

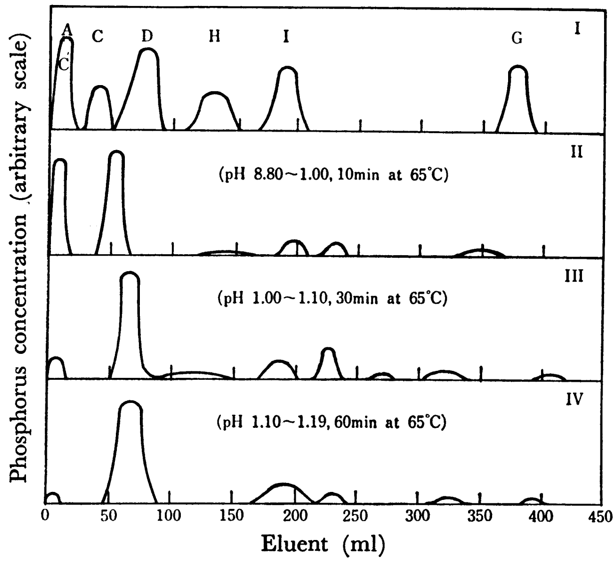

Fig. 6. Gradient elution analysis of various phosphorus compounds and hydrolysis products of $N_4P_4(NH_2)_8$ in acid solution.

Eluent: 1 l H_2O in mixing bottle, 400 ml 0.8 mol/l KCl in stock bottle.

I: Mixture of amide phosphorus compounds and phosphates [A: $N_4P_4(NH_2)_8$, C: $P_2O_2(NH)(NH_2)_4$, C': $PO(NH_2)_3$, D: $PO(ONa)(NH_2)_2$, H: $PO(ONa)_2NH_2$, I: Na_2HPO_4, G: $Na_4P_2O_7$].

II—IV: Hydroysis products of $N_4P_4(NH_2)_8$.

Process of Hydrolysis: The process of the neutral or acid hydrolysis is shown in Fig. 7.

A proton from water coordinates to an N atom on the ring of $N_4P_4(NH_2)_8$, one in a double bond between the N and P atoms is cut off, and then the P atom has a positive charge. This coordinates to an OH group, and then the ring is opened. An intermediate (B), which has an asymmetrical structure and is unstable, is formed. It immediately decomposes into unknown compounds (B' and B''), tetramidoimidodiphosphate (C), and phosphoryl triamide (C'). The arrows shown in Fig. 7 denote the course of the hydrolysis. The hy-

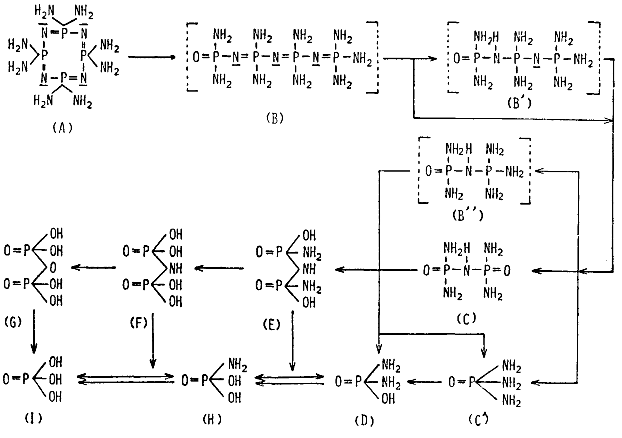

Fig. 7. Hydrolysis of $N_4P_4(NH_2)_8$ in neutral or acid solution.

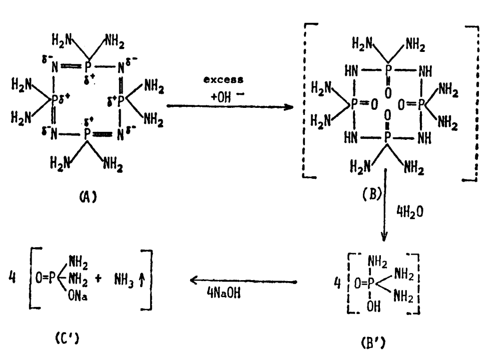

Fig. 8. Hydrolysis of $N_4P_4(NH_2)_8$ in alkali solution.

drolysis of $N_4P_4(NH_2)_8$ roughly progresses up to the formation of diamidophosphate in the neutral solution.

The alkali hydrolysis of $N_4P_4(NH_2)_8$ can be expressed as follows:

$$N_4P_4(NH_2) + 4H_2O + 4NaOH \rightarrow 4PO(ONa)(NH_2) + 4NH_3 \qquad (3)$$

The process of the reaction is shown in Fig. 8.

In the P–N ring of $N_4P_4(NH_2)_8$, the electronegativity of phosphorus (2.1) is less than that of nitrogen (3.0). Thus there is the possibility of a polarization such as $N^{\delta-}$–$P^{\delta+}$. In an alkali aqueous solution, the ionic strength of OH^- is large, and this OH group coordinates to the $P^{\delta+}$ atom. Consequently, the double bond between the P and N atoms is cut off and a single bond forms simultaneuosly, since the N atom has an electron. At the same time, the P atom is combined by a co-coordinate bond to the O atom in the previously coordinated OH group, and the H in the OH group is separated as an ion; it reacts with the N atom in the P–N ring and then an imido group is formed. This state can be represented as an unknown compound (B). Further, (B) is immediately hydrolyzed into an unknown compound (B′). (B′) separates ammonia by the reaction with sodium hydroxide, and is converted directly into diamido phosphate, which is of a stable structure of the sp^3 hybridization.

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