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The Synthesis and Thermal Behavior of Hydrated Sodium Tetra-μ-imido-*cyclo*-tetraphosphate

Makoto SAKURAI and Makoto WATANABE*
Department of Industrial Chemistry, College of Engineering, Chubu University, Matsumoto-cho, Kasugai, Aichi 487

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Hydrated tetrasodium tetra-μ-imido-*cyclo*-tetraphosphate, $(NaPO_2NH)_4 \cdot 2.5H_2O$, has been prepared by hydrolyzing 2,2,4,4,6,6,8,8-octachloro-$2\lambda^5,4\lambda^5,6\lambda^5,8\lambda^5$-cyclotetraphosphaza-1,3,5,7-tetraene in an aqueous sodium acetate solution. The tetra-μ-imino-*cyclo*-tetraphosphate reorganized to produce trisodium tri-μ-imido-*cyclo*-triphosphate and then changed to make chain and ring condensed phosphates containing imino groups upon heating above 180 °C in air according to the following reactions:

$$(NaPO_2NH)_4 \rightarrow 4/3(NaPO_2NH)_3,$$
$$(NaPO_2NH)_3 + H_2O \rightarrow Na_3P_3O_7(NH)_2,$$
$$(NaPO_2NH)_3 + 2H_2O \rightarrow Na_3P_3O_8NH,$$
$$n(NaPO_2NH)_4 + mH_2O \rightarrow Na_{4n}P_{4n}O_{8n+m}(NH)_{4n-m} + mNH_3,$$

and

$$n(NaPO_2NH)_3 + mH_2O \rightarrow Na_{3n}P_{3n}O_{6n+m}(NH)_{3n-m} + mNH_3.$$

All kinds of the imidopolyphosphates were finally converted to sodium *cyclo*-triphosphate above 550 °C by the substitution of imino groups for bridging oxygens and reorganization of the thermal products.

There have been hundreds of P–N compounds. Among them, ammonium polyphosphates are used as flame-proof materials, and phosphazenes are expected to be used as inorganic gums. Many papers concerning P–N compounds have been published. Imidopolyphosphates are very interesting compounds, since they can be used as flame retardants, precursors of phosphate glass containing nitrogen, biochemical materials, chemical fertilizers, etc. Inspite of their use, there have only been a few papers concerning these compounds. The present authors have produced papers concerning the synthesis, thermal behavior, complexation, and hydrolitic property of several imidooligophosphates.[1—9] This paper describes the synthesis and thermal behavior of tetra-μ-imodo-*cyclo*-tetraphosphate.

Experimental

Preparation of Tetra-μ-imido-*cyclo*-tetraphosphate. 2,2,4,4,6,6,8,8-octachloro-$2\lambda^5,4\lambda^5,6\lambda^5,8\lambda^5$-1,3,5,7-tetraene was made by reacting phosphorus pentachloride with ammonium chloride in 1,2-tetrachloroethane and distilling the product under reduced pressure.[10] The phosphazene (15 g) was dissolved in dioxane (200 cm^3). Sodium acetate (120 g) was dissolved in water (40 cm^3). The solutions were warmed at 45—50 °C and then mixed. After the resulting mixture was reacted with stirring for 3 h at 45—50 °C, a white precipitate was produced, which was quickly filtered off and washed with 70 and 90 v% aqueous ethanol solutions. The product (1 g) was dissolved in water (40 cm^3). After sodium chloride (2 g) was added into the solution, it was stirred for 15—20 min, producing a white precipitate. The product was first washed with 70 and 90 v% aqueous ethanol solutions and then acetone.

Chemical Analysis. The phosphorus, nitrogen, and sodium in a sample were determined, respectively, by Molybdenum Blue colorimetric analysis, the Kjeldahl technique, and an atomic absorption spectrophotometric measurement. The solubility was measured by putting 0.2 g of sample in 10 cm^3 of water and stirring the mixture for 1 h at room temperature (15—20 °C).

High-Performance Liquid Chromatography (HPLC). An HPLC analysis with the gradient technique, which was developed by Baba et al.,[11—13] was employed in order to separate and determined the phosphate species in a sample by using a Shimadzu and/or JASXO HPLC apparatus. A separation column (4 mm×240 mm) with TSK-gel (SAX-F0011) and KCl eluent (0.45 mol dm^{-3}) were used for the analysis. About 10 mg of a sample was dissolved in 10 cm^3 of water; then 200 mm^3 of the sample solution was injected into the column.

X-Ray Diffractometry (XRD). An X-ray diffraction diagram of a sample was taken with nickel-filtered Cu $K\alpha$ radiation by using a Rigaku X-ray diffractometer (RAD-1B).

^{31}P Nuclear Magnetic Resonance (NMR) Measurement. A sample was dissolved in water and a ^{31}P NMR spectrum of the solution was taken using a JNM-GX 270 spectrograph. The chemical shifts are reported relative to external 85% orthophosphoric acid, with the positive shifts being downfield.

Thermogravimetry (TG) and Differential Thermal Analysis (DTA). TG and DTA measurements were used to study the thermal behavior of the product using a Rigaku and/or Seiko Instruments TG-TDA apparatus in air at a heating rate of 10 °C min^{-1}.

Results and Discussion

Chemical Composition. As Fig. 1 shows, the product gave only one HPLC peak; the result means that the product was a pure compound. Further, it is reasonable that the retention time of the product was caused by tetra-μ-imido-*cyclo*-tetraphosphate. The product showed one singlet ^{31}P NMR peak at −3.5 ppm, indicating that it comprised the same kind of $P(O_2)$ NH group. Found: Na, 20.1; P, 26.5; N, 11.9%. Calcd for $(NaPO_2NH)_4\cdot 2.5H_2O$: Na, 20.5; P, 27.6; N, 12.5%. Accordingly, it can be concluded that the product was hydrated tetrasodium tetra-μ-imido-*cyclo*-tetraphosphate. The XRD data of the product are given in Table 1. The product was stable in air at room temperature.

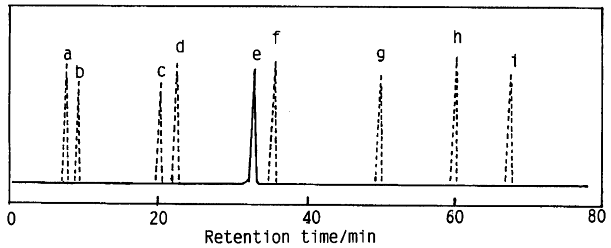

Fig. 1. HPLC profiles of the product (—) and known phosphates (- - -). a: Phosphoramidate, b: orthophosphate, c: tri-μ-imido-*cyclo*-triphosphate, d: diphosphate, e: product, f: μ-oxo-di-μ-imido-*cyclo*-triphosphate, g: di-μ-oxo-μ-imido-*cyclo*-triphosphate, h: *cyclo*-tetraphosphate, i: *cyclo*-triphosphate.

Table 1. XRD Data of $(NaPO_2NH)_4\cdot 2.5H_2O$

d value/Å	I/I_0	d value/Å	I/I_0	d value/Å	I/I_0
8.386	37	3.396	30	2.311	18
8.125	25	3.343	33	2.282	17
7.086	37	3.114	32	2.179	32
6.732	41	3.047	16	2.157	35
5.878	15	2.922	10	2.121	16
5.824	11	2.871	91	2.114	25
4.797	100	2.810	58	2.108	12
4.647	18	2.789	43	2.050	14
4.383	12	2.731	57	1.906	9
4.215	26	2.705	92	1.783	18
4.141	27	2.655	12	1.754	18
4.092	53	2.624	49	1.745	9
4.033	37	2.609	21	1.685	21
3.983	45	2.594	16	1.680	12
3.776	93	2.560	10	1.633	15
3.729	19	2.484	12	1.626	11
3.704	35	2.398	10	1.603	10
3.624	25	2.374	25		
3.561	11	2.352	12		
3.482	37	2.331	33		

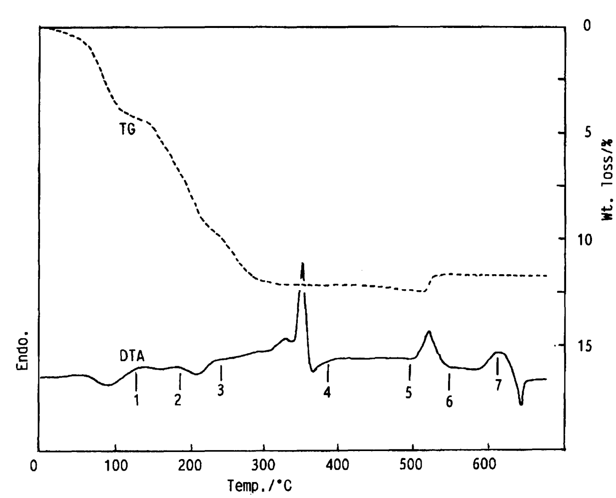

Fig. 2. TG and DTA curves of $(NaPO_2NH)_4\cdot 2.5H_2O$.

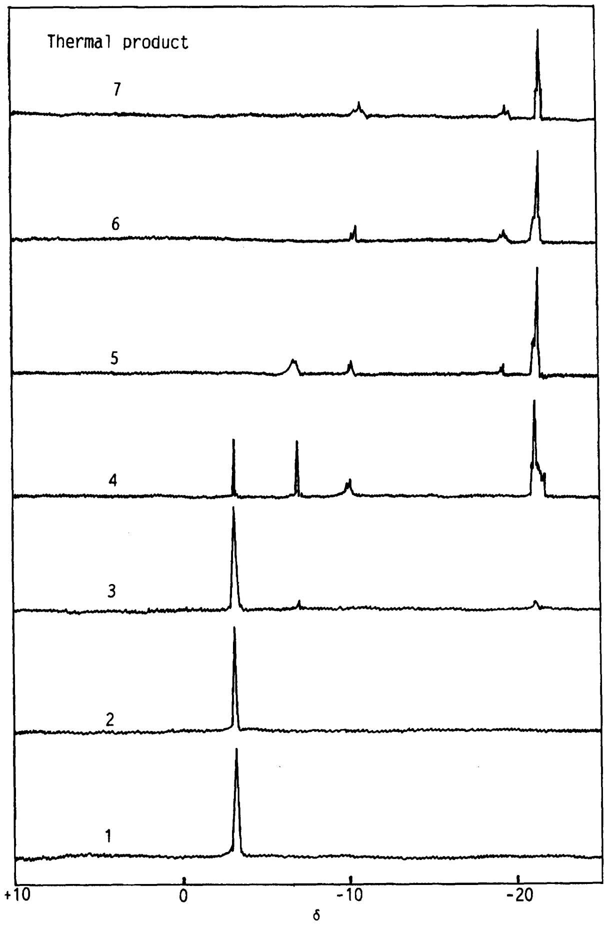

Fig. 3. ^{31}P NMR spectra of the thermal products.

Thermal Behavior. TG and DTA curves of the product are given in Fig. 2. The thermal products (as numbered in the figure) were removed from a furnace and subjected to further analysis in order to study any thermal changes. The ^{31}P NMR spectra and composition of the thermal products are given in Fig. 3 and Table 2 respectively. Thermal product 1 comprised only tetra-μ-imido-*cyclo*-tetraphosphate. This means that the endothermic process accompanied by a weight loss was due to the removal of a part of the water of crystallization according to the following reaction:

$$(NaPO_2NH)_4\cdot 2.5H_2O \rightarrow (NaPO_2NH)_4\cdot(2.5-x)H_2O + xH_2O \quad (0 < x \leq 2.5). \qquad (1)$$

Since thermal product 1 showed the XRD pattern of $(NaPO_2NH)_4\cdot 2.5H_2O$, the produced sodium tetra-μ-

Table 2. Weight Loss and Composition of the Thermal Products

Thermal product	Temp °C	Wt loss %	Total N %	Phophates/P% Tetraimido-cyclotetra	Triimido-cyclotri	Diimido-cyclotri	Monoimido-cyclotri	cyclotri
1	135	3.7	12.4	100	—	—	—	—
2	185	9.5	12.4	97.6	2.4	—	—	—
3	240	11.2	11.0	79.7	8.2	6.5	4.5	1.1
4*	380	12.1	5.5	6.5	42.9	20.0	9.9	20.7
5*	490	12.6	4.4	—	10.9	35.5	3.1	50.5
6	550	11.7	1.8	—	—	—	8.8	91.2
7	600	11.6	0.5	—	—	—	3.6	96.4

The thermal product contained water-insoluble substance (solubility: 4, 38; 5*, 18%).

imido-*cyclo*-tetraphosphate was X-ray diffractometrically amorphous. The weight loss of thermal product 2 was near to the value for the process of $x=2.5$ in Eq. 1, and the second endothermic process may have been caused by the reaction. Thermal product 2 showed XRD peaks other than the weak peaks due to $(NaPO_2NH)_4 \cdot 2.5H_2O$. The XRD peaks can be concluded to be due to the anhydrous tetrasodium tetra-μ-imido-*cyclo*-tetraphosphate, $(NaPO_2NH)_4$. Thermal product 2 contained a small amount of tri-μ-imido-*cyclo*-triphosphate other than tetra-μ-imido-*cyclo*-tetraphosphate. The following conversion can be written for the process:

$$(NaPO_2NH)_4 \rightarrow 4/3(NaPO_2NH)_3. \qquad (2)$$

The XRD pattern of thermal product 3 was considered to be responsible for the anhydrous tetra-μ-imido-*cyclo*-tetraphosphate, because nearly 80 P% of the phosphate species in the thermal product was tetra-μ-imido-*cyclo*-tetraphosphate. The XRD data of the anhydrous tetra-μ-imido-*cyclo*-tetraphosphate is given in Table 3. Thermal product 3 contained small amounts of tri-μ-imido-*cyclo*-tri-, μ-oxo-di-μ-imido-*cyclo*-tri-, di-μ-oxo-μ-imido-*cyclo*-tri-, and *cyclo*-triphosphates. The following thermal reactions are expressed for the process:

(successive reactions)

$$(NaPO_2NH)_3 + H_2O \rightarrow Na_3P_3O_7(NH)_2 + NH_3 \qquad (3)$$

$$Na_3P_3O_7(NH)_2 + H_2O \rightarrow Na_3P_3O_8NH + NH_3 \qquad (4)$$

$$Na_3P_3O_8NH + H_2O \rightarrow (NaPO_3)_3 + NH_3 \qquad (5)$$

(slmultaneous reactions)

$$(NaPO_2NH)_3 + H_2O \rightarrow Na_3P_3O_7(NH)_2 + NH_3 \qquad (3)$$

$$(NaPO_2NH)_3 + 2H_2O \rightarrow Na_3P_3O_8NH + 2NH_3 \qquad (6)$$

$$(NaPO_2NH)_3 + 3H_2O \rightarrow (NaPO_3)_3 + 3NH_3 \qquad (7)$$

It was difficult to determine which reactions were reasonable for the process. The ^{31}P NMR peaks between −7.0 and −19.5 ppm are due to μ-oxo-di-μ-imido- and di-μ-oxo-μ-imido-*cyclo*-triphosphates and that at −21 ppm was caused by the middle PO_4 group of *cyclo*-triphosphate. The NMR spectra agree well with the HPLC data. A large part of thermal product 4 was a water-insoluble product, which may have been highly polymerized condensed phosphate containing imino groups produced by the following reactions:

Table 3. XRD Data of $(NaPO_2NH)_4$

d value/Å	I/I_0	d value/Å	I/I_0	d value/Å	I/I_0
9.321	30	3.482	17	2.370	13
7.506	10	3.453	14	2.265	12
7.272	9	3.390	13	2.257	10
7.155	22	3.341	84	2.219	10
6.921	17	3.211	11	2.212	10
6.375	21	3.153	15	2.163	16
4.662	66	3.122	21	2.153	18
4.299	17	2.871	15	2.147	17
4.259	40	2.857	25	2.137	19
4.018	37	2.848	31	2.099	10
3.983	100	2.836	22	2.045	9
3.893	12	2.799	26	2.038	12
3.776	14	2.784	38	1.966	12
3.735	27	2.752	25	1.876	9
3.698	31	2.701	57	1.734	9
3.621	16	2.668	43	1.681	10
3.592	24	2.643	26	1.676	10
3.567	33	2.634	20	1.671	13
3.547	34	2.619	10		
3.528	30	2.528	42		

$$n(NaPO_2NH)_4 + mH_2O$$
$$\rightarrow Na_{4n}P_{4n}O_{8n+m}(NH)_{4n-m} + mNH_3 \qquad (8)$$
$$(4n > m)$$

$$n(NaPO_2NH)_3 + mH_2O$$
$$\rightarrow Na_{3n}P_{3n}O_{6n+m}(NH)_{3n-m} + mNH_3 \qquad (9)$$
$$(3n > m)$$

The large exothermic peak at about 350 °C can be considered to have been caused by the formation and crystallization of the water-insoluble imidopolyphosphate, since a new XRD pattern appeared after the exothermic process. The XRD data of the imdopolyphosphate

Table 4. XRD Data of the Water-Insoluble Imidopolyphosphate

d value/Å	I/I_0	d value/Å	I/I_0	d value/Å	I/I_0
6.815	9	3.206	30	2.457	10
6.671	13	3.188	29	2.294	10
5.381	14	3.161	28	2.052	8
5.317	14	3.142	20	2.044	11
5.110	100	3.070	15	2.038	12
4.792	16	3.039	20	2.030	18
4.756	15	3.025	12	2.023	19
4.618	14	2.980	12	1.797	10
4.480	16	2.953	26	1.792	10
4.226	24	2.926	20	1.765	9
3.853	21	2.915	19	1.661	10
3.578	12	2.857	55		
3.533	11	2.837	64		
3.458	38	2.823	58		
3.439	29	2.759	23		
3.408	31	2.612	11		
3.336	37	2.596	15		
3.321	34	2.574	18		
3.299	21	2.567	15		
3.222	25	2.466	11		

are listed in Table 4. The exothermic process at about 520 °C could have been caused by the substitution of imino groups of the imidophosphates for bridging oxygens, and the reorganization and crystallization of the produced condensed phosphates to sodium *cyclo*-triphosphate, because the thermal process accompanied a weight gain and thermal product 6 showed an XRD pattern of sodium *cyclo*-triphosphate. This process can be exhibited by the following equations:

$$\mathrm{Na_3P_3O_8NH + H_2O \rightarrow (NaPO_3)_3 + NH_3} \qquad (5)$$

$$\mathrm{Na_3P_3O_7(NH)_2 + 2H_2O \rightarrow (NaPO_3)_3 + 2NH_3} \qquad (4)\ \text{and}\ (5)$$

$$\mathrm{(NaPO_2NH)_3 + 3H_2O \rightarrow (NaPO_3)_3 + 3NH_3} \qquad (7)$$

$$\mathrm{Na}_{4n}\mathrm{P}_{4n}\mathrm{O}_{8n+m}(\mathrm{NH})_{4n-m} + (4n-m)\mathrm{H_2O} \rightarrow n(\mathrm{NaPO_3})_3 + (4n-m)\mathrm{NH_3} \qquad (10)$$

$$\mathrm{Na}_{3n}\mathrm{P}_{3n}\mathrm{O}_{6n+m}(\mathrm{NH})_{3n-m} + (3n-m)\mathrm{H_2O} \rightarrow n(\mathrm{NaPO_3})_3 + (3n-m)\mathrm{NH_3} \qquad (11)$$

All kinds of thermally produced phosphates were finally converted to sodium *cyclo*-triphosphate by substitution of the imino groups for bridging oxygens and reorganization of the produced condensed phosphates above 550 °C. The overall conversion of the sodium tetra-μ-imido-*cyclo*-tetraphosphate to sodium *cyclo*-triphosphate can be written by the following chemical equation:

$$\mathrm{(NaPO_2NH)_4 + 4H_2O \rightarrow 4/3(NaPO_3)_3 + 4NH_3}. \qquad (12)$$

The last endothermic process was caused by melting of the *cyclo*-triphosphate.

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