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Synthesis and thermal behaviour of ammonium and guanidine *cyclo*-hexaphosphates

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Ammonium *cyclo*-hexaphosphate monohydrate and guanidine *cyclo*-hexaphosphate dihydrate were prepared by a wet chemical process from an aqueous solution of lithium *cyclo*-hexaphosphate. Thermal properties of the compounds were studied by using a TG–DTA apparatus.

1. Introduction

Condensed phosphates are well known materials. They are used in many industrial fields as water treatment, food additives, detergents, chemical fertilizers, biomaterials, electroceramics, optoceramics, etc. [1–5]. Among them, several phosphates (di-, tri-, *cyclo*-tri-, *cyclo*-tetra-, *cyclo*-hexa-, *cyclo*-octa, *cyclo*-deca-, and long-chain polyphosphates including phosphate glasses) have been made and isolated. There have been hundreds of studies on di-, tri-, *cyclo*-tri-, *cyclo*-tetra-, and long-chain polyphosphates, while only a few papers on the other condensed phosphates have been published. Ammonium and guanidine phosphates are important materials as flame retardants [6]. Lithium and sodium *cyclo*-hexaphosphates have been prepared and their thermal and hydrolytic properties were investigated [7–12]. This paper describes wet chemical syntheses and thermal properties of ammonium and guanidine *cyclo*-hexaphosphates.

2. Experimental procedure

2.1. Preparation of *cyclo*-hexaphosphates

Lithium *cyclo*-hexaphosphate hexahydrate was made by the method described previously [8]. The *cyclo*-hexaphosphate (1.0 g) was dissolved in water (10 cm^3) and lithium ions in the solution were removed by passing through a column of cation-exchange resin. Aqueous ammonia (29%, 10 cm^3) was added into the *cyclo*-hexaphosphoric acid solution. The resulting solution was cooled in a refrigerator (at 3 °C) overnight. The white precipitate was filtered off, washed with 80 vol % aqueous acetone, and then dried in the atmosphere. The yield was about 1.5 g. To produce guanidine *cyclo*-hexaphosphate, guanidine phosphate (1.0 g) or guanidine carbonate (1.0 g) was added to the *cyclo*-hexaphosphoric acid solution and the resulting solution was allowed to stand in a refrigerator (at 3 °C) overnight. The white precipitate was filtered off, washed, and dried with the same method as above. The yield was about 1.5 g.

2.2. Chemical analysis

The determination of phosphorus and nitrogen was achieved by the Molybdenum Blue method and the Kjeldahl technique, respectively. The amount of water in the samples was measured thermogravimetrically.

2.3. High-performance liquid chromatography (HPLC)

A phosphate sample (0.01 g) was dissolved in water (10 cm^3) and the solution (100 mm^3) was injected into a column. The HPLC method developed by Baba and co-workers [13, 14] was used for the separation and determination of phosphates. The eluents of 0.24, 0.40, 0.45, and 0.50 $mol\,dm^{-3}$ solutions of potassium chloride were employed.

2.4. X-ray diffractometry (XRD)

An XRD pattern of a powdered sample was taken with nickel filtered CuK_α radiation using a Rigaku RAD-1B diffractometer.

2.5. Thermogravimetry (TG) and differential thermal analysis (DTA)

TG and DTA curves of a phosphate sample were recorded on a Rigaku TAS-100 or a Seiko SSC/5200 apparatus at a heating rate of 5 $°C\,min^{-1}$ in dry air.

3. Results and discussion

3.1 Ammonium *cyclo*-hexaphosphate

The result of HPLC showed that the product was *cyclo*-hexaphosphate. Chemical analysis of the product gave the contents of phosphorus, nitrogen, and water as P 30.7%, N 14.6%, H_2O 2.4%. The calculated contents of phosphorus, nitrogen, and water for $(NH_4PO_3)_6 \cdot H_2O$ were 31.6%, 14.3%, and 3.0%, respectively. From the results, it was found that the product was ammonium *cyclo*-hexaphosphate monohydrate. XRD data of the product are given in Table I.

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TABLE I XRD data of $(NH_4PO_3)_6 \cdot H_2O$

d (nm)	I/I_0	d (nm)	I/I_0
0.6583	100	0.2290	2
0.4467	13	0.2232	1
0.4203	36	0.2186	3
0.3867	8	0.2143	2
0.3630	28	0.2105	7
0.3346	2	0.2027	2
0.3285	8	0.1970	2
0.3060	6	0.1904	3
0.3024	13	0.1765	4
0.2921	20	0.1704	2
0.2843	8	0.1681	2
0.2645	21	0.1630	2
0.2577	2	0.1605	1
0.2513	5	0.1559	1
0.2383	3		

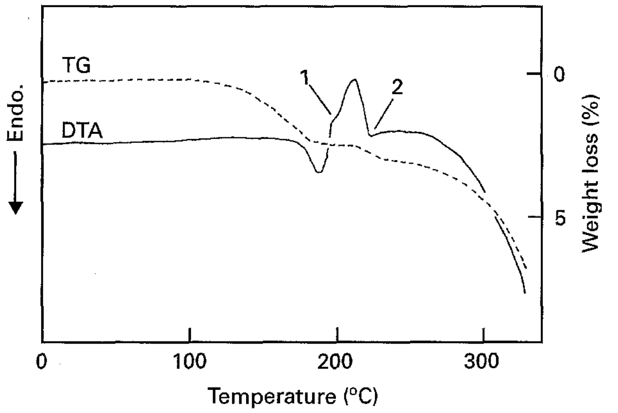

Figure 1 TG and DTA curves of $(NH_4PO_3)_6 \cdot H_2O$.

TG and DTA curves of the product are shown in Fig. 1, and analytical results of the thermal products 1 and 2 as numbered in Fig. 1 are listed in Table II. The first endothermic reaction accompanying weight loss seemed to be due to the removal of water of crystallization. The weight loss of thermal product 1 was near to the following dehydration

$$(NH_4PO_3)_6 \cdot H_2O \rightarrow (NH_4PO_3)_6 + H_2O \qquad (1)$$

Thermal product 1 gave the XRD pattern of $(NH_4PO_3)_6 \cdot H_2O$, indicating that a small part of the water of crystallization still remained in the product. Thermal product 1 also indicated weak XRD peaks other than those of ammonium *cyclo*-hexaphosphate monohydrate. The weak peaks were the same as those of thermal product 2 and the XRD pattern was assigned to that of ammonium polyphosphate form I (JCPDS 22-0061). The result in Table II shows that part of the *cyclo*-hexaphosphate decomposes to other phosphates. The following general equation can be written for the decomposition

$$(NH_4PO_3)_6 + 3/nH_2O \rightarrow 3/n(NH_4)_{2n}H_2P_{2n}O_{6n+1} \qquad (2)$$

From the above results, the thermally produced phosphates other than ammonium polyphosphate were amorphous. Because thermal product 2 gave an XRD pattern of ammonium polyphosphate form I, the exothermic reaction at about 220 °C was caused by crystallization of the amorphous phosphate produced to the ammonium polyphosphate according to the reaction

$$(NH_4)_{2n}H_2P_{2n}O_{6n+1} \rightarrow 2(NH_4PO_3)_n + H_2O \qquad (3)$$

$$(NH_4PO_3)_6 \rightarrow 6/n(NH_4PO_3)_n \qquad (4)$$

At a higher temperature, the release of ammonia and decomposition of the polyphosphate to phosphates with shorter chain lengths, were observed.

3.2. Guanidine *cyclo*-hexaphosphate

The products which were obtained from guanidine carbonate and guanidine phosphate as starting materials gave the same XRD pattern. HPLC analysis

TABLE III XRD data of $[(NH_2)_3C]_6(PO_3)_6 \cdot 2H_2O$

d (nm)	I/I_0	d (nm)	I/I_0
1.0250	54	0.3678	8
0.8751	61	0.3579	31
0.8185	39	0.3443	60
0.7689	36	0.3204	7
0.5949	6	0.3114	9
0.5110	6	0.3097	7
0.5035	15	0.3034	59
0.4672	52	0.3006	16
0.4567	13	0.2910	27
0.4485	68	0.2824	10
0.4454	58	0.2805	8
0.4371	14	0.2741	8
0.4271	14	0.2654	8
0.4153	15	0.2570	9
0.4092	9	0.2510	8
0.3990	15	0.2495	11
0.3942	7	0.2414	7
0.3897	10	0.2374	12
0.3847	31	0.2220	11
0.3739	100	0.2115	4

TABLE II Analytical data of the thermal products of $(NH_4PO_3)_6 \cdot H_2O$

Thermal product	Temperature (°C)	Weight loss (%)	XRD	Phosphates (P%)[a]					
				1P	2P	3P	4P	6M	Higher
1	200	2.4	$(NH_4PO_3)_6 \cdot H_2O$ +APPI[b]	6.3	4.8	5.1	3.7	72.7	7.4
2	230	2.7	APPI	13.2	18.6	7.3	2.4	–	58.5

[a] 1P, 2P, 3P, 4P, and 6M are ortho-, di-, tri-, tetra-, and *cyclo*-hexaphosphates, respectively.
[b] Ammonium polyphosphate form I.

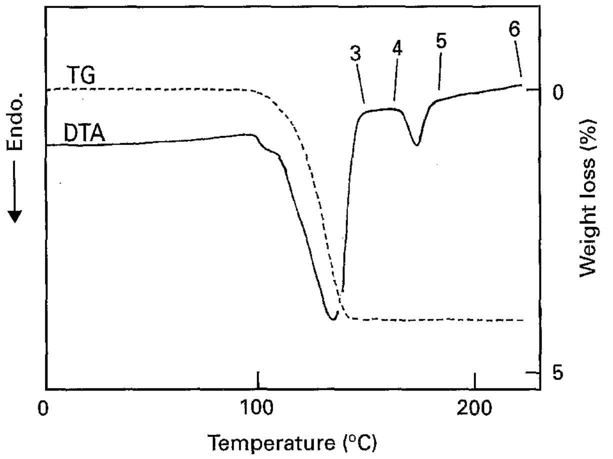

Figure 2 TG and DTA curves of $[(NH_2)_3C]_6(PO_3)_6 \cdot 2H_2O$.

TABLE V XRD data of $[(NH_2)_3C]_6(PO_3)_6$ form I

d (nm)	I/I_0	*d* (nm)	I/I_0
1.0250	17	0.3278	11
0.8734	36	0.3229	24
0.8499	100	0.3125	63
0.8200	15	0.3036	21
0.7979	8	0.3002	7
0.7880	11	0.2959	6
0.7675	17	0.2906	7
0.6544	31	0.2820	5
0.5941	3	0.2790	5
0.5640	21	0.2736	7
0.5494	4	0.2720	10
0.5029	19	0.2699	10
0.4662	34	0.2656	5
0.4489	30	0.2574	6
0.4243	33	0.2555	11
0.4153	6	0.2494	13
0.4063	40	0.2479	10
0.3962	56	0.2444	10
0.3904	23	0.2406	11
0.3847	12	0.2334	5
0.3742	35	0.2306	5
0.3576	10	0.2246	8
0.3520	47	0.2182	5
0.3443	23	0.2133	6
0.3353	23	0.1946	5

TABLE VI XRD data of $[(NH_2)_3C]_6(PO_3)_6$ form II

d (nm)	I/I_0	*d* (nm)	I/I_0
1.0934	7	0.3361	13
1.0274	56	0.3218	13
0.8768	82	0.3123	29
0.8499	53	0.3054	33
0.8216	35	0.3034	70
0.7702	39	0.2912	15
0.6554	14	0.2800	7
0.5965	5	0.2743	11
0.5647	10	0.2717	11
0.5116	7	0.2701	8
0.5035	24	0.2660	8
0.4682	61	0.2641	9
0.4549	24	0.2563	11
0.4462	69	0.2516	9
0.4380	16	0.2498	14
0.4271	22	0.2482	8
0.4239	16	0.2411	11
0.4157	14	0.2381	10
0.4063	17	0.2371	12
0.3998	21	0.2335	6
0.3962	31	0.2243	6
0.3907	17	0.2224	11
0.3844	38	0.2205	6
0.3742	100	0.2113	6
0.3681	10	0.2035	7
0.3579	30	0.1990	6
0.3523	22	0.1923	6
0.3445	57		

showed that the product was *cyclo*-hexaphosphate. Chemical analysis gave the contents of phosphorus, carbon, nitrogen, and water as P 21.6%, C 8.2%, N 28.2%, H_2O 4.1%. The calculated contents of the elements and water for $[(NH_2)_3C]_6(PO_3)_6 \cdot 2H_2O$ were P 21.4%, C 8.3%, N 29.0%, H_2O 4.1%, respectively. From these results, the product was found to be guanidine *cyclo*-hexaphosphate dihydrate. XRD data of the *cyclo*-hexaphosphate are listed in Table III. TG and DTA curves of the *cyclo*-hexaphosphate dihydrate are shown in Fig. 2, and analytical results of the thermal products 3–6 as numbered in Fig. 2 are presented in Table IV. The *cyclo*-hexaphosphate showed a large endothermic reaction accompanying a large weight loss at about 100–140 °C. The weight loss corresponds to the dehydration

$$[(NH_2)_3C]_6(PO_3)_6 \cdot 2H_2O \rightarrow [(NH_2)_3C]_6(PO_3)_6 + 2H_2O \qquad (5)$$

The analytical results in Table IV show that thermal product 3 is composed of only *cyclo*-hexaphosphate. Accordingly, the endothermic reaction was caused by the removal of water of crystallization. XRD data of the anhydrous guanidine *cyclo*-hexaphosphate are

TABLE IV Analytical data of the thermal products of $[(NH_2)_3C]_6(PO_3)_6 \cdot 2H_2O$

Thermal product	Temperature (°C)	Weight loss (%)	XRD[a]	Phosphates (P%)[b]					
				1P	2P	3P	4P	6M	Higher
3	150	4.1	ANHI	–	–	–	–	100	–
4	160	4.1	ANHI	–	–	–	–	100	–
5	185	4.1	ANHII	–	–	–	–	100	–
6	220	4.1	ANHI	–	–	–	–	100	–

[a] ANHI and II are anhydrous guanidium *cyclo*-hexaphosphate, forms I and II, respectively.
[b] 1P, 2P, 3P, 4P and 6M are ortho- di-, tri-, tetra-, and *cyclo*-hexaphosphates, respectively.

given in Table V. The anhydrous guanidine *cyclo*-hexaphosphate indicated a phase transition through the endothermic reaction at about 160–180 °C. XRD data of the *cyclo*-hexaphosphate are given in Table VI. The anhydrous *cyclo*-hexaphosphate obtained at 100–140 °C was named form I and the *cyclo*-hexaphosphate obtained at 160 to 180 °C, form II. Form II gradually changed to form I at a higher temperature and the anhydrous guanidine *cyclo*-hexaphosphate melted at about 230 °C. Decomposition of the *cyclo*-hexaphosphate to other phosphates was not observed up to 230 °C.

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