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Synthesis and thermal reorganization of sodium cyclo-hexaphosphate

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Sodium cyclo-hexaphosphate hexahydrate was prepared by passing an aqueous solution of lithium cyclo-hexaphosphate through cation-exchange resin, neutralizing the resulting solution with an aqueous sodium hydroxide solution, and then adding ethanol into the solution. The sodium cyclo-hexaphosphate was dehydrated upon heating above 180 °C without decomposing to other phosphates and anhydrous sodium cyclo-hexaphosphate was produced. The anhydrous cyclo-hexaphosphate was stable and did not exhibit any thermal change up to 450 °C, and was transformed to sodium cyclo-triphosphate above 450 °C. The cyclo-triphosphate melted at about 650 °C.

1. Introduction

Some oligophosphates and long-chain polyphosphates have been made by thermal condensation of orthophosphates. These polyphosphates have been used for water treatment, food additives, detergents, the ceramic industry, etc. [1–3]. Griffith and Buxton [4] have reported the synthesis of cyclo-hexaphosphates by heating a mixture of phosphoric acid and di-lithium carbonate and then crystallizing cyclo-hexaphosphates from an aqueous solution of the thermal product. It was pointed out that the synthetic method had several problems and proposed a modified process to prepare lithium cyclo-hexaphosphate hexahydrate [5]. Griffith and Buxton [4] also reported that it was possible to dehydrate the cyclo-hexaphosphate to form anhydrous lithium cyclo-hexaphosphate without it decomposing to other phosphates, but it was found in our previous paper that a small part of the cyclo-hexaphosphate decomposed to phosphates with shorter chain lengths upon heating above 100 °C. This paper describes the synthesis of sodium cyclo-hexaphosphate using lithium cyclo-hexaphosphate as a starting material, and the thermal dehydration and reorganization of the sodium cyclo-hexaphosphate.

2. Experimental procedure

2.1. Preparation of sodium cyclo-hexaphosphate

Lithium cyclo-hexaphosphate hexahydrate was prepared by the method described previously [5]. The lithium cyclo-hexaphosphate (4 g) was dissolved in water (6 cm^3). Lithium ions in the solution were removed by passing the phosphate solution through cation-exchange resin. The resulting solution was neutralized with an aqueous 1 mol dm^{-3} solution of sodium hydroxide. Ethanol (200–250 cm^3) was added to the neutralized solution. The white precipitate was filtered off and washed with a 75 vol % aqueous solution of acetone and then acetone.

2.2. Chemical analysis

Atomic absorption analysis was employed for determination of sodium ions in a sample solution, using a Shimazu atomic absorption spectrophotometer (AA-646). Phosphorus was determined according to the Molybdenum Blue method [6]. The amount of bound water was measured by heating loss.

2.3. High-performance liquid chromatography (HPLC)

An HPLC technique was used for separation and determination of phosphate species in a sample solution [7]. Aqueous 0.24, 0.40, and 0.60 mol dm^{-3} solutions of potassium chloride were run at a flow rate of 1 cm^3 min^{-1}.

2.4. Nuclear magnetic resonance (NMR)

A ^{31}P NMR spectrum of an aqueous phosphate solution was taken using a JNM-GX270 instrument. Phosphoric acid (85%) was employed as a reference with the positive chemical shifts being downfield.

2.5. X-ray diffractometry (XRD)

An XRD diagram of a powder sample was taken with nickel-filtered CuK_α radiation using a Rigaku X-ray diffractometer, RAD-1B.

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

TG–DTA measurement was used to study the thermal behaviour of the product using a Rigaku TG–DTA apparatus in air with a heating rate of 5 °C min^{-1}.

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3. Results and discussion

3.1. Composition of the product

The chemical analysis of the product gave the following data: Na 18.9%, P 25.6%, H_2O 15.0%. The calculated contents of sodium, phosphorus, and bound water for $(NaPO_3)_6 \cdot 6H_2O$ are as follows: Na 19.1%, P 25.8%, H_2O 15.0%. The ^{31}P NMR spectrum of the product gave only one singlet at -22.1 p.p.m. and the peak is due to a middle-PO_4 group. The product also showed only one HPLC peak in the profile. Accordingly, the product is sodium cyclo-hexaphosphate hexahydrate, $(NaPO_3)_6 \cdot 6H_2O$. The XRD data of the product and those given by Griffith and Buxton [4] are indicated in Table I. The yield of the product was about 88%. The cyclo-hexaphosphate was stable at room temperature (10–30 °C) and its solubility was 9.3 at 15 °C.

TABLE I XRD data of $(NaPO_3)_6 \cdot 6H_2O$

This study				Griffith and Buxton [4]	
d (nm)	I/I_0	d (nm)	I/I_0	d (nm)	I/I_0
0.928	48	0.212	6	0.719	–
0.717	39	0.211	21	0.509	–
0.525	21	0.207	7	0.492	–
0.506	41	0.201	10	0.359	–
0.490	59	0.196	5	0.330	–
0.484	51	0.193	3		
0.463	100	0.189	10		
0.456	17	0.188	5		
0.358	58	0.187	5		
0.355	22	0.185	18		
0.347	16	0.184	3		
0.334	15	0.181	4		
0.329	37	0.175	4		
0.312	32	0.172	5		
0.308	63	0.171	6		
0.297	9	0.167	4		
0.294	11	0.165	3		
0.293	19				
0.289	3				
0.279	4				
0.276	7				
0.272	38				
0.267	19				
0.263	20				
0.259	42				
0.253	3				
0.250	5				
0.244	3				
0.242	24				
0.239	27				
0.231	34				
0.223	4				
0.215	16				
0.213	3				

3.2. TG and DTA measurements

TG–DTA curves of sodium cyclo-hexaphosphate hexahydrate are shown in Fig. 1. Thermal products as numbered in Fig. 1 were removed from a furnace and subjected to further analysis to study thermal changes. The analytical data of the thermal products are listed in Table II and XRD diagrams of the thermal products are given in Fig. 2. The cyclo-hexaphosphate showed a large endothermic peak and a large (14.8%) rapid weight loss at about 180 °C. As Table II shows, the phosphate contained in thermal product 1 was only cyclo-hexaphosphate. Therefore, the following dehydration can be progressed through the thermal change without decomposition of the cyclo-hexaphosphate to other phosphates

$$(NaPO_3)_6 \cdot 6H_2O \rightarrow (NaPO_3)_6 + 6H_2O \quad (1)$$

The measurement of weight loss of the sample at this step supported the dehydration. The XRD diagram of thermal product 1 is, accordingly, due to anhydrous sodium cyclo-hexaphosphate. XRD data of the anhydrous sodium cyclo-hexaphosphate are listed in Table III together with those of Griffith and Buxton [4]. The HPLC analysis of the thermal products in Table II shows that the anhydrous cyclo-hexaphosphate is stable up to 450 °C. Thermal product 5 indicated unknown XRD peaks other than those of the anhydrous sodium cyclo-hexaphosphate and known sodium cyclo-triphosphate, $NaPO_3I$ (JCPDS card 11-0648). Because thermal product 5 was composed of cyclo-hexa- and cyclo-triphosphates, the un-

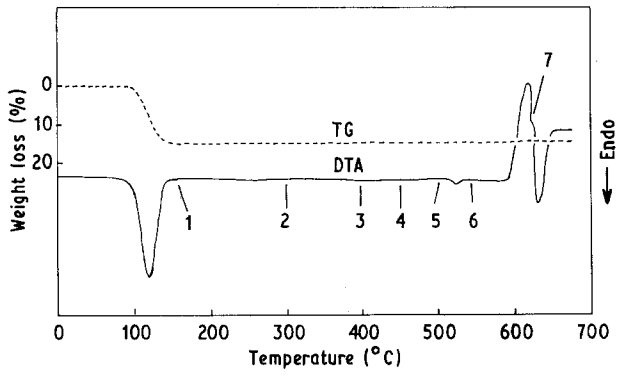

Figure 1 DTA and TG curves of $(NaPO_3)_6 \cdot 6H_2O$.

TABLE II Weight loss and composition of the thermal products of $(NaPO_3)_6 \cdot 6H_2O$

Thermal product	Temperature (°C)	Weight loss (%)	XRD	Phosphates (P%)	
				Cyclotri	Cyclohexa
1	180	14.8	$(NaPO_3)_6$	–	100
2	300	14.8	$(NaPO_3)_6$	–	100
3	400	14.9	$(NaPO_3)_6$	–	100
4	450	15.0	$(NaPO_3)_6$	–	100
5	500	15.0	$(NaPO_3)_3$, $(NaPO_3)_6$	43.9	56.1
6	550	15.0	$(NaPO_3)_3$	100	–
7	610	15.0	$(NaPO_3)_3$	100	–

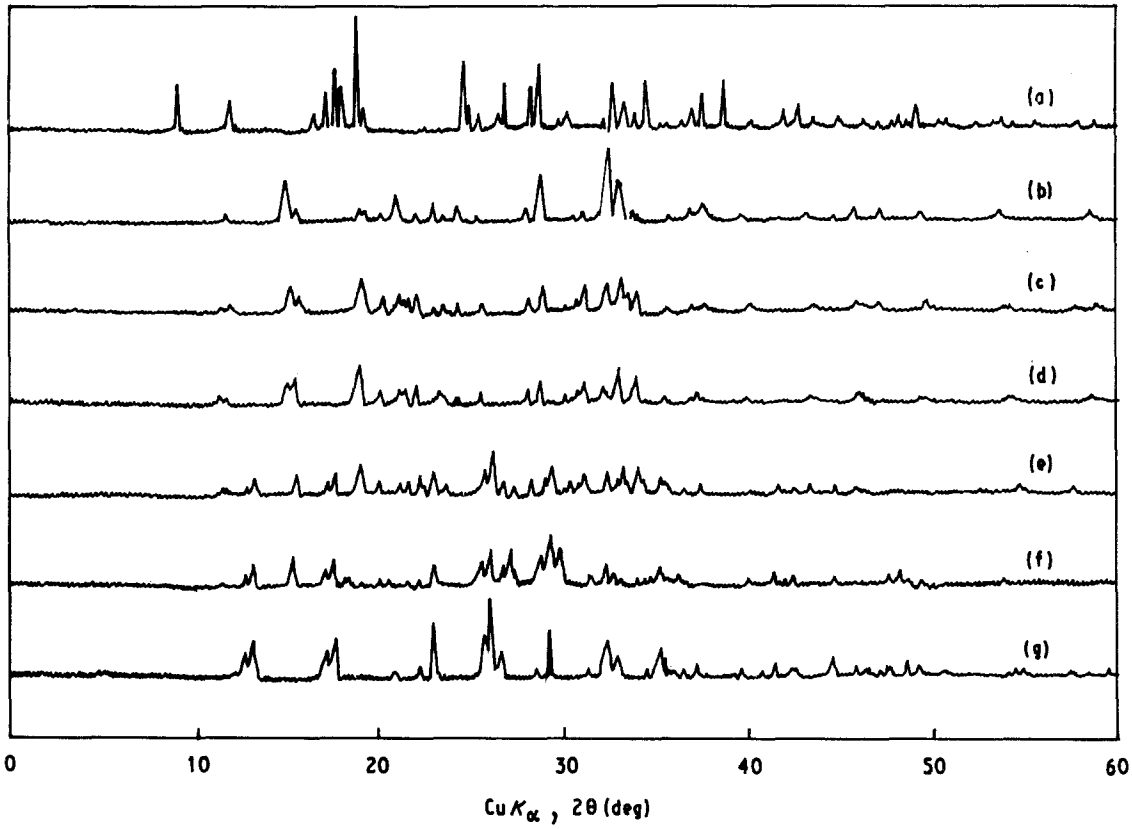

Figure 2 XRD diagrams of the thermal products of $(NaPO_3)_6 \cdot 6H_2O$: (a) $(NaPO_3)_6 \cdot 6H_2O$, (b) 1, (c) 2, (d) 3, (e) 5, (f) 6, (g) 7.

TABLE III XRD data of $(NaPO_3)_6$

This study				Griffith and Buxton [4]	
d (nm)	I/I_0	*d* (nm)	I/I_0	*d* (nm)	I/I_0
0.749	14	0.234	8	0.564	–
0.727	15	0.224	9	0.460	–
0.575	80	0.223	13	0.435	–
0.566	62	0.217	11	0.269	–
0.471	16	0.216	11		
0.463	71	0.209	10		
0.460	100	0.207	16		
0.435	40	0.205	10		
0.420	43	0.203	8		
0.415	35	0.198	21		
0.408	35	0.197	27		
0.399	46	0.195	12		
0.384	16	0.192	11		
0.377	23	0.191	18		
0.364	22	0.190	10		
0.345	25	0.189	12		
0.316	40	0.184	17		
0.313	13	0.176	8		
0.307	73	0.171	9		
0.297	13	0.170	13		
0.294	15	0.169	11		
0.290	26	0.168	9		
0.286	63	0.167	13		
0.279	11	0.159	10		
0.275	87				
0.269	95				
0.267	50				
0.263	56				
0.251	12				
0.250	9				
0.242	12				
0.240	23				
0.239	23				
0.237	26				
0.236	12				

known XRD peaks can be considered to be due to an unknown phase of sodium cyclo-triphosphate. After a small endothermic change at about 550°C, thermal product 6 contained only cyclo-triphosphate. Therefore, the XRD peaks of the thermal product are due to the known and unknown phases of sodium cyclo-triphosphate. The thermal change at 450–550°C can be written as follows:

$$(NaPO_3)_6 \begin{cases} \longrightarrow (NaPO_3)_3, NaPO_3I \\ \searrow (NaPO_3)_3 \text{(unknown phase)} \end{cases} \quad (2)$$

Because thermal product 7 showed XRD peaks due to only $NaPO_3I$, the large exothermic peak at about 600 °C could be responsible for the transformation of the unknown phase of sodium cyclo-triphosphate to the known phase, $NaPO_3I$. The last large endothermic change was caused by melting of the sample.

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