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The thermal property of alkaline earth diphosphates made by a wet process

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Alkaline earth diphosphates [$K_2Mg_3(P_2O_7)_2 \cdot 6H_2O$, $2Mg_2P_2O_7 \cdot 15H_2O$, $Sr_2P_2O_7 \cdot 3H_2O$, and $Ba_2P_2O_7 \cdot 2H_2O$] were made by mixing solutions of tetrapotassium diphosphate and alkaline earth dichlorides. These diphosphates showed the following thermal reactions when they were heated up to 1000 °C:

1. dehydration

$$M_4P_2O_7 \cdot nH_2O \rightarrow M_4P_2O_7 \cdot (n-x)H_2O + xH_2O \qquad (0 < x \leqslant n)$$

2. degradation

$$M_4P_2O_7 + H_2O \rightarrow 2M_2HPO_4$$

3. disproportionation or metathesis

$$2M_2HPO_4 \rightarrow M_3PO_4 + MH_2PO_4$$

4. polymerization

$$2M_2HPO_4 + nMH_2PO_4 \rightarrow M_{n+4}P_{n+2}O_{3n+7} + (n+1)H_2O$$

5. reorganization or degradation to diphosphate

$$M_{n+2}P_nO_{3n+1} + (n-2)M_3PO_4 \rightarrow (n-1)M_4P_2O_7$$

6. reorganization or degradation to tri- and/or diphosphates (for only $Ba_2P_2O_7 \cdot 2H_2O$)

$$M_{n+2}P_nO_{3n+1} + \tfrac{1}{2}(n-3)M_3PO_4 \rightarrow \tfrac{1}{2}(n-1)M_5P_3O_{10} \qquad (n \geqslant 3)$$

$$M_{n+2}P_nO_{3n+1} + (n-3)M_3PO_4 \rightarrow M_5P_3O_{10} + (2n-4)M_4P_2O_7 \qquad (n \geqslant 3)$$

where M stands for K and/or $\frac{1}{2}$Mg, $\frac{1}{2}$Sr, or $\frac{1}{2}$ Ba.

1. Introduction

Polyphosphates have been used for chemical fertilizers, water softeners, food additives, chemical manufacture, ceramic industry, and so on [1]. The usage of the compounds has recently extended to other fields, for example, electrical manufacture and biomaterials [2, 3]. Diphosphates and diphosphoric acid solution have been used for water treatment, food additives, metal plating chemicals [4], and so on. In spite of the increasing utility of the compounds, the physical and chemical research on the synthesis and property of these phosphates has not been well established yet. The preparation of some calcium diphosphates by a wet process was investigated by Brown *et al.* [5], but the other alkaline earth diphosphates have not been well studied. This paper describes the wet chemical preparation of magnesium, strontium, and barium diphosphates and their thermal behaviour.

2. Experimental procedure

2.1. Preparation of diphosphates

Tetrapotassium diphosphate was made by heating dipotassium hydrogenorthophosphate at 600 °C for 6 h. The diphosphate was dissolved in water to prepare 1.0 and 0.1 mol dm^{-3} aqueous solutions. The aqueous solutions of magnesium, strontium, and barium dichlorides with the same concentration as that of the diphosphate were added dropwise to the diphosphate solution. The pH of the solution was controlled with hydrochloric acid and an aqueous solution of potassium hydroxide. The temperature of the reaction mixture was kept at 22 °C during the treatment.

2.2. Determination of metals

Alkaline earth metals in a sample were determined by EDTA (disodium dihydrogen ethylenediaminetetraacetate dihydrate) titration analysis. Atomic absorption analysis was employed for the determination of potassium in a sample by using a Shimazu AA-646 spectrophotometer.

2.3. Separation and quantitative analysis of phosphates

One-dimensional paper chromatographic separation

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and colorimetric determination of phosphates were achieved [6]. A modified stock solution of a molybdenum(V)–molybdenum(VI) reagent was used for the determination [7].

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

A sample was heated at a heating rate of 10 °C/min in air by using Cho Balance TRDA-H apparatus.

2.5. X-Ray diffractometry

An X-ray diffraction diagram of a powder sample was taken with nickel filtered Cu*K*α radiation by using a Rigaku X-ray diffractometer, RAD-1B.

2.6. I.r. spectrophotometry

An i.r. spectrum of a sample was recorded on a JASCO IR spectrophotometer, A-3, using the KBr disc method.

2.7. Measurement of particle size

Particle size distribution was measured according to the centrifugal sedimentation technique, with isobutyl alcohol as sedimentation medium, using a Shimazu SA-CP3.

3. Results and discussion

3.1. Composition of the products

The diphosphates obtained are listed in Table I together with modal diameter and yield. When $1.0\,\text{mol}\,\text{dm}^{-3}$ solutions of tetrapotassium diphosphate and magnesium dichloride were used, the diphosphate contained potassium in every pH range. When the $0.1\,\text{mol}\,\text{dm}^{-3}$ solutions were employed, dimagnesium diphosphate was produced. In the preparations of the strontium and barium salts, distrontium and dibarium diphosphates were made in every experimental condition. These diphosphates were stable in a usual environment. In every case, particle size and yield of the diphosphates, respectively, decreased and increased with an increase in the pH of the solution. A precipitate was not produced in a solution with a pH value lower than those indicated in Table I. The size of the precipitate obtained from a solution with a pH value higher than those in Table I was too small to be filtered off. Product I is a new type of magnesium potassium diphosphate.

3.2. TG and DTA

3.2.1. $K_2Mg_3(P_2O_7)_2 \cdot 6H_2O$

TG and DTA curves of product I are shown in Fig. 1. The thermal products as numbered in Fig. 1 were removed from a furnace and subjected to further analysis to study the thermal change. The result of chemical analysis and the i.r. spectra of the thermal products are indicated in Table II and Fig. 2, respectively. The first and second small endothermic change associated with a little weight loss seemed to be due to removal of the bound water. The result in Table II shows that a small amount of the diphosphate degraded to orthophosphate at the second endothermal step. The process can be described by the equation

$$K_2Mg_3(P_2O_7)_2 + 2H_2O \rightarrow K_2Mg_3(HPO_4)_4 \quad (1)$$

The above equation can be rewritten by the general equation

$$M_4P_2O_7 + H_2O \rightarrow 2M_2HPO_4 \quad (2)$$

where M stands for K and/or 1/2 Mg. The third large endothermic peak accompanying a large weight loss can be caused by the elimination of the rest of the bound water and the condensation of the orthophosphate produced according to Equation 1. The thermal product 3 included tri- and higher polyphosphates other than ortho- and diphosphates. The orthophosphate made according to Equation 1 can only produce

TABLE I Composition, particle size, and yield of the diphosphates (a) Concentration of the solutions of tetrapotassium diphosphate and alkaline earth dichloride

Metal ion	Conc.[a] mol dm^{-3}	pH	Product	Composition	Modal diameter (μm)	Yield (%)
Mg^{2+}	1.0	3–4	I	$K_2Mg_3(P_2O_7)_2 \cdot 6H_2O$	13.8	86
		4–5	"	"	4.4	87
		5–6	"	"	3.8	90
	0.1	4–5	II	$2Mg_2P_2O_7 \cdot 15H_2O$	7.5	30
Sr^{2+}	1.0	2–3	III	$Sr_2P_2O_7 \cdot 3H_2O$	22.7	40
		3–4	"	"	21.0	48
		4–5	"	"	8.6	79
		5–6	"	"	7.2	80
	0.1	4–5	"	"	23.1	75
		5–6	"	"	11.9	76
Ba^{2+}	1.0	2–3	IV	$Ba_2P_2O_7 \cdot 2H_2O$	13.4	73
		3–4	"	"	6.6	74
		4–5	"	"	4.5	79
		5–6	"	"	4.5	80
	0.1	2–3	"	"	13.4	73
		3–4	"	"	6.6	74
		4–5	"	"	4.5	79
		5–6	"	"	4.5	80

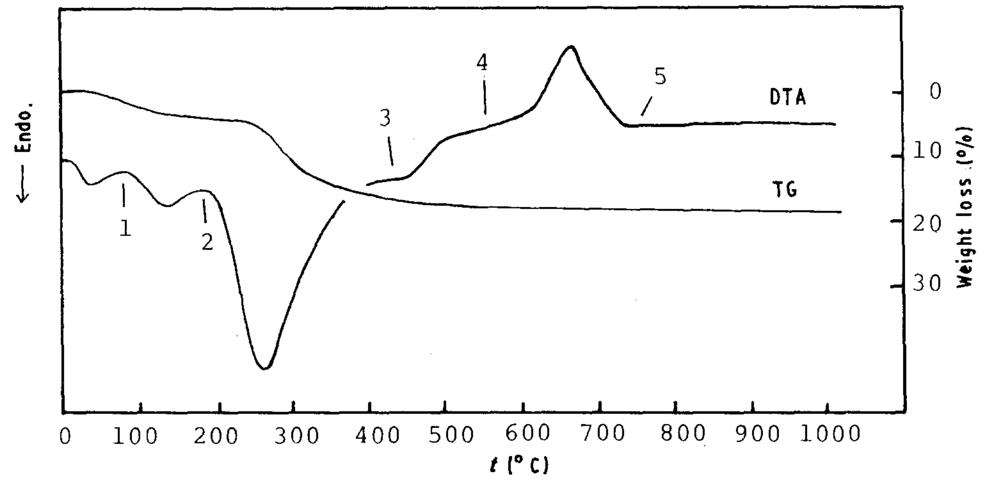

Figure 1 TG and DTA curves of the product I.

TABLE II Weight loss and composition of the thermal products of I. UC and AM stand for the unknown crystalline and amorphous products, respectively.

Thermal product	Weight loss (%)	XRD	Phosphates (%)			
			Ortho	Di	Tri	Higher
1	1.9	UC	–	100	–	–
2	3.8	"	4.4	95.6	–	–
3	16.8	AM	4.0	22.2	31.0	42.8
4	17.5	"	–	20.5	35.5	44.0
5	17.8	$Mg_2P_2O_7$	–	20.2	28.3	51.5

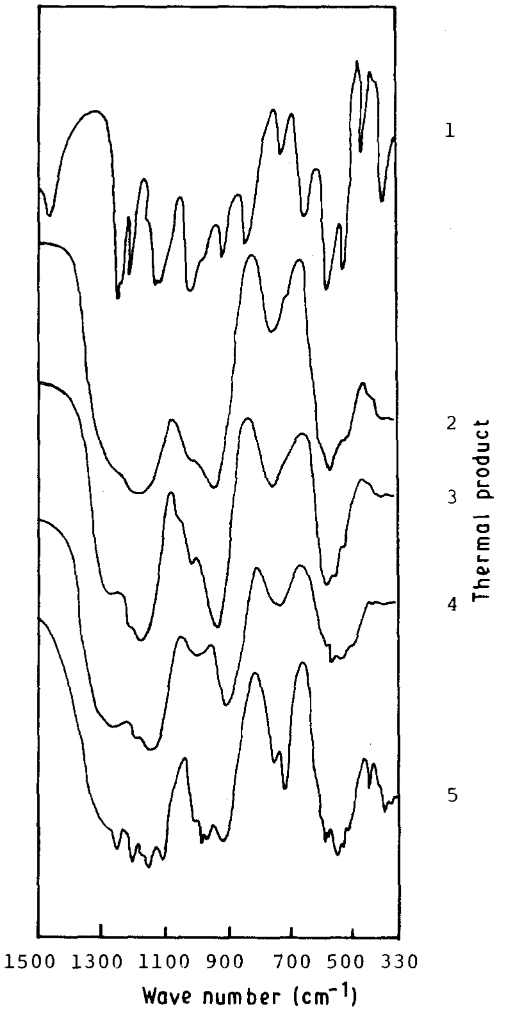

Figure 2 I.r. spectra of the thermal products of I.

diphosphate by the following equation

$$2M_2HPO_4 \rightarrow M_4P_2O_7 + H_2O \qquad (3)$$

The following polymerization reactions are unreasonable for the temperature range (200–450 °C)

$$3M_2HPO_4 \rightarrow \begin{cases} M_5P_3O_{10} + MHO + H_2O \\ M_4HP_3O_{10} + M_2O + H_2O \\ M_3H_2P_3O_{10} + M_2O + MHO \\ M_2H_3P_3O_{10} + 2M_2O \end{cases} \qquad (4)$$

$$M_4P_2O_7 + M_2HPO_4 \rightarrow \begin{cases} M_5P_3O_{10} + MHO \\ M_4HP_3O_{10} + M_2O \end{cases} \qquad (5)$$

Since the existence of the radical species like $[P(O_2)O]^-$ is unbelievable at low temperatures, the formation of polyphosphates with chains longer than that of diphosphate can be explained by the following disproportionation or metathesis of the orthophosphate:

$$2M_2HPO_4 \rightarrow M_3PO_4 + MH_2PO_4 \qquad (6)$$

The MH_2PO_4 species can produce polyphosphates with polymerization degrees larger than 2 in the temperature region by the condensations:

$$2M_2HPO_4 + MH_2PO_4 \rightarrow M_5P_3O_{10} + 2H_2O \qquad (7)$$

$$2M_2HPO_4 + 2MH_2PO_4 \rightarrow M_6P_4O_{13} + 3H_2O \qquad (8)$$

$$2M_2HPO_4 + nMH_2PO_4 \rightarrow M_{n+4}P_{n+2}O_{3n+7} + (n+1)H_2O \qquad (9)$$

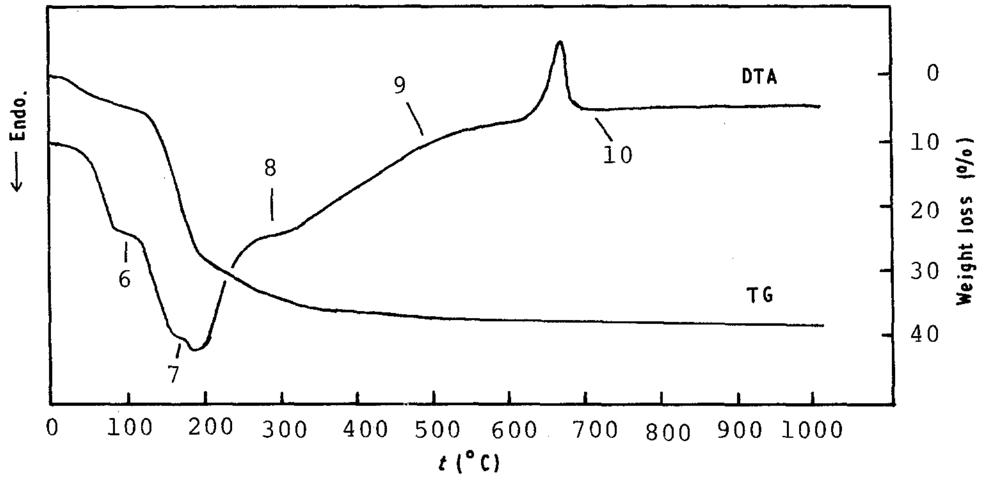

Figure 3 TG and DTA curves of the product II.

The polymerization was proceeded a little by successive heating up to 600 °C. The i.r. spectra of the thermal products 3 and 4 exhibited an absorption at 1250 cm^{-1} which corresponds to a $(PO_2)^-$ group. The i.r. result supports the above discussion. The thermal products 3 and 4 were X-ray diffractometrically amorphous. The exothermic peak at about 650 °C was considered to be caused by the crystallization of the amorphous phosphates to dimagnesium diphosphate, because the thermal product 5 showed the X-ray diffraction pattern of $Mg_2P_2O_7$. The i.r. absorption of the thermal product 5 at 1250 cm^{-1} indicates that the product contains also polyphosphates with chain lengths longer than diphosphate and the result agrees well with the analytical one in Table II. The successive heating up to 1000 °C did not cause any thermal change.

3.2.2. $2Mg_2P_2O_7 \cdot 15H_2O$

TG and DTA curves of the product II are shown in Fig. 3. The analytical data and the i.r. spectra of the thermal products are indicated in Table III and Fig. 4, respectively. The endothermic change with weight loss was caused by the removal of the bound water and the thermal product 6 was composed of diphosphate. The next large endothermic change accompanying rapid weight loss seemed to be due to the elimination of the bound water. It was also concluded that the degradation of the diphosphate to orthophosphate according to Equation 2, the disproportionation of the orthophosphate (Equation 6) and the polymerization of the phosphates to triphosphate (Equation 7) took place through the endothermic reaction, because the thermal product 7 was composed of ortho- and diphosphates and a small amount of triphosphate. The degradation of the diphosphate to orthophosphate progressed much by successive heating up to 300 °C and the polymerization of the phosphates to phosphates with chain lengths longer than diphosphate was proceeded by heating up to 500 °C. The i.r. spectral consideration based on an absorption at 1250 cm^{-1} supports the above discussion. After the exothermic peak at about 670 °C, the thermal product

TABLE III Weight loss and composition of the thermal products of II. UC and AM stand for the unknown crystalline and amorphous products, respectively.

Thermal product	Weight loss (%)	XRD	Phosphates (P%)			
			Ortho	Di	Tri	Higher
6	4.9	UC	–	100	–	–
7	25.8	AM	15.7	81.8	2.5	–
8	34.0	"	46.2	47.2	6.6	–
9	36.5	"	28.2	46.8	14.0	11.0
10	37.9	$Mg_2P_2O_7$	–	100	–	–

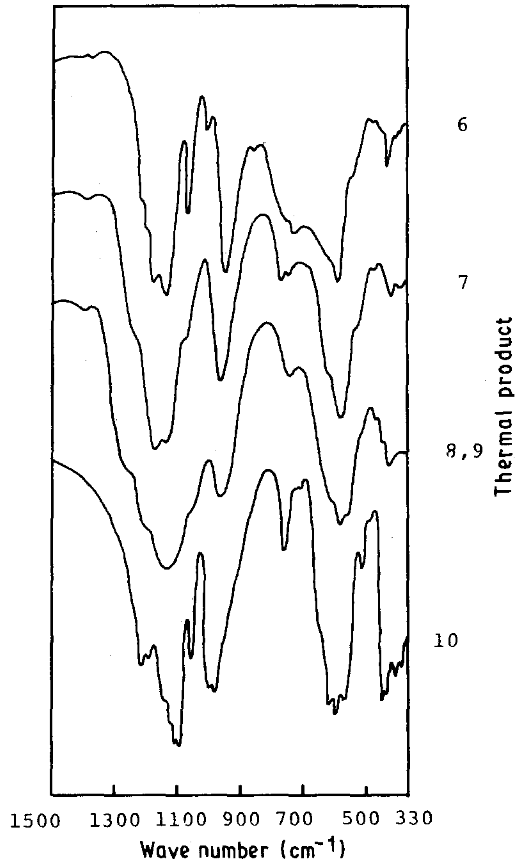

Figure 4 I.r. spectra of the thermal products of II.

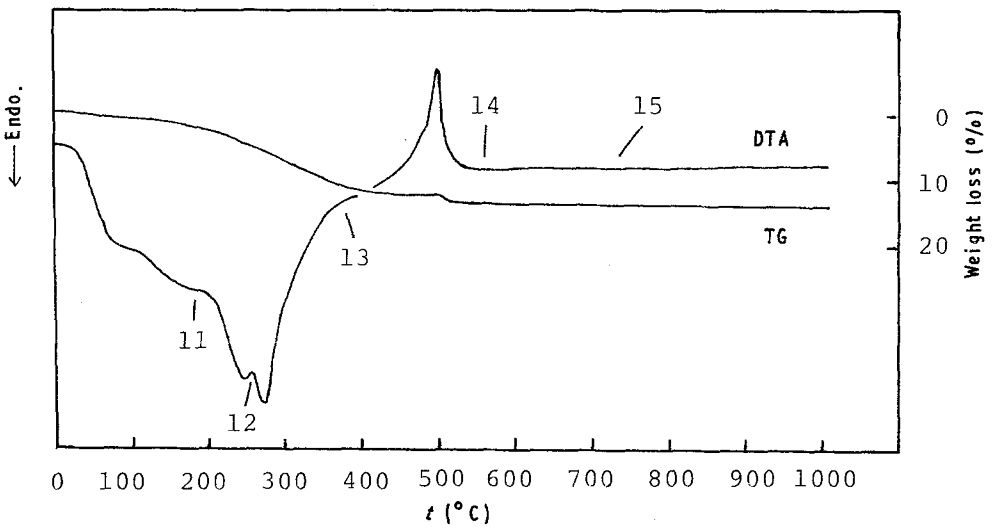

Figure 5 TG and DTA curves of the product III.

TABLE IV Weight loss and composition of the thermal products of III. UC stands for the unknown crystalline product.

Thermal product	Weight loss (%)	XRD	Phosphates (P%)			
			Ortho	Di	Tri	Higher
11	2.4	UC	12.1	87.9	–	–
12	6.9	"	20.7	73.5	5.8	–
13	11.8	"	33.4	60.1	6.5	–
14	13.1	$Sr_2P_2O_7$	7.8	92.2	–	–
15	13.3	"	–	100	–	–

showed the X-ray diffraction pattern of dimagnesium diphosphate. The thermal product was slightly soluble in a 6% EDTA aqueous solution and the solution contained only diphosphate. The i.r. spectrum of the thermal product 10 did not exhibit an absorption of a $(PO_2)^-$ group at 1250 cm^{-1}. Accordingly, it was concluded that the thermal product 10 was composed of only $Mg_2P_2O_7$. This means that the amorphous phosphates with a variety of chain lengths were reorganized to $Mg_2P_2O_7$ through the exothermal process. The reorganization of triphosphate to diphosphate can be written as follows

$$M_5P_3O_{10} + M_3PO_4 \rightarrow 2M_4P_2O_7 \qquad (10)$$

The reorganization can be described generally by the equation

$$M_{n+2}P_nO_{3n+1} + (n-2)M_3PO_4 \rightarrow (n-1)M_4P_2O_7 \qquad (11)$$

The reorganization of the phosphates was not observed in the thermal reaction of product I.

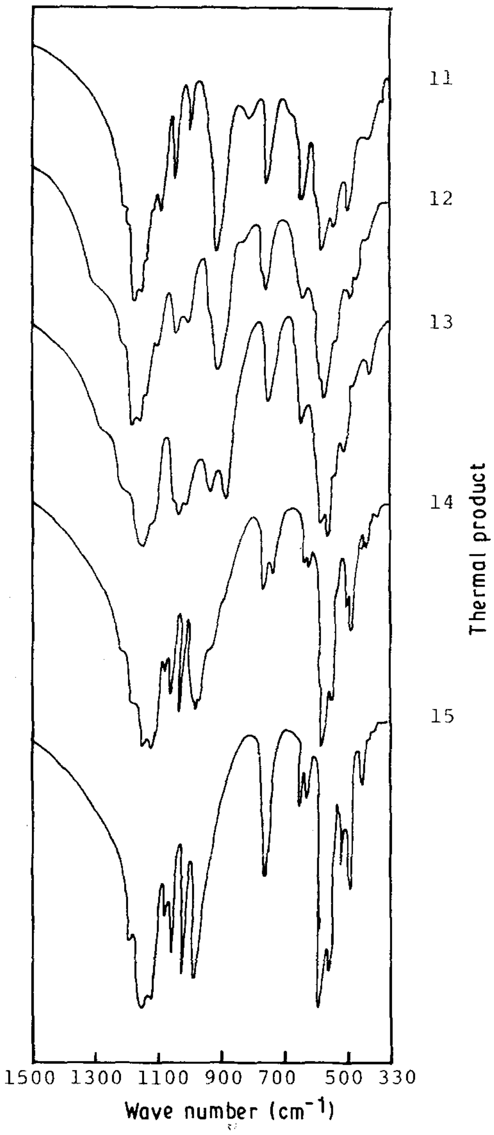

Figure 6 I.r. spectra of the thermal products of III.

3.2.3. $Sr_2P_2O_7 \cdot 3H_2O$

TG and DTA curves of the product III are shown in Fig. 5. The analytical result and i.r. spectra of the thermal products are indicated in Table IV and Fig. 6, respectively. The first endothermic reaction with gradual weight loss at the temperature range lower than 200 °C was caused by the dehydration of the bound water. A portion of the diphosphate was decomposed to orthophosphate at the same time by Equation 2. Through the next endotherm up to 400 °C, the metathesis (Equation 6) and the polymerization (Equation 9) took place other than the dehydration of the bound

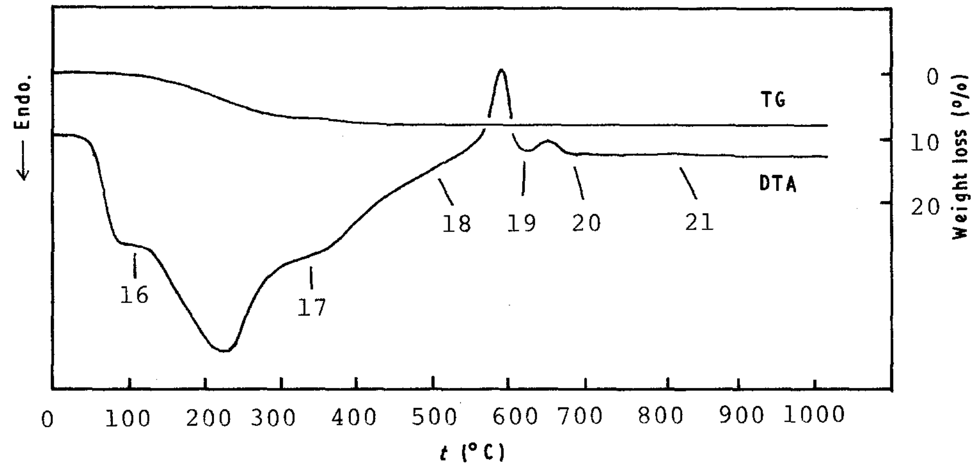

Figure 7 TG and DTA curves of the product IV.

TABLE V Weight loss and composition of the thermal products of IV. UC stands for the unknown crystalline product.

Thermal product	Weight loss (%)	XRD	Phosphates (%)			
			Ortho	Di	Tri	Higher
16	1.3	UC	4.8	95.2	–	–
17	7.1	”	10.2	64.6	11.5	13.7
18	7.3	”	7.3	45.8	21.2	25.7
19	7.4	”	–	64.4	35.6	–
20	”	”	–	55.0	45.0	–
21	”	”	–	52.5	47.5	–

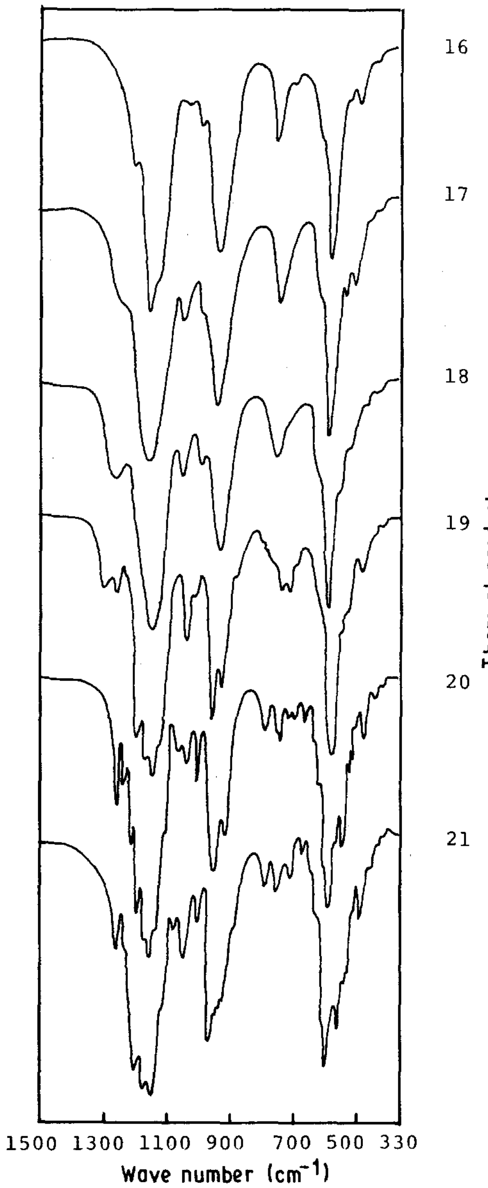

Figure 8 I.r. spectra of the thermal products of IV.

water. The degradation of the diphosphate to orthophosphate was also proceeded through endothermic change. The i.r. spectra of the thermal products 12 and 13 indicated a shoulder peak at 1250 cm^{-1}. The spectral result agrees well with the one of the phosphate contents in Table IV. The exothermic change at about 500 °C seemed to be due to the reorganization of the phosphates to diphosphate according to Equation 11 because the thermal product 14 contained about 92% of diphosphate, exhibited an X-ray diffraction diagram of $Sr_2P_2O_7$, and did not show an i.r. absorption of $(PO_2)^-$. The reorganization was progressed by the successive heating.

3.2.4. $Ba_2P_2O_7 \cdot 2H_2O$

TG and DTA curves of the product IV are shown in Fig. 7. The analytical result and i.r. spectra of the thermal products are indicated in Table V and Fig. 8, respectively. The first endothermic reaction at about 100 °C was due to the removal of the bound water. As Table V shows, the degradation of the diphosphate to orthophosphate took place at the same time. Through the next large endothermic reaction, the metathesis (Equation 6) and the polymerization (Equation 9) occurred beside the dehydration of the bound water and the degradation of the diphosphate to orthophosphate. The successive heating up to 450 °C progressed the polymerization and the contents of tri- and higher polyphosphates increased. The i.r. spectra of thermal products 17 and 18 showed an i.r. absorption of $(PO_2)^-$ at 1250 cm^{-1}. The spectral result agrees well with the analytical one in Table V. The thermal product 18 gave several very weak X-ray diffraction peaks and was nearly amorphous. After the exothermic peak at about 600 °C, the thermal product 19 exhibited sharp X-ray diffraction peaks. The exothermic change can be attributed to the crystallization of the amorphous polyphosphates. The thermal product was composed of di- and triphosphates. It could be concluded that the polyphosphates with chain lengths longer than triphosphate were reorganized to di- and triphosphates at the same time. The reorganization to diphosphate can be described by Equation 11 and that to triphosphate can be written as follows

$$M_{n+2}P_nO_{3n+1} + \tfrac{1}{2}(n-3)M_3PO_4 \rightarrow \tfrac{1}{2}(n-1)M_5P_3O_{10} \quad (n \geqslant 3) \qquad (12)$$

$$M_{n+2}P_nO_{3n+1} + (n-3)M_3PO_4 \rightarrow M_5P_3O_{10} + (2n-4)M_4P_2O_7 \quad (n \geqslant 3) \qquad (13)$$

The reorganization or degradation to di- and triphosphates is specific for the thermal behaviour of dibarium diphosphate and was not observed in the thermal processes of the magnesium and strontium diphosphates.

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