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# The synthesis and thermal behaviour of zinc diphosphates

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Zinc diphosphates ($Zn_2P_2O_7 \cdot 5H_2O$, $Zn_2P_2O_7 \cdot 3H_2O$, $5K_{1.4}Zn_{1.3}P_2O_7 \cdot 16H_2O$, and $5K_{0.8}Zn_{1.6}P_2O_7 \cdot 9H_2O$) were made by the wet process. The composition of the products was dependent on the conditions (concentration, pH, and dropping rate of the solution) of the process. When the products were heated, decomposition of the diphosphates to orthophosphate took place below about 150° C. Polymerization of the phosphates to phosphates with longer chains was observed in the temperature range 150 to 400° C. The amorphous phosphates thermally produced by heating diphosphates other than $5K_{1.4}Zn_{1.3}P_2O_7 \cdot 16H_2O$, showed reorganization to diphosphate above 400° C according to the reaction

$$M_2O_3PO[P(O_2M)O]_nPO_3M_2 + nM_3PO_4 \rightarrow (n+1)M_4P_2O_7$$

where M represents K and/or 1/2Zn.

## 1. Introduction

Polyphosphates have been used in the fields of agriculture, water treatment, chemical manufacture, ceramic industry, food additives, and so forth [1]. Although the use of the compounds is expanding to other fields, e.g. electrical manufacture and biomaterials, the physical and chemical properties of these compounds have not yet been fully investigated. Diphosphates have been used for water treatment, food additive, etc., and a solution of diphosphate for plating [2]. Zinc diphosphate has been employed as a zinc plating reagent, and is usually made by mixing solutions of tetrapotassium diphosphate and zinc dichloride or zinc sulphate, but the relationship between the conditions and chemical composition for the synthesis of the diphosphate has not yet been well established. This paper describes the synthesis of zinc diphosphates by the wet process and their thermal behaviour.

## 2. Experimental procedure

### 2.1. Materials and methods

Tetrapotassium diphosphate was prepared by heating dipotassium hydrogenorthophosphate at 600° C for 6 h. The diphosphate was dissolved in water to make 1.0 and 0.1 mol dm$^{-3}$ solutions. An aqueous solution of zinc dichloride with the same concentration as that of the diphosphate was added dropwise to the diphosphate solution at a regulated dropping rate. 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

The presence of zinc in a sample was determined using the disodium dihydrogen ethylenediaminetetraacetate dihydrate (EDTA) titration method with an XO indicator. Atomic absorption analysis was used for the quantitative analysis of potassium using a Shimadzu AA-646 spectrophotometer.

### 2.3. Separation and determination of phosphates

The one-dimensional paper chromatographic separation and the colorimetric determination of phosphates were used [3]. A modified stock solution of a molybdenum(V)–molybdenum(VI) reagent was employed for the determination [4].

### 2.4. Thermogravimetric and differential thermal analyses

A sample was heated at 10° C min$^{-1}$ in air using a Cho Balance TRDA-H apparatus.

### 2.5. X-ray diffraction

An X-ray diffraction (XRD) pattern of a powder sample was recorded on a Rigaku X-ray diffractometer, RAD-1B, with nickel-filtered Cu*Kα* radiation.

### 2.6. Measurement of particle size

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

## 3. Results and discussion

### 3.1. Composition of the products

The compositions of the zinc diphosphates made by the wet process are shown in Table I together with the conditions of synthesis (concentration, pH, and dropping rate of the solution), particle size, and yield. In all reaction systems, the precipitates were aged for 1 h in

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TABLE I Composition, particle size, and yield of zinc diphosphates

| Concentration* ($mol\,dm^{-3}$) | pH | Dropping† time (min) | Product | Composition | Modal diameter ($\mu m$) | Yield (%) |
|---|---|---|---|---|---|---|
| 1.0 | 2.0–4.0 | 420 | [I] | $5K_{1.4}Zn_{1.3}P_2O_7 \cdot 16H_2O$ | 23.5 | 79 |
| | 2.0–3.0 | 30 | [II] | $5K_{0.8}Zn_{1.6}P_2O_7 \cdot 9H_2O$ | 11.9 | 80 |
| | 3.0–5.0 | 30 | [III] | $5K_{0.8}Zn_{1.6}P_2O_7 \cdot 9H_2O$ | 8.3 | 90 |
| | 5.0–6.0 | 30 | [IV] | $5K_{0.8}Zn_{1.6}P_2O_7 \cdot 9H_2O$ | 2.7 | 91 |
| 0.1 | 2.0–3.0 | 30 | [V] | $Zn_2P_2O_7 \cdot 5H_2O$ | 24.1 | 51 |
| | 3.0–4.0 | 30 | [VI] | $Zn_2P_2O_7 \cdot 5H_2O$ | 23.0 | 60 |
| | 4.5–5.5 | 30 | [VII] | $Zn_2P_2O_7 \cdot 3H_2O$ | 12.0 | 61 |
| | 5.5–6.0 | 30 | [VIII] | $5K_{0.8}Zn_{1.6}P_2O_7 \cdot 9H_2O$ | 4.1 | 62 |

*Concentration of the solutions of tetrapotassium diphosphate and zinc dichloride.

†Time to mix the two solutions dropwise; 40 $cm^3$ 1.0 $mol\,dm^{-3}$ zinc dichloride solution was added to 25 $cm^3$ 1.0 $mol\,dm^{-3}$ tetrapotassium diphosphate solution, and 120 $cm^3$ 0.1 $mol\,dm^{-3}$ zinc dichloride solution was added to 75 $cm^3$ 0.1 $mol\,dm^{-3}$ tetrapotassium diphosphate solution.

the solution. When the 1.0 $mol\,dm^{-3}$ solutions of tetrapotassium diphosphate and zinc dichloride were used, the diphosphates obtained contained potassium and zinc at pH 2.0 to 6.0 and the potassium content and particle size of the products increased with decreasing dropping rate. When a dropping time of 30 min was employed, potassium zinc diphosphate, $5K_{0.8}Zn_{1.6}P_2O_7 \cdot 9H_2O$, was obtained at pH 2.0 to 6.0. The particle size of the diphosphate decreased and the yield of the product increased with increasing pH of the solution. When the 0.1 $mol\,dm^{-3}$ solutions of tetrapotassium diphosphate and zinc dichloride were used, dizinc diphosphates ($Zn_2P_2O_7 \cdot 5H_2O$ and $Zn_2P_2O_7 \cdot 3H_2O$) were obtained at pH 2.0 to 5.5 and potassium zinc diphosphate, $5K_{0.8}Zn_{1.6}P_2O_7 \cdot 9H_2O$ was produced at pH 5.5 to 6.0. The yield of these diphosphates was 50 to 60% and the particle size decreased with increasing pH of the solution. The X-ray diffraction patterns of the diphosphates are shown in Fig. 1. The data for $Zn_2P_2O_7 \cdot 5H_2O$ and $Zn_2P_2O_7 \cdot 3H_2O$ made in this study agree well with the JCPDS index.

## 3.2. Thermal analysis

### 3.2.1. Product I

Thermogravimetric (TG) and differential thermal analysis (DTA) curves of Product I are shown in Fig. 2. The thermal products as numbered in Fig. 2 were removed from the furnace and subjected to further analysis. The analytical results are listed in Table II. A weak endothermic peak with a small weight loss was observed below 100° C. A small amount of diphosphate decomposed to orthophosphate at the same time. The decomposition can be written as

$$M_4P_2O_7 + H_2O \rightarrow 2M_2HPO_4 \qquad (1)$$

where M represents K and/or 1/2Zn. The water in the equation can come from the water of crystallization. The next large endothermic peak accompanying a rapid weight loss may mainly be due to an elimination of the water of crystallization. The results in Table II indicate that the decomposition of the diphosphate to orthophosphate and the polymerization of the phosphates to phosphates with longer chains take place at the same time. The orthophosphate which is produced

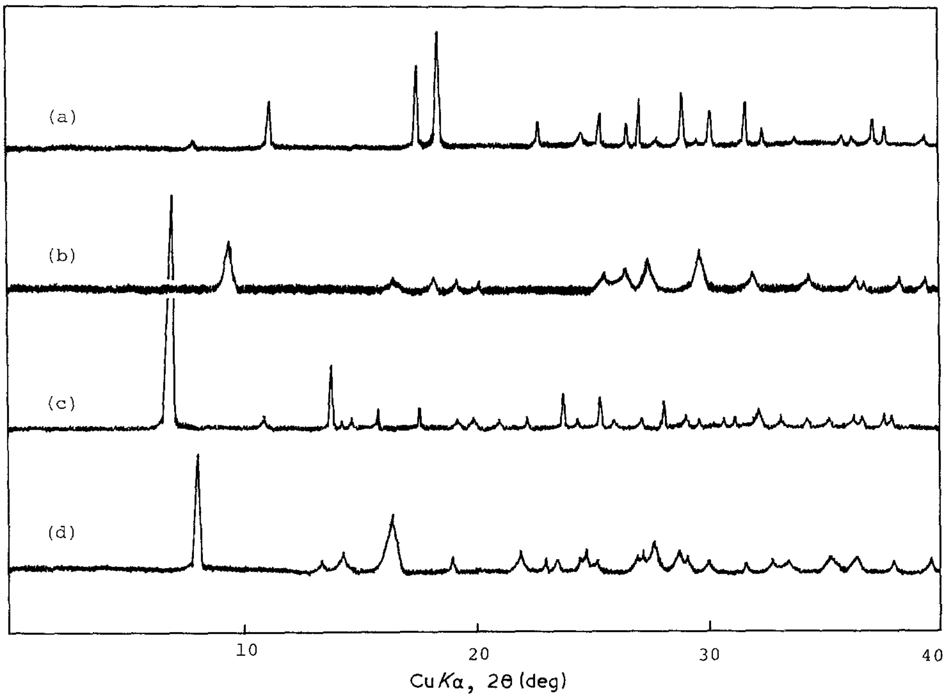


*Figure 1* X-ray diffraction diagrams of the products: (a) Product I, (b) Product II, (c) Product V, (d) Product VII.

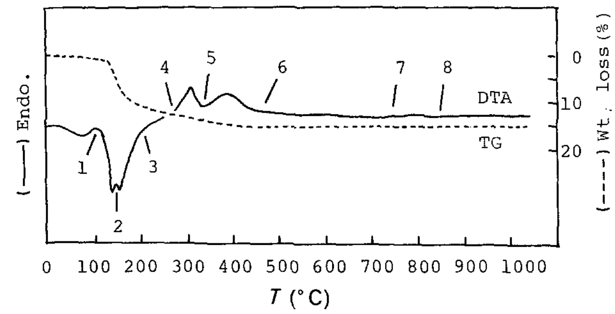


*Figure 2* DTA and TG curves of I.

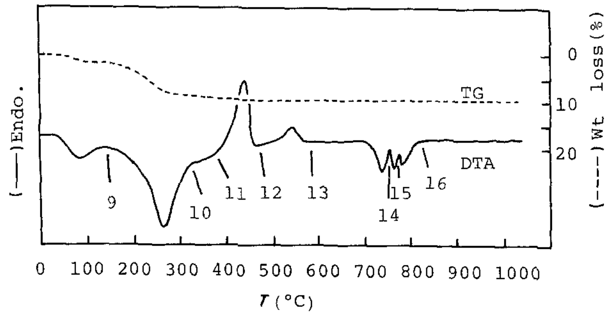


*Figure 3* DTA and TG curves of II.

through Equation 1 can only give diphosphate by condensation

$$2M_2HO_4 \rightarrow M_4P_2O_7 + H_2O \qquad (2)$$

It is impossible to produce phosphates with chains longer than the diphosphate by the following condensation process in the temperature range used

$$3M_2HPO_4 \rightarrow M_5P_3O_{10} + MHO + H_2O \qquad (3)$$

$$3M_2HPO_4 \rightarrow M_4HP_3O_{10} + M_2O + H_2O \qquad (4)$$

$$3M_2HPO_4 \rightarrow M_3H_2P_3O_{10} + M_2O + MHO \qquad (5)$$

$$3M_2HPO_4 \rightarrow M_2H_3P_3O_{10} + 2M_2O \qquad (6)$$

$$3M_3PO_4 \rightarrow M_5P_3O_{10} + 2M_2O \qquad (7)$$

$$M_4P_2O_7 + M_2HPO_4 \rightarrow M_5P_3O_{10} + MHO \qquad (8)$$

$$M_4P_2O_7 + M_2HPO_4 \rightarrow M_4HP_3O_{10} + M_2O \qquad (9)$$

$$M_4P_2O_7 + M_3PO_4 \rightarrow M_5P_3O_{10} + M_2O \qquad (10)$$

The formation of polyphosphates with chains longer than diphosphate can be explained by the following disproportionation or metathesis of the orthophosphate

$$2M_2HPO_4 \rightarrow M_3PO_4 + MH_2PO_4 \qquad (11)$$

$MH_2PO_4$ can produce polyphosphates with chains longer than diphosphate in the temperature range studied as follows

$$2M_2HPO_4 + MH_2PO_4 \rightarrow M_5P_3O_{10} + 2H_2O \qquad (12)$$

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

$$2M_2HPO_4 + nMH_2PO_4 \rightarrow M_{n+4}P_{n+2}O_{3n+7} + (n+1)H_2O \qquad (14)$$

The polymerization proceeded through the next two exothermic reactions which are associated with a small weight loss. After the last exothermic peak at about 390° C, part of the thermal product fused. Complete melting was observed at a temperature higher than 550° C.

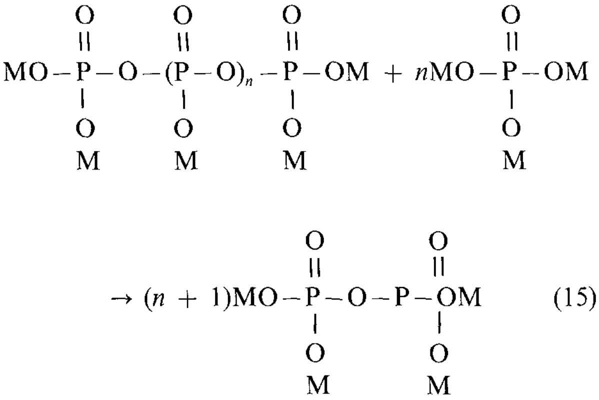
TABLE II Weight loss and composition of thermal products from I

| Thermal product | Wt loss (%) | X-ray diff. | Phosphates (% P) | | | |
|---|---|---|---|---|---|---|
| | | | Ortho | Pyro | Tri | Higher |
| 1 | 1.8 | UC | 4.9 | 95.1 | - | - |
| 2 | 8.1 | UC | 36.6 | 56.0 | 7.4 | - |
| 3 | 11.2 | AM | 37.9 | 52.4 | 9.7 | - |
| 4 | 12.1 | AM | 24.9 | 50.0 | 17.9 | 7.2 |
| 5 | 13.5 | UC | 16.7 | 52.7 | 11.8 | 18.8 |
| 6 | 15.5 | partly melted | 3.2 | 39.8 | 12.0 | 44.8 |
| 7 | 15.6 | melted | 2.0 | 22.6 | 23.9 | 51.6 |
| 8 | 15.6 | melted | 2.0 | 20.3 | 24.4 | 53.3 |

UC, unknown crystalline product; AM, amorphous.

### 3.2.2. *Product II*

TG and DTA curves of Product II are shown in Fig. 3 and the analytical results are listed in Table III. A small endothermic reaction accompanying a small weight loss was observed below 150° C. This thermal process may be due to a removal of part of the water of crystallization. As Table III shows, the thermal product contained a small amount of orthophosphate, indicating that the decomposition of diphosphate to orthophosphate through Equation 1 took place at the same time. The next large endothermic reaction and weight loss could be caused by an elimination of the rest of the water of crystallization. The analytical data show that the polymerization of the produced phosphates to phosphates with longer chains took place through Reactions 12, 13 and 14. The large exothermic peak is caused by the crystallization of the amorphous phosphates. After the thermal reaction, the diphosphate content increased and the contents of the other phosphates decreased. Therefore, it can be concluded that the reorganization of ortho- and polyphosphates to diphosphate takes place through the thermal reaction. The reorganization can be written as



$$MO-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle M}{\displaystyle O}}{\underset{|}{P}}}-O-(\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle M}{\displaystyle O}}{\underset{|}{P}}}-O)_n-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle M}{\displaystyle O}}{\underset{|}{P}}}-OM + nMO-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle M}{\displaystyle O}}{\underset{|}{P}}}-OM$$

$$\rightarrow (n+1)MO-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle M}{\displaystyle O}}{\underset{|}{P}}}-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle M}{\displaystyle O}}{\underset{|}{P}}}-OM \qquad (15)$$

The reorganization proceeded through the next exothermic reaction and the thermal product contained only diphosphate. The next two endothermic peaks were caused by a fusion of part of the thermal product and the redistribution of the diphosphate to orthophosphate and various sorts of polyphosphates occurred again through the thermal processes. Complete melting was observed after the last endothermic peak.

TABLE III Weight loss and composition of thermal products from II

| Thermal product | Wt loss (%) | X-ray diff. | Phosphates (% P) | | | |
|---|---|---|---|---|---|---|
| | | | Ortho | Pyro | Tri | Higher |
| 9 | 2.1 | UC | 5.1 | 94.9 | – | – |
| 10 | 8.7 | AM | 20.4 | 64.4 | 11.5 | 3.7 |
| 11 | 9.2 | AM | 17.9 | 61.2 | 16.0 | 4.9 |
| 12 | 9.6 | UC | 3.4 | 86.7 | 6.4 | 3.5 |
| 13 | 9.6 | UC | – | 100 | – | – |
| 14 | 9.6 | partly melted | 3.6 | 90.4 | 6.0 | – |
| 15 | 9.6 | partly melted | 3.9 | 84.4 | 7.5 | 4.2 |
| 16 | 9.6 | melted | 15.2 | 61.2 | 18.7 | 4.9 |

UC, unknown crystalline product; AM, amorphous.

TABLE IV Weight loss and composition of thermal products from V

| Thermal product | Wt loss (%) | X-ray diff. | Phosphates (% P) | | | |
|---|---|---|---|---|---|---|
| | | | Ortho | Pyro | Tri | Higher |
| 17 | 12.7 | UC | – | 100 | – | – |
| 18 | 16.7 | UC | 12.4 | 87.6 | – | – |
| 19 | 20.3 | AM | 30.5 | 53.7 | 11.1 | 4.7 |
| 20 | 21.1 | AM | 23.2 | 45.2 | 16.1 | 15.5 |
| 21 | 22.4 | UC | 9.1 | 90.9 | – | – |
| 22 | 22.5 | $Zn_2P_2O_7$<br>(JCPDS 8-238) | – | 100 | – | – |
| 23 | 22.5 | melted | 27.2 | 54.8 | 18.0 | – |

UC, unknown crystalline product; AM, amorphous.

### *3.3.3. Product V*

TG and DTA curves of Product V are shown in Fig. 4 and the analytical data are listed in Table IV. The large endothermic peak accompanying rapid weight loss was due to removal of the water of crystallization and no other thermal reactions were observed below 120° C. Although the next endothermic reaction up to 200° C was considered to be due mainly to an elimination of the rest of the water of crystallization, degradation of the diphosphate to orthophosphate also occurred at the same time. The next endothermic peaks accompanying weight loss were considered to be caused by the polymerization of the phosphates to phosphates with longer chains, according to reactions similar to Equations 12, 13 and 14. The amorphous product was crystallized through the exothermic reaction at about 500° C and the reorganization of the ortho- and polyphosphates to diphosphate took place at the same time. The reorganization proceeded up to about 800° C and the product was dizinc diphosphate. The diphosphate melted completely through the last large endothermic reaction and part of the diphosphate was reorganized into ortho- and triphosphates.

### *3.2.4. Product VII*

TG and DTA curves of Product VII are shown in Fig. 5 and the analytical data are listed in Table V. Several endothermic processes accompanying weight loss were observed up to 300° C. The main reaction below 170° C may be due to a removal of the water of crystallization and the analytical data show that the decomposition of the diphosphate to orthophosphate and the polymerization of the phosphates to higher polyphosphates were taking place at the same time. The decomposition and polymerization proceeded up to 450° C. After the large exothermic peak at about 480° C, the amorphous phosphates were crystallized and reorganized to diphosphate. The reorganization was seen to run gradually up to 700° C. Part of the thermal product fused at 730° C. Complete melting of the product was observed after the last endothermic reaction at about 1000° C, and part of the diphosphate was transformed to various sorts of phosphates through the thermal process.

## 4. Conclusion

Potassium zinc diphosphates ($5K_{1.4}Zn_{1.3}P_2O_7 \cdot 16H_2O$ and $5K_{0.8}Zn_{1.6}P_2O_7 \cdot 9H_2O$) were made by mixing 1.0 mol dm$^{-3}$ solutions of tetrapotassium diphosphate and zinc dichloride. When 0.1 mol dm$^{-3}$ solutions of tetrapotassium diphosphate and zinc dichloride were used, zinc diphosphates ($Zn_2P_2O_7 \cdot 5H_2O$, $Zn_2P_2O_7 \cdot 3H_2O$, and $5K_{0.8}Zn_{1.6}P_2O_7 \cdot 9H_2O$) were produced. The composition, particle size, and yield of the products depended on the experimental conditions (the pH and dropping rate of the solution). The diphosphates showed the thermal reactions below 400° C as follows.

1. Dehydration

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

2. Decomposition

$$M_4P_2O_7 + H_2O \rightarrow 2M_2HPO_4$$

3. Condensation

$$2M_2HPO_4 \rightarrow M_4P_2O_7 + H_2O$$

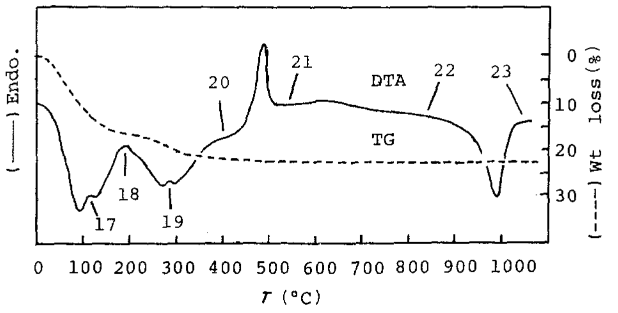


*Figure 4* DTA and TG curves of V.

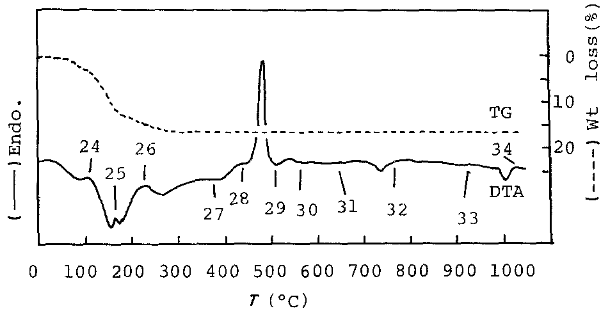


*Figure 5* DTA and TG curves of VII.

TABLE V Weight loss and composition of thermal products from VII

| Thermal product | Wt loss (%) | X-ray diff. | Phosphates (% P) | | | |
|---|---|---|---|---|---|---|
| | | | Ortho | Pyro | Tri | Higher |
| 24 | 2.6 | $Zn_2P_2O_7 \cdot 3H_2O$ | 3.5 | 96.5 | – | – |
| 25 | 10.8 | UC | 20.3 | 78.7 | 1.0 | – |
| 26 | 12.7 | UC | 26.3 | 69.4 | 4.3 | – |
| 27 | 15.5 | AM | 20.8 | 59.5 | 13.3 | 6.4 |
| 28 | 15.5 | AM | 18.6 | 58.3 | 18.4 | 4.7 |
| 29 | 15.7 | $Zn_2P_2O_7$ and UC | 5.9 | 91.0 | 3.1 | – |
| 30 | 15.7 | $Zn_2P_2O_7$ and UC | 4.9 | 92.0 | 3.1 | – |
| 31 | 15.9 | $Zn_2P_2O_7$ | 1.4 | 96.2 | 2.4 | – |
| 32 | 15.9 | partly melted | 3.3 | 93.2 | 3.5 | – |
| 33 | 16.0 | partly melted | 3.4 | 93.3 | 3.3 | – |
| 34 | 16.0 | melted | 29.5 | 49.8 | 12.9 | 7.8 |

UC, unknown crystalline product; AM, amorphous.

4. Disproportionation or metathesis and condensation

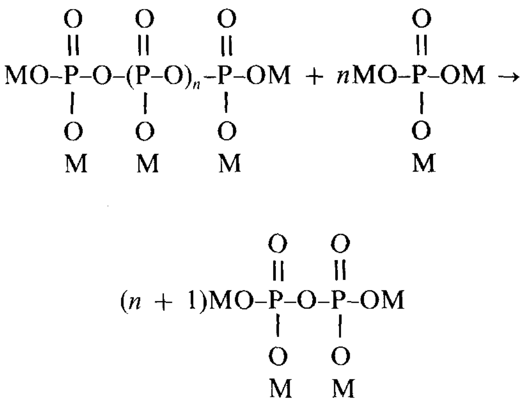
$$2M_2HPO_4 \rightarrow M_3PO_4 + MH_2PO_4$$

$$2M_2HPO_4 + nMH_2PO_4$$

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

The phosphates which were thermally produced from diphosphates other than $5K_{1.4}Zn_{1.3}P_2O_7 \cdot 16H_2O$ according to the above reactions showed the following reorganization to diphosphate above 400° C.

5. Reorganization



$$\mathrm{MO{-}\overset{\overset{O}{\|}}{\underset{\underset{\underset{M}{O}}{|}}{P}}{-}O{-}(\overset{\overset{O}{\|}}{\underset{\underset{\underset{M}{O}}{|}}{P}}{-}O)_{\mathit{n}}{-}\overset{\overset{O}{\|}}{\underset{\underset{\underset{M}{O}}{|}}{P}}{-}OM} + n\mathrm{MO{-}\overset{\overset{O}{\|}}{\underset{\underset{\underset{M}{O}}{|}}{P}}{-}OM} \rightarrow$$

$$(n + 1)\mathrm{MO{-}\overset{\overset{O}{\|}}{\underset{\underset{\underset{M}{O}}{|}}{P}}{-}O{-}\overset{\overset{O}{\|}}{\underset{\underset{\underset{M}{O}}{|}}{P}}{-}OM}$$

The reorganized diphosphate transformed to a mixture of various types of phosphates through fusion.

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