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A DETAILED STUDY OF THE CONDENSATION OF THE $Ca(H_2PO_4)_2 \cdot H_2O$–$CaHPO_4 \cdot 2H_2O$ SYSTEM UNDER THERMAL TREATMENT

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ABSTRACT

The thermal condensation of an equimolecular mixture of $Ca(H_2PO_4)_2 \cdot H_2O$–$CaHPO_4 \cdot 2H_2O$ has been studied from room temperature up to 620 °C by a thermogravimetric continuous mode method, and by a batch method, heating the mixture at 140, 190, 240, 300, 360, 420 and 620 °C. The batches were cooled after heating at each temperature, and examined by X-ray diffraction (XRD) and IR to identify the intermediate products. The thermal condensation towards the final products, which were identified as β-$Ca(PO_3)_2$, $Ca_4P_6O_{19}$ and $7CaO \cdot 5P_2O_5$ (tromelite), proceeds through initial removal of the crystal water molecules (140–190 °C) and subsequent condensation and removal of additional water (190–360 °C). A detailed reaction pathway has been constructed, made up of parallel and consecutive chemical transformations, taking into account the intermediate products observed by XRD and IR, and also maintaining the mass balance of the system. It should be noted that the second constituent of the starting mixture $Ca(H_2PO_4)_2 \cdot H_2O$–$CaHPO_4 \cdot 2H_2O$ appears to suffer initially a kind of mechanochemical dehydration at room temperature towards $CaHPO_4$.

INTRODUCTION

An important step in the production of phosphate fertilizers as calcium polyphosphates is the acid–thermal treatment of phosphate raw materials, which is accompanied by polycondensation of decomposition products. Polycondensation in the $Ca(H_2PO_4)_2$–$CaHPO_4$ system, or the corresponding hydrated system $Ca(H_2PO_4)_2 \cdot H_2O$–$CaHPO_4 \cdot 2H_2O$, can act as a precise model of these processes. However, work aiming at a detailed examination of the reactions occurring during heating is rather scarce, probably because of the complexity of the systems. The only relatively detailed study known to us is of the system $Ca(H_2PO_4)_2 \cdot H_2O$–$CaHPO_4$ up to 900 K using various methods (thermogravimetry, conductivity, NMR) [1]. The main conclusion of this work is that heating results in gradual copolymerization of the two components towards a final product of general formula $Ca_{n/2+1}P_nO_{3n+1}$, with n reaching values around 5. Nevertheless, a detailed discussion of the mechanism of condensation–polymerization is no available. We also note that some work on the system $Ca(H_2PO_4)_2 \cdot H_2O$–$CaHPO_4 \cdot 2H_2O$–SiO_2 has recently been accomplished in our laboratory [2]. As comparable work on the $Ca(H_2PO_4)_2 \cdot H_2O$–$CaHPO_4 \cdot 2H_2O$ system was not available, we decided to examine this system rather closely. We note that the two components of the system are usually formed as intermediate products during the treatment of phosphate ores with H_3PO_4 at high temperatures, resulting finally in complete dehydration of the system. IR, thermogravimetric and X-ray diffraction (XRD) techniques were used to study and identify the intermediates and final products, and elucidate the mechanism of transformation.

EXPERIMENTAL AND RESULTS

The raw materials used in the study were commercial $Ca(H_2PO_4)_2 \cdot H_2O$ and $CaHPO_4 \cdot 2H_2O$. The $CaHPO_4 \cdot 2H_2O$ (Carlo Erba, Ph. Eu.) was of composition 41.2% P_2O_5, 33.5% CaO and 25.1% H_2O. Its IR spectrum, shown in Fig. 2 together with other spectra of intermediate products, is in complete agreement with data from the literature [3,4]. The $Ca(H_2PO_4)_2 \cdot H_2O$ used (Merck, extra pure) as a starting material was of composition 56.5% P_2O_5, 21.5% CaO and 21.7% H_2O. The "free H_3PO_4" content was determined after washing with acetone, and was found to be 2.97% H_3PO_4 (or 2.15% P_2O_5). The IR spectrum after washing with acetone is also shown in Fig. 2, and is in agreement with other results in the literature [3,5–7].

Equimolecular mixtures of the two solids were prepared by mixing corresponding amounts of each in a porcelain mortar under strong grinding.

TABLE 1

Percentage weight losses of equimolecular mixture of $Ca(H_2PO_4)_2 \cdot H_2O$–$CaHPO_4 \cdot 2H_2O$ ($\approx$15 g) after 7 h of heating at each temperature

Sample number	Temperature (° C)						
	140	190	240	300	360	420	620
1	12.76	–	–	–	–	–	–
2	12.72	13.56	–	–	–	–	–
3	11.88	13.28	16.36	–	–	–	–
4	12.50	13.15	17.40	20.78	–	–	–
5	11.12	13.44	17.27	21.02	21.99	–	–
6	8.66	13.80	16.12	20.61	22.16	22.65	–
7	–	13.62	16.33	20.25	21.38	21.86	23.09
Mean values:	12.20	13.48	16.70	20.66	21.84	22.26	–

Maximum theoretical weight loss: 23.35%

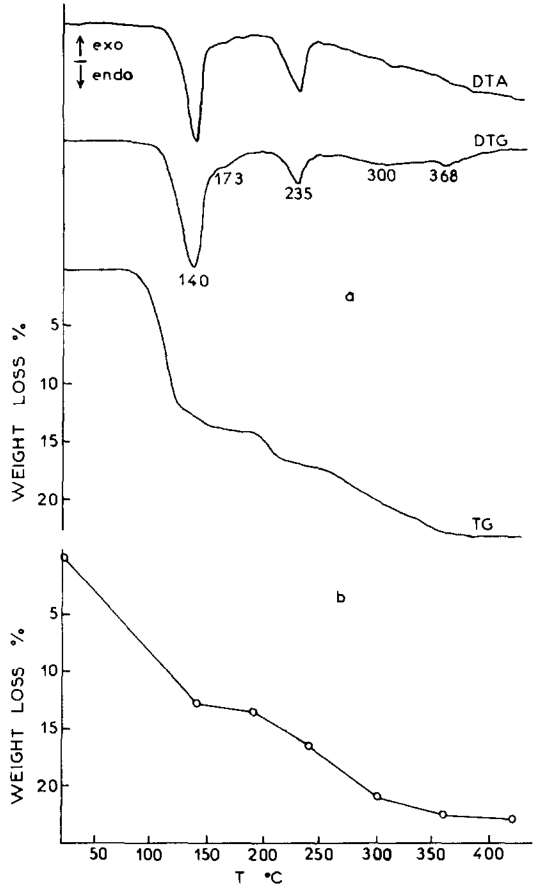

Fig. 1. (a) TG, DTG and DTA curves for the equimolecular mixture $Ca(H_2PO_4)_2 \cdot H_2O$–$CaHPO_4 \cdot 2H_2O$ heated at 2.2° C min^{-1}; (b) percentage weight loss of the same mixture (~ 15 g) after 7 h of heating at each temperature.

The $Ca(H_2PO_4)_2 \cdot H_2O$ used had in each case been washed with acetone to remove the "free H_3PO_4". Samples (= 15 g) from this mixture were heated separately in porcelain crucibles at 140, 190, 240, 300, 360, 420 and 620° C for 7 h each. The weight losses of these batch experiments, calculated after cooling, are given in Table 1 and are also shown in Fig. 1, as a function of temperature. (For comparison, the same figure also shows the thermogravimetric results taken by continuous mode, as described below.) Each of the samples was then examined by IR and XRD techniques.

IR spectra of the samples, taken with a Perkin-Elmer 577 spectrophotometer, are shown in Fig. 2.

In the XRD studies we used a Philips system (PW 2253 lamp, PW 1050 Goniometer, PW 1965/50 Analog Detector) with Co $K\alpha$ radiation ($\lambda = 1.7902$ Å). The results are shown in Fig. 3.

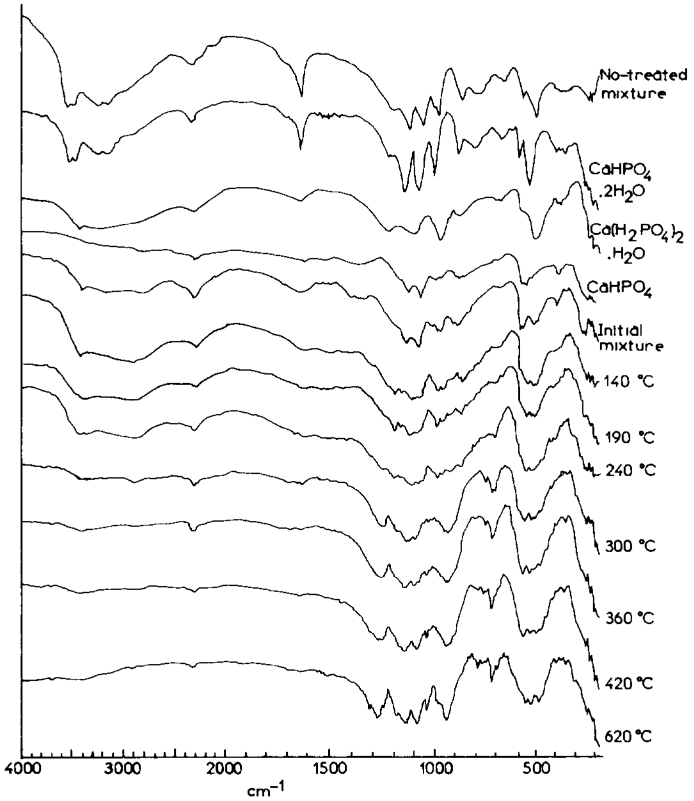

Fig. 2. IR spectra of the equimolecular mixture of $Ca(H_2PO_4)_2 \cdot H_2O$–$CaHPO_4 \cdot 2H_2O$ heated at the temperatures indicated. The spectra of the initial components are also shown.

The thermogravimetric study of the unheated mixture was carried out using a thermograph TRDA$_3$-H (Chyo Balance Corporation), which provided signals for the temperature *T*, and thermogravimetric (TG), differential thermogravimetric (DTG) and differential thermal analysis (DTA). A sample graph for the equimolecular mixture at a heating rate of 2.2 °C min^{-1} is shown in Fig. 1, where the weight loss from the TG curve can be compared with the results from the batch experiments.

DISCUSSION

The unheated equimolecular mixture of the two components, prepared by strong grinding in a porcelain mortar, does not consist of the mixed phases, but instead shows the fingerprints of $Ca(H_2PO_4)_2 \cdot H_2O$ and traces of $CaHPO_4$. This behaviour is apparent in both the IR and XRD measurements (Figs. 2 and 3). By contrast, the equimolecular unheated mixture, without grinding shows a rather normal behaviour, with strong IR absorp-

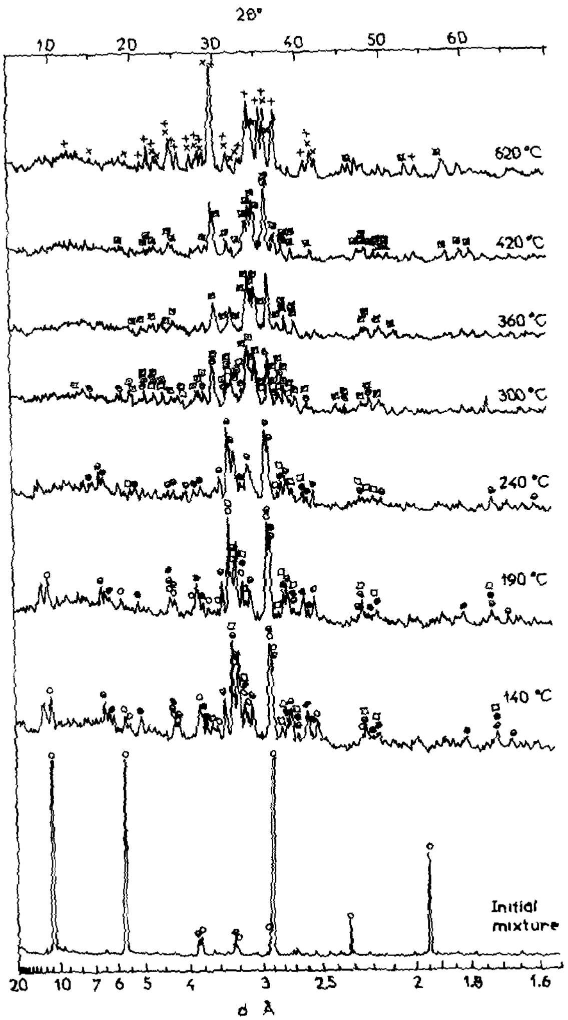

Fig. 3. XRD pattern of the equimolecular mixture of $Ca(H_2PO_4)_2 \cdot H_2O$–$CaHPO_4 \cdot 2H_2O$ heated at the temperatures indicated. The pattern of the initial (unheated) mixture is also shown. (○) $Ca(H_2PO_4)_2 \cdot H_2O$, (◒) $CaHPO_4$, (◓) $H_3PO_4 \cdot 0.5\ H_2O$, (●) $Ca(H_2PO_4)_2$, (□) $CaH_2P_2O_7$, (⊡) $Ca_3(HP_2O_7)_2$, (◩) $Ca_2HP_3O_{10}$, (◪) $\gamma Ca_2P_2O_7$, (◨) γ-$Ca(PO_3)_2$, (◧) $7CaO \cdot 5P_2O_5$, (×) β-$Ca(PO_3)_2$, (+) $Ca_4P_6O_{19}$. (Radiation Co $K\alpha$, Fe filter, recording 2° C min^{-1}.)

tion bands for $CaHPO_4 \cdot 2H_2O$. We note that, visually, the initial commercial sample of $Ca(H_2PO_4)_2 \cdot H_2O$ gives the impression of a layered structure, and indeed its XRD lines correspond to 0*k*0 levels (010, 020, 030, etc.), which are also apparent in the strongly treated mixture. Indeed a neutron diffraction study of this compound [8] has shown that crystal water molecules occur along the *k* direction and separate two different kinds of $H_2PO_4^-$ group. That there are two different conformations of $H_2PO_4^-$ group in the $Ca(H_2PO_4)_2 \cdot H_2O$ structure has also been confirmed by an IR study [6], in which double peaks were observed.

The disappearance of the $CaHPO_4 \cdot 2H_2O$ (brushite) phase and some indications in the XRD pattern (Fig. 3) of traces of anhydrous $CaHPO_4$ (monetite) can be attributed to a mechanochemical transformation according to the reaction

$$CaHPO_4 \cdot 2H_2O \xrightarrow{\text{Mechanochemical activation}} CaHPO_4 + 2H_2O(ads) \qquad (1)$$

In support of such a reaction is the observation that the initial treated mixture gives the impression of humidity on its surface. Nevertheless, the fate of this free water is not clear. It may be that it remains physically adsorbed on the surface and is removed by heating at $T > 100\,°C$.

The thermogravimetric batch experiments, as well as those conducted in continuous mode (Fig. 1), indicate that the mixture loses water in two main steps. The first is strongly endothermic, and takes place at around 140 °C with a weight loss of −13%. This loss corresponds to the removal of all three crystal water molecules from the initial equimolecular mixture

$$\begin{aligned} &Ca(H_2PO_4)_2 \cdot H_2O + CaHPO_4 + 2H_2O(ads) \\ &\quad \rightarrow Ca(H_2PO_4)_2 + CaHPO_4 + 3H_2O \qquad (2) \end{aligned}$$

The second weight loss takes place between 200 and 300 °C in the batch experiments, and at around 235 °C in the continuous thermograph. This weight loss corresponds to almost 8% of the initial weight, and is probably due to some kind of condensation of the simple molecules to polyphosphates. The remaining 2% weight loss, which takes place up to 600 °C, can be attributed to some further condensation to higher polyphosphates. We shall try to identify the final products of these successive condensations on the basis of the results of the IR and XRD studies.

XRD data

The XRD patterns (Fig. 3) show that the initial equimolecular mixture heated to 140 as well as to 190 °C takes on the structure of $CaHPO_4$ and $Ca(H_2PO_4)_2$, and a small amount of $Ca(H_2PO_4)_2 \cdot H_2O$ is also apparent. However, there remain three rather strong peaks, corresponding to $d =$ 13.01–12.75 and 3.302 Å, with relative intensities 28 and 91, respectively, which have not been identified according to the corresponding ASTM data.

Upon heating to 240 °C, the $CaHPO_4$ and $CaH_2P_2O_7$ phases are still apparent, while the previously noted unidentified peaks have moved slightly ($d = 13.10$ and 2.298 Å), and their intensities are reduced by nearly 20% (21 and 74, respectively).

At 300 °C the phases $CaH_2P_2O_7$, $Ca_3(HP_2O_7)_2$, $Ca_2HP_3O_{10}$ and $H_3PO_4 \cdot 0.5H_2O$ can be positively identified. We also observe two very strong reflections corresponding to $d = 3.325$ and 2.911 Å, with relative intensities 45 and 89, respectively, which cannot be easily identified according to ASTM data. It may be that the second peak corresponds to free H_3PO_4 ($d = 2.908$ Å, according to ASTM), but its intensity appears extraordinarily high, whereas according to ASTM it should be around 15. We should bear in mind that the stronger peak of H_3PO_4 appears at $d = 3.500$ Å according to the literature. In our data, a peak does appear at $d = 3.555$ Å, with $I/I_0 = 69$ but this can also be attributed to the tripolyphosphate ($d = 3.580$ Å and $I/I_0 = 80$, according to the literature).

Heating at 360 ° C results in the appearance of phases $Ca_2HP_3O_{10}$ and γ-$Ca(PO_3)_2$ in small quantities. Three rather strong peaks, corresponding to $d = 3.702$, 3.331 and 2.917 Å with $I/I_0 = 25$, 44 and 100, respectively, could not be identified. Nevertheless, the last two of these correspond to those which also remained unidentified at 300 ° C, so again these peaks may be due to tripolyphosphates.

After heating at 420 ° C we observe the crystal phases γ-$Ca_2P_2O_7$ and γ-$Ca(PO_3)_2$, while two strong peaks corresponding to $d = 3.530$ and 2.958 Å with $I/I_0 = 80$ and 28, respectively, remain unidentified.

Finally, after heating at 620 ° C we observe the crystal phases of β-$Ca(PO_3)_2$, $Ca_4P_6O_{19}$ and $7CaO \cdot 5P_2O_5$ (tromelite) [9]. One strong peak ($I/I_0 = 53$) corresponding to $d = 3.031$ Å remains unidentified.

IR data

The results obtained from the IR experiments (Fig. 2) are in agreement with the basic assumptions made previously on the basis of the XRD studies. Thus, the initial equimolecular mixture after the strong mechanical treatment shows the absorption bands of both $Ca(H_2PO_4)_2 \cdot H_2O$ and $CaHPO_4$, while the non-treated mixture shows the bands of $Ca(H_2PO_4)_2 \cdot H_2O$ and $CaHPO_4 \cdot 2H_2O$. According to the literature [6,10,11], the crystal water molecules of $Ca(H_2PO_4)_2 \cdot H_2O$ absorb at 3450 and 3220 cm^{-1} (stretching), at 1640 cm^{-1} (bending in plane), and at 685 and 667 cm^{-1} (liberation modes). Our spectra indeed showed absorptions at 1640 and 685 cm^{-1}, in agreement with the above data.

The absorption bands for the crystal water are quite apparent up to 240 ° C. We also note that up to 420 ° C there exist some absorptions around 3300 cm^{-1}, which correspond to zeolitic H_2O, as indicated in a recent work [12] on $Ca_2HP_3O_{10}$. In this compound the zeolitic water remains up to 527 ° C.

The absorption bands of acidic phosphoric groups P–OH appear at 2910–2900 (stretching), 1393–1192 (δ) and 978–980 (stretching) cm^{-1}, and are quite strong up to 240 ° C. Then, after treatment at 360 ° C, they become much weaker, as is to be expected for the gradual dehydration–condensation.

The vibrations of middle groups O–P–O (PO_2) of the poly- and metaphosphates which appear at 1304–1027 cm^{-1} overlap with those of PO_3 terminal groups at 1200–988 cm^{-1} (ν_{as}, ν_s). These bands become more apparent after heating at 300 °C, and are quite distinct after heating at 620 °C, as is to be expected for the continuously increasing amount of polymerized phosphoric salts.

Finally, the absorption bands of P–O–P bridging groups of the poly- and metaphosphates appear at 978–681 cm^{-1} (ν_{as}, ν_s) and, as with the PO_2 and PO_3 groups, and for similar reasons, they become more apparent above 300 °C and much more distinct at 620 °C.

The mechanism

On the basis of the above data we set out to construct a scheme to represent the detailed pathway of the reactions that occur during heating up to 620 °C. This scheme, shown in Fig. 4, maintains the mass balance of the system precisely.

There follows a detailed analysis and justification of this pathway. Reactions (I), (II), (III) and (VII) of Fig. 4, which occur at 140 190, 240 and 360 °C, are typical dehydrations upon heating.

$$Ca(H_2PO_4)_4 \cdot H_2O \xrightarrow{140\text{–}190\,^{\circ}C} Ca(H_2PO_4)_2 + H_2O \qquad (I)$$

$$CaHPO_4 \cdot 2H_2O \rightarrow CaHPO_4 + 2H_2O \qquad (II)$$

$$Ca(H_2PO_4)_2 \xrightarrow{240\,^{\circ}C} CaH_2P_2O_7 + H_2O \qquad (III)$$

$$CaH_2P_2O_7 \xrightarrow{360\,^{\circ}C} Ca(PO_3)_2 + H_2O \qquad (VII)$$

Reactions (IV) and (V), also of Fig. 4, result in the formation of free H_3PO_4 with or without increment of the degree of polymerization.

$$CaH_2P_2O_7 + \tfrac{2}{3}H_2O \xrightarrow{300\,^{\circ}C} \tfrac{1}{3}[Ca_3(HP_2O_7)_2] + \tfrac{2}{3}[H_3PO_4 \cdot 0.5H_2O] \qquad (IV)$$

$$CaH_2P_2O_7 + \tfrac{1}{4}H_2O \xrightarrow{300\,^{\circ}C} \tfrac{1}{2}Ca_2HP_3O_{10} + \tfrac{1}{2}[H_3PO_4 \cdot 0.5H_2O] \qquad (V)$$

We note that a reaction similar to reaction (V) is given the literature [13] for the double salt $RbMn(H_2P_2O_7)_2$ at 280 °C. The same products give $Ca(H_2PO_4)_2$ when heated at 200 °C under 5 atm steam pressure [14], but with the difference that the resulting phosphoric acid contains four water molecules instead of one.

$$RbMn(H_2P_2O_7)_2 \xrightarrow{280\,^{\circ}C} \text{II-}RbMnHP_3O_{10} + H_3PO_4 \qquad (3)$$

$$8Ca(H_2PO_4)_2 + 8H_2O \xrightarrow{200\,^{\circ}C,\ 5\ \text{atm steam}} 4Ca_2HP_3O_{10} + 4[H_3PO_4 \cdot 4H_2O] \qquad (4)$$

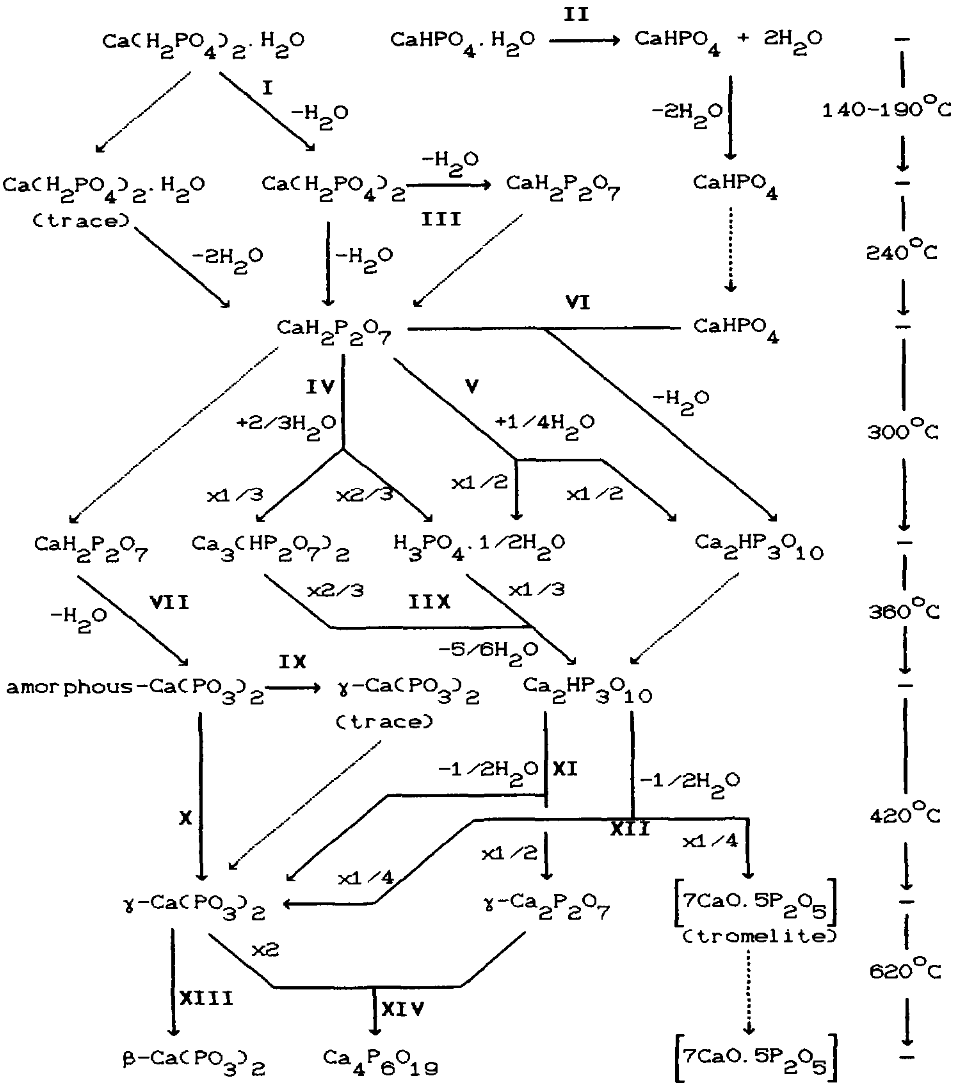

Fig. 4. Reaction pathways for the thermal condensation of equimolecular mixture of $Ca(H_2PO_4)_2 \cdot H_2O$ and $CaHPO_4 \cdot 2H_2O$ up to 620 °C. The reactions are coded using roman numerals, and are referred to by the same numerals in the text.

A similar mechanism for reaction (IV) has also been proposed elsewhere [15].

Reactions (VI) and (IIX) (see Fig. 4) are typical of the build-up of polyphosphates by successive addition of $CaHPO_4$ or $H_3PO_4 \cdot 0.5H_2O$ groups

$$\frac{n+2-2m}{2}Ca(H_2PO_4)_2 \rightarrow Ca_{(n+2-2m)/2}H_{2m}P_nO_{3n+1} + (2-2m)H_3PO_4 + (n-1)H_2O \qquad [0 < m < 1] \qquad (5)$$

$$\mathrm{Ca}_{(n+2-2m)/2}\mathrm{H}_{2m}\mathrm{P}_n\mathrm{O}_{3n+1} + \tfrac{1}{2}\mathrm{Ca(H_2PO_4)_2} \rightarrow \mathrm{Ca}_{(n+3-2m)/2}\mathrm{H}_{2m}\mathrm{P}_{n+1}\mathrm{O}_{3n+4} + \mathrm{H_2O} \tag{6}$$

$$\frac{n+2-2m}{2}\mathrm{Ca(H_2PO_4)_2} + (2m-2)\mathrm{H_3PO_4} \rightarrow \mathrm{Ca}_{(n+2-2m)/2}\mathrm{H}_{2m}\mathrm{P}_n\mathrm{O}_{3n+1} + (n-1)\mathrm{H_2O} \tag{7}$$

Reactions (XI) or (XII) (Fig. 4) are typical routes by which the decomposition of $Ca_2HP_3O_{10}$ can proceed.

$$\mathrm{Ca_2HP_3O_{10}} \rightarrow \tfrac{1}{2}\gamma\text{-}\mathrm{Ca_2P_2O_7} + \gamma\text{-}\mathrm{Ca(PO_3)_2} + \tfrac{1}{2}\mathrm{H_2O} \tag{XI}$$

$$\mathrm{Ca_2HP_3O_{10}} \rightarrow \tfrac{1}{4}[\mathrm{7CaO \cdot 5P_2O_5}] + \tfrac{1}{4}\gamma\text{-}\mathrm{Ca(PO_3)_2} + \tfrac{1}{2}\mathrm{H_2O} \tag{XII}$$

Mechanism (XI) is noted in the scheme [13,16]

$$\mathrm{P_3O_{10}^{5-}} \rightarrow \mathrm{P_2O_7^{4-}} + \mathrm{PO_3^-} \tag{8}$$

In that case, the mechanism is given by the reaction

$$\mathrm{RbMnHP_3O_{10}} \xrightarrow{600\,^\circ\mathrm{C}} \mathrm{RbMnP_2O_7} + \text{amorphous phase (?)} \tag{9}$$

which in our case can be written as

$$\mathrm{2Ca_2HP_3O_{10}} \rightarrow \mathrm{2Ca_2P_2O_7} + \text{amorphous } \mathrm{P_2O_5} + \mathrm{H_2O} \tag{10}$$

$$\mathrm{2Ca_2HP_3O_{10}} + \mathrm{P_2O_5} \rightarrow \mathrm{4Ca(PO_3)_2} + \mathrm{H_2O} \tag{11}$$

whose sum corresponds to reaction (XI). Also in support of the same mechanism is a work in which the synthesis of condensed double cesium manganese phosphate [13] is reported to proceed via the reactions

$$\mathrm{CsMnHP_3O_{10}} \xrightarrow{650\,^\circ\mathrm{C}} \mathrm{CsMnP_2O_7} + [\mathrm{P_2O_5}] + \mathrm{H_2O} \tag{12}$$

$$\mathrm{CsMnHP_3O_{10}} + \mathrm{O_2} \xrightarrow{650\,^\circ\mathrm{C}} \mathrm{CsMnP_3O_9} + \mathrm{CsMn(PO_3)_3} + \mathrm{H_2O} \tag{13}$$

Mechanism (XII) has also been proposed elsewhere [12].

Reaction (XIV) corresponds to the build-up of polyphosphates according to the general scheme [16]

$$\mathrm{P_2O_7^{4-}} + \mathrm{PO_3^-} \rightarrow \mathrm{P_3O_{10}^{5-}} \tag{14}$$

$$\mathrm{P_2O_7^{4-}} + \mathrm{2PO_3^-} \rightarrow \mathrm{P_4O_{13}^{6-}} \tag{15}$$

$$\mathrm{P_2O_7^{4-}} + \mathrm{3PO_3^-} \rightarrow \mathrm{P_5O_{16}^{7-}} \tag{16}$$

$$\mathrm{P_2O_7^{4-}} + \mathrm{4PO_3^-} \rightarrow \mathrm{P_6O_{19}^{8-}} \tag{17}$$

which in our case can be written as

$$\mathrm{Ca_2P_2O_7} + \mathrm{2Ca(PO_3)_2} \rightarrow \mathrm{Ca_4P_6O_{19}} \tag{XIV}$$

Finally, the conversion of calcium metaphosphate from the γ to the β form is well known, and takes place at around 550 °C [1] or 570 °C [2] at a heating rate of 5 °C min^{-1}.

$$\gamma\text{-}\mathrm{Ca(PO_3)_2} \xrightarrow{550\text{–}570\,^\circ\mathrm{C}} \beta\text{-}\mathrm{Ca(PO_3)_2} \tag{XIII}$$

The remaining paths, (X) and (IX), in Fig. 4 correspond to the crystallization of amorphous metaphosphates to the γ form.

In conclusion, upon heating, the system $Ca(H_2PO_4)_2 \cdot H_2O$–$CaHPO_4 \cdot 2H_2O$ appears to lose water in two main steps: about 13% of its weight between 140 and 190 ° C, and about 8% between 240 and 300 ° C, with the remaining 2% loss occurring up to 620 ° C. The products obtained are the result of a number of parallel and consecutive chemical transformations. The first step noted above yields mainly the anhydrous raw materials $Ca(H_2PO_4)_2$ and $CaHPO_4$, as well as $CaH_2P_2O_7$. The second step yields mainly tripolyphosphates, $Ca_2HP_3O_{10}$ and amorphous $Ca(PO_3)_2$. The final products were identified as β-$Ca(PO_3)_2$, $Ca_4P_6O_{10}$, and to a lesser degree, $7CaO \cdot 5P_2O_5$ (tremolite). Intermediate products of degree of polymerization $n = 4$ or 5 were not identified. Finally, an interesting feature of the $CaHPO_4 \cdot 2H_2O$ component of the initial mixture was its non-reversible dehydration at room temperature.

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