

## STUDY OF THE THERMAL DEHYDRATION OF $\text{Zn}_{0.5}\text{Ca}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$

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### ABSTRACT

The dehydration and condensation reactions taking place during calcination of  $\text{Zn}_{0.5}\text{Ca}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  have been followed by means of thermal analyses under quasi-isothermal–isobaric conditions. Isothermal calcination of the starting binary dihydrogen phosphate has been carried out in an electric oven at various temperatures. The reaction products obtained were analysed by chromatography, IR spectroscopy, X-ray diffraction analysis, electron microscopy and atomic absorption spectroscopy. The compositions of the calcination products were determined by extraction with solutions of inorganic compounds and with organic reagents. The effect of water vapour partial pressure has been monitored on the course, rate, and yield of the condensation reactions and on the formation of the main and a further product, the binary cyclotetraphosphate (tetrametaphosphate)  $c\text{-ZnCaP}_4\text{O}_{12}$ .

### INTRODUCTION

Cyclotetraphosphates (tetrametaphosphates) [1] of general formula  $c\text{-M}_2^{\text{II}}\text{P}_4\text{O}_{12}$  ( $\text{M}^{\text{II}}$  being, for example, Zn, Mn, Co, Mg, Cd or Ni) can be prepared by thermal dehydration of the dihydrogen phosphates of bivalent metals. In our laboratory they have been tested as microadditives to fertilizers with long-term action [2,3] and in some cases as special thermostable inorganic pigments (luminescent [4–6], anticorrosive [7–9] or coloured [10,11]). Their synthesis has been studied using the methods of thermal analysis (TA), especially under quasi-isothermal–isobaric conditions (Q-TA) [12–15]. Recently, we have dealt with the preparation of binary cyclotetraphosphates, i.e., of the type where part of the cation of the bivalent (non-ferrous) metal is substituted by the cheaper cation of an alkaline earth metal (Ca or Mg in particular). The cost of the products is thus lower, and their application properties are improved. Such products have not been described in the literature up to the present (nor in the latest literature reviews [16–18]); in fact, doubt has been cast on the possible existence of cyclotetraphosphate-type products containing calcium as one of the cations (including  $c\text{-ZnCaP}_4\text{O}_{12}$ ) [16]. (This follows from the fact that dicalcium

cyclotetraphosphate does not exist [1,16–18]). Our latest work [19–21] goes contrary to this opinion by showing that some binary products of type  $c\text{-M}_{2-x}^{\text{II}}\text{Ca}_x\text{P}_4\text{O}_{12}$  with a limited Ca content ( $x \leq 1$ , as a rule) can be prepared. The starting material for their preparation is a mixture containing calcium compounds and those of the appropriate bivalent metal having volatile anions, together with phosphoric acid. The mixture is treated by a thermal method [22] to give the desired product. In laboratory experiments used to determine the basic conditions of synthesis and to explain the mechanism of dehydration and condensation reactions forming the binary product, it is more useful, however, to start with the binary dihydrogenphosphate in a hydrated form prepared in advance. The present paper gives a survey of the results obtained in the thermal treatment of  $\text{Zn}_{0.5}\text{Ca}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ .

## EXPERIMENTAL

The starting binary dihydrogenphosphate  $\text{Zn}_{0.5}\text{Ca}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  (white or colourless crystals) was prepared in our laboratory by the crystallization of a solution containing  $\text{Zn}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{PO}_4^{3-}$  ions and concentrated

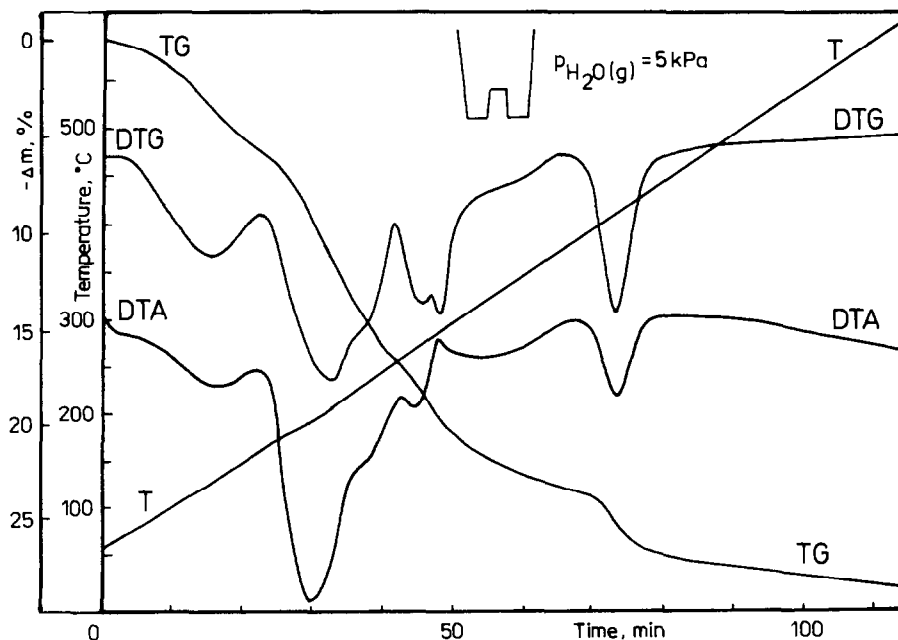


Fig. 1. Simultaneous TG, DTG and DTA curves of  $\text{Zn}_{0.5}\text{Ca}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  under dynamic (non-isothermal) conditions. Apparatus, Derivatograph C; temperature increase,  $5^\circ\text{C min}^{-1}$ ; sample weight, 303.1 mg; sensitivity of TG balance, 100 mg, of DTG balance, 2 and of DTA, 2; open Pt-crucible; standard,  $\alpha\text{-Al}_2\text{O}_3$ ; atmosphere, air.

at 60°C. Its quality was confirmed by analytical atomic absorption spectroscopy (AAS) and X-ray diffraction, and its morphology by electron microscopy.

For elucidation of the mass and energy transformations during calcination, the sample was thermoanalysed by the classical dynamic method (i.e. non-isothermally) using a Derivatograph C apparatus (Hungarian Optical Works, MOM Budapest). The measurement was carried out in an open crucible with a temperature increase of 5°C min<sup>-1</sup>, sample weight 303.1 mg, and sensitivity of thermogravimetry (TG) 100 mg, differential thermal analysis (DTA), 6 and differential TG (DTG) 2. The temperature interval was 40 to 600°C, and the examination was carried out in the presence of air (Fig. 1).

In order to differentiate better between the individual processes taking place during the calcination, and to follow the effect of water vapour on their course, we submitted the starting dihydrogenphosphate to TA under quasi-isothermal–isobaric conditions (Q-TA) [23–25]. The decomposition rate chosen was 0.3 mg min<sup>-1</sup> (calculated for a 100 mg total weight change). Under these conditions, the first measurement was carried out on the Derivatograph C, a labyrinth crucible being used as the sample carrier (Fig. 2) (sample weight 243.45 mg, temperature increase 2°C min<sup>-1</sup>, sensitivity of TG 100 mg, DTG 0.5, and DTA 2). Further measurements were carried out only by thermogravimetry (Q-TG) on the Derivatograph Q-1500 apparatus (MOM Budapest), using four different platinum crucible types as carriers for the thermoanalysed sample (Fig. 3; sample weight ca. 250 mg): a multi-plate sample holder (A), an open crucible (B), a crucible with a lid (C) and a six-component labyrinth crucible (D). The last-mentioned arrangement makes it possible to trap the water vapour released during calcination of the dihydrogenphosphate, its partial pressure being about 100 kPa (quasi-isobaric conditions) [23–25]. In contrast, in the case of the multiplate crucible A, the partial pressure of water vapour in the calcined sample is so low (ca. 1 kPa) that in the course of calcination it can be neglected. The corresponding pressure values with crucibles B and C were 5 and 20 kPa, respectively [23–25].

The conditions determined from the results of thermal analysis were then adopted for the preparation of the main condensation products and intermediates, i.e. by calcination of the starting dihydrogen phosphates in an L 112.2 electric oven (GDR) with controlled temperature increase of 2°C min<sup>-1</sup> (Chinotherm 10A, Chinoi Budapest, Hungary) at various temperatures (in the interval 100–600°C). Each sample was heated for 30 min under isothermal conditions in a flat corundum pan (corresponding to the multi-plate crucible, i.e. 1 kPa) and in a compound of corundum crucibles (corresponding to the labyrinth crucible, i.e. 100 kPa water vapour pressure).

On the basis of the introductory experiments, the calcination products were extracted with organic solvent (acetone), water or a solution of an

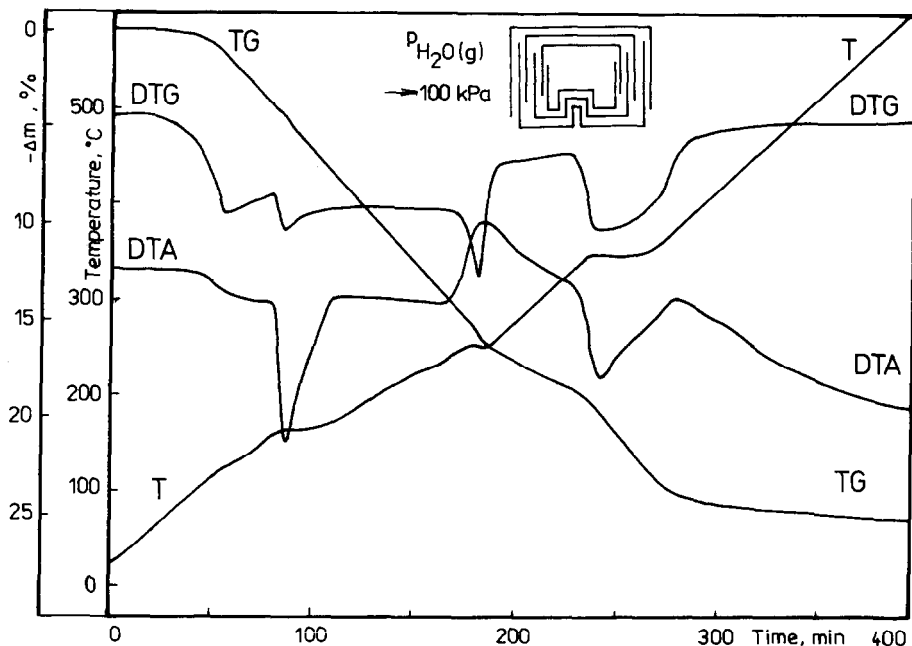


Fig. 2. Simultaneous TG, DTG and DTA curves of  $\text{Zn}_{0.5}\text{Ca}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  under quasi-isothermal, quasi-isobaric conditions. Apparatus, Derivatograph C; decomposition rate,  $0.3 \text{ mg min}^{-1}$ ; temperature increase,  $2^\circ \text{C min}^{-1}$ ; sample weight, 243.35 mg; sensitivity of TG balance, 100 mg, of DTG balance, 0.5, and of DTA balance, 2; standard,  $\alpha\text{-Al}_2\text{O}_3$ ; labyrinth crucible; atmosphere, air.

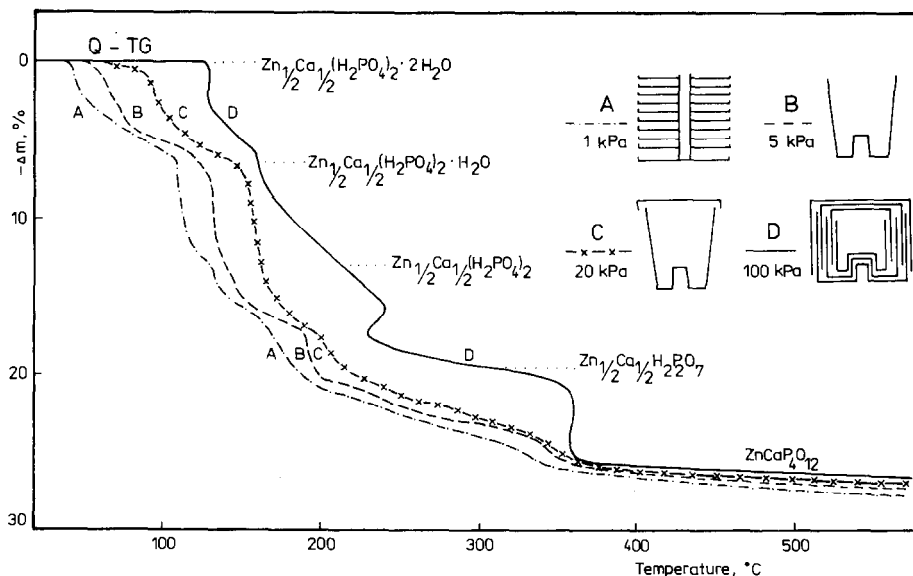


Fig. 3. Thermogravimetric curves of  $\text{Zn}_{0.5}\text{Ca}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  under quasi-isothermal, quasi-isobaric conditions. Apparatus, Derivatograph Q-1500; sample weight, 250 mg; decomposition rate,  $0.3 \text{ mg min}^{-1}$ ; Atmosphere, air. A, Multiplate crucible,  $p_{\text{H}_2\text{O}}(\text{g}) = 1 \text{ kPa}$ ; B, open crucible,  $p_{\text{H}_2\text{O}}(\text{g}) = 5 \text{ kPa}$ ; C, crucible with a lid,  $p_{\text{H}_2\text{O}}(\text{g}) = 20 \text{ kPa}$ ; D, labyrinth crucible,  $p_{\text{H}_2\text{O}}(\text{g}) = 100 \text{ kPa}$ .

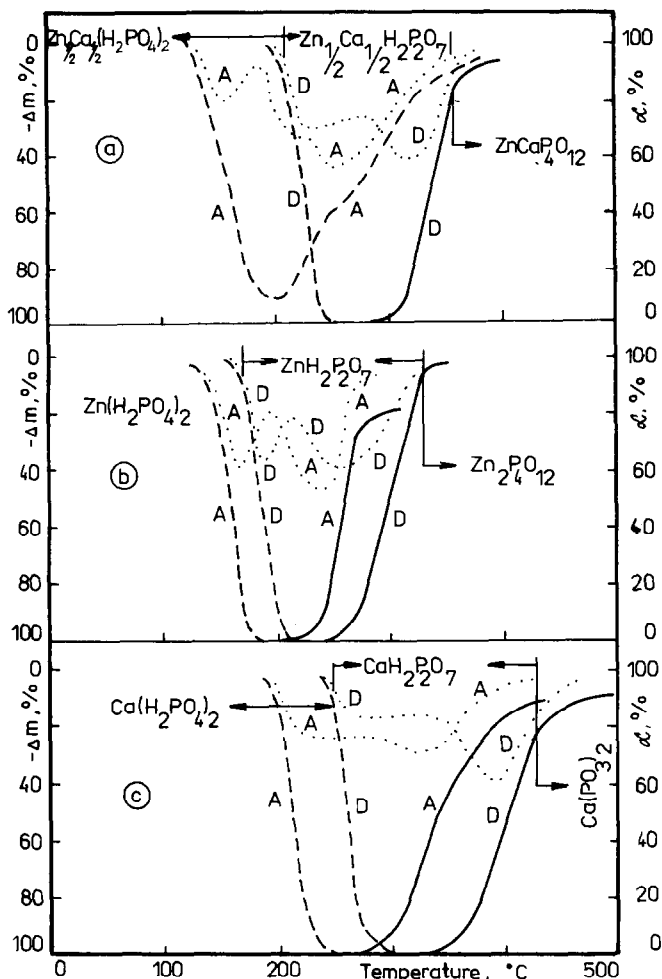


Fig. 4. Extraction experiments on calcinates of  $\text{Zn}_{0.5}\text{Ca}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Zn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ . Calcination conditions,  $2^\circ\text{C min}^{-1}$ ;  $p_{\text{H}_2\text{O}}(\text{g})$  1 kPa (A) or 100 kPa (D). Weight changes determined by extraction: acetone (.....); water (---); 0.3 M HCl (—) (degree of conversion ( $\alpha$ ) with respect to the cyclotetraphosphates).

inorganic compound (0.3 M HCl) [26] (Fig. 4). The extraction experiments allowed the investigation of the formation and existence of various intermediates, especially dihydrogendiphosphate, and the formation of the main product cyclotetraphosphate.

The extraction of the phosphorus component (in the form of phosphoric acid or diphosphoric acid from the dihydrogendiphosphate formed) by acetone is expressed by the weight decrease after extraction of the calcinate and as the  $\text{P}_2\text{O}_5$  portion of the total amount in the calcinate. The calcinates were then extracted with water, as the intermediate dihydrogendiphosphate  $\text{Zn}_{0.5}\text{Ca}_{0.5}\text{H}_2\text{P}_2\text{O}_7$  is water soluble. The samples calcined above  $120^\circ\text{C}$  were extracted with 0.3 M HCl, only the final product  $c\text{-ZnCaP}_4\text{O}_{12}$  (or  $c\text{-}$

$\text{Zn}_2\text{P}_4\text{O}_{12}$  and  $\text{Ca}(\text{PO}_3)_2$ ) being insoluble, to determine the conversion degree of  $\text{Zn}_{0.5}\text{Ca}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  into  $c\text{-ZnCaP}_4\text{O}_{12}$  (or  $c\text{-Zn}_2\text{P}_4\text{O}_{12}$  and  $\text{Ca}(\text{PO}_3)_2$ ).

The starting phosphate and these calcination products were analysed and individual products formed in the thermal analysis under quasi-isothermal–isobaric conditions were identified by means of TLC [27,28], IR spectroscopy [29] (Perkin Elmer 684 IR spectrometer), X-ray diffraction analysis [30,31] (HZG-4 apparatus, G.D.R.) and electron microscopy (Tesla BS 300, Czechoslovakia). The solid residues from each of the extraction experiments were also analysed by the above-mentioned instrumental methods. On boiling with dilute (1:1) hydrochloric acid the residues were dissolved, and the  $\text{Me}^{\text{II}}\text{O}/\text{P}_2\text{O}_5$  ratios were determined by AAS [32].

## RESULTS AND DISCUSSION

### *Thermal analysis of $\text{Zn}_{0.5}\text{Ca}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ under dynamic conditions*

It is evident from the thermoanalytical curves of the starting dihydrate of the binary zinc–calcium dihydrogenphosphate (Fig. 1), taken under dynamic conditions with the use of an open crucible, that altogether six endothermal processes take place. They are always connected with mass losses, whose sum (up to a TA temperature of  $600^\circ\text{C}$ ) equals 28.7% of the original mass of the thermoanalysed sample. After the last (sixth) endothermal process was complete, the total mass loss was about 26%; this agrees accurately with the liberation of all four water molecules (two of water of crystallization and two of constitutional water) from the starting dihydrogenphosphate (theoretical mass loss 25.17%). The first molecule of water of crystallization is released in the endothermal process over the temperature interval  $70\text{--}150^\circ\text{C}$ . The second water of crystallization molecule is liberated during the most significant endothermal process in the range  $150\text{--}210^\circ\text{C}$ . The first molecule of constitutional water is evidently released in two equivalent parts under these conditions: the first part in the interval  $210\text{--}245^\circ\text{C}$ , and the second one at  $245\text{--}270^\circ\text{C}$ ; such liberation is accompanied by two smaller endothermal effects. The release of the second constitutional water molecule can also be considered under these TA conditions in two equivalent parts: the first in the interval  $270\text{--}365^\circ\text{C}$  and the second at  $365\text{--}460^\circ\text{C}$ ; the release of the first part is accompanied by a small endothermal process, and that of the second by a more pronounced endothermal process.

### *Thermal analysis of $\text{Zn}_{0.5}\text{Ca}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ under quasi-isothermal–isobaric conditions*

Figure 2 presents as examples individual thermoanalytical curves obtained by Q-TA using the Derivatograph C apparatus. A labyrinth crucible

was used as the sample carrier so that the vapour pressure in the sample area approached the surrounding atmospheric pressure, i.e. 100 kPa. The curves show that, in this instance, liberation of the four water molecules from the starting phosphate takes place in the four temperature intervals 130–165 °C, 165–225 °C, 225–350 °C and 350–400 °C; the first, second and fourth of these processes are endothermally significant. It was interesting to find that a notable exothermal effect appears within the third temperature interval (255–350 °C), in which a perceptible dip on the temperature curve occurs at 225 °C. This can be explained by the way in which, within the release of water of crystallization, the sample first melts in its own water (confirmed with a high-temperature microscope), losing its crystalline nature. After reaching a certain degree of dehydration (the release of two water of crystallization molecules and about a third of the constitutional water molecule), crystallization of the sample takes place, which is an exothermal process. The heat generated by this action will speed up the process of release of the first constitutional water molecule, which causes a discontinuity in the TG curve close to the temperature of 255 °C. This break, representing a sharper mass decrease than hitherto, causes the temperature in the Derivatograph oven to stop rising (or even to drop slightly) as the apparatus tends to bring the decomposition rate back to the originally set  $0.3 \text{ mg min}^{-1}$ . The mass loss at the temperature when the last endothermal process is finished (400 °C) equals 25.1%, which is in good correlation with the release of four water molecules from the starting  $\text{Zn}_{0.5}\text{Ca}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ .

Only the thermal analyses under quasi-isothermal–isobaric conditions on the Derivatograph Q-1500 apparatus, using four different crucibles as sample carriers (Fig. 3), have given a more concrete conception of individual processes taking place in the course of calcining the starting  $\text{Zn}_{0.5}\text{Ca}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ . These analyses allowed the two principal reaction mechanisms to be defined, which are closely connected with water vapour pressure within the space of the calcined sample. The first of these holds for vapour pressures approaching 100 kPa (corresponding to the use of a labyrinth crucible as carrier for the thermoanalysed sample); however, the second mechanism is preferred if the vapour pressure is very low or negligible (multi-plate crucible). The former mechanism alone leads to the desired product of binary zinc–calcium cyclotetraphosphate. In the latter case the products are mainly of non-binary type.

*Labyrinth crucible:  $p\text{H}_2\text{O} (g)$  ca. 100 kPa*

When using a labyrinth crucible as the sample carrier (Fig. 3, curve D), the water of crystallization of the starting  $\text{Zn}_{0.5}\text{Ca}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  liberated first corresponds to one  $\text{H}_2\text{O}$  molecule. This stage takes place in the temperature interval 130–160 °C, when a part of this water (about one third) is isothermally released at 130 °C. (This corresponds to the tempera-

ture at which the liberation of water of crystallization from the single zinc dihydrogenphosphate,  $\text{Zn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ , starts under the equivalent isothermal conditions [33].) Liberation of the second molecule of water of crystallization from the starting binary zinc–calcium dihydrogenphosphate then starts in the temperature interval 160–210 °C. (This agrees exactly with the temperatures of release of water of crystallization under corresponding isothermal–isobaric conditions from the single dihydrogenphosphates, both that of zinc,  $\text{Zn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  [33] and that of calcium,  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  [34].) These first two, clearly dehydration, processes consequently lead to intermediate products of anhydride type. They still have a binary nature under conditions of water vapour pressures approaching 100 kPa. X-ray analysis has confirmed that they are not mixtures of two or more substances.

The next process, which corresponds to release of the first molecule of constitutional water and is also connected with the first condensation reaction (forming the binary dihydrogendiphosphate), takes place within the temperature interval 210–330 °C. In this process, a significant break in the TG curve occurs at a temperature of 230–240 °C, which is connected with the above mentioned and explained crystallization of the thermoanalysed sample within this temperature zone. The temperature interval of formation of the binary dihydrogendiphosphate is slightly shifted to higher temperatures as compared with the temperature intervals determined for the corresponding processes (forming dihydrogendiphosphates) under equivalent conditions the calcination of simple dihydrogenphosphates,  $\text{Zn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  (170–250 °C) [33] and  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  (195–250 °C) [34]. The formation and existence of the binary dihydrogendiphosphate in calcinates prepared in an electric oven under corresponding conditions (temperature and water vapour pressure) have been proved (by means of instrumental analytical methods (IMA) and extraction experiments; see Fig. 4) within a temperature interval practically identical with that in Q-TA. The increased portion of calcinate extractable by acetone in the temperature interval 200–300 °C provides evidence for this (Fig. 4a). For comparison, calcinates were prepared and analysed starting from single dihydrogenphosphates (Figs. 4b and 4c). In the case of zinc dihydrogenphosphate, the interval is slightly shifted to lower temperatures (190–280 °C). In the case of calcium dihydrogenphosphate the temperature interval of the intermediate  $\text{CaH}_2\text{P}_2\text{O}_7$  formation and existence is shifted to even higher temperatures (250–375 °C). Comparison of these intervals with the above-given interval for  $\text{Zn}_{0.5}\text{Ca}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  calcination provides some verification that the intermediate product formed is also a binary type— $\text{Zn}_{0.5}\text{Ca}_{0.5}\text{H}_2\text{P}_2\text{O}_7$ —and not a mixture of  $\text{ZnH}_2\text{P}_2\text{O}_7$  and  $\text{CaH}_2\text{P}_2\text{O}_7$ . The results of electron microscopic observation (both of the calcinates and their extraction residues) and of IR spectroscopy provide proof.

The last-observed Q-TA process, the release of the second molecule of constitutional water connected with the second condensation reaction (for-



ming cyclotetraphosphate), takes place in a labyrinth crucible (i.e. at a water vapour pressure near 100 kPa) in the temperature interval 330–400 °C; the main part of the reaction (more than 80%) then occurs in a relatively narrow interval, 360–370 °C. The product obtained under these conditions is explicitly binary zinc–calcium cyclotetraphosphate,  $c\text{-ZnCaP}_4\text{O}_{12}$  (confirmed by IMA methods). This product is a new compound which has not until now been mentioned in the literature, and for that reason has been the subject of our Czech patent [35]. We determined its crystal structure as being monoclinic, group  $C/2c$ , with structural parameters  $a = 1.2195$  nm,  $b = 0.8448$  nm,  $c = 1.0148$  nm,  $\beta = 118.36^\circ$ , elementary cell volume  $V = 0.9200$  nm<sup>3</sup> and density 3.05 g cm<sup>-3</sup> ( $\rho$  calculated) or 3.042 g cm<sup>-3</sup> ( $\rho$  experimental). When comparing the temperature zones for formation of the binary  $c\text{-ZnCaP}_4\text{O}_{12}$  product recorded in Q-TA with those of the corresponding single products  $c\text{-Zn}_2\text{P}_4\text{O}_{12}$  and  $\text{Ca}(\text{PO}_3)_2$  under equivalent conditions, it can be seen that they differ: the zinc product is formed at lower temperatures (ca. 300 °C) [33], while the calcium product is formed mostly at temperatures around 400 °C [34]. This conclusion about the calcinates was confirmed by extraction experiments carried out with 0.3 M HCl (Fig. 4). In the calcination of different starting dihydrogenphosphates [ $\text{Zn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  or  $\text{Zn}_{0.5}\text{Ca}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ ] at vapour pressures near 100 kPa, the first portions of the final products [cyclotetraphosphates or  $\text{Ca}(\text{PO}_3)_2$ ] can be obtained above temperatures of 250 °C (Zn), 290 °C (Zn–Ca) and 370 °C (Ca). The major portion of calcinate reacted to give the final product at 325 °C (Zn), 350 °C (Zn–Ca) and 430 °C (Ca). The final (stabilized) extent of reaction for individual calcinates as determined under these conditions was ca. 97%  $c\text{-Zn}_2\text{P}_4\text{O}_{12}$  (at 350 °C), ca. 93%  $c\text{-ZnCaP}_4\text{O}_{12}$  (at 400 °C) and ca. 90%  $\text{Ca}(\text{PO}_3)_2$  (at 475 °C).

*Multi-plate crucible:  $p\text{H}_2\text{O}$  (g) ca. 1 kPa*

When using a multi-plate crucible as carrier for the thermoanalysed sample (Fig. 3, curve A), water of crystallization is again liberated first from the starting  $\text{Zn}_{0.5}\text{Ca}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ . The amount corresponding to the first molecule of water of crystallization is released in the temperature interval 60–110 °C. A further amount corresponding to the second water of crystallization molecule is then released in a relatively narrow temperature interval, 110–130 °C. Comparison with earlier work [33,34] and with the results of both extraction experiments (Fig. 4) and IMA method analyses shows that the calcination product at this stage comprises a mixture of dihydrogenphosphate anhydrides with products obtained by their decomposition (splitting); i.e. lower hydrogenphosphate hydrates [ $\text{M}^{\text{II}}\text{HPO}_4 \cdot x\text{H}_2\text{O}$ ;  $\text{M}^{\text{II}} = \text{Zn}$  or  $\text{Ca}$ ] and phosphoric acid; lower hydrates are next dehydrated [36] and phosphoric acid condenses separately to diphosphoric acid and later to higher polyphosphoric acids.

The next process, corresponding to the release of the next water molecule (which this time is constitutional water) takes place within the interval 130–190 °C. For the greater part, zinc dihydrogendiphosphate,  $\text{ZnH}_2\text{P}_2\text{O}_7$ , is formed from the zinc component of the calcinate, and  $\text{CaH}_2\text{P}_2\text{O}_7$  from the calcium component. The given temperature interval for forming the zinc intermediate product under these conditions accords exactly with that in ref. 33.

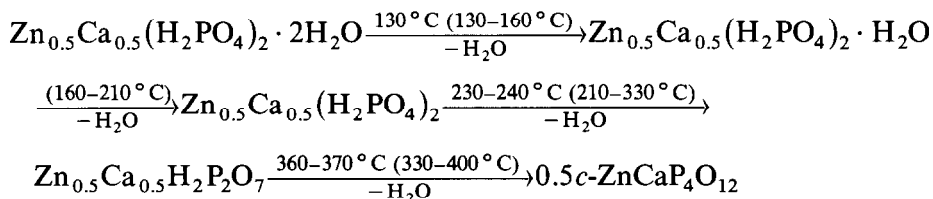
With further temperature rise above 190 °C, the zinc and calcium dihydrogenphosphates condense separately to form the final by-products  $c\text{-Zn}_2\text{P}_4\text{O}_{12}$  and  $\text{Ca}(\text{PO}_3)_2$  [33,34]. The part of the calcinate corresponding to binary zinc–calcium dihydrogenphosphate then condenses to form the main final product, binary zinc–calcium cyclotetraphosphate, which makes up only the smaller part of the calcinate. However, these processes are complicated by a separate condensation of the cleaved phosphoric acid to form higher phosphoric acids,  $\text{H}_{n+2}\text{P}_n\text{O}_{3n+1}$ , and by a partial rise in content of diphosphates ( $\text{Ca}_2\text{P}_2\text{O}_7$  and  $\text{Zn}_2\text{P}_2\text{O}_7$ ). This fact can even lead to formation of ultraphosphates to a small extent. A steady but slight decrease in the sample mass to below that for the total theoretical amount of water [contained in the starting  $\text{Zn}_{0.5}\text{Ca}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ ] at temperatures above 450 °C can be explained thus. Extraction experiments (Fig. 4) and IMA analyses of calcinates have proved that calcination leads to formation of the binary product  $c\text{-ZnCaP}_4\text{O}_{12}$  to only a small degree under these conditions (water vapour pressure negligible). The last-named product was present at about 15% at 500 °C, while the main portion was made up by  $c\text{-Zn}_2\text{P}_4\text{O}_{12}$  and  $\text{Ca}(\text{PO}_3)_2$ . These also form a substantial part of the insoluble portion determined by extraction experiments (with 0.3 M HCl), making ca. 70% of the calcinate in total.

#### *Using other crucible types*

Thermal analyses under quasi-isothermal–isobaric conditions using two other crucible types as sample carriers, the open crucible (with a water vapour pressure about 5 kPa) and a crucible with a lid (20 kPa), gave thermogravimetric curves B and C in Fig. 3. The curves cannot provide such an explicit account for reaction mechanisms as the above-described curves A and D. At vapour pressures around 5 kPa the mechanism of dehydration and condensation reactions approaches closer to that with the multi-plate crucible (water vapour pressure 1 kPa). Comparing curves A and B, the temperatures of individual processes do not differ by more than 20 °C in the most part. The content of the final binary cyclotetraphosphate,  $c\text{-ZnCaP}_4\text{O}_{12}$ , in the calcinate after the TA is ca. 25%. At a vapour pressure of 20 kPa, the reaction mechanisms lie somewhere in the middle between those described for the labyrinth crucible (100 kPa) and for the multi-plate crucible (1 kPa), the yield of the main product,  $c\text{-ZnCaP}_4\text{O}_{12}$ , being 40%.

## CONCLUSION

The course and conditions of the calcination of the starting  $\text{Zn}_{0.5}\text{Ca}_{0.5}\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  at water vapour pressure approaching 100 kPa in the sample region can be expressed by the following scheme (with the temperature intervals of individual processes given in parentheses and the temperatures of the specific part of each process given before the parentheses).



In this way [27] binary zinc-calcium cyclotetraphosphate,  $c\text{-ZnCaP}_4\text{O}_{12}$  (with yield ca. 93% w/w), can be prepared, which appears to be a prospective special pigment [38].

If calcination is carried out at lower water vapour pressures, the temperatures of the individual processes decrease, and some of the intermediate products split to form other intermediates, which condense separately. The portion of the main product,  $c\text{-ZnCaP}_4\text{O}_{12}$ , in the final calcination residue can fall to 15% (at water vapour pressures approaching 1 kPa). The final by-products are  $c\text{-Zn}_2\text{P}_4\text{O}_{12}$  and  $\text{Ca}(\text{PO}_3)_2$ , which can, however, constitute the major part of the calcinate at low vapour pressure. Higher phosphoric acids, diphosphates and, eventually, products with ultraphosphate-type anions can form as well to a lesser extent.

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