

A STUDY OF THE THERMAL PREPARATION OF $c\text{-Cd}_{4/3}\text{Ca}_{2/3}\text{P}_4\text{O}_{12}$

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ABSTRACT

The possibility of preparing binary cadmium-calcium cyclotetraphosphate (tetrametaphosphate) by means of thermal dehydration of the appropriate binary dihydrogen phosphate has been studied. The possible formation of this condensation product from the cadmium ions that are often present in the starting phosphoric compound used in the technological preparation of binary calcium cyclotetraphosphates (serving as new special pigments) would represent an important, hygienic method of binding them to an insoluble, less harmful cadmium compound. The maximum proportion of calcium in the binary product, as found by the authors of this paper, amounts to half of the cadmium constituent (in molar terms). That is why $\text{Cd}_{2/3}\text{Ca}_{1/3}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ was used as the starting material. Its dehydration was observed mainly by thermal analytical methods under quasi-isothermal-isobaric conditions. Isothermal calcination of the initial binary dihydrogenphosphate was 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 AAS. The compositions of the calcinates were determined through extraction with solutions of inorganic compounds and with organic reagents.

INTRODUCTION

Cyclotetraphosphates (tetrametaphosphates) [1] of the common formula $c\text{-Me}_2(\text{II})\text{P}_4\text{O}_{12}$ (Me being, for example, Zn, Mn, Co, Mg, Cd or Ni) can be prepared by thermal dehydration of the dihydrogenphosphates of bivalent metals. In our laboratory they have been tested as microadditives to fertilizers with long-term action [2,3], and some of them are thermostable inorganic pigments, exceptional for their luminescence [4–6], anti-corrosive properties [7–9] or colour [9–11]. Their synthesis can be studied using the methods of thermal analysis (TA), mainly under quasi-isothermal-isobaric conditions (Q-TA) [12–15]. Recently, we have been attempting to prepare binary cyclotetraphosphates, i.e. those in which a proportion of the cation of a bivalent metal (non-ferrous) is substituted with cheaper cations of alkaline earth metals (mainly Ca and Mg). In this way, the price of the products is lowered and their possible applications become increased. Until now, such products have not been described, even in the latest reviews. Predictions

concerning the possible existence of cyclotetraphosphate-type products containing calcium as one of the cations have been considered dubious [16]: this is due to the fact that dicalcium cyclotetraphosphate does not exist [1,16–18]. Our latest work [19–21] has altered this opinion by showing that some binary products of $c\text{-Me}_{2-x}(\text{II})\text{Ca}_x\text{P}_4\text{O}_{12}$ with a limited Ca content (as a rule $x \leq 1$) can be prepared. The starting material for their preparation is a suitable mixture containing compounds of calcium and of the appropriate bivalent metal with volatile anions, together with phosphoric acid. The mixture is converted to the desired product using a thermal method [22]. It should be noted that the phosphoric acid used in technological processes will often contain cadmium at levels which constitute a health risk. The problem is to determine the behaviour of the cadmium ions when the starting mixture is converted to binary calcium cyclotetraphosphate using thermal methods. The possible formation of a binary cadmium-calcium product, such as an insoluble cyclotetraphosphate, would be a useful means of their elimination. This resulting product would then be included in the major binary products, of $\text{M}_{2-x}(\text{II})\text{Ca}_x\text{P}_4\text{O}_{12}$ -type ($\text{M}(\text{II}) \equiv \text{Zn}, \text{Mn}$ or Co), and could be left there as it is insoluble in the matrix, yielding a harmless mixture. Our recent paper [23] has shown that the maximum possible calcium content in the binary cadmium-calcium cyclotetraphosphate equals one-half of the cadmium ions. In the above-mentioned synthesis of binary calcium cyclotetraphosphates with other bivalent metals, however, an excess of calcium ions over cadmium ions will always occur. Therefore, in this sense $c\text{-Cd}_{4/3}\text{Ca}_{2/3}\text{P}_4\text{O}_{12}$ will be a so-called boundary product. The present paper considers its preparation by a thermal method. In the laboratory experiments used to determine the basic conditions of the synthesis and to explain the mechanism of the dehydration and condensation reactions forming the cyclotetraphosphate-type binary product, it is, however, preferable to begin with previously prepared binary dihydrogenphosphate in the hydrated form. This paper presents a survey of the results obtained in the thermal treatment of $\text{Cd}_{2/3}\text{Ca}_{1/3}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$.

EXPERIMENTAL

The starting material, binary dihydrogenphosphate $\text{Cd}_{2/3}\text{Ca}_{1/3}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (white or colourless crystals), was prepared in our laboratory by crystallisation of a solution containing Cd^{2+} , Ca^{2+} and PO_4^{3-} ions in stoichiometric quantities, condensed at 60°C . Its quality was confirmed by AAS and X-ray diffraction analyses; its morphology was verified by electron microscopy.

To elucidate the mass and energy transformations during calcination, a $\text{Cd}_{2/3}\text{Ca}_{1/3}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ sample was thermoanalysed under quasi-isothermal–isobaric conditions (Q-TA) [24–26] using a Derivatograph C apparatus (Hungarian Optical Works, MOM Budapest). The measurement was

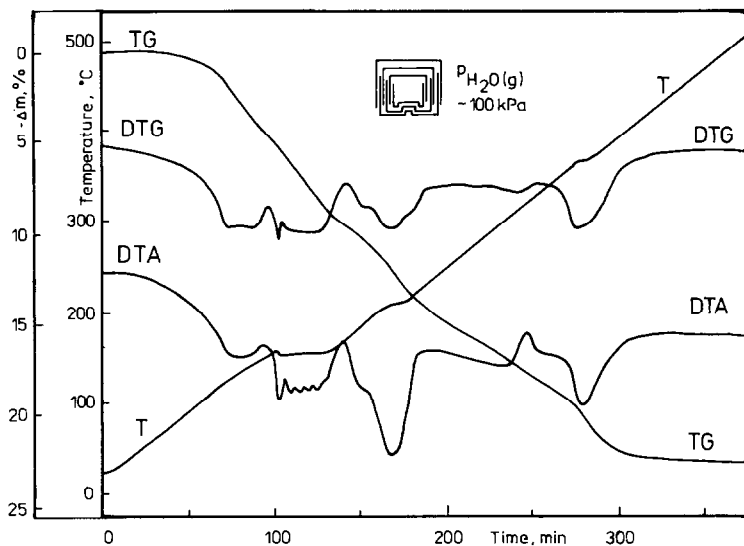


Fig. 1. Simultaneous TG, DTG and DTA curves for $\text{Cd}_{2/3}\text{Ca}_{1/3}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ under quasi-isothermal–quasi-isobaric conditions, Apparatus, Derivatograph C; decomposition rate, 0.2 mg min^{-1} ; heating rate, $1.5^\circ\text{C min}^{-1}$; sample weight, 141.4 mg. Sensitivity of the balances: TG, 100 mg; DTA, 2; DTG, 0.5. Labyrinth crucible, $p_{\text{H}_2\text{O}(\text{g})} = 100 \text{ kPa}$; standard $\alpha\text{-Al}_2\text{O}_3$; atmosphere, air.

carried out in a labyrinth crucible with a temperature increase of $1.5^\circ\text{C min}^{-1}$, a sample weight of 141.4 mg, a decomposition rate of 0.2 mg min^{-1} , a TG sensitivity of 100 mg, a DTA sensitivity of 2, a DTG sensitivity of 0.5 and in a temperature interval from 25 to 500°C ; the examination was performed in the presence of air (Fig. 1).

In order to better separate the individual processes taking place during the calcination and to follow the effect of water vapour on their course, the starting dihydrogenphosphate was investigated by Q-TA using a Derivatograph Q-1500 apparatus (MOM Budapest), with four different types of platinum crucible being used to contain the thermoanalysed sample (Fig. 2): a multi-plate sample holder (curve A), an open crucible (B), a crucible with a lid (C) and a six-component labyrinth crucible (D). This last arrangement makes it possible to trap the water vapour released during calcination of the starting dihydrogenphosphate, its partial pressure being about 100 kPa. In contrast, in the case of the multi-plate crucible, A, the partial pressure of water vapour in the calcinated sample is so low (about 1 kPa) that it can be neglected. The corresponding pressure values of crucibles B and C were 5 and 20 kPa, respectively [24–26]. The decomposition rate chosen was 0.2 mg min^{-1} (calculated for a 100 mg total weight change) with a sample weight of about 250 mg.

The conditions determined from the results of the thermal analyses were then adopted for preparation of the main condensation products and

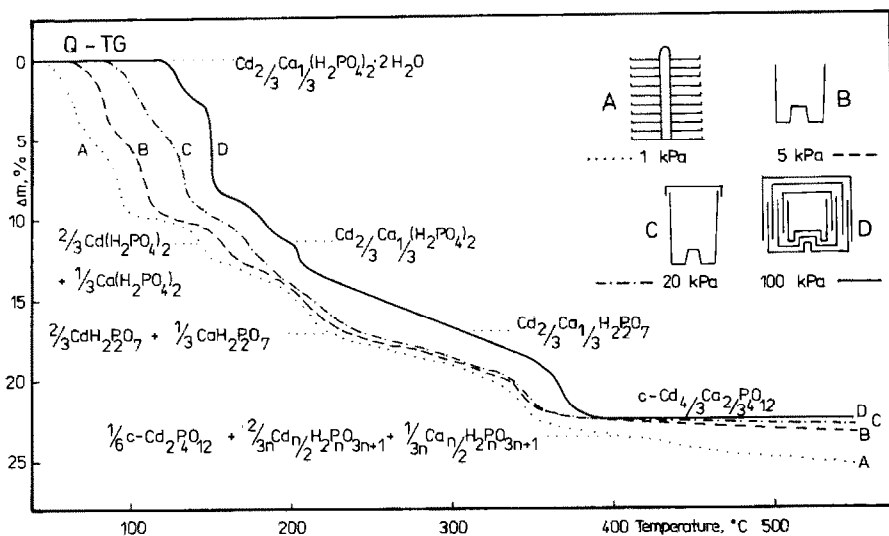


Fig. 2. Thermogravimetric curves of $\text{Cd}_{2/3}\text{Ca}_{1/3}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ under quasi-isothermal, quasi-isobaric conditions; Apparatus, Derivatograph Q-1500; decomposition rate 0.2 mg min^{-1} ; sample weight, 250 mg; atmosphere, air. A, Multiplate crucible, $p_{\text{H}_2\text{O}}(\text{g}) = 1 \text{ kPa}$; 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, $p_{\text{H}_2\text{O}}(\text{g}) = 100 \text{ kPa}$.

intermediates, i.e. by calcination of the starting dihydrogenphosphates in an electric oven (L 112.2 (GDR)) with a controlled temperature rise of $2^\circ \text{C min}^{-1}$ (Chinotherm 10A, Chinoin, Budapest) at various temperatures in the range $100\text{--}600^\circ \text{C}$. Each sample was heated for 30 min at isothermal conditions in a flat corundum pan which corresponds to the multi-plate crucible, i.e. 1 kPa, and in a set of corundum crucibles corresponding to the labyrinth crucible, i.e. 100 kPa water-vapour pressure.

Using information obtained from the introductory experiments, the calcinates were extracted with some organic solvents (acetone), water and solutions of inorganic compounds (0.3 M HCl) [27] (Fig. 3). The extraction experiments made possible the investigation of the formation and existence of various intermediates, especially dihydrogendiphosphate, and the formation of the main product, cyclotetraphosphate. The phosphorus extracted in acetone (in the form of phosphoric acid or diphosphoric acid) from the dihydrogendiphosphate formed, is expressed as the weight decrease after extraction of the calcinate and as the fraction of P_2O_5 relative to the total in the calcinate. Then, the calcinates were extracted with water as the dihydrogendiphosphate intermediate, $\text{Cd}_{2/3}\text{Ca}_{1/3}\text{H}_2\text{P}_2\text{O}_7$, is water soluble. The calcinate samples were then extracted with 0.3 M HCl only, because the final products $c\text{-Cd}_{4/3}\text{Ca}_{2/3}\text{P}_4\text{O}_{12}$ (or $c\text{-Cd}_2\text{P}_4\text{O}_{12}$ and $\text{Ca}_{n/2}\text{H}_2\text{P}_n\text{O}_{3n+1}$), are insoluble.

The starting phosphate and these calcinates were analysed, and the

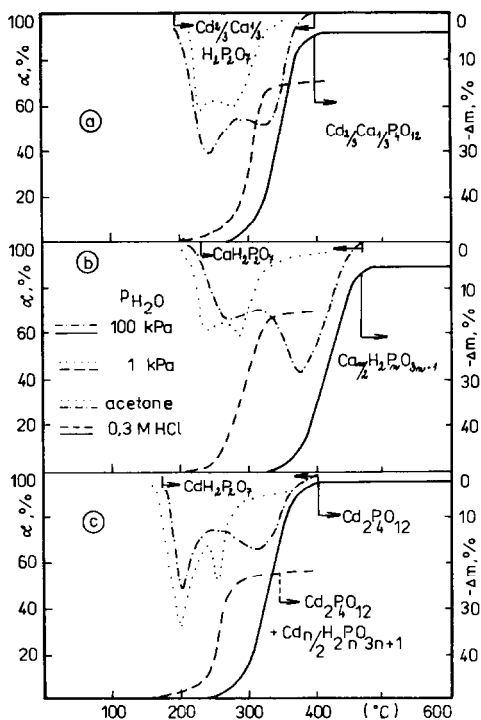


Fig. 3. Extraction experiments on calcinates of $\text{Cd}_{2/3}\text{Ca}_{1/3}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (a), $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ (b) and $\text{Cd}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (c). Calcination conditions: $2^\circ \text{C min}^{-1}$; $p_{\text{H}_2\text{O}(\text{g})} = 1 \text{ kPa}$ (in crucible A) (\cdots and $---$), 100 kPa (in crucible D) ($---$ and $---$). Weight changes determined by extraction using acetone (\cdots and $---$) or 0.3 M HCl ($---$ and $---$) (α , degree of conversion to the cyclotetraphosphates).

individual products prepared in the thermal analysis under quasi-isothermal-isobaric conditions were identified by means of TLC [28,29], IR spectroscopy [30] (Perkin-Elmer 684 IR spectrometer), X-ray diffraction analysis [31,32] (HZG-4 apparatus, G.D.R.) and electron microscopy (Tesla BS 300 C.S.S.R.). The solid residues from each extraction experiment were also analysed by the above instrumental methods. The residues were dissolved by boiling with dilute (1 : 1) hydrochloric acid and the $\text{Me}(\text{II})\text{O}/\text{P}_2\text{O}_5$ ratios were determined by atomic absorption spectrometry [33].

RESULTS AND DISCUSSION

Individual thermoanalytical curves obtained with the Derivatograph C apparatus are plotted in Fig. 1. Because the labyrinth crucible was used as sample carrier, the vapour pressure in the space area approached that of the surrounding atmosphere, i.e. 100 kPa . The curves show that, with these conditions, the release of four water molecules from the starting phosphate

(two of water of crystallisation and two of constitutional water) takes place in five temperature intervals: 125–150 °C, 150–167 °C, 167–205 °C, 205–305 °C and 305–395 °C. All have an explicit endothermic nature, although it is interesting that a perceptible exothermic effect appears at the beginning of the last temperature interval (305–395 °C). This can only be ascribed to the crystallisation of the amorphous intermediate product, $\text{Cd}_{2/3}\text{Ca}_{1/3}\text{H}_2\text{P}_2\text{O}_7$ (which will be discussed later). The total mass loss of the sample is 22.75% at the final temperature of the last endothermic process, which is in exact accordance with the release of four water molecules from the initial $\text{Cd}_{2/3}\text{Ca}_{1/3}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$. The five separate processes correspond exactly to the release of 0.5, 1, 0.5, 1 and 1 water molecule, respectively.

A more concrete conception of the course of the individual processes taking place in the calcination of the initial $\text{Cd}_{2/3}\text{Ca}_{1/3}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ was obtained by means of thermogravimetric analyses under quasi-isothermal-isobaric conditions (Q-TA) with the use of four different crucible types as sample carriers (Fig. 2). This revealed two basic reaction mechanisms, closely connected with the water-vapour pressure in the area of the calcined sample. The first mechanism is for vapour pressures approaching 100 kPa, corresponding to the use of the labyrinth crucible; the second, in contrast, is the preferred mechanism when the vapour pressure is very low, nearly negligible, as with the multi-plate crucible. Only the first mechanism (100 kPa) leads to the desired product, binary cadmium-calcium cyclo-tetraphosphate. In the other case, products of a non-binary nature are mostly formed.

Labyrinth crucible ($p\text{H}_2\text{O}(\text{g}) \sim 100 \text{ kPa}$)

With the labyrinth crucible as sample holder (Fig. 2, curve D), the first weight loss is water of crystallisation corresponding to half a molecule of H_2O being released from the initial $\text{Cd}_{2/3}\text{Ca}_{1/3}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ in the temperature interval 125–150 °C. This corresponds to the temperature at which most of the water of crystallisation is released from the simple cadmium dihydrogenphosphate, $\text{Cd}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ in the same isothermal conditions [34]. The remaining water of crystallisation binary cadmium-calcium dihydrogenphosphate is lost in two processes in the temperature intervals 150–167 °C and 167–205 °C: the first represents the release of one whole molecule and is explicitly isothermal (nearly 90% of this water of crystallisation is liberated at 150 °C); the second process is the loss of the rest of the water of crystallisation, half a molecule. This agrees with the temperatures of the release of all the water of crystallisation from the corresponding simple dihydrogenphosphates, that of cadmium $\text{Cd}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ [34] and of calcium $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ [35], at equal isothermal and isobaric conditions. These dehydrating processes lead to an intermediate product of anhydride type, $\text{Cd}_{2/3}\text{Ca}_{1/3}(\text{H}_2\text{PO}_4)_2$, which, in conditions where

the water-vapour pressure approaches 100 kPa, is still binary in nature (the X-ray diffraction analysis confirmed that it was not a mixture of two or more substances).

The next process, taking place in the 205–305 °C range, corresponds to the release of the first molecule of constitutional water and is associated with the first condensation reaction to form binary dihydrogendiphosphate. About a third of this process occurs practically isothermally at 205 °C. (The temperature interval for the formation of binary dihydrogendiphosphate is in good agreement with the temperature intervals determined with the same conditions for the corresponding processes forming dihydrogendiphosphates in the calcination of simple dihydrogenphosphates: $\text{Cd}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, 175–215 °C [34]; and $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, 195–250 °C [35]).

The formation and existence of binary dihydrogendiphosphate in the calcinates prepared in corresponding conditions in the electric oven was confirmed as occurring within practically the same temperature interval as in Q-TA. A further proof is the increased portion of calcinate extractable by acetone within the temperature interval 200–300 °C (Fig. 3a). The preparation and analysis of calcinates was also carried out in the same way using the simple dihydrogenphosphates as starting materials for comparison (Fig. 3b and c). In the case of the calcinates of cadmium dihydrogenphosphate, this interval is somewhat wider (180–350 °C). For calcinates of calcium dihydrogenphosphate, the interval for the appearance and existence of the intermediate $\text{CaH}_2\text{P}_2\text{O}_7$ shifts to higher temperatures (250–375 °C). Comparing these intervals with the corresponding interval given above for the calcination of $\text{Cd}_{2/3}\text{Ca}_{1/3}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ may confirm, to some extent, that the intermediate formed, $\text{Cd}_{2/3}\text{Ca}_{1/3}\text{H}_2\text{P}_2\text{O}_7$, is also binary in nature, and not a mixture of $\text{CdH}_2\text{P}_2\text{O}_7$ and $\text{Ca}_2\text{H}_2\text{P}_2\text{O}_7$. This was also verified by electron microscopy (for calcinates and their extraction residues) and IR spectroscopy.

The last process recorded with Q-TA, the release of the second molecule of constitutional water connected with the second condensation reaction (the formation of cyclotetraphosphate), takes place in the labyrinth crucible, i.e. with a water-vapour pressure of nearly 100 kPa, within the temperature interval 305–395 °C; much of the reaction (over a half) takes place in a relatively narrow interval 365–370 °C. With these conditions, the product is explicitly binary cadmium-calcium cyclotetraphosphate, $c\text{-Cd}_{4/3}\text{Ca}_{2/3}\text{P}_4\text{O}_{12}$ (confirmed with instrumental analytical methods (IAMs)). This is a new compound, not mentioned in the literature until now, and is the subject of our Czechoslovak patent [23]. It was found to crystallise in the monoclinic system, group $C/2c$ with structural parameters: $a = 1.2457$ nm, $b = 0.8732$ nm, $c = 1.0443$ nm, $\beta = 119.45^\circ$, the elementary cell volume $V = 0.9891$ nm³ and density 3.29 g cm⁻³ (ρ calculated) or 3.3 g cm⁻³ (ρ experimental). The temperature zones recorded with Q-TA for the formation of the binary product $c\text{-Cd}_{4/3}\text{Ca}_{2/3}\text{P}_4\text{O}_{12}$ were compared with the temperatures of forma-

tion of the corresponding simple products, $c\text{-Cd}_2\text{P}_4\text{O}_{12}$ and $\text{Ca}_{n/2}\text{H}_2\text{P}_n\text{O}_{3n+1}$ (in the same conditions). They are slightly different: the cadmium product is formed at 380–390 °C, for the most part, while the calcium product is mostly formed at about 400 °C [35]. The extraction experiments on calcinates treated with 0.3 M HCl (Fig. 3) confirmed these conclusions. In the calcination of individual starting dihydrogenphosphates, $\text{Cd}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ or $\text{Cd}_{2/3}\text{Ca}_{1/3}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, at vapour pressures of nearly 100 kPa, the first portions of final products (cyclo-tetraphosphates or possibly $\text{Ca}_{n/2}\text{H}_2\text{P}_n\text{O}_{3n+1}$) appear above temperatures of 300 °C (Cd), 280 °C (Cd-Ca) and 370 °C (Ca). Most of the calcinate has been converted to the final product by 360 °C (Cd), 350 °C (Cd-Ca) and 430 °C (Ca). The final (steady state) conversion degree found in the individual calcinates with these conditions was about 95% for $c\text{-Cd}_2\text{P}_4\text{O}_{12}$ (at 400 °C), about 92% for $c\text{-Cd}_{4/3}\text{Ca}_{2/3}\text{P}_4\text{O}_{12}$ (at 400 °C) and about 90% for $\text{Ca}_{n/2}\text{H}_2\text{P}_n\text{O}_{3n+1}$ (at 475 °C).

Multi-plate crucible ($p\text{H}_2\text{O}_7(\text{g}) \approx 1 \text{ kPa}$)

When the multi-plate crucible is used as the carrier of the thermoanalysed sample (Fig. 2, curve A), the first weight-loss from the initial $\text{Cd}_{2/3}\text{Ca}_{1/3}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ is water of crystallisation, once again: 4/3 molecules of water of crystallisation are released in the temperature interval 50–90 °C. Next, water corresponding to the second third of the second molecule of water of crystallisation is released in a relatively narrow temperature interval, 90–110 °C, much of this process taking place within 95–100 °C. The last third of the second molecule of water of crystallisation is liberated within the temperature range 110–150 °C, most of it being released in the range 135–145 °C. According to previous papers [34,35] and the results of extraction experiments (Fig. 3), at this stage the calcinate is mostly an anhydrous mixture of dihydrogenphosphates, also including some of their decomposition or splitting products, i.e. lower hydrates of the hydrogenphosphates $\text{Me}(\text{II})\text{HPO}_4 \cdot x\text{H}_2\text{O}$, where $\text{Me}(\text{II}) \equiv \text{Cd}, \text{Ca}$, and some phosphoric acid. The lower hydrates are then dehydrated in the next process, and phosphoric acid condenses separately to diphosphoric acid and then to higher polyphosphoric acids. As early as the liberation of water of crystallisation, the binary dihydrogenphosphate decomposes into the two simple dihydrogenphosphates of cadmium and calcium. Therefore the temperature intervals in which both this water and the constitutional water are released (as will be said later) correspond roughly to the temperatures of the appropriate processes in the thermal dehydration of these two simple dihydrogenphosphates [34,35].

The next two processes, taken together, correspond to the release of a constitutional water molecule in the interval 150–230 °C. The cadmium

constituent of the calcinate forms cadmium dihydrogendiphosphate, mostly in the first process (150–205 °C), and the calcium component yields $\text{CaH}_2\text{P}_2\text{O}_7$, mostly in the second process (205–230 °C). (According to ref. 34 the temperature of formation for the cadmium intermediate at these conditions is in exact agreement with the given interval.)

With a further rise in temperature above 230 °C, under these conditions the cadmium and calcium dihydrogendiphosphates condense separately to form the final products, $c\text{-Cd}_2\text{P}_4\text{O}_{12}$, $\text{Cd}_{n/2}\text{H}_2\text{P}_n\text{O}_{3n+1}$ and $\text{Ca}_{n/2}\text{H}_2\text{P}_n\text{O}_{3n+1}$ [34,35]. (A small part of the calcinate corresponding to the binary cadmium-calcium dihydrogendiphosphate then condenses to form the main final product, binary cadmium-calcium cyclotetraphosphate, which constitutes, however, only a very small part of the calcinate.) These processes are complicated by the separate condensation of the released phosphoric acid to form higher phosphoric acids, $\text{H}_{n+2}\text{P}_n\text{O}_{3n+1}$, and by the partial formation of diphosphates ($\text{Ca}_2\text{P}_2\text{O}_7$ and $\text{Cd}_2\text{P}_2\text{O}_7$). These processes can also lead, to a lesser extent, to the formation of ultraphosphates. A steady slight decrease in the sample mass at temperatures above 360 °C, exceeding the total theoretical amount of water in the starting $\text{Cd}_{2/3}\text{Ca}_{1/3}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, can be thus explained. The extraction experiments (Fig. 3) and the analysis of calcinates by IAMs confirmed that calcination under these conditions of negligible vapour pressure results in the formation of only a small amount of the binary product, $c\text{-Cd}_{4/3}\text{Ca}_{2/3}\text{P}_4\text{O}_{12}$: it formed only 5% of the calcinates prepared at 500 °C, the main products being $c\text{-Cd}_2\text{P}_7\text{O}_{12}$, $\text{Ca}_{n/2}\text{H}_2\text{P}_n\text{O}_{3n+1}$ and $\text{Cd}_{n/2}\text{H}_2\text{P}_n\text{O}_{3n+1}$; the first two also make up a substantial part of the insoluble residue determined by extraction experiments (using 0.3 M HCl), constituting about 2/3 of the calcinate (Fig. 3).

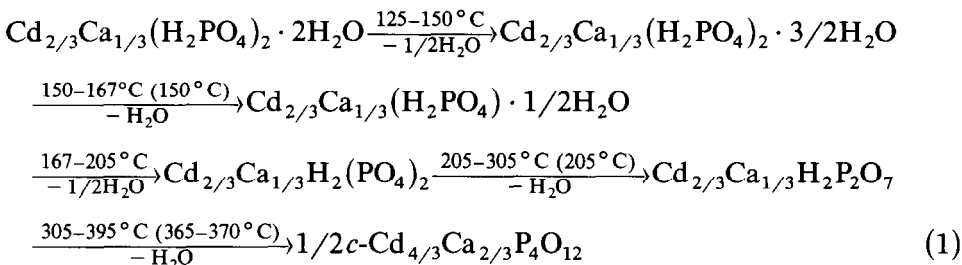
The use of other crucible types

Thermogravimetric curves B and C were obtained in thermal analyses at quasi-isothermal-isobaric conditions using two other crucible types as sample holders: the open crucible (with water-vapour pressure of about 5 kPa) and the crucible with a lid (20 kPa). Their courses do not provide such an unequivocal explanation of the reaction mechanism as those described above for the A and D curves. At vapour pressures of about 5 and 20 kPa, the mechanism of the dehydration and condensation reactions seems to approach that described for the multi-plate crucible (1 kPa). A comparison of curves A and B, and possibly C, shows that the temperatures of individual processes do not differ by more than 20 °C, possibly by 40 °C.

The content of final binary cyclotetraphosphate in the calcinate after thermal analysis is about 10% in the open crucible and about 30% in the crucible with a lid.

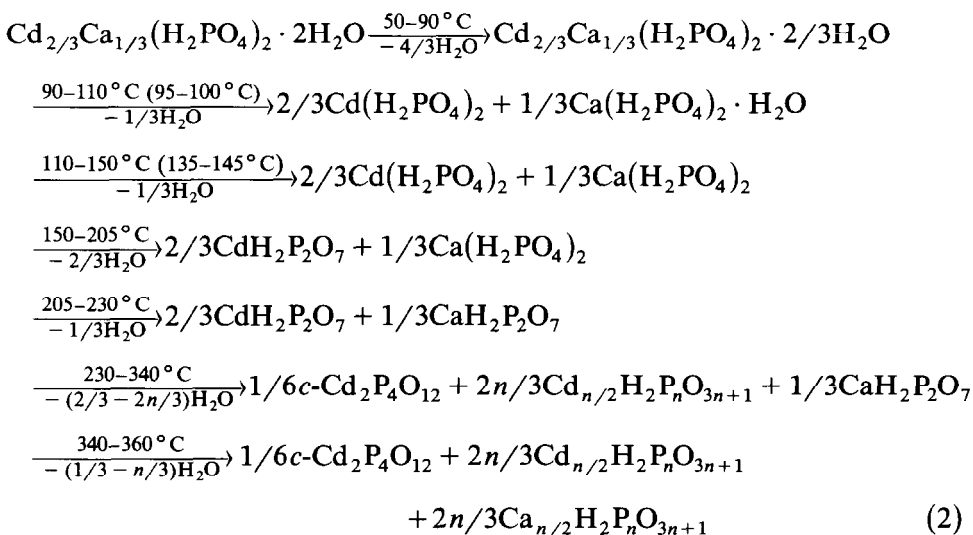
CONCLUSION

The course and conditions of formation of $c\text{-Cd}_{4/3}\text{Ca}_{2/3}\text{P}_4\text{O}_{12}$ in the calcination of $\text{Cd}_{2/3}\text{Ca}_{1/3}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, with water-vapour pressure in the space approaching 100 kPa, is shown below (the temperatures of the main part of the process are given in parentheses)



Binary cadmium-calcium cyclotetraphosphate, $c\text{-Cd}_{4/3}\text{Ca}_{2/3}\text{P}_4\text{O}_{12}$, with a yield of about 92% is obtained in this way.

If the calcination takes place at lower water-vapour pressures, the initial binary cadmium-calcium dihydrogenphosphate decomposes partly (at 20 kPa) or fully (at 1 kPa) to simple cadmium and calcium dihydrogenphosphates. These are then dehydrated and condensed separately, and the starting temperatures of the individual processes are lowered. The percentage of the main product, $c\text{-Cd}_{4/3}\text{Ca}_{2/3}\text{P}_4\text{O}_{12}$, in the final calcinate also decreases, to even under 5% at vapour pressures approaching 1 kPa. At very low vapour pressures, the course of the main processes can be described as follows



Higher polyphosphoric acids, diphosphates and some products with ultra-phosphate-type anions may also be formed to a small extent.

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