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The thermal synthesis of cadmium(II) cyclo-tetraphosphate

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Abstract

The preparation of c-$Cd_2P_4O_{12}$ reported here is based on the thermal dehydration of $Cd(H_2PO_4)_2 \cdot 2H_2O$. Thermal analysis under quasi-isothermal-isobaric conditions was used. The calcinates obtained under comparable conditions in an electric oven were analysed with instrumental analytical methods and extraction experiments.

INTRODUCTION

The thermal dehydration of $Cd(H_2PO_4)_2 \cdot 2H_2O$ has been studied by various authors, see, for example, refs. 1–4, some of whom also report thermoanalytical measurements. According to the cited papers, the main product of the thermal dehydration of cadmium dihydrogenphosphate is always a mixture of cadmium cyclo-tetraphosphate (tetramethaphosphate) (c-$Cd_2P_4O_{12}$) with higher linear cadmium phosphates $[(Cd(PO_3)_2]_n$, the proportion of which is said to rise with increasing temperature. Reference 1 gives the temperatures of the individual hydration and condensation reactions in the interval 100–200°C, i.e. liberation of crystal water (100°C), and formation of $CdH_2P_2O_7$ (180°C), and c-$Cd_2P_4O_{12}$ (200°C). Paper 2, however, implied that some of these temperatures may be 30–210°C higher. Reference 3, dealing with the thermal dehydration at very low pressures or in a vacuum, has shown that the intermediate condensation product, $CdH_2P_2O_7$, can only be produced in the presence of water vapour, otherwise normal diphosphate $Cd_2P_2O_7$ is formed in a mixture with split phosphoric or diphosphoric acid. Evidently, a sufficient amount of the $CdH_2P_2O_7$ intermediate must be formed in order that the course of the next condensation reaction, connected with obtaining the desired product

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c-$Cd_2P_4O_{12}$, should proceed. This also follows from our previous papers [5–11] which reported the thermal dehydration of dihydrogenphosphates of other divalent metals and the synthesis of corresponding cyclo-tetraphosphates. These conclusions were drawn from the results of thermal analyses under quasi-isothermal-isobaric conditions and from the analysis of calcinates prepared under comparable conditions in an electric oven, which were carried out by means of instrumental analytical methods (IAM) and extraction experiments. Therefore, we have applied the same methodologies here to observe the conditions of c-$Cd_2P_4O_{12}$ synthesis. The aim was to obtain the highest possible yields of the cyclo-tetraphosphate, which constitutes the insoluble portion of the calcinate. This would provide a possible binding of the problematic cadmium ions that are often present in phosphoric acid, when this is used in the preparation of cyclo-tetraphosphates of bivalent metals serving as special inorganic pigments [12].

EXPERIMENTAL

The initial binary dihydrogenphosphate $Cd(H_2PO_4)_2 \cdot 2H_2O$ (with crystals) was prepared in our laboratory.

To clarify the mass and energy transformations taking place during calcination, the sample was thermoanalysed by the classical dynamic method, i.e. non-isothermal, using a Q-1500 derivatograph apparatus (MOM Budapest). The measurement was carried out in two types of crucibles.

In order better to separate 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) [13–15]. The first measurements under these conditions were carried out by means of a Derivatograph C (MOM Budapest), with a labyrinth crucible being used as a sample carrier (Fig. 2). The next quasi-isothermal, quasi-isobaric experiments were carried out on a Q-1500 derivatograph, using four types of crucibles (Fig. 3) [13–15].

On the basis of the TA and Q–TA results, larger calcinate samples for analyses were then prepared in an electric furnace. The samples to be calcinated were placed in special vessels corresponding, with respect to the water vapour pressure, to the crucibles A and D illustrated in Fig. 3. At first, the starting phosphate was calcinated at various temperatures (10°C steps) in the range from 100 to 400°C, the heating rate corresponding to that of TA.

The calcinate prepared at 400°C at water vapour pressures approaching 100 kPa was then tempered to the higher temperatures of 500, 600, 700 and 770°C.

Then, the calcinations of $Cd(H_2PO_4)_2 \cdot 2H_2O$ were repeated at 300–350°C for various time periods (up to 500 min) using either the starting $Cd(H_2PO_4)_2 \cdot 2H_2O$ or the intermediates $Cd(H_2PO_4)_2$ and $CdH_2P_2O_7$ (Fig. 5). The kinetic curves obtained from this calcination experiments were submitted to a mathematical treatment [16].

All the calcinates were analysed by IAM and/or by our extraction experiments (see papers 5–11).

RESULTS AND DISCUSSION

Non-isothermal TA

Under the conditions of non-isothermal TA, see Fig. 1, four water molecules (two of crystal water and two constitutional water molecules) are released from the initial $Cd(H_2PO_4)_2 \cdot 2H_2O$ in four steps. These are accompanied by endothermal effects in the temperature intervals 130–160, 160–210, 210–320 and 360–450°C. When an open crucible is used (vapour pressure, 5 kPa) the temperatures are 20–40°C lower. The DTA and DTG

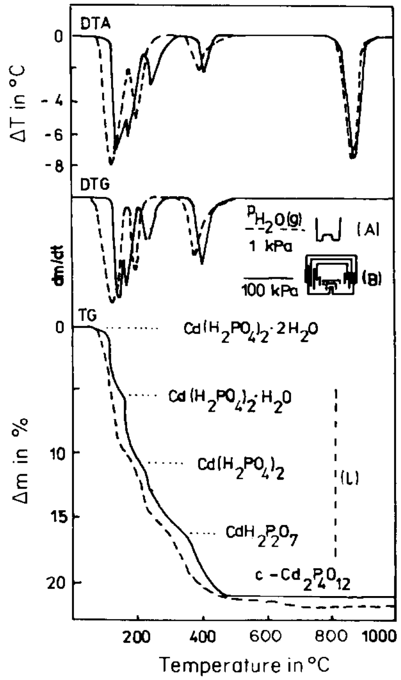

Fig. 1. Simultaneous TG, DTG and DTA curves of $Cd(H_2PO_4)_2 \cdot 2H_2O$, recorded under dynamic (non-isothermal) conditions on a Q-1500 derivatograph; temperature increase, 2.5°C min^{-1}; sample weight, 600 mg; standard, $\alpha\text{-}Al_2O_3$; sensitivity of the balance, TG 200 mg, DTA and DTG 1/3; atmosphere, air. (A) Open crucible, $pH_2O(g) = 5$ kPa; (B) labyrinth crucible, $pH_2O(g) = 100$ kPa.

curves indicate that the release of the two molecules of crystal water occurs in only one step at lower vapour pressures. Another interesting difference can be seen in the course of the TG curves after reaching the mass corresponding to the loss of four water molecules from the starting phosphate (21.04%): in the labyrinth crucible, there is no further mass change, while in the open crucible a slight mass loss continues steadily up to 750°C (by about another 1% of the original sample mass). This can only be explained by the phosphate component splitting off at lower vapour pressures, and a portion of this condensing to form higher polyphosphoric acids, finally up to phosphorous pentoxide which can volatilize from the mixture at higher temperatures. An endothermal effect with calcinate melting is observed in the DTA curve beginning at 800°C, which corresponds to the melting temperature of c-$Cd_2P_4O_{12}$ given in our previous paper [17].

Quasi-isothermal, quasi-isobaric TA

The thermal analysis at quasi-isothermal–isobaric conditions on the Derivatograph C apparatus using a labyrinth crucible (Fig. 2) confirmed the results of the dynamic TA in general. The release of four water molecules from $Cd(H_2PO_4)_2 \cdot 2H_2O$ is noted, accompanied by four endothermal processes. The starting temperatures of the individual processes could be

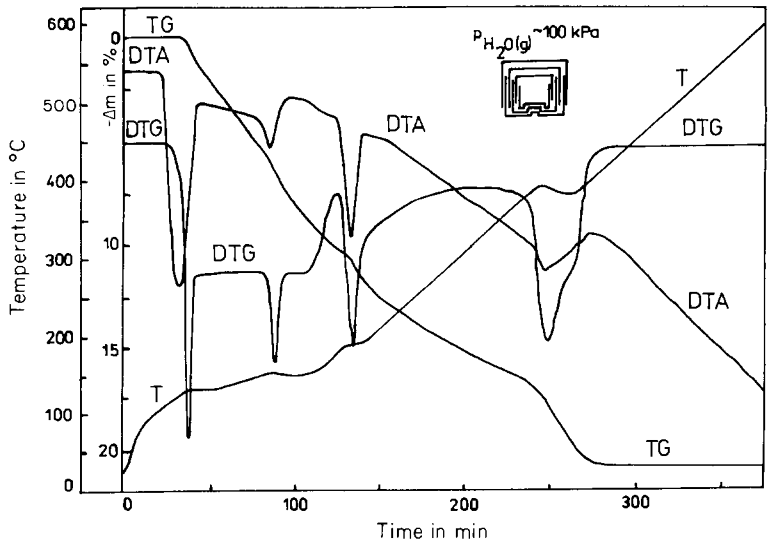

Fig. 2. Simultaneous TG, DTG and DTA curves of $Cd(H_2PO_4)_2 \cdot 2H_2O$ recorded under quasi-isothermal, quasi-isobaric conditions on a derivatograph C; decomposition rate, 0.2 mg min^{-1}, temperature increase, 1°C min^{-1}; sample weight, 334 mg; sensitivity of the balance, TG 100 mg, DTA 2, DTG 0.5; labyrinth crucible $pH_2O(g) = 100$ kPa; standard, α-Al_2O_3; atmosphere, air.

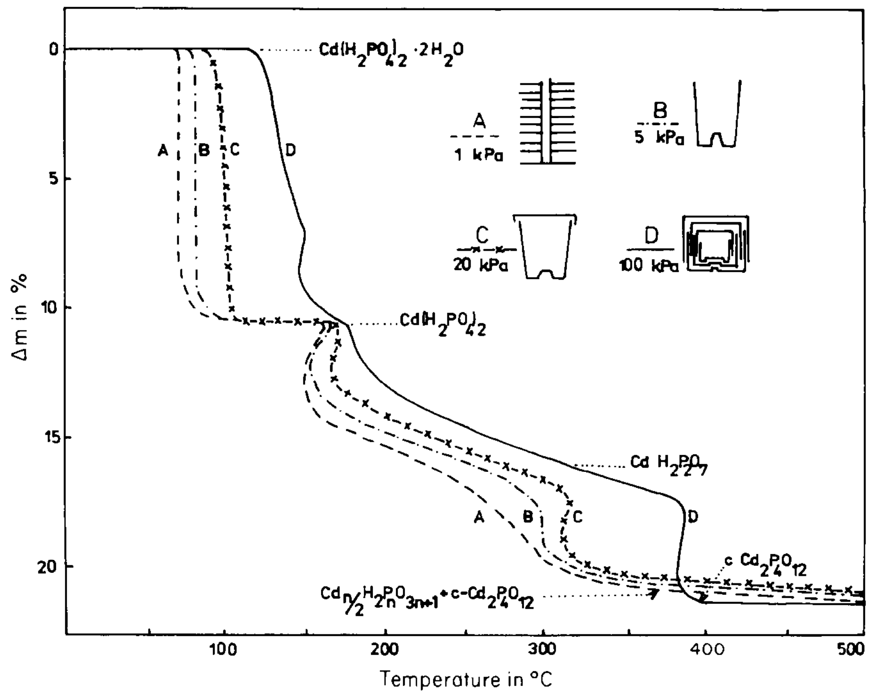

Fig. 3. Thermogravimetric curves of $Cd(H_2PO_4)_2 \cdot 2H_2O$ recorded under quasi-isothermal, quasi-isobaric conditions on a Q-1500 derivatograph; sample weight, 300 mg; decomposition rate, 0.2 mg min^{-1}; atmosphere, air. Curve A, multi-plate crucible, $pH_2O(g) = 1$ kPa; curve B, open crucible, $pH_2O(g) = 5$ kPa; curve C, crucible with a lid, $pH_2O(g) = 20$ kPa; curve D, labyrinth crucible, $pH_2O(g) = 100$ kPa.

determined more exactly as 130, 155, 190 and 330°C. There is quite a great difference between the start of the first condensation reaction (forming $CdH_2P_2O_7$) and the second (forming c-$Cd_2P_4O_{12}$); this is interesting because the main part of the second reaction does not take place until 370–385°C. In the case of thermal analyses of dihydrogenphosphates of other bivalent metals [5–11], this difference was lower by about a third.

The thermogravimetric curves obtained under quasi-isothermal–isobaric conditions on the Q-1500 derivatograph using four crucible types (Fig. 3) has elucidated the dehydration of $Cd(H_2PO_4)_2 \cdot 2H_2O$ with possible c-$Cd_2P_4O_{12}$ formation.

Labyrinth crucible, $pH_2O(g) = 100$ kPa

When the labyrinth is used under Q–TA conditions, the first molecule of crystal water and a third of the second are liberated in the interval 120–150°C. The remaining two thirds of the crystal water molecule are released in the second process in the interval 150–175°C. This liberation of crystal water in two unequal parts can be explained by the fact that the sample is melting in its own crystal water under conditions of higher water vapour pressure. The sample takes on a pastey consistency which makes the liberation of crystal water difficult (see the course of the D curve in the 120–150°C interval as compared with corresponding parts of the A, B, and C curves). When a sufficient amount of $Cd(H_2PO_4)_2$ anhydride is formed the paste becomes more pervious, which facilitates the release of the rest of the crystal water. Dehydration takes place with the chosen decomposition rate of 0.2 mg min^{-1} at the temperature corresponding to the partial water vapour pressure; therefore, the temperature in this part of the D curve dropped to 145°C. The first molecule of constitutional water is slowly released within a wide temperature interval to form the first condensation product $CdH_2P_2O_7$, although nearly a half of this process takes place within the narrow interval of 175–190°C. Thus, this cadmium dihydrogenphosphate, whose formation is necessary for sufficient yield of the required cyclo-tetraphosphate final product [3], is formed with greater difficulty than with other divalent cations [5–11]. This is also connected with the presence of the above-mentioned crust, typical for the formation of intermediate products with divalent cations; its porosity decreases with increasing vapour pressure in the calcination space, as observed by an electron microscope.

Acetone extraction of the calcinate samples prepared in an electric oven (Fig. 4) under comparable conditions confirms that the temperature zone for the existence of dihydrogendiphosphate is really very wide — from 180 to 350°C. This zone corresponds to a certain extractability of the phosphoric component from the calcinate which, according to our previous works [5–11], is associated with the very existence of the dihydrogendiphosphate. A temporary decrease in the extractable portion of the phosphoric

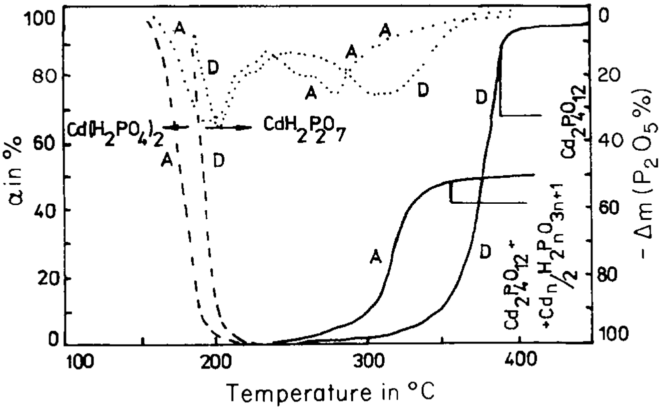

Fig. 4. Extraction experiments on calcinates of $Cd(H_2PO_4)_2 \cdot 2H_2O$ (calcination conditions, 2.5°C min^{-1}; $pH_2O(g)$; A, 1 kPa; D, 100 kPa. Weight changes determined by extraction: with acetone (· · ·), and 0.3 M HCl (—), with α being the degree of conversion to the cyclo-tetraphosphate.

component at about 250°C could be caused by the temporary formation of the intermediate $CdH_2P_2O_7 \cdot 3H_2O$ corresponding to the hypothesis suggested in ref. 3. Another explanation could be that the crystallization of the intermediate $CdH_2P_2O_7$, which was first amorphous reduces the possibility of extracting the phosphoric component until it is destroyed again, when it begins to lose the second constitutional water, as was observed with zinc intermediates [10].

The first mass losses corresponding to the beginning of the release of the second constitutional water molecule and thus to the beginning of the second condensation reaction (to form the cyclo-tetraphosphate) were recorded in the labyrinth crucible (curve D, Fig. 3) from 315°C. From this temperature, the nuclei are gradually formed, reaching a sufficient amount at 390°C for the reaction to proceed at a considerable speed. In accordance with the chosen decomposition rate of $0.2\ \mathrm{mg\ min^{-1}}$ which is kept constant in the apparatus, the temperature drops by about 10°C. This is why about 75% of the process took place almost isothermally. The extraction of calcinates prepared under comparable conditions with 0.3 M HCl (Fig. 4) confirmed that c-$Cd_2P_4O_{12}$ first forms above 300°C. A stable rate in the reaction changing the calcinate into cyclo-tetraphosphate is reached above 380°C when the calcinate contains more than 95% c-$Cd_2P_4O_{12}$. The amount of this desired product in the calcinate does not change up to its melting temperature of 800°C (as shown below). (Almost equal values of the reaction rate were reached with the sample in the labyrinth crucible following Q-TA, i.e. after reaching 500°C.)

Multi-plate crucible, $pH_2O(g) = 1$ kPa

When using a multi-plate crucible as the sample carrier in Q-TA (Fig. 3, curve A) all the crystal water is lost in one step, isothermally at 70°C. The first condensation reaction corresponding to $CdH_2P_2O_7$ formation in its first phase, starts with the increase in the nuclei from 160°C. This evidently takes place at a higher temperature than the reaction itself (i.e. with a higher energy content of the compound) under conditions of negligible water vapour pressure. After a sufficient amount of nuclei are formed, the balance becomes stabilized, and the reaction proceeds with the chosen decomposition rate ($0.2\ \mathrm{mg\ min^{-1}}$) and at the temperature corresponding to actual water vapour pressure (a temperature drop to 150°C). The mass loss corresponding to the first constitutional water molecule is reached at 220°C. This process, however, proceeds without any conspicuous break in the Q-TA curve up to 300°C, when about 3/4 of the second constitutional water molecule has already been released. Then the mass decrease slows down, and at the temperature of completing the Q-TA (500°C), it equals the loss of four water molecules from the starting $Cd(H_2PO_4)_2 \cdot 2H_2O$. The analysis of the thermoanalysed sample after completion of Q-TA showed that it contained about half c-$Cd_2P_4O_{12}$, the other half being intermediate products, mainly higher linear cadmium phosphates $Cd_{n/2}H_2P_nO_{3n+1}$. The formation of this intermediate in a practically endless range of successive reactions, reaction (1), is probably the cause of the continuous ('breakless') course of the Q-TA curve A within the interval 160–500°C.

$$Cd(H_2PO_4)_2 = (2/n)\,Cd_{n/2}H_2P_nO_{3n+1} + (1 - 2/n)H_2O \qquad (n = 1, 2\ldots) \qquad (1)$$

In addition, the splitting of the intermediates (especially of the dihydrogendiphosphate) to hydrogenphosphate and phosphoric or diphosphoric acid takes place at this negligible water vapour pressure. The acids then condense separately. $Cd_2P_2O_7$ and higher polyphosphoric acids are formed as further intermediate products. The final product of the separate condensation of the phosphoric constituent, phosphorous pentoxide, becomes volatile at higher temperatures. Therefore the total mass decrease above 500°C surpasses the theoretical decrease corresponding to four water molecules from the starting phosphate (see Fig. 1).

Extraction experiments (Fig. 4) with calcinates prepared under comparable conditions (water vapour pressure ≈ 1 kPa) confirmed these results. In the acetone extraction, a part of the phosphoric constituent is extracted during the period from a calcinate preparation temperature of 150°C up to 400°C. The greatest portions were extracted in the interval 180–300°C. A local minimum, similar to the extraction of calcinates prepared at water vapour pressure approaching 100 kPa, is observed on the curve characterizing the share of the extracted phosphoric constituent. This minimum is not so obvious, appears at lower temperatures (220–230°C) and its temperature zone is not so wide. This may serve as a proof, to some extent, that a part of the intermediate product condensed in a different mechanism under these conditions, eqn. (1). The extraction with 0.3 M HCl shows that the first small portions of insoluble c-$Cd_2P_4O_{12}$ are already present in the calcinate from temperatures of 230–240°C under these conditions. A stabilized degree of calcinate conversion into cyclo-tetraphosphate is reached from 350°C when it reaches nearly 55%.

Open crucible and crucible with a lid, $pH_2O(g) = 5$ and 20 kPa

When using the other two types of crucibles for the thermoanalysed samples (open crucible at a vapour pressure of 5 kPa (curve B) and crucible with a lid at 20 kPa (curve C, Fig. 3), the dehydration and condensation mechanism represents a transition between the mechanisms suggested for 1 kPa vapour pressure (multi-plate crucible (curve A)) and for 100 kPa pressure (labyrinth crucible (curve D)). In both cases, all the crystal water is released in one process, practically isothermally, at 80°C in the open crucible and at 95–105°C in that with a lid. Condensation reactions connected with liberating constitutional water from the anhydride $Cd(H_2PO_4)_2$ begin from 165 and 170°C, respectively. A temperature drop to 155 or 165°C, respectively, follows immediately. The mass decrease corresponding to the release of the first constitutional water molecule is reached at 250 or 270°C, respectively. From these temperatures, water corresponding to the second constitutional water molecule is then released. When the open crucible is used, a more distinct mass decrease occurs at 300°C (corresponding to the release of about 1/4 of the water molecule). In the case of the crucible with a lid, a more distinct mass decrease (corresponding to nearly a half of the water molecule) occurs at 315°C, during which the temperature drops to 310°C. After finishing Q-TA (at 500°C), the content of c-$Cd_2P_4O_{12}$ determined in the cooled sample was about 60% in the open crucible, and 80% in the crucible with a lid. Higher linear cadmium phosphates were mainly obtained as by-products.

Calcination experiments

In order to verify that the content of higher linear cadmium phosphates in the calcinates increases with rising temperature to the detriment of cyclo-tetraphosphates, calcinates were prepared at vapour pressures of 1 kPa and 100 kPa, at temperatures of 500, 600, 700 and 770°C. The c-$Cd_2P_4O_{12}$ content determined in all cases remained almost unchanged with the temperature: at 100 kPa, it was 94–97%; at 1 kPa, 52–56%. Similarly, within the interval 400–770°C, some other properties of these calcinates (prepared at 100 kPa) remained unchanged: the pycnometrically determined density was 3.75 g cm^{-3}, the structural parameters correspond to c-$Cd_2P_4O_{12}$ (monoclinic system, group C_{2c}: $a = 1.2328(4)$ nm, $b = 0.8639(3)$ nm, $c = 1.0388(3)$ nm, $\beta = 119.33(2)°$, the elementary cell volume is 0.9645 nm^3). This shows that further tempering (to temperatures higher than those corresponding to the end of the reaction forming cyclo-tetraphosphate) has no influence on the proportion of cyclo-tetraphosphate (and its structure), or on the yield of higher linear phosphates in the calcinates. This holds, of course, up to the melting temperature of c-$Cd_2P_4O_{12}$ (800°C) only, as shown in our previous work.

Temperatures of 300°C (1 kPa water vapour pressure) and 350°C (100 kPa) were chosen for the kinetic investigation of the formation of c-$Cd_2P_4O_{12}$. The results are given in Fig. 5. For 100 kPa water vapour pressure in the calcinate area, more than 97% conversion of the calcinate into c-$Cd_2P_4O_{12}$ was reached in 500 min of calcination, with all the starting compounds. For 1 kPa water vapour pressure, the values were preceptibly lower. The highest conversion degree at this water vapour pressure, and, hence, the lowest difference from the results at 100 kPa, was reached when $CdH_2P_2O_7$ was used as the starting compound. This indicates that side reactions leading to a reduction in the product yield take place especially during formation of $CdH_2P_2O_7$. Mathematical treatment of the kinetic curves (Fig. 5) and of the TG curves from dynamical TA (Fig. 1) revealed

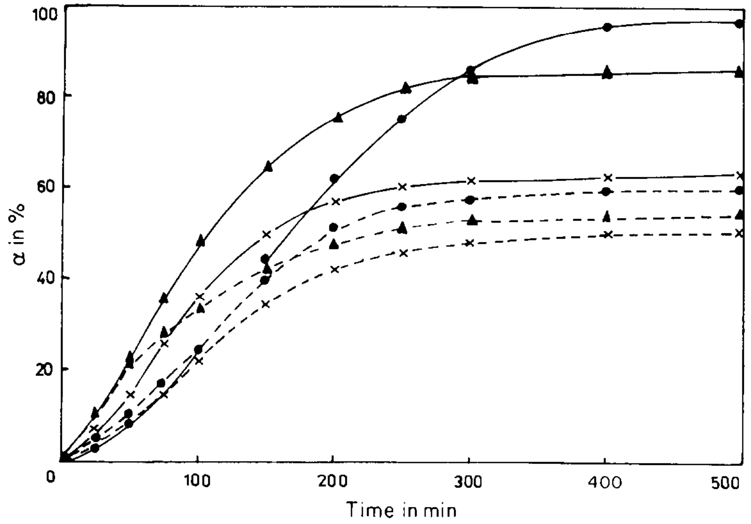

Fig. 5. The dependence of the conversion degree (α) to c-$Cd_2P_4O_{12}$ of the initial cadmium(II) phosphates: $Cd(H_2PO_4)_2 \cdot 2H_2O$ (●), $Cd(H_2PO_4)_2$ (×), $CdH_2P_2O_7$ (▲), on the calcination time, for the calcination temperatures: A, 300°C ($pH_2O(g) = 1$ kPa); B, 350°C ($pH_2O(g) = 100$ kPa).

that diffusion is the controlling process of the condensation reaction. This is best expressed by the anti-Jander equation $[(1+\alpha)^{1/3} - 1]^2 = kt$ (for the so-called countercurrent diffusion) [16]. In this way it was possible to confirm the results by electron microscopy, which revealed distinct porosity in the intermediate $CdH_2P_2O_7$. Taking into account all the circumstances, however, we can state that the condensation reaction, the formation of c-$Cd_2P_4O_{12}$ (especially in the labyrinth crucible), probably leads to an equilibrium, but that its course is affected by the porosity of the upper layer of the calcinate which is formed on the nuclei.

CONCLUSIONS

The course and temperature conditions of the reaction taking place in the calcination of the initial $Cd(H_2PO_4)_2 \cdot 2H_2O$, under conditions when the water vapour pressure in the calcination space approaches 100 kPa, is described by

$$Cd(H_2PO_4)_2 \cdot 2H_2O \xrightarrow[-(4/3)H_2O]{120\text{–}150°C\ (130\text{–}140°C)} Cd(H_2PO_4)_2 \cdot (2/3)H_2O \xrightarrow[-(2/3)H_2O]{150\text{–}175°C\ (150°C)}$$

$$Cd(H_2PO_4)_2 \xrightarrow[-H_2O]{175\text{–}315°C\ (175\text{–}190°C)}$$

$$CdH_2P_2O_7 \xrightarrow[-H_2O]{315\text{–}400°C\ (380\text{–}390°C)} c\text{-}Cd_2P_4O_{12}$$

The data given in parentheses represent the temperatures of the decisive parts of individual processes. Dicadmium cyclo-tetraphosphate c-$Cd_2P_4O_{12}$ can be prepared with this method giving a yield of up to 97% w/w. The conditions of calcination after the intermediate anhydride $Cd(H_2PO_4)_2$ is formed in the calcinate are vital for obtaining a sufficient yield of the cyclo-tetraphosphate. If the calcination temperature is increased after the formation of cyclo-tetraphosphate, i.e. above 400°C, neither the share of c-$Cd_2P_4O_{12}$ nor its structure changes until its melting temperature (800°C) is reached.

If the calcination of the starting dihydrogenphosphate is carried out at lower water vapour pressures, higher linear cadmium phosphates are partially formed, having the common formula $Cd_{n/2}H_2P_nO_{3n+1}$. Their share can make up nearly one half of the final calcinate mass at vapour pressures of about 1 kPa. Moreover, the intermediate products (dihydrogendiphosphate) may partially split to form hydrogenphosphates and phosphoric acid, or diphosphates and diphosphoric acid. These compounds then dehydrate with further increase in temperature, and eventually may condense to other by-products. The share of c-$Cd_2P_4O_{12}$ in the final calcinate can thus decrease to 50–55% at water vapour pressures approaching 1 kPa.

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