

MECHANISM OF THE THERMAL DEHYDRATION OF $\text{Co}_{1/2}\text{Ca}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$

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The mechanism of the dehydration and condensation reaction taking place during calcination of $\text{Co}_{1/2}\text{Ca}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ has been followed by means of thermal analyses at non-isothermal (dynamic) and at quasi-isothermal-isobaric conditions. Isothermal calcination of starting binary dihydrogenphosphate was carried out in electric oven at various temperatures. The reaction intermediates and products obtained were analyzed by instrumental analytical methods and extraction experiments with solutions of inorganic compounds and with organic reagents. Effect of water vapour pressure has been followed on course, rate and yield of the condensation reactions and of the formation of main considered product-binary cyclo-tetraphosphate (tetrametaphosphate) $c\text{-CoCaP}_4\text{O}_{12}$.

Cyclo-tetraphosphate (tetrametaphosphate) of the common formula $c\text{-Me}_2^{\text{II}}\text{P}_4\text{O}_{12}$ (Me^{II} being e. g. Zn, Mn, Co, Mg, Cd, Ni) can be prepared by thermal dehydration of the dihydrogen phosphates of bivalent metals [1-5]. The evaluation of physico-chemical and application properties of cyclo-tetraphosphates shows the prospect of their utilizing as special inorganic pigments, especially for high-temperature (e. g. in ceramics [6, 7]), anti-corrosive [8, 9] and luminescent [10, 11] purposes. Recently we have aimed at preparing binary cyclo-tetraphosphates, i. e. those in which a part of the bivalent (non-ferrous) metal cation is substituted with cations of alkaline earth metals (mainly Ca and Mg) [12-14]. The possible existence prognosis for the cyclo-tetraphosphate type products containing calcium as one of the cations (that means the $c\text{-CoCaP}_4\text{O}_{12}$ as well) is quite sceptical [1, 12-14]. Our last papers [15-17] have disproved this opinion showing that several binary products of the $c\text{-Me}_{2-x}^{\text{II}}\text{Ca}_x\text{P}_4\text{O}_{12}$ type with a limited Ca content (as a rule $x = 1$) can be prepared. Suitable mixture containing a volatile anion of

calcium and of the appropriate bivalent metal together with phosphoric acid serves as starting material. It is treated by the thermal method [18] to the desired product. The presented paper gives a survey of the results obtained with thermal treating $\text{Co}_{1/2}\text{Ca}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$.

Experimental

Starting binary dihydrogenphosphate $\text{Co}_{1/2}\text{Ca}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (blue-violet crystals) was prepared by crystallization from the solution containing Co^{2+} , Ca^{2+} and PO_4^{3-} ions in stoichiometric quantities. Its quality was confirmed by X-ray diffraction analysis and its morphology by electron microscopy.

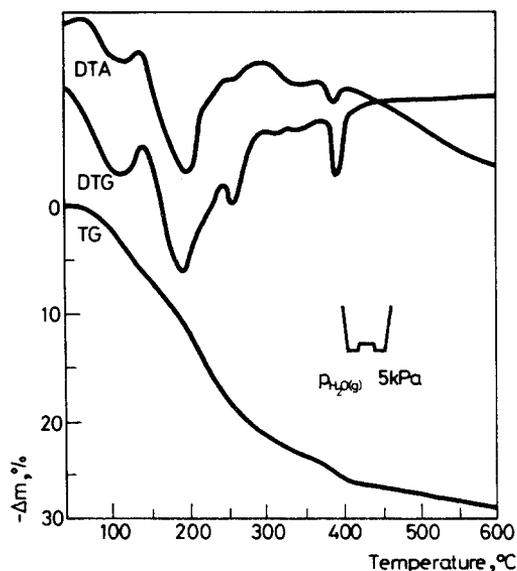


Fig.1 Simultaneous TG, DTG and DTA curves of $\text{Co}_{1/2}\text{Ca}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ traced under dynamic (non-isothermal) conditions. Temperature increase: 5 deg. min^{-1} ; Sample weight: 301 mg; Standard: $\alpha\text{-Al}_2\text{O}_3$; Sensitivity of the balance: TG 100 mg; Open crucible, $p\text{H}_2\text{O}(\text{g}) = 5 \text{ kPa}$; Atmosphere: air

The sample was thermoanalyzed by the classical dynamic method (i. e. non-isothermal) using a Derivatograph C apparatus (MOM Budapest). The

measurement was carried out in an open crucible with the temperature increase of 5 deg. min^{-1} , sample weight 301.1 mg, sensitivity of TG 100 mg, DTA 6, DTG 2, temperature interval from 20 to 600° , the examination was carried out in the presence of air (Fig. 1).

The binary phosphate was also submitted to TA under quasi-isothermal-isobaric conditions [19-21]. The decomposition rate, was $0.3 \text{ mg} \cdot \text{min}^{-1}$, various types of crucibles were used for measurements by means of Derivatograph Q-1500 viz. multiplate crucible (A), open crucible (B), crucible with a lid (C), and a six-component labyrinth crucible (D). The last arrangement (D) allows to retain water vapour released during the calcination of starting dihydrogenphosphate, so that its partial pressure is maintained at about 100 kPa (quasi-isobaric conditions) [19]. In the cases (A), (B) and (C) partial pressure corresponded approximately to 1 kPa, 5 kPa and 20 kPa, resp. [20-21].

The condensation products and intermediates of the calcination of the starting dihydrogenphosphate were prepared in an electric oven at various temperatures ($80, 100, 120, \dots 300, 350, \dots 600^{\circ}$) under isothermal conditions in the flat corundum set (part water pressure corresponds to 1 kPa) and in a set of special shaped crucible (100 kPa) were maintained for 30 min.

The inorganic solvent (dilute hydrochloric acid) [22] was used for extraction of the prepared calcinates. The samples prepared by calcination in the electric oven at isothermal conditions were extracted with acetone (Fig. 4). The extractable phosphate components (phosphoric or diphosphoric acid), were expressed as the P_2O_5 proction of the total amount in the calcinate. There after the calcinates were extracted with water dissolving the $\text{Me}^{\text{II}}\text{H}_2\text{P}_2\text{O}_7$ intermediate formed. The samples calcined above 120° were extracted with 0.3 M HCl in which only the final product $c = \text{CoCaP}_4\text{O}_{12}$ (or $c\text{-Co}_2\text{P}_4\text{O}_{12}$ and $\text{Ca}(\text{PO}_3)_2$) is insoluble.

The starting phosphate and its calcinates were analyzed and the individual products were identified by means of TLC [23, 24], IR spectroscopy [25] (Perkin-Elmer 684 infrared spectrometer), X-ray diffraction analysis [26, 27] (on HZG-4 apparatus, DDR) and electron microscopy (Tesla BS-300, ČSSR).

Results and discussion

The thermoanalytical curves of the starting binary cobalt-calcium dihydrogenphosphate $\text{Co}_{1/2}\text{Ca}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (Fig. 1), recorded under dynamic conditions using the open crucible, show that the first distinct en-

dothermic process starts in the interval 60-140°. This process passes into the next, even more distinct process within the 140-215° interval. The two processes are accompanied with a considerable mass loss making altogether 13 % up to the temperature of 215°; this is in good correspondence with the release of two crystal water molecules from the starting phosphate. Next two, this time distinct endothermic processes (within the intervals 215-250° and 250-275°) are also connected with a mass loss, each of them corresponds to releasing half a molecule of water (one water molecule is thus released within the interval 215-275° altogether). The last two endothermic processes - an unexpressive one in the 300-370° interval and a more distinct from 300 to 400° - make in a whole a mass loss corresponding to the release of the last (fourth) water molecule (i. e. the second molecule of constitutional water). As the course of the TG-curve shows, the weight of the sample, however, still decreases even after the last, energetically distinct process (above 400°); it is a steady but mild decrease up to 600°, when the measurement was finished. These facts demonstrate that the dehydration and mainly condensation reactions will have a more complicated mechanism than that described in our previous paper [2] on the thermal dehydration of $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$.

Figures 2 and 3 show the DTA, DTG a TG curves obtained in experiments carried out under quasi-isothermal and quasi-isobaric conditions by using various types of sample holders. The course of the curves allowed to state two mechanisms which are depended on the water vapour tension, within the grains. One of them holds for the vapour tension approaching 100 kPa (Fig. 2 and Fig. 3 curve D) on the contrary the other is preferred if the vapour tension is very low (curve A, B and C). Only the former mechanism leads to the derived product of binary cobalt-calcium cyclo-tetraphosphate. In the latter case the products of non-binary type are mostly produced. (The X-ray analysis of the intermediate and final products confirmed this supposition). So e. g. in the Q-TG curves, obtained using the labyrinth crucible (curve D) the first waterloss processes (two moles of crystal water) could clearly be distinguished in contrast to curves A, B and C. Curve D traced by using the labyrinth crucible showed viz. the dehydration as some step process while the Q-TG curves picked up by using the other three types of sample holders showed this period of the dehydration as a two step reaction.

The analysis of the Q-TG curve (curve D in Fig. 2), traced by using the labyrinth crucible ($p_{\text{H}_2\text{O}} = 100 \text{ kPa}$) shows that the course and conditions of the reaction taking place in the calcination of starting $\text{Co}_{1/2}\text{Ca}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ can be expressed by the following diagram (the temperature intervals

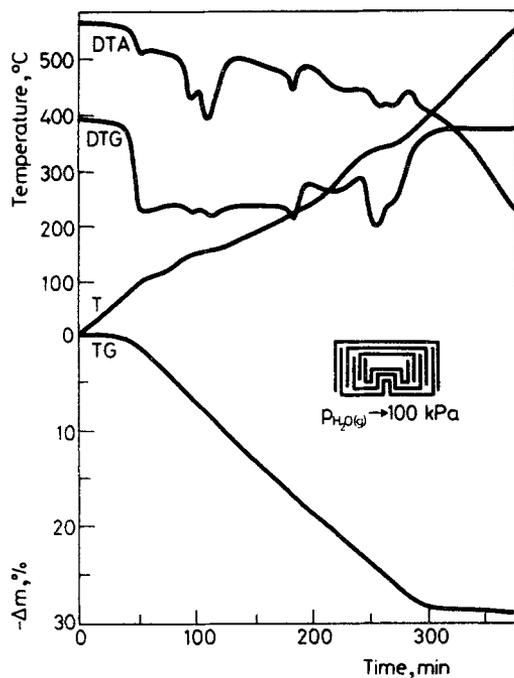
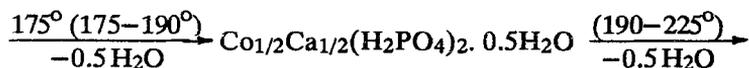
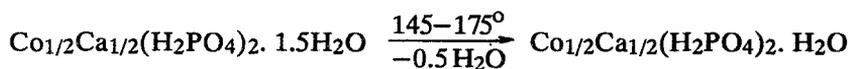
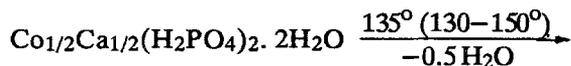
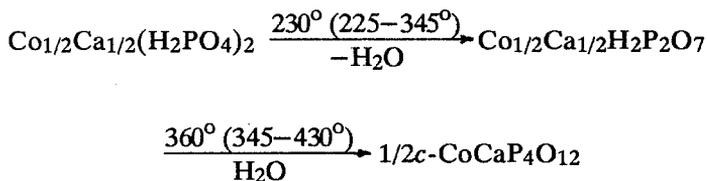


Fig.2 Simultaneous TG, DTG and DTA curves of $\text{Co}_{1/2}\text{Ca}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ traced under quasi-isothermal, quasi-isobaric conditions. Decomposition rate: $0.3 \text{ mg} \cdot \text{min}^{-1}$; Temperature increase: $2 \text{ deg} \cdot \text{min}^{-1}$; Sample weight: 259.6 mg ; Sensitivity of the balance: TG 100 mg ; Labyrinth crucible, $p_{\text{H}_2\text{O}(\text{g})} = 100 \text{ kPa}$; Atmosphere: air

of individual processes are given in brackets, the temperature of the decisive part of the process are given before the brackets):





The splitting off of the constitutional water from the double salt $\text{Co}_{1/2}\text{Ca}_{1/2}(\text{H}_2\text{PO}_4)_2$ took place in two steps and probably according to two different mechanism. first the crystal waterfree sample lost viz. in a broad temperature interval between 225-345° (about a third of it is released nearly isothermally at 230°) gradually one molecule of water. In contrast, the greater part of the second molecule of constitutional water became liberated in the vicinity of 360° while it was not necessary to increase the temperature significantly. However the last traces of the water could be expelled from the sample only by the gradual increasing of the temperature with about 200 degrees. As a matter of fact it counts as an exception if the departure of water takes place in rapid way.

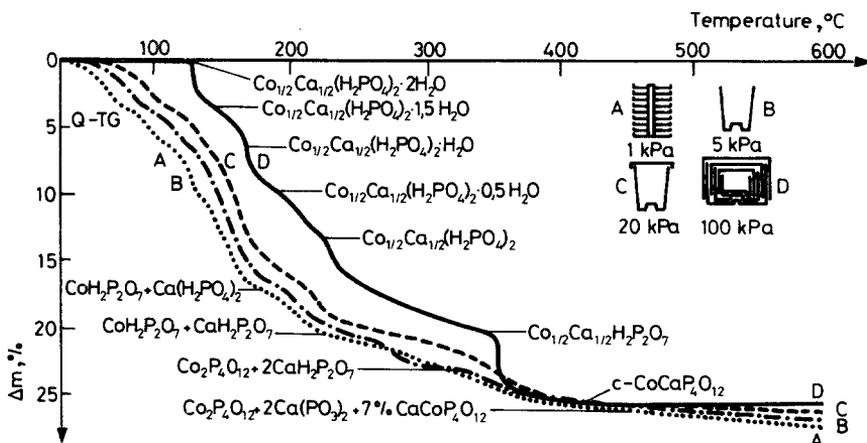


Fig.3 TG curves of $\text{Co}_{1/2}\text{Ca}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ traced under quasi-isothermal, quasi-isobaric conditions. Decomposition rate: $0.2 \text{ mg} \cdot \text{min}^{-1}$; Sample weight: 300 mg; Atmosphere: air; (A) Multiplate crucible, $p_{\text{H}_2\text{O}(\text{g})} = 1 \text{ kPa}$; (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, $p_{\text{H}_2\text{O}(\text{g})} = 100 \text{ kPa}$

The fact that the intermediate $\text{Co}_{1/2}\text{Ca}_{1/2}\text{H}_2\text{P}_2\text{O}_7$ as well as the end product of first condensation reaction. $\text{CoCaP}_4\text{O}_{12}$ are binary salts and not

the simple mixtures of the corresponding cobalt and calcium compounds, could convincingly be proved in experiments carried out by extraction. As it can be seen in Fig. 4, the course of curves 1 and 2 in picture *a* do not show any likeness with those to be seen in pictures *b* and *c*. Based on the results of electron microscopic examinations and IA spectroscopic examinations of the calcinated samples and the extraction residues we also came to the above conclusion. Binary cobalt-calcium cyclo-tetraphosphate $c\text{-CoCaP}_4\text{O}_{12}$ with the yield about 95 % w. w. can be prepared with this method [18]. It appears to be a perspective special pigment of an intensive blue-violet colour [31].

The binary cobalt-calcium cyclo-tetraphosphate ($c\text{-CoCaP}_4\text{O}_{12}$) presents a new compound not mentioned in literature till now and which has become the subject of Czechoslovak patent [30]. Its crystal structure has been determined in monoclinic system group C 2c, with structure parameters: $a = 1.2130(7)$ nm, $b = 0.8676(5)$ nm, $c = 0.9895(5)$ nm, $\beta = 118.46(3)^\circ$, the volume of an elementary cell $V = 0.9135$ nm³ and density 3.017 g . cm⁻³ (ρ calculated) or 3.02 g . cm⁻³ (ρ experimental).

The water loss process of $\text{Co}_{1/2}\text{Ca}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ took place in another way if the compound was examined on the other sample holder in the presence of water vapour of about 1-20 kPa pressure under quasi-isothermal conditions. In this case namely the course of the curves (curves A, B and C) differed from that of the Q-TG curves obtained by using the labyrinth crucible (curve D). The former curves were not only shifted in the direction of lower temperatures, according to the lower vapour content, but the break points presented themselves also at temperatures-different from those corresponding composition of the intermediates formed within the labyrinth crucible. The results of the extraction experiments (Fig. 4) similarly prove the change of the decomposition mechanism. According to these, in a significantly lower temperature range became the intermediates water soluble (curve 3, Fig. 4) and the final product insoluble in 0.3 M HCl solution (curve 4) respectively.

Based on the analogy of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ [29] and $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ [2], as well as on earlier experiences one can draw conclusion regarding the character of the changed reaction mechanism. Accordingly, it can be supposed that in the presence of water vapour of low partial pressure beside $\text{Co}_{1/2}\text{Ca}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 1.5\text{H}_2\text{O}$ also hydrogenphosphate hydrates of other composition ($\text{Me}^{\text{II}}\text{HPO}_4 \cdot \text{H}_2\text{O}$; $\text{Me}^{\text{II}} = \text{Co}, \text{Ca}$) and phosphoric acid could be formed. After it these intermediate hydrates may lose their residual crystal water content while of the phosphoric acid, diphosphoric acid may be released. These are condensed separately to form higher polyphosphoric

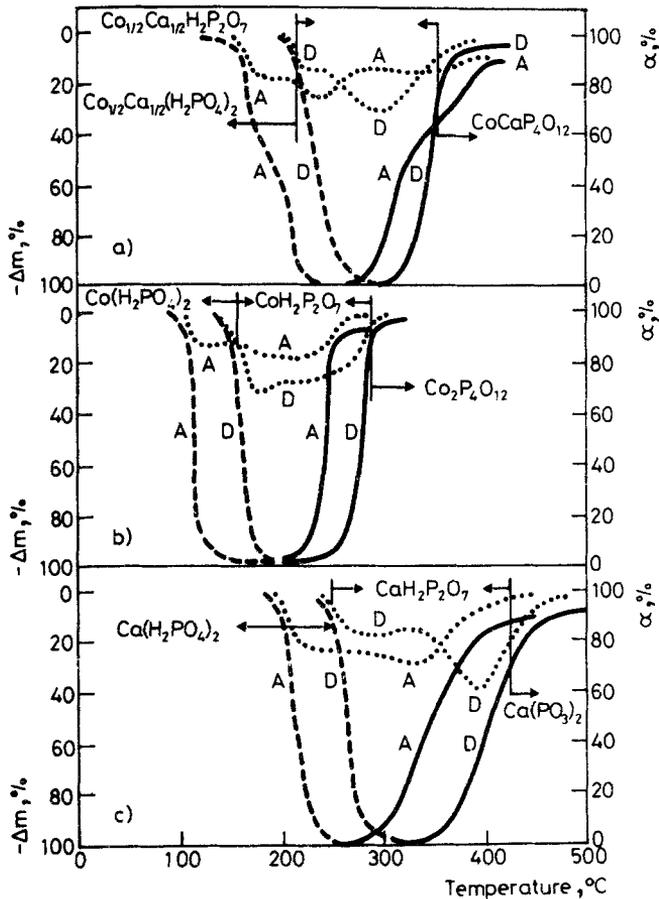


Fig.4 Extraction experiments on calcinates of $\text{Co}_{1/2}\text{Ca}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (a), $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (b) and $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ (c). (Calcination conditions 2 deg. min^{-1} , $p\text{H}_2\text{O}(\text{g}) = 1 \text{ kPa}$ - A, 100 kPa - D). Weight changes determined by extraction: acetone (·····); water (---); 0.3M HCl (—) (degree of conversion (α) to the cyclo-tetraphosphates)

acids in the calcination to higher temperatures. After release of all crystal water the intermediate product is a mixture of anhydrides of the cobalt and calcium dihydrogenphosphate. The first molecule of constitutional water is liberated in the temperature interval $155\text{--}270^\circ$ and corresponds to the formation of the $\text{CoH}_2\text{P}_2\text{O}_7$ and $\text{CaH}_2\text{P}_2\text{O}_7$ intermediate products in the calcinate at this conditions. The next process in the interval of $225\text{--}310^\circ$ caused again the release of 0.5 water molecules. Parallel dicobalt cyclo-tetraphosphate $c\text{-Co}_2\text{P}_4\text{O}_{12}$ and $\text{CaH}_2\text{P}_2\text{O}_7$ were formed [29]. With further tempera-

ture increase the end compounds were condensed. Beside dicobalt tetraphosphate was formed (225-310°) also $\text{Ca}(\text{PO}_3)_2$ (310-420°). The formation of final product only about 7 % of $\text{CoCaP}_4\text{O}_{12}$ could be detected. Other by products formed in lesser extent are higher polyphosphoric acids, diphosphates (of cobalt and calcium), and event. products with ultra-phosphate type anions.

Summing up, it can be stated the mechanisms of the reactions taking place under two different conditions (100 and 1 kPa resp.) is, that in pure water vapour atmosphere of 100 kPa pressure the reactions take place in a uniform and unambiguous way (*sec equis*), and the intermediary and final products are of binary type double salts, while in water vapour atmosphere of low (1 kPa) partial pressure the starting compound decomposes soon after the beginning, breaks up into its constituent parts and many partial reactions take place in a parallel way.

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Zusammenfassung – Mittels Thermoanalyse bei nichtisothermen (dynamischen) und bei quasi-isothermen-isobaren Bedingungen wurde der Mechanismus der Dehydratations- und der Kondensationsreaktion bei der Kalzinierung von $\text{Co}_{1/2}\text{Ca}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ untersucht. Die isotherme Kalzinierung des binären Dihydrogenphosphates als Ausgangsstoff wurde in einem Elektroofen bei verschiedenen Temperaturen durchgeführt. Zwischen- und Endprodukte der Reaktion wurden durch instrumentelle analytische Methoden und durch Extraktionsexperimente mit Lösungen von anorganischen Verbindungen und mit organischen Reagenzien analysiert. Es wurde weiterhin der Einfluß des Wasserdampfdruckes auf Weg, Geschwindigkeit und Ausbeute der Kondensationsreaktionen und auf die Bildung des Hauptproduktes (binäres Cyclotetraphosphat (Tetramethaphosphat) $c\text{-CoCaP}_4\text{O}_{12}$) untersucht.