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THERMAL DECOMPOSITION OF BINARY DIHYDROGENPHOSPHATES

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Cyclo-tetraphosphates $M^{II}_{2-x}M^{II}_xP_4O_{12}$ have been synthetized by thermal dehydration of dihydrogenphosphates. The syntheses of the binary cyclo-tetraphosphates c–$Zn_{2-x}Ca_xP_4O_{12}$ and c–$Mn_{2-x}Mg_xP_4O_{12}$ are presented as examples.

Binary cyclo-tetraphosphates have been tested as special thermostable anticorrosive inorganic pigments. The main attention was focused on elucidation of the mechanism of the reactions taking place during the formation of these compounds, and determination of the reaction conditions necessary for their preparation. The method of synthesis gave a possibility to obtain them and define them as new inorganic compounds [1], because they have not yet been described in the literature [2-3].

Experimental

The measurements were carried out with a Derivatograph C (Fig. 1) and a Derivatograph Q-1500 (Fig. 2) (MOM, Budapest). Platinum crucibles of various types (Fig. 2) were used, which permitted trapping of the water vapour released from the phosphate sample at various tensions. Individual products and intermediates were prepared by calcination of the starting phosphate in an electric oven, and they were analyzed by instrumental methods (IMA): thin-layer chromatography, infrared spectroscopy and X-ray diffraction analysis. The surface changes were observed by means of electron microscopy. Extraction of the calcinates with various solvents allowed determination of the temperature regions of existence of the individual intermediates.

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Results and discussion

Individual thermoanalytical curves obtained in Q-TA by using the Derivatograph C apparatus are given as examples in Fig. 1. A labyrinth crucible was used as the sample holder: the vapour tension in the sample space approached that of the surrounding atmosphere, i.e. 100 kPa. The curves show that the liberation of the water molecules from the dihydrogenphosphate $Zn_{1/2}Ca_{1/2}(H_2PO_4)_2 \cdot 2H_2O$ takes place in the temperature intervals 130-165°, 165-225° and 350-400°, the first, second and fourth of these intervals having a marked endothermic nature. All four crystal water molecules of $Mn_{1/2}Mg_{1/2}(H_2PO_4)_2 \cdot 4H_2O$ seem to be released within one continuous process in the temperature interval 120-190°, and the two molecules of water of constitution in two steps (190-270° and 270-360°).

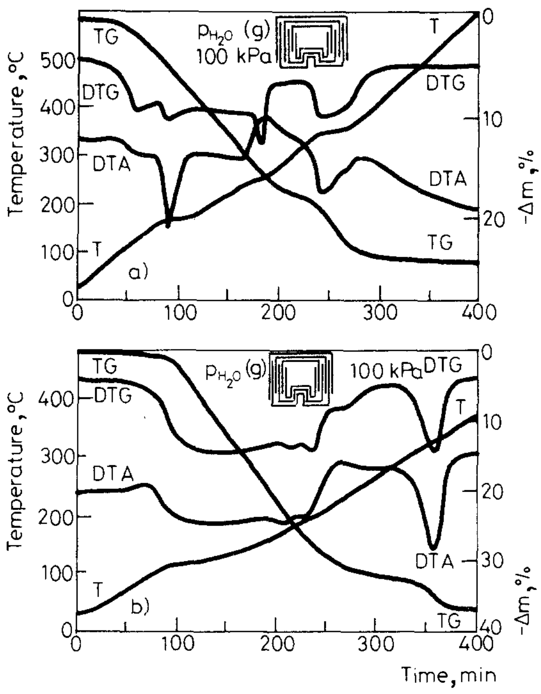

Fig. 1 Simultaneous TA curves of $Zn_{1/2}Ca_{1/2}(H_2PO_4)_2 \cdot 2H_2O$ (a) and $Mn_{1/2}Mg_{1/2}(H_2PO_4)_2 \cdot 4H_2O$ (b) recorded under quasi-isothermal, quasi-isobaric conditions. Apparatus: Derivatorgraph C; decomp. rate: 0.3 mg·min^{-1}; heating rate: 1 deg·min^{-1}; sample weight: 240 mg (a), 150 mg (b)

Only Q-TA with the use of two different crucibles as sample holders (Fig. 2) gave a more concrete conception of the individual processes taking place in the course of calcination of the starting dihydrogenphosphates. This allowed establishment of the two principal reaction (decomposition) mechanisms that are closely connected with the water vapour pressure within the space of the calcined sample. The first of them holds for the vapour pressure approaching 100 kPa (corresponding to the use of a labyrinth crucible as the holder of the thermoanalyzed sample): in contrast, the second is preferred if the vapour pressure is very low, and quite negligible (multi-plate crucible). The former mechanism leads only to the desired product, the binary cyclo-tetraphosphate. In the latter case, mostly products of non-binary type are produced.

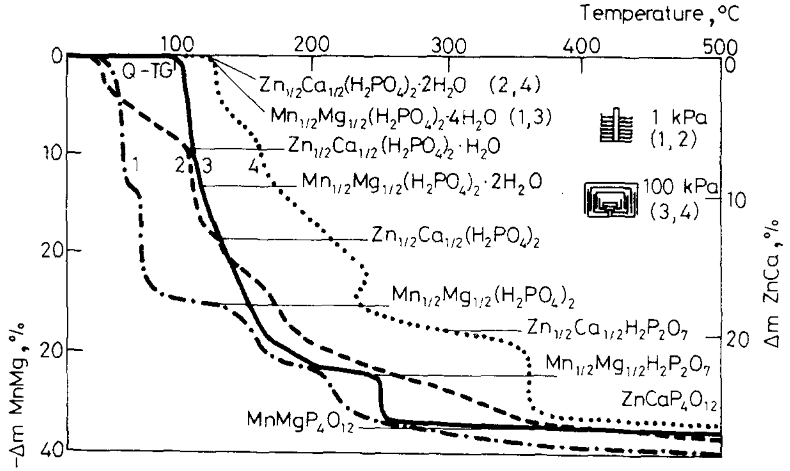

Fig. 2 TG curves of $Zn_{1/2}Ca_{1/2}(H_2PO_4)_2 \cdot 2H_2O$ and $Mn_{1/2}Mg_{1/2}(H_2PO_4)_2 \cdot 4H_2O$, recorded under quasi-isothermal-isobaric conditions (decomp. rate: 0.3 $mg \cdot min^{-1}$)

The course and conditions of the calcination of the starting zinc-calcium and manganese-magnesium dihydrogenphosphates at a water vapour pressure in the space approaching 100 kPa can be expressed as follows, with the temperature intervals of the individual processes (the temperature intervals of the processes for $Mn_{1/2}Mg_{1/2}(H_2PO_4)_2 \cdot 4H_2O$ are given in brackets):

$$Zn_{1/2}(Mn)Ca_{1/2}(Mg)(H_2PO_4)_2 \cdot xH_2O \xrightarrow[-x\,H_2O]{130-210^{\circ}(120-190^{\circ})}$$

$$Zn_{1/2}(Mn)Ca_{1/2}(Mg)(H_2PO_4)_2 \xrightarrow[-\,H_2O]{210-330^{\circ}(190-250^{\circ})}$$

$$Zn_{1/2}(Mn)Ca_{1/2}(Mg)H_2P_2O_7 \xrightarrow[-\,H_2O]{330-400^{\circ}(250-400^{\circ})}$$

$$\rightarrow 1/2\ c\text{-}ZnCaP_4O_{12}\ (c\text{-}MnMgP_4O_{12})$$

In this way [4], binary zinc-calcium and manganese-magnesium cyclotetraphosphates, which appear to be perspective special pigments, can be prepared in yields of about 93 and 97 wt.%, respectively.

If calcination is carried out at lower water vapour pressures, the temperatures of the individual processes decrease, and some of the intermediates split to form other intermediates that are condensed separately. The proportion of the main product, c–$ZnCaP_4O_{12}$, in the final calcinate falls to 15% (60% of c-$MnMgP_4O_{12}$) at a water vapour pressure approaching 1 kPa. The final by-products are c–$Zn_2P_4O_{12}$ and $Ca(PO_3)_2$; however, these can constitute the bulk of the product at low vapour pressure, together with higher phosphoric acids, diphosphates and smaller amounts of products with ultraphosphate-type anions. In the case of $Mn_{1/2}Mg_{1/2}(H_2PO_4)_2$, certain intermediates (anhydride or dihydrogendiphosphate) partly split to hydrogenphosphates and phosphoric acid or diphosphates and diphosphoric acid, respectively, and to individual manganese and magnesium intermediates (i.e. not of binary type). The latter are then dehydrated and condensed separately to by-products, in this way decreasing the proportion of the main product, c–$MnMgP_4O_{12}$, in the calcinate.

References

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Zusammenfassung — Durch thermische Dehydratation von Dihydrogenphosphaten wurden cyclische Tetraphosphate der Formel $M^{II}_{2-x}M^{II}_{x}P_4O_{12}$ synthetisiert. Als Beispiel wird die Synthese der binären Cyclotetraphosphate c–$Zn_{2-x}Ca_xP_4O_{12}$ und c–$Mn_{2-x}Mg_xP_4O_{12}$ beschrieben.