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INVESTIGATION OF REACTIONS CONNECTED WITH FORMATION OF CONDENSED PHOSPHATES BY TA METHODS

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ABSTRACT

Dynamic and quasi-isothermal-isobaric TA curves were used to follow the condensation reactions taking place during calcination of manganese and cobalt dihydrogenphosphates. The products of calcination obtained were analyzed by chromatography, IR and NMR spectroscopy, and X-ray diffraction analysis.

INTRODUCTION

Recently, condensed phosphates of some divalent metals have proved to be significant compounds. They have been tested as microadditives to fertilizers of long-term action, and some of them are special thermostable inorganic pigments[1]. Therefore, main attention was focused on elucidation of mechanisms of the reaction taking place during formation of these compounds and determination of the reaction conditions necessary for their preparation. With respect to the above-mentioned applications, the most favourable seem to be cyclo-tetraphosphates (c-$Mn_2P_4O_{12}$ and c-$Co_2P_4O_{12}$) which can be prepared by calcination of dihydrogenphosphates.[2]

RESULTS AND DISCUSSION

Thermogravimetric curves (Q-TG) of $Mn(H_2PO_4)_2.2H_2O$ at quasi-isothermal-isobaric conditions (Fig.1) showed, at first, the release of the two crystal water molecules from the said substance: the process occurs in a single step in the case of Mn^{II} phosphate[3]. The corresponding temperature for the individual crucibles were : (A) 60-75°C, (B) 80-100°C, (C) 100-110°C, (D) 120°C. Hence the temperature of the crystal water release is decreased with decreasing partial pressure of water vapour above the analyzed sample. From the Q-TG curves it also follows that the reaction proceeded practically isothermally, i.e. to an equilibrium. With Co^{II} dihydrogenphosphate (Fig.2) the crystal water is released in two steps. In the crucible (D) the two water molecules escape independently at 105-150°C and 150-180°C. In the other crucibles (A-C) this process takes place at the temperature of 60-150°C. The existence of anhydrous $Me(H_2PO_4)_2$ was proved in the interval above the temperatu-

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res mentioned and its crystalline character was confirmed.

The first molecule of the constitutional water begins to escape from manganese (II) dihydrogenphosphate at the same temperature (190°C) in all the crucibles used. Then the sample temperature spontaneously decreases to 155, 165 and 170°C in the crucibles (A),(B) and (C), respectively, about one half of water molecule being released. This phenomenon can be explained in the following way: Formation of the nuclei which intitiate the transformation begins at a higher temperature than that corresponding to the temperature of the transformation, i.e. at a higher energy content of the compound[4]. As soon as a sufficient amount of the nuclei is formed, the equilibrium is reestablished, and the reaction proceeds at the chosen rate of 0•4 mg min^{-1} and at the temperature corresponding to the actual partial pressure of water vapour. In the labyrinth crucible (D), the first water molecule is released at constant temperature corresponding to the reaction course at the partial pressure of water vapour 100 kPa and at the chosen rate at 190°C. The temperature slowly increases during releasing of the second half of water molecule. It can be presumed that porosity of the upper layer of the calcinate decreases with increasing partial pressure of water vapour. Thereby the escape of water vapour from the phase boundary is made increasingly difficult as the thickness of the said layer increases.

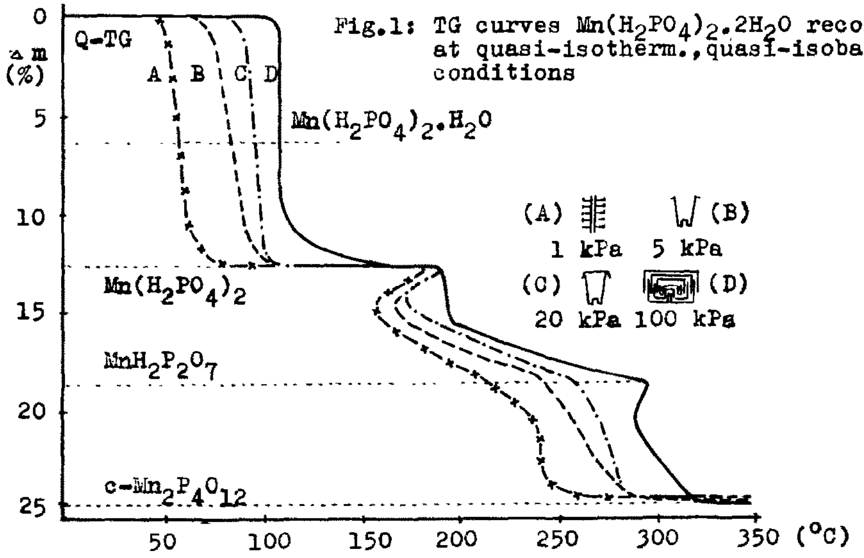

Fig.1: TG curves $Mn(H_2PO_4)_2.2H_2O$ recorded at quasi-isotherm.,quasi-isobaric conditions

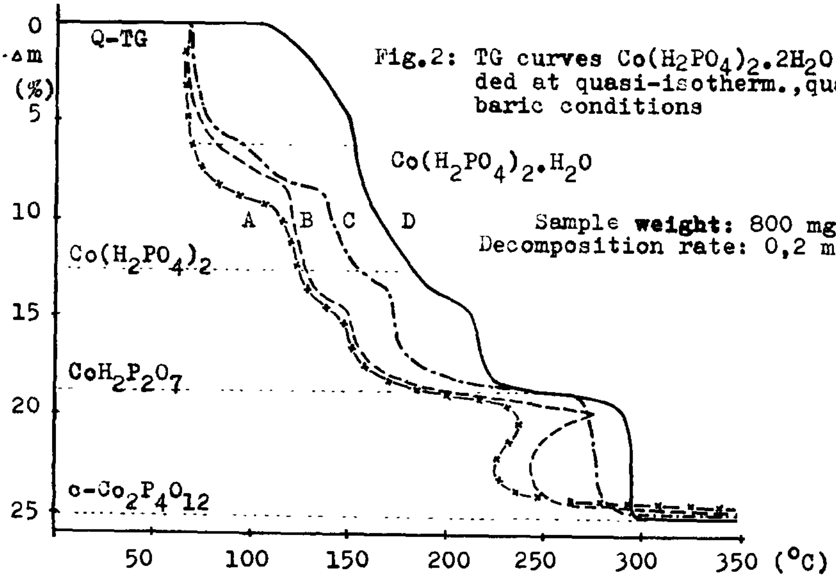

Fig.2: TG curves $Co(H_2PO_4)_2.2H_2O$ recorded at quasi-isotherm.,quasi-isobaric conditions

Sample **weight:** 800 mg
Decomposition rate: 0,2 $mg.min^{-1}$

The intermediate prepared also by calcination of the starting sample at isothermal conditions was submitted to extraction analyses to determine the material balance. The results of the extraction experiments show that a part of the phosphorus component is split off in the form of phosphoric acid from the intermediate anhydrous dihydrogenphosphate or in the form of diphosphoric acid from the first condensation product - dihydrogendiphosphate. Simultaneously, a part of this component is transformed into the diphosphate $Me_2P_2P_7$. At the same time, however, the released part of the phosphorus component can be condensed independently, whereby the yield of the second condensation reaction is lowered (the cyclo-tetraphosphate formation). This condensation reaction proceeds even at the temporarily decreased temperature, higher condensates of polyphosphoric acid being formed gradually during further increase of temperature.

The temperatures of liberation of the last part of water correspond to the second molecule of the constitutional water of the starting dihydrogenphosphate and to the second condensation reaction - formation of $c-Me_2P_4O_{12}$. They again depend on the crucible type used, i.e. on the partial pressure of water vapour. At the same time, however, it was shown that this transformation only proceeds by the isothermal way (280-295°C) and, hence, leads to an equilibrium in the case of Co^{II} phosphate in the labyrinth crucible. In the different crucible types used, this process with Mn^{II} phosphate proceeds at temperature : (A) 220-265°C, (B) 250-295°C, (C) 270--300°C, (D) 320-330°C. With Co^{II} dihydrogenphosphate, the release of the second molecule of the constitutional water was observed practically at the temperatures of 240°C (A) and 270°C (B,C). In the crucible types (A) and (B), this process is accompanied by a distinct temperature decrease again: viz. to 225°C (A) and 245°C (B). This value corresponds - to the partial pressure at which the decomposition proceeds at the chosen rate (0·4 mg/min). Taking into account all the circumstances, however, we can state that the condensation reaction - formation of c-$Me_2P_4O_{12}$ - probably leads to an equilibrium, but its course is affected by porosity of the upper layer of the forming calcinate. The overall weight decrease in the case of the labyrinth crucible corresponds to the theoretical value of complete release of 4 water molecules from the starting phosphate. In the other crucible types (where, in the course of the condensation reaction giving $MnH_2P_2O_7$, partial release and independent condensation of phosphoric acid took place) such weight decrease was not reached up to the temperature 380°C. This result is due to the fact that the condensation to higher degrees of the split off phosphoric acid as well as the partial formation of $Mn_2P_2O_7$ are shifted to higher temperatures, i.e. above the temperature of formation of c-$Mn_2P_4O_{12}$.

The existence and the quality of the cyclo-tetraphosphate formed were confirmed by the above-mentioned methods of instrumental analysis[5,6]. The results given partially disagree with the published findings: the authors give different temperatures and also describe formation of linear tri- and tetraphosphates (Mn^{II})[7] and even higher (up to eight-membered) condensed phosphates (Co^{II})[8] as the reaction intermediates.

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