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A STUDY OF CONDENSATION REACTIONS DURING FORMATION OF c-$Cu_2P_4O_{12}$ BY MEANS OF QUASI-ISOTHERMAL-ISOBARIC THERMAL ANALYSES

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ABSTRACT

Calcination of a mixture of copper (II) oxide and phosphoric acid (mol. ratio $CuO/P_2O_5 = 1$) produces dicopper (II) cyclo-tetraphosphate as the main product. At first, various intermediates of the type of simple copper (II) phosphates are formed. Then, at higher temperatures, condensation of phosphate anions takes place. Temperature and rate of the individual reactions as well as yields of the main product are distinctly affected by water vapour pressure in the calcinate.

INTRODUCTION

Influence of water vapour pressure on the reactions producing cyclo-tetraphosphate by calcination of cobalt (II) dihydrogenphosphate was examined in our previous paper (ref.1). As the pure copper(II) dihydrogenphosphate does not exist (ref.2), the preparation of dicopper(II) cyclo-tetraphosphate must start from a mixture of copper(II) oxide (or hydroxide or carbonate) and phosphoric acid with the molar ratio $CuO/P_2O_5 = 1$ (ref.3). The data (refs 3,4,5) on conditions of this preparation show considerable discrepancies. Their reason is explained in this paper by the given effect of water vapour pressure in the calcinate on the reaction course and on yield of the cyclo-tetraphosphate. (The accompanying poster also gives data on formation and existence of the individual intermediates.

MEASURING METHODS

The thermal analyses were carried out with a Q-Derivatograph type Q-1500 (MOM Budapest, system F.Paulik, J.Paulik, L.Erdey). Various types of platinum crucibles were used as sample carriers (see Figs 1 and 2). These arrangements enabled the water vapour released from the thermoanalyzed mixture to be retained with various partial pressures (ref.6). Calcination of the original mixture in an electric oven was used for preparation of the individual products and intermediates. These substances were analyzed by means of TLC, IR spectroscopy, and X-ray diffraction analysis. Also they

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were observed by means of electron microscopy, extracted with organic solvents and with mineral acids, and the extracts were analyzed by means of complexometry and by AAS.

RESULTS AND DISCUSSION

TA of the starting mixture (which can be expressed as CuO + $+2H_3PO_4 + 2\cdot1\ H_2O$) at dynamic conditions gave considerably different results for different crucibles used as the sample carriers. Figure 1 gives (as an example, others are presented in the poster) the TA curves with two types of Pt crucibles with extreme values of water vapour pressure (ref.6). The first type is the so-called multiplate crucible (A), in which the water vapour pressure can practically be neglected (1 kPa), and the other is a labyrinth arrangement (B) in which the pressure of water vapour approaches atmospheric pressure (100 kPa). In the TA range up to 1000°C the overall weight decrease of the mixture was 29·3 % in the labyrinth arrangement (which corresponds to practically quantitative formation of c-$Cu_2P_4O_{12}$). In the etage crucible, the respective value was 44·2 %. In the labyrinth crucible the weight of the sample did not further change after the formation of cyclo-tetraphosphate (450°C) was finished. In the etage crucible, however, the weight continued to decrease after partial reaction of formation of c-$Cu_2P_4O_{12}$ which was most marked within the interval from 400 to 600°C but perceptible even above 820°C when the cyclo-tetraphosphate melts. These facts indicate that, besides the condensation reactions connected only with release of water and leading to the cyclo-tetraphosphate, there take place still other reactions characterized by relatively distinst loss of the phosphate component due to its volatility.

The TA at quasi-isothermal-isobaric conditions (Fig.2) confirmed these conclusions. As compared with the TA at dynamic conditions, the individual processes were recorded more distinctly and the temperatures connected therewith were more accurate. Analysis of the calcinates prepared at various temperatures showed that there obviously takes place formation of an intermediate whose formula is $3(CuHPO_4.H_2O).H_3PO_4.2\cdot5H_2O$ (ref.3). Besides that, the mixture contains excess phosphoric acid and water. Further reactions then proceed in dependence on the crucible type, i.e. on the water vapour pressure in the calcinate. In the labyrinth arrangement free water is released at first, followed by bound water

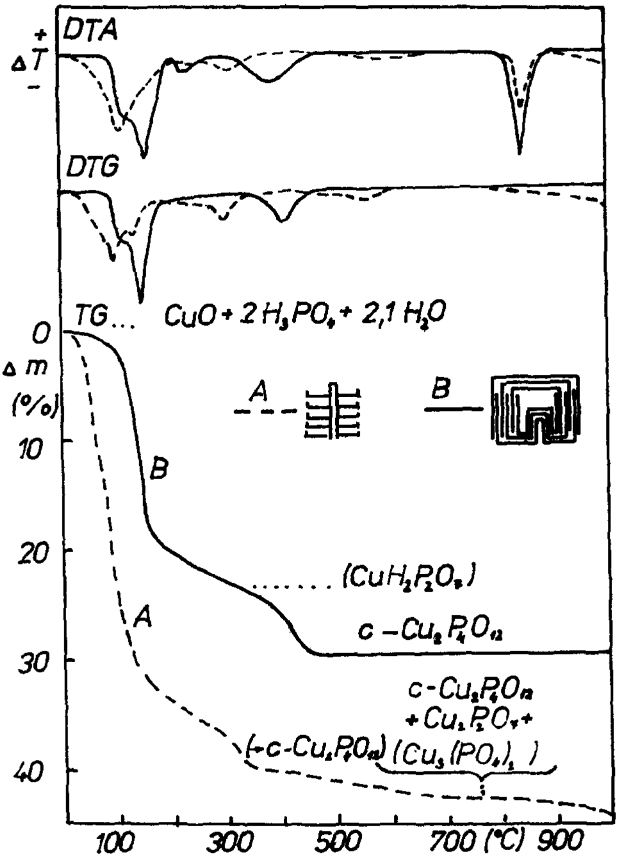

Fig. 1. DTA, DTG, TG curves starting mixture ($CuO+2H_3PO_4+2,1H_2O$) recorded at dynamic conditions

Sample weight: 400 mg
Standard: α-Al_2O_3
Atmosphere: air
Sensitivity of the balance: TG 200 mg
DTA, DTG 1/3
Temperature increase: 2,5°C.min^{-1}

Derivatograph Q-1500
System: F.Paulik, J.Paulik, L.Erdey

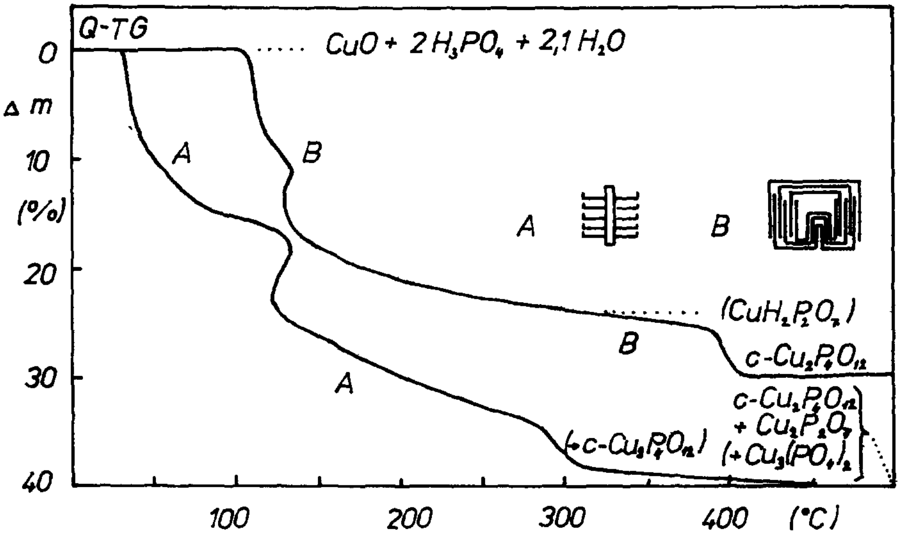

Fig. 2. TG curves starting mixture ($CuO+2H_3PO_4+2,1H_2O$) recorded at quasi-isothermal-isobaric conditions

Sample weight: 400 mg
Decomposition rate: 0,4 mg.min^{-1}
Atmosphere: air

and finally by that from free orthophosphoric acid. At the same time the condensation product $CuH_2P_2O_7$ is already formed. This product is then converted quantitatively into c-$Cu_2P_4O_{12}$ by the second condensation reaction. At low water vapour pressure - in the etage crucible - the processes are somewhat different. Again free water and bound water (from the first intermediate) are released first. At the same time, however, free phosphoric acid present in the mixture begins to boil and to condense independently into polyphosphoric acid. After complete dehydration of the first intermediate a mixture of condensation products $Cu_2P_2O_7$ and c-$Cu_2P_4O_{12}$ (approximately in molar ratio 2:1) are formed. The highly condensed polyphosphoric acid is finally decomposed (at high temperatures of the TA) into P_2O_5 which escapes from the mixture (Fig.1). At these conditions, about a quarter of phosphoric acid is lost and does not take part in the formation of the required product - c-$Cu_2P_4O_{12}$. Besides that, in the etage crucible we can also expect formation of small amount of some further types of copper(II) phosphates (ref.2). The latter are decomposed above 500°C to give $Cu_2P_2O_7$ and $Cu_3(PO_4)_2$, the losses of the phosphate component being further increased. Thereby the yields of c-$Cu_2P_4O_{12}$ are decreased to about one half of that obtained in the labyrinth arrangement.

CONCLUSIONS

The TA at dynamic and at quasi-isothermal-isobaric conditions showed that the preparation of c-$Cu_2P_4O_{12}$ via calcination of the mixture of copper(II) oxide and phosphoric acid is distinctly affected by water vapour pressure in the calcinate. If this pressure approaches atmospheric pressure, the condensation reaction of formation of the cyclo-tetraphosphate proceeds practically quantitatively at the temperatures 380-410°C. On the contrary, if the water vapour pressure is negligible, the process takes place at the temperatures lower by 100°C, the yields being roughly 50 %.

REFERENCES

1 M.Trojan,D.Brandová,Z.Šolc, 3 ESTAC'84, Interlaken, Switzerland 1984 (special issue Thermochim.Acta - in press)
2 E.Hayek,P.Reinthaler,J.Adamietz, Monats.Chem. 107 (1976)
3 E.Thilo,H.Grunze, Z.Anorg.Allg.Chem. 290 (1957) 209
4 R.A.Mannanova, IVUZ Chim. chim.technol. 19 (1976) 1831
5 A.V.Lavrov,T.A.Bykanova, IAN SSSR Neorg.mater. 11 (1975) 901
6 J.Paulik,F.Paulik, Comprehensive Analytical Chemistry, ed.G.Svehla, Vol.XII, Part A, Elsevier Sci.Pub.Comp. Amsterdam 1981.