

## **MECHANISM OF DEHYDRATION AND CONDENSATION OF $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$**

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The dehydration of  $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$  was followed by means of thermogravimetric measurements under quasi-isothermal–quasi-isobaric conditions. The intermediates and products formed during the thermal analysis and during the calcination of the starting hydrogen phosphate in an electric furnace at various temperatures were analysed by means of thin-layer chromatography, IR spectroscopy, X-ray diffraction analysis and electron microscopy.

The condensed phosphates are thermally and chemically highly stable compounds [1, 2], which can be applied as micro-element fertilizers with long-term action [3, 4], and as special inorganic pigments [5–7]. One of the phosphates investigated is dicopper(II) diphosphate, which can be obtained of copper(II) hydrogen phosphate or of a mixture of phosphoric acid and a suitable copper(II) compound [8]. Several authors [9–11] have paid attention to the formation of  $\text{Cu}_2\text{P}_2\text{O}_7$ . Others [12–14] have investigated the  $\text{CuO-P}_2\text{O}_5\text{-H}_2\text{O}$  and/or  $\text{CuO-P}_2\text{O}_5$  and  $\text{Cu}_2\text{O-P}_2\text{O}_5$  phase equilibria, which can contribute to the decomposition of the diphosphate during its melting [15]. The available papers dealing with formation of diphosphate do not provide uniform data on the temperatures of release of the crystal water and the condensation reaction and the existence of two modifications [16, 17]. Certain authors [18] consider that the monoclinic  $\alpha\text{-Cu}_2\text{P}_2\text{O}_7$  is transformed in a reversible way into the high-temperature  $\beta$ -modification (monoclinic) in the interval 348–373°.

## Experimental

### *Material*

For the preparation of copper(II) hydrogen phosphate, the reaction of an aqueous suspension of dicopper(II) dihydroxide carbonate with phosphoric acid [19] in stoichiometric ratio was used. Under continuous stirring at 60°, the reaction took place in 5 h. The quality of the product was confirmed by X-ray diffraction analysis and electron microscopy [20].

### *Method*

In order to separate the individual processes taking place during the calcination and to determine the influence of the water vapour pressure on their course, the starting hydrogen phosphate was submitted to thermogravimetric measurement under quasi-isothermal–quasi-isobaric conditions (Q–TG) [21, 22] by means of a derivatograph–C [23, 24], produced by the Hungarian Optical Works, MOM, Budapest. The preselected decomposition rate was 0.2 mg min<sup>-1</sup>. The experiment was performed in the presence of air by applying a sample amount of about 350 mg. Various types of platinum sample holders [21, 22] were used for the measurements (labyrinth crucible: curve 1, covered crucible: curve 2, uncovered crucible: curve 3, and multiplate sample holder: curve 4 in Fig. 1). The labyrinth crucible retains the water vapour released during the calcination of the starting hydrogen phosphate, the partial pressure of which attains 100 kPa immediately after the beginning of the decomposition and remains constant until the end of the reaction (quasi-isobaric). The application of the multiplate sample holder leads to a practically negligible water vapour pressure (about 1 kPa). The water vapour pressures in the case of the covered and uncovered crucibles are about 5 and 20 kPa. In this case the linear rise of temperature was 5 deg min<sup>-1</sup>, the sample was about 350 mg and the open crucible was applied as sample holder.

By means of an electric furnace stepwise heated up to various temperatures, condensation products were prepared. For this process, the multiplate sample holder and the labyrinth crucible were used. The intermediates were analysed by means of thin-layer chromatography (the TLC II set) [25], IR spectroscopy [26, 27] (Perkin–Elmer 684 infrared spectrophotometer) and x-ray diffraction analysis [28, 29] on a HZG–4 apparatus (GDR).

## Results and discussion

Of the Q-TG and TG curves in Fig. 1, curve 1, which was traced under the conditions of quasi-isothermal heating and by using the labyrinth crucible, provides the most comprehensive information about the decomposition mechanism of  $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ . This curve clearly shows that the decomposition of  $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$  took place in two steps. First, the sample lost its water of crystallization in an isothermal way at  $145^\circ$ , after which its constitutional water was released in the broad temperature interval between  $145$  and  $320^\circ$ . From the fact that the break-point in curve 1 and the weight constancy period of the curve above  $350^\circ$  accorded to the stoichiometrically computed levels can be drawn that the water molecules bound in the two different way were released separately.

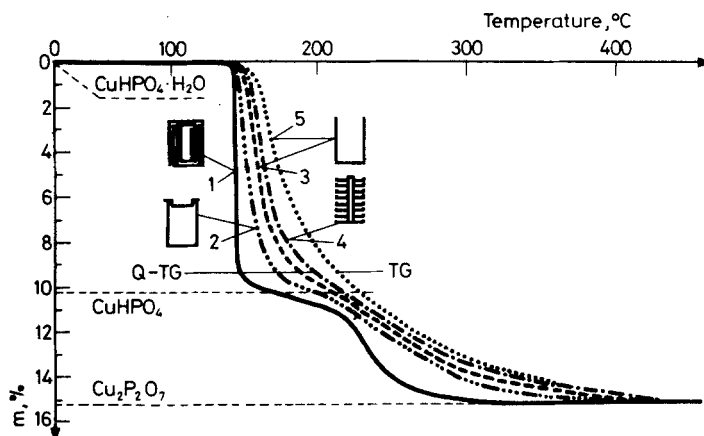


Fig. 1 Q-TG curves of hydrogen phosphate obtained by various types of platinum sample holders

It also turned out that the first period of the decomposition is a process taking place between solid and gaseous phases. The simultaneously traced DTA curve (not illustrated) did not show any enthalpy change indicative of the melting of the salt. Consequently, a liquid phase was even transitionally not formed. The literature data also support the general opinion that this material does not melt.

From the circumstance that one mole of water of crystallization departed in an isothermal way in the case of curve 1, it follows that this is a process leading to equilibrium [21, 22]. However, there are certain conditions which seemingly contradict this statement. First, curves 2, 3 and 4, traced with the use of various sample holders, did not run in isothermal way. Secondly, the curves were shifted in comparison to one another, and the sequence of their shifts was just the reverse (1, 2, 3, 4) what one would expect for the various sample holders [21, 22]: for the

labyrinth, covered and uncovered crucible and the multiplate sample holder, the partial pressure of water vapour was about 100, 20, 5 and 1 kPa, respectively, i.e. in the event of reactions leading to equilibrium the curves should follow one another in the sequence 4, 3, 2, 1.

The above phenomena can probably be explained by presuming that the crust-like new phase formed on the surface of the  $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$  grains tends, like many other metal acid phosphates [21, 22, 33], to form a compact structure. With the progress of the transformation, the poor porosity rendered it more and more difficult for the water vapour to depart from the interior of the grains. The rate at which the thickness of the crust elevated the temperature of the decomposition increased continuously up to the end of the transformation. Accordingly, the conversion became anisothermal (curves 2, 3 or 4) despite the fact that it was originally isothermal (curve 1), i.e. it was a process leading to equilibrium.

If this idea is accepted as correct, then it can also be presumed that the porosity of the new phase was greatly influenced by the liberated water vapour still in contact with the grains. The higher the concentration of the water vapour, the greater was the porosity.

In this sense, the differences between the curves in Fig. 1 can already be interpreted. In the case of curve 1, it can be assumed that, in the pure water vapour atmosphere (100 kPa) within the labyrinth crucible, the porosity of the new phase became high enough to ensure that the water of crystallization could still depart in an isothermal way. However, in the case of curves 2, 3 and 4, the reaction-retarding effect of the poor porosity prevailed.

The sequence of the curves (4, 3, 2, 1) is also in conformity with the above picture. The higher the partial pressure of the sample in contact with the water vapour, the higher the temperature domain in which the transformation took place.

Also, in conformity with this explanation are the results obtained from the examination of the crystal structure and morphology of the  $\text{CuHPO}_4$  intermediate. x-ray diffraction analysis for example, showed that the crystal structure of the grains became better ordered in the labyrinth crucible than on the multiplate sample holder. Electronmicroscopic examinations proved further that the breaking up into small pieces of the grains did not occur to such an extent, and the grains preserved their original size and shape better, if the experiment was carried out by using the labyrinth crucible instead of the multiplate sample holder.

In the second period of the decomposition, the  $\text{CuHPO}_4$  intermediate lost its water of constitution. From the broad temperature interval (160–320°) of the second step of curve 1, the conclusion can be drawn that not a simple, but a very complex decomposition mechanism prevails here. It seems probable that in this period of the transformation many strongly overlapping elementary condensation

reactions take place. Otherwise, this assumption is supported by the analogy of the decomposition mechanism of metal hydrogen phosphates investigated earlier [21, 22, 30–33].

The end-product of condensation was mostly  $\text{Cu}_2\text{P}_2\text{O}_7$ , as shown by the Q–TG curves, but this was also indicated by the results of x-ray diffraction and chromatographic analyses.

From the latter examinations it turned out further that other condensation products, e.g. simple phosphates, diphosphoric acid, polyphosphoric acid, etc. were formed in small amount in the course of the reaction. Polyphosphoric acid is formed from diphosphoric acid through polycondensation, even if the temperature is not further increased.

Polyphosphoric acid forms a compact crust, with poor porosity, on the surface of the grais. The crust formation and the porosity-increasing effect of the water vapour can probably explain the phenomenon that, similarly to the process of water loss, in this case too the sequence of the curves is 4, 3, 2, 1, instead of the courses of the four curves being congruent, as usually occurs in the case of anisothermal reactions [21, 22].

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**Zusammenfassung** — Mittels thermogravimetrische Messungen wurde die Dehydration von  $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$  unter quasiisothermen-quasiisobaren Bedingungen untersucht. Die bei der Thermoanalyse und dem Kalzinieren des ursprünglichen Hydrogenphosphates in einem elektrischen Ofen bei verschiedenen Temperaturen entstehenden Produkte und Zwischenprodukte wurde mit Hilfe von Dünnsichtchromatographie, IR-Spektroskopie, Röntgendiffraktion und Elektronenmikroskopie untersucht.

**Резюме** — Термогравиметрическим методом в квазиизотермических-квазиизобарных условиях была изучена дегидратация  $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ . Методами тонкослойной хроматографии, ИК спектроскопии, рентгенофазового анализа и электронной микроскопии изучены промежуточные и конечные продукты, образующиеся в процессе термического анализа, а также при обжиге исходного гидрофосфата в электрической печи при различных температурах.