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THERMAL TRANSFORMATIONS OF $CuNH_4PO_4 \cdot H_2O$

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Abstract

The isothermal and non-isothermal transformations of polycrystalline $CuNH_4PO_4 \cdot H_2O$ in vacuum and in various gas atmospheres (in open air and in gaseous ammonia atmosphere) were studied at 20–800°C by means of differential thermal analysis, thermogravimetry, X-ray diffraction, paper chromatography, optical microscopy and chemical analyses. The effects of the gas phase composition on the kinetic peculiarities of total gas evolution and on the partial processes of dehydration, ammonia removal and rearrangement of the anionic sub-lattice were considered.

Keywords: kinetics and mechanism, phosphates, thermal transformation, topochemistry

Introduction

Metal ammonium phosphates, capable of forming a number of monohydrates of the form $M^{II}NH_4PO_4 \cdot H_2O$ (where M^{II} is Mg, Mn, Co, Ni or Cu), are considered as prospective fertilizers [1]. As potential sources of complex mineral fertilizers they are characterised by optimal ratios and high concentrations of nutritive elements. In addition, the low solubility of metal ammonium phosphates in water gives rise to their long lifetimes as sources of fertilizers. They decompose slowly in the soil, under the action of bacteria, to give soluble forms available for the plants [2]. The use of metal ammonium phosphates as fertilizers gives rise to many technological problems, in particular, investigation of the possibility of removing balast crystallization water without loss of ammonia. This problem is interesting also from the scientific viewpoint, because its solution requires the study of the mechanism of a complex topochemical process. In fact, the heating of a metal ammonium phosphate is associated with a number of consecutive and parallel chemical reactions [3], such as:
dehydration of the crystal hydrate:

$$M^{II}NH_4PO_4 \cdot H_2O \rightarrow MNH_4PO_4 + H_2O, \qquad (1)$$

removal of ammonia from the anhydrous salt formed:

$$MNH_4PO_4 \rightarrow MHPO_4 + NH_3 \qquad (2)$$

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and elimination of the so-called 'structural' water with associated anionic condensation and subsequent crystallization of the diphosphate formed:

$$2MHPO_4 \rightarrow M_2P_2O_7 + H_2O \quad (3)$$

The behavior of metal ammonium phosphates on heating has been the subject of a number of thermoanalytical studies [4–8], but in many cases the results have been contradictory. The ratio of reaction rates of the processes (1)–(3) and, thus, the composition of the intermediate products varies markedly, not only within a series of metal ammonium phosphates [3], but also for one and the same compound, depending on conditions of the thermal treatment. One of the possible causes of the observed discrepancies in the results cited in literature is that , as a rule, the composition of the gas phase over the sample has not been controlled in the experiments performed. It has been shown [5, 8], in the thermal decomposition of $CoNH_4PO_4{\cdot}H_2O$, that the role of the gas phase is decisive for the course of the processes under consideration.

Unlike other metal ammonium phosphates, the copper salt has not been studied sufficiently [3, 5, 10]. There has been mention of neither the composition of the intermediate products formed nor the structure of the initial monohydrate [10]. In this work we present the results of studies of isothermal and non-isothermal transformations of copper ammonium phosphate monohydrate occurring on heating in air, in vacuum and in gaseous ammonia atmospheres in the temperature range 20–800°C.

Experimental

Crystalline $CuNH_4PO_4{\cdot}H_2O$ was prepared by mixing 1 M solutions of ammonium phosphate hydrate (analytical grade) and copper(II) chloride (analytical grade) in a volume ratio 2:1. After ageing for seven days at T=20°C, the product crystals (square platelets of average dimension 0.1–0.2 mm) were separated on a ceramic filter, washed with water and dried to constant mass in air of relative humidity RH=60%. As found by chemical analyses, the product contained Cu 32.8, P 15.8, NH_3 8.7 and H_2O 13.9%, which are the values close to those calculated for the monohydrate. The powder X-ray diffraction pattern was practically identical with [10] for $CuNH_4PO_4{\cdot}H_2O$.

In non-isothermal experiments in air, use was made of a Derivatograph OD-103 MOM with different sample holders and different heating rates. Kinetic studies of the isothermal evolution of gaseous products were carried out in a vacuum setup provided with a quartz spiral microbalance (of sensitivity 0.65 mm mg^{-1}), capable of keeping either a high vacuum (final pressure of $1{\cdot}10^{-5}$ hPa) or a required pressure of air or gaseous ammonia. A 60 mg sample, uniformly spread in a flat-bottomed aluminium pan, was suspended on the weighing spiral and introduced, through a ground quartz junction, to the reaction vessel in which a pre-determined temperature (T±0.1°C) and gas phase composition and pressure (p±1 hPa) were previously settled and the kinetic experiment was performed. The kinetic data obtained were treated with the use of the equation $\alpha=1-\exp(-k't^n)$, where α is the transformation degree, t is time, and k' is a constant related to the rate constant by $k=n(k')^{1/n}$ [11].

The products formed at different stages of the isothermal and non-isothermal transformations of the samples were subjected to X-ray diffraction (Diffractometer DRF-2,0, radiation CuK_α) and chemical analyses. Copper was determined by complexometric titration with methylthymol blue as indicator; phosphorus – by a photocolorimetric method; nitrogen – by the Kjeldahl method, and water – from mass loss on ignition, after subtraction of ammonia. The contents of condensed anionic forms (di- and tripolyphosphate) in the dehydration products were determined by ascending paper chromatography using FN 12 paper. The interfering effect of Cu^{2+} cations was eliminated by addition of EDTA, or by pretreatment of the analysis solution with sodium sulfide. In addition, characteristic changes on the crystal surface, occurring during the thermal treatment, were observed by optical microscope MIN-8 and recorded photographic all.

Results and discussion

Non-isothermal transformations of $CuNH_4PO_4 \cdot H_2O$ in air

The results of thermal analysis (Fig. 1) show that under conditions of heating in air, the monohydrate is stable up to a temperature about 140°C, at which its decomposition begins. The elimination of the main part of its crystal water is reflected in an asymmetric endotherm on the DTA curve with a peak temperature of 164°C. The anhydrous salt formed is fairly crystalline (Fig. 2), but the absence of any distinct effect due to its formation may be accounted for by a low stability of that compound. The chemical analysis of the product formed on heating the sample under the conditions of thermogravimetric experiment up to 185°C (Δm=9.3 mass%, corresponding to elimination of 1 mol of crystal water) shows that, under these conditions, the elimination of the crystal water is accompanied by a loss of 0.1 mol NH_3. In addition, according to the results of chromatographic analysis, the product contains about 5% of phosphorus in the form of diphosphate, which is equivalent to elimination of 0.025 mol of structural water.

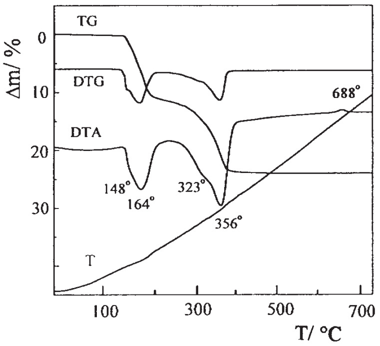

Fig. 1 Thermal analysis curves of $CuNH_4PO_4 \cdot H_2O$ obtained in humid air atmosphere (*RH*=60%); platinum pan, sample mass – 500 mg, heating rate 10 K min^{-1}

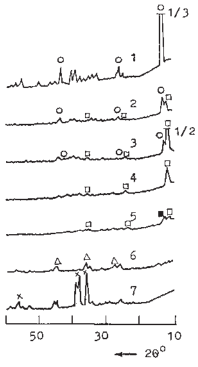

Fig. 2 X-ray diffraction patterns of products obtained on heating $CuNH_4PO_4{\cdot}H_2O$ under thermogravimetric conditions:
1 – 20°C, 2 – 146°C, 3 – 165°C, 4 – 185°C, 5 – 314°C, 6 – 364°C, 7 – 688°C
(o – $CuNH_4PO_4{\cdot}H_2O$; □ – $CuNH_4PO_4$; ■ – $CuHPO_4$; Δ – γ-$Cu_2P_2O_7$;
x – α-$Cu_2P_2O_7$, the X-ray phase analyses were performed on samples cooled to room temperature)

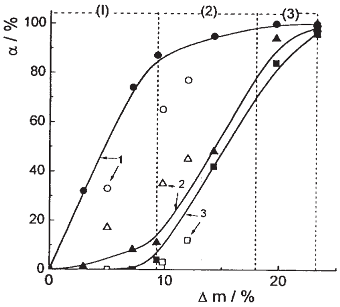

Fig. 3 Changes of transformation degree, α, in reactions (1), (2) and (3) depending on total mass loss Δ*m* during the heating of $CuNH_4PO_4{\cdot}H_2O$ in humid air (*RH*=60%);
1 – reaction (1), 2 – reaction (2), 3 – reaction (3). The vertical dashed lines correspond to the calculated values of Δ*m* corresponding to successive occurence of reactions (1)–(3); solid symbol – under conditions of thermogravimetric experiment, open symbol – under isothermal conditions

Decomposition of the anhydrous salt begins at above 290°C. This process is manifested on the DTA curve by an endotherm with a peak temperature of 356°C. A small deflection at 323°C suggests that the reactions (2) and (3) follow each other, although the results of chemical analyses (Table 1) show that the release of ammonia and water, formed in the course of the anionic condensation, proceeds practically simultaneously. So, for example, for a sample heated to 314°C under the conditions of thermogravimetric experiment (Δ*m*=14.3%), the degree of ammonia elimination and the degree of anionic condensation were practically identical and amounted to 48 and 46%, respectively (Fig. 3).

Table 1 Composition of gaseous and solid products of thermal treatment of $CuNH_4PO_4 \cdot H_2O$ (P_1 – mono-, P_2 – di-, P_3 – triphosphate)

T / °C	Δm			Contents of phosphorus in the form/wt%			Crystalline phases*
	Σ /%	mol H_2O	mol NH_3	P_1	P_2	P_3	
Under the thermogravimetric experimental conditions (in humid air (*RH*=60%); platinum crucible, the mass of sample=500 mg, heating rate 10 K min^{-1})							
20	0	0	0	100	0	0	I
146	2.9	0.32	0.01	100	0	0	I,II
165	7.2	0.74	0.08	100	0	0	II,I
185	9.3	0.91	0.11	95.0	5.0	0	II
314	14.3	1.19	0.48	54.0	46.0	0	II,III
364	19.7	1.42	0.94	10.4	79.3	10.3	IV
373	22.7	1.48	0.98	9.4	69.0	21.6	IV
688	22.9	1.51	1.00	2.8	74.1	23.1	V
800	22.8	1.5	1.00	0	100	0	V
Isothermal heating in air (*RH*=60%)							
146	1.8	–	–	100	0	0	I,II
153	5.0	0.35	0.20	100	0	0	I,II
158	5.5	–	–	100	0	0	I,II
167	7.3	–	–	100	0	0	I,II
172	9.8	0.68	0.40	93.7	6.3	0	II,I
180	11.0	–	–	95.8	4.2	0	II
Isothermal heating in vacuum ($p=1 \cdot 10^{-4}$ kPa)							
118	0.6	–	–	100	0	0	I
131	4.2	–	–	100	0	0	I,II
137	5.8	0.48	0.15	100	0	0	I,II
144	8.9	0.76	0.23	100	0	0	II,I
157	11.0	–	–	93.7	6.3	0	II
167	12.2	0.93	0.37	99.2	0.8	0	II
Isothermal heating in ammonia atmosphere (p_{NH_3}=13 kPa)							
110	9.0	0.97	0	100	0	0	II
130	9.4	1.0	0	100	0	0	II
157	9.4	1.0	0	100	0	0	II

*I – $CuNH_4PO_4 \cdot H_2O$; II – $CuNH_4PO_4$; III – $CuHPO_4$; IV – γ-$Cu_2P_2O_7$; V – α-$Cu_2P_2O_7$ (X-ray phase analyses were performed for samples cooled to room temperature)

As the decomposition progressed, the amount of the anhydrous salt diminished and a new phase, not described in literature, was formed. A feature of the new phase is a peak on the diffraction spectrum at the reflection angle 2θ=14°26'. As will be shown below, on isothermal heating of $CuNH_4PO_4{\cdot}H_2O$ this phase may be obtained in a pure state. It has been identified as anhydrous copper hydrophosphate. The products of the anionic condensation (mixture of di- and tripolyphosphates) are initially amorphous, but as the temperature increases their composition becomes simpler due to increased accumulation of the diphosphate form. The X-ray diffraction pattern of the product obtained on heating the monohydrate at 364°C reveals the presence of γ–$Cu_2P_2O_7$, the modification described in [10]. According to literature data this phase should be transformed, on further heating, into the high temperature modification, β–$Cu_2P_2O_7$ [12]. Such a transformation is evidently the case in our experiment (exotherm with a peak at 688°C on the DTA curve), but, on cooling the thermally treated sample to room temperature, the high-temperature modification is converted into the low-temperature α–$Cu_2P_2O_7$ occurring in X-ray diffraction patterns recorded in our experiments (Fig. 2).

Isothermal transformations of $CuNH_4PO_4{\cdot}H_2O$ in air

The data presented above show that, under the conditions of non-isothermal heating existing during the thermogravimetric experiment, the temperature ranges of the reactions (1)–(3) overlap and it becomes impossible to isolate the intermediate products in their stoichiometric composition, in particular the anhydrous copper ammonium phosphate. It also proved impossible to obtain this compound on isothermal heating of the monohydrate in air. The results of chemical analyses of the products obtained (Table 1, Fig. 3) show that, under such conditions, the dehydration is accompanied by even stronger decomposition of the complex cation. Even at relatively small degrees of transformation considerable amounts of ammonia are released. The curves of Δm *vs*. t, which represent the kinetics of the overall release of gaseous products, are shown in Fig. 4a. In the initial stages, which feature an overwhelming release of water vapour, the kinetic curves have the S-shaped form, which is characteristic for dehydration of most crystal hydrates of phosphate salts, but that process slows down rapidly. The kinetic parameter n from the equation $\alpha=1-\exp(-kt^n)$ used in approximation of the experimental data (we took $\alpha=1.0$ for mass loss $\Delta m=18.0\%$ corresponding to release of 1 mol H_2O and 1 mol NH_3) changed from $n_1=1.7$–1.8 to $n_2=0.5$–0.6. According to [11] thus may be accounted for by the fact that the process, first proceeding in the kinetic range, passes further into the diffusion-controlled form.

It should be pointed out that the solid products of dehydration of phosphate crystal hydrates, irrespective of their ease of formation of stable pseudomorphic structures, do not form kinetic barriers for diffusion of water vapour from the reaction zone [13]. The presence of transport pores in the solid laminar structure of the phosphates enables the reaction to proceed in the kinetic regime. The retardation of the isothermal process of dehydration, observed in some cases, is usually accounted for by some associated processes, such as disproportionation [14] or anionic condensation [8]. In the former case, the retardation effect is due to the decrease of mobility of

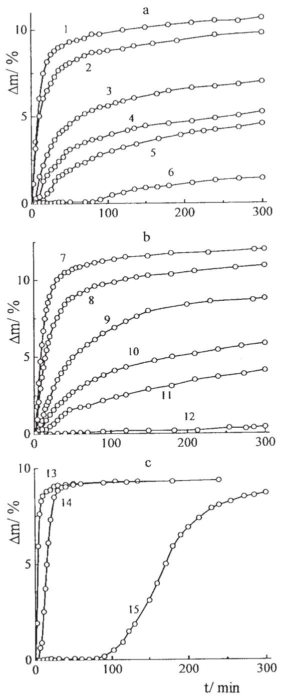

Fig. 4 Kinetic curves of gas liberation for isothermal heating of $CuNH_4PO_4{\cdot}H_2O$ a – in humid air (*RH*=60%), b – in vacuum, c – in ammonia (p_{NH_3}=13 kPa);
1 – 180°C, 2 – 172°C, 3 – 167°C, 4 – 158°C, 5 – 153°C, 6 – 146°C, 7 – 167°C, 8 – 157°C, 9 – 144°C, 10 – 137°C, 11 – 131°C, 12 – 118°C, 13 – 157°C, 14 – 130°C, 15 – 110°C

water vapour because of its combining with phosphoric acid (product of disproportionation of hydrophosphate) and, in the latter, due to lattice distortion and a decrease of its penetrability for gaseous products.

The process of thermal decomposition of $CuNH_4PO_4{\cdot}H_2O$, dealt with in this work, presents some peculiarities. Firstly, the initial monohydrate, on crystallochemical transformation to the anhydrous salt retains, not only the external form of the initial crystals (pseudomorphism), but also their transparency. Thus, the relationship between the increasing reaction rate, observed in the initial stages, and its location has not been determined. There are no optically distinguishable separation zones between the reacted and non-reacted parts of the crystal. Secondly, the causes of retardation of the reaction, observed in later stages, are not evident, because the anionic condensation, which seems to be the cause of an analogous hampering effect in the thermal decomposition of $MgNH_4PO_4{\cdot}H_2O$ [15] and $MnNH_4PO_4{\cdot}H_2O$ [9] is manifested here only in the advanced stages. It has already been mentioned that the occurrence of diffusion retardation may be due not only to the formation of inhibiting layer of the solid product, but also to the change in mobility of the gaseous products. In fact, the start of ammonia release may give rise to an interaction of the gaseous reac-

Table 2 Kinetic characteristics of isothermal decomposition of $CuNH_4PO_4·H_2O$ in various gas atmospheres

T/°C	Δm/%	n	K min^{-1}
in air, 100 kPa (RH=60%)			
146	0.4–1.2 1.2–1.8	n_1=1.7 n_2=0.5	$2.7·10^{-3}$ $2.9·10^{-5}$
153	0.5–1.6 1.6–5.0	n_1=1.8 n_2=0.5	$5.6·10^{-1}$ $2.0·10^{-4}$
172	5.3–7.7 7.8–9.8	n_2=0.5 n_3=0.1	$5.4·10^{-3}$ $9.8·10^{-5}$
180	7.8–8.9 8.9–11.0	n_2=0.5 n_3=0.1	$3.7·10^{-3}$ $1.4·10^{-4}$
In vacuum, p=10^{-4} kPa			
118	0.3–0.7	n_1=1.5	$5.4·10^{-4}$
131	0.2–1.7 1.7–4.2	n_1=1.4 n_2=0.5	$5.2·10^{-3}$ $1.5·10^{-4}$
144	0.7–2.0 3.6–8.2 8.2–9.0	n_1=1.4 n_2=0.6 n_3=0.2	$2.1·10^{-2}$ $1.9·10^{-3}$ $9.3·10^{-5}$
157	2.2–6.0 6.0–9.0 9.0–11.0	n_1=1.0 n_2=0.5 n_3=0.2	$2.2·10^{-2}$ $5.5·10^{-3}$ $3.8·10^{-4}$
167	3.4–8.2 8.2–10.6 10.6–12.2	n_1=1.1 n_2=0.5 n_3=0.1	$4.7·10^{-2}$ $8.0·10^{-3}$ $1.6·10^{-3}$
p_{NH_3}=13 kPa			
110	0.1–9.35	5.0	$3.1·10^{-1}$
130	0.1–9.3	4.1	$8.1·10^{-2}$
157	0.1–9.4	2.3	$2.6·10^{-2}$

Table 3 Values of the Arrhenius activation energy E_v (kJ mol^{-1}) at different steps of the isothermal decomposition of $CuNH_4PO_4·H_2O$

Atmosphere	α						
	0.1	0.2	0.3	0.4	0.5	0.7	0.9
In air	161	203	243	–	–	–	–
In vacuum	–	184	195	216	233	226	168
p_{NH_3}=13 kPa	–	96	–	100	–	97	–

tion products (ammonia and water vapour) either with each other (to form less mobile association forms) or with acidic centers of the hydrophosphate formed. There remains a question, why such interactions do not appear in the thermal decompositions of other metal ammonium phosphates. It should be taken into account, however, that the product remaining after ammonia elimination from copper ammonium phosphate has much stronger proton-donor properties and, besides, copper has a much stronger complexing capacity. As a result, not only quantitative but also qualitative changes are observed in the mobility of the gaseous reaction products formed.

At higher transformation degrees, where elimination of the structural water begins, the crystal lattice starts to decompose (the crystals become dull although they retain their outer structural form) and the diffusion retardation increases (n_3=0.1). The kinetics of this process are very complex. The results of the experiments do not permit the determination of reliable values of the Arrhenius' activation energy E_k for the above-mentioned three reaction stages, which differ in the nature of the rate-limiting process because their borders (based on Δm values) shift depending on temperature (Table 2). The values of activation energy E_v (Table 3) derived from the temperature dependence of the reaction rate at different transformation degrees must therefore be considered as only approximate. Nevertheless, they show clearly the regular increase of activation energy in the process of isothermal reaction (from 161 kJ mol^{-1} at Δm=1.8% to 243 kJ mol^{-1} at Δm=5.4%).

Isothermal transformations of $CuNH_4PO_4 \cdot H_2O$ in vacuum

If $CuNH_4PO_4 \cdot H_2O$ is heated in a vacuum, the isothermal process develops analogously to that observed in air with the exception that the temperature region, in which the reaction proceeds with comparable rates, is slightly shifted towards lower values. The kinetic curves (Fig. 4b) also exhibit sections of increasing rate with subsequent retardation, which is reflected in changes of value of the kinetic parameter. Relating to these values it is possible to distinguish three stages of the process: 'pure' dehydration (kinetic range, $n>1$), complex dehydration and ammonia release (stationary diffusion, $n\approx0.5$), and dehydration associated with ammonia release and anionic condensation (non-stationary diffusion, $n\approx0.1$). On passage from the first to the second stage, the value of E_v increases from 166 kJ mol^{-1} for Δm=3.5% to 233 kJ mol^{-1} for Δm=8.0%, but then decreases again, irrespective of the increasing diffusion retardation. This may be accounted for by the change in the nature of diffusion. At this stage, the concentration of acidic (Lewis) centers on the surface of the transporting pores is decreased as a consequence of dehydroxylation accompanying the process of anionic condensation (Eq. (2)). The limiting stage becomes the molecular diffusion of the gaseous products, which has a lower activation energy. An identical effect is observed also on heating $CuNH_4PO_4 \cdot H_2O$ in air. In this case, however, we failed to determine the decrease of E_v because of the insufficient number of kinetic experiments in the high-temperature region (although they were carried out in intervals of 5–8°C).

Thus, the experiments performed have shown that, under conditions of isothermal heating of $CuNH_4PO_4 \cdot H_2O$ in vacuum and in air, it is impossible to separate the processes (1) and (2). The values of Δm, at which the kinetic curves pass into practically horizontal sections, increase monotonously with increasing temperature, including also the ranges of Δm corresponding to the formation of anhydrous salt.

Isothermal transformations of $CuNH_4PO_4·H_2O$ in ammonia atmosphere

Although the transition from air atmosphere to vacuum was not associated with a considerable increase in the dehydration rate of $CuNH_4PO_4·H_2O$, an attempt was made to separate processes (1) and (2) by retardation of the ammonia elimination (and thus also the anionic condensation). With this aim, the heating of the monohydrate was carried out in an atmosphere of gaseous ammonia. Figure 4 shows the kinetic curves obtained on isothermal heating of the monohydrate at p_{NH_3}=13 kPa. It is clearly seen that, in a wide temperature range of 110–157°C, the curves of Δm *vs.* t attain a plateau at Δm=9.3%. The results of both chemical and X-ray diffraction analyses (Table 1) have shown that, under these conditions, a fairly crystalline anhydrous salt of stoichiometric composition is formed.

Comparison of the kinetic curves obtained in different gas atmospheres (Fig. 4) shows that the use of gaseous ammonia not only inhibits the process of ammonia elimination, but also increases the rate of dehydration. Thus, for heating under vacuum for 6 h at T=110°C the loss of mass Δm was below 0.5%, while in the ammonia atmosphere (p_{NH_3}=13 kPa) under identical conditions the dehydration was practically complete (Δm=9.0%). The accelerating effect of the gas atmosphere in relation to a vacuum is a rather rare phenomenon in the case of reversible reactions. In fact, even gases not participating in a given reaction usually have a retarding effect of the so-called ‘gaseous envelope’ [16], as they interfere with gas removal from the sample surface. It should be taken into account, however, that gaseous ammonia is not an inert gas in the case of dehydration of $CuNH_4PO_4·H_2O$. From the very beginning of ammonia release one can observe diffusional inhibition of the removal of gaseous products, including also water vapour. If, however, the dehydration is not associated with ammonia removal, the whole process proceeds in the kinetic regime (n=1.5). This is evidently the reason why the reaction rate is higher in cases where it proceeds in the atmosphere of ammonia.

The results of X-ray diffraction analyses show that the products formed during isothermal dehydration in the ammonia atmosphere, in vacuum, as well as in air, have identical structures. We have found only one of the two modifications of $CuNH_4PO_4$ described in [5]. Visual observations have shown, however, that the product of stoichiometric composition, obtained in the ammonia atmosphere, exhibits a change in colour. In the course of dehydration the crystals obtain an intense blue colour which, on cooling, changes into turquoise. This transition, connected with the change in structure of the coordination polyhedron, is not associated with a change in mass of the sample, so it is advisable to regard it as being due to a phase transformation. Unfortunately, the equipment used in the work did not allow high-temperature X-ray diffraction measurements in ammonia atmosphere to be done. These phenomena were not observed in experiments where the products were obtained on isothermal heating of $CuNH_4PO_4·H_2O$ in air or in vacuum.

Isothermal transformations of anhydrous salt

The influence of the gas phase is also observed during decomposition of anhydrous copper ammonium phosphate. Figure 5 shows kinetic curves of total gas release during isothermal heating of $CuNH_4PO_4$ (samples of the anhydrous salt were obtained in ammonia atmosphere at T=130°C) in various gas atmospheres at 250°C. In order to simplify the comparison of these data with those presented previously, the mass losses have been calculated with reference to the monohydrate.

From the kinetic viewpoint, the nature of the decomposition of $CuNH_4PO_4$ in various gas atmospheres was practically identical. The curves of Δm *vs.* t are parabolic, which is characteristic of diffusion-controlled processes, as evidenced by the values of the kinetic parameter (n=0.3–0.4). The highest rates were observed when the process was carried out in vacuum, which conforms to the general laws of reversible topochemical reactions [16]. The results of chemical and chromatographic analyses of the solid residue (Table 4) show that isothermal heating in vacuum, under the conditions specified above, results in release of ammonia (0.81 mol NH_3) and water (0.18 mol H_2O). It also proved impossible to separate the processes (2) and (3) from each other in experiments carried out in ammonia atmosphere. In this case the total loss of mass corresponding to identical values of T and t was much lower than in vacuum, but the molar ratio of the gaseous products was practically identical (0.57 mol NH_3 and 0.12 mol H_2O).

Because water vapour should hamper the process of anionic condensation, it might have been supposed that use of an atmosphere of humid air would promote the separation of processes (2) and (3). In fact, the results of chemical analysis (Table 4) have shown that, on isothermal heating of $CuNH_4PO_4$ at 250°C in air at relative humidity RH=60%, only gaseous ammonia was released. The solid product formed under such conditions does not contain the condensed anionic forms produced on heating anhydrous copper ammonium phosphate in vacuum and in ammonia atmosphere. The X-ray diffraction pattern of that residue contained, along with the peaks due to the anhydrous salt, the peaks due to a phase not previously described in the literature, that we identify as anhydrous copper hydrophosphate. Unfortunately, diffusional hampering of the process did not allow us to obtain, under these conditions, complete transformation conforming to Scheme (2). An increase of temperature, for instance to 280°C, resulted in occurrence of anionic condensation. The polymeric products obtained (about 20% diphosphate with small admixtures of higher condensed forms) appear from the X-ray diffraction pattern, to be amorphous hence the only crystalline phase is copper hydrophosphate.

Effect of conditions of thermal treatment

The effect of the gas phase on the relation of reaction rates of the processes (1)–(3) may be manifested also by other factors, apparently independent of the gas phase composition. So, for example, the results cited above lead to the conclusion, that the composition of the products corresponding to a particular loss in mass, Δm, depends on the parameters of thermal treatment of the sample. In fact, the data of Table 1 and

Table 4 Composition of gaseous and solid products of isothermal treatment of $CuNH_4PO_4$ (T=250°C, t=180 min, Δm was calculated with reference to the monohydrate)

Δm			Contents of phosphorus in the form/wt%			Crystalline phases*
Σ/%	mol H_2O	mol NH_3	P_1	P_2	P_3	
			in vacuum ($p=1\cdot10^{-4}$ kPa)			
18.1	1.18	0.82	64	34	2	III, II
			p_{NH_3}=13 kPa			
15.3	1.11	0.57	89	11	0	III, II
			In air, 1000 hPa (RH=60%)			
13.4	1.0	0.47	100	0	0	III, II

*I – $CuNH_4PO_4·H_2O$; II – $CuNH_4PO_4$; III – $CuHPO_4$; IV – γ-$Cu_2P_2O_7$; V – α-$Cu_2P_2O_7$

Fig. 3 show clearly, that, under the conditions of thermogravimetric experiments, processes (1) and (2) overlap to a lesser degree and (2) and (3) to a greater degree than during the isothermal heating. However, in the kinetic and the thermogravimetric experiments different sample masses were used, of the order of 60 and 500 mg, respectively. Besides, in the kinetic experiments the weighed sample was spread in a thin layer, and in the thermogravimetric experiments a compact sample was placed in the pan. Such differences may be reflected in conditions of transport of the gaseous products formed and, consequently, on their partial pressure in the reaction space. To check on this, a thermogravimetric experiment was carried out with the use of a multibottomed sample holder in which it was possible to spray a 500 mg sample in a thin layer. Figure 6 shows the thermogravimetric data obtained under such conditions compared with the data obtained with a conventional sample pan. As may be seen, the inflexion on the TG curve, that separates the processes (1) and (2), is much weaker in the conventional pan and is shifted towards greater values of Δm. At the same time

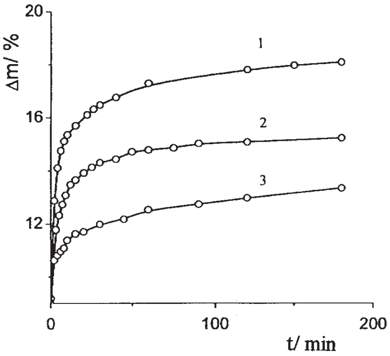

Fig. 5 Kinetic curves of release of gas products on isothermal heating of $CuNH_4PO_4·H_2O$ at T=250°C; 1 – in vacuum, 2 – in ammonia atmosphere (p_{NH_3}=13 kPa), 3 – in humid air (RH=60%)

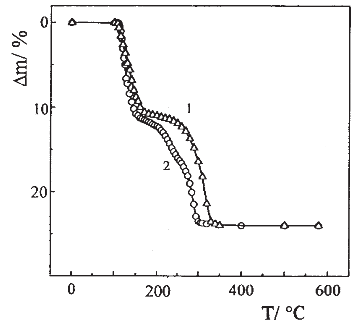

Fig. 6 Thermogravimetric curves of $CuNH_4PO_4{\cdot}H_2O$ on heating under conditions: sample mass – 500 mg, heating rate 10 K min^{-1}, 1 – platinum crucible, 2 – flat pan holder

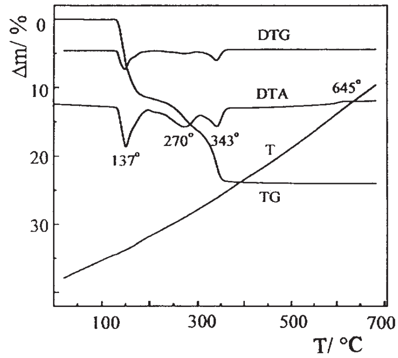

Fig. 7 Thermal analysis curves of polycrystalline $CuNH_4PO_4{\cdot}H_2O$ obtained in humid air (*RH*=60%); flat platinum holder, sample mass – 500 mg, heating rate 10 K min^{-1}

another inflexion, corresponding to separation of the processes (2) and (3), appears on the TG curve. The second endotherm on the DTA curve (Fig. 7) splits into two with peak temperatures of 270 and 343°C, respectively.

The results obtained conform with the above data on the effect of gaseous products on the relation between the reactions (1)–(3) proceeding under isothermal heating of the samples. Figure 4 and Tables 1 and 4 show that water vapour (humid air) has practically no effect (as compared with vacuum) on the rate of elimination of crystal water and ammonia, but it hampers anionic condensation. The gaseous ammonia greatly accelerates dehydration, sharply slows ammonia elimination and little influences upon the anionic condensation process.

As a consequence, decreases of pressure of the two gases should lead to more pronounced overlapping of processes (1) and (2) and to partial separation of processes (2) and (3). This was observed in the experiment with the sample material spread in a thin layer (Figs 6 and 7).

A similar effect was observed for other factors which increase diffusional transport of the gaseous products. Thus, decreasing the sample mass on non-isothermal heating, or slowing down the heating rate (the isothermal experiment is a limit from such a viewpoint), leads to a stronger overlapping of processes (1) and (2) and promotes the separation of processes (2) and (3).

Conclusions

1. The studies have shown that the nature of the chemical and phase transformations of $CuNH_4PO_4{\cdot}H_2O$ during heating depends strongly on the composition of the gas phase over the sample.
2. The observed effect of conditions of the thermal treatment (isothermal and non-isothermal heating), as well as of the rate of temperature increase and sample mass distribution (in non-isothermal heating) on the composition of the intermediate compounds depends on differences in the conditions of removal of the gaseous products (water vapour and ammonia) from the sample and on changes in their partial pressure in the reaction zone.

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