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Thermal transformations of $Pb_2PO_4NO_3.H_2O$

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Abstract

Gravimetric, thermogravimetric, and X-ray diffraction analyses, IR spectroscopy, and optical spectroscopy were used in the studies of iso- and non-isothermal transformations of crystalline $Pb_2PO_4NO_3.H_2O$ in air at temperature range 20–1000°C. At $t > 100°C$ the process proceeds with dehydration of crystal hydrates, accompanied by crystallisation of anhydrous $Pb_2PO_4NO_3$ which, on heating above 400°C, is decomposed to yield nitrogen dioxide and molar oxygen. The resulting mixture of lead oxide and orthophosphate, which crystallises in monoclinic system, undergoes a transformation at $t > 500°C$ to give an oxo-phosphate $Pb_4P_2O_9$ melting at 960°C. The paper includes space-time models of development of the thermochemical process involved in the dehydration of initial monohydrate and thermal decomposition of the anhydrous salt formed. © 1997 Elsevier Science B.V.

Keywords: Thermal transformation; Phosphate

1. Introduction

Lead phosphates have become highly interesting due to their piezo- and ferroelectric properties [1–4]. In particular, the electric conductivity [5], dielectric [6] and magnetic [7] properties of $Pb_2PO_4NO_3.H_2O$ were studied in a wide temperature range of 20–500°C. No account was taken, however, of the possibility of substantial changes in the crystal composition and structure of the salt on heating. Indeed, no information on thermal transformation of lead nitrophosphate has been available in chemical literature.

The present work includes the results of studies on iso- and non-isothermal heating of crystalline $Pb_2PO_4NO_3.H_2O$ in air. The results enable to determine the sequence of chemical reactions and of associated phase transformations involved in the process, as well as to put forward the mechanism of their development.

2. Experimental

The starting material used in the experimental work was obtained in reaction of polycrystalline $MgNH_4PO_4.H_2O$ (synthesised in our laboratory) with 0.1 N solution of $Pb(NO_3)_2$ (100 mg of the salt in 30 ml of solution) at $t = 25°C$. The initially formed lead hydroxyphosphate $Pb_5(PO_4)_3OH$, with a pyromorphite structure [8], underwent in 20 days complete spontaneous transformation to $Pb_2PO_4NO_3.H_2O$.

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Transparent prismatic crystals ($D = 0.1 - 0.3$ mm), precipitated from the solution, were filtered off on sintered glass filter, washed with water, and dried in air at $t = 20°C$ and relative humidity 45%. The dried substance contained 70.3% Pb, 5.4% P, 2.3% N, and 3.1% H_2O, which corresponded well with the formula $Pb_2PO_4NO_3.H_2O$ (70.29% Pb, 5.26% P, 2.38% N, and 3.06% H_2O). The X-ray diffraction pattern of powdered sample corresponded with that found in literature for $Pb_2PO_4NO_3.H_2O$ [9].

The non-isothermal studies were performed with the use of derivatograph 3434-C with microprocessor control (open platinum crucible, sample weight 100 mg, heating rate 10°C/min). The isothermal experiments involved a vacuum device with quartz spiral balance (sensitivity 1 mg/mm, the 60 mg sample material spread in a thin layer on the bottom of glass pan), in which the kinetics of evolution of gaseous reaction products was studied in air, under high vacuum, and under fixed pressure of water vapour. The products formed in individual stages of iso- and non-isothermal transformations were subjected to X-ray diffraction analyses (diffractometer DPF-2,0, radiation FeK_α) and IR spectroscopic analyses (spectrometer UR-20, KBr tablets).

In a separate series of experiments the crystal changes due to isothermal dehydration were observed in a thermostated vacuum cell provided with optical quartz windows. The anionic composition of both the initial sample and the thermally treated materials was controlled by quantitative ascending chromatography on FN 12 paper with addition of EDTA and cation exchanger KU-2 aiming to eliminate the effect of Pb^{2+} cations on the chromatographic process and facilitating the solubilisation of sparingly soluble products of thermal treatment [10].

3. Results and discussion

The results of the experiments have shown that the thermal treatment of $Pb_2PO_4NO_3.H_2O$ gives rise to two independent, consecutive, topochemical processes – dehydration of the monohydrate and thermal decomposition of the anhydrous salt formed. Let us consider shortly each of the two individual processes.

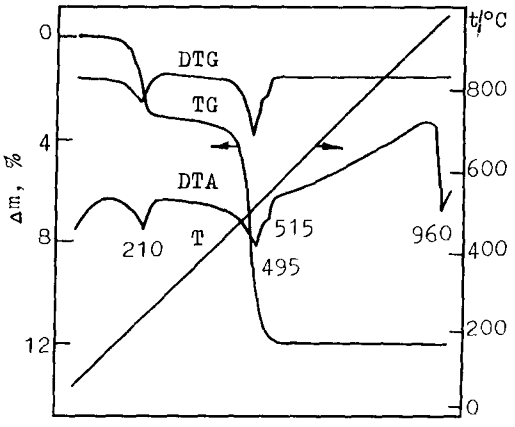

Fig. 1. Results of thermogravimetric studies of $Pb_2PO_4NO_3$ ($m = 100$ mg, $\Delta m = 12.1$ mg, heating rate 10 mg K^{-1}; platinum crucible).

3.1. Dehydration

As results from the thermogravimetric data (Fig. 1), the monohydrate crystals are stable on heating up to 100°C. Heating to higher temperatures results in dehydration, which gives an endothermic effect on DTA curve with a peak temperature of 210°C. The loss in weight recorded by the TG curve is $\Delta m = 3.1\%$, which corresponds to elimination of 1 molecule of H_2O. The resulting anhydrous salt is fairly crystalline (Fig. 2) and stable on heating up to about 400°C.

Under isothermal conditions the dehydration of monohydrate proceeds at lower temperatures and the anhydrous salt can be obtained at $t = 125°C$ (Fig. 3). It should be pointed out that this temperature is relatively high, since most crystal hydrates of phosphate salts studied under isothermal conditions loose water below 100°C [11]. Evidently water molecules in monoclinic lattice of $Pb_2PO_4NO_3.H_2O$ are fairly tightly bound with the essential structure-forming elements of the crystal. This fact is also confirmed by the results of IR spectroscopy studies (Fig. 4). The changes in the spectrum of the dehydration product (as compared with the spectrum of the initial monohydrate) are not confined to disappearance of the bands corresponding to δH_2O deformation (1600 cm^{-1}) and asymmetrical valency vibrations δ_3OH (3550 cm^{-1}) of hydroxyl groups of water molecules. Substantial changes are also observed in the structure of spectrum of symmetrical ν_1 and antisymmetrical ν_3 valency

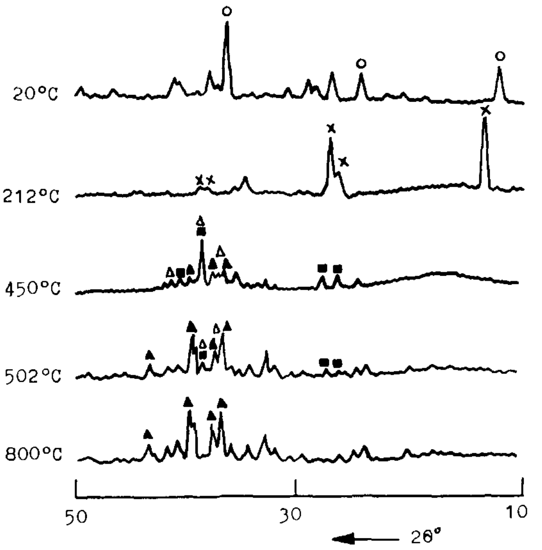

Fig. 2. X-Ray diffraction patterns of $Pb_2PO_4NO_3.H_2O$ and of products of its thermal decomposition (heating rate = 10 K min^{-1}; o-$Pb_2PO_4NO_3.H_2O$; x-$Pb_2PO_4NO_3$; ●-$Pb_9(PO_4)_6$; △-PbO(yellow); △-$Pb_4P_2O_9$).

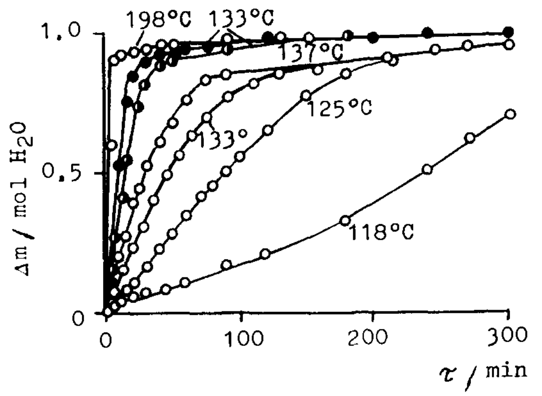

Fig. 3. Kinetic curves of thermal dehydration of $Pb_2PO_4NO_3.H_2O$ crystal hydrate in air (o-p = 1000 hPa, p_{H_2O} = 13.3 hPa), in vacuum (●-p = 10^{-5} hPa), and in atmosphere of water vapour (o-p_{H_2O} = 13.3 hPa).

vibrations of the PO_4 group (900–1100 cm^{-1}), as well as in the region of valency vibrations of the Pb–O bond (500–600 cm^{-1}). The substantial electrostatic effect of the cationic and anionic fields on the water molecule does not lead, however, to its proteolytic dissociation. For this reason we failed to find, in the products of monohydrate dehydration, any condensed phosphate phases claimed to occur during dehydration of some neutral phosphates of transition elements [12].

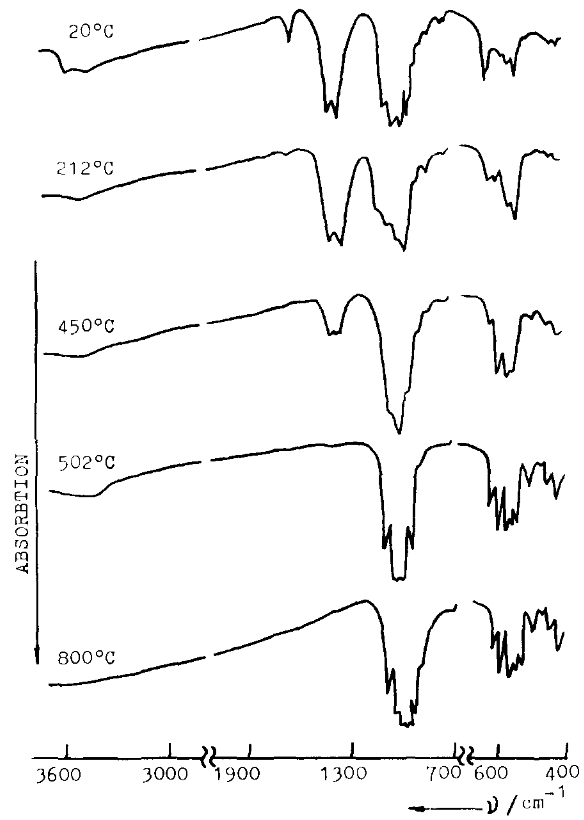

Fig. 4. IR spectra of $Pb_2PO_4NO_3.H_2O$ crystal hydrate and products of its thermal decomposition (heating rate = 10 K min^{-1}).

Isothermal dehydration of $Pb_2PO_4NO_3.H_2O$ is characteristic by a number of features. Microscopic investigations have shown that progressive dehydration is accompanied by loss in transparency, leading gradually to complete opacity, without visible reaction centres on surface edges. Irrespective of the associated structural transformation the developing pseudomorphose retains not only the form of the initial crystal, but also a relatively high mechanical strength. In such cases the reaction rate is usually slowed down because of diffusion limitations in the release of gaseous reaction product from the reaction zone and the kinetic curves have a parabolic shape [13,14]. But the $\Delta m-\tau$ curves shown in Fig. 3 are S-shaped, which is characteristic for self-accelerating topochemical processes proceeding within the kinetic region. Such a feature is characteristic of the dehydration of phosphates. Rigid tridimensional structure of such compounds, associated with a laminar arrangement of bulk of the crystal favours the situation, in which the anhydrous product forms a network of microchannels capable of transporting water vapour molecules toward the crystal surface [11]. The formation of porous dehydration product of considerable mechanical strength was confirmed in number of references [15,16] by measurements of specific surface of the samples during the course of reaction.

The increase of reaction rate observed during the isothermal dehydration of $Pb_2PO_4NO_3.H_2O$ is apparently due to its propagation in the bulk of the crystal and not in a uniform frontal zone but preferentially along some branching planes. Such a development of the process considered in detail in our paper on dehydration of potassium dihydrophosphate [17] may be explained in terms of the known model of branching chains [18,19]. The localisation of most reaction sites in the bulk of the crystal instead of its surface results in a situation where the reaction rate is almost independent of water vapour pressure at the crystal surface. The kinetic curves of Δm vs. τ obtained in a high vacuum are practically identical with those obtained for $p_{H_2O} = 13.3\,hPa$ (Fig. 3).

Taking into account the complexity of the process under consideration we abstained from its detailed kinetic analysis because of difficulties in the interpretation of the data obtained. It should be noted, however, that the values of the Arrhenius' activation energy E_v, as calculated from the temperature dependence of the reaction rate $v_{\Delta m}$ for different values of Δm, undergo only slight changes in the course of isothermal reaction from 150 ± 10 kJ/mol for $\Delta m = 0.3$ mole H_2O to 124 ± 10 kJ/mol for $\Delta m = 0.7$ mole H_2O. This fact provides a support for the above given statement concerning the lack of diffusion obstacles in the development of the process despite propagation of the reaction front into the bulk of the crystal. It would not be fully correct, however, to give a meaning of energy characteristics to the obtained values of E and to relate them to the kinetic stage of the reaction. They should only be considered as effective values describing the overall process.

3.2. *Thermal decomposition of anhydrous salt*

The process of $Pb_2PO_4NO_3$ decomposition proceeds in a relatively narrow temperature range and it gives endothermic effects on DTA and DTG curves, with a peak temperature at 495°c. The loss of mass at that stage, as calculated for anhydrous salt, is 9.4%, which corresponds to release of 1.0 mole NO_2 and 0.25 mole O_2 per 1 mole of $Pb_2PO_4NO_3$. Such a composition of gaseous reaction products occurs normally during the decomposition of lead nitrates[20], as far as solid products are concerned, the following two variants may be assumed:

$$Pb_2PO_4NO_3 \rightarrow \tfrac{1}{2}PbO + \tfrac{1}{2}Pb_3(PO_4)_2 + NO_2 + \tfrac{1}{4}O_2 \quad (1)$$

or

$$Pb_2PO_4NO_3 \rightarrow \tfrac{1}{2}Pb_4P_2O_9 + NO_2 + \tfrac{1}{4}O_2 \quad (2)$$

According to the data of X-ray diffraction analysis the composition of the solid reaction products varies depending on the decomposition temperature and conditions of thermal treatment (iso- or non-isothermal heating). In non-isothermal heating under conditions of thermogravimetric experiment below 450°C, when the degree of decomposition is about 75%, the product is a complex mixture of crystalline phases (Fig. 2). The mixture includes lead oxide (PbO) (its presence is evidenced also by bright yellow colour of the mixture), neutral lead phosphate crystallising in the hexagonal (vacancy) form pyromorphite $Pb_9\square^{2+}(PO_4)_6\square^{-}_2$ (this phase has been described in [21]), and oxy-phosphate $Pb_4P_2O_9$ (in its monoclinic modification [22]). Such a composition enables to conclude that the process proceeds with participation of each of the 2 schemes, the (1) being prevalent, according to the heights of the peaks on the X-ray diffraction pattern.

Upon temperature increase to 500°C the dominating phase, formed in complete decomposition of $Pb_2PO_4NO_3$, appears to be the monoclinic oxy-phosphate, whereas $Pb_9(PO_4)_6$ is present only in trace amounts (a reflex at $2\theta = 38°C$). At still higher temperatures the only solid product appears to be $Pb_4P_2O_9$. Such changes in the structure of decomposition products is also evidenced by the IR spectra (Fig. 4). The increase of temperature is accompanied by decrease of intensity of absorption bands due to valency vibrations of NO_3-group (1335–1385 cm^{-1}) and decrease in number of bands due to vibrations of PO_4-group and Pb–O bonds, probably as a consequence of formation of highly symmetrical phases (orthorhombic PbO and hexagonal $Pb_9(PO_4)_6$). The formation of monoclinic oxy-phosphate is accompanied by increase in complexity of IR spectrum of the reaction product.

The results obtained in the non-isothermal decomposition of $Pb_2PO_4NO_3$ do not allow to state univocally, if the oxy-phosphate is formed in reaction (1) or as a result of a secondary reaction of solid products formed in reaction (1), according to the following scheme:

$$PbO + Pb_3(PO_4)_2 \text{ (in this case } \tfrac{1}{3}Pb_9(PO_4)_6) \rightarrow Pb_4P_2O_9$$

The 2-stage mechanism of the reaction is confirmed by the composition of solid reaction products obtained in the isothermal heating of $Pb_2PO_4NO_3$ at $t = 440°C$ ($\tau = 5$ h). Under such conditions the decomposition ends with quantitative release of gaseous products (Fig. 5) and formation of a mixture of PbO and $Pb_9(PO_4)_6$ (Fig. 6). The oxy-phosphate $Pb_4P_2O_9$ is formed at higher temperatures conforming to reaction (3). The compound melts at $t = 960°C$, which is in a good agreement with literature data [23].

Despite of the complex structural transformations associated with the decomposition of $Pb_2PO_4NO_3$ the obtained product, like in the case of dehydration of monohydrate, retains the form of the initial crystal. Also, in this case the formation of pseudomorphose does not result in diffusional obstacles in evolution of gaseous products from the reaction zone. But in the case of thermal decomposition of the anhydrous salt the kinetic curves of gas evolution $\Delta m - \tau$ (Fig. 5) are clearly different from analogous curves obtained during the dehydration. Their linearity shows that the rate of the process practically does not change in the course of isothermal decomposition.

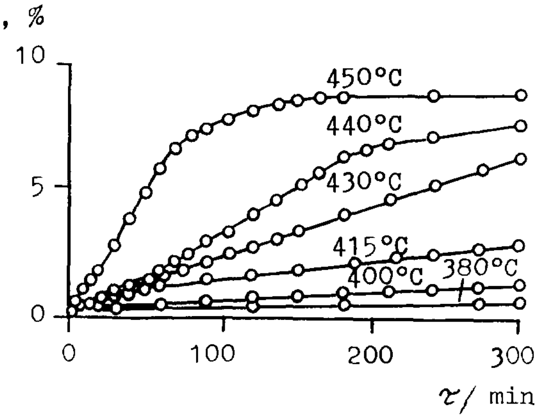

Fig. 5. Kinetic curves of thermal decomposition of $Pb_2PO_4NO_3$ in air (p = 1000 hPa, p_{H_2O} = 13.3 hPa

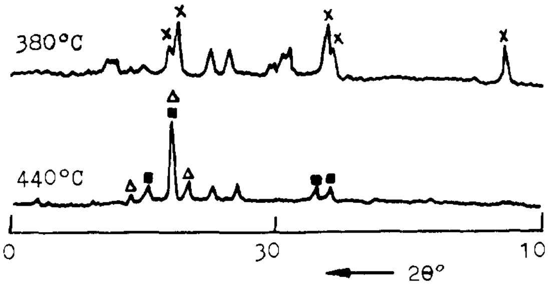

Fig. 6. X-Ray diffraction curves of the products of $Pb_2PO_4NO_3$ thermal decomposition under isothermal conditions (x-$Pb_2PO_4NO_3$; □-$Pb_9(PO_4)_6$; △-PbO(yellow)).

Such a kinetics is usually accounted for the fact that in the course of isothermal reaction the area of the reaction zone remains constant. In such a type of model it is assumed that the propagation of the reaction zone in the bulk of the crystal proceeds frontally, starting from two opposite sides. An excellent illustration of such a model has been given by Reller and Oswald [24] who have provided its confirmation by optical microscopy based on an example of decomposition of $Ni(SCN)_2.(py)_2$ single crystal. Unfortunately, such a study was not possible in our case because of opacity of the crystals in the stage of decomposition. It seems, however, that the above described model is fully applicable to our case, if we take into account the laminar structure of $Pb_2PO_4NO_3$. Evidently, the liberation of coarser (as compared with H_2O) molecules of nitrogen dioxide and molecular oxygen does not make use of all channels and pores available, as in the course of dehydration, but proceeds only along the planes characterised by maximum values of interplanar distances.

During the course of thermal decomposition of $Pb_2PO_4NO_3$ the value of E_v increases slightly in isothermal process from 230 kJ/mol at $\Delta m = 3.5\%$ to 315 kJ at $\Delta m = 5.7\%$ (complete decomposition of the anhydrous salt corresponds to $\Delta m = 9.4\%$).

At high degrees of decomposition ($\Delta m > 7\%$) the rate of the isothermal reaction slows down abruptly (Fig. 5); the remaining gaseous products are released in a wide range of temperature (up to 520°C). This is evidently the cause of splitting of the endothermic effect corresponding to the decomposition of the anhydrous salt and formation of a shoulder at 515°C. This shoulder does not correspond to formation of an intermediate compound, but it results from purely kinetic reasons.

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