Thermochimica Acta, 126 (1988) 355–363
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL TRANSFORMATIONS OF TRIPHOSPHATES $Na(NH_4)_4P_3O_{10} \cdot 4H_2O$ AND $(NH_4)_9H(P_3O_{10})_2 \cdot 2H_2O$

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(Received 13 July 1987)

ABSTRACT

The methods of thermogravimetry (TG), infrared spectroscopy (IRS), X-ray diffraction (XRD), thin-layer chromatography (TLC) and chemical analysis were used to investigate isothermal and non-isothermal transformations of triphosphates $Na(NH_4)_4P_3O_{10} \cdot 4H_2O$ and $(NH_4)_9H(P_3O_{10})_2 \cdot 2H_2O$ in air, in a stream of nitrogen and in an ammonia atmosphere at temperatures ranging from 20 to 600 °C. It was shown that in the course of heating in the gaseous ammonia atmosphere, which has a stabilizing influence on surface NH_4^+ groups, triphosphates lose crystal water according to the non-degradative mechanism with crystallization of the final anhydrous products $Na(NH_4)_4P_3O_{10}$ and $(NH_4)_9H(P_3O_{10})_2$.

INTRODUCTION

The results of investigating the composition of products formed during the heating of the known crystallohydrates $Na(NH_4)_4P_3O_{10} \cdot 4H_2O$ [1,2] and $(NH_4)_9H(P_3O_{10})_2 \cdot 2H_2O$ [3,4], in vacuum and in a water vapour atmosphere indicate that the synthesis of anhydrous salts directly from crystallohydrates is not an easy task. Anhydrous salts which are formed during the dehydration of $Na(NH_4)_4P_3O_{10} \cdot 4H_2O$ [5] and $(NH_4)_9H(P_3O_{10})_2 \cdot 2H_2O$ [6], are generally tainted with products of triphosphate deammonation, as well as the products of anionic degradation. The direct transformation of hydrated sodium ammonium triphosphate according to the non-degradative mechanism is possible; however, it is necessary to use as the starting material a non-stoichiometric triphosphate sample, $Na_{1.2}(NH_4)_{3.8}P_3O_{10} \cdot 3.9H_2O$, which has a deficit of ammonia [7].

It was assumed that in a certain pressure interval gaseous ammonia would stabilize ammonium salts, which would enable dehydration according to the non-degradative mechanism, independently of whether the initial crystallohydrates have stoichiometric or non-stoichiometric composition. Previous

0040-6031/88/$03.50

experiments have shown that a pressure of about 1 atm is sufficient for this. In order to obtain data for comparison, comparable with those of experiments performed in an ammonia atmosphere, an independent series of experiments was carried out at the same pressure in an air atmosphere and in a stream of previously dried nitrogen.

EXPERIMENTAL

TG investigations in an ammonia atmosphere were performed in a high vacuum apparatus with a quartz spiral microbalance (sensitivity, 1.2 mg mm^{-1}; sample mass (m), 20–25 mg). Upon evacuation, the apparatus was filled with gaseous ammonia previously dried over granulated KOH until a pressure of $P_{NH_3} = 986$ kPa was attained; the non-isothermal experiment was then started with a given heating rate. In the isothermal experiments the sample was lowered into a previously thermostatted part of the reactor in which the temperature was maintained constant with an accuracy of $\pm 0.1°$ C. The same apparatus was used for investigating thermal transformations in air atmosphere.

Experiments in a stream of previously dried nitrogen (flow rate 17 cm^3 min^{-1}) were undertaken with the Perkin–Elmer Thermal Analysis Lab 1, using the TGS-2 block, Model FDC-1. The samples of mass $m = 9$–12 mg were placed in the standard Perkin–Elmer platinum vessel.

IR spectra were performed at temperatures of 20 ° C and −180 ° C on a SPECORD 75 IR spectrophotometer using KBr pellets. In order to determine the phase composition by XRD analysis a DRF-2.0 (Cu K_α radiation) diffractometer was used. Samples of partially decomposed salts for XRD analysis were prepared in a separate series of experiments with sample masses of $m = 100$–150 mg.

Quantitative TLC analysis was carried out using a complete KTH-0.1 kit for thin layer chromatography.

Chemical analysis was performed according to standard methods: phosphorus was determined photocolorimetrically, nitrogen according to Kjeldahl, sodium by flame-photometry, water from the difference of mass loss after heating and the ammonium content.

The initial salts were synthesized according to known methods [1–4] somewhat modified due to the application of our data [5,6]. The sample of $Na(NH_4)_4P_3O_{10} \cdot 4H_2O$ was a fine crystalline powder (crystal size $D =$ 0.02–0.07 mm) which, according to the results of TLC analysis, contained 0.1% phosphorus in the form of monophosphate (P_1), 2.2% phosphorus in the form of diphosphate (P_2) and 97.7% phosphorus in the form of triphosphate (P_3). In the sample of $(NH_4)_9H(P_3O_{10})_2 \cdot 2H_2O$ ($D = 0.1$–0.3 mm) 0.9% P_1, 2.2% P_2 and 96.9% P_3 were found. Both samples, according to XRD analysis results, did not contain impurities of foreign crystalline phases.

RESULTS AND DISCUSSION

IR analysis of the initial crystallohydrates (Fig. 1) confirmed the data obtained previously by Raman and IR spectroscopic methods using deuterated samples [8,9] that, in principle, the evolution of crystal water is possible without breaking the P–O bridge bond. In that sense the investigated crystallohydrates differ from other triphosphate crystallohydrates, for example, in the analysis of $Na_5P_3O_{10} \cdot 6H_2O$ and $K_5P_3O_{10} \cdot 4H_2O$, their vibrational spectra do not indicate such a possibility.

Taking into consideration the influence of temperature on the position of the maxima of the absorption bands of the IR spectra, absorption bands in the region 3300–2700 cm^{-1} correspond to valence vibrations of the ammonium ion (ν_1, ν_3), 1500–1370 cm^{-1} to antisymmetric deformational vibrations (ν_4), 1730–1690 cm^{-1} to symmetric deformational vibrations (ν_2) and 544–400 cm^{-1} to internal vibrations. On the basis of literature data for various ammonium salts [10–15], some of the absorption bands, intense at room temperature, correspond to the combinations $\nu_2 + \nu_6$ (2190–2170 cm^{-1}) and $\nu_4 + \nu_6$ (1960–1900 cm^{-1}). Corresponding absorption bands of water molecule vibrations in the crystal lattice are at 3415–3300 cm^{-1} ($\nu_{OH}(H_2O)$) and 1640–1630 cm^{-1} ($\delta(H_2O)$).

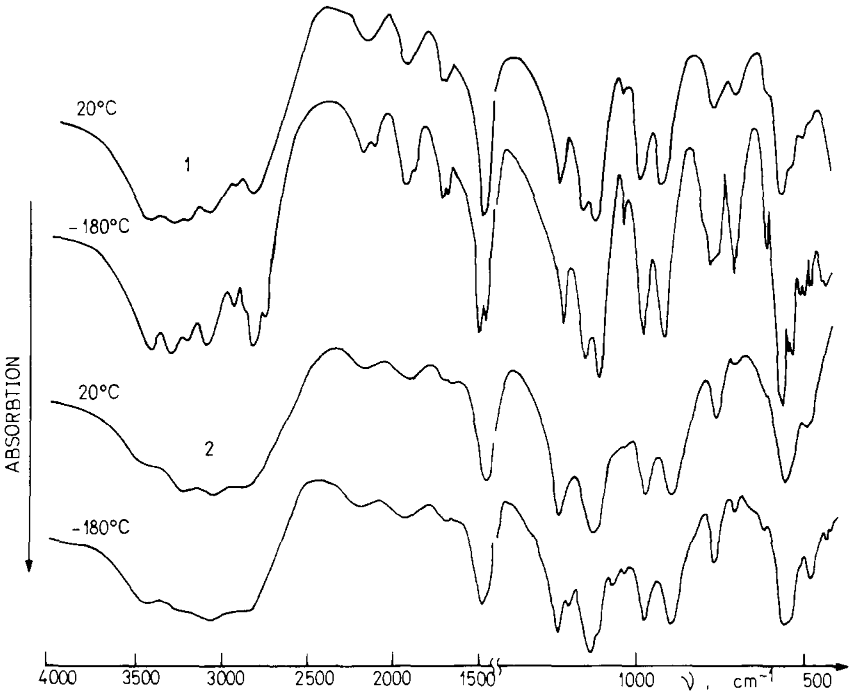

Fig. 1. IR spectra of the triphosphate crystallohydrates $Na(NH_4)_4P_3O_{10} \cdot 4H_2O$ (1) and $(NH_4)_9H(P_3O_{10})_2 \cdot 2H_2O$ (2).

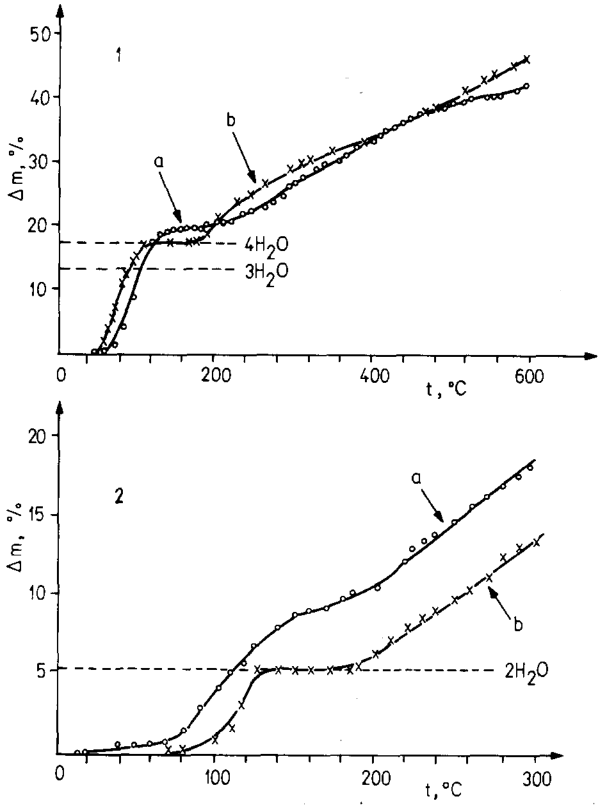

Fig. 2. TG curves of $Na(NH_4)_4P_3O_{10} \cdot 4H_2O$ (1) and $(NH_4)_9H(P_3O_{10})_2 \cdot 2H_2O$ (2) in air (a) and in an ammonia atmosphere (b); heating rate HR = 1 K min^{-1}.

Estimation of the hydrogen bond energy on the basis of the low frequency shift ν_{OH} yields a value of 21–25 kJ mol^{-1}. Water molecules with such a low hydrogen bond energy should be relatively easily separated from the crystalline lattice according to the direct mechanism without anion degradation. However, in order to achieve the non-degradative mechanism certain conditions are necessary. Especially in vacuum and in a water vapour atmosphere, the non-degradative mechanism is not attained in its pure form [5,6].

This mechanism is also not achieved in the dehydration of crystallohydrates in streams or atmospheres of other gases (except in gaseous ammonia). The TG curves of crystallohydrates in an air atmosphere (Fig. 2) and a stream of nitrogen (Fig. 3) do not have clearly defined horizontal plateaus during mass loss which would correspond to the complete removal of crystal water without simultaneous ammonia loss: $\Delta m = 17.1\%$ for $Na(NH_4)_4P_3O_{10} \cdot 4H_2O$ and $\Delta m = 5.1\%$ for $(NH_4)_9H(P_3O_{10})_2 \cdot 2H_2O$. A reaction degree of $\alpha = 1$ (Fig. 3) corresponds to the complete removal of water and ammonia from the crystallohydrate. Analogous results were obtained at other heating rates, besides the ones presented.

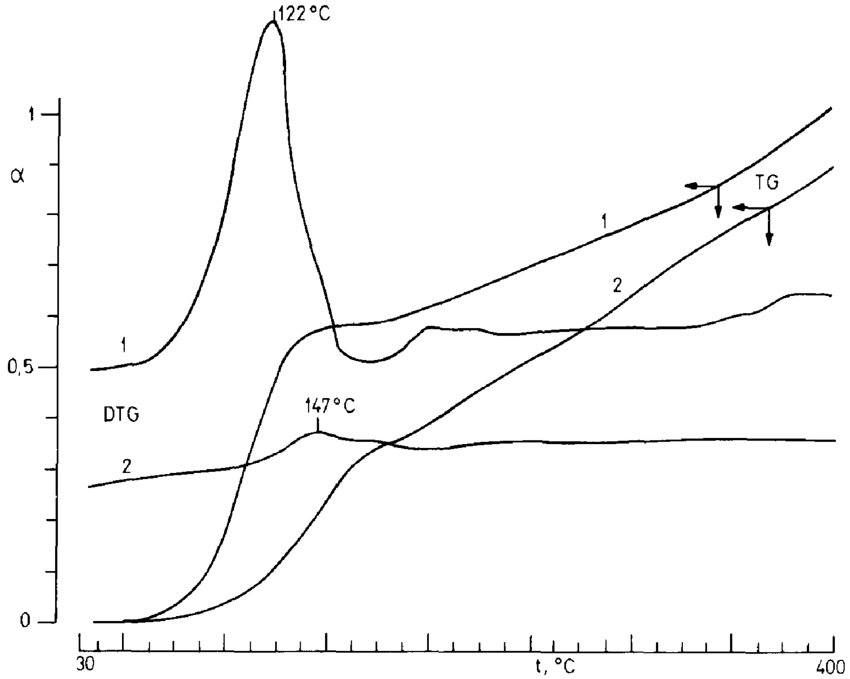

Fig. 3. TG curves and DTG curves of $Na(NH_4)_4P_3O_{10}\cdot 4H_2O$ (1) and $(NH_4)_9H(P_3O_{10})_2\cdot 2H_2O$ (2) in a stream of nitrogen; HR = 20 K min^{-1}.

Only in a gaseous ammonia atmosphere, which has a stabilizing effect on the surface NH_4^+ groups and thus stops ammonia loss in crystallohydrate dehydration, are the horizontal plateaus clearly seen at the calculated values of crystal water loss: $\Delta m = 4H_2O$ in the case of sodium ammonium triphosphate and $\Delta m = 2H_2O$ in the case of acidic ammonium triphosphate (Fig. 2). Both plateaus are limited by the temperature interval 120–180 °C.

Samples of anhydrous salts, obtained in the region of the first half of the plateau, according to chemical analysis data, have the following composition (mass %)

sodium ammonium salt (experimental)	NH_3, 19.6; P, 26.7; H_2O, 0.1
$Na(NH_4)_4P_3O_{10}$ (theoretical)	NH_3, 19.6; P, 26.7; H_2O, 0
acidic salt (experimental)	NH_3, 23.0; P, 27.4; H_2O, 0
$(NH_4)_9H(P_3O_{10})_2$ (theoretical)	NH_3, 22.9; P, 27.8; H_2O, 0

By TLC the following were determined: 1.1%P_1, 4.6% P_2, 94.3% P_3 in $Na(NH_4)_4P_3O_{10}$ and 1.6 P_1, 4.7% P_2, 93.7% P_3 in $(NH_4)_9H(P_3O_{10})_2$.

Both salts were characterized by X-ray diffractograms, which are in agreement with reference diffractograms obtained under isothermal conditions at 110 °C for the sodium ammonium salt and 150 °C for the acidic salt (Fig. 4).

Isothermal experiments have shown that non-degradative dehydration does not occur as a simple reaction of direct transformation of the initial

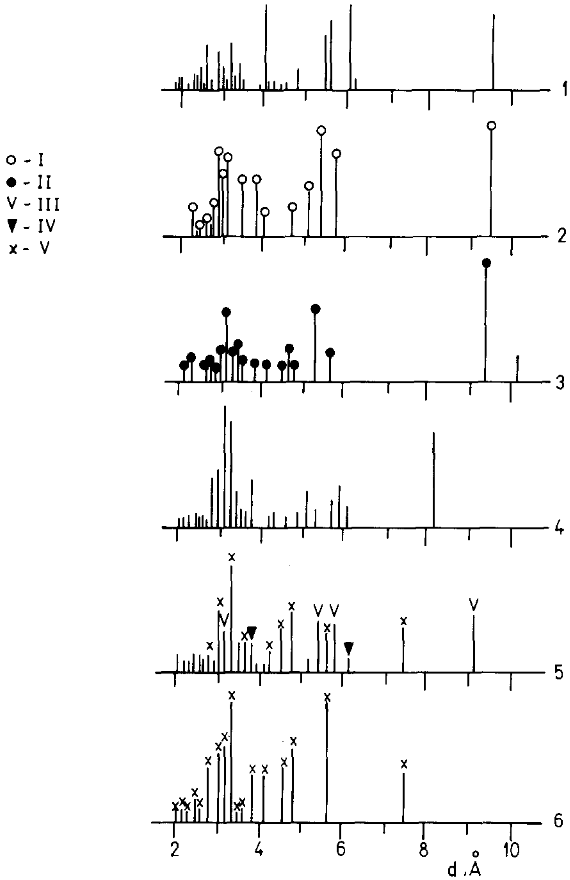

Fig. 4. Scheme of the diffractogram of the products of isothermal dehydration of $Na(NH_4)_4P_3O_{10}\cdot 4H_2O$ (1–3) and $(NH_4)_9H(P_3O_{10})_2\cdot 2H_2O$ (4–6) in an ammonia atmosphere: 1, $Na(NH_4)_4P_3O_{10}\cdot 4H_2O$; 2, $\Delta m = 13.0\%$, $t = 84\,^\circ C$, $\tau = 300$ min; 3, $\Delta m = 17.1\%$, $t = 110\,^\circ C$, $\tau = 200$ min; 4, $(NH_4)_9H(P_3O_{10})_2\cdot 2H_2O$; 5, $\Delta m = 4.5\%$, $t = 120\,^\circ C$, $\tau = 300$ min; 6, $\Delta m = 5.4\%$, $t = 150\,^\circ C$, $\tau = 300$ min. Designations of crystalline phases: I, $Na(NH_4)_4P_3O_{10}\cdot H_2O$; II, $Na(NH_4)_4P_3O_{10}$; III, $(NH_4)_5P_3O_{10}$; IV, $(NH_4)_4HP_3O_{10}$; V, $(NH_4)_9H(P_3O_{10})_2$.

crystallohydrate to anhydrous salts. In both cases the process takes place with the formation of intermediate crystalline products.

During the heating of $Na(NH_4)_4P_3O_{10}\cdot 4H_2O$ it was noted by the XRD method that an intermediate monohydrate was formed

$$Na(NH_4)_4P_3O_{10}\cdot 4H_2O \xrightarrow[60\text{–}80\,^\circ C]{-3H_2O} Na(NH_4)_4P_3O_{10}\cdot H_2O \xrightarrow[100\text{–}110\,^\circ C]{-H_2O} Na(NH_4)_4P_3O_{10}$$

which has the same diffractogram as the previously described monohydrate [5]. Its formation is reflected in the kinetic curves of isothermal dehydration (Fig. 5) in the form of a plateau at 57–84 °C and in the TG curve (Fig. 2) in the form of a mild saddle at $\Delta m = 3H_2O$.

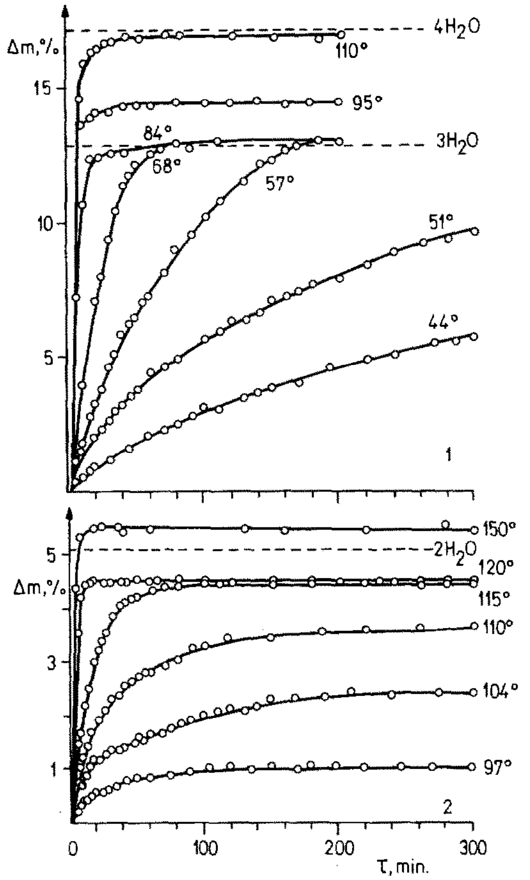

Fig. 5. Kinetic curves of the isothermal dehydration of $Na(NH_4)_4P_3O_{10}\cdot 4H_2O$ (1) and $(NH_4)_9H(P_3O_{10})_2\cdot 2H_2O$ (2) in an ammonia atmosphere.

Besides crystalline $(NH_4)_9H(P_3O_{10})_2$ in the products of heating $(NH_4)_9H(P_3O_{10})_2\cdot 2H_2O$, the presence of crystalline $(NH_4)_5P_3O_{10}$ and $(NH_4)_4HP_3O_{10}$ were noted, which, during the temperature increase 125–180 °C, disappear, transforming to $(NH_4)_9H(P_3O_{10})_2$. Their appearance, as in the case of dehydration in vacuum [6], can be explained by the partial disproportionation of the initial crystallohydrate with accompanying dehydration of the formed disproportionation products

$$\begin{tikzcd}
(NH_4)_5P_3O_{10}\cdot H_2O \arrow[r, "-H_2O", "90\text{–}120\,^{\circ}C"'] & (NH_4)_5P_3O_{10} \arrow[dr] & \\
\boxed{(NH_4)_9H(P_3O_{10})_2\cdot 2H_2O} \arrow[u] \arrow[d] & 125\text{–}180\,^{\circ}C & \boxed{(NH_4)_9H(P_3O_{10})_2} \\
(NH_4)_4HP_3O_{10}\cdot H_2O \arrow[r, "-H_2O", "90\text{–}120\,^{\circ}C"'] & (NH_4)_4HP_3O_{10} \arrow[ur] &
\end{tikzcd}$$

Besides dehydration, according to this scheme, direct dehydration also occurs

$$(NH_4)_9H(P_3O_{10})_2 \cdot 2H_2O \rightarrow (NH_4)_9H(P_3O_{10})_2 + 2H_2O\uparrow$$

the product of which can be already determined by XRD at 100–120 °C.

The thermal transformation of tetrahydrate to monohydrate

$$Na(NH_4)_4P_3O_{10} \cdot 4H_2O \rightarrow Na(NH_4)_4P_3O_{10} \cdot H_2O + 3H_2O\uparrow$$

judging by the value of the kinetic parameter $n = 0.8$–1.0 in the equation

$$\alpha = 1 - \exp(-c\tau^n) \qquad \text{and} \qquad k = nc^{1/n}$$

(α = degree of conversion, τ = time, c = constant, k = rate constant), takes place in the kinetic region as a first order reaction. The temperature dependence of the rate constant is of the form

$$k = 10^{15.6 \pm 0.5} \exp\left(-\frac{113000 \pm 400}{RT}\right) \text{min}^{-1} \quad (317\text{–}341\text{K})$$

The first order of the reaction is of formal character and is not connected to the described cases of homogeneous reactions of crystals [16].

The more complicated process of $(NH_4)_9H(P_3O_{10})_2 \cdot 2H_2O$ dehydration is demonstrated as diffusion limited ($n = 0.4$–0.7), while the temperature dependence of the rate constant is characterized by increased values of the pre-exponential factor and effective activation energy

$$k = 10^{46.9 \pm 2.9} \exp\left(-\frac{360000 \pm 400}{RT}\right) \text{min}^{-1} \quad (370\text{–}388 \text{ K})$$

Without additional data it is not possible to perform a kinetic analysis of the component stages of the total process.

CONCLUSIONS

(1) Gaseous ammonia, as opposed to other gases, shows a stabilizing effect on surface NH_4^+ groups and thus prevents deammonation and degradation in the process of crystal water removal from $Na(NH_4)_4P_3O_{10} \cdot 4H_2O$ and $(NH_4)_9H(P_3O_{10})_2 \cdot 2H_2O$ during their heating to 150–180 °C.

(2) The dehydration of $Na(NH_4)_4P_3O_{10} \cdot 4H_2O$ and $(NH_4)_9H(P_3O_{10})_2 \cdot 2H_2O$ in an ammonia atmosphere takes place according to the non-degradative mechanism, by the direct transformation of the initial crystallohydrates to the anhydrous crystalline salts $Na(NH_4)_4P_3O_{10}$ and $(NH_4)_9H(P_3O_{10})_2$, as well as by the intermediate stage of formation of crystalline $Na(NH_4)_4P_3O_{10} \cdot H_2O$ in the case of sodium ammonium triphosphate and of crystalline $(NH_4)_5P_3O_{10}$ and $(NH_4)_4HP_3O_{10}$ in the case of acidic triphosphate.

(3) The isothermal transformation of tetrahydrate to monohydrate $Na(NH_4)_4P_3O_{10} \cdot 4H_2O$ to $Na(NH_4)_4P_3O_{10} \cdot H_2O$ formally presents a first

order reaction which is not connected to homogeneous reactions of crystals. The more complex reaction of $(NH_4)_9H(P_3O_{10})_2 \cdot 2H_2O$ dehydration involves diffusion limited processes, the component stages of which are not subject to simple kinetic analysis.

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