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THERMAL CONVERSIONS OF SODIUM CYCLOTRIPHOSPHATE MONOHYDRATE, $Na_3P_3O_9 \cdot H_2O$

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ABSTRACT

Isothermal and non-isothermal conversions of $Na_3P_3O_9 \cdot H_2O$ in flowing nitrogen and in air were investigated. It was shown that $Na_3P_3O_9 \cdot H_2O$, in contrast to $Na_3P_3O_9 \cdot 3H_2O$ and $Na_3P_3O_9 \cdot 6H_2O$, loses crystal water irreversibly at $t > 100°C$ in two stages (DSC effects at 124–132 and 210–216°C), their rates being slightly sensitive to water vapour pressure. Isothermal dehydration in the first stage ($t \leqslant 155°C$; mass loss, $\Delta m < 0.5$ mol H_2O) represents a decelerating process. The second stage is characterized by self-acceleration which is explained by the surface accumulation of P–OH groups.

INTRODUCTION

According to earlier published works [1,2] the monohydrate $Na_3P_3O_9 \cdot H_2O$ holds a special position in the series of sodium cyclotriphosphate crystal hydrates. First, in contrast to $Na_3P_3O_9 \cdot 3H_2O$ and $Na_3P_3O_9 \cdot 6H_2O$, which on heating lose the main part of crystal water at temperatures below 100°C without rupture of the anion cycle, $Na_3P_3O_9 \cdot H_2O$ loses crystal water at temperatures above 100°C according to a degradation mechanism. Second, though the crystal structures of $Na_3P_3O_9 \cdot H_2O$ and $Na_3P_3O_9$ are similar to each other [3], the crystal lattice of a single crystal does not pass directly into the crystal lattice of an anhydrous salt. This process proceeds by means of intermediate stages of structure rearrangement and destruction of the cyclic anion. The main reason for this difference is attributed [1] to the low value of the molar volume of crystal water in the monohydrate as compared to other crystal hydrates: 4.7 cm^3 mol^{-1} H_2O for $Na_3P_3O_9 \cdot H_2O$ and 15.4 cm^3 mol^{-1} H_2O for $Na_3P_3O_9 \cdot 6H_2O$.

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The specific features of crystal water removal from a monohydrate must, in a particular way, affect the kinetic characteristics of dehydration. In order to obtain kinetic data (preliminary investigations were carried in ref. 1) we studied the isothermal (100–220°C) and non-isothermal (40–350°C) dehydrations of $Na_3P_3O_9 \cdot H_2O$ in a flow of dry nitrogen. Non-isothermal dehydrations of $Na_3P_3O_9 \cdot 3H_2O$ and of $Na_3P_3O_9 \cdot 6H_2O$ were studied in air at 20–550°C for comparison.

EXPERIMENTAL

A fine crystalline sample of $Na_3P_3O_9 \cdot H_2O$ (crystal size 0.01–0.1 mm) was obtained according to a well-known method [2] modified by the fact that crystals were precipitated from an aqueous solution of chromatographically pure sodium cyclotriphosphate with methanol at 20°C. According to thin layer chromatography (TLC) analysis data (KTH, 0.1; equipment set for TLC) and to XRD analysis data (DRF, 2.0; diffractometer; $\mathrm{Cu}K_\alpha$ irradiation) the sample was a chromatographically pure substance free of admixtures of other anionic phosphate forms and foreign crystal phases. Its X-ray pattern corresponded to the known data for $Na_3P_3O_9 \cdot H_2O$ [2–5], including data for $Na_3P_3O_9 \cdot H_2O$ (form II) [1]. Crystals of $Na_3P_3O_9 \cdot 3H_2O$ obtained according to the method of ref. 2 and used for comparative experiments were approximately the same size as $Na_3P_3O_9 \cdot H_2O$ crystals. The experiments were carried out with freshly prepared samples, because during storage $Na_3P_3O_9 \cdot 3H_2O$ decomposes into $Na_3P_3O_9 \cdot 6H_2O$ and $Na_3P_3O_9 \cdot H_2O$. Hexahydrate was obtained by a well-known method [6]. On mild grinding it represented a fine crystalline sample with a crystal size of 0.05–0.1 mm. The samples were free from other phosphates and foreign crystal phases.

Non-isothermal conversions of the samples in air were studied by the derivatographic method with a MOM OD-102-T derivatograph (Budapest) at a heating rate, HR = 10 K min^{-1}. Powder-like samples ($m = 300$ mg) were placed in an open ceramic pan.

Isothermal conversions in a flow of nitrogen containing up to 20–30 ppm of water vapour, 7 ppm of oxygen and 2–3 ppm of argon were studied by TG. Non-isothermal conversions were studied by TG, DSC and DTG. The experiments were carried out using a Perkin-Elmer thermal analysis Lab 1 with DSC-2 Scan Auto Zero (nitrogen flow rate, 37 ml min^{-1}) and TGS-2, Model FDC-1 (nitrogen flow rate, 14 ml min^{-1}) units. The powder-like sample ($m = 1$–10 mg) was placed into standard Perkin-Elmer platinum, gold or aluminium pans or was encapsulated in aluminium foil. During isothermal TG experiments the temperature at the beginning of the experiments was increased at HR = 160 K min^{-1} up to $t < 160$°C or at HR = 320 K min^{-1} up to $t > 160$°C and then kept at a constant level within ± 0.1°C.

Initial and thermally treated $Na_3P_3O_9 \cdot H_2O$ crystals were studied using a Philips E.M. 300 electron microscope by the carbon replica method. A thin film of spectrally pure carbon was deposited on the sample in vacuum, then the replica-film was separated, by dissolving the sample in distilled water, and studied microscopically.

RESULTS AND DISCUSSION

On non-isothermal heating, tri- and hexahydrates lose a large portion of their crystal water at around or below 100°C practically in a single stage with a corresponding main endothermal effect at 100°C for $Na_3P_3O_9 \cdot 3H_2O$ and at 110°C for $Na_3P_3O_9 \cdot 6H_2O$ (Fig. 1). According to XRD and TLC data the dehydration proceeds without destruction of the anion cycle and crystalline $Na_3P_3O_9$ is formed, which could be heated up to its melting temperature (620–623°C) without changes in mass, phase or anion composition.

On heating the monohydrate under the same conditions the water is removed in two stages with endothermal effects at 128 and 210°C. Two endothermal effects are known in the literature for $Na_3P_3O_9 \cdot H_2O$ (form II) at 130 and 170°C [7]. Within the above-mentioned temperature range, and

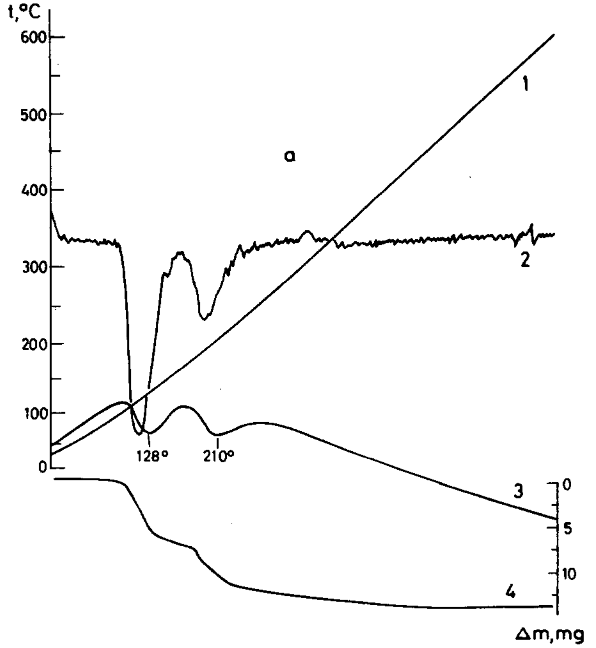


Fig. 1. Derivatograms of $Na_3P_3O_9 \cdot H_2O$ (a), $Na_3P_3O_9 \cdot 3H_2O$ (b) and $Na_3P_3O_9 \cdot 6H_2O$ (c): (1) *T*, (2) DTG, (3) DTA, (4) TG.

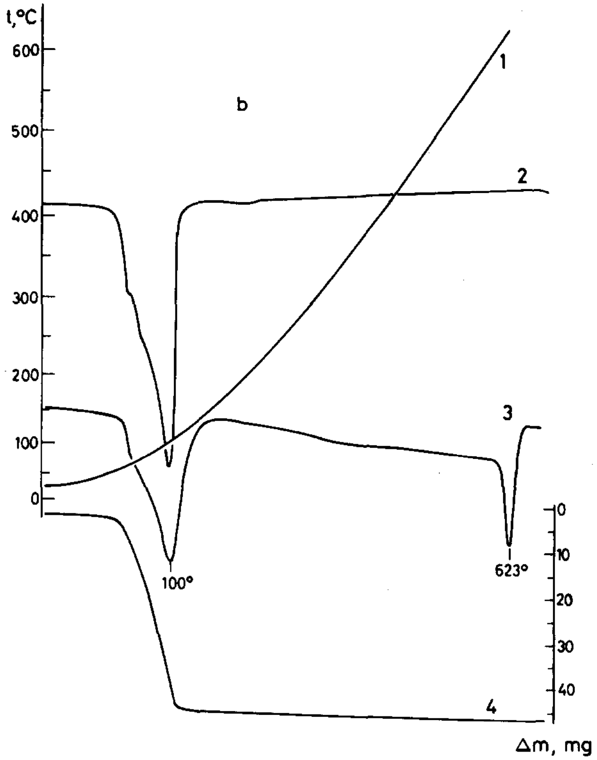


Fig. 1 (continued).

especially around the second endothermal effect, dehydration is accompanied by anion decyclization. The decyclization products are amorphous and at the end of dehydration they are transformed into crystalline $Na_3P_3O_9$ due to recondensation. The latter product behaves as described above.

Hydrolytic rupturing of the anion cycle takes place either directly under the action of crystal water, i.e., according to the intrinsic hydrolysis mechanism, or under the action of water vapour. The above-mentioned results and published data [3] that, in the case of $Na_3P_3O_9$ and $Na_3P_3O_9 \cdot H_2O$, water cannot enter or leave the crystalline structure without rearrangement, allows us to conclude that the dehydration of $Na_3P_3O_9 \cdot H_2O$ is an irreversible topochemical reaction. This is the important distinction between monohydrate and hexahydrate, because the isothermal–isobaric dehydration of the latter at temperatures below 180°C proceeds in direct compliance with the laws of reversible topochemical reactions of the type $A_s \rightleftarrows B_s + C_g$ [8].

This distinction explains some specific features of the dehydration of $Na_3P_3O_9 \cdot H_2O$ as compared with $Na_3P_3O_9 \cdot 6H_2O$; it particularly explains the different sensitivity of dehydration rates to water vapour pressure.

The reversible dehydration of $Na_3P_3O_9 \cdot 6H_2O$ is sensitive to experimental conditions, which determine the possibility of an unhindered removal of

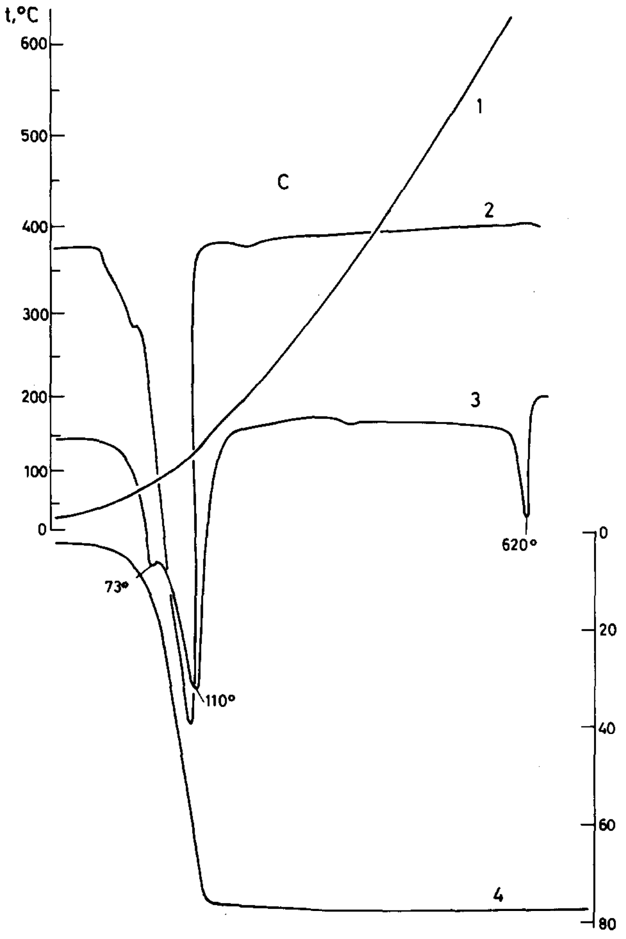


Fig. 1 (continued).

water vapour into the gas phase. The use of an open pan for $Na_3P_3O_9 \cdot 6H_2O$ being heated in a flow of nitrogen results in the appearance on the DSC curve of an endothermal effect (66°C) of single-stage crystal water removal. In the case of the encapsulated sample, three endothermal effects at 62, 92 and 103°C (Fig. 2) are observed. Splitting of the endothermal effect is caused by the accumulation of water vapour inside the non-pierced capsule. In this case the dehydration of $Na_3P_3O_9 \cdot 6H_2O$ proceeds, not directly to $Na_3P_3O_9$, but by the formation of intermediate crystal hydrates. The thermal treatment of $Na_3P_3O_9 \cdot 6H_2O$ in a humid atmosphere serves as the basis of one of the methods for obtaining $Na_3P_3O_9 \cdot H_2O$ [1]. This has been proved by XRD analysis. The same explanation is true for the splitting of the endothermal effect during DTA (Fig. 1C).

On the other hand, the DSC curves of encapsulated and open-pan

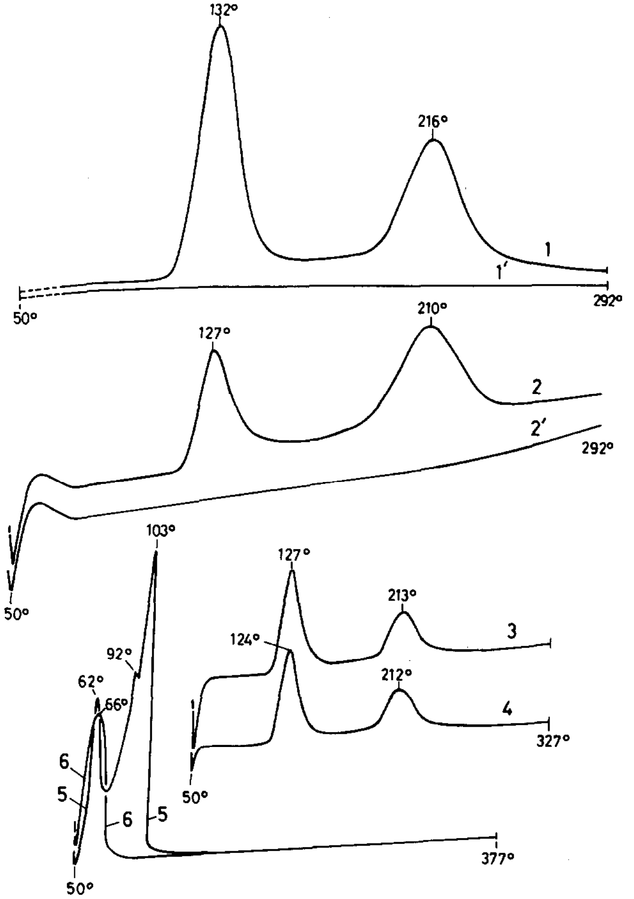


Fig. 2. DSC curves of $Na_3P_3O_9 \cdot H_2O$ (1–4) and $Na_3P_3O_9 \cdot 6H_2O$ (5, 6) heated in a flow of nitrogen: (1) $m = 10.16$ mg, Al-capsule; (2) $m = 8.27$ mg, ground sample, Al-capsule; (1′) and (2′) baselines; (3) $m = 4.40$ mg, open Al-pan; (4) $m = 3.63$ mg, Al-capsule; (5) $m = 6.19$ mg, Al-capsule; (6) $m = 1.14$ mg, open Al-pan; HR = 20 K min^{-1} (1–4); HR = 10 K min^{-1} (5, 6).

$Na_3P_3O_9 \cdot H_2O$ heating coincide (Fig. 2, curves 3 and 4). In this case the rate of dehydration is slightly sensitive to water vapour pressure in both stages. Usually, water vapour accelerates recondensation due to the mineralizing effect, however, in our case this effect is not observed, because the crystallization of $Na_3P_3O_9$ proceeds at a high rate and does not represent a limiting stage of the process.

The second endothermal effect on heating $Na_3P_3O_9 \cdot H_2O$ (210–216°C), in contrast to the first effect (127–132°C), does not change substantially with respect to the granulometric composition of the sample. Figure 2 (curve 2) shows data for the $Na_3P_3O_9 \cdot H_2O$ sample, ground to a fine powder (particle size < 0.005–0.01 mm). The energy of mechanically induced strains accumulated during sample grinding is released in the first dehydration

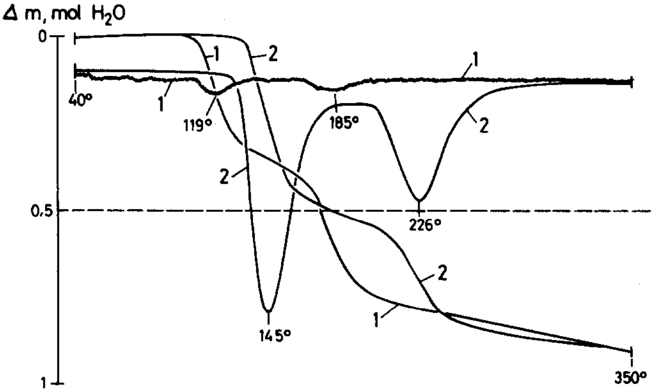


Fig. 3. TG and DTG curves of $Na_3P_3O_9 \cdot H_2O$ heated in a flow of nitrogen (Pt-pan): (1) HR = 1.25 K min^{-1}, $m = 5.91$ mg; (2) HR = 80 K min^{-1}, $m = 6.65$ mg.

stage. Thus, the heat of conversion, calculated by the planimetric method using the areas under the peaks, diminishes in the first stage as a result of mechanical activation from $\Delta H_1 = 26.9$ kJ mol^{-1} to $\Delta H_1 = 14.8$ kJ mol^{-1}. In the second dehydration stage the heat of conversion undergoes an insignificant change ($\Delta H_2 = 23.5$ kJ mol^{-1}; $\Delta H_2 = 22.7$ kJ mol^{-1} before and after activation, respectively).

Optimal heating rates (HR = 10–20 K min^{-1}) were used in the DSC studies. The change of HR within the range 1.25–80 K min^{-1} does not affect the general picture of the process, but leads to a shift of the peaks. In TG and DTG experiments the shift attains 20° for the first effect and 40° for the second effect (Fig. 3). Besides, the amount of water removed during the first effect increases with HR.

Kinetic curves of the reversible isothermal dehydration of $Na_3P_3O_9 \cdot 6H_2O$ have a specific S-form with self-acceleration and deceleration regions [6,9]. The curves of the irreversible dehydration of $Na_3P_3O_9 \cdot H_2O$ are characterized by a different form (Fig. 4). Within the temperature range 100–155°C the curves have a typical form for diffusion-limited processes, they consist of an initial section of rapid dehydration and further sections of slow dehydration. The latter sections shift towards low Δm with decreasing temperature. At $t = 157$–185°C these sections become straight and pass into self-acceleration regions. At $t > 200$°C the curves resume the form they had at low temperature.

According to XRD and TLC analyses rapid initial dehydration at $t < 155$°C is not connected with significant anion decyclization or with $Na_3P_3O_9$ crystallization. These processes take place in the stage of slow dehydration, where the $Na_3P_3O_9$ phase and amorphous decyclization products gradually accumulate in the sample with increasing isothermal treatment time. It thus follows that shortening of the isothermal treatment time allows an increase of the amount of water that could be removed from $Na_3P_3O_9 \cdot H_2O$ without

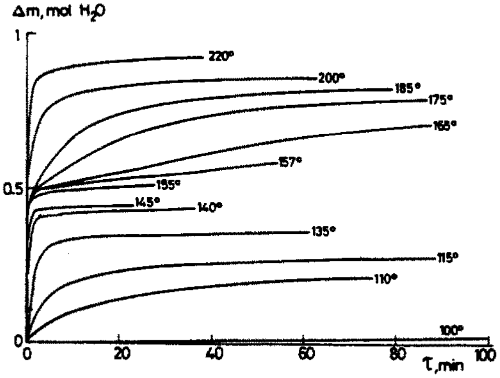
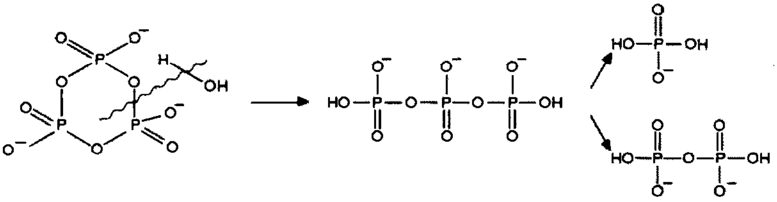


Fig. 4. Kinetic curves of isothermal dehydration of $Na_3P_3O_9 \cdot H_2O$ in a flow of nitrogen (Pt-pan, $m = 5$–10 mg).

anion destruction. Under the conditions of non-isothermal experiments this amount is equal to the amount of water removed before the first effect. This amount increases with HR (see TG curves 1 and 2, Fig. 3).

The irreversibility of rapid initial dehydration, which is not connected with decyclization, has a diffusion nature that seems to be conditioned by diffusional difficulties the water is subjected to during migration from the interior to the surface of the crystals. At this stage the effective activation energy, calculated from the temperature dependence of the initial dehydration rate, has a value of $E = 190$–200 kJ mol^{-1}, that exceeds the known values for hydrolytic anion decyclization in the solid phase and in aqueous solutions ($E = 84$–100 kJ mol^{-1}). Increased E values are typical for diffusion-limited processes, $A_s \rightarrow B_s + C_g$, which take place in the atmosphere of gaseous reaction products [8,10].

Self-accelerated dehydration within the range $t = 157$–185°C is not caused by the appearance of cracks or crystal fragmentation. The results of electron microscopy indicate that the contours of the crystals do not change during dehydration, though the possibility of micropore formation is not excluded (Fig. 5). At such temperatures, the degradation processes resulting in the formation of acid ortho- and pyrophosphates are intensified.



The effective activation energy ($E = 145$–160 kJ mol^{-1}) calculated from the temperature dependence $1/\tau_{0.6}$ ($\Delta m = 0.6$ mol H_2O) or $1/\tau_{0.7}$ ($\Delta m = 0.7$ mol H_2O), is somewhat lower than values obtained earlier. However, even

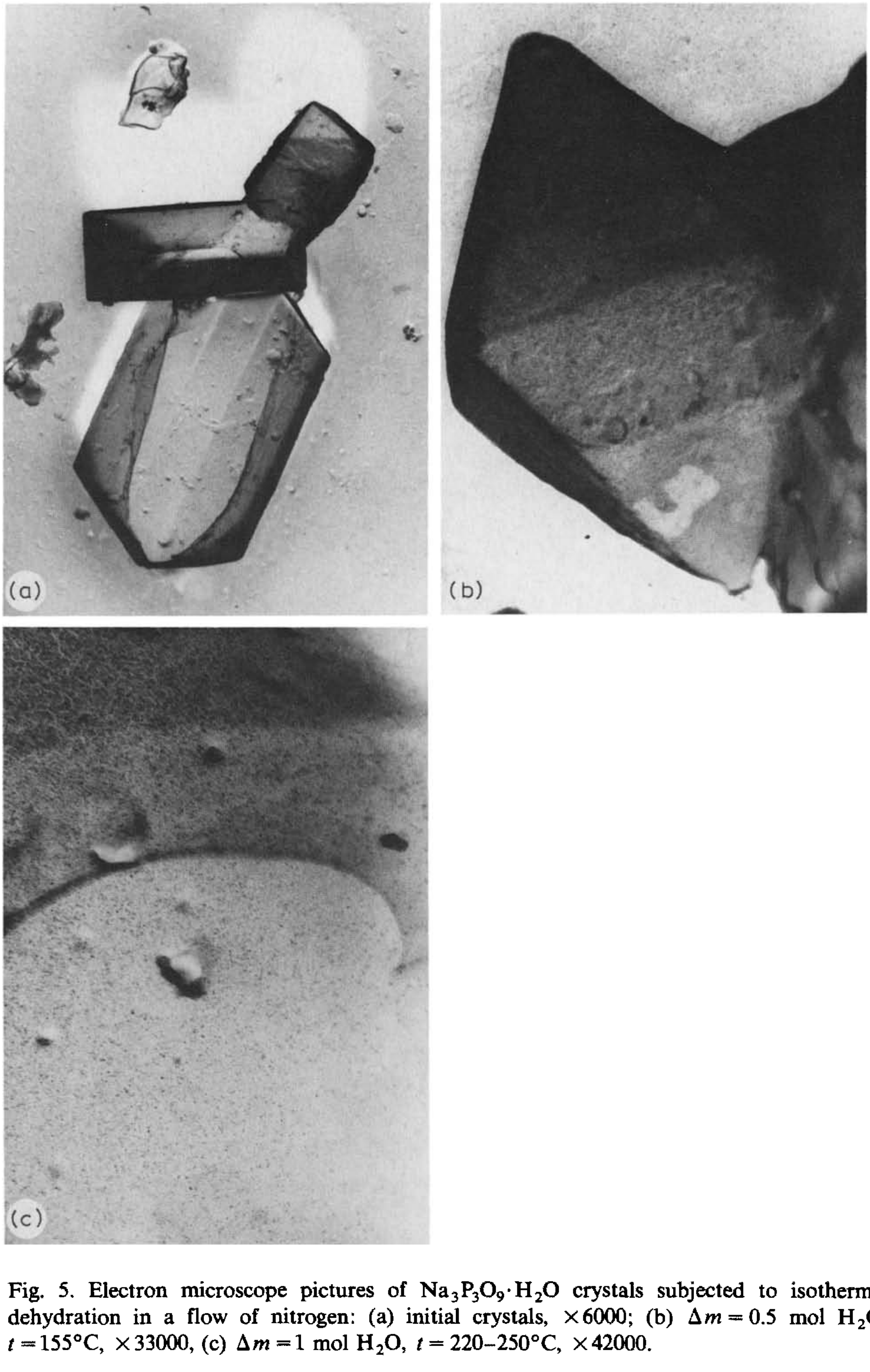


Fig. 5. Electron microscope pictures of $Na_3P_3O_9 \cdot H_2O$ crystals subjected to isothermal dehydration in a flow of nitrogen: (a) initial crystals, $\times 6000$; (b) $\Delta m = 0.5$ mol H_2O, $t = 155°C$, $\times 33000$, (c) $\Delta m = 1$ mol H_2O, $t = 220$–$250°C$, $\times 42000$.

this value does not correspond to that of P–O–P bond rupturing, because degradation is accompanied by the processes of anion condensation.

Accumulation of acid phosphates and increased mobile proton concentration can be logically considered by taking into account the proton mechanism of the above process as the main reason for reaction self-acceleration and for transition of the reaction from the diffusional to the kinetic region. The reaction is localized mainly on the surface of the crystals and in micropores; the accumulating P–OH groups have good access to the gaseous phase and interact easily with gaseous ammonia forming NH_4^+ ions, which could be determined by IR spectroscopy. At temperatures below 155°C the samples do not absorb gaseous ammonia. In this case hydrolytic rupturing of P–O–P bonds takes place according to the intrinsic hydrolysis mechanism, localized mainly in the volume of the crystals, and P–OH groups have practically no access to the gaseous phase.

CONCLUSIONS

(1) The monohydrate $Na_3P_3O_9 \cdot H_2O$, in contrast to $Na_3P_3O_9 \cdot 3H_2O$ and $Na_3P_3O_9 \cdot 6H_2O$, loses crystal water irreversibly at $t > 100°C$ in two stages (DSC effects at 124–132 and 210–216°C). The rates and other characteristics of these two stages are a slight sensitivity to water vapour pressure, and, in the second stage, the characteristics are slightly sensitive to mechanical activation of the sample.

(2) Isothermal dehydration within the limits of the first stage ($t < 155°C$; mass loss, $\Delta m = 0.5$ mol H_2O) represents a decelerating process, which is stopped at various values of Δm. The halting of the process at various Δm values and its irreversibility are interpreted on the basis of the intrinsic hydrolysis mechanism and diffusion-limited dehydration scheme.

(3) Isothermal dehydration in the second stage ($t \geqslant 155°C$; $\Delta m > 0.5$ mol H_2O) represents a self-accelerating process connected with hydrolytical rupturing of the P–O bonds and with anion condensation. Self-acceleration is explained by accumulation of the P–OH groups localized mainly on the surface of the crystals. These groups are capable of interaction with gaseous ammonia.

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