THERMOCHEMISTRY OF SODIUM TRIPHOSPHATE AND SODIUM CYCLOTRIPHOSPHATE TRANSFORMATIONS

V.M. GALOGAZA *

University of Belgrade, Faculty of Technology and Metallurgy, 11000 Belgrade (Yugoslavia)

S.G. TERESHKOVA and E.A. PRODAN

Institute of General and Inorganic Chemistry, Academy of Sciences of Belorussian SSR, 220606 Minsk (U.S.S.R.)

(Received 7 June 1988)

ABSTRACT

Thermal transformations taking place on heating $Na_5P_3O_{10} \cdot 6H_2O$, $Na_5P_3O_{10}(II)$ and $Na_3P_3O_9 \cdot 6H_2O$ in dry nitrogen at 293–880K are investigated using DSC, TG and TLC methods. The obtained standard enthalpies of the main reactions and the constituent stages of reactions of the $Na_5P_3O_{10}(II) \rightarrow Na_5P_3O_{10}(I)$ transition are discussed. A universal formula for thermochemical calculations is proposed which allows the determination of thermodynamic characteristics for complex multistage and multicycle topochemical processes. The cyclic character of $Na_5P_3O_{10} \cdot 6H_2O$ dehydration is explained on the basis of a zonary mechanism of reaction which spreads through the crystals.

INTRODUCTION

The results of investigations into the kinetics and mechanism of the dehydration of sodium triphosphate hexahydrate $Na_5P_3O_{10} \cdot 6H_2O$ and of sodium cyclotriphosphate hexahydrate $Na_3P_3O_9 \cdot 6H_2O$ suggest fundamental differences in their behaviour when heated. As a rule, $Na_5P_3O_{10} \cdot 6H_2O$ dehydration proceeds via a degradation mechanism and only rarely, for instance in the case of rapid heating at high water vapour pressure, is there a probability of direct dehydration to $Na_5P_3O_{10}(II)$ without anion destruction [1,2]. In contrast, under the same conditions $Na_3P_3O_9 \cdot 6H_2O$ dehydrates with the direct transformation of hexahydrate into the anhydrous salt

$$Na_3P_3O_9 \cdot 6H_2O \rightarrow Na_3P_3O_9 + 6H_2O \uparrow \qquad (1)$$

---
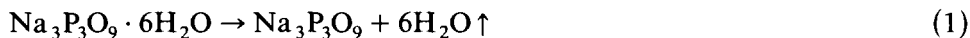
* Author to whom all correspondence should be addressed.

Due to the high rate of crystallization of $Na_3P_3O_9$, reaction (1) takes place in a kinetic regime and is not complicated by diffusion processes [3,4].

The literature provides scanty data on the thermodynamic characteristics of these processes [5]. Using solution calorimetry, Irving and McKerrell [6] determined the standard heats of formation of $Na_5P_3O_{10} \cdot 6H_2O$, $Na_3P_3O_9$ and of two crystalline forms of anhydrous sodium triphosphate: low temperature $Na_5P_3O_{10}(II)$ and high temperature $Na_5P_3O_{10}(I)$. Andon et al. [7] measured heat capacities of these compounds and obtained the entropy values S_{298}. Using a differential scanning calorimeter, Ashcroft et al. [8] measured the heats of formation of $Na_5P_3O_{10}(II)$ and $Na_3P_3O_9$ and calculated the enthalpies of reaction.

In order to obtain comparable thermochemical data on the processes taking place during heating $Na_5P_3O_{10} \cdot 6H_2O$, $Na_5P_3O_{10}(II)$ and $Na_3P_3O_9 \cdot 6H_2O$, we investigated their thermal transformations under identical conditions using the methods of differential scanning calorimetry (DSC), thermogravimetry (TG) and thin layer chromatography (TLC). Polycrystalline samples with known crystal dimensions were used in the experiments which were performed in a flow of dry nitrogen. The obtained experimental $\Delta H_r^{\ominus}$ (r, reaction) and $\Delta H_t^{\ominus}$ (t, transition) values were compared with the values calculated from the known thermodynamic characteristics of the crystalline reaction participants.

EXPERIMENTAL SECTION

TLC-pure and X-ray-diffraction (XRD)-pure substances were used *: $Na_5P_3O_{10} \cdot 6H_2O$ (crystal size $D = 0.02-0.2$ mm) was prepared by a five-fold recrystallization of the technical product, as reported by Quimby [9]; $Na_3P_3O_9 \cdot 6H_2O$ ($D = 0.01-0.3$ mm) was prepared by a known method [10]; and $Na_5P_3O_{10}(II)$ ($D = 0.005-0.02$ mm and specific surface area $S = 3 \pm 1$ m^2 g^{-1}) was obtained by thermal treatment of $Na_5P_3O_{10} \cdot 6H_2O$ in water vapour steam at 623 K. The XRD characteristics of the samples correspond to the ASTM table data. TLC analysis was performed using a KTC-0.1 equipment set. Before the experiments the samples were kept in hermetically sealed ampoules with minimal free volume.

Thermochemical experiments were conducted using a Perkin–Elmer Thermal Analysis Lab 1 with DSC-2 Scan Auto Zero Accessory (nitrogen flow rate 37 cm^3 min^{-1}). For recording TG curves and for monitoring mass loss, the TGS-2 model FDC-1 unit was used (nitrogen flow rate 17 cm^3 min^{-1}).

In the temperature range from 293 to 750 K, which is sufficient for complete removal of water from both the crystal hydrates, the samples

($m = 4$–17 mg) were arranged in standard open Perkin–Elmer aluminium pans. The preferred procedure for DSC experiments is to encapsulate the samples, but in our case this method is not suitable. Inside the capsule the process proceeds in an autogenerated atmosphere of water vapour which, starting from a definite critical pressure, changes the direction of the reaction and the composition of reaction products. The same happens when a pierced capsule or a pan covered with a disc is used. Thus, the DSC curve of the $Na_3P_3O_9 \cdot 6H_2O$ sample covered with an aluminium disc shows two endo-effects of dehydration instead of only the one, which is observed when an open aluminium pan is used [4]. For the investigation of the transformation of $Na_5P_3O_{10}(II)$ into $Na_5P_3O_{10}(I)$ in the range of temperatures up to 880 K, a standard open platinum or gold sample pan was used.

In DSC and TG experiments, the temperature was increased at heating rates (HR) in the range 0.3–20 K min^{-1}. For isothermal investigations, the temperature was brought to the required value at an HR of 160 K min^{-1} and then kept constant within ± 0.1 K. The area under the DSC peaks was measured by a precision planimeter and was also determined gravimetrically. The experiments for enthalpy determination were repeated 3–5 times using intermediate temperature calibration and baseline adjustment control.

RESULTS AND DISCUSSION

In conformity with the results obtained earlier [4], $Na_3P_3O_9 \cdot 6H_2O$ dehydration proceeds according to reaction (1) with rapid $Na_3P_3O_9$ crystallization and completion of the process at 350 K (Fig. 1). HR variation in the range 0.3–20 K min^{-1} somewhat changes the latter value as well as the position of the DSC curve maximum, but the process is usually completed below 360–370 K and is not accompanied by any cycle rupture. The TLC analysis indicates that the mass content of phosphorus in the form of cyclotriphosphate (P_{3c}) does not fall below 98–99% P_{3c}.

The enthalpy of reaction (1) established experimentally ($\Delta H_r^{\ominus} = 76.5$ kcal mol^{-1}) does not essentially differ from the calculated value $\Delta H_{r298}^{\ominus} = 77.4$ kcal mol^{-1}. Because no data on the standard enthalpy of $Na_3P_3O_9 \cdot 6H_2O$ formation were available, the calculation derived from the standard enthalpy of formation of $Na_3P_3O_9$ ($\Delta H_{f298}^{\ominus} = -878.6 \pm 1.5$ kcal mol^{-1}) [6] and the standard enthalpy of formation of $6H_2O$ in the state of ice ($\Delta H_{f298}^{\ominus} = -424.2$ kcal mol^{-1}). In choosing the latter value we took into account the known $\Delta H_{f298}^{\ominus}$ data for the salt hydrate series of mono-, di- and triphosphates (on average, $\Delta H_{f298}^{\ominus} = -70.7$ kcal mol^{-1} per mol of H_2O).

One of the peculiarities of $Na_3P_3O_9 \cdot 6H_2O$ dehydration is that it begins to lose water in dry atmosphere at room temperature. Therefore, when determining the $\Delta H_r^{\ominus}$ value for reaction (1), a correction was introduced to allow for the exact water content of the sample at the beginning of the DSC
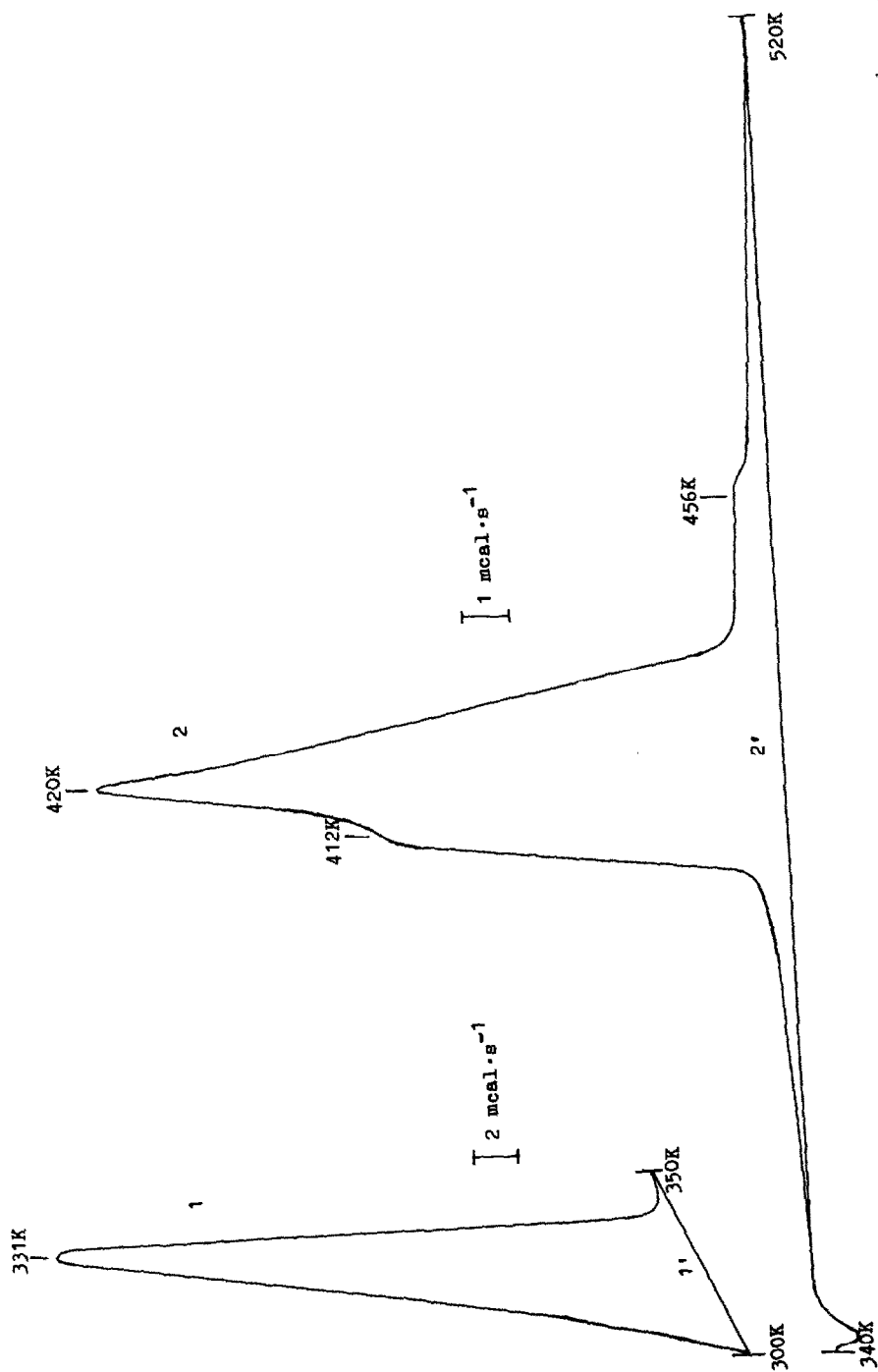
Fig. 1. DSC curves for hexahydrates: 1, $Na_3P_3O_9 \cdot 6H_2O$, HR = 5 K min^{-1}, m = 4.50 mg; 2, $Na_5P_3O_{10} \cdot 6H_2O$, HR = 20 K min^{-1}, m = 4.83 mg; 1′ and 2′, baselines.

experiment. For the sample used here, the value of the correction is insignificant, but when the sample is in the form of a powder, it becomes important; in particular, the final parts of the isothermal and non-isothermal TG curves correspond to a mass loss Δm of 4–5 mol H_2O instead of 6 mol H_2O. In some experiments, relatively large single crystals were used in which case the value of the correction was close to zero.

For the dehydration of $Na_5P_3O_{10} \cdot 6H_2O$, in contrast to that of $Na_3P_3O_9 \cdot 6H_2O$, there is no need for such a correction because the more stable $Na_5P_3O_{10} \cdot 6H_2O$ crystals begin to lose water at 350–360 K. But there are difficulties in removing residual water which is not a problem with $Na_3P_3O_9 \cdot 6H_2O$ dehydration. For this and other reasons, the DSC curve has a more complicated shape (Fig. 1) than in the case of $Na_3P_3O_9 \cdot 6H_2O$.

The overall reaction can be formulated as follows

$$Na_5P_3O_{10} \cdot 6H_2O \rightarrow Na_5P_3O_{10}(\mathbf{II}) + 6H_2O\uparrow \qquad (2)$$
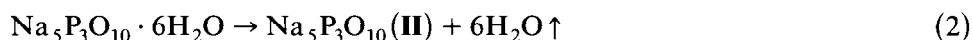
with only the initial and final crystalline products being considered. The experimental value of the enthalpy, $\Delta H_r^{\ominus} = 79.6$ kcal mol^{-1}, for (2) is close to the value $\Delta H_{r298}^{\ominus} = 79.8$ kcal mol^{-1} calculated from the known standard enthalpies of formation of H_2O in the vapour state ($\Delta H_{f298}^{\ominus} = -57.8$ kcal mol^{-1}), $Na_5P_3O_{10}(\mathbf{II})$ ($\Delta H_{f298}^{\ominus} = -1059.1 \pm 1.5$ kcal mol^{-1}) and $Na_5P_3O_{10} \cdot 6H_2O$ ($\Delta H_{f298}^{\ominus} = -1485.7 \pm 1.5$ kcal mol^{-1}) [6].

In reality the process is much more complicated, which is apparent from the comparatively complex shape of the DSC curve. The proximity of the experimental and calculated $\Delta H_r^{\ominus}$ values only means that under the given conditions, reaction (2) proceeds with complete removal of H_2O and a high yield of $Na_5P_3O_{10}(\mathbf{II})$. In practice, we did not manage to achieve direct dehydration via reaction (2).

Reaction (2) is industrially important, and its kinetics and mechanism have been extensively discussed in the literature [5,11–14]. Here, we shall only consider the points pertaining to the problems discussed.

In general, taking into account the latest data [15], the process of removing water of crystallization from $Na_5P_3O_{10} \cdot 6H_2O$ can be divided into several stages.

Stage (a)

This is the reversible non-degradative removal of a comparatively small quantity of water (usually $\Delta m \leqslant 0.6$ mol H_2O) in a kinetic regime corresponding to the slowly increasing initial sections of the DSC curve (Fig. 1) and the non-isothermal TG curve (Fig. 2). The amount of water that can be removed in such a way is largely determined by the crystal size and, to a smaller degree, by the HR or treatment time. This is the only reversible stage of the dehydration process and the only stage at which the equilibrium pressure of water vapour over $Na_5P_3O_{10} \cdot 6H_2O$ crystals is relevant. Taking
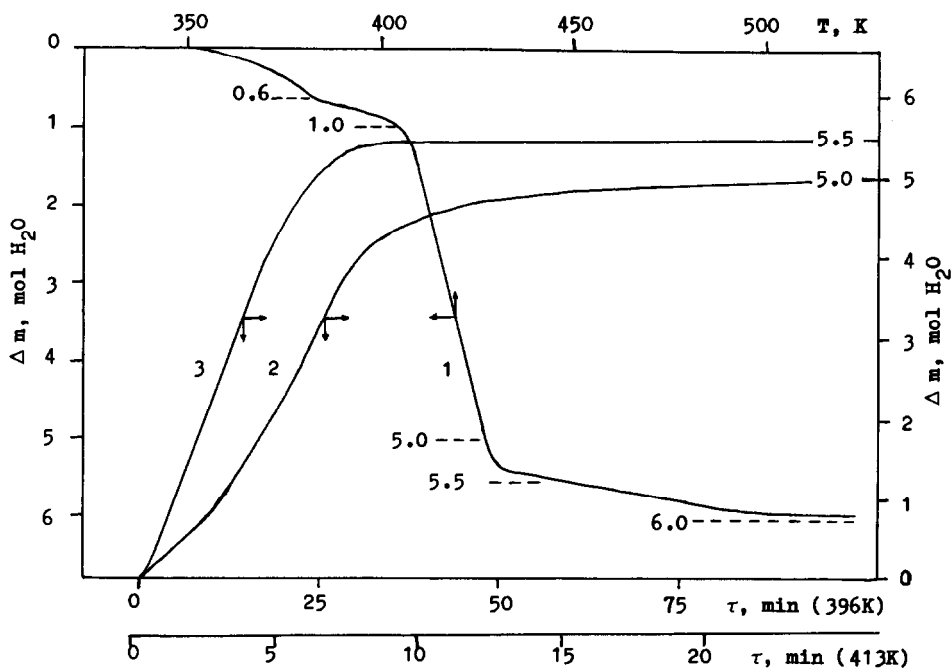
Fig. 2. TG curves for $Na_5P_3O_{10} \cdot 6H_2O$: 1, non-isothermal, HR = 5 K min^{-1}, $m = 8.82$ mg; 2, isothermal, 396 K, $m = 4.65$ mg; 3, isothermal, 413 K, $m = 4.59$ mg.

into consideration the $\Delta H_{r298}^{\ominus}$ value for the removal of this amount of water and the $\Delta S_{r298}^{\ominus}$ value of 21.25 e.u., we obtain the equilibrium constant $K_{298} = 6.19 \ 10^{-2}$.

Stage (b)

This involves the removal of water in the Δm interval between 0.6 and 2.0 mol H_2O in a diffusion regime with no deep anion degradation. A point of inflection in the DSC and TG curves corresponds to the finish/start of this stage. At high HR, the degree of anion degradation is insignificant, but it increases with decreasing HR and increasing isothermal treatment time. The peculiarity of degradation at this stage is that the diphosphate : monophosphate molar ratio in the resulting products exceeds 1 : 1, sometimes reaching 4 : 1. If the degree of degradation is insignificant, the process, in spite of its diffusion regime, may be reversed and the initial content of water of crystallization (6 mol H_2O) may be re-established. In some cases, with the help of moist air treatment, it is possible to restore the original transparency to cloudy crystals. The diffusion regime is considered to be accompanied by diffusion of water molecules from the interior of the crystal to its external geometrical surfaces.

TABLE 1

Standard enthalpies of the reactions occurring during the heating of $Na_3P_3O_9 \cdot 6H_2O$ and $Na_5P_3O_{10} \cdot 6H_2O$

Reaction	$\Delta H^{\ominus}_{r298}$ (kcal mol^{-1})	$(\Delta H^{\ominus}_{r298})^{\star a}$ (kcal mol^{-1})
(1)	+77.4	+12.9
(2)	+79.8	+13.3
(3)	+26.6	+13.3
(4)	+37.4	+12.5
(5)	+46.05	+13.16
(6)	+15.8	+15.8
(7)	+7.15	+14.3
(7')	+3.575	+14.3
(8)	−4.325	−17.3
(9)	−4.325	−17.3
(10)	+4.325	+17.3
(11)	+4.325	+17.3
(12)	+1.0	0
(13)	+13.3	+13.3

^{a} Standard enthalpy of reaction recalculated for evolution or absorption of 1 mol H_2O.

In view of the above considerations, stages (a) and (b) were treated as one reaction without degradation in the thermochemical calculations (Table 1)
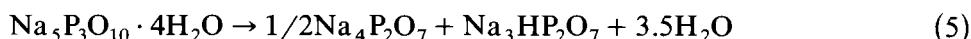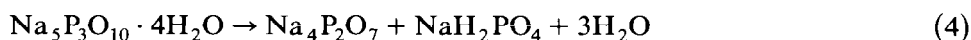
$$Na_5P_3O_{10} \cdot 6H_2O \rightarrow Na_5P_3O_{10} \cdot 4H_2O + 2H_2O\uparrow \qquad (3)$$
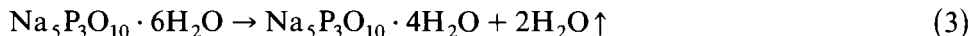
This reaction is reversible under the conditions mentioned above.

Stage (c)

The removal of the main part of water (Δm between 2 and 5.0–5.5 mol H_2O) proceeds with deep anion degradation in the vicinity of the DSC curve maximum (Fig. 1) and in the region of major sections of the TG curves (Fig. 2). The TLC data indicate that the mass content of phophorus in the form of triphosphate (P_3) decreases to 0–10% P_3, and in the form of mono-(P_1) and diphosphate (P_2) increases to 20–30% P_1 and 60–70% P_2 respectively. The diphosphate: monophosphate molar ratio varies between 1:1 and 2:1. The reaction can proceed both in a diffusion and kinetic regime.

The main processes at this stage can be generalized into two schemes

$$Na_5P_3O_{10} \cdot 4H_2O \rightarrow Na_4P_2O_7 + NaH_2PO_4 + 3H_2O \qquad (4)$$

$$Na_5P_3O_{10} \cdot 4H_2O \rightarrow 1/2Na_4P_2O_7 + Na_3HP_2O_7 + 3.5H_2O \qquad (5)$$
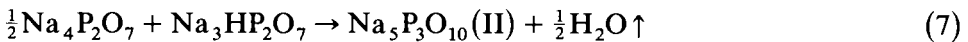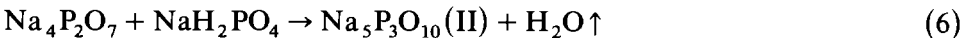
of which the second explains the excess of diphosphate in the dehydration products (monophosphate appears as a result of diphosphate disintegration into two monophosphate fragments). According to reaction (4), stage (c) should be complete at $\Delta m = 5.0$ mol H_2O, and according to reaction (5), at $\Delta m = 5.5$ mol H_2O. Figure 2 shows two isothermal TG curves which become

almost horizontal in the final section near $\Delta m = 5.0$ mol H_2O (396 K) and $\Delta m = 5.5$ mol H_2O (413 K). But such a coincidence does not prove the validity of either reaction (4) or reaction (5) because, firstly, due to the slowness of the diffusion processes, the curve in the final section is not exactly horizontal, and secondly, the position of the final section of the curve is not strictly fixed in relation to the Δm scale; it corresponds to different Δm values depending on the chosen T values. Reactions (4) and (5) can proceed simultaneously together with other reactions, such as those leading to the formation of crystalline dihydrogendiphosphate, $Na_2H_2P_2O_7$, which was found in the reaction mixture.

Stage (d)

This stage represents the removal of residual water (Δm between 5.0–5.5 and 6 mol H_2O) corresponding to the extended final sections of the DSC curve (Fig. 1) and the non-isothermal TG curve (Fig. 2) as well as the final sections of the isothermal TG curves at $T \geqslant 396$ K. This process takes place in a diffusion regime, and the diphosphate: monophosphate molar ratio, similar to that in stage (b), reaches values of up to $4:1$ and $5:1$. At this stage recondensation of earlier formed products takes place

$$Na_4P_2O_7 + NaH_2PO_4 \rightarrow Na_5P_3O_{10}(II) + H_2O\uparrow \qquad (6)$$

$$\tfrac{1}{2}Na_4P_2O_7 + Na_3HP_2O_7 \rightarrow Na_5P_3O_{10}(II) + \tfrac{1}{2}H_2O\uparrow \qquad (7)$$

The final product is contaminated with unreacted residual $Na_4P_2O_7$ and by
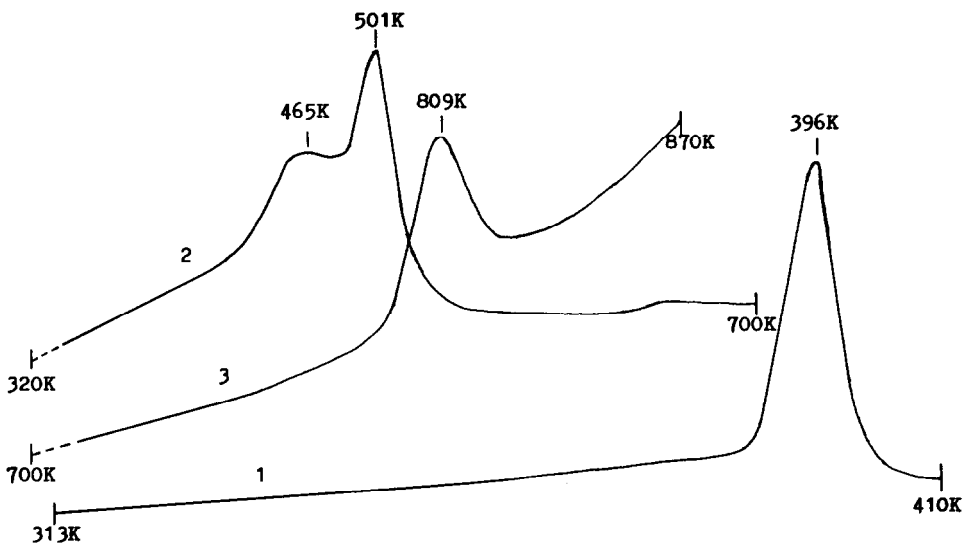
Fig. 3. DSC curves for $Na_5P_3O_{10}\cdot 6H_2O$ and its dehydration products: 1, $Na_5P_3O_{10}\cdot 6H_2O$, HR $= 0.62$ K min^{-1}, $m = 16.47$ mg; 2, product with $\Delta m = 5.218$ mol H_2O, HR $= 20$ K min^{-1}, $m = 13.22$ mg; 3, product with $\Delta m = 6$ mol H_2O, HR $= 20$ K min^{-1}, $m = 12.73$ mg.
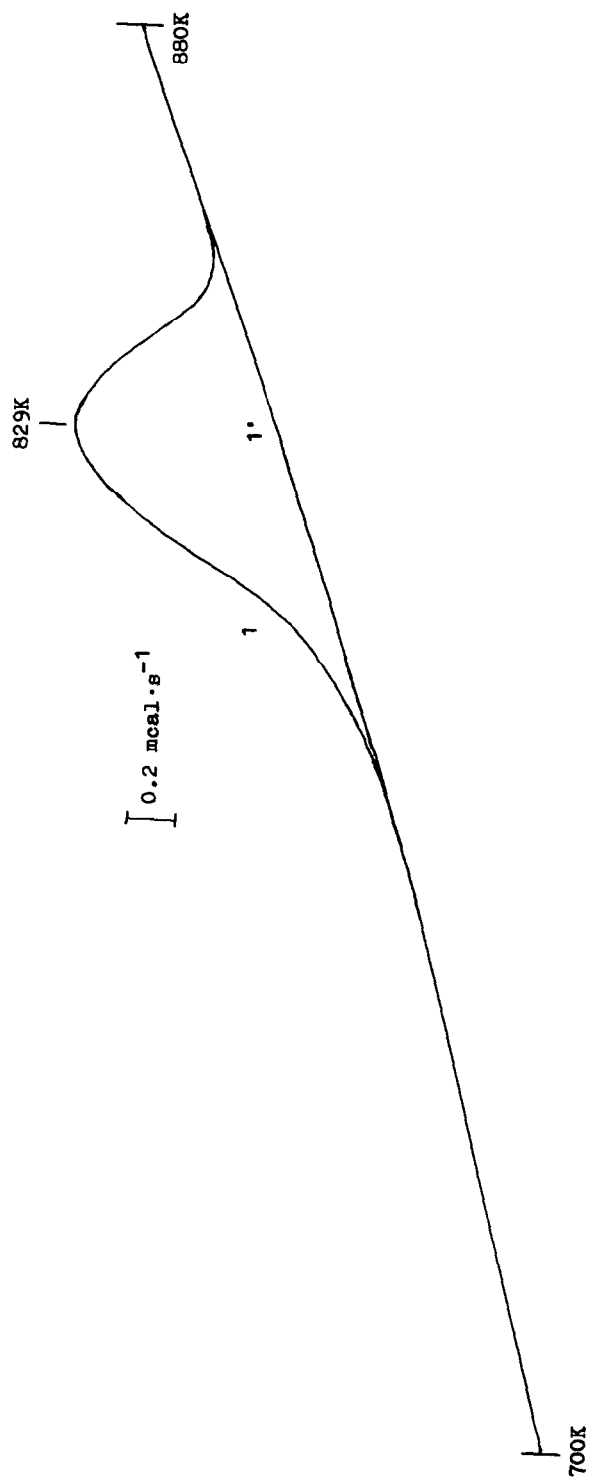
Fig. 4. DSC curve for $Na_5P_3O_{10}(II)$: 1, $HR = 20$ K min^{-1}, $m = 16.30$ mg; 1′, baseline.

admixtures of $Na_3P_3O_9$ (formed from $Na_2H_2P_2O_7$), $Na_5P_3O_{10}(I)$ and other phosphates. In these experiments $Na_5P_3O_{10}(I)$ was not found, at least not at $T < 520$ K.

Stage (d) is further subdivided, depending on the HR and on other factors, into several substages which cannot be simply ascribed to the separate reactions (6) and (7). Figure 3 illustrates this: a $Na_5P_3O_{10} \cdot 6H_2O$ sample was heated to 410 K at an HR of 0.62 K min^{-1} (curve 1), cooled to 320 K at a cooling rate (CR) of 160 K min^{-1} and then weighed; the mass of lost water was determined ($\Delta m = 5.218$ mol H_2O) and the sample was heated again to 700 K at an HR of 20 K min^{-1} (curve 2); then, after a short pause, heating continued to 870 K at an HR of 20 K min^{-1} (Curve 3). The maximum at 809 K on curve 3 has shifted compared with the earlier value of 829 K determined for the transition of $Na_5P_3O_{10}(II)$ to $Na_5P_3O_{10}(I)$ [15]. A shift is usually observed when insufficiently pure samples of $Na_5P_3O_{10}(II)$ are used. An experiment with a TLC-pure $Na_5P_3O_{10}(II)$ sample shows (Fig. 4) that the maximum at 829 K of the transition $Na_5P_3O_{10}(II) \rightarrow Na_5P_3O_{10}(I)$ is easily reproduced, and that the experimental $\Delta H_t^{\ominus}$ value of the transition ($\Delta H_t^{\ominus} = 2.3$ kcal mol^{-1}) is not essentially different from the value $\Delta H_{t298}^{\ominus} = 2.6$ kcal mol^{-1} calculated as the difference between the $\Delta H_{f298}^{\ominus}$ for $Na_5P_3O_{10}(II)$ formation and the $\Delta H_{f298}^{\ominus} = -1056.5 \pm 1.5$ kcal mol^{-1} for $Na_5P_3O_{10}(I)$ formation.

THERMOCHEMISTRY OF THE PROCESSES

It should be noted that the enthalpy of the transition of $Na_5P_3O_{10}(II)$ to $Na_5P_3O_{10}(I)$, in contrast to the DSC maximum temperature of the transition, is only slightly sensitive to the purity of the $Na_5P_3O_{10}(II)$. The enthalpy of the transition estimated on the basis of curve 3 (Fig. 3) is $\Delta H_t^{\ominus} = 2.2$ kcal mol^{-1}. The other values obtained fall within the range 2.3–2.6 kcal mol^{-1} (Table 2) i.e. they cover the entire interval between the calculated and the experimental values for pure $Na_5P_3O_{10}(II)$, although in some cases a splitting of the DSC maximum is observed (the temperature of the second maximum is given in brackets in Table 2). The average value of the experimental data for the transition is $\Delta H_t^{\ominus} = 2.4 \pm 0.2$ kcal mol^{-1}.

The experimental values given in Table 2 were obtained using the same heating and cooling rates as were used to obtain the data shown in Fig. 3. The only difference is that at stages (a)–(c), the HR was varied between 0.31 and 10 K min^{-1}. Moreover, at HR = 1.25 K min^{-1}, one of the experiments (marked with a and b in Table 2) was interrupted not after $\Delta m = 5$ mol H_2O but after $\Delta m = 1.303$ mol H_2O. At stage (d), overall $\Delta H_r^{\ominus}$ experimental values were determined irrespective of the number of substages.

When choosing the general scheme for the calculation of $\Delta H_{r298}^{\ominus}$, we took into account its regular changes in the homologous series of chain and cyclic

TABLE 2

Thermal effects of the processes developing on heating $Na_5P_3O_{10}\cdot 6H_2O$

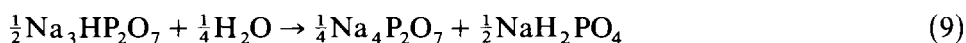| HR (K min⁻¹)	Stages (a), (b), (c)			Stage (d), HR = 20 (K min⁻¹)				$\Delta H_r^{\ominus}$ for $\Delta m = 6$, experimental (kcal mol⁻¹)	Transition $Na_5P_3O_{10}$(I) → $Na_5P_3O_{10}$(II), HR = 20 (K min⁻¹)	
	$\Delta m_{(a-c)}$ (mol H₂O)	$\Delta H^{\ominus}$ (kcal mol⁻¹)		$6 - \Delta m_{(a-c)}$ (mol H₂O)	$\Delta H_r^{\ominus}$ (kcal mol⁻¹)				$\Delta H_t^{\ominus}$, experimental (kcal mol⁻¹)	T for DSC maximum (K)
		Experimental	Calculated, 298 K		Experimental		Calculated, 298 K			
					For $6 - \Delta m_{(a-c)}$	For 1 mol H₂O				
0.31	5.230	–	68.6	0.770	12.7	–	10.6	–	2.6	811
0.62	5.218	65.2	68.4	0.782	11.5	14.7	10.8	76.7	2.2	809
1.25	5.377	69.6	70.5	0.623	8.8	14.1	8.7	78.4	2.5	803 (835)
1.25	1.303 [a]	13.4 [a]	17.3 [a]	4.697 [b]	67.2 [b]	14.3 [b]	61.9 [b]	80.6	2.5	804 (835)
10.0	5.097	66.5	66.8	0.903	13.5	14.9	12.4	80.8	2.3	812

[a] Data refer to stage (a).
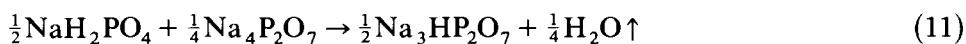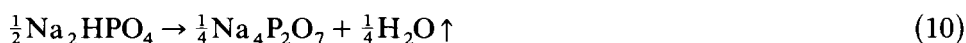[b] Data refer to stages (b), (c) and (d).

phosphates, as mentioned earlier [16], as well as the zonary (gradient) mechanism of the development of topochemical processes in crystals [17], which is applicable to the diffusion of water molecules from the bulk of the crystal to its surface. At stage (c), preference is given to reaction (5) which explains the accumulation of excessive diphosphate in the reaction mixture. A proportion of the water molecules, diffusing through the diphosphates layer formed according to (5), take part in the degradation of the latter i.e. along with reaction (5) other reactions take place

$$\tfrac{1}{4}Na_4P_2O_7 + \tfrac{1}{4}H_2O \rightarrow \tfrac{1}{2}Na_2HPO_4 \tag{8}$$

and/or

$$\tfrac{1}{2}Na_3HP_2O_7 + \tfrac{1}{4}H_2O \rightarrow \tfrac{1}{4}Na_4P_2O_7 + \tfrac{1}{2}NaH_2PO_4 \tag{9}$$

The absorbed water is then released

$$\tfrac{1}{2}Na_2HPO_4 \rightarrow \tfrac{1}{4}Na_4P_2O_7 + \tfrac{1}{4}H_2O\uparrow \tag{10}$$

$$\tfrac{1}{2}NaH_2PO_4 + \tfrac{1}{4}Na_4P_2O_7 \rightarrow \tfrac{1}{2}Na_3HP_2O_7 + \tfrac{1}{4}H_2O\uparrow \tag{11}$$

The cycle of water absorption and evolution can be repeated indefinitely.
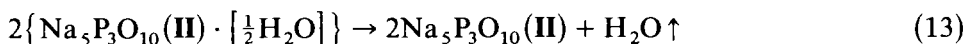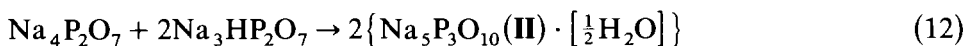
In the case of a single cycle, the products formed according to reactions (10) and (11) at stage (d) interact

$$\tfrac{1}{4}Na_4P_2O_7 + \tfrac{1}{2}Na_3HP_2O_7 \rightarrow \tfrac{1}{2}Na_5P_3O_{10}(II) + \tfrac{1}{4}H_2O\uparrow \tag{7'}$$
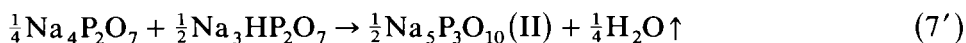
The rest of the products remaining after reaction (5) interact according to the same scheme (7').

According to reactions (8)–(11), no more than 0.5 mol H_2O takes part in one cycle. It may be that the water escaped via the diffusion mechanism both at stage (c) and stage (d). It is logical to assume that during the second, third and subsequent cycles, the percentage of water taking part in each cycle is the same: during the first cycle, 0.5 out of 6 mol H_2O (8.3(3)%) takes part; during the second, 0.0416(6) mol H_2O out of the remaining 0.5 mol H_2O; during the third, 0.003472(2) mol H_2O, etc. In other words, with an increased number of cycles, the quantity of water taking part in each cycle decreases in geometrical progression.

At the same time, the amount of heat necessary to remove 1 mol H_2O increases from cycle to cycle. This can be illustrated using hypothetical processes as an example

$$Na_4P_2O_7 + 2Na_3HP_2O_7 \rightarrow 2\{Na_5P_3O_{10}(II) \cdot [\tfrac{1}{2}H_2O]\} \tag{12}$$

$$2\{Na_5P_3O_{10}(II) \cdot [\tfrac{1}{2}H_2O]\} \rightarrow 2Na_5P_3O_{10}(II) + H_2O\uparrow \tag{13}$$

according to which the water released is not immediately evolved into the gas phase, but remains somehow bound for a time to $Na_5P_3O_{10}(II)$, for instance in the form of the hypothetical $Na_5P_3O_{10}(II) \cdot [\tfrac{1}{2} H_2O]$ complex. Later the complex disintegrates and the water enters the gas phase according to reaction (13).

The term $(\Delta H^{\ominus}_{r298})^{\star}$ is now introduced to represent the standard enthalpy of reaction recalculated for evolution or absorption of 1 mol H_2O. For reaction (12), $(\Delta H^{\ominus}_{r298})^{\star}$ is 0, because it is not connected with the removal of water (see Table 1). Consequently, between $(\Delta H^{\ominus}_{r298})^{\star} = 14.3$ kcal mol^{-1} for reactions (7) or (7'), on the one hand, and $(\Delta H^{\ominus}_{r298})^{\star} = 13.3$ kcal mol^{-1} for reactions (12) and (13), on the other, there is a difference of 1.0 kcal mol^{-1}. If every cycle includes (12)- and (13)-type reactions, the enthalpy of removing 1 mol H_2O increases with each cycle by 1.0 kcal mol^{-1} i.e. $(\Delta H^{\ominus}_{r298})^{\star}$ increases in an arithmetic progression. While calculating the values given in Tables 1 and 2, we used, apart from the data in the literature mentioned, the standard enthalpies of formation of $Na_4P_2O_7$ ($\Delta H^{\ominus}_{f298} = -763.7 \pm 1.0$ kcal mol^{-1}) [6], of $Na_3HP_2O_7$ ($\Delta H^{\ominus}_{f298} = -713.3$ kcal mol^{-1}, calculated by a comparative method using literature data [6]), of NaH_2PO_4 ($\Delta H^{\ominus}_{f298} = -368.96 \pm 0.5$ kcal mol^{-1}) [18] and of Na_2HPO_4 ($\Delta H^{\ominus}_{f298} = -419.42 \pm 0.5$ kcal mol^{-1}) [18].

When the process proceeds without cycles, $\Delta H^{\ominus}_{r298}$ can be calculated according to the formula

$$\Delta H^{\ominus}_{r298} = 2\left(\Delta H^{\ominus}_{r298}\right)^{\star}_{(3)} + 3.5\left(\Delta H^{\ominus}_{r298}\right)^{\star}_{(5)} + 0.5\left(\Delta H^{\ominus}_{r298}\right)^{\star}_{(7)} \tag{14}$$

In the case of a single cycle process, $\Delta H^{\ominus}_{r298}$ is calculated either according to the formula

$$\Delta H^{\ominus}_{r298} = 2\left(\Delta H^{\ominus}_{r298}\right)^{\star}_{(3)} + 3.5\left(\Delta H^{\ominus}_{r298}\right)^{\star}_{(5)} + 0.25\left(\Delta H^{\ominus}_{r298}\right)^{\star}_{(7)} - 0.25\left(\Delta H^{\ominus}_{r298}\right)^{\star}_{(8,9)}$$
$$+ 0.25\left(\Delta H^{\ominus}_{r298}\right)^{\star}_{(10,11)} + 0.25\left(\Delta H^{\ominus}_{r298}\right)^{\star}_{(7')} \tag{15}$$

if the water taking part in the cycle was evolved at stage (c), or according to the formula

$$\Delta H^{\ominus}_{r298} = 2\left(\Delta H^{\ominus}_{r298}\right)^{\star}_{(3)} + 3.5\left(\Delta H^{\ominus}_{r298}\right)^{\star}_{(5)} + 0.5\left(\Delta H^{\ominus}_{r298}\right)^{\star}_{(12,13)} \tag{16}$$

if the water taking part in the cycle was evolved at stage (d).

The general formula for the multicycle process is

$$\Delta H^{\ominus}_{r298} = \Delta m_{(a,b)}\left(\Delta H^{\ominus}_{r298}\right)^{\star}_{(3)} + \Delta m_{(c)}\left(\Delta H^{\ominus}_{r298}\right)^{\star}_{(5-9)}$$
$$+ (m - m')\left(\Delta H^{\ominus}_{r298}\right)^{\star}_{(7-13)} \sum_{i=1}^{\infty} x^i$$
$$+ (m - m')\left(\Delta H^{\ominus}_{r298}\right)^{\star}_{i \geqslant 3} \sum_{i=3}^{\infty} x^{(i-1)}(i-2) \tag{17}$$

where m is the number of moles of H_2O in the crystal hydrate (in our case, $m = 6$), m' is the number of moles of H_2O remaining in the substance after stage (c), $\Delta m_{(a,b)}$ and $\Delta m_{(c)}$ are the numbers of moles of H_2O evolved at stages (a,b) and (c), respectively, i is the number of cycles, x is the percentage of moles of H_2O taking part in the cycle e.g. $x = m'/m$ or $x = m'/(m - m')$ ($x = 8.3(3)\%$ or $x = 9.09(09)\%$, respectively); and

$(\Delta H_{r298}^{\ominus})_{i \geqslant 3}^{\star}$ is the enthalpy increment calculated for the evolution or absorption of 1 mol H_2O in each cycle beginning with the third one (for $i = 3$ $(\Delta H_{r298}^{\ominus})^{\star} = 1.1$ kcal mol^{-1}).

Calculation according to eqn. (17) with $x = m'/m$ and $m' = 0.5$ produces the value $\Delta H_{r298}^{\ominus} = 79.3$ kcal mol^{-1}, which is not essentially different from the values calculated using eqns. (14), (15) and (16) ($\Delta H_{r298}^{\ominus} = 79.8$ kcal mol^{-1}), nor from that determined experimentally ($\Delta H_{r298}^{\ominus} = 79.6$ kcal mol^{-1}). The values of $\Delta H_{r298}^{\ominus}$ given in Table 1 were calculated using eqn. (17). The experimental values $\Delta H_r^{\ominus}$ and $\Delta H_t^{\ominus}$ are presented without any correction for the temperature dependence of the reaction/transition enthalpy.

Equation (17) is useful from a number of different points of view. It reflects the real development of the process when the overall reaction of removing water from the crystal hydrate consists of a number of parallel and consecutive stages. These stages can be reversible and irreversible, can proceed in a kinetic or in a diffusion regime, with or without degradation of the anion, and with or without anion condensation. The formula takes into account the possibility of absorption of part of the water and the repetition of absorption evolution cycles, which explains the case of stepped removal of residual water. This is reflected in the shape of the isothermal kinetic curve Δm versus τ which becomes horizontal in its final section: with the increase of T, the horizontal section gradually shifts to higher values of Δm, approaching the theoretical limit.

Such a phenomenon is characteristic not only of the reaction studied and not only for crystal hydrate decomposition; it is well-known in inorganic topochemistry [17]. Thus, it seems reasonable to believe that the formula in eqn. (17) may be used in thermochemical investigations of various topochemical reactions involving evolution/absorption of a gas when there are difficulties concerning the chemical transformations of residual quantities of substances. Assumption of a diffusion mechanism is not obligatory because the cyclic character and the zonal mechanism may also be caused by other reasons.

CONCLUSIONS

Using DSC, iso- and non-isothermal TG and quantitative TLC methods, a thermochemical investigation was carried out into the processes occurring during heating of $Na_5P_3O_{10} \cdot 6H_2O$ (crystal size, $D = 0.02$–0.2 mm), $Na_5P_3O_{10}(II)$ ($D = 0.005$–0.02 mm) and $Na_3P_3O_9 \cdot 6H_2O$ ($D = 0.01$–0.3 mm) in a flow of dry nitrogen at 293–880 K. For the transition of $Na_5P_3O_{10}(II)$ to $Na_5P_3O_{10}(I)$, the experimental enthalpy $\Delta H_t^{\ominus}$ was estimated to be 2.4 ± 0.2 kcal mol^{-1} which is close to the calculated value of 2.6 kcal mol^{-1} and does not essentially depend on the purity of the $Na_5P_3O_{10}(II)$. The temperature of the DSC curve maximum of the transition, in contrast to the

$\Delta H_t^{\ominus}$ value, varies, depending on the $Na_5P_3O_{10}(\textbf{II})$ purity, between 803 and 835 K (in some cases a splitting of the maximum is observed).

The non-degradative dehydration of $Na_3P_3O_9 \cdot 6H_2O$ which proceeds in one stage with rapid crystallization of $Na_3P_3O_9$, is characterized by $\Delta H_r^{\ominus} = 76.5$ kcal mol^{-1} (experimental) and $\Delta H_{r298}^{\ominus} = 77.4$ kcal mol^{-1} (calculated).

The dehydration of $Na_5P_3O_{10} \cdot 6H_2O$ as distinct from that of $Na_3P_3O_9 \cdot 6H_2O$, consists of a series of parallel and consecutive stages: reversible and irreversible, diffusion limited and non-limited, with and without anion degradation, and with and without anion condensation.

For calculating $\Delta H_{r298}^{\ominus}$ for the $Na_5P_3O_{10} \cdot 6H_2O$ dehydration, a general formula (eqn. 17)) of a universal nature is suggested. As well as the multistage nature of the dehydration, the formula takes into account the possibility of a repeated absorption of a proportion of the water and repetition of the absorption evolution cycles. Calculations using this formula have produced the value $\Delta H_{r298}^{\ominus} = 79.3$ kcal mol^{-1} which does not essentially differ from $\Delta H_{r298}^{\ominus} = 79.8$ kcal mol^{-1}, the value calculated for direct transformation of $Na_5P_3O_{10} \cdot 6H_2O$ into $Na_5P_3O_{10}(\textbf{II})$, or from $\Delta H_{r298}^{\ominus} = 79.6$ kcal mol^{-1}, which is the estimated experimental value. The multicycle character of $Na_5P_3O_{10} \cdot 6H_2O$ dehydration is explained on the basis of a zonary (gradient) mechanism of reaction spreading through the crystals.

An opinion is advanced concerning the possibility of using the general formula (eqn. (17)) for thermochemical investigations of other topochemical processes with gas evolution/absorption which are characterized by a multistage and multicycle nature and by a difficulty of the chemical transformations of residual quantities of the substances.

REFERENCES

1 A.C. Zettlemoyer, C.H. Schneider, H.V. Anderson and R.J. Fuchs, J. Phys. Chem., 61 (1957) 991.
2 W.O. Groves and J.W. Edwards, J. Phys. Chem., 65 (1961) 645.
3 E. Thilo and M. Wallis, Chem. Ber., 86 (1953) 1213.
4 V.M. Galogaza, E.A. Prodan, S.I. Pytlev and I. Ristić, Thermochim. Acta, 97 (1986) 23.
5 R.K. Osterheld, in E.J. Griffith and M. Grayson (Eds.), Topics in Phosphorus Chemistry, Vol. 7, Interscience, New York, London, 1972, p. 103.
6 R.J. Irving and H. McKerrell, Trans. Faraday Soc., 64 (1968) 875, 879.
7 R.J.L. Andon, J.F. Counsell, J.F. Martin and C.J. Mash, J. Appl. Chem., 17 (1967) 65.
8 S.J. Ashcroft, E. Keen and C.T. Mortimer, Trans. Faraday Soc., 65 (1969) 2851.
9 O.T.Quimby, J. Phys. Chem., 58 (1954) 603.
10 H.M. Ondik and J.W. Gryder, J. Inorg. Nucl. Chem., 14 (1960) 240.
11 E. Thilo, Ueber den Mechanismus der Kristallwasserabgabe aus kondensierten Phosphaten, Akademie-Verlag, Berlin, 1952, p. 16.
12 J.R. Van Wazer, Phosphorus and Its Compounds, Vol. 1, Interscience, New York, 1958, p. 968.

13 D.E.C. Corbridge, Phosphorus: An Outline of Its Chemistry, Biochemistry and Technology, 3rd edn., Elsevier, Amsterdam London, 1985, p. 762.
14 E.A. Prodan, L.I. Prodan and N.F. Ermolenko, Tripolyfosfaty i Ikh Primenenie (Tripolyphosphates and Their Use), Nauka i Tekhnika, Minsk, 1969, p. 533 (in Russian).
15 V.M. Galogaza, E.A. Prodan, V.A. Sotnikova-Yuzhik, D.U. Scala, N.V. Bulavkina and S.I. Pytlev, Thermochim. Acta, 106 (1986) 141.
16 S.G. Tereshkova, Zh. Fiz. Khim., 54 (1980) 1018 (in Russian).
17 E.A. Prodan, Neorganicheskaya Topokhimiya (Inorganic Topochemistry), Nauka i Tekhnika, Minsk, 1986, p. 240 (in Russian).
18 R.J. Irving and H. McKerrell, Trans. Faraday Soc., 63 (1967) 2913.