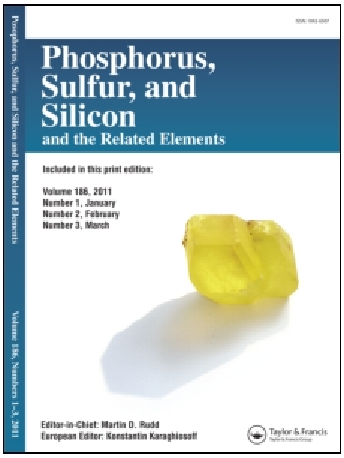

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INFLUENCE OF WATER VAPOR ON $P_3O_9^{3-}$ RING OPENING DURING THE THERMAL DEHYDRATION OF $NaCaP_3O_9,3H_2O$

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The study of the heterogeneous system $NaCaP_3O_9,3H_2O–H_2O_{(g)}$ allowed the internal hydrolysis of $P_3O_9^{3-}$ rings to be shown, which explains its instability. In the absence of water vapor pressure, $NaCaP_3O_9,3H_2O$ loses its $3H_2O$'s reversibly.

INTRODUCTION

The extent of hydration of sodium calcium trimetaphosphate ranges from $2H_2O$ to $3H_2O$, depending on authors.[1–4] A. Durif noticing that it depended on the ambient water vapor pressure, concluded that some zeolitic water was present in this compound.[5] W. Feldmann[3] noticed, first a partial cutting of $P_3O_9^{3-}$ rings yielding monophosphate, diphosphate and an anhydrous trimetaphosphate, around 150°C, then the presence of the anhydrous trimetaphosphate alone, between 250°C and 300°C and finally polyphosphate formation about 500°C. We resumed the thermal dehydration of $NaCaP_3O_9,3H_2O$ to show the extent to which this compound contains mobile water and to clarify the transformation process of hydrated trimetaphosphate to anhydrous trimetaphosphate.

EXPERIMENTAL

Thermogravimetry (MacBain-type thermobalance), differential thermal analysis coupled with thermogravimetry and x-ray diffractometry in a heating cell were used. These methods specially adapted to fix a given water vapor pressure on the sample are well known.[6–8] Thin-layer cellulose chromatography allowed the extent of condensation of the various phosphates formed to be identified.[9]

ADSORPTION CAPACITY

Water adsorption-desorption isotherms, at 25°C, were plotted for several plugs of sodium calcium trimetaphosphate prepared by alcohol precipitation of an aqueous solution of $Na_3P_3O_9$ and $CaCl_2$ (Figure 1). Depending on the plugs obtained, this trimetaphosphate

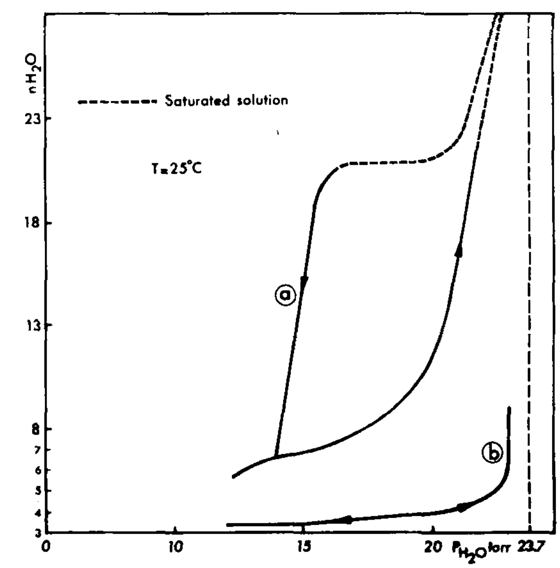


FIGURE 1 Sorption isotherms of two $NaCaP_3O_9,3H_2O$ characteristic plugs.

appeared to absorb variable amounts of water, far larger than $3H_2O$. SEM (stereoscan-type) analysis showed that the highly-adsorbant samples were made of hollow needles, 1 μ wide (internal diameter) whereas the others were made of needles closed at both tips (Figures 2 and 3). The high adsorption capacity noticed for certain plugs is, thus, certainly due to the presence of these macrochannels within which a capillary condensation occurs. We also noticed that a fresh material prepared by alcohol precipitation and composed of needles closed at both ends contains $2H_2O$ and has a hydration extent fluctuating around $3H_2O$, depending on the hygrometric degree of the

FIGURE 2 $NaCaP_3O_9,3H_2O$ morphology of high-adsorption capacity: curve a, Figure 1.

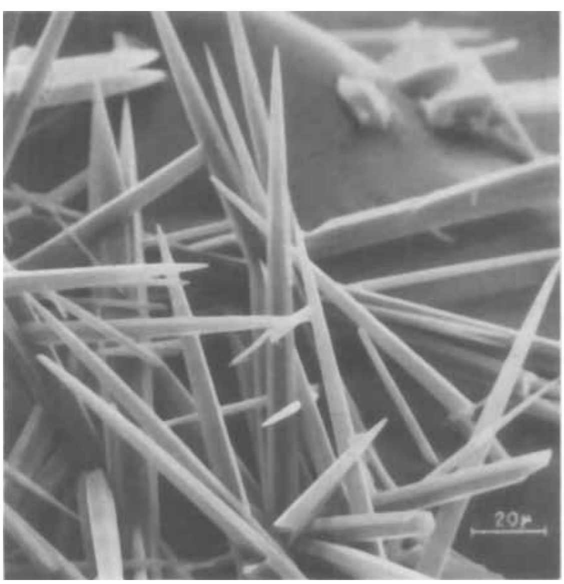


FIGURE 3 $NaCaP_3O_9,3H_2O$ morphology of low-adsorption capacity: curve b, Figure 1.

ambient atmosphere, only when it is left in ambient air, after 48 hours. The molecule belonging to range $3H_2O$-$2H_2O$ is probably loosely-bonded to the lattice. Thus, depending on the solid morphology and room water pressure, the hydration rate varies considerably from one plug to another.†

† It has not been possible, as yet, to determine the factor allowing numerous, hollow needles to be obtained reproducibly.

STABILITY IN AMBIENT PRESSURE AND TEMPERATURE CONDITIONS

A few months following preparation (6 months maximum), the trimetaphosphate, in room conditions, is converted into NaH_2PO_4, H_2O and $CaH_2P_2O_7$. Two facts tend to prove that the amount of both compounds formed is stoichiometric and satisfies:

$$NaCaP_3O_9,3H_2O \rightarrow NaH_2PO_4,H_2O + CaH_2P_2O_7$$

Moreover, at 600°C, an ignition loss of the mixture obtained through conversion of the trimetaphosphate shows the loss of $3H_2O$ and the formation of polyphosphate according to:

$$NaH_2PO_4,H_2O + CaH_2P_2O_7 \rightarrow NaCa(PO_3)_3 + 3H_2O$$

Furthermore, a mole to mole mixture of NaH_2PO_4 (anhydrous or hydrated form) and $CaH_2P_2O_7$ raised to 600°C gives a similar result (Table I). The transformation of the trimetaphosphate being relatively slow, the study of its dehydration could be anticipated taking care to change the plugs frequently and checking their purity (TLC, XR).

DEHYDRATION AND REHYDRATION OF $NaCaP_3O_9$, $3H_2O$ UNDER FIXED WATER VAPOR PRESSURE

The hydration degree of the plugs used was close to $3H_2O$ in room conditions and they were composed

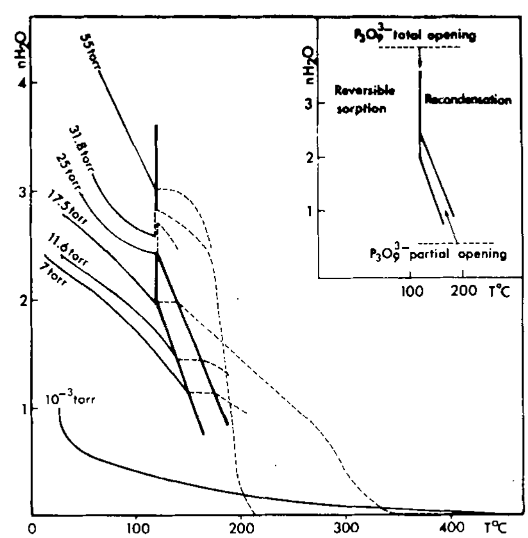
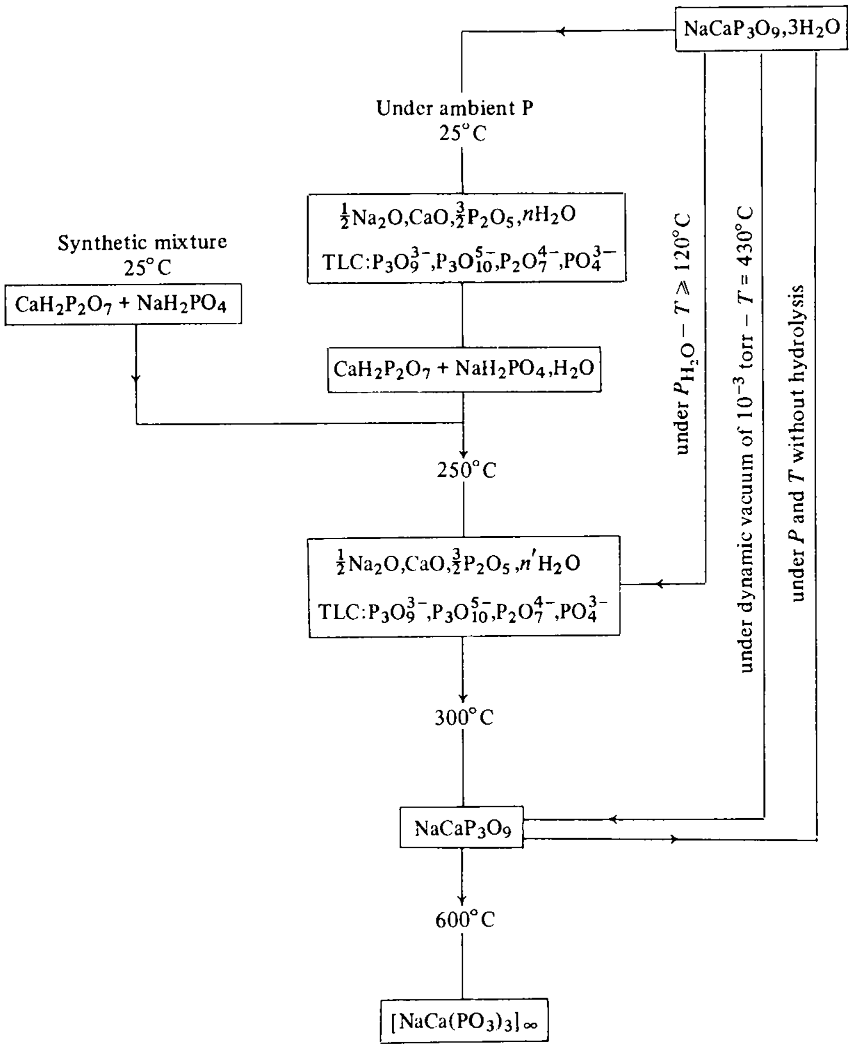


FIGURE 4 $NaCaP_3O_9,3H_2O$ dehydration under fixed P_{H_2O} and by successive temperature steps.

TABLE I



of thin needles closed at both tips. The range investigated was between $3H_2O$ and the anhydrous material. The thermal dehydration, under fixed water vapor pressure, by successive temperature steps, shows three stages defining three domains (Figure 4).

1 A Domain of Reversible Sorption of the H_2O Molecules

An amount of H_2O's, whose variation depends on the water pressure fixed, leaves the lattice reversibly. At the lower boundary pressure, (dynamic vacuum of about 10^{-3} torr), the trimetaphosphate may be entirely dehydrated without a $P_3O_9^{3-}$ ring splitting by raising the temperature progressively from 25°C to 430°C. The $NaCaP_3O_9$, then obtained at 430°C, placed in water vapor pressure and temperature conditions such that the ring does not hydrolyse (next paragraph) rehydrates slowly and yields the initial compound, $NaCaP_3O_9$, $3H_2O$. In these conditions the reversible sorption range overlaps entirely the $3H_2O$ anhydrous material hydration range. At the higher boundary pressure ($P = 55$ torr), the $3H_2O$ trimetaphosphate hydrolyses entirely at 120°C. In these conditions, therefore, there is no stability domain. In between, part of the H_2O's only dehydrates reversibly and the XR diffractograms of $NaCaP_3O_9$, $3H_2O$, remain unchanged while they are removed. The H_2O's, thus, are loosely-bonded to the lattice. In this domain, $NaCaP_3O_9, xH_2O\text{-}H_2O_g$ is

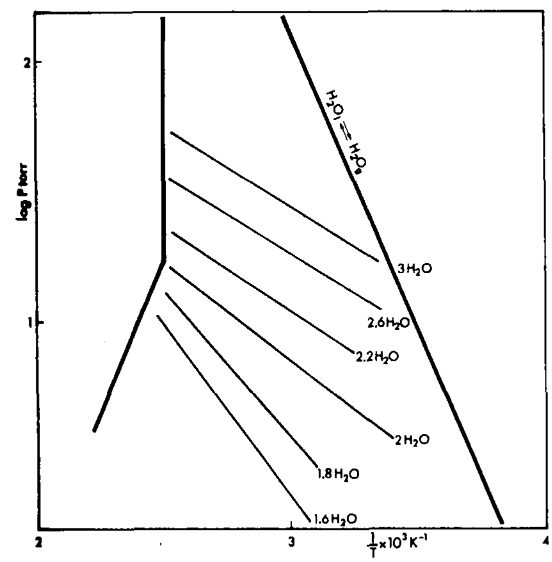


FIGURE 5 Linear transformed isosters.

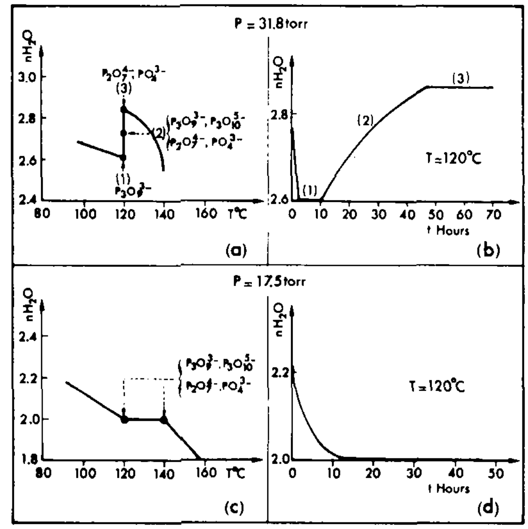


FIGURE 6 $P_3O_9^{3-}$ ring opening process.

divariant. The extent of hydration, then, is water vapor pressure and temperature dependent; this accounts for the fact that hydration degrees lower than $3H_2O$ are reported in the literature. An isobar network was experimentally plotted (Figure 4) and the linear transformed curves $\log P = f(1/T)_{nH_2O}$ were deduced from them (Figure 5). The enthalpy and entropy normal isosteric values calculated from these curves (Table II) are abnormally low as they are less than those of water vaporization†. A contrary and reversible effect, thus, coincides with dehydration.

2 *A $P_3O_9^{3-}$ Ring Opening Domain*

The investigation of the reversible sorption domain of the trimetaphosphate showed that, under water vapor pressure, there is a temperature boundary beyond which a $P_3O_9^{3-}$ ring opening occurs. Under a high water vapor pressure ($P > 22$ torr), the rings open entirely, the final material being a mixture of mono and diphosphate anions yielding no XR diffractograms. This decondensation occurs around 120°C and is accompanied by a water gain. This rehydration requiring some time, it is then possible to follow the ring opening progress through thin-layer chromatography (Figure 6a and b). Thus, the intermediate formation of a tripolyphosphate anion $P_3O_{10}^{5-}$ showing a mechanism similar to that noticed, several times, in an aqueous medium could be observed:

$$P_3O_9^{3-} \xrightarrow{H_2O} P_3O_{10}^{5-} \xrightarrow{H_2O} PO_4^{3-} + P_2O_7^{4-}$$

However, under lower pressures ($P < 22$ torr) the ring opening is only partial, the final material obtained being a poorly-crystallized mixture of $P_3O_9^{3-}$, $P_3O_{10}^{5-}$, $P_2O_7^{4-}$, PO_4^{3-} anions. The XR spectrum shows a few bands attributable to the anhydrous form $NaCaP_3O_9$, and as we can shift from the hydrated form to the anhydrous one, the partial opening may be expressed as follows:

$$P_3O_9^{3-} \begin{cases} \nearrow P_3O_9^{3-} \\ \searrow P_3O_{10}^{5-},\ P_2O_7^{4-},\ PO_4^{3-} \end{cases}$$

This ring opening resulting from an actual hydrolysis, starts under conditions such that the higher the water vapor pressure the higher the hydration extent and the lower the temperature. The thermograms, $nH_2O = f(T)_p$ show a slowing down of dehydration resulting in a weight step over a temperature range of about 20°C (Figure 6c and d). Water vapor, thus, plays a

† The H_2O molecule of a hydrated solid has freedom degrees lower than those of the water molecule. Its enthalpy and entropy, thus, are lower than those of the water molecule.

$$H_{H_2O(g)} - H_{H_2O(c)} > H_{H_2O(g)} - H_{H_2O(l)}$$

i.e.

$$\Delta H_{\text{observed for hydrate}} > \Delta H_{\text{water vaporization}}$$

A similar reasoning may be done for the entropy.

prevailing part in the $P_3O_9^{3-}$ ring opening and it is to be noticed that under a dynamic vacuum of 10^{-3} torr, $NaCaP_3O_9,3H_2O$ dehydrates reversibly without any decondensation.

3 A Recondensation Domain, as $P_3O_9^{3-}$ Rings

The dehydration, by heating, of the hydrated, poorly-crystallized mixture formed during the more or less partial opening of the $P_3O_9^{3-}$ rings, leads to a total recondensation, as $P_3O_9^{3-}$ rings. When the anhydrous state is attained, only the crystallized phase, $NaCaP_3O_9$ remains. This re-ringing occurs in such a way that the higher the water vapor pressure fixed, the lower the temperature. Thus, the anhydrous phase formation by recondensation of the mono and diphosphate mixture (200°C-350°C), occurs at a much lower temperature, than by direct dehydration of $NaCaP_3O_9,3H_2O$ under dynamic vacuum (430°C). The anhydrous phase, identified as the trimetaphosphate $NaCaP_3O_9$, being stable over a temperature range of 50°C, is converted to polyphosphate $[NaCa(PO_3)_3]_\infty$ by heating. Its inter-planar spacings are listed in Table III.

TABLE II

nH_2O	ΔH kcal. mole^{-1}	ΔS^o cal. k^{-1}. mole^{-1}
3	2.9	2.2
2.6	2.8	1.0
2.2	3.1	1.3
2	3.6	1.6
1.8	5.3	5.3
1.6	6.2	7.4

INFLUENCE OF HEATING ON DEHYDRATION

The thermograms recorded during the dehydration of $NaCaP_3O_9,3H_2O$ by a linear temperature rise (300°C/h), under water vapor pressure (10^{-3} torr-31.8 torr) (Figure 7), coincide during the removal of the first two H_2O's and show a change in their slope at the 1.6 H_2O hydration level, when a more or less partial opening of the $P_3O_9^{3-}$ rings occurs under water vapor pressure, whereas this phenomenon is not noticed under a dynamic vacuum of 10^{-3} torr. These thermograms are differentiated during the removal of the last H_2O, the anhydrous phase being attained at a temperature which is all the lower as the water vapor pressure is higher, a result which is similar to that observed in the case of dehydration by equilibrium points. The product obtained at a temperature of

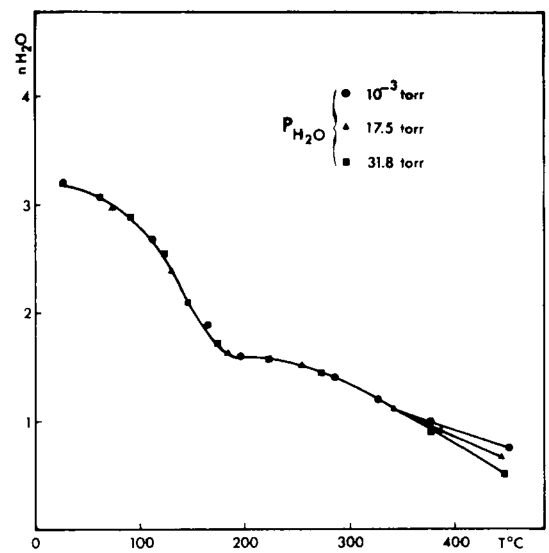


FIGURE 7 $NaCaP_3O_9,3H_2O$ dehydration under fixed P_{H_2O} and by linear temperature rise of about 300°C/h.

about 500°C, either under water vapor pressure or dynamic vacuum, still contains a certain amount of water (0.4 to 0.6 H_2O) and appears as a mixture of $NaCaP_3O_9$ and $[NaCa(PO_3)_3]_\infty$, the anhydrous phase being made of polyphosphate only. The anhydrous trimetaphosphate, thus, cannot be isolated by a temperature rise, whatever the water vapor fixed.

ASSUMPTION OF AN INTERNAL HYDROLYSIS

The ease with which sodium calcium trimetaphosphate hydrolyses in the presence of water vapor pressure leads us to assume an internal hydrolysis, a phenomenon already observed for cadmium trimetaphosphate, $Cd_3(P_3O_9)_2,14H_2O$.[10,11] Indeed, the study of this trimetaphosphate dehydration along with a study of the mobility of water molecules by NMR showed that part of the $14H_2O$'s is retained by the $P_3O_9^{3-}$ rings. This hydrolysis results from the transfer of one of the protons initially belonging to an H_2O molecule into an external oxygen of the anionic $P_3O_9^{3-}$ rings. Group $[3H^+,P_3O_9^{3-}]$, highly unstable in presence of water vapor, then, breaks down all the more easily as the water vapor pressure fixed is higher.

To check this assumption, several experiments were carried out to find out the nature of the H_2O bonds within the lattice. NMR and IR spectroscopy show several types of water molecules: highly-mobile H_2O's, H_2O's loosely-bonded to the lattice and most probably OH^-'s. These spectra are just being interpreted. Heterogeneous catalysis tests, however, gave positive results. Sodium calcium trimetaphosphate was partially dehydrated under a dynamic vacuum of 10^{-3} torr at 160°C and, at this temperature, it was noticed, that a flow of isobutene (yield: 0.2 mmole/h) led to the formation of an isooctene dimer (3.5%) and a trimer in $C_{12}H_{36}$ (1%). These results, specific to a Brönstedt acid can be obtained in the same experimental conditions as the monophosphoric acid. The H^+ catalytic ions can only come from a dissociation of the H_2O's contained in the trimetaphosphate and behave, regarding catalysis, like the protons of monophosphoric acid. The catalyst, $CaNaP_3O_9, xH_2O$, thus, is liable to act as group $[3H^+, P_3O_9^{3-}]$. This result, thus, sustains the internal hydrolysis assumption, accounting for the abnormally low values of the normal isosteric enthalpies and entropies. Indeed, it results in water retention at ring level i.e. by a phenomenon opposed to dehydration.

COMPARED DEHYDRATIONS OF MIXTURE $NaH_2PO_4 + CaH_2P_2O_7$ AND $NaCaP_3O_9,3H_2O$

In the same way as for $NaCaP_3O_9,3H_2O$, the thermal dehydration of the stoichiometric mixture, $NaH_2PO_4 + CaH_2P_2O_7$ leads to the final formation of polyphosphate, $[NaCa(PO_3)_3]_\infty$. It, thus, seemed interesting to investigate whether, in the case of this mixture, the formation of the anhydrous trimetaphosphate preceded that of the polyphosphate. For this purpose, $NaH_2PO_4 + CaH_2P_2O_7$, was heated at room pressure and around 250°C. $NaCaP_3O_9$ actually formed. The compared dehydration of the mixture and $NaCaP_3O_9$ is summed up in Table I.

TABLE III

$NaCaP_3O_9$ our values		$NaCaP_3O_9$ by W. FELDMANN	
I/I_0	$d_Å$	I/I_0	$d_Å$
15	7.67		7.7
20	5.95		
100	{5.13	100	5.2
	{5.09	100	5.0
2	4.61		
2	4.53		
5	4.10		
30	3.84	50	3.8
2	3.74		
2	3.58		
45	{3.24	50	3.2
	{3.22		
10	2.92	25	3.0
40	{2.85	50	2.9
	{2.82		
2	2.78		

CONCLUSION

The normal extent of hydration for sodium calcium trimetaphosphate is possibly $3H_2O$ and the large amounts of water that it can further fix result from a capillary condensation within macrochannels formed during crystallization. The $3H_2O$'s show the characteristic features of loosely-bonded molecules, located in micropores. In the presence of water vapor an internal hydrolysis leads to a more or less partial opening of the $P_3O_9^{3-}$ rings (hence this compound instability at room conditions), whereas under a dynamic vacuum of 10^{-3} torr, the trimetaphosphate may be entirely dehydrated without any decondensation. Whatever the dehydration process, the thermal dehydration yields the stable anhydrous trimetaphosphate within a narrow temperature range, preceding the occurrence of polyphosphate. Placed in specific temperature and pressure conditions the anhydrous trimetaphosphate may recover the extent, $3H_2O$.

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REFERENCES AND NOTES

1. C. G. Lindbom, *Ber* 8, 122 (1875).
2. C. Martin and A. Durif, *Bull. Soc. Fr. Mineral Cristallogr.* 95, 149 (1972).
3. W. Feldmann, *Z. anorg. allgem. chem.* **400** n° 2, 97 (1973).
4. E. Thilo and I. Grunze, *Z. anorg. allgem. chem.* **290**, 223 (1957).
5. A. Durif, *C. R. Acad. Sc. Paris* **275**, 1379 (1972).
6. F. Lavanant, Thèse Ingénieur-Docteur Dijon (1963).
7. D. Michot, Thèse Docteur 3ème Cycle Dijon (1975).
8. P. Barret and N. Gerard, Brevet CNRS n° P 921010.
9. J. Aurenge, M. Degeorges and J. Normand, *Bull. Soc. chim. Fr.* 508 (1964).
10. D. Michot and M. H. Simonot-Grange, Ier Symposium International de la Chimie Hétérocyclique Minérale, Besançon, France, Juin 1975.
11. C. Doremieux-Morin, Ier Symposium International de la Chimie Hétérocyclique Minérale, Besançon, France, Juin 1975.