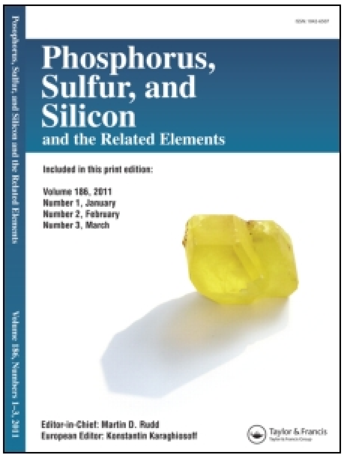

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THERMAL DEHYDRATION OF BARIUM AND CALCIUM TRIMETAPHOSPHATE HEXAHYDRATES: $Ba_3(P_3O_9)_26H_2O$ AND $Ca_3(P_3O_9)_26H_2O$

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$Ba_3(P_3O_9)_2$ $6H_2O$ and $Ca_3(P_3O_9)_2$ $6H_2O$ have mobile H_2O's which, under a dynamic vacuum of about 0.133 Pa, leave the lattice without disrupting it. Under water-vapor pressure, dehydration is accompanied by hydrolysis of $P_3O_9{}^{3-}$ rings. The final product of dehydration is the β polyphosphate.

I INTRODUCTION

This study of the dehydration of barium and calcium trimetaphosphate hexahydrates[1] is part of a more general and systematic investigation in our laboratory on the inflence of water vapor on the trimetaphosphate hydrates of alkaline and alkaline-earth metals. It supplements those studies already effected on $NaBaP_3O_93H_2O$,[2] $NaCaP_3O_93H_2O$,[3] $NaSrP_3O_93H_2O$ and $Sr_3(P_3O_9)_27H_2O$.[4]

II EXPERIMENTAL

In addition to the experimental techniques usually used: thermogravimetry (TG), differential thermal analysis (DTA), X-ray powder diffractomerty (XRD), and thin layer chromatography (TLC),[5] infrared spectroscopy (IR) was employed here. The experiments were carried out in successive temperature steps, either under a dynamic vaccuum of about 0.133 Pa or with a controlled water-vapor pressure.

$Ba_3(P_3O_9)_26H_2O$ and $Ca_3(P_3O_9)_26H_2O$ were prepared according to the Boulle method[6] by the exchange reaction between silver trimetaphosphate and barium or calcium chloride. In both cases the crystals obtained were stable in ambient room conditions.

III RESULTS

(*a*) $Ba_3(P_3O_9)_26H_2O$

$Ba_3(P_3O_9)_26H_2O$ is the only trimetaphosphate hydrate reported in the literature. Its crystal structure was described by MASSE *et al.*[7] It crystallizes in the triclinic system[8] space group $P\bar{1}$. Half the water molecules lie in the channels formed by the $P_3O_9^{3-}$ rings. Two H_2O's do not take part in the cohesion of the lattice.

Under dynamic vacuum and ambient temperature, the TG thermograms (Figure 1a) show that $3H_2O$'s rapidly leave the lattice. A fourth follows more slowly. The removal of these $4H_2O$'s does not disturb the structure of the trimetaphosphate. After atmospheric pressure has been reestablished, the XR pattern of the sample remains characteristic of $Ba_3(P_3O_9)_26H_2O$. On heating, this pattern disappears at about 90°C, and progressive ring opening occurs, leading to a mixture, first of PO_4^{3-}, $P_2O_7^{4-}$, $P_3O_9^{3-}$ anions, then of $P_3O_9^{3-}$, PO_3^- anions. Finally, when dehydration is complete at about 450°C, only perfectly crystallized $\beta[Ba(PO_3)_2]_\infty$ remains.[9]

Under a constant water-vapor pressure, the TG thermograms (Figure 1a) show that dehydration proceeds in three steps:

1) A continuous and slow water loss without opening of $P_3O_9^{3-}$ rings. This domain starts with the original $6H_2O$'s and is essentially complete at an extent of hydration and a temperature, symbolized by n_0 and T_0; n_0 is larger and T_0 is smaller for high water-vapor pressure P, as shown in Table I. In every case, rehydration leads to $Ba_3(P_3O_9)_26H_2O$. Study of the reversibility shows a hysteresis phenomenon: the rehydration curve is always located under the dehydration curve (Figure 1b). In addition, for each pressure, there are several rehydration curves depending on the

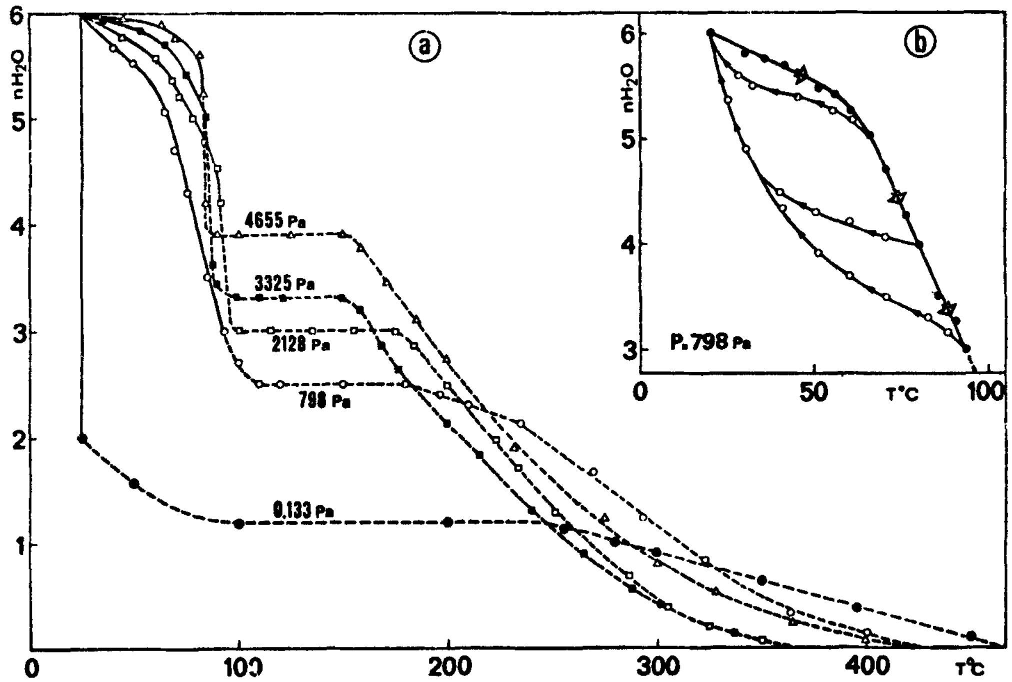

FIGURE 1 TG thermograms of $Ba_3(P_3O_9)_26H_2O$ under water vapor by successive temperature steps: —— $P_3O_9^{3-}$ rings; ---- $P_3O_9^{3-}$ ring opening (a) dehydration; (b) rehydration.

temperature where cooling begins. But, the new dehydration curve of the rehydrated sample is the same as the original one.

2) A very rapid water loss, and then a mass step (i.e. the dehydration has stopped although the temperature increases). Before the mass step begins a partial opening of the $P_3O_9^{3-}$ ions occurs resulting in the formation of a mixture of $P_3O_9^{3-}$, $P_3O_{10}^{5-}$, $P_2O_7^{4-}$, PO_4^{3-} anions. This mixture then can take up water again when the temperature is lowered; on the contrary, as soon as the mass step is reached there is no further

TABLE I

Coordinates of common limits of the conservation domains of rings and of hydrolysis and coordinates of mass steps

		$Ba_3(P_3O_9)_26H_2O$				$Ca_3(P_3O_9)_26H_2O$		
beginning of ring opening	P Pa	798	2128	3325	4655	798	2128	3325
	n_0 mol	3.0	4.2	5.0	5.2	5.4	5.8	6.0
	T_0 °C	93	92	85	82		110	
mass step	n mol	2.5	3.0	3.3	3.9			
	T°C beginning	110	100	95	88		no mass step	
	T°C end	180	175	150	150			

water intake by lowering temperature. This mass step is such that the higher the water vapor level is fixed, the higher is the extent of hydration (Table I). By raising the temperature during the mass step, the decondensation of anions continues: LTC then shows the gradual disappearance of the $P_3O_9^{3-}$ and $P_3O_{10}^{5-}$ ions for the benefit of $P_2O_7^{4-}$ and PO_4^{3-} ions.

3) A continuous and slow water loss occurs up to total dehydration brings about a recondensation of the various compounds into polyphosphate $\beta[Ba(PO_3)_2]_\infty$ at about 300°C. The temperature of final dehydration is about 400°C.

These dehydration curves thus characterize three domains: one where cyclic structures are conserved one domain of ring opening and one of anion recondensation to yield polyphospates.

Under atmospheric pressure, the DTA thermograms (300°C/h) show: Figure 2 (a) Two endothermic peaks, the first beginning at 70°C and the second before the first ends (maximum at 85°C). (b) Two exothermic peaks, the first following immediately after the second endothermic peak (maximum at 165°C) and the second beginning at 440°C.

TG, XRD and TLC analysis carried out at the level of each peak maximum show that the first two peaks may be assigned to the water loss (no lattice disruption; phases of $5.5H_2O$ and $3H_2O$ rehydrate into $Ba_3(P_3O_9)_26H_2O$), the third to the conversion of trimetaphosphate into polyphosphate (no XRD pattern; no rehydration of the mixture in $2H_2O$) and the last to the crystallization of the polyphosphate (TLC: PO_3^-, XRD: $\beta[Ba(PO_3)_2]_\infty$).

IR spectra (conditions: suspension in mineral oil (nujol) between two pellets of thallous bromide and iodide (KRS-5)) effected at room temperature and at −150°C show several bands specific to the OH stretching and bending frequencies (Table II). By vacuum dehydration at room temperature, the most mobile OH and H_2O bands located at 3560 cm^{-1} and 1615 cm^{-1} disappear whereas the $P_3O_9^{3-}$ bands (between 1300 cm^{-1} and 600 cm^{-1}) are not altered.

The analysis of the crystal structure shows that, on the one hand if two H_2Os are not bound to the lattice, two other H_2Os are also able to leave without breaking it up: one because of its important thermal parameter, and the other because the Ba-H_2O bond is weak; on the other hand, two H_2Os are strongly bound to the trimetaphosphate lattice.

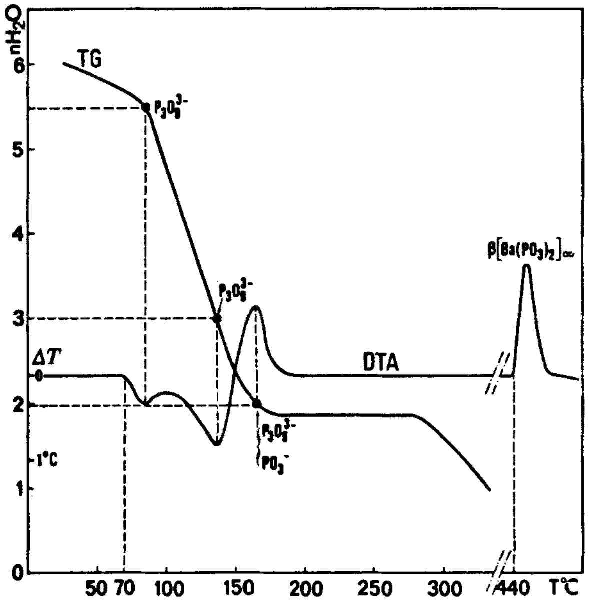

FIGURE 2 (DTA and TG thermograms of $Ba_3(P_3O_9)_26H_2O$ under room pressure by a linear temperature rise (300°C/h).

Our experimental results agree perfectly with these structural facts. Indeed, on the one hand, in the hydration range $6H_2O$-$2H_2O$, without water vapor, four H_2Os can be removed without disrupting the lattice (IR, XRD). The decondensation observed with water vapor may then be interpreted as resulting from a hydrolysis; on the other hand, it is impossible to reach a hydration extent less than $2H_2O$ without causing the trimetaphosphate to break up.

(*b*) $Ca_3(P_3O_9)_26H_2O$

Several calcium trimetaphosphate hydrates are reported in the literature: $10H_2O$,[10] $9H_2O$,[6,11] $7H_2O$[12] and $6H_2O$[13] hydrates. Using the BOULLE method[6] two of those were obtained: the hexahydrate, either in powder form by precipitation from ethyl alcohol or in crystal form by the fast evaporation of a highly concentrated solution, the decahydrate by slow evaporation of a diluted solution. Both of them can be prepared from the same solution, the hexahydrate precipitating after 24 hours and the decahydrate after about a week. Only the hexahydrate is reported in this paper; the crystals prepared have a hydration extent of $6.3H_2O$. The structure of this compound is unknown.

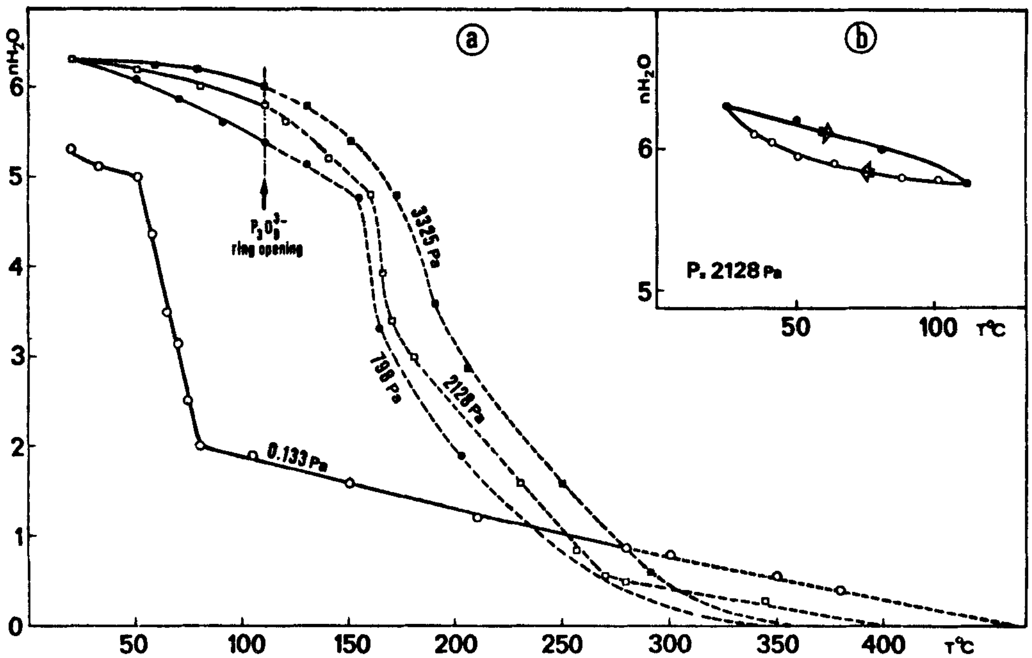

FIGURE 3 TG thermograms of $Ca_3(P_3O_9)_2 6H_2O$ under water vapor by successive temperature steps: — $P_3O_9^{3-}$ rings; ---- $P_3O_9^{3-}$ ring opening (a) dehydration; (b) rehydration.

Under vacuum and at ambient temperature, the TG thermograms show (Figure 3a) that the loss of one H_2O is observed and the setting up of atmospheric pressure again leads to the trimetaphosphate hexahydrate. On heating, between 50°C and 80°C, the removal of three H_2Os is rapid, and at 80°C and above the loss of the last two H_2Os is slower. From 65°C XRD analysis shows that the characteristic pattern of $Ca_3(P_3O_9)_2 6H_2O$ disappears slowly. However, TLC analysis from 65°C to 280°C shows the sole presence of the $P_3O_9^{3-}$ anion. Therefore nearly total dehydration, probably up to a hydration extent of $1H_2O$, does not cause any deterioration of the trimetaphosphate ring. From 280°C, TLC analysis reveals the presence of polyphosphate anions. At 450°C the dehydration is complete and the final material is β-$Ca(PO_3)_2$.[10,13]

Under water-vapor pressure, three steps are observed during dehydration: (Figure 3a).

1) A continuous and solw water loss without opening of $P_3O_9^{3-}$ rings occurs. The domain starts with the original $6.3H_2O$s and is essentially complete at an extent of hydration and a temperature, symbolized by n_0 and T_0; n_0 is larger, and T_0 is constant, for high water-vapor pressure P, as shown in Table I. As for barium trimetaphosphate, rehydration occurs with a hysteresis phenomenon (Figure 3b) and the XRD pattern of the rehydrated compound is characteristic of that of $Ca_3(P_3O_9)_2$ $6H_2O$.

2) Whatever the pressure, at 110°C the opening of the $P_3O_9^{3-}$ rings begins leading to a mixture of di- and monophosphates. Under low pressure ($\simeq 0.8$ kPa) the opening is only partial; under higher pressure ($\simeq 3.3$ kPa) it is total with formation of a mixture of mono- and diphosphates. At about 200°C, XRD analysis shows the intermediate formation of $Ca_3(HP_2O_7)_2$.[14]

3) A continuous and slow water loss occurs until total dehydration takes place at about 350°-400°C, leading to the formation of the β polyphosphate. The three domains characterized in the barium trimetaphosphate study are formed again.

Under atmospheric pressure, the DTA and TG thermograms (300°C/h) show: (Figure 4): (a) Two endothermic peaks beginning at 80°C and 160°C, and at $6H_2O$ and $5H_2O$. (b) One exothermic peak beginning at 500°C.

XRD and TLC analyses carried out at different temperatures thus show that both endothermic peaks are attributable to water losses (until 185°C: no opening of the $P_3O_9^{3-}$ rings; XRD pattern of

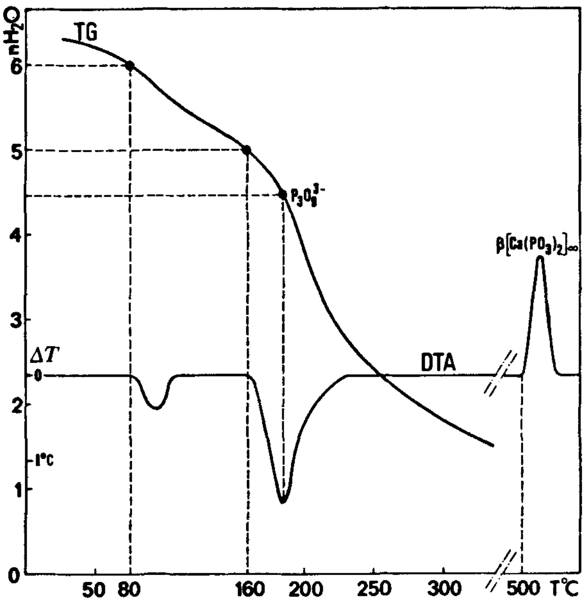

FIGURE 4 DTA and TG thermograms of $Ca_3(P_3O_9)_2 6H_2O$ under room pressure by a linear temperature rise (300°C/h).

the rehydrated phases characteristic of $Ca_3(P_3O_9)_2$ $6H_2O$ and the exothermic peak to the polyphosphate crystallization[10,13] (at 400°C: PO_3^{3-} and $P_3O_9^{3-}$, no XRD pattern, no rehydration; at 510°C: XRD characteristic of $\beta[Ca(PO_3)_2]_\infty$).

The IR spectra (see above for experimental conditions) show the occurrence of two very mobile OH^- bands (Table II). This is in agreement with the TG study showing that it is possible, in the absence of water vapor, to almost entirely dehydrate the trimetaphosphate without breaking up the rings. The ring opening observed during dehydration under water-vapor pressure must, in this case also, be assigned to a hydrolysis.

IV CONCLUSION

The processes of dehydration of $Ba_3(P_3O_9)_2 6H_2O$ and $Ca_3(P_3O_9)_2 6H_2O$ are similar to those observed in our previous studies. They may be summed up as follows: (a) In the absence of water vapor, removal of mobile H_2O without breaking up of the $P_3O_9^{3-}$ rings. (b) In presence of water vapor, three steps are evident: ring conservation, hydrolysis, and recondensation. It should be noted that in the latter step, contrary to what has been observed in previous studies, the recondensation as anhydrous trimetaphosphate is not observed.

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TABLE II

Vibration frequencies of trimetaphosphate H_2O's

	Frequency cm^{-1}		
	$Ba_3(P_3O_9)_2 6H_2O$		$Ca_3(P_3O_9)_2 6H_2O$
	25°C	−150°C	25°C
stretching	3570 narrow	3640 3560 very narrow	3600 narrow 3580 shouldering
	3370 2190 broad	3460 3420 3300 3190 narrow	3520 narrow 3360 3200 broad
bending	1640 broad 1615 shouldering	1650 1625 narrow	1645 1605 narrow

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