Contribution from the Department of Inorganic and Analytical Chemistry, the Hebrew University, Jerusalem, Israel

An I.R., T.G. and D.T.A. Study of some Hydrated Metal Phosphates

L. Ben-Dor and I. Felner[*]

Received October 13, 1969

The dehydration of the hydrated phosphates (normal and acid) of sodium, potassium and calcium and also those of iron, nickel, copper and zinc were studied by infrared spectrometry, thermal gravimetry and differential thermal analysis. In most cases a gradual dehydration was found from the phosphate polyhydrate to the anhydride (sometimes to the pyrophosphate) without the formation of an extra-energetically stable monohydrate phase.[1]

Introduction

The dehydration of metal phosphate hydrates has not been extensively studied as compared to dehydration studies of metal sulphates. Since metal sulphate monohydrates exhibit certain acidic properties[1] it was of interest to see whether the metal phosphate monohydrates exhibit similar characteristics, in view of the structural and configurational similarity between the sulphates and the phosphates.

Of the alkali earth phosphates, the dehydration of $CaHPO_4 . 2H_2O$ was the most extensively studied[2-6a] by thermal means. In all cases the anhydrous salt was first formed, followed by the pyrophosphate. The same was true of $Mg(H_2PO_4)_2 . H_2O$ and $Ca(H_2PO_4)_2 . H_2O$.[7,8] The phosphates of sodium and potassium show step-dehydration and also condensation steps.[9-11] The dehydration of some transition-metal phosphates, although showing loss of water in more than one distinct step, does not show the formation of stable monohydrate intermediaries.[12,13]

Infrared data for the hydrated phosphates has been reported by various authors,[14-17**] although only few phosphates were studied, and Berry,[17] who gives complete detailed assignment for $H_2PO_4^-$ and H_2O species, deals only with monocalcium phosphate monohydrate with no attempt at comparing the various hydrates.

Experimental Section

Samples. The following were Baker Analyzed Reagents: $K_3PO_4 . H_2O$, $K_3PO_4 . nH_2O$, $Na_3PO_4 . 12H_2O$, $Na_2HPO_4 . 12H_2O$, $Na_2HPO_4 . 7H_2O$, $Na_2HPO_4 . 2H_2O$, $NaH_2PO_4 . H_2O$, $Ca(H_2PO_4)_2 . H_2O$ and $Cu_3(PO_4)_2 . 3H_2O$. The following were obtained from Chemicals and Phosphates, Ltd., Haifa, Israel: $Fe_3(PO_4)_2 . 8H_2O$, $Ni_3((PO_4)_2 . 7H_2O$, $Zn_3(PO_4)_2 . 2H_2O$ and $CaHPO_4 . 2H_2O$. In Table I are listed some monohydrates, anhydrides and pyro salts prepared by heating the respective polyhydrate phosphate at specific temperatures for 1-2 hrs. as found from T.G. and D.T.A. data.

Measurements. Thermal analysis runs were carried out on a Stone D.T.A. KA-2H unit using the techniques and equipment described in a previous paper

Table I. Dehydrating temperatures of various phosphates prepared from the appropriate polyhydrates

Compound	Temp. (°C)
$Ni_3(PO_4)_2 . xH_2O$	200
$Ni_3(PO_4)_2$	400
$Cu_3(PO_4)_2 . H_2O$	180
$Zn_3(PO_4)_2 . H_2O$	200
$Na_3PO_4 . H_2O$	170
Na_2HPO_4	200
$CaHPO_4$	200
$Ca_2P_2O_7$	450

(*) Based on M. Sc. thesis of I. F., Hebrew University, Jerusalem, 1968.

(1) L. Ben-Dor and R. Margalith, *Inorg. Chim. Acta, 1,* 49 (1967).

(2) J. G. Rabatin, P, H. Gale, and A. E. Newkirk, *J. Phys. Chem., 64,* 491 (1960).

(3) S. Matsumo, *Kogyo Kagaku Zasshi, 70,* 269 (1967). [C.A., *69,* 74701e (1968)]

(4) S. Matsumo, M. Watenabe, and Y. Mitsutomi, *Kogyo Kagaku Zasshi, 70,* 2124 (1967) [C.A., *69,* 73575a (1968)].

(5) V. V. Pechkovskii, L. N. Shchegrov, A. S. Shul'man, R. Y. Mel'nikova, and M. D. Mochalina, *Zh. Neorg. Khim., 13,* 2360 (1968).

(6) P. Dugleux and A. de Sallier Dupin, *Bull. Soc. Chim. France,* 144, 973, 978 (1967).

(6a) P. Dugleux, A. de Sallier Dupin, and A. Boullé, *Bull. Soc. Chim. France, no. spécial,* 1683 (1968).

(7) V. V. Pechkovskii, L. N. Shchgerov, A. S. Shulman, R. Y. Mel'nikova, and S. S. Gusev, *Vestsi Akad. Navuk Belarus. SSR, Ser. Khim. Navuk, 1,* 36 (1968) [C.A., *69,* 31668c (1968)].

(8) A. B. Bekturov, D. Z. Serazetdinov, Yu. A. Kushnikov, E. V. Poletoaev, and S. M. Dionenko, *Zh. Neorg. Khim., 12,* 2355 (1967).

(9) L. G. Berg, *Bull. Acad. Sci. URSS, Classe Sci. Chim.,* 887 (1940) (ref. no. 42 *in:* J. W. Mellor, *Comprehensive Treatise on Inorganic and Theoretical Chemistry,* Vol. II, Suppl. III, part. 2, p. 1958 (1963)).

(10) W. Behl and G. Gaur, *Z. Phys. Chem.,* 29, 289 (1961).

(11) L. Steinbrecher and J. Fred Hazel, *Inorg. Nucl. Chem. Letters, 4,* 559 (1968).

(**) These are a selection of some of the pertinent references. More are cited in ref. (23) and (25).

(12) N. S. Kurnakoff and I. A. Andreevsky, *Ann. Inst. Anal. Phys. Chem.,* 2, 485 (1924).

(13) G. Brauer, *Handbook of Preparative Inorganic Chemistry,* Academic Press, New York, 1963, p. 1081.

(14) F. A. Miller and G. H. Wilkins, *Anal. Chem., 24,* 1253 (1952).

(15) J. V. Pustinger, W. T. Cave and M. L. Nielsen, *Spectrochim. Acta, 15,* 909 (1959).

(16) R. Blinc and D. Hadži, *Mol. Phys., 1,* (1958).

(17) E. E. Berry, *Spectrochim. Acta, 24A,* 1727 (1968).

Table II. The dehydration of some hydrated phosphates

Salt	DTA bands	TG steps	Peaks °C	Steps °C	H_2O molecules lost
$Fe_3(PO_4)_2 \cdot 8H_2O$	1	1 (gradual)	110	100-400	~8
$Ni_3(PO_4)_2 \cdot 7H_2O$	2	2	90; 205	90; 200	1; 5
$Cu_3(PO_4)_2 \cdot 3H_2O$	2	2	180; 320	150; 330	2; 2/3
$Zn_3(PO_4)_2 \cdot 2H_2O$	2	2	110; 270	120; 290	1; 1
$Zn_3(PO_4)_2 \cdot H_2O$	1	—	270	—	—

from this laboratory.[1] I. R. spectra were taken on a Perkin Elmer model 21 instrument in the range 2-15 μ. The technique is the same as the one used before.[1] T.G. runs were carried out on a Chevenard thermobalance manufactured by A.D.A.M.E.L. The rate of heating was maintained at 5°C/min. The temperature measured by a chromel-alumel couple was read off a potentiometer to ±10°C. Full scale deflection on the thermogram recorder was calibrated to 70±0.5 mg. The thermograms were redrawn for better and clearer presentation and the appropriate weight loss unit indicated.

Results and Discussion

(7) Table II shows the D.T.A. and T.G. data of the hydrated transition metal phosphates. All the D.T.A. peaks are endothermic.

$Fe_3(PO_4)_2 \cdot 8H_2O$. The T.G. data show a weight loss corresponding to *ca.* 8 molecules of water which are lost gradually rather than sharply. The dehydration starts at 100°C and by the time the temperature reaches 175°C, 5 water molecules have been lost. Thence to 400°C, 3 more water molecules are slowly lost. The DTA sustains these data and shows a well-formed endothermic band peaking at 110°. The subsequent slow loss of water could not be followed owing to the slight energetic changes involved.

$Ni_3(PO_4)_2 \cdot 7H_2O$. The dehydration of this compound takes place in two sharp steps (Figure 1). Contrary to expectation, only 6 molecules of water are lost, the resulting compound above 200° being the anhydride, or very close to it. Both T.G. and D.T.A. were carried to 500°C without further detectable loss of water. The dehydration of the octahydrate carried out by Kurnakoff *et al.*[12] proceeds in 3 steps, namely 110° 220° and 260°, the first two being similar to our findings, and the third being possibly due to the extra water molecule. The stage at which the 7th water molecule was lost from the sample studied by us cannot be definitely stated.

$Cu_3(PO_4)_2 \cdot 3H_2O$. This compound is dehydrated in 2 steps: 2 molecules of water are lost at 150° and then 2/3 of the third molecule is gradually lost between 210°-330°, a weak endothermic band peaking at 320° appearing in the DTA graph (Figures 2, 3).

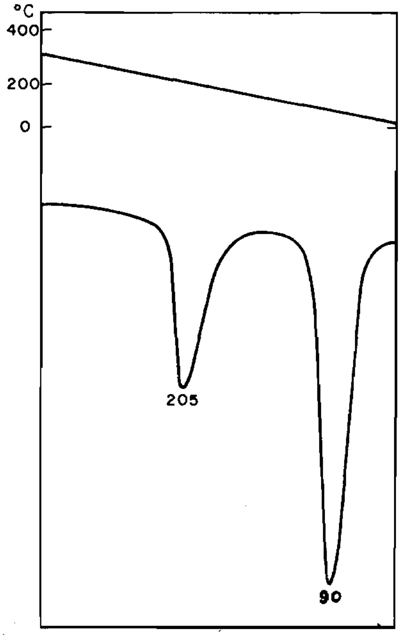

Figure 1. D.T.A. of $Ni_3(PO_4)_2 \cdot 7H_2O$.

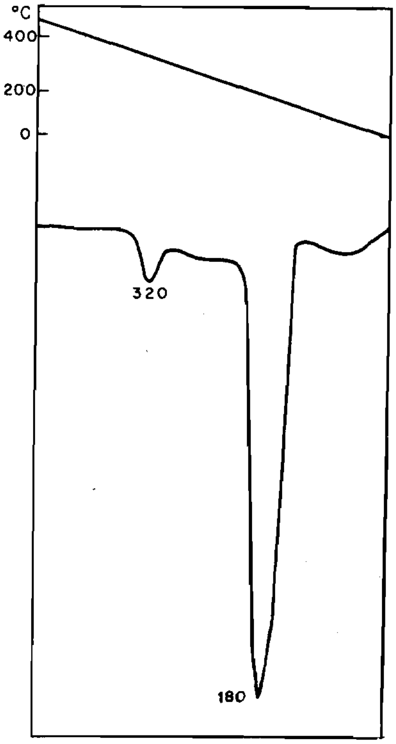

Figure 2. D.T.A. of $Cu_3(PO_4)_2 \cdot 3H_2O$

Table III. D.T.A. and T.G. data on alkali phosphates (including Ca).

Salt	DTA bands	TG steps	Peak temps. °C	Step temps. °C	H_2O molecules lost
$Na_3PO_4 . 12H_2O$	2 [a]	2	(90); 110; 290	20-150; 300	10; 1
$Na_3PO_4 . H_2O$	1	—	290	—	
$K_3PO_4 . nH_2O$	3	2	85; 140; 190	70-110; 150-210	2; 2
$K_3PO_4 . H_2O$	1 [b]	—	(90); 280	—	
$Na_2HPO_4 . 12H_2O$	3	2	60; 110; 300	60-120; 300	9; ½
$Na_2HPO_4 . 7H_2O$	2	2	80; 300	40-100; 290	6½; ½
$Na_2HPO_4 . 2H_2O$	3	2	110; 310; 330	90; 300	2; ½
$NaH_2PO_4 . H_2O$	4	4	100; 220; 310; 350	110; 220; 310; 360	1; ½; ½
$Ca(H_2PO_4)_2 . H_2O$	2	2	90; 280	90-130; 270	1; 1
$CaHPO_4 . 2H_2O$	3	2	150 (wk.); 185; 390	120-200; 410	2; ½

[a] (+ shoulder); [b] (+ weak band).

This comparatively weak peak could be observed only when the rate of heating was increased to 12°C/min.

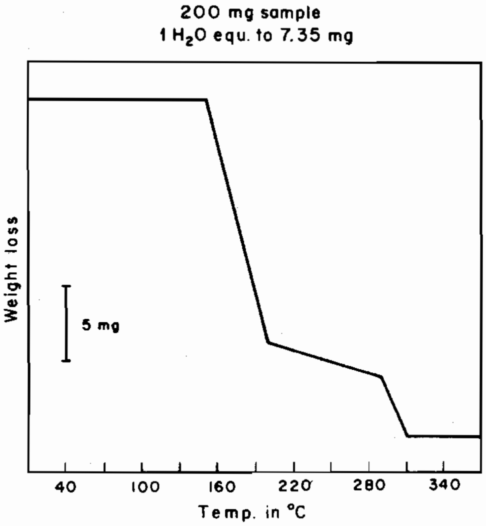

Figure 3. T.G. curve of $Cu_3(PO_4)_2 . 3H_2O$.

$Zn_3(PO_4)_2 . 2H_2O$. Whereas the above compounds each show an individual pattern of dehydration, this compound follows the well known pattern exhibited by the hydrated metal sulphates.[1] The monohydrate forms at 120°C and reaches complete dehydration at 280° (Figures 4, 5).

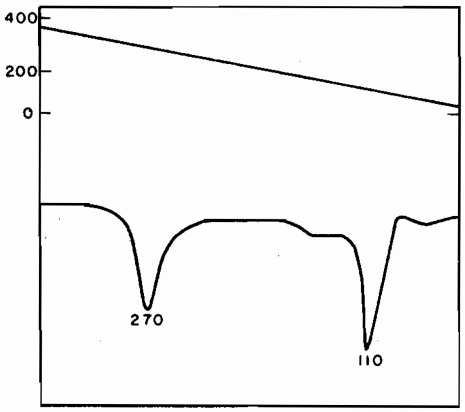

Figure 4. D.T.A. of $Zn_3(PO_4)_2 . 2H_2O$

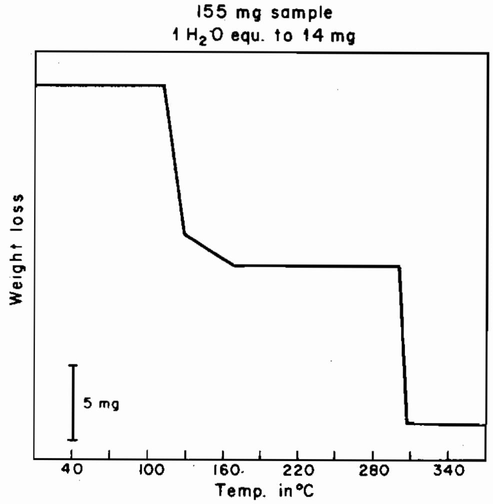

Figure 5. T.G. curve of $Zn_3(PO_4)_2 . 2H_2O$

(2) Table III gives dehydrating data for the various alkaly phosphates (including Ca).

$Na_3PO_4 . 12H_2O$. The dehydrating experiments on this compound show it to contain (on average) 11 molecules of water rather than 12. Duval[18,19] demonstrated this salt to be a mixture of the dodeca, deca and heptahydrates. In addition, this is the only compound amongst the alkali phosphates that shows on dehydration the clearcut formation of a monohydrate stable between 120-280° (Figures 6, 7). Neither Duval[18] nor Steinbrecher *et al.*[11] observed the formation of this monohydrate, nor in fact any weight loss above 230° and 200°, respectively. Their sample may possibly have been a lower hydrate.

$K_3PO_4 . nH_2O$. From our data it is obvious that this polyhydrate contains 4 molecules of water. The dehydration is not sharp, and it seems that 2 moles of water are lost successively, and at the higher temperature 2 extra moles are lost simultaneously. The formation of a monohydrate was thus not detected. However, if the starting material is the monohydrate it shows strong bonding, the water being lost at 280°, a temperature very close to that shown by the dehydration of $Na_3PO_4 . H_2O$.

(18) C. Duval, *Inorganic Thermal Gravimetric Analysis*, Elsevier Publ. Co., New York, 1963, pp. 201, 258.
(19) C. Duval, *Anal. Chim. Acta*, *13*, 32 (1955).

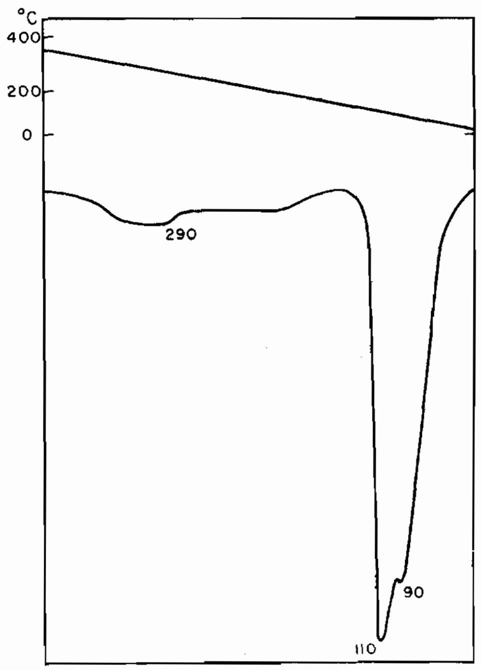

Figure 6. D.T.A. curve of $Na_3PO_4 . 12H_2O$.

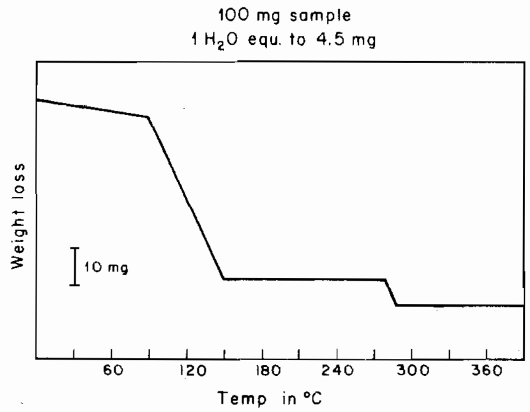

Figure 7. T.G. curve of $Na_3PO_4 . 12H_2O$.

Na_2HPO_4 polyhydrates. In these phosphates, the dehydration step to the anhydride is followed by a condensation step to the pyrophosphate. On the whole our results agree with those of Duval[18,19] and Steinbrecher *et al.*[11] The dodecahydrate melts at 60° and its water of hydration is completely evaporated at 110° Condensation occurs at 300°, causing the loss of ½ mole of water and formation of the pyrophosphate. The heptahydrate loses its water when heated up to 100°C, and at 280° condensation to the pyrophosphate occurs ($Na_4P_2O_7$). In the dihydrate one can observe the energetics involved in an extra step when the anhydride is submitted to structural reorganization before its condensation (DTA band peaking at 310°C). This weak step could not be detected in the other disodium salts owing to their comparatively high water content (Figures 8-10).

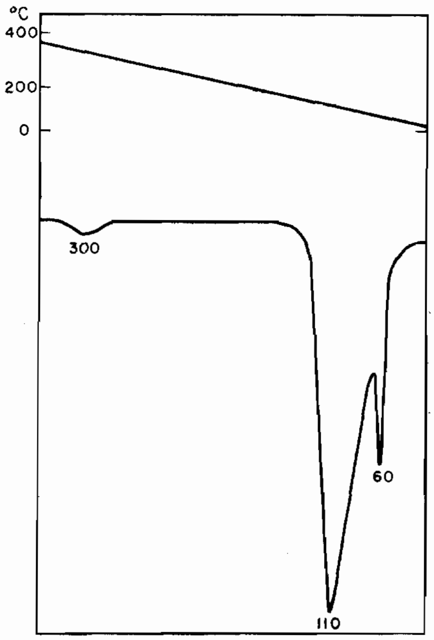

Figure 8. D.T.A. curve of $Na_2HPO_4 . 12H_2O$.

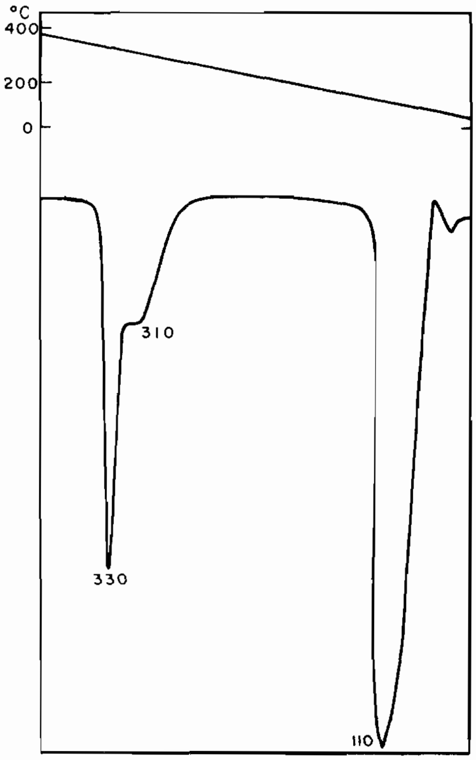

Figure 9. D.T.A. curve of $Na_2HPO_4 . 2H_2O$.

$NaH_2PO_4 . H_2O$. After losing its water of hydration (1 mole) at *ca.* 100°C, this compound goes through 2 well known condensation steps.[20] It first forms the acid pyrophosphate in a sharp step around 220°, and in a second step the metaphosphate polymer in the range 300-360°C. The DTA bands also show three groups: a peak at 100° — the anhydride range; 220° — condensation to acid pyrophosphate; $Na_2H_2P_2O_7$; 310° and 360° — condensation and struc-

---

(20) J. R. Van Wazer, *Phosphorus and its Compounds*, Interscience publ. Inc., New York, Vol. I, 1958, pp. 607, 616.

Table IV. I. R. band (in cm^{-1}) of some hydrated metal phosphates

Salt	strong str. H_2O (ν_1, ν_3)	medium ben. H_2O (ν_2)	strong str. deg. PO_4^{3-} (ν_3)	H-bonding ν_1 (OH)	Remarks
$Cu_3(PO_4)_2 . 3H_2O$	3320	1630	1080	2310 (m)	is partly hydrolysed
$Cu_3(PO_4)_2 . H_2O$	3270	1630	1080	2320 (m)	is partly hydrolysed
$Zn_3(PO_4)_2 . 2H_2O$	3400	1660	1095	2360 (w)	is slightly hydrolysed
$Zn_3(PO_4)_2 . H_2O$	3450	1610	1110	2360 (w)	is slightly hydrolysed
$Ni_3(PO_4)_2 . 7H_2O$	3400	1620	1050	—	—
$Ni_3(PO_4)_2 . xH_2O$	3400	1620	1050	2320 (w)	is slightly hydrolysed
$Ni_3(PO_4)_2$	—	—	1050	—	anhydrous
$Fe_3(PO_4)_2 . 8H_2O$	3450	1640	1000	—	—

tural reorganization to metaphosphate $(Na_3PO_4)_n$ (Figure 11). In the last two steps, ½ mole H_2O is lost për step. The two condensation steps were observed by Steinbrecher *et al.*[11] for NaH_2PO_4 anhydride, the first also by Boullé *et al.*[21] Seiyama *et al.*[22] observed a very similar D.T.A. curve.

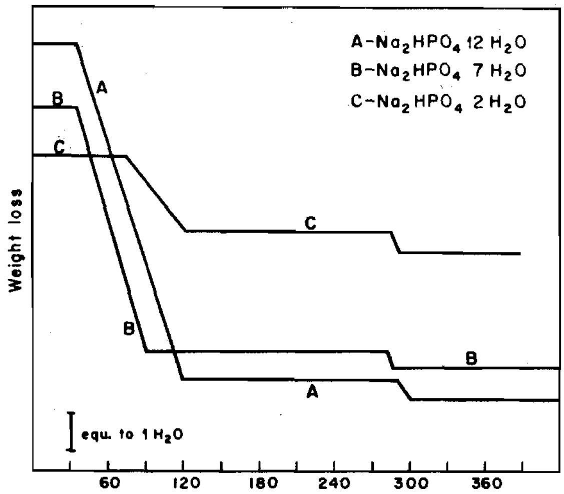

Figure 10. T. G. curves of $Na_2HPO_4 . 12, 7$ and 2 H_2O.

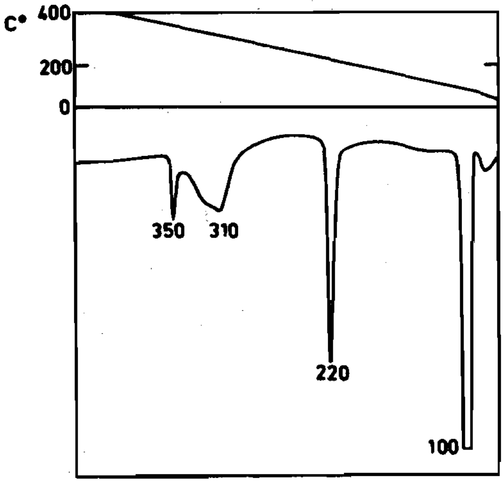

Figure 11. D.T.A. curve of $NaH_2PO_4 . H_2O$.

$Ca(H_2PO_4)_2 . H_2O$ and $CaHPO_4 . 2H_2O$. Both these salts lose their water of hydration at comparatively low temperatures, this step being followed by a condensation step. The former salt forms the acid pyrophosphate: $CaH_2P_2O_7$ and the latter the normal pyrophosphate $Ca_2P_2O_7$. It is of interest to note that the acid pyrophosphate of Ca is resistant to further condensation.

(3) Table IV shows the prominent I. R. bands of the transition-metal phosphates.

Only zinc and copper phosphate show a « monohydrate » spectrum (Figures 12, 13). The other salts studied show no difference in spectrum between the different polyhydrates, a result expected from their D.T.A. and T.G. curves. The « monohydrate » spectra show the shift of the bending vibration of H_2O–ν_2 from 1660 to 1610 cm^{-1} (Zn salt) and the appearance of the strong forbidden librational modes of H_2O at 815 cm^{-1} (Cu salt).[1]

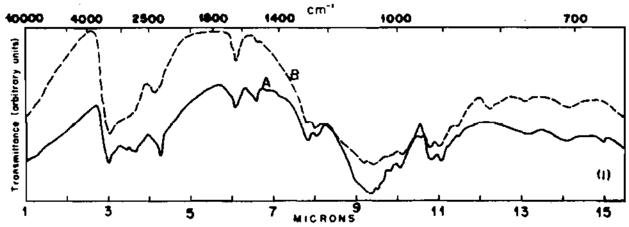

Figure 12. I.R. spectrum of $Cu_3(PO_4)_2$. A: polyhydrate; B: monohydrate.

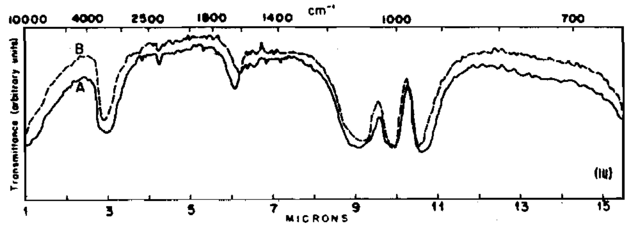

Figure 13. I.R. spectrum of $Zn_3(PO)_4)_2$. A: polyhydrate; B: monohydrate.

---

(21) A. Boullé, Dominé-Bergès, and C. Morin, *Comptes rendus*, *241*, 1772 (1955).

(22) T. Seiyama and A. Kato, *Thermal Analysis '65*, ed. J. R. Redfern, Macmillan & Co. Ltd., London, 1965, p. 116.

Table V. I.R. bands (in cm^{-1}) of some alkali metal phosphates (including Ca)

	strong ν_3 H_2O	weak ν_1 OH	strong ν_2 H_2O	strong ν_3 PO_4^{3-}	strong ν_1 PO_4^{3-}	a-sym. str. $P(OH)_2$	sym. str. $P(OH)_2$	a-sym. sym	str. PO_2 str. PO_2
$Na_3PO_4 . 12H_2O$	3550	2340	1670 (1610)	1020	broad	—	—	—	—
$Na_3PO_4 . H_2O$	3350	2330	1440	1040	1010	—	—	—	—
	3450	(2350)	1645	1000	(broad)				
$K_3PO_4 . 4H_2O$	3300		1650	1080	1010	—	—	—	—
$K_3PO_4 . H_2O$	3350	2350	1700	—	—	—	—	—	—
$Na_2HPO_4 . 12H_2O$	3350	2350	1700	—	—	1135	1060	995, 952	865
$Na_2HPO_4 . 2H_2O$	3350	2400	1720	—	—	1135	1060	995, 952	865
Na_2HPO_4	3600	2420	1660	—	—	1150	1010	950	840
$NaH_2PO_4 . H_2O$		2320				1170	1110, 1035	960	895
$Ca(H_2PO_4) . H_2O$	3400	2420 2320	1650	—	—	1170	1120	975	870
$CaHPO_4 . 2H_2O$	3550	2330	1655	—	—	1175	1055	985	870

Following Tanabe[25] we tried to estimate the « acidity » of these monohydrates qualitatively. Using 0.01% p-dimethylaminoazo-benzene in hexane as indicator, we followed the change of colour of the indicator, upon introduction of the various phosphates into the indicator solution. Only $Cu_3(PO_4)_2 . H_2O$ and $Zn_3(PO_4)_2 . H_2O$ showed « acidity », although comparatively weaker than the sulphate monohydrates. Thus, although the former might show catalytic activity their usefulness is probably limited.

Most phosphate salts are hydrolysed comparatively easily even on grinding in air, so that besides the H_2O and PO_4^{3-} vibrations other vibrations such as those due to $H_2PO_4^-$ and HPO_4^{2-} appear. These latter species are characterized by P—O symmetrical stretching at 870 cm^{-1} and P—O antisymmetrical stretching at 930 cm^{-1} and 995 cm^{-1}. Thus copper salts show weak-medium bands peaking at 995, 930, 910, 870 cm^{-1}. The zinc salts which are less hydrolysed do not show all these bands, except for one peaking at 950 cm^{-1}, while they do show the strong 1015 cm^{-1} band expected in normal phosphates owing to the I.R. forbidden symmetrical stretching ν_1 of PO_4^{3-}. Similar spectra were observed by Miller *et al.*[14] and Chapman *et al.*[23] The spectrum of $Fe_3(PO_4)_2 . 8H_2O$ showed rather weak and broad bands in contrast with the above sharp ones, probably because of the poor quality of the material, which could not be improved by recrystallization. Heating the material at 110°C causes complete loss of water, so that there was no point in recording spectra of the dried salt. Both the iron and nickel salts show the sym. str. of H_2O (ν_1) (3200 cm^{-1} and 3100 cm^{-1}), but not ν(OH). When the nickel salt is partly dehydrated, it shows ν(OH) 2320 cm^{-1} and a medium band peaking at 875 cm^{-1} due to hydrolysis. The complete anhydrous salt shows only PO_4^{-3} vibrations.

(4) Table V shows the prominent I.R. bands of the alkali metal phosphates (including Ca). Comparison of the spectra of the monohydrates of the normal phosphates with the polyhydrates reveals a shift of the bending vibration of H_2O (ν_2), and both spectra show the forbidden librational modes of H_2O: 850 cm^{-1} for the sodium salt and 845 cm^{-1} for the potassium salt (Figure 14). In $K_3PO_4 . H_2O$ a band peaking at 674 cm^{-1} appears owing to deformation of PO_4^{3-} (also shown by monohydrate sulphates[1]).

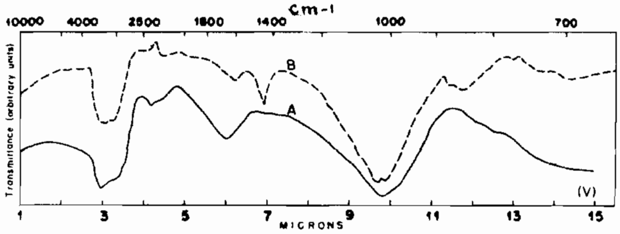

Figure 14. I.R. spectrum of Na_3PO_4. A: polyhydrate; B: monohydrate.

In the region 2280-2380 cm^{-1} all the acid phosphates show bands of strengths increasing with the number of P-O-H groups in the molecule,[17,24] and arising through strong hydrogen bonding. (This assignment is still a subject of controversy). In all the polyhydrates a strong *sym.* str. vibration ν_1 of H_2O is observed in the region 3075-3100 cm^{-1}, as well as the anti-sym. str. vibration ν_3 (see Table V). In the monohydrates only the anti-sym. str. vibration was observed, in contrast to the case of the hydrated sulphates.[1] The spectra of $NaH_2PO_4 . H_2O$ (Figure 15) and $Ca(H_2PO_4)_2 . H_2O$ are very similar and agree well with that observed by Berry[17] for the latter salt. The normal phosphates show the sym. str. vibration and the a-sym. degenerate str. vibration of PO_4^{-3}, while the acid phosphates show the sym. and a-sym. str. vibration of O-P-O and HO-P-OH.

Conclusion

DTA, TG and IR studies carried out for a number of phosphate hydrates showed that although dehydration is usually stepwise, on the whole there is no intermediate richly-energetic monohydrate species. $Zn_3(PO_4)_2 . H_2O$ loses its water of hydration in a sharp step appearing in both TG and DTA curves.

---

(23) A. C. Chapman and L. E. Thirlwell, *Spectrochim. Acta, 20,* 937 (1964).
(24) G. M. Murphy and G. Weiner, *J. Chem. Phys., 22,* 1322 (1954).
(25) K. Nakamoto, « I.R. spectra of Inorganic & Co-ordination Compounds », John Wiley & Sons, N. Y., 1963.

In the IR spectrum there is a shift in the bending vibration of H_2O. $Cu_3(PO_4)_2 . H_2O$ loses its water in a more gradual step, but its IR spectrum indicates both a shift in ν_2 H_2O and the ilibrational modes of H_2O, 815 cm^{-1}, which characterizes a lowering of symmetry of the molecule. $Na_3PO_4 . H_2O$ and $K_3PO_4 . H_2O$ show very similar behaviour in general. However, there is one main point of difference: whereas the sodium salt is formed during the dehydration of the polyhydrate, it is impossible to obtain the potassium salt in a similar manner, although in itself it is a stable well defined compound showing all the expected bands in its IR spectrum. In the hydrogen phosphates the dehydration step is followed by condensation step(s) all well shown in the DTA and TG curves. Their IR spectra, except for the H_2O vibrations, are different from those of the normal phosphates, as is expected from their different symmetry.

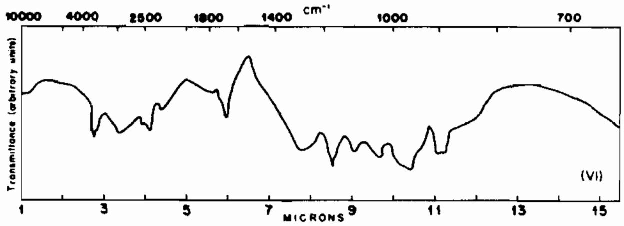

Figure 15. I.R. spectrum of $NaH_2PO_4 . H_2O$.

Acknowledgment. The authors wish to extend their thanks to Chemicals and Phosphates Ltd., Haifa, for kindly supplying a variety of phosphates used in this research.