Thermochimica Acta, 67 (1983) 341–349
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

PHYSICO-CHEMICAL PROPERTIES OF METAL PHOSPHATES *

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(Received 14 March 1983)

ABSTRACT

DTA, TG and DTG techniques are employed to study the thermal behaviour of the orthophosphates $M_3(PO_4)_2$ (where M = Cu, Zn, Mn and Cd), and $TiPO_4 \cdot 2\ H_2O$, and $Zr(HPO_4)_2 \cdot X\ H_2O$. The phosphates are characterized by X-Ray diffraction and IR spectroscopy. All the phosphates except titanium phosphate are found to be thermally stable up to 1000°C and crystalline in nature. From the kinetics of the dehydration the activation energies are found to be 14, 7, 9.5 and 9.4 kcal $mole^{-1}$ for Mn, Cd, Zr and Zn phosphate, respectively. The order of reaction for dehydration is nearly one for all the phosphates.

INTRODUCTION

The dehydration of the hydrated phosphates of manganese, copper and zinc has been reported previously [1,2]. 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 intermediates [3]. It is of interest to study the physico-chemical properties of the phosphates which are in turn related to the catalytic activity. These phosphates are characterized by thermal analysis, followed by IR spectra and X-ray diffraction.

MATERIALS

Aqueous solutions of metal chlorides and phosphoric acid (1 : 1 mole ratio) were mixed and ammonia (14% v/v) was added to control the pH of

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0040-6031/83/$03.00

the resulting mixtures. The solutions were stirred for about 2 h at room temperature and then allowed to stand for a further 24 h. The precipitates were filtered, washed with distilled water, and dried in air at 100°C for 8 h.

CHEMICAL ANALYSIS

The percent metal oxide and phosphorus pentoxide of the synthetic phosphates was determined by wet chemical analysis [4]. The compositions of metal oxide, phosphorus pentoxide and water are compared with theoretically calculated values in Table 1.

THERMAL ANALYSIS

The thermoanalytical curves were recorded on a MOM derivatograph (type CO-102 B) [5] in the temperature range 0–1000°C, using 200 mg samples and a heating rate of 10°C min^{-1} in air. α-Alumina was used as reference material.

X-RAY DIFFRACTION

The X-ray diffraction patterns of all the phosphates were recorded on a Philips X-ray diffractometer (model PW 100) using nickel filtered CuK_α radiation.

IR SPECTRA

Infrared spectra were recorded on a Perkin-Elmer 221 spectrometer in Nujol mull in the frequency range 600–3700 cm^{-1} at room temperature.

TABLE 1

Chemical analysis

Phosphate	MO%		P_2O_5%		H_2O%	
	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.
$Mn_3(PO_4)_2 \cdot 5\ H_2O$	47.83	47.76	31.91	31.83	20.26	20.41
$Cu_3(PO_4)_2 \cdot 3\ H_2O$	54.89	54.72	32.68	32.59	12.43	12.69
$Cd_3(PO_4)_2 \cdot 3\ H_2O$	66.30	66.15	25.00	24.85	08.70	09.00
$Zn_3(PO_4)_2 \cdot 4\ H_2O$	53.23	53.12	31.03	30.88	15.72	15.98
$TiPO_4 \cdot 2\ H_2O$	29.25	29.18	50.00	49.75	20.75	20.25
$Zr(HPO_4)_2 \cdot 10\ H_2O$	27.61	27.51	28.88	29.75	43.51	44.13

RESULTS AND DISCUSSION

Differential thermal analysis

Figure 1 shows the DTA curves of the metal phosphates $M_3(PO_4)_2 \cdot X H_2O$ (where M = Cu, Zn, Cd and Mn), and $TiPO_4 \cdot 2 H_2O$ and $Zr(HPO_4)_2$ 10 H_2O. The DTA curve of zirconium phosphate shows a single sharp endothermic peak with the maximum at 122°C for dehydration. The manganese phosphate pentahydrate shows a broad endotherm with the maximum at 260°C and a shoulder at 350°C while an exothermic peak is observed at 415°C. The dehydration of cadmium phosphate takes place in a step with the endothermic peak maximum at 320°C. In the case of

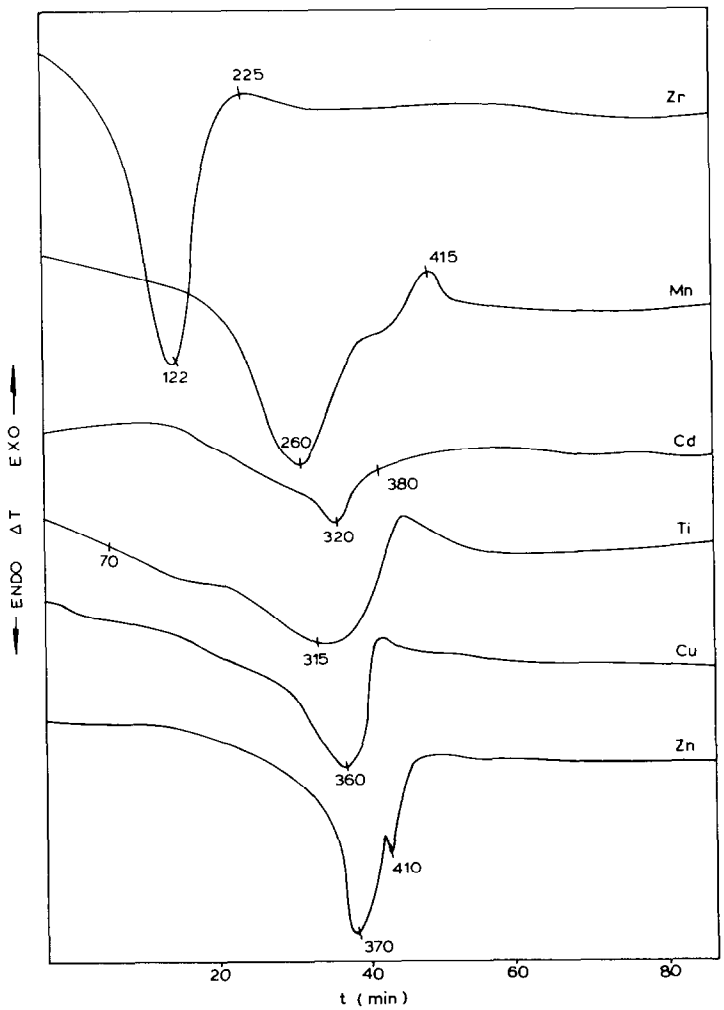

Fig. 1. DTA curves of the phosphates.

titanium(III) phosphate dihydrate only a single broad peak with the maximum at 315°C is observed. Zinc phosphate tetrahydrate shows two endotherms, the first at 370°C and the second at 410°C, and an exotherm appears at 960°C which is due to phase transition. A single endothermic peak is observed with the maximum at 360°C for copper phosphate trihydrate.

Thermogravimetry (TG, DTG)

Figure 2 shows the TG and DTG curves of the phosphates under study. In the case of zinc phosphate tetrahydrate a two-step dehydration is observed. In the first step, dehydration starts at 320°C and is complete at

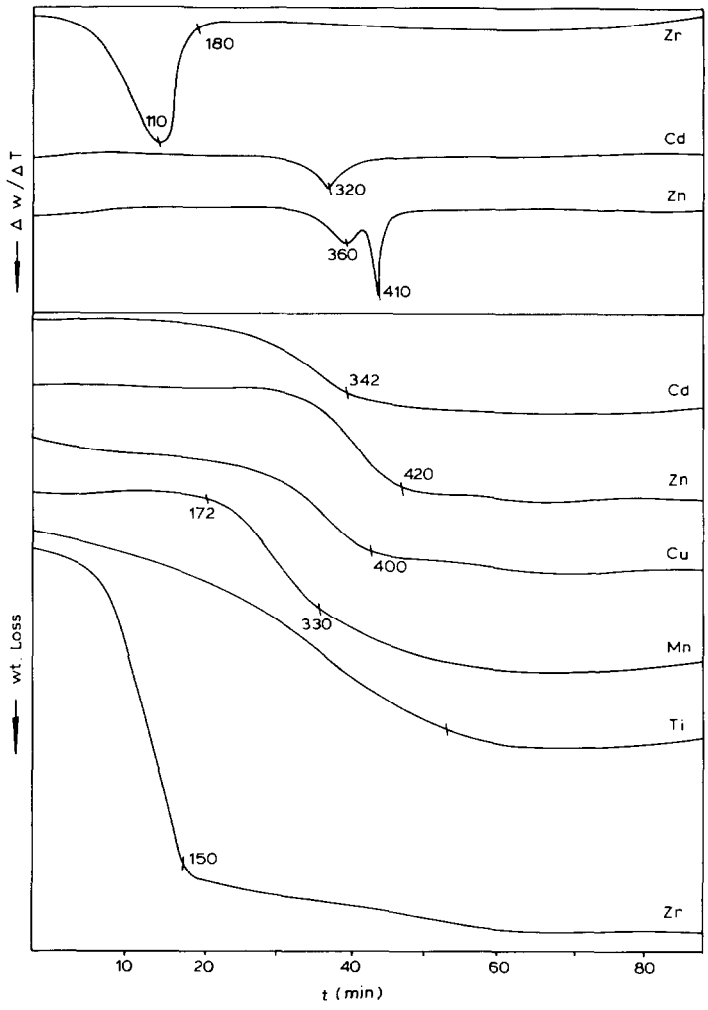

Fig. 2. TG and DTG curves of the phosphates.

385°C; two molecules of water are lost. The second step starts at 385°C and dehydration is complete at 420°C, with loss of the remaining water. The total weight loss is observed to be 15%. The exotherm at 960°C indicates phase transition from α-$Zn_3(PO_4)_2$ to β-$Zn_3(PO_4)_2$ [6–8]. Variation in the temperature range may be due to differences in the method of sample preparation.

The TG data of manganese phosphate pentahydrate show a total mass loss of 22% which is due to dehydration. It occurs in two steps: the first is sharp while the second is broad. In the first step, three molecules of water are lost in the temperature range 172–330°C and the other two molecules of water are removed up to 405°C. The exothermic peak between 405 and 430°C may be due to the formation of nuclei of crystalline manganese orthophosphate. Thermal analysis of the hexa and heptahydrates has been reported [9–12].

The TG data of copper phosphate trihydrate show 12.4% weight loss in the temperature range 200–400°C with the loss of all the water molecules [3]. Cadmium phosphate trihydrate loses three water molecules in a single step in the temperature range 210–350°C, with a total weight loss of 8.9%.

The dehydration of titanium(III) phosphate dihydrate takes place in two steps. The first commences at 210°C and is complete at 320°C, and loses half a molecule of water. The second step starts at 320°C and is complete at 450°C, and loses the remaining water molecules. The total weight loss is observed to be 26%. The exotherm appearing at 815°C is due to the phase transition from α- to β-TiPO4,

$$TiPO_4 \cdot 2\ H_2O \rightarrow TiPO_4 \cdot 1.5\ H_2O \rightarrow \alpha\text{-}TiPO_4 \rightarrow \beta\text{-}TiPO_4$$

According to TG data, zirconium phosphate decahydrate loses all the water molecules in a single step in the temperature range 80–150°C. The total weight loss is 45%, which corresponds to 11 molecules of water. Finally, anhydrous zirconium pyrophosphate is formed.

Kinetics of dehydration

The kinetics of the dehydration reaction were studied using DTA and TG equations and the energy of activation was determined. The kinetic parame-

TABLE 2

Kinetic parameters of dehydration

Phosphate	E_{DTA}[13]	E_{TG}[13]	E_{TG}[14]	Order of reaction
Manganese	14.27	10.76	14.48	1.07
Cadmium	7.86	6.00	7.41	1.04
Zirconium	8.86	9.50	9.54	1.00
Zinc	9.21	9.56	9.65	1.10

ters were calculated using the Piloyan equation for DTA and TG [13] and the Coates and Redfern equation for TG [14]. The order of reaction was determined by shape index method [15]. The dehydration process is of first order and values of reaction order and energy of activation are summarized in Table 2. From the results, it is clear that the water molecules are physically adsorbed on the phosphates.

X-Ray diffraction

The X-ray diffraction patterns of Zn, Cu, Mn, Zr and Cd phosphates calcined at 500°C for 2 h and recorded at room temperature are shown in Fig. 3. The structure of zinc phosphate is monoclinic, in agreement with the

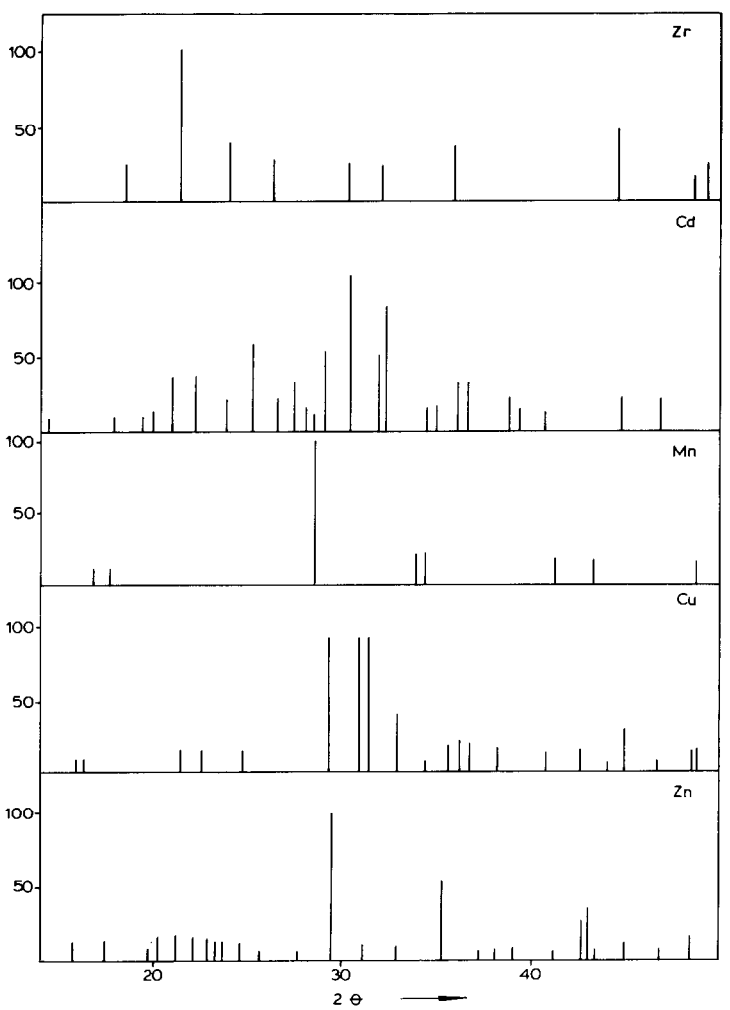

Fig. 3. X-Ray diffraction patterns of the phosphates.

work reported in ref. 16. The X-ray diffraction pattern of copper phosphate is concurrent with its literature pattern [17] and it crystallizes in the triclinic group. Manganese phosphate crystals show a similar structure to that of the mineral graftonite [18]. Two crystalline modifications have been reported at 630 and 850°C [19]. However, in the present case manganese phosphate crystallizes at a lower temperature.

Cadmium phosphate contains some crystals of the pyrophosphate group, thus giving a mixture of ortho- and pyrophosphates. The line intensities and interplanar distances are compared with reported data [20]. However, the structural parameters have not yet been reported. Zirconium pyrophosphate crystallizes as cubic crystals, with the lattice parameter $a = 8.258$ Å [21–23]. The X-ray diffraction pattern of titanium phosphate shows the amorphous state.

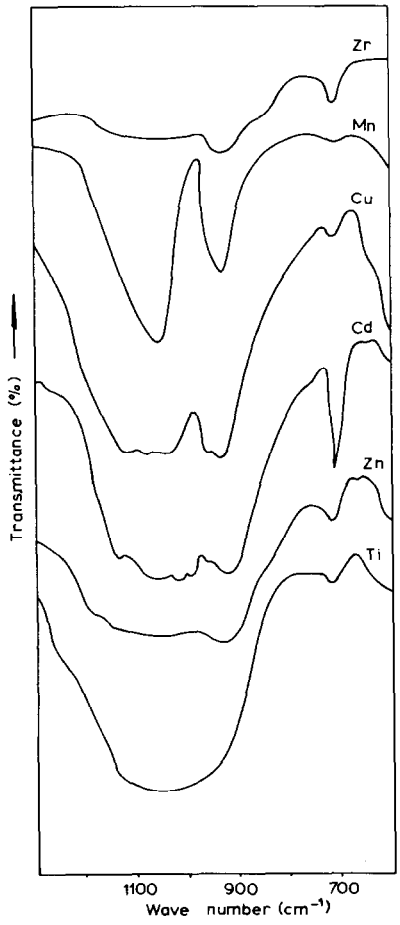

Fig. 4. IR spectra of the phosphates.

IR spectra

Figure 4 shows the IR spectra of Ti, Mn, Cu, Zn, and Cd orthophosphates and zirconium pyrophosphate calcined at 400°C. The anhydrous orthophosphates show the stretching frequencies (V_3) in the range 1015–1060 cm^{-1} and the deformation frequencies (ν_1) in the range 880–940 cm^{-1} [24–28]. The IR spectra of titanium phosphate and cadmium phosphate trihydrate have not yet been reported. The IR spectrum of zirconium phosphate shows a sharp band at 970 cm^{-1} and broad band at 1050–1250 cm^{-1} which are comparable with reported work [29].

From the present work it is concluded that Mn, Cu, Zn, and Cd orthophosphates are crystalline and thermally stable up to 900°C. Although titanium phosphate is amorphous it gives acidic centres. These phosphates can be used as catalysts. The dehydration process helps the formation of acidic centres.

ACKNOWLEDGEMENT

R.G. Sarawadekar is grateful to the Director, National Chemical Laboratory, Pune, for permission to carry out this work.

REFERENCES

1 M. Giorgini, M. Bertolozzi, F. Morelli and A. Di Manno, Ann. Chim. (Rome), 65 (1975) 29.
2 N.S. Kurnakoff and I.A. Andrersky, Ann. Inst. Anal. Phys. Chem., 2 (1924) 485.
3 L. Bendor and I. Felnar, Inorg. Chim. Acta, 4 (1970) 49.
4 A.I. Vogel, A Textbook of Quantitative Inorganic Analysis, Longmans, Green and Co. Ltd., 3rd edn., 1969.
5 F. Paulik, J. Paulik and L. Erdey, Talanta, 13 (1966) 1405.
6 A.G. Kotlova, N.I. Shchepokkina and B.M. Kooster, Inorg. Mater. (U.S.S.R.), 11 (1976) 1247.
7 M.A. De Schutlen, Bull. Soc. Chim. Fr., 27 (1904) 100.
8 L.J. Spencer, Mineral. Mag. (1876–1968), 15 (1908) 68.
9 A.A. Varlanov, Kh.Z. Sekushova, K.M. Mekhliev and T.G. Alkhazov, Russ. J. Inorg. Chem., 23 (1978) 341.
10 M.V. Goloschcapov, Z. Neorg. Khim., 1 (1956) 2635.
11 M.V. Goloschcapov, B.V. Martyneko and Ya.T. Torgashin, Z. Neorg. Khim., 15 (1970) 670.
12 I.V. Tananev and N.N. Chudinova, Z. Neorg. Khim., 8 (1963) 1076.
13 G.O. Piloyan and O.S. Novikova, Russ. J. Inorg. Chem., 12 (1967) 313.
14 A.W. Coates and J.P. Redfern, Nature (London), 201 (1964) 68.
15 H.E. Kissinger, Anal. Chem., 29 (1957) 1702.
16 C. Calvo, Can. J. Chem., 43 (1965) 436.
17 G.L. Schoemaker, J.B. Anderson and E. Kastiner, Acta Crystallogr., Sect. B, 33 (1977) 2969.

18 J.S. Stephans, Ph.D. Thesis, MacMaster Univ., Hamilton, Ontario, 1967.
19 C. Calvo, Am. Mineral., 53 (1958) 742.
20 R.C. Ropp, R.W. Mooney and C.W.W. Hoffman, Anal. Chem., 33 (1961) 1687.
21 D.E. Harrison, H.A. Mokinsby and F.A. Hummel, J. Am. Ceram. Soc., 37 (1954) 277.
22 H. McD. Macheachin, Acta. Crystallogr., 14 (1961) 1286.
23 C.B. Schar, L.C. Carrison and C.M. Schwartz, Nature (London), 204 (1964) 573.
24 B.V. Martyneko, M.V. Goloschapov and Ya.T. Torgashin, Inorg. Mater., 1 (1971) 1064.
25 A.N. Lazarev and T.F. Tenishera, Izv. Akad. Nauk S.S.S.R., Ser. Khim., 3 (1964) 403.
26 S.Z. Haider, Anal. Chim. Acta, 24 (1961) 250.
27 E. Steger and G. Leuoroth, Z. Anorg. Allg. Chem., 303 (1960) 189.
28 T. Kagiya, T. Shimizu, T. Suno, K. Azuma and K. Fukui, Kagaku Zasshi, 67 (1964) 261.
29 S.E. Horseley, D.V. Novel and D.T. Stewart, Spectrochim. Acta, Part A, 30 (1974) 535.