on the phosphorus. The inductive effect of the fluorine atoms may decrease the electron density on the phosphorus to such an extent that an appreciable dipole moment is produced which leads to a much greater intermolecular attraction. The melting point, 156°, of triphenylphosphine oxide is also increased 12 degrees by fluorine substitution. Increased hindrance to rotation of the phenyl groups would seem the better explanation here.

Thermal Stability.—The thermal decomposition of the newly synthesized compounds I, III, IV, and of decafluorodiphenyl were studied qualitatively. The hydrocarbon analogs, except for that of IV, were also studied. The results are shown in Table I. The relative thermal stability of the compounds appears to be in the order: $(C_6F_5)_2 \geq (C_6H_5)_2 > (C_6H_5)_4Si \geq (C_6F_5)_4Si > (C_6F_5)_3P > (C_6H_5)_3P > (C_3F_5)_3PO$.

It should be emphasized that these experiments were conducted in glass. Even so, perfluorodiphenyl is unchanged until held at 575° for 1 hr. It is believed that, in appropriate metal apparatus, it would show somewhat greater thermal stability than its hydrocarbon analog. Of the aromatic hydrocarbons in general, diphenyl is one of the most thermally stable. We have also studied in a similar manner about forty hydrocarbon aryl silanes without finding any with greater thermal stability than tetraphenylsilane, $[(C_6H_5)_4Si]$, which is considerably less stable than diphenyl.

The effect of the pentafluorophenyl group on the thermal stability undergoes a reversal in direction between the silane and phosphine. The presence of fluorine decreases the stability of the silane but increases the stability of the phosphine. However, the fluorophosphine oxide is less stable than the triphenylphosphine. These phenomena are obviously connected with the pair of coördinating electrons on the phosphine. The trends in the results suggest fairly marked differences in the bond strengths of the Si–C and P–C bonds in these compounds as a result of the fluorine substitution.

Table I

Comparison of Thermal Stabilities

Compound	M.p., °C.	Heating conditions Temp., °C.	Time, hr.	Condition of sample
$(C_6F_5)_4Si$	249	500	1	Charred, not coked
(I)		500	2	Charred, definite etching
		500	3	Coked, etched tube
$(C_6H_5)_4Si$	232	500	1	Yellow color
		500	2	Yellow, decomposition started
$(C_6F_5)_2$	70	325	1	Unchanged
		366	1	Unchanged
		420	2	Unchanged
		500	1	Unchanged
		575	1	Slight coloration
		660	1	Charred
$(C_6H_5)_2$	69	500	1	Unchanged
		500	2	Unchanged
		500	3	Unchanged
		660	1	Tube burst, some decomposition indicated
$(C_6F_5)_3P$	116–117	200	20	Unchanged
(III)		300	20	Slight yellowing
		400	6	Slight yellowing, m.p. 115°
		450	3	Tan crystals, m.p. 110–113°
		450	20	Dark brown oil
$(C_6H_5)_3P$	79	300	20	Unchanged
		400	6	Yellow liquid, some crystals, m.p. 73°
		400	20	Dark brown oil
$(C_6F_5)_3OP$	169–170	200	20	Unchanged
(IV)		300	20	Dark brown oil

[Contribution from the Chemical and Metallurgical Division, Sylvania Electric Products, Inc., Towanda, Pennsylvania]

Phosphates of Cadmium

By R. C. Ropp and R. W. Mooney

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The phosphate, $Cd_5H_2(PO_4)_4(H_2O)_4$, is stable over wide concentration, temperature and *p*H limits, converting in the presence of ammonia at *p*H 7.5 or above to one of two forms of cadmium ammonium phosphate hydrate, depending on ammonia concentration. In contrast to earlier results, no other basic phosphates could be precipitated, although cadmium hydroxylapatite was readily prepared by prolonged hydrolysis. A study of the thermal behavior of the compounds by means of differential thermal and thermogravimetric analysis showed that $Cd_5H_2(PO_4)_4(H_2O)_4$ dehydrates readily, losing up to four molecules of water before a change in structure is apparent, thus revealing properties somewhat similar to alkaline-earth hydroxylapatites. The ammonium phosphates form an intermediate $(CdHPO_4)_3 \cdot NH_3$ and finally convert to the pyrophosphate.

Introduction

The preparation of the cadmium phosphates was explored many years ago by several authors[1-3] who, for the most part, described the forms obtained and a method of precipitation, but gave

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[1] F. Stromeyer, *Schweiggers J.*, **22**, 362 (1818).

[2] A. deShulten, *Bull. soc. chim.*, France, **1**, 472 (1889).

[3] E. H. Miller and R. W. Page, *School Mines Quart.*, **22**, 391 (1900). See also: J. W. Mellor," A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. IV, Longmans, Green and Co., New York, N. Y., 1940, pp. 658–665.

little attention to thermal behavior. The quantitative determination of cadmium *via* precipitation as cadmium ammonium phosphate hydrate and ignition to $Cd_2P_2O_7$, presented by several workers,[4,5] remains the gravimetric procedure usually recommended. The acid phosphate, $Cd(H_2PO_4)_2 \cdot 2H_2O$, prepared by deShulten[2] and the condensed phosphates obtained during the dehydration of the acid phosphate were recently studied in detail as part of a comprehensive investigation of condensed phosphates and arsenates.[6]

There even has been some disagreement between the various authors regarding which basic phosphates of cadmium may be precipitated from solution. Although deShulten reported a voluminous amorphous precipitate which approached the composition $Cd_3(PO_4)_2$, as well as the crystalline $Cd_5H_2(PO_4)_4 \cdot 4H_2O$, later workers[7] could only obtain the latter compound. Klement and Zureda[8] reported that $Cd_5H_2(PO_4)_4 \cdot 4H_2O$ as well as $Cd_3(PO_4)_2 \cdot 5H_2O$ could be obtained from solution but not $CdHPO_4$. Since the hydroxylapatites are most easily formed by hydrolysis of secondary metal phosphates and since $CdHPO_4$ did not appear to exist, these authors found it necessary to resort to hydrothermal synthesis to prepare cadmium hydroxylapatite. $Cd_3(PO_4)_2$ was also reportedly prepared[9] by the method of "acidimetric precipitation."

The object of the present work was to define more clearly the regions of stability of the various basic phosphates of cadmium including the cadmium ammonium phosphates and to study their solid-state reactions and products obtained on pyrolysis to present a more comprehensive report than previously available. This work was part of a general study of the raw materials used in the preparation of some of the common inorganic phosphors.

Experimental

A. Preparation of $Cd_5H_2(PO_4)_4(H_2O)_4$.—This compound was prepared at temperatures ranging from 0–100° by the addition of cadmium solutions (usually $Cd(NO_3)_2 \cdot 4H_2O$) to phosphate solutions prepared from H_3PO_4, or solutions of mono-di-, or trisodium phosphate, as well as mono- or diammonium hydrogen phosphate. A variety of concentrations ranging from 0.1 to 3.0 molar of both cadmium and phosphate ions were employed. The same compound was obtained irrespective of the manner, rate or order of addition of reagents, although the degree of crystallinity was dependent upon these variables. The largest crystals, acicular in habit, were obtained by the addition of the phosphate to the cadmium solution at elevated temperatures. In the absence of ammonium ions, the compound was found to be stable over a wide *p*H range from 3 to 11, whereas in the presence of ammonia, it was stable only over the region *p*H 3–7.5, since at the upper range the compound $CdNH_4PO_4 \cdot H_2O$ began to form as described below.

$Cd_5H_2(PO_4)_4(H_2O)_4$ may also be prepared by heating a solution of the monobasic phosphate, $Cd(H_2PO_4)_2 \cdot 2H_2O$, to 80°. All samples were dried for 16 hr. at 100–120°.

Anal. Calcd. for $Cd_5H_2(PO_4)_4(H_2O)_4$: Cd, 55.3; P, 12.2; H_2O, 7.1. Found: Cd, 54.5; P, 12.0; H_2O (Karl Fischer), 6.7, Cd/P ratio, 1.25.

B. Preparation of $(CdHPO_4)_3 \cdot 3NH_3 \cdot 3H_2O$.–This compound was prepared by the addition of an ammonium phosphate solution to a solution of cadmium ions with subsequent adjustment of the *p*H with NH_4OH to values between 7.5 and 10.5. The precipitation was found to be essentially a conversion of $Cd_5H_2(PO_4)_4(H_2O)_4$, prepared at any *p*H value, to $(CdHPO_4)_3 \cdot 3NH_3 \cdot 3H_2O$ by adjustment of the *p*H with NH_4OH—preferably to *p*H 9.0–9.5. Conversion occurred in minutes.

A preferred method involved the addition of NH_3 gas to a $Cd(NO_3)_2$ solution to form the tetraammino complex, $Cd(NH_3)_4{}^{+2}$, which was buffered at *p*H 9.5, a point where $(CdHPO_4)_3 \cdot 3NH_3 \cdot 3H_2O$ was readily precipitated by the addition of any soluble ammonium phosphate.

The precipitation of $(CdHPO_4)_3 \cdot 3NH_3 \cdot 3H_2O$ at elevated temperatures gave a coarse precipitate which was very crystalline and had a laminar micaceous habit as determined by microscopic examination. Material precipitated at room temperature was less crystalline and highly aggregated. All samples were dried for 16 hr. at 110–120°.

Anal. Calcd. for $(CdHPO_4)_3 \cdot 3NH_3 \cdot 3H_2O$: Cd, 46.2; P, 12.7; NH_3, 7.0; H_2O, 7.4. Found: average of 2 preparations; Cd, 46.0; P, 12.5; NH_3, 8.2; H_2O (Karl Fischer), 7.4; Cd/P ratio, 1.01; NH_3/H_2O ratio (based on 7 preparations), 1.13.

C. Preparation of $(CdHPO_4)_3 \cdot 4NH_3 \cdot 2H_2O$.—A second form of cadmium ammonium phosphate hydrate was prepared by adding NH_3 gas in very great excess to $Cd(NO_3)_2$ solution until the *p*H approached 11.5. Precipitation by adding a phosphate solution to this ammonia-saturated solution gave a second form of cadmium ammonium phosphate hydrate having a two to one ratio of NH_3 to H_2O. Samples were dried for 16 hr. at 110–120°.

Anal. Calcd. for $(CdHPO_4)_3 \cdot 4NH_3 \cdot 2H_2O$: Cd, 46.2; P, 12.7; NH_3, 9.3; H_2O, 4.9. Found: average of 3 preparations; Cd, 44.5; P, 12.4; NH_3, 9.0; H_2O (Karl Fischer), 3.9; Cd/P ratio, 0.99; NH_3/Cd ratio, 1.34; NH_3/H_2O ratio (based on 7 preparations), 2.05.

D. Preparation of $5CdO \cdot 2P_2O_5$ ($Cd_3(PO_4)_2 \cdot Cd_2P_2O_7$).—If the compound $Cd_5H_2(PO_4)_4(H_2O)_4$ is heated to constant weight at 700°, the samples lose weight almost exactly equivalent to five moles of H_2O per mole of $Cd_5H_2(PO_4)_4(H_2O)_4$ yielding a compound containing five gram-atoms cadmium per four gram-atoms of phosphorus—stoichiometrically $Cd_3(PO_4)_2 \cdot Cd_2P_2O_7$.

Anal. Calcd. for $Cd_3(PO_4)_2 \cdot Cd_2P_2O_7$: Cd, 60.7; P, 13.4. Found: Cd, 56.9; P, 12.6; Cd/P ratio, 1.24.

E. Preparation of $(CdHPO_4)_3 \cdot NH_3$.—An intermediate, having a distinct and characteristic X-ray diffraction pattern, in the conversion of cadmium ammonium phosphate hydrate to cadmium pyrophosphate was prepared by heating a sample of $(CdHPO_4)_3 \cdot 3NH_3 \cdot 3H_2O$ or $(CdHPO_4)_3 \cdot 4NH_3 \cdot 2H_2O$ for approximately 64 hr. at 200° or 5 hr. at 280° with a loss in weight equivalent to five molecules of water plus ammonia yielding the compound $(CdHPO_4)_3 \cdot NH_3$.

Anal. Calcd. for $(CdHPO_4)_3 \cdot NH_3$: Cd, 52.5; P, 14.5; NH_3, 2.65. Found: Cd, 52.6; P, 14.0; NH_3, 2.5; H_2O (Karl Fischer), 0.33; Cd/P ratio, 1.04; Cd/NH_3 ratio, 3.2.

F. Preparation of $Cd_2P_2O_7$.—The pyrophosphate was easily prepared by heating $(CdHPO_4)_3 \cdot 3NH_3 \cdot 3H_2O$ for 2 hr. at 980°.

Anal. Calcd. for $Cd_2P_2O_7$: Cd, 56.4; P, 15.5. Found: Cd, 56.6; P, 15.1, Cd/P ratio, 1.03.

G. Preparation of $Cd_3(PO_4)_2$.—The compound $Cd_3(PO_4)_2$ was prepared by solid-state reaction of $(CdHPO_4)_3 \cdot 3NH_3 \cdot 3H_2O$ with CdO_2[10] in a mole ratio of 2:1 at temperatures equal to or exceeding 650° for 3 to 4 hr.

Anal. Calcd. for $Cd_3(PO_4)_2$: Cd, 64.0; P, 11.8. Found: Cd, 64.1; P, 11.4; Cd/P ratio, 1.55.

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(4) A. Carnot and P. M. Proromant, *Compt. rend.*, **101**, 59 (1885).

(5) M. Austin, *Am. J. Sci.*, **8**, 206 (1889).

(6) E. Thilo and I. Grunze, *Z. anorg. allgem. Chem.*, **290**, 209 (1957).

(7) F. Ephraim and C. Rossetti, *Helv. Chim. Acta*, **12**, 1025 (1929).

(8) R. Klement and F. Zureda, *Z. anorg. allgem. Chem.*, **245**, 229 (1940).

(9) W. Rathje, *Ber.*, **74B**, 357 (1941).

(10) C. W. W. Hoffman, R. C. Ropp and R. W. Mooney, THIS JOURNAL, **81**, 3830 (1959).

H. Preparation of Cadmium Hydroxylapatite.—Cadmium hydroxylapatite could not be precipitated from solution but was easily prepared by the hydrolysis of $(CdHPO_4)_3 \cdot 3NH_3 \cdot 3H_2O$ by refluxing in water for a few days. The hydrolysis of $Cd_3(PO_4)_2$ or $Cd_5H_2(PO_4)_4(H_2O)_4$ also gave the apatite, but only at a very slow rate requiring over a week for partial conversion. An alkali hydroxide, such as NaOH, could not be used to speed the hydrolysis since it resulted eventually in the precipitation of $Cd(OH)_2$. The X-ray diffraction pattern of the cadmium hydroxylapatite, so produced, was in fair agreement with that reported by Klement and Zureda.[8]

Anal. Calcd. for $Cd_5OH(PO_4)_3$: Cd, 65.2; P, 10.8. Found: Cd, 64.8; P, 11.2; Cd/P ratio, 1.59.

J. X-ray Diffraction, Differential Thermal and Thermogravimetric Analyses.—The methods used for identification by Debye–Scherrer patterns and the techniques of differential thermal and thermogravimetric analyses were the same as those used during a recent study of the dibasic phosphates of strontium.[11]

Results

The effect of *p*H on the precipitation of $Cd_5H_2(PO_4)_4(H_2O)_4$ was readily determined by titration of a solution of cadmium nitrate in phosphoric acid with NaOH and NH_4OH. Crystals of $Cd_5H_2(PO_4)_4(H_2O)_4$ began to appear in both cases at approximately *p*H 3 corresponding to the first ionization of H_3PO_4 to give $H_2PO_4^-$ ions. With further addition of NaOH, this precipitate remained stable up to *p*H 11 where $Cd(OH)_2$ was finally formed. However, in the case of NH_4OH, $Cd_5H_2(PO_4)_4(H_2O)_4$ was converted to cadmium ammonium phosphate hydrate at *p*H 7.5 corresponding to the ionization of $H_2PO_4^-$ ions to give HPO_4^{-2} ions. This latter precipitate dissolved at *p*H 10 and $Cd(OH)_2$ was again formed at approximately *p*H 11.

The conversion of $Cd_5H_2(PO_4)_4(H_2O)_4$ to $(CdHPO_4)_3 \cdot 3NH_3 \cdot 3H_2O$ appeared to be reversible since a dried sample of the latter refluxed in boiling water for 4 hr. underwent conversion to a mixture of approximately 30% $Cd_5H_2(PO_4)_4(H_2O)_4$ and 70% cadmium hydroxylapatite. Both forms of the cadmium ammonium phosphate hydrate gave these products in a few hours while the rate of conversion of pure $Cd_5H_2(PO_4)_4(H_2O)_4$ to cadmium hydroxylapatite by refluxing in water was much slower, requiring weeks for partial conversion.

Differential thermal analyses of $Cd_5H_2(PO_4)_4(H_2O)_4$ disclosed that the compound went through five resolvable endothermic reactions during its dehydration, namely: (1) a low energy reaction at approximately 200° following the loss of absorbed water, (2) three high energy endothermic changes between 250 and 300°, and (3) a final low energy change between 350 and 400°. However, thermogravimetric analyses did not resolve the weight losses corresponding to these endothermic changes since the rate and amount of weight loss was roughly proportional to the temperature to which the sample was subjected. At a constant temperature below 300°, the system never came to a constant weight even at extremely long firing times, whereas, for a linearly increasing temperature, the samples began to lose weight at 260° and a smooth curve of weight loss *vs.* temperature was obtained up to 475° corresponding to a weight loss of 5.02–5.10 moles H_2O/mole $Cd_5H_2(PO_4)_4(H_2O)_4$ (Av. = 5.05 for 4 runs).

X-Ray examination of a sample prepared at increasing temperatures showed that the $Cd_5H_2(PO_4)_4(H_2O)_4$ pattern was maintained up to 270°, even though approximately three molecules of water had been lost. At about 290°, and a loss of 3.9 moles H_2O, the diffraction pattern of the product changed to that characteristic of the final form and remained unchanged during the loss of the final molecule of water.

X-ray diffraction patterns of the two cadmium ammonium phosphate hydrates differed mainly in the intensities of a few lines as illustrated by the selected data of Table I.

Table I

X-ray Diffraction Patterns of the Cadmium Ammonium Phosphate Hydrates

$(CdHPO_4)_3 \cdot 3NH_3 \cdot 3H_2O$ d(Å.)	I	$(CdHPO_4)_3 \cdot 4NH_3 \cdot 2H_2O$ d(Å.)	I
8.78	vs	8.70	vs
4.85	w	4.85	w
4.38	m	4.38	m
3.81	w	3.83	w
3.50	s	3.50	m
2.94	w	2.94	vs
2.91	m	2.91	w
2.88	vs	2.88	s
2.77	m	2.78	m
2.42	w	2.43	w
2.33	m	2.32	w

Differential thermal analyses of $(CdHPO_4)_3 \cdot 3NH_3 \cdot 3H_2O$ and $(CdHPO_4)_3 \cdot 4NH_3 \cdot 2H_2O$ gave approximately the same results showing two endothermic peaks; the first at 205–230° and a second at 355–360°. With large laminar crystals of $(CdHPO_4)_3 \cdot 3NH_3 \cdot 3H_2O$ obtained by precipitation at high temperatures, the first endothermic peak was observed at lower temperatures around 155°, but the temperature of the second reaction remained unchanged. By careful pyrolysis the intermediate, $(CdHPO_4)_3 \cdot NH_3$, was isolated as described in the Experimental section. Thus, a sample of laminar $(CdHPO_4)_3 \cdot 3NH_3 \cdot 3H_2O$ heated to constant weight at 280° exhibited a weight loss of 13.9% while a sample of $(CdHPO_4)_3 \cdot 4NH_3 \cdot 2H_2O$ heated to constant weight at 200° had a 12.3% loss in weight corresponding to a loss of 5 molecules of NH_3 plus H_2O. Further heating of $(CdHPO_4)_3 \cdot NH_3$ above 360° gave rise to an amorphous phase and finally to the cadmium pyrophosphate structure with a total weight loss of 18.0%.

All attempts to prepare a crystalline tribasic phosphate by precipitation following the method of Klement and Zureda[8] or a slight modification of Rathje's method[9] failed since either an amorphous precipitate or the compound $Cd_5H_2(PO_4)_4(H_2O)_4$ was formed. However, the tribasic phosphate was prepared by solid-state reaction as described in the Experimental section. Cadmium hydroxylapatite could not be precipitated from solution but was easily prepared by hydrolysis.

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(11) R. W. Mooney, M. A. Aia, C. W. W. Hoffman and R. C. Ropp, This Journal, **81**, 826 (1959).

Discussion

From a perusal of previous literature, it might be inferred that cadmium ammonium phosphate hydrate is the form which would be most likely to be encountered. Actually, this form is stable only over a narrow range of precipitation conditions and it is $Cd_5H_2(PO_4)_4(H_2O)_4$ which is found over a wide range of precipitation variables. The precipitation of $Cd_5H_2(PO_4)_4(H_2O)_4$ from cadmium and phosphate solutions over a wide *p*H range resembles in many aspects the precipitation of the dibasic phosphates of the alkaline-earth metals. However, its appearance over a wide range of preparation temperatures is not characteristic of either the calcium or strontium dibasic phosphates where transitions occur from $CaHPO_4 \cdot 2H_2O$ to $CaHPO_4$ and from β-$SrHPO_4$ to α-$SrHPO_4$ with increasing temperature. Obviously, this compound has great stability as also evidenced by its occurrence at *p*H 10 where a more basic phosphate might be expected to precipitate. In many respects, therefore, it resembles $BaHPO_4$ which is formed over wide *p*H and temperature intervals. Its preparation from a monobasic phosphate by the application of heat according to the reaction

$$5Cd(H_2PO_4)_2 \cdot 2H_2O \xrightarrow{\Delta} Cd_5H_2(PO_4)_4(H_2O)_4 + 6H_3PO_4 + 6H_2O \quad (1)$$

is also characteristic of the preparation of a dibasic alkaline-earth phosphate from a monobasic phosphate.

However, the thermal behavior of $Cd_5H_2(PO_4)_4(H_2O)_4$ is more characteristic of a hydroxylapatite in view of its continuous loss of water depending upon dehydration time and temperature. The observation that the X-ray diffraction pattern changes rather sluggishly to the final product with no evidence of any intermediate phases is also striking. The fact that the Cd/P ratio is unchanged after firing would be consistent with the equation

$$Cd_5H_2(PO_4)_4(H_2O)_4 \longrightarrow Cd_3(PO_4)_2 \cdot Cd_2P_2O_7 + 5H_2O \quad (2)$$

and, in fact, the final X-ray pattern is similar in some respects to the diffraction pattern of $Cd_2P_2O_7$. However, the diffraction pattern of the fired product is not equivalent to a pattern of a mechanical mixture of $Cd_3(PO_4)_2$ plus $Cd_2P_2O_7$ or a mixture of these two obtained by firing cadmium ammonium phosphate with cadmium peroxide in a ratio of four to one.

It is suggested that the compound $Cd_5H_2(PO_4)_4(H_2O)_4$ is not a hydrate in the usual sense but rather is structurally similar to the hydroxylapatites which can lose water continuously without a serious change in structure occurring simultaneously. This assumption is corroborated by the fact that the water molecules are so tightly bound that the Karl Fischer reagent does not readily react with them. However, the compound dissolves sluggishly in the reagent releasing the water molecules slowly. As a result, the formula for this compound is written in a manner which suggests that the water molecules are bound in the crystal by forces greater than those normally associated with hydrates.

Another basic phosphate also has traits characteristic of a dibasic phosphate. Cadmium ammonium phosphate hydrate reacts to form $Cd_2P_2O_7$, but despite the known gravimetric procedure for cadmium,[12] it is $Cd_5H_2(PO_4)_4(H_2O)_4$ which is first precipitated and then transformed to $(CdHPO_4)_3 \cdot 3NH_3 \cdot 3H_2O$. This transformation with the addition of ammonia takes place at approximately *p*H 7.5 according to the equation

$$3Cd_5H_2(PO_4)_4(H_2O)_4 + 3HPO_4^{-2} + 15NH_4^+ + 9OH^- \longrightarrow 5(CdHPO_4)_3 \cdot 3NH_3 \cdot 3H_2O + 6H_2O \quad (3)$$

The reactions start at the hydrogen ion concentration where the equilibrium of the second ionization reaction of phosphoric acid is shifted to the right thus increasing the concentration of HPO_4^{2-} ions appreciably. Under the above conditions, the transformation takes place with ease in minutes. The reverse reaction, namely, the conversion of cadmium ammonium phosphate hydrate to $Cd_5H_2(PO_4)_4(H_2O)_4$ and finally to cadmium hydroxylapatite by hydrolysis may be represented by the equations

$$5(CdHPO_4)_3 \cdot 3NH_3 \cdot 3H_2O \xrightarrow[NH_3]{H_2O} 3Cd_5H_2(PO_4)_4(H_2O)_4 + 3H_3PO_4 + 3H_2O \quad (4)$$

and

$$Cd_5H_2(PO_4)_4(H_2O)_4 \xrightarrow{H_2O} Cd_5OH(PO_4)_3 + H_3PO_4 + 3H_2O \quad (5)$$

These reactions are also characteristic of the hydrolysis of a dibasic phosphate to the hydroxylapatite compound. Elevated temperatures markedly increase the rates of reaction which are normally very slow. Hydrolysis of $Cd_5H_2(PO_4)_4(H_2O)_4$ to cadmium hydroxylapatite occurs only after several weeks, again denoting the stability of this compound in solution.

The present study has suggested the complexity of cadmium ammonium phosphate hydrate since for the special form containing four mols NH_3 and two mols H_2O, three mols of cadmium and phosphate are requisite. On the same basis then, the compound previously written $CdNH_4PO_4 \cdot H_2O$ becomes $(CdHPO_4)_3 \cdot 3NH_3 \cdot 3H_2O$.

The slight differences between the X-ray diffraction patterns of $(CdHPO_4)_3 \cdot 3NH_3 \cdot 3H_2O$ and $(CdHPO_4)_3 \cdot 4NH_3 \cdot 2H_2O$ are not surprising since the replacement of a molecule of H_2O by a molecule of NH_3 should not affect the diffraction pattern appreciably. The differences might be due to preferred orientation since a corresponding effect was observed between the low and high temperature preparations of $(CdHPO_4)_3 \cdot 3NH_3 \cdot 3H_2O$. However, the differences are believed to be real since the non-laminar material was used for the X-ray work and the possibility of preferred orientation effects should be minimized. The analytical data

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(12) W. Wagner, C. J. Hull and G. E. Markle, "Advanced Analytical Chemistry," Reinhold Publishing Co., New York, N. Y., 1956, p. 138.

strongly support the existence of the two forms and calculations of bond energies for $Cd(H_2O)_6^{+2}$ and $Cd(NH_3)_6^{+2}$ are very close, being 41.7 and 39.5 kcal./bond, respectively, indicating that at high enough NH_3 concentrations, a replacement of a water molecule by an ammonia molecule would be possible.

Upon heating, both forms convert to an intermediate which analytically may be represented by the formula $(CdHPO_4)_2\cdot NH_3$, according to the equation

$$\left.\begin{array}{l}(CdHPO_4)_3\cdot 3NH_3\cdot 3H_2O\\ (CdHPO_4)_3\cdot 4NH_3\cdot 2H_2O\end{array}\right\}\xrightarrow{200-280^\circ} (CdHPO_4)_3\cdot NH_3 + \left\{\begin{array}{l}2NH_3 + 3H_2O\\ \text{or}\\ + 3NH_3 + 2H_2O\end{array}\right. \qquad (6)$$

The calculated weight loss of about 12.1% agrees reasonably well with the thermogravimetric results of 13.9 and 12.3% loss. The experimental data indicate that at least one NH_3 molecule in $(CdHPO_4)_3\cdot 3NH_3\cdot 3H_2O$ may differ in its bonding as evidenced by the mode of decomposition. It may well be that it is complex-bound and not equivalent to the other NH_3 molecules.

As with many of the phosphates obtained on pyrolysis, the possibility exists that $(CdHPO_4)_3\cdot NH_3$ may not be a distinct chemical specie but instead may be a mixture of cadmium ortho- and pyrophosphates combined with amorphous material as found by Edwards and Herzog[13] in their dehydration experiments on sodium orthophosphate. The final total weight loss of 18.0% is in good agreement with the theoretical weight loss of 18.1% for the conversion to the pyrophosphate. In contrast to the polymorphic alkaline-earth pyrophosphates,[14] only one modification of $Cd_2P_2O_7$ was observed up to the melting point.

Contrary to some earlier results[8,9] the precipitation of a crystalline tribasic cadmium phosphate from solution was not achieved in this study. In fact, it is doubtful if such a species exists since earlier workers[2,7] were careful to point out that these precipitates were often voluminous and amorphous. Further, it is suggested that the presumed formation of a tri-basic phosphate could have been confused with the precipitation of $Cd_5H_2(PO_4)_4(H_2O)_4$ which in this study was found to be the stable cadmium phosphate precipitate over a wide range of precipitation variables.

The difficulty in achieving the precipitation of a tribasic phosphate is attributed to the observation that at high *p*H values $Cd(OH)_2$ is more stable than any cadmium phosphate. Thus, neither $Cd_3(PO_4)_2$, $Cd_3(PO_4)_2\cdot 5H_2O$ or $Cd_5OH(PO_4)_3$ could be precipitated from solution.

The preparation of cadmium hydroxylapatite was achieved by rather conventional means, namely, the hydrolysis of a cadmium ammonium phosphate hydrate. This result is in contrast to the predictions of Klement and Zureda[8] who used a hydrothermal synthesis method since they did not believe hydrolysis possible. Their conclusion was based upon the non-existence of $CdHPO_4$, which is confirmed by this study, but the substitution of $(CdHPO_4)_3\cdot 3NH_3\cdot 3H_2O$ for the normal dibasic phosphate leads to the expected results.

Finally, it is suggested that the chemistry of Cd most resembles that of Mn rather than that of Mg and Zn as proposed by previous authors. According to Ephraim and Rossetti,[7] manganese forms the compound $Mn_5H_2(PO_4)_4\cdot 4H_2O$ as well as other forms. No other phosphate compounds are known in which the cation to anion ratio is five to four.

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