[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF THE NATIONAL BUREAU OF STANDARDS]

Pyrophosphate Formation Upon Ignition of Precipitated Basic Calcium Phosphates[1]

BY ALLEN GEE AND VICTOR R. DEITZ

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Precipitated basic calcium phosphates were found to yield substantial quantities of pyrophosphate on ignition at 400° to 600°. This pyrophosphate formation most likely resulted from the presence of acid phosphate groups in the precipitates. Under given conditions of ignition the amount of pyrophosphate was greater when the precipitate had a ratio of calcium to phosphate lower than that in hydroxyapatite. The slow rate of conversion suggested that diffusion might be the rate-controlling factor. Above 600° the pyrophosphate reacted with the hydroxyapatite to form β-tricalcium phosphate, and this accounted for the decrease in pyrophosphate with increase in temperature. The evidence presented gives additional support to the current view that $Ca_3(PO_4)_2 \cdot xH_2O$ does not exist as a unique compound in precipitates from aqueous solutions.

I. Introduction

It has been shown that the chemical composition of basic calcium phosphates (BCP) varies considerably with the conditions of precipitation. In addition to a varying water content the precipitates studied had atomic ratios of calcium to phosphorus ranging from 1.33 to 2.0.[2,3,4] Some investigators, as for instance, Eisenberger, Lehrman and Turner,[2] concluded that the observed composition range represents an unbroken series of solid solutions. According to their views, hydrated tricalcium phosphate is not a unique compound, but is merely one member of a solution series. Other workers, notably Cameron and Bell[5] and Hendricks and Hill,[6] have maintained that precipitated BCP having the composition of tricalcium phosphate is, in fact, hydroxyapatite with surface-adsorbed acid phosphate groups. Hendricks and Hill based their opinion mainly on the circumstance that the materials generally possess large surface areas and at the same time exhibit X-ray diffraction patterns[7,8] closely similar to those of hydroxyapatite.

If acid phosphate were present, gentle ignition of the preparations should cause the formation of a dehydrated phosphate. Although Hirschman, Sobel, Kramer and Fankuchen[9] demonstrated by X-ray diffraction the presence of pyrophosphate in ignited mechanical mixtures of dicalcium phosphate and hydroxyapatite, they were unable to detect it in ignited precipitates of BCP which had the same ratios of calcium to phosphate as the mixtures. This paper reports a successful detection and determination of pyrophosphate in ignited BCP, the conditions of ignition which govern the conversion, and the possible significance to the knowledge of the structure of BCP.

II. Materials

The precipitated basic calcium phosphates used were (1) commercial products (designated by "S"), (2) samples furnished by other investigators (see footnote of Table I), or (3) samples prepared in this Laboratory for a general study (designated by "P"). All of the commercial products were C.P. or N.F. grade, and partial analyses of the other samples indicated them to be of equal quality. The materials prepared in this Laboratory[10] were contaminated by strontium (originating from the reagent grade $CaCO_3$) amounting to 1 mole per cent. of the calcium, by silica and alumina, about 0.2% each by weight, and by carbon dioxide less than 1%. Chemical impurities other than $HPO_4^{=}$ and $H_2PO_4^-$ ions appeared not to have any bearing on the semi-quantitative relationships to be presented.

Preparations P-22 and P-23 were made from dilute solutions of monocalcium phosphate and calcium bicarbonate. All other "P" samples listed in Table I were precipitated from large volumes of water at selected temperatures by the slow addition from burets of calcium hydroxide and monocalcium phosphate solutions.[10-12] These preparations had B.E.T. surface areas ranging from 4 to 130 square meters per gram, a variety of physical appearances, and different chemical compositions.

A number of the samples were examined under the polarizing microscope, by X-ray diffraction and by electron microscopy for the presence of a separate phase of dicalcium phosphate. The materials with discernible crystals showed negligible amount of birefringence characteristic of $CaHPO_4 \cdot 2H_2O$, the others with finer particle sizes approaching the colloidal range have no recognizable birefringence. All of the X-ray diffraction patterns were entirely apatitic, although the sharpness of the patterns varied considerably. None of the preparations, including P-22 which has been examined thoroughly, gave any evidence from these tests of a separate phase.

III. Experimental

a. **Ignition.**—Samples of BCP in covered porcelain crucibles, usually containing less than a gram, were maintained at a given temperature in an electric muffle furnace[13] for 15 to 360 hours. The various times of ignition are shown in Table I.

b. **Analysis.**—The values for pyrophosphate shown in Table I were obtained by spectrophotometric determinations of orthophosphate before and after acid hydrolysis. Since condensed phosphates are converted to orthophosphates by boiling in dilute acid, the difference between the results by the two procedures is the value for condensed phosphate. The ratio of this difference to the total phosphate times 100 was used to represent the percentage of phosphate converted.

Fifty mg. of ignited BCP was dissolved as rapidly as possible (1 to 10 min. at room temperature) in 10 ml. of perchloric acid (0.2 M), and the solution was diluted to 100 ml. immediately. Two 5-ml. aliquots were placed in separate 25-ml. volumetric flasks. To one was added 1 ml. of perchloric acid (6 M) and the flask placed on a boiling water-bath for an hour to hydrolyze the pyrophosphate. After cooling, the mixture was diluted to about 15 ml. To the aliquot in the other flask after dilution with 10 ml. of water,

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(2) S. Eisenberger, A. Lehrman and W. D. Turner, *Chem. Revs.*, **26**, 257 (1940).

(3) W. F. Neuman and M. W. Neuman, *ibid.*, **53**, 1045 (1953).

(4) B. Kurmies, *Phosphorsaure*, **13**, 57 (1953).

(5) F. K. Cameron and J. M. Bell, THIS JOURNAL, **27**, 1512 (1905).

(6) S. B. Hendricks and W. L. Hill, *Proc. Natl. Acad. Sci.*, **36**, 731 (1950).

(7) H. C. Hodge, M. LeFevre and W. F. Bale, *Ind. Eng. Chem., Anal. Ed.*, **10**, 156 (1938).

(8) A. S. Posner and S. R. Stephenson, *J. Dental Research*, **31**, 371 (1952).

(9) A. Hirschman, A. E. Sobel, O. Kramer and I. Fankuchen, *J. Biol. Chem.*, **171**, 285 (1947).

(10) A. Gee, *Proc. Third Tech. Sess. Bone Char*, 337 (1953).

(11) A. V. Kazakov, *Trans. Sci. Inst. Fertilizers Insectofungicides (U.S.S.R.)*, **139**, 3 (1937).

(12) H. G. McCann, *J. Biol. Chem.*, **201**, 247 (1953).

(13) The accuracy of temperature was ±5°, although a slight defect in the furnace control may have caused some of the temperatures to be as much as 20° from the indicated reading.

TABLE I

PYROPHOSPHATE FORMATION IN BASIC CALCIUM PHOSPHATES

Sample no.	Ratio, Ca/PO₄	Surface area, m.²/g.	Ignition Time, hr.	Ignition Temp., °C.	Mole % phosphate converted X_P
P-22	1.424	63	60	600	25.7
			120	600	31.7
P-23	1.531	49.5	60	600	11.2
P-26	1.542	52.8	60	600	12.4
P-J[a]	1.557		60	600	11.9
P-25	1.558	128	60	600	9.6
P-28	1.58	20.4	60	600	8.0
BPI-2186[a]	1.585	10.2	60	600	6.7
P-13	1.606		60	600	7.4
P-20	1.665	4.5	60	600	1.6
II[a]	1.667		60	600	2.7
L-apatite[a]	1.67	67.8	60	600	0.5
P-24	1.68	3.1	60	600	0.4
P-11	1.709	6.4	60	600	0.8
S-95B	1.65		60	600	2.2
S-96	1.67	58.1	60	600	1.4
S-97	1.66		60	600	2.0
S-93	1.548	27.5	15	600	7.3
			60	600	10.0
			120	600	10.2
			240	600	12.8
			300	600	11.7
			360	600	12.5
			15	400	4.4
			15	800	8.2
			15	950	0.8

[a] These samples were kindly furnished as follows: P-J, R. S. Bowman, Mellon Institute, Pittsburgh, Pa.; BPI-2186, W. L. Hill, Bur. Plant Industry, Beltsville, Md.; II, H. G. McCann, Natl. Inst. of Health, Bethesda, Md.; L-apatite, W. F. Neuman, Univ. of Rochester, Rochester, N. Y.

1 ml. of 6 *M* perchloric acid was added. Then 1 ml. of a solution containing ammonium molybdate (80 g./liter) and ammonium vanadate (4.0 g./liter) was pipetted into each flask and both solutions were diluted to volume. The intensities of the resulting yellow color, indicating the orthophosphate concentration, were measured by differential spectrophotometry.[14]

c. **Results.**—The results of the analyses for pyrophosphate in a variety of BCP are listed in order of composition in Table I. Figure 1a shows how the amount of orthophosphate (mole per cent.) transformed into pyrophosphate after a period of 15 hours varied with ignition temperature. From 400 to about 700°, the amount increased because of a higher rate of reaction. Above 800° the amount decreased abruptly because of the competing reaction whereby β-tricalcium phosphate was formed.[9,15]

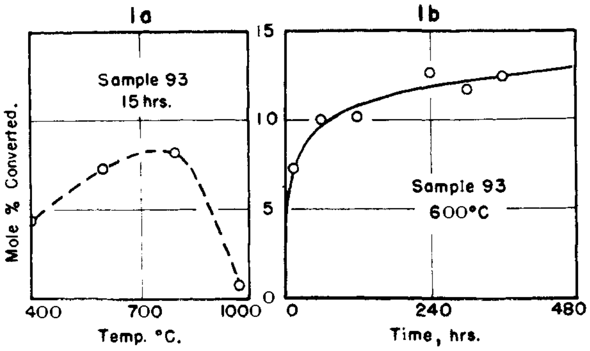

Fig. 1.—Pyrophosphate formation in sample 93 as a function of time (1a) and temperature (1b).

In order to obtain a reasonable rate of pyrophosphate formation without excessive conversion to β-tricalcium phosphate, a temperature of 600° was chosen for most of this work. At this temperature the formation of the pyrophosphate increased with ignition time as shown in Fig. 1b. The rate was relatively fast initially, but became very slow after 120 hours. For convenience most samples were heated for only 60 hours, a period which gives a point at just above the "knee" of the curve. How closely different samples arrived at the same stage under the same ignition conditions is a question not fully investigated.

For homogeneous samples of BCP under the same ignition conditions the amount of pyrophosphate formed was found to depend on composition. This dependency on the molal ratio of Ca to PO₄ is shown by the circles in Fig. 2. Samples having a composition corresponding to, or more basic than, that of hydroxyapatite yielded very small but detectable amounts of pyrophosphate. The amount of pyrophosphate became larger as the ratio of calcium to phosphate fell below 1.67.

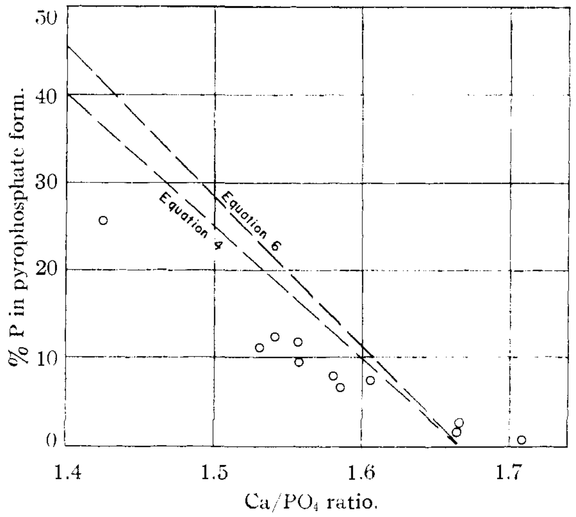

Fig. 2.—Formation of pyrophosphate in various basic calcium phosphates upon ignition for 60 hours at 600°; experimental points in circles and dotted lines theoretical curves.

At 600° the chief product in the pyrolysis of dicalcium phosphate is pyrophosphate. The formation of pyrophosphate during the ignition is apparently unaffected by the presence of hydroxyapatite[9] and/or lime. The latter was demonstrated by the ignition of one commercial sample of "tricalcium phosphate" which was found to be predominately a mixture of lime and dicalcium phosphate having an over-all ratio of calcium to phosphorus of 1.52. After 60 hours at 600° 86.5% of the phosphate appeared in the pyroform. This observation suggests that the reason why samples having the composition of hydoxyapatite may still yield some pyrophosphate upon ignition is that they may contain incompletely reacted dicalcium phosphate and lime. The possible existence of CaO in BCP is not discussed.

IV. Identification of Pyrophosphate

Since acid phosphates condense in a number of ways, some work was done to determine the reaction product. Sodium acid phosphates condense into polymers, and the degree of polymerization decreases as the starting material is made more basic.[16] The dibasic salt forms largely the dimeric pyrophosphate. Calcium acid phosphates behave similarly,

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(14) A. Gee and V. R. Deitz, *Anal. Chem.*, **25**, 1320 (1953).

(15) M. J. Dallemagne, H. Brasseur and J. Melon, *Bull. soc. chim. France*, **3-4**, 138 (1949).

(16) J. R. Van Wazer, THIS JOURNAL, **72**, 647, 655 (1950).

and the following reaction begins at about 300° and proceeds rapidly at 400°[17]

$$2CaHPO_4 \longrightarrow Ca_2P_2O_7 + H_2O \tag{1}$$

Tribasic phosphates have not been known to undergo condensation because there is no acid hydrogen to react. Should any condensation occur in BCP, the degree of polymerization might be expected by analogy with the sodium phosphate system not to go beyond the pyrophosphate stage.

Two incidental observations pointed to the existence of a condensed phosphate in samples of ignited BCP: (a) In titrations with ethylenediamine tetraacetate ion for calcium after dissolution of the samples, competition for the calcium with the chelating agent was observed. This competition is characteristic of condensed phosphates. (b) The amount of orthophosphate determined spectrophotometrically[14] in the ignited sample was less than that in the same sample before ignition, but the phosphate reappeared very slowly as orthophosphate in an acid medium at a rate similar to that for known solutions of pyrophosphate. The existence of the latter in one sample of the ignited BCP was confirmed by chemical separation as manganous pyrophosphate:

A 25-mg. portion of sample S-93, ignited for 360 hours at 600°, was dissolved in 5 ml. of 0.2 *M* perchloric acid, and 0.10 g. of sodium acetate trihydrate was added immediately after dissolution. The precipitation was carried out by the method of Jones.[18] The *p*H of the solution was adjusted to 4.1 by the addition of 25 mg. of chloroacetic acid. This was followed by the addition of 50 mg. of manganous chloride tetrahydrate and 0.3 ml. of acetone. Precipitation began within a few minutes and was allowed to proceed overnight. The precipitate was centrifuged and washed first with 3 ml. of 25% acetone and then with larger portions of 50% acetone. Finally, the precipitate was air-dried at room temperature.

Similar precipitates were made from sodium metaphosphate (of unknown degree of polymerization, J. T. Baker Chemical Co., Lot 12795) and calcium pyrophosphate (Monsanto Chemical Co., Lot 235), all with sufficient calcium nitrate added to maintain the same calcium–phosphorus ratio as S-93. The small amount of precipitate from the metaphosphate tended to show that only a small quantity of pyrophosphate was present in this sample. All three precipitates were dissolved in 0.3 *N* perchloric acid, hydrolyzed at 100°, and analyzed for manganese (colorimetrically after oxidation to permanganate with persulfate) and total phosphate. The atomic ratios of manganese to phosphorus for the precipitates from the ignited BCP was 1.00. The ratios in the precipitates from the pyrophosphate and the metaphosphate, which may contain higher polymers, were 0.92 and 0.88, respectively.[19]

It is known that triphosphate ions are not precipitated by manganous ions[18] and higher phosphate polymers which might be precipitated would form salts that would contain still lower manganese to phosphate ratios. Hence, the proximity of the above ratios to unity means that the precipitates were largely pyrophosphate. Spectrophotometric determinations showed that the orthophosphate incorporated in the precipitate was below 8%.

Tests on solutions of ignited BCP were negative for the presence of long-chain polyphosphates as determined by precipitation with barium chloride in acid medium. Tests were also negative for triphosphate as determined by examination for phosphorus after precipitation of barium phosphate in a weakly basic medium. The amount of phosphorus precipitated as manganese pyrophosphate in BCP sample S-93 accounted for 90% of the total condensed phosphate determined by the method described in IIIb. Hence, pyrophosphate is the predominant condensed form in ignited BCP just as one expects from an analogy to the sodium phosphate systems.

V. Discussion

Kinetics of Reaction.—The rate of formation of pyrophosphate in BCP as indicated by Fig. 1b is much slower than that observed for the condensation from a pure phase of dicalcium phosphate.[17] Although the temperature which initiates the reaction may not be appreciably higher than that for a pure phase of dicalcium phosphate, the reaction rate in BCP up to 700° appears to have a much smaller temperature coefficient. Both the low rate and the small temperature coefficient strongly suggest that the rate-controlling factor is the solid diffusion or surface migration of some reactant such as the acid hydrogen. Experiments designed to study the mechanism of the reaction by measuring changes in surface properties have thus far been inconclusive.

Hirschman, Sobel, Kramer and Fankuchen[9] found that pyrophosphate reacted with hydroxyapatite at 900° to form the β-tricalcium phosphate. The pyrophosphate in the BCP samples of Table I, formed with prolonged ignition appears to react similarly. Thus, with a portion of sample S-93 which had already been ignited at 600° for 360 hours, it was found that all of the pyrophosphate was converted after ignition in a platinum crucible over a Meker burner for 1 hour. This formation of β-tricalcium phosphate explains why the curve in Fig. 1a falls off at high temperatures.

Since water is evolved in the formation of pyrophosphate, there might seem to be some connection between the water loss and the amount of pyrophosphate formed. Inasmuch as water is always found in precipitates of BCP to an extent ranging from 1 to 7%, some loss of water occurs upon ignition even when negligible amounts of pyrophosphate are found. The loss of weight upon ignition is appreciable,[10,20] generally several times that computed for the reaction alone.

Relation to Structure.—Numerous investigators[6–9,18] have concluded from X-ray diffraction evidence that BCP which had a ratio of calcium to phosphate lower than that in hydroxyapatite has adsorbed or occluded phosphate in one of the acid forms. The results above prove the existence of acid phosphate groups in precipitates of BCP having ratios of calcium to phosphate from 1.4 to 1.67. Therefore, the view that $Ca_3(PO_4)_2 \cdot xH_2O$, commonly referred to as tricalcium phosphate hydrate, is a chemical compound is now questionable.

Formulations of the following type may be in reasonable accord with the observations

$$Ca_{10}(PO_4)_6(OH)_2 \cdot nCaHPO_4 \tag{I}$$

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[17] Andre Boulle, *Compt. rend.*, **226**, 1617 (1948).

[18] L. T. Jones, *Ind. Eng. Chem., Anal. Ed.*, **14**, 536 (1942).

[19] If one assumes 2 atoms of manganese per molecule, the molecular weight computed from the last two precipitates is 339 ± 8. On the basis of a 1 to 1 ratio of manganese to phosphorus this corresponds to the formula $Mn_2P_2O_7 \cdot 3H_2O$. Experiments show this substance to be stable at room temperature and above 50% relative humidity. The anhydrous form is stable at 105°.

[20] P. W. Arnold, *Trans. Faraday Soc.*, **46**, 1061 (1950).

or

$$Ca_{10}(PO_4)_6(OH)_2 \cdot mCa(H_2PO_4)_2 \qquad (II)$$

where n or m is either zero or positive with an uncertain limit (m in no case can be >4).

If formula I is correct, then the limit of the amount of pyrophosphate which can form according to reaction 1 can be derived. This limit can be expressed as a function of the molar ratio of calcium to phosphate, R, where

$$R = \frac{10 + n}{6 + n} \qquad (2)$$

Since the maximum amount of phosphate which can change into pyrophosphate is equal to the quantity of acid phosphate initially present, it follows that

$$X_P = \text{phosphate convertible (mole \%)} = \frac{n}{6 + n} \times 100 \qquad (3)$$

By the elimination of n between (2) and (3), one obtains

$$X_P = \frac{1}{2}(5 - 3R) \times 100 \qquad (4)$$

Equation 4 is represented by the lower broken line in Fig. 2.

According to formula II

$$R = \frac{10 + m}{6 + 2m}$$

If the reaction

$$H_2PO_4^- + PO_4^{\equiv} \longrightarrow P_2O_7^{4-} + H_2O \qquad (5)$$

is assumed to occur, then

$$X_P = \frac{4}{7}(5 - 3R) \times 100 \qquad (6)$$

This equation gives values somewhat greater than those of equation 4.

BCP with ratios of calcium to phosphate less than the ratio in hydroxyapatite (1.67) yielded amounts of pyrophosphate after 60 hours of heating which were considerably below the limiting value prescribed by equation 4. Three possible reasons for this general trend are the following.

(a) Some reversion of pyrophosphate to β-tricalcium phosphate occurs even at 600°. The X-ray diffraction pattern for P-22 shows evidence for the formation of β-tricalcium phosphate.

(b) Some labile condensed phosphate may have formed which would be quickly hydrolyzed upon the solution of the sample in dilute acid. However, the amount of pyrophosphate hydrolyzed has been found to be negligible under the conditions of analysis.

(c) The reaction is not complete after 60 hours at 600°.

Table II shows the way in which two samples of BCP approach the limiting value, computed from equation 4, with continued ignition. The curve in Fig. 1b appears to approach asymptotically 78% of the limiting value. Since P-22, with a lower ratio of calcium to phosphate, is more likely to form labile polyphosphates, the fact that the formation of pyrophosphate in this sample approaches more closely the limiting value may be an indication that reason (b) above is unimportant.

TABLE II

APPROACH OF PYROPHOSPHATE FORMATION TO THE LIMITING VALUE OF X_P FROM EQUATION 4 WITH TIME OF HEATING AT 600°

BCP	Limiting value of X_P from eq. 4, mole %	% of limiting value 60 hr.	 120 hr.	 360 hr.
S-93	18.0	56	57	70
P-22	36.4	71	87	

The pH of the water extracts of BCP generally rose only slightly when the BCP was subjected to higher ignition temperatures. Sample S-93 before ignition gave a water extract (1 g. BCP in 50 ml.) of pH 6.3 but yielded an extract of pH 6.0, 6.5, 7.1 and 7.6 after ignition for 15 hours at 400, 600, 800 and 950°, respectively. This rise in pH may be related to the loss of acid phosphate, first through the pyrophosphate reaction and at higher temperatures through the formation of β-tricalcium phosphate.

There is no direct experimental evidence which would favor either formula I or formula II. Formula I may be preferred because (1) the relative insolubility of $CaHPO_4$ would favor its being adsorbed, and (2) it is not possible to form solid $Ca(H_2PO_4)_2$ above pH 4, in which region the basic calcium phosphates are precipitated. The slow rate of formation of the pyrophosphate during the ignition would suggest a reaction in which the rate-controlling factor is diffusion rather than the chemical reaction given by equation 5 wherein the acid phosphate can react immediately with a close neighbor in the substrate.

The amount of pyrophosphate formed upon ignition of BCP could not be correlated with properties other than chemical composition. Surface areas, for instance, do not appear to have an effect. Several pairs of substances can be chosen to support a possible relation. However, a comparison between P-26 and P-25, which have B.E.T. surface areas of 53 and 128 m.^{2}/g., respectively (see Table I), shows that a large difference in measurable surface areas had no significant effect on the amount of pyrophosphate formed.

Conclusion

Evidence has been presented which indicates that precipitated BCP may contain acid phosphate groups. This conforms with previously published[2-4] postulations which were based on less direct evidence. The presence of acid phosphate was indicated by the pyrolysis reaction to form pyrophosphate which was proven chemically to be present by the precipitation of manganese pyrophosphate. The pyrophosphate was in all probability distributed uniformly throughout the BCP as a consequence of the homogeneous location of the acid phosphate groups. The absence of organized multilayers of pyrophosphate was confirmed by the lack of a pyrophosphate X-ray diffraction pattern for an ignited material containing as much as 25.7% pyrophosphate.

The results presented do not answer the question of where the acid phosphate groups reside. These groups may constitute an adsorbed phase solely, they may be in a solid solution, or they may be partially disssolved in a depth of several molecular layers at the surface of the crystallites. The important facts which have been established are (a) the formation of pyrophosphate upon the ignition of precipitated BCP, (b) the slow rate of pyrophosphate formation relative to a macrophase of acid phosphate, and (c) the correlation of the amount of pyrophosphate formed with the observed ratio of Ca to PO_4, as shown by Table I.

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Exchange of Chlorine in Aqueous Systems Containing Chloride and Tetrachloroplatinate(II)[1,2]

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The kinetics of exchange of chlorine has been measured in aqueous solutions containing Cl^-, $[PtCl_4]^=$ and $[PtCl_3(H_2O)]^-$ by the use of Cl^{36}. Addition of $[Pt(NH_3)_4](NO_3)_2$ to the solutions yielded precipitates of $[Pt(NH_3)_4][PtCl_4]$ (Magnus' green or pink salts) and $[Pt(NH_3)_4][PtCl_3(H_2O)]_2$ without fractionation or induced exchange. Exchange occurred by means of the reversible aquation process: $[PtCl_4]^= + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [PtCl_3(H_2O)]^- + Cl^-$, for which $\Delta H_1^{\ddagger} = 21$ kcal., $\Delta S_1^{\ddagger} = -8$ e.u., $\Delta H_2^{\ddagger} = 15$ kcal. and $\Delta S_2^{\ddagger} = -18$ e.u. In addition to this process one other detectable exchange occurred between Cl^- and $[PtCl_3(H_2O)]^-$ with a rate, $R = k'[PtCl_3(H_2O)]^-$, for which $\Delta H^{\ddagger} = 25$ kcal. and $\Delta S^{\ddagger} = 2$ e.u.

Introduction

The exchange of chlorine between chloride ion and the $[PtCl_4]^=$ ion in aqueous solution has been found to proceed with a conveniently measurable rate at room temperatures. The tetrachloroplatinate(II) ion, representative of the square, planar complexes of platinum(II), is inert toward substitution in the sense defined by Taube.[3] Although it has been recognized that water or hydroxide can be substituted for chloride in this ion,[4] it is surprising that for so familiar a system a quantitative treatment of such aquation (or hydrolysis) has not appeared in the literature.

The rate of exchange of a ligand in a complex with its corresponding entity in solution gives very fundamental information about the nature of the species in the solution. The work of Adamson, Welker and Volpe,[5] who observed diverse rate of exchange between cyanide ion and the cyanide ligand in a number of coördination complexes, illustrates the use which can be made of these techniques. Grinberg and Nikol'shaga[6] have studied the exchange in systems with a number of the square platinum(II) complexes. They reported that the exchange rate decreases in order with the ligands: $CN^- > I^- > Br^- > Cl^-$. For the tetrachloroplatinate(II) ion the exchange periods were reported to be long compared to the 38-minute half-life of the Cl^{38} isotope available. The abstract of their work does not mention the possibility of a photo-effect on the rates of exchange, although this effect has frequently been noted in exchange work with related compounds. For example, Adamson and Grunland[7] indicated that the exchange of Br between $[PtBr_6]^=$ and Br^-, undetected in the dark, was exceedingly rapid in light.

Rich and Taube[8] recently have reported studies of the exchange of Cl between $[PtCl_6]^=$ and Cl^- and of the exchange of Pt between $[PtCl_4]^=$ and $[PtCl_6]^=$ with a discussion of the role of Pt^{III}. They had previously described the exchange system $[AuCl_4]^-:Cl^-$.[9] The complex $[AuCl_4]^-$ is closely related to $[PtCl_4]^=$ in that it also exists as the square, coplanar complex.

A number of observations by Flikkema and Hammond[10] have been of great assistance in the interpretation of the results of the present exchange experiments. They found that a chloride ligand of $[PtCl_4]^=$ in its aqueous solution was replaced reversibly by H_2O with a reaction period of a few hours according to the reaction

$$[PtCl_4]^= + H_2O \underset{k_1}{\overset{k_2}{\rightleftharpoons}} [PtCl_3(H_2O)]^- + Cl^- \quad (1)$$

The resulting ion, $[PtCl_3(H_2O)]^-$, is a weak acid which can be titrated by hydroxide with a glass electrode. The extent of aquation can be followed by measuring the acid titer of the solution. Flikkema and Hammond found that the replacement of chloride by water was first order in $[PtCl_4]^=$, and the replacement of water by chloride in the reverse reaction was first order in $[PtCl_3(H_2O)]^-$ and first order in Cl^-. In addition, a second aquation occurred with a much longer period. The formation of $[PtCl_2(H_2O)_2]$ was catalyzed by hydroxide, and the formation of appreciable concentrations of this diaquo-species was accompanied by the formation

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(2) Work performed in the Ames Laboratory of the Atomic Energy Commission.

(3) H. Taube, *Chem. Revs.*, **50**, 69 (1952).

(4) J. N. Friend, "Textbook of Inorganic Chemistry," Vol. IX, Part I, 2nd Edition, Charles Griffin and Company, Ltd., London, 1922, pp. 286–288.

(5) A. W. Adamson, J. P. Welker and M. Volpe, THIS JOURNAL, **72**, 4030 (1950).

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(9) R. L. Rich and H. Taube, *J. Phys. Chem.*, **58**, 1 (1954).

(10) D. S. Flikkema and G. S. Hammond, private communication.